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To Jim Phelan	From Melinda Trizinsky	
Co. Sandia	Co.	
Dept.	Phone # 703-739-1217	
Fax # 505-848-0543	Fax # 703-548-8773	

Field Demonstration of Slurry Reactor Biotreatment of Explosives- Contaminated Soils

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by J.F. Manning, Jr., R. Boopathy,
and E.R. Breyfogle

Bioremediation Group, Environmental Research Division
Argonne National Laboratory, 9700 South Cass Avenue,
Argonne, Illinois 0439-4843

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Field Demonstration of Slurry Reactor Biotreatment of Explosives-Contaminated Soils

1 Summary

The U.S. Army Environmental Center (USAEC) has conducted field demonstration studies at the Joliet Army Ammunition Plant (JAAP), located at Joliet, Illinois, on a bioslurry soil treatment system. These studies were conducted between July 1994 and August 1995. The overall goal was to determine the effectiveness and cost of bioslurry systems for degrading explosives in soil. The bioslurry system is another biological treatment technology (in addition to composting) that could represent an acceptable, cost-effective alternative to incineration for the treatment of explosives-contaminated soils. The bioslurry system achieved > 99% removal of explosives from the input soil and demonstrated mineralization of TNT. We estimate that bioslurry technology could be implemented for S290-350/yd³.

Bioslurry technology requires excavation of soil, screening of the soil to remove large rocks (larger than 0.25 in.) and plant roots, mixing of the soil with water to form a slurry, mixing of the slurry in a reactor, and finally removal of the slurry from the reactor. In addition, biodegradation of explosives requires a co-substrate (molasses in this case), pH adjustment (to pH > 6), and an aerobic-anoxic operating strategy. The bioslurry system can be operated as a batch or semibatch process, depending on site-specific conditions. The operation described in this report relied on the native microbial population to degrade explosives in soil.

Four reactors were operated at JAAP: a control with no co-substrate, a 20% weekly replacement (by volume) reactor, a 10% weekly replacement (by volume) reactor, and a 5% daily (four days per week) replacement (by volume) reactor. This design allowed investigation of different soil loading rates and therefore different TNT (2,4,6-trinitrotoluene) mass loading rates. All reactors had a target soil slurry of 15% (weight/weight [W/W]); in reality, the reactors operated with a 10-16% W/W soil slurry. The reactors were subjected to identical environmental conditions, and the temperature, pH, and dissolved oxygen level were approximately the same in all systems. The composition of molasses was consistent throughout the field demonstration. Explosives concentrations in soil were 2,000-8,000 mg/kg. The reactors had working volumes of 350-380 gal.

The results from the study indicated that the control reactor did not have the conditions necessary to achieve degradation of explosives. No co-substrate was added to this system. Over the period of the study, no explosives (TNT, RDX [hexahydro-1,3,5-trinitro-1,3,5-triazine], or TNB [1,3,5-trinitrobenzene]) were removed from the soil. In addition, none of the intermediates associated with TNT degradation was observed. These results confirmed that added co-substrate is needed for degradation of TNT.

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The 20% weekly replacement reactor (with a soil retention time of five weeks) demonstrated the capability to degrade TNT effectively. When the temperature was above 25°C, the residual TNT concentration in the soil was less than 50 mg/kg, and the 4-amino-2,6-dinitrotoluene (4A26DNT) concentration was less than 100 mg/kg. In addition, RDX and TNB levels were below 10 mg/kg. When the temperature was below 25°C, the biological system could not maintain this high rate of TNT degradation, and significant accumulation of the 4A26DNT intermediate occurred.

The 10% weekly replacement reactor (with a soil retention time of ten weeks) had a large capability to degrade TNT. In addition, RDX and TNB were effectively removed to residual concentrations in soil of less than 10 mg/kg. When the temperature was above 25°C, the residual TNT in the soil was less than 20 mg/kg, and the 4A26DNT level was below 10 mg/kg. When the temperature was below 25°C, TNT removal continued with very little change in soil concentrations, but 4A26DNT accumulated to concentrations of 100 mg/kg.

The 5% daily replacement reactor (with a soil retention time of five weeks) had a large capability to degrade TNT. On the basis of mass, this reactor was similar to the 20% weekly replacement reactor, but the concentrations of explosives surrounding the microorganisms at any particular time were significantly less. In this system, TNT was removed to levels below 20 mg/kg, and the 4A26DNT concentration was less than 50 mg/kg. When temperatures were below 25°C, the TNT concentration was less than 200 mg/kg, and 4A26DNT accumulated significantly in the system.

