

SERDP FINAL REPORT



Removal, Degradation, and Recovery of Energetics Residues from Range Scrap CP-1196



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CP-1196 Removal, Degradation and Recovery of Energetics Residues from Range Scrap

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PROJECT BACKGROUND

This research project addressed DoD's need for more effective, lower cost methods for treatment of energetics residues on scrap materials at military training/testing installations as identified in SEEDSON-01-08. There is an immense backlog of scrap from closed ranges and training areas in both the United States and Canada that have not yet been cleared as well as on active ranges that will have to be removed routinely in the future. Although the total mass of residual energetics materials (EM) remaining on range scrap is likely to be quite small compared to the amount of EM delivered, there is a significant potential risk for soil and groundwater contamination from EM that are exposed to weathering processes (Appendix B, Figure 1). Of course, if a critical mass of EM is present, there is also the risk of a detonation occurring during recycling or other processing of the scrap.

Following normal operating procedures, Explosive Ordnance Detonation (EOD) personnel segregate all scrap with visible indications of energetics residues, as well as scrap materials that contain hidden recesses, and treat it as Unexploded Ordnance (UXO) material destined for either open burning or open detonation - a process that is no longer considered an acceptable disposal alternative. The segregated items are considered too dangerous to remove from the range and have been "blown-in-place" using either a supplemental explosive charge or by gunfire. Neither procedure produces a reliable high-order detonation wherein nearly 100% of the EM is consumed. The resulting low-order detonation results in additional residual EM being distributed around the range.

There is also scrap with a difficult to detect surface coating of unexploded EM. The presence of an "invisible" surface coating was first discovered by this project's Principal Investigator (PI) on LAW rocket scrap recovered from a Canadian military site. The rocket scrap was contaminated with 50 mg/kg (50 g/metric ton) of HMX and trace level TNT. Although the more concentrated energetics residues in cracks and fissures or on surfaces overlooked by EOD personnel are potential sources of detonations during thermal treatment or other processing methods (as little as 1-mm thick deposits can support a detonation), regulations require that scrap also be free of the "invisible" energetic coatings.

To date, the most advanced energetics residue treatment technology is a hot-gas system developed by the US Army Environmental Center to decontaminate high-value scrap recovered during the decommissioning of manufacturing and processing facilities. The ability to reclaim valuable fittings, valves, pumps, blowers and processing assemblies and to sell recyclable scrap at premium prices helps offset the high cost of procurement, operation and maintenance of this technology. Indeed, hot-gas treatment requires expensive capital equipment (e.g., temperature resistant chambers, burners, stack-gas scrubbers, controllers) and continuous energy inputs. Range scrap, however, is typically found as small pieces that are deteriorated from exposure to detonation, burning and/or weathering. It is not a high-value product, offering little opportunity for recouping costs through the sale of decontaminated material. Furthermore, many types of range scrap contain volatile toxic metals, plastics and rubber components that produce hazardous emissions during hot-gas exposure, and are therefore not treated by that technology. Nevertheless, a recent ESTCP project considered a less expensive embodiment of the process wherein large piles of scrap were covered with insulating blankets and treated with hot gas. Results from that investigation are pending.

A second approach that has been awarded an ESTCP contract is the UXBase hot caustic treatment. Decontamination with UXBase is restricted to materials (i.e., metals) that will not be dissolved by 3M NaOH at 80°C and to scrap that is not visibly contaminated with residual energetics since the first step in the process is shredding.

