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SAND2005-0345

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Printed January 2005

Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – Project CP-1227 FY04 Annual Technical Report

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Abstract

Military test and training ranges operate with live fire engagements to provide realism important to the maintenance of key tactical skills. Ordnance detonations during these operations typically produce minute residues of parent explosive chemical compounds. Occasional low order detonations also disperse solid phase energetic material onto the surface soil. These detonation remnants are implicated in chemical contamination impacts to groundwater on a limited set of ranges where environmental characterization projects have occurred. Key questions arise regarding how these residues and the environmental conditions (e.g., weather and geostatigraphy) contribute to groundwater pollution impacts. This report documents interim results of a mass transfer model evaluating mass transfer processes from solid phase energetics to soil pore water based on experimental work obtained earlier in this project. This mass transfer numerical model has been incorporated into the porous media simulation code T2TNT. Next year, the energetic material mass transfer model will be developed further using additional experimental data.

Acknowledgements

This work was sponsored by the Strategic Environmental Research and Development Program (SERDP), under the technical direction of Jeff Marqusee and programmatic direction of Brad Smith. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

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1.0 Introduction

SERDP is seeking techniques and knowledge that will permit assessment of the environmental impact of residual energetic material from test and training operations. Low-order detonations that disperse discrete solid phase particles onto and into the soil leave the greatest legacy of energetic material residues. One principal environmental impact is contamination of aquifers. The energetic material most likely to impact aquifers is RDX due to its low drinking water advisory limits, low retardation during soil transport and low rate of environmental degradation.

Understanding the mass transfer rate from discrete solid phase particles into the soil pore water is critical to the impact analysis of these residues for groundwater contamination. Weather is an important process that drives the mass transfer phenomena. This work seeks to analyze this mass transfer process using laboratory measurement and numerical simulation methods. The results from this work will create a new predictive ability to assess the migration potential of residual energetic materials.

Objective

This work seeks to develop an energetic material source function that describes the mass transfer of solid phase energetic materials to a solute in soil pore water, and to incorporate this process in a solute transport model with linkages to time dependent weather phenomena. This energetic material source function can be used in a screening level simulation tool to assess groundwater pollution management strategies for residual energetic materials left by military testing and training operations.

2.0 Project Plan

This project began in FY01 as a two year effort to develop the preliminary data and mass transfer properties for use in a screening model. At the end of each year, the annual technical reports have documented the methods and results for work that occurred that year (Phelan et al., 2001; Phelan et al., 2003). At the Fall 2002 IPR, sufficient evidence was shown to extend the experimental work and explore certain mass transfer phenomena in more detail and create a screening model to evaluate the environmental impacts of low order detonation debris. The project extension proposal was for a one year extension; however funding constraints extended the task scope to three years. Table 1 shows the major project tasks in experimental and modeling areas for each year. Table 2 shows the detail tasks and milestones for the entire project.

Table 1. Project Task Schedule

FY	Experimental	Modeling
2001	Method Development Phase I, Test Group A and B	Initial Formulation
2002	Phase II, Test Group A and B	Revised Formulation and Data/Model Comparisons
2003	Phase III	
2004		2-d Model Enhancement
2005		Screening Assessments

The experiments completed in FY03 are summarized in the annual report (Phelan et al., 2004). Modification of the Energetic Material Source Function to include the Phase III experimental data was planned to occur during FY04. However, the funds for FY04 were received over 7 months late on May 19, 2004, which has caused a significant delay in the work. The modified Energetic Material Source Function should be completed by May 2005.

The present plan is that the screening assessments scheduled for 2005 will not be performed and the project will be completed in the Fall 2005. The development of screening models is the subject of a recent SON (CPSON-06-02, November 10, 2004). Work on screening models under the present project is not appropriate given the recent SON. Therefore, after the modified Energetic Material Source Function is completed in May 2005, the project will be complete and the final project report will be written.