A laboratory study with radiolabeled TNT was conducted on samples from the control reactor, the 20% weekly replacement reactor, and the 5% daily replacement reactor. The purpose of this study was to measure the mineralization of TNT by the reactors. The sample from the control reactor generated essentially no radiolabeled carbon dioxide; in samples from the active reactors, approximately 20-23% radiolabeled carbon dioxide was generated from the radiolabeled TNT, indicating that ring cleavage had occurred. Most of the remainder of the radiolabel was distributed in water-soluble biomass and fatty acid intermediates. A very small fraction was incorporated into 4A26DNT.

Overall, the important process parameters, as determined in this field demonstration, are the need for an organic co-substrate (molasses), the operation of the reactors in an aerobic-anoxic sequence, and temperature. In warm temperatures, operation of the system at 20% (or higher) replacement will achieve removal of explosives. Cold temperatures did not destroy the microbial activity, but they slowed the rate of microbial metabolism. In particular, degradation of TNT continued with the accumulation of 4A26DNT. The reactors were operated successfully at lower replacement rates ($\leq 10\%$) in cold weather. The treated soil (bioslurry) can be applied directly to land and will not affect plant growth. In summary, the bioslurry system has a real potential to remove explosives, particularly TNT, from soil.

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The purpose of this report is to summarize all procedures and activities associated with the bioslurry field demonstration. The results of the field activities are presented, along with a discussion.

Previous studies supporting the field demonstration described here were reported in the following documents:

- Montemagno, C.D., and Irvine, R.L., 1990. *Feasibility of Biodegrading TNT-Contaminated Soils in a Slurry Reactor*, Technical Report CETHA-TE-CR-90062, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland, prepared by Argonne National Laboratory, Argonne, Illinois, June.
- Montemagno, C.D., 1991, *Evaluation of the Feasibility of Biodegrading Explosives-Contaminated Soils and Groundwater at the Newport Army Ammunition Plant*, Technical Report CETHA-TS-CR-92000, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland, prepared by Argonne National Laboratory, Argonne, Illinois, June.
- Manning, Jr., J.F., Boopathy, R., and Kulpa, C.F., 1995, *A Laboratory Study in Support of the Pilot Demonstration of a Biological Soil Slurry Reactor*, Technical Report SFIM-AEC-TS-CR-94038, U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, prepared by Argonne National Laboratory, Argonne, Illinois, July (available in print and on CD-ROM).

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6 Conclusions

On the basis of the data presented in Section 5, the following major conclusions are drawn from the bioslurry field demonstration:

- Bioslurry systems can be used effectively to bioremediate soils contaminated with TNT, RDX, TNB, and DNT to a variety of treatment goals. This study demonstrated that TNT can be removed to levels below 20 mg/kg. In warm weather, the 20% replacement strategy will meet all treatment goals.
- Aerobic-anoxic operation and co-substrate are necessary for removal of explosives from soil.
- The treated material is suitable for land application, as demonstrated by removal and mineralization of explosives and by the plant growth studies. Residual carbon is removed by natural soil degradation.
- The systems achieved different removal levels of TNT from soil, depending on the mass of soil replaced each week and the temperature. Under similar conditions, the 10% replacement reactor performed slightly better than the others.
- Temperature plays a major role in determining the amount of TNT degraded and the subsequent degradation of the 4A26DNT intermediate. Degradation of intermediates is affected at temperatures below 25°C, and accumulation of intermediates becomes a significant operational concern at temperatures below 15°C.
- Readaptation after temperatures fell below 25°C took longer than adaptation at start-up. The biological mechanism for this phenomenon is unknown, but it might have to do with changes in the microbial population.
- Recycled process water after dewatering is an acceptable source of water for slurry preparation. The crucial factors affecting the use of recycled process water seem to be accumulated salts (Na^+ , Mg^{2+} , and Ca^{2+}). In addition, K^+ and HCO_3^- were found in the process water and soil (Griest et al. 1997).
- Significant reaeration by the mixing equipment occurred in these systems, resulting in conditions where oxygen was added to the system constantly in

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small quantities, in addition to the aeration accomplished by the forced-air diffusers.

- Approximately 20-23% mineralization was achieved in a laboratory study on samples removed from the reactors. Approximately 55% of the remaining radiolabel was converted to biomass and fatty acids, representing ring cleavage but not mineralization.
- The bioslurry system is relatively simple to operate and can be implemented with commercially available equipment. A safety review addressing explosives should be conducted before any equipment is used in areas where explosives can concentrate and become a hazard to human health or equipment.