A cleaner, less expensive, more reliable (simpler), and more widely applicable technology is clearly needed for treating range scrap, *particularly fragments contaminated with detonable residues and bulk (chunk) energetic materials ejected from low-order detonations.*

During the course of a previous research project aimed at investigating the effects of lime (which is used to improve the friability of soils during *ex situ* remediation) on the analysis of explosives by EPA Method 8330, the PI discovered that solid TNT and RDX residues on soils could be completely dissolved in aqueous solutions containing small quantities of inexpensive, agricultural lime. In the basic limewater (calcium oxide) solutions, complete dissolution of crystalline explosives occurred in a few weeks; surprisingly, the quantities dissolved far exceeded the reported aqueous solubilities of these compounds. Following dissolution, it was observed that insoluble polymers of TNT and RDX formed and precipitated from solution. Preliminary characterization of the precipitates as well as mass balance determinations indicated that nearly all of the dissolved energetics were reacted and recovered as polymers. The remaining mass consisted of small quantities of benign formate, acetate, and nitrite ion degradation products of the explosives.

The current research project investigated limewater as a low-cost, simple, environmentally benign decontaminant with potential to remove and degrade energetics residues from scrap materials of virtually any size or type (metal, wood, rubber, plastic, cardboard, etc.) found on training/testing ranges at DoD installations. Formation of insoluble polymers that can be collected as solids was investigated as an efficient means to minimize the volume of waste produced from large volumes of contaminated scrap and facilitate waste handling.

OBJECTIVE

Our objective in this project was to investigate limewater-based approaches to decontaminating range scrap. Effort was focused on developing solvent formulations and procedures for the aqueous treatment (dissolution, degradation, and polymerization/recovery) of TNT and RDX, including Composition B (CompB), on scrap materials. Specific technical objectives of the project were the following:

- (1) Determine limewater solution conditions that maximize the speed of solid energetics dissolution and degradation.
- (2) Determine limewater solution conditions that provide maximum yield of polymers from degraded energetics.
- (3) Establish an optimum treatment formulation and laboratory scale procedure for treating energetics residues on real range scrap.
- (4) Perform a preliminary cost analysis of the most favorable treatment schemes.

TECHNICAL APPROACH

Our approach offers to advance the state-of-the-art in scrap decontamination in several key areas. First, by converting the energetics to innocuous ions and solid polymers, a compact, easily isolated and handled waste product will be formed. Air emissions and large volumes of highly contaminated hazardous liquid waste are avoided. Second, start-up equipment and formulation costs for treating up to 4 tons (5 cu yd) of scrap at a time are estimated to be less than \$50K - at least an order of magnitude lower than baseline technologies. Operational costs are also expected to be exceptionally low as minimal labor is required and energy costs are restricted to one modestly sized pump. Third, the simplicity of the soaking treatment approach enhances its reliability - there is little equipment to malfunction. Fourth, because the proposed treatment is chemically mild, it will be compatible with most scrap material - metal, wood, plastic, rubber, etc.

The technical research program consisted of three major tasks. A brief overview of the work conducted under each task is provided below. The experimental methods and results for each task are described in greater detail in the Project Accomplishments section of this report.

Task 1. *Limewater Treatment Formulation Development.* Experimentation began with the simple limewater solution (1 lb lime/100 gal water) that was observed to dissolve and polymerize explosives in a previous study. Although that solution was an effective polymerizer of TNT and RDX, the dissolution process for the solid energetics was exceedingly slow. Therefore, under this task we investigated modifications to the basic limewater formulation to increase both the dissolution and polymerization rates of secondary high explosives (HE).

Task 2. *Treatment of Real Military Range Scrap.* The U.S. Army's Cold Regions Research and Engineering Laboratory (CRREL), which is local to ARA's New England Division, provided us with a limited number of low order detonation fragments from a hand grenade range. The fragments were contaminated with thin layers (<1 mm) and thicker "chunks" (>3 mm) of CompB. These few fragments were tested in only the best candidate decontamination solutions as determined in Task 1.

Task 3. *Biological Treatment of Decontamination Solutions.* This task was added to the research plan after it became clear that residual, colored polymeric reaction products could remain dissolved or suspended in the decontamination solutions for considerable periods of time.