Table 2. Master List of Tasks, Milestones and Deliverables

Task Name	Milestone	Date	Status	Deliverable
1 - Phase I Experiments	Complete solubility kinetics pretest	8/01	Completed	Phelan, J.M., J.L. Barnett, J.V. Romero, D.R. Parker, 2002. Solubility and Dissolution Kinetics of Composition B in Water. Sandia National Laboratories Report SAND2002-2420, December 2002.
	Complete Phase I, Test Group A	11/01	Completed	
	Complete Phase I, Test Group B	01/02	Completed	
2- Initial Model Development	Develop Preliminary Form of Energetic Material Source Function	8/01	Completed	
	Integrate with T2TNT	11/01	Completed	
	Compare Modified T2TNT with Experimental Data	02/02	Completed	
3 – Phase II Experiments	Phase II Test Plan	02/02	Completed	
	Complete Phase II, Test Group A	06/02	Completed	
	Complete Phase II, Test Group B	09/02	Completed	
4 – Revised Energetic Material Source Function	Complete New Energetic Material Source Function	06/02	Completed	
	Compare Energetic Material Source Function with Phase II Experimental Data	11/02	Completed	
	Develop the 2-d effects model for pore water effluent concentrations	9/04	Initiated	Delayed
	Analyze 2-d effects on energetic material mass transfer	3/05	Not Started	Delayed
5 – Phase III Experiments	Complete Phase III Tests	12/03	Completed	
6 – Roadmap	Develop application roadmap	12/03	Completed	
7 – Application analysis tools	Develop application analysis tools	12/05	Not Started	Cancelled
	Complete screening assessments of range contamination	12/05	Not Started	Cancelled
	Complete systems analysis to evaluate relationships for exceeding groundwater criteria	4/06	Not Started	Cancelled
8 – Technical Reports to SERDP	Annual Technical Report	12/01	Completed	Phelan, J.M., S.W. Webb, J.V. Romero and J.L. Barnett, 2001. FY01 Interim Technical Report, Strategic Environmental Research and Development Program, Project 1227, Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water.
	Annual Technical Report	12/02	Completed	Phelan, J.M., S.W. Webb, J.V. Romero, J.L. Barnett, F. Griffin, M. Eliassi and J.L. Brainard, 2003. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2003-0153, January 2003.
	Annual Technical Report	12/03	Completed	Phelan, J.M., J.L. Barnett, and D.R. Kerr, 2004. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – FY03 Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2004-0039, January 2004.
	Annual Technical Report	12/04	This Report	Webb, S.W., and J.S. Stein, 2005. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – FY04 Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2005-0345, January 2005.

3.0 Modeling Approach

3.1 Experimental Data

Table 3 summarizes the experimental data obtained in this project (Phelan, et al., 2001, 2002, 2004). The initial model for the Energetic Material Source Function (EMSF) was based on the Phase I and II experimental data (Phelan et al., 2003). The present work will modify the EMSF to include the Phase III experimental data.

Table 3. Experimental Test Phases and Principal Factors

Test Phase	Principal Factors	Mass Transfer Test Designator
Phase I, Test Group A	Flow, temperature, EM particle size	MT1, MT2, MT3
Phase I, Test Group B	Porous media saturation	MT5, MT12
Phase II, Test Group A	Bed loading, bed depth, initial wetting rate	MT6, MT7, MT8, MT8b, MT8c, MT8d, MT9b2, 9b3
Phase II, Test Group B	Flow, EM particle size, detonation debris	MT10, MT13, MT14, MT11, MT15, MT16, MT17, MT18
Phase III	Surface vs. buried deposits, EM particle size, low order detonation debris	MT 19-1, 2, 3, 4; MT20-1, 2, 3; MT21-1, 2; MT22-1, 2, 3; MT23-1, 2; MT24-1; MT25-1; MT26-1, MT27-1; MT28-1.