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7 Lessons Learned

In addition to the specific technical data and discussion already presented, a variety of observations were made that might prove valuable in implementing a bioslurry process at a large scale. These lessons relate to the specific conditions of the JAAP field demonstration and are not directly quantifiable; however, they do result from extensive operating experience. Actions taken in response to these observations should not directly affect the bioslurry process but could enhance operation of a bioslurry system. The following are the general observations:

- The major lesson learned concerns the adaptability of the bioslurry treatment process to a variety of different cleanup standards. The frequency of replacements and the volume of replacements could be increased greatly, depending on the amount of explosives that could remain in the soil. For example, with a risk-based cleanup standard for TNT of 150 mg/kg, a 10% reactor could be operated all winter, and then in the summer, replacements could be increased to 50%. This strategy would greatly increase the throughput of soil and reduce the cleanup time and cost. In some cases, the determining factor in reactor operations will be DNT, which often has a risk-based cleanup concentration below that of any other explosive. DNT can be removed from soil by microorganisms.
- Process monitoring could be reduced from the intensive sampling regime implemented in this field demonstration. Daily sampling for pH and DO is not necessary, particularly after the operating characteristics of the reactors have been determined. Automatic recording of pH and DO levels might be suitable.
- Foaming of the reactor contents upon the addition of air through the diffusers needs to be monitored and controlled. No foam control was attempted in this demonstration, but additives are available for that purpose. Foam control is difficult and expensive. The addition of a foam warning system or an antifoam addition system would be a cost consideration. Foam can be controlled by careful monitoring of air addition.
- The reduction in soil particle size needs to be monitored, because the size of the particles after bioslurry treatment directly affects dewatering or ultimate land disposal. It might be possible to operate reactors with different mixing configurations or strategies to diminish the particle size reduction. It might also be possible to operate the reactors with intermittent mixing if the motors used can resuspend the slurry. The ability of a mixing system to suspend the material to be treated must be investigated. The torque, horsepower, and shape of the mixer are significant considerations.

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- Water supply requirements for a full-scale facility need to be examined. The source of water and its constituents (particularly heavy metals) must be evaluated for potential negative effects on the biological process.
- EPA Method 8330 should be used to analyze the initial soil and the treated slurry at the end of processing. EPA Method 8330 is the method of choice for determining accurately when intermediates have been removed.
- Field test kits should be evaluated for use in monitoring TNT concentrations approximately weekly during adaptation and operation.
- Adaptation might proceed faster than indicated in this report. The operators in this study allowed the system to adapt very slowly to develop operating experience. Molasses could be added aggressively on a weekly basis during adaptation. This strategy would shorten the adaptation period.
- Adaptation after temperatures fall below 25°C needs to be examined carefully. Operation as a batch process to remove intermediates might improve throughput. This procedure could reduce the operating problems encountered at temperatures below 25°C and could alleviate accumulation of 4A26DNT.
- pH control is required if the pH drops to below 6.0. The process can operate at a wide range of pH values between 6.0 and 8.0. The process tended to operate naturally at pH 6.0.
- Final soil disposition should be considered as part of the feasibility study process. Depending on how the soil is ultimately disposed, significant cost savings could result. After this demonstration, direct land application was used for disposal of the soil.
- The steps in operating a full-scale system are excavation, soil screening, slurry preparation, molasses addition, air addition, mixing, chemical analysis (particularly for explosives and pH), and soil disposition.
- Sampling is designed to maximize process efficiency. Field test kits can identify when TNT and other explosives have been removed from the system. Test kits can also estimate when EPA Method 8330 should be used. This determination will be based in part on site-specific operational experience, but the analyses should begin approximately five days after molasses addition. An appropriate pH level is required to operate the microbial process efficiently: pH should be measured every other day. Dissolved oxygen levels should be measured every day after air addition.

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- The bioslurry process is extremely flexible and resilient in its operation. In this demonstration, the performance of the 20% replacement reactor in warm weather was equivalent to that of the 10% replacement reactor. In cold weather, a 10% replacement reactor can be operated to achieve desired cleanup standards. This observation supports the *potential* for year-round operation. The decision to operate year-round is an economic consideration, not a performance issue.
- The complete removal of explosives in the 20% replacement reactor during warm weather indicates that higher replacement volumes could potentially be accommodated.
- A potential problem with operating a bioslurry system to more stringent cleanup levels (i.e., TNT levels of 150 mg/kg) is the accumulation of intermediates in the slurry.
- The amount of soil in the slurry (15% in this study) was limited by mixer design. Other mixing systems might allow operation with a 20-40% slurry.
- Heating methods investigated included heat tape wrapped around the reactors, addition of steam to the slurry, and heating the input water. These methods were not implemented because of safety concerns or cost. Insulation and area heating were used in this demonstration. Insulation of a full-scale system would probably be cost-effective and would take advantage of heat generation by the microbes during metabolism. Area heating systems are not cost-efficient.