SUMMARY

This final report constitutes the deliverable for this exploratory research project. It includes a detailed discussion of the experiments performed, their results, and conclusions drawn from the results along with recommendations for future development and implementation of the new technology. As part of the conclusions and recommendations for future work, a conceptual design for a pilot-scale treatment system is presented. The system allows for a few chemical parameters to be measured in the field to ensure the efficacy of the treatment process (this can be extremely difficult in other processes). Another important element of the report is an initial cost analysis estimate for a field-scale version of the two most promising treatment schemes. Key parameters in the analysis are reagents, equipment, and energy costs.

PROJECT ACCOMPLISHMENTS

Introduction

The general treatment approach we proposed to investigate was to soak scrap in a mildly alkaline solution of aqueous lime (calcium oxide and/or calcium hydroxide). The reaction chemistry of energetics in base solution is an active area of research. Of particular relevance to this project, researchers in Germany recently demonstrated that TNT hydrolyzed with an equal weight of strong base (sodium hydroxide) produced polymers of molecular weight (MW) 1,000-30,000 daltons. In another study, RDX was degraded to nitrite, organic acids, formaldehyde and various gases under strong base conditions and no polymers were formed. Similar reaction mechanisms and end products can be produced *in situ* by stimulating natural, biological degradation. Our approach is markedly different from others in that we will use commercial lime, a comparatively weaker base, as the active chemical ingredient in our formulation. During a previous investigation, the PI discovered that both TNT and RDX, as well as mixtures of the two explosives, formed large quantities of insoluble polymers when added to aqueous calcium oxide solutions. Characterization of the TNT-polymers by N-15 and C-13 NMR and elemental analysis (Appendix B, Figure 2) clearly indicated that calcium was incorporated into the polymers via binding to carboxylate, phenolate, and other functional group moieties. The complex structures (i.e., functional groups) formed by TNT and RDX in limewater were very similar to the TNT-humic compounds that were studied by the PI and others in an earlier SERDP project (CU-715). It is notable that the humic bound TNT was discovered to be bio-unavailable. Thus, it is reasonable to expect that energetics treated with limewater may be similarly rendered bio-inert by binding to organic biomass (e.g., sludge or compost). The sequestration of energetics in bio-unavailable products is a proven and accepted solution to eliminating the toxicity of energetics-contaminated soils.

Methods

Task 1. Limewater Treatment Formulation Development.

Under this task we investigated various formulations of basic limewater solution with the objective of increasing the dissolution rate of secondary HE. Test materials were neat TNT and CompB. These materials were selected for initial study because they represent over 90% of the HE present at contaminated military sites. Experiments were performed with 1-5mg solid HE (Kodak technical grade TNT or military grade CompB) and 5-10mL decontaminant solution contained in 22mL capped glass vials. Dissolution rates were determined visually, i.e., by observing the time required for complete dissolution of the energetics. Small aliquots (10 μ L) of the test solutions were analyzed periodically by High Performance Liquid Chromatography (HPLC) to follow the formation of degradation products during dissolution.

In addition to room temperature testing (ca. 65 $^{\circ}$ F), dissolution experiments were performed at the extremes of ambient temperatures (e.g., at 35 and 100 $^{\circ}$ F) by placing samples in a cold anti-room and a furnace room. Although it will not be our objective to ultimately control the temperature of the treatment formulation in the field, as this would add considerable cost to the treatment process, our goal in this task was to understand the effect of temperature on dissolution, degradation and polymerization so that a formulation could be developed which was effective and predictable at all ambient temperatures. Experiments were performed under both static and dynamic (stirred solution) conditions.

The first approach to enhancing the dissolution kinetics of energetics was to maximize the lime concentration (increase the pH). The solubility limits and solution pH of both calcium oxide (quicklime) and calcium hydroxide (slaked or hydrated lime) were determined. Sodium hydroxide was also investigated as a low-cost additive to lime to determine if even more alkaline conditions accelerate dissolution.