3.2 Modeling

The modeling approach has been presented previously (Phelan et al., 2003) and is summarized below. There are no new modeling results in this report.

In order to simulate the mass transfer tests, modifications have been made to the T2TNT code (Webb et al., 1999). A separate solid phase and mass transfer from the solid phase to water have been added to the code. The details of the mass transfer model are discussed below.

3.2.1 Mass Transfer Formulation

The mass transfer rate from a solid to the surrounding fluid is given by:

$$\dot{m} = k A_i S_\ell \rho_f (C_s - C) \quad [1]$$

where \dot{m} is the mass transfer rate from the solid to the liquid phase (kg/s), k is the mass transfer coefficient (m/s), A_i is the solid phase interfacial area (m^2), S_ℓ is the liquid saturation, ρ_f is the fluid density (kg/m^3), C is the concentration of the solid material in the far-field fluid (mass fraction), and C_s is the saturation concentration of the solid material in the fluid (mass fraction). In equation [1], the mass transfer from the solid mass to the liquid phase is calculated. The liquid saturation, S_ℓ , is included to account for the wetted solid surface area.

The mass transfer coefficient, k , and the interfacial area, A_i , are unknowns in the above equation. The interfacial area, A_i , varies dramatically over time as the mass is transferred from the solid phase into the water phase. The interfacial area is assumed to be a direct function of the time-dependent mass of the solid particles raised to an exponent X , or:

$$A_i = a M^X \quad [2]$$

where a is a constant (m^2/kg^X), M is the mass of the solid particles (kg), X is the exponent on the solid mass. The constant a is determined using the initial solid mass and the initial surface area, which is based on initially spherical particles.

Using the definition of the interfacial area, the mass transfer relationship can then be written as:

$$\dot{m} = k a M^X S_\ell \rho_f (C_s - C) \quad [3]$$

The fitting parameters for any given simulation run are the mass transfer coefficient, k , and the exponent X . The mass transfer model presented here is intentionally kept simple to easily vary k and X parameters to fit the experimental data and to determine their influence on this fit.

One-dimensional simulation models were developed for the saturated and pulsed tests. In this initial model development phase, only dissolution of RDX was considered. As shown in Figure 1, there are two stages of the outlet concentration data from the experiments; an initial excess mass capacity stage where the exit concentration is essentially constant, and a mass depletion stage where the exit concentration decreases dramatically with time.

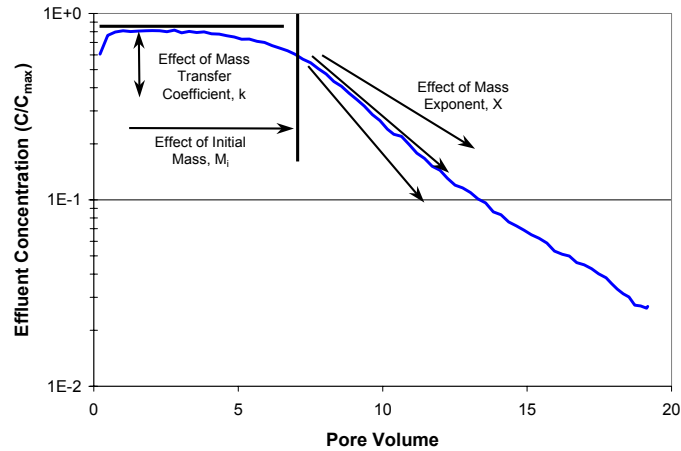


Figure 1. Effluent Concentration Stages

Figure 2 shows some representative results from the data-fitting process. The overall agreement is encouraging. The initial peak is reasonably well predicted as is the mass depletion stage for this test (MT14).