A second means to enhance dissolution kinetics is to add miscible organic solvents to the limewater. It is well known that pure acetone dissolves large quantities of solid HE in just a few seconds; however, the flammability of neat acetone presents some risk at explosives-handling facilities. We investigated the high-boiling solvents, 2-butoxyethanol (butyl cellosolve), available as Dowex-EB (DX), and isopropanol in addition to dilute acetone as dissolution agents for TNT and RDX. We also investigated formulations composed of various light alkanes, detergents and emulsifiers available commercially as biodegradable, "green" cleaners. Two formulations, SuperSolve (SC) and SC-1000, procured from GEMTEK (Phoenix, AZ), were studied. Both are proprietary mixtures of alcohol ethoxylates, tall-oil fatty acids and surfactants. The DoD has already invested heavily in adopting such environmentally benign formulations to replace hazardous, ozone-depleting or toxic chemicals. Adapting a "green" washing system that is already part of military operations for the present application would create a substantial dual-use benefit; although costs of these cleaning additives are higher than polar solvents. The "green" cleaners were tested full strength and diluted in limewater solution, as was the DX additive.

The second major element of this task was to identify and optimize conditions promoting the polymerization and precipitation of HE. Lime concentration, sodium hydroxide additive and the alternative solvents described above were investigated for their effect on polymerization as well as their solvating properties. For the polymerization and precipitation tests, we used the HE solutions produced in the dissolution tests. The progress of polymerization/precipitation was assessed by observing the accumulation of precipitate and by estimating the residual color of the supernatant. The supernatant solutions were also analyzed by HPLC for un-reacted explosive as well as to follow the formation and transformation of degradation products into dimers, polymers or other products. HPLC analyses were performed on solutions withdrawn from vials used in the 100°F experiments and from additional combinations of TNT and Comp B dissolved in various decontaminant solutions of interest. TNT and RDX as well as polar degradation products were analyzed using reverse-phase chromatography with UV absorbance detection at 254nm. The ionic degradation products nitrite and acetate were analyzed by mobile-phase ion-pair chromatography with conductivity detection. Nitrite is released from both TNT and RDX, while acetate is formed when the hydrazine ring of RDX is cleaved and the daughter products rearrange. Column chromatography using a size exclusion gel (Sephadex G-15) was used to fractionate solutions into molecular weight ranges. Our goal was to ensure that only benign, low concentration degradation products such as acetate and nitrite are ultimately formed (in addition to polymer) during treatment. Inexpensive and innocuous metals including zero-valent iron, zinc, and titanium dioxide were investigated as catalysts for polymerization and precipitation of HE. Flocculation with bentonite was also evaluated as a means to enhance polymer precipitation (i.e., reducing polymer solubility).

Task 2. Treatment of Military Range Scrap.

Low order detonation fragments from a hand grenade range that were coated with thin (<1 mm) and thick (>3 mm) layers of CompB were soaked in various acetone/limewater and SC/limewater formulations and periodically withdrawn for observation. The pieces of scrap and decontaminant solutions were placed in 400-mL beakers and stirred using a magnetic stir-bar. The soaking times required to remove the deposits were determined visually.

Task 3. Biological Treatment of Decontamination Solutions.

This task was not included in the original proposal. However, it was added after it became evident that although acetone and "green" cleaner significantly increased the rates of dissolution vs. limewater alone, they also slowed down the yields of precipitated polymers. Elevated pH, metal catalysts, and flocculent did not significantly enhance the production of solid polymers. Two biological treatments were investigated for the removal of reaction products from the limewater wash solutions - (1) activated sludge wastewater treatment, and (2) composting. For these experiments, solutions of CompB dissolved in 25% solutions of acetone/limewater and SC/limewater were added incrementally to 2L batches of mixed liquor from a local treatment facility and to 250-mL beakers of a compost mixture (manure, woodchips, grass clippings and garden soil). After 10 days, the supernatant from the liquor was decanted and analyzed. The sludge and compost were dried and extracted with water, then dried again and extracted with acetone. Both the aqueous and acetone extracts were examined visually for color (red) and by HPLC to determine if residual HE or low concentrations of their reaction products were present.

Results and Discussion

Task 1. Limewater Treatment Formulation Development.

Preliminary experiments were carried out to determine which formulations would be used for the first round of dissolution experiments. The quantity of lime (calcium oxide) that was first proposed (1lb/100 gal water) was actually close to the solubility limit. Because lime is not an especially strong, or water-soluble base, it was expected that concentrations near the solubility limit would be required for rapid treatment of energetics. This proved true, as lime concentrations less than about 0.01% did not effectively dissolve the HE. Therefore, a 0.1% mixture of lime in reagent-grade water was used for the initial soaking experiments. The solution was measured to be pH 12.4.

In the first major round of dissolution tests with TNT, the solutions were left undisturbed at room temperature. The test matrix included 10%, 25%, and 50% solutions of DX and acetone in 0.1% limewater, as well as 100% SC and SC-1000 cleaners. The solution of 50% acetone in 0.1% limewater was the most effective solvent, dissolving a 1mg TNT chip in just a few hours. A deep red solution was produced almost immediately upon mixing, indicating the formation of Meisenheimer anions. The rest of the test solutions turned red but did not dissolve the entire chip within a day. After three days in the test solutions, the entire chip had been dissolved by the 25% acetone and 100% SC cleaner and an appreciable portion of a chip was dissolved by the 50% DX formulation. Little or no TNT was solubilized by the SC-1000 cleaner in three days, so it was eliminated from further experimentation.

In the course of the static tests, it was observed that the dissolution process was diffusion-limited. The test chips turned very dark red, as did the immediately surrounding solution. After three days, the intact chips were surrounded by an almost opaque red solution that remained at the bottom of the vials. It was hypothesized that under static conditions the formation of a coating of red hydrolysis products on the chip surface would eventually impede further dissolution and degradation. To test this theory, a second set of dissolution experiments was performed with a small amount of mixing to distribute the dissolved and hydrolyzed material away from the chip surface. The gentle washing action was accomplished by mounting a set of vials on a tilted wheel that rotated slowly so that the fluid was moving relative to the chip, but without producing any mechanical agitation. For comparison, replicate samples were tested statically. Chips of 5mg TNT or CompB were tested in the following solutions: 0.1% lime; 10%, 25%, and 50% acetone; 10%, 25%, and 50% DX; and 50%, 75%, and 100% SC. The tests were performed at 100°F. The beneficial effect of even minimal stirring was apparent in a few days, as several of the stirred samples were completely dissolved (Appendix B, Figure 3). Since the

stirred SC formulations were working well, two additional samples of TNT with 25% and 10% SC solutions were added to the rotating wheel after two weeks. The 100°F experiments were terminated after 30 days. The results (Appendix B, Figure 3) clearly show that stirring had a strong positive influence on dissolution and that 50% acetone was the most effective formulation tested. High concentration SC formulations (75% or more) were also effective. At 100% SC, dissolution was complete within two days, even without stirring.

The experiments were repeated at 35°F. A slightly modified set of formulations was used and included 0.1% lime; 10%, 25% and 50% acetone; 50% DX; 10%, 50% and 75% SC; and 0.1% NaOH. As shown in Appendix B, Figure 4, the effect of reduced temperature was dramatic. Except for the 50% acetone formulation, which effected dissolution in two days with stirring, only the 50%DX and 75% SC had dissolved the chips after 40 days, even with gentle stirring. The addition of NaOH did not improve results measurably compared to limewater alone. Clearly, the decontamination process will require longer periods with high concentrations of additives during spring and fall clean-up at far northern ranges.