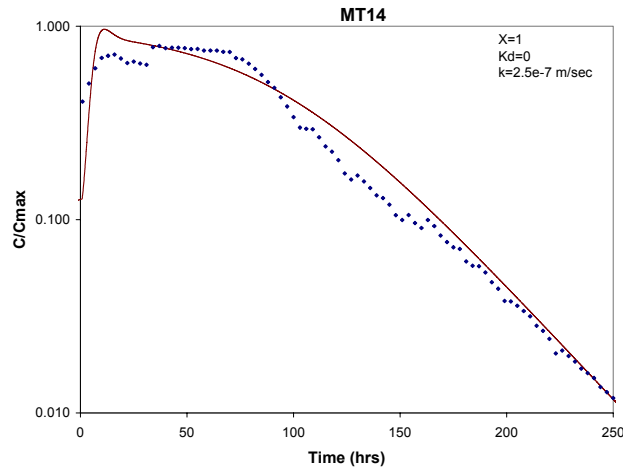


Figure 2. Representative Data-Model Comparison

Figures 3 and 4 plot the values of k and X as a function of the initial RDX mass per unit area, respectively. The trend of decreasing values of k and X with increasing mass per unit area is clearly seen in the two plots. In addition, the MT12 pulsed test parameters are plotted on the curves indicating consistency between the parameters derived from the saturated flow test and for unsaturated conditions.

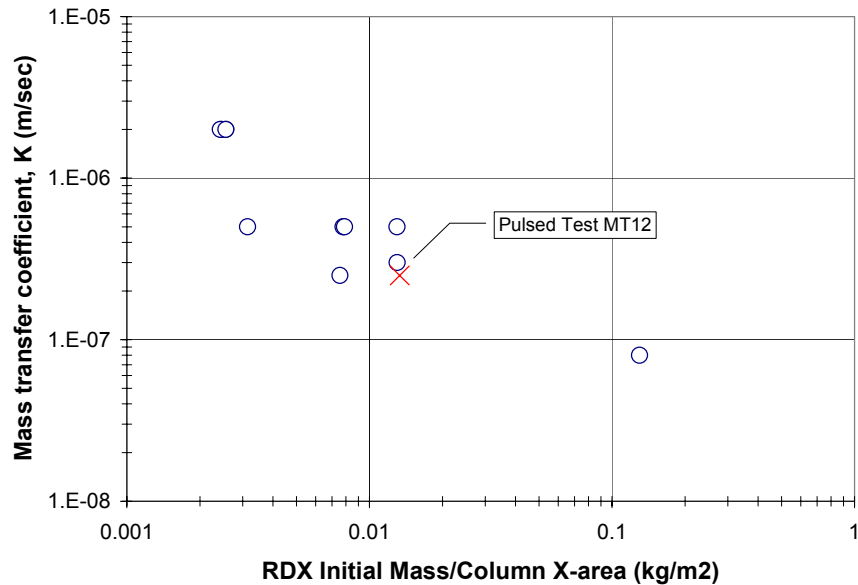


Figure 3. Effect of Initial RDX Mass per Unit Area on Mass Transfer Coefficient, k