All of the soaking solutions discussed above resulted in mixtures that initially contained TNT, RDX and red-colored Meisenheimer complexes when analyzed by HPLC. Following complete dissolution of a TNT or CompB chip, the dissolved explosives persisted for a time and then disappeared as they degraded. Typically, several new species appeared in the reverse-phase chromatograms and increased in quantity for a time before also disappearing. To further elucidate those species, aliquots of the decontamination solutions were spiked with a pink colored molecular weight tracer (Rhodamine WT, MW 480) and passed through the G-15 gel filtration column. The fractions were collected and re-injected onto the HPLC. The major peak that appeared in the lime, acetone, and SC containing solutions appears to have a molecular weight of almost 400 daltons (Appendix B, Figure 5) and is probably a dimer derived from de-nitrated TNT. Interestingly, the dimer did not appear in the formulations containing DX. The formation of the dimer was fastest in the solutions containing acetone and SC; however, it also persisted longer in those formulations than for limewater alone, probably due to better solvation. Nevertheless, as polymerization progressed, the dimer intermediate concentration decreased. In the case of the limewater and mixed acetone formulations, the loss of dimer and formation of larger MW polymers was observed as a solution color change from deep red to pale yellow. As the concentration of acetone increased, the color remained darker and less precipitate was formed because the acetone enhanced polymer solubility. The SC solutions, although no longer containing the dimer, remained dark red with no precipitate. Presumably, the polymers that formed were maintained in solution by the SC detergent micelles - as is intended for this type of cleaning product. The DX solutions also remained a deep red color with no precipitate, no detectable dimer and no evidence of polymerization (all components were of molecular weight less than the dimer).

Ion pair HPLC analysis revealed that the degradation products acetate and nitrite did not appear until after the explosives were completely dissolved. Surprisingly, some acetate appeared in the TNT dissolution experiments when NaOH was included in the limewater formulation - the source of the acetate is unclear. Some acetate was removed from the acetone solutions during polymerization, presumably having been incorporated into the polymers. Approximately a third of the nitro groups that were present in the TNT and RDX were recovered from the acetone and SC formulations as inorganic nitrite that remained in solution.

Overall, the HPLC results indicate that the predominant products formed from TNT and RDX by the most effective decontaminant solutions (acetone or SC in limewater) are the desired polymers and innocuous anions such as nitrite and acetate. No residual EM persists in the soak solutions. The most effective dissolution formulations (100% SC and 50% acetone) are also most effective at solubilizing the polymers. The products of DX treatment are uncertain.

We were initially concerned with the potential flammability hazard associated with the use of acetone and recommended that alternative high-boiling solvents should be investigated in this project. The performance of DX was generally poor, so an additional high-boiling solvent, 70% aqueous isopropanol, was also tested at 0.1% lime concentration. The isopropanol formulation dissolved the TNT and CompB chips at a rate comparable to 10% acetone; however, the RDX that dissolved did not degrade substantially and no evidence for polymerization of TNT was observed (i.e., a gel filtration separation indicated that all red colored products were of lower molecular weight than the dimer that was produced in the basic acetone solutions). In short, neither DX nor isopropanol is a suitable substitute for acetone.

The excellent performance of dilute solutions of acetone in limewater suggested reconsideration of its flammability. It is a critical point that the volatilization rate of acetone from aqueous solutions is substantially reduced in direct relation to the concentration. Acetone evaporates from a 10% aqueous solution at 10% of the rate of neat acetone because only 10% of the molecules at the solution-air interface are acetone. To test this further, a portable gas detection instrument (Photovac PID) was used to measure the concentration of acetone vapor above a 4L open bucket containing a 35% solution of acetone in aqueous limewater at 90°F. A magnetic stir bar was used to agitate the solution and the surface was covered with a 3-inch layer of 1-inch diameter plastic balls commonly used to reduce evaporation from open vessels. The measured Short Term Exposure Limit (STEL, a 15 minute moving average) value never exceeded 700ppm, which is well below the 25,000ppm LEL (Lower Explosion Limit) for acetone. Thus, aqueous formulations of up to the 50% acetone used in this study should be acceptable as scrap decontaminants.