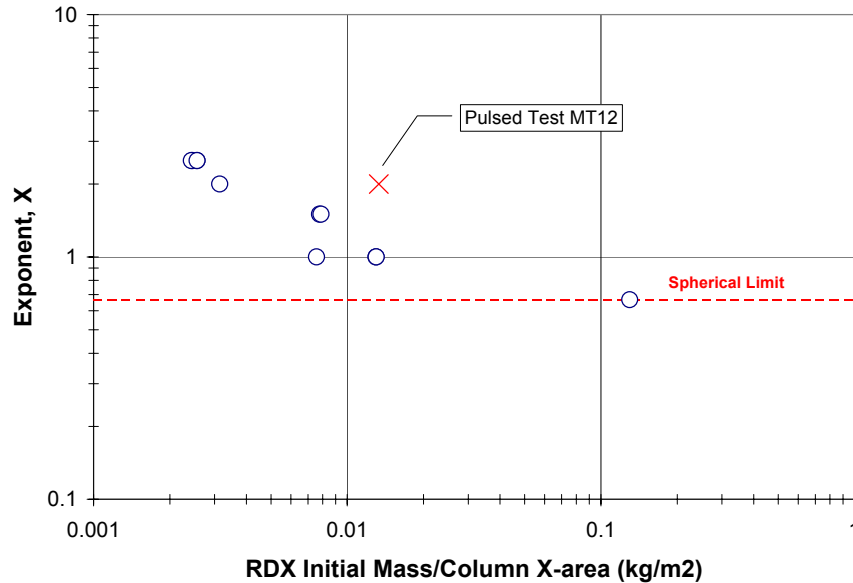


Figure 4. Effect of Initial RDX Mass per Unit Area on Interfacial Area Exponent, X

Overall, this initial mass transfer model has successfully fit the experimental data for the 100 μm particles. Further development of the model is needed to include the Phase III experimental data and data for other particle diameters. This model development will be completed by May 2005.

3.2.2 Sensitivity Study

In addition to the fitting of the experimental data, work has started looking in detail at the full range of energetic material mass transfer column experiments done in the laboratory using formal sensitivity analysis techniques to identify the most important variables. While the most important parameters are summarized in Table 3 shown earlier, this ranking was based on observations and not on any analytical procedure. The present, more formal approach, will be used to define either one or more statistical regression models based on the data that can be used to predict quantities such as normalized effluent concentration or effluent saturation as a function of selected input parameters. The value of such a model would be that it could provide not only predictions based on the experimental data but perhaps just as important, it could provide estimates of the uncertainty in the predictions. A quantification of uncertainties is especially useful if such data is to be used for site assessments and decision analysis applications.

Preliminary work has begun by assembling all the experimental data into a uniform digital format for analysis. Initial observations and analysis of the data indicate that out of the numerous input parameters that were varied in the experiments, only a few appear to control mass transfer processes.

Results also indicate that there are external factors influencing the experimental results that appear to add additional uncertainty into the analysis. One of the major external factors appears to be the degradation behavior of these energetic materials, especially TNT during the experiments. The extent of material degradation varied significantly between the experiments and makes comparisons between different experiments more challenging. The next stage will be the formal model development stage. This work will examine relationships between combinations of input and output data and identify important correlations that should be included in the final model.

4.0 Summary

4.1 Modeling Efforts

The Energetic Material Source Function is being extended to include Phase III experimental data and data. The effort will include a formal sensitivity study to identify the most important variables.

4.2 Path Forward – Near Term

The Energetic Material Source Function will be extended to include Phase III experimental data and data from different particle sizes. This extension will occur by May 2005. At that time, the project final report will be written.

4.3 Path Forward – Long Term

The Energetic Material Source Function generated by this project can be used in the development of screening models, which is the subject of a recent SON (CPSON-06-02, November 10, 2004).

4.4 Action Item Response

Action Item

In your Annual and Final Reports discuss the effect of the particle size on the movement of the material, i.e., the bi-modal behavior. The question is whether the 1000 μm particle is solid or collection of smaller particles that will easily break apart under these conditions (see work with 500 μm particle movement RDX-22 to RDX-25 and MT-22 to MT-25).

Response

The CompB material was not easy to break up. The 1000 μm material stayed as single particles when we put it into the test columns. We do not believe that the particles break apart from test column setup, and definitely not during the test.

References

Phelan, J.M., J.L. Barnett, and D.R. Kerr, 2004. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – FY03 Project CP-1227 Annual Technical Report. Sandia National Laboratories Report SAND2004-0039, January 2004.

Phelan, J.M., S.W. Webb, J.V. Romero, J.L. Barnett, F. Griffin and M. Eliasi, 2003. Measurement and Modeling of Energetic Material Mass Transfer to Soil Pore Water – Project CP-1227 Annual Technical Report, SAND2003-0153, January 2003.

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