Additional experiments were conducted to determine if the rate of polymerization/precipitation of TNT and RDX degradation products could be enhanced. Flasks containing 100mg of CompB in 100mL of limewater solutions of 25% acetone, 25% SC or 70% isopropanol were stirred with a magnetic bar until the EM dissolved. The solution was distributed as 10mL aliquots in separate vials. Powdered catalysts were added to see if these affected the reaction rates. Titanium dioxide, zinc and iron dust (10-20 μ m particle size) had no measurable effect on polymerization rates. Bentonite was added to determine if flocculation would precipitate the polymers. This flocculent did not enhance precipitation over the control samples, even when pH adjustments were made either to neutralize or acidify the solutions. The results indicate that further work with catalysts and flocculents offers little promise for improving the yield of insoluble polymers. However, the more aggressive stirring used in this series of experiments revealed that the rate of RDX degradation is slow in SC compared to acetone. With minimal agitation, many days were required for dissolution in 25% SC and the solution concentration of RDX remained low at all times (TNT was dissolved more efficiently). With stronger agitation, the RDX was dissolved quickly, but the subsequent degradation was slow. The faster EM destruction rate in acetone can be explained by its participation in the chemical degradation reactions. Acetone is a Lewis acid, losing a proton to form the enolate ion ($\text{CH}_3\text{-C}=\text{O-CH}_2^-$) in base. This ion is then available to react with TNT and RDX, increasing the rate of hydrolysis. Thus, it appears that acetone is not only a superior solvent but also an accelerator of degradation (Appendix B, Figure 5).

Task 2. Treatment of Military Range Scrap.

A fortuitous discussion with a civil engineer brought to the PI's attention the burn hazards associated with quicklime (CaO) as opposed to hydrated (slaked) lime (Ca(OH)₂). It is unlikely that military personnel or contractors will want to handle the bulk quantities of quicklime that the proposed decontamination protocol will require. Thus, quicklime was replaced by an equal weight of hydrated lime for the tests with authentic range scrap. The substitution did not measurably affect decontamination performance, but improved the safety of the method.

Fragments from low order detonations of hand grenades were obtained from several ranges. The pieces of scrap contained visible deposits of residual CompB that ranged from thin (<1mm) coatings to residues over 3mm thick. Removal of the deposits from authentic ordnance scrap proved much more difficult than the dissolution of isolated chips of TNT and CompB that had been achieved in prior experiments. This was most likely due to strong adhesion to the scrap metal surfaces. For example, vigorous agitation over 14 days was required to remove the *thin* residues from fragments placed into either 25% solutions of acetone/limewater or SC/limewater (Appendix B, Figure 6). Microscopic examination of particles of CompB from the laboratory test batch that was used for preliminary experiments were compared to the military-grade CompB removed from the hand grenade. The most important observation was that neither CompB mixture was uniformly composed of RDX and TNT. Rather, CompB consists of RDX crystals suspended in a matrix of TNT. The laboratory-grade CompB had smaller, more uniformly sized RDX crystals compared to the military-grade material. When the decontaminant formulations were added to the samples, the TNT dissolved first, releasing RDX crystals (Appendix B, Figure 7). Thus, thin layers of CompB were both dissolved and disintegrated (decomposed in EOD terminology) by the formulations.

Fragments containing *thick* CompB deposits were also placed in beakers containing either 25% solutions of acetone/limewater or SC/limewater and agitated for 14 days. The results for the thick deposits were considerably different than for the thin residues (Appendix B, Figure 8). CompB was removed almost completely by the SC solution; however, a large amount of the disintegrated (released) RDX remained as crystals that settled out when stirring was stopped. In acetone solution, the thick deposit became dark red-brown and was resistant to removal. The deposit was later pried from the scrap and broken open to reveal that polymerization of TNT had occurred throughout the entire mass of CompB, resulting in the RDX becoming trapped in an insoluble polymer matrix (Appendix B, Figure 9). Furthermore, we observed that CompB from the thinly covered parts of the fragments was also transformed into polymeric products that redeposited on metal surfaces, coating the entire fragment inside and out. This precipitate was not easily removed by rinsing with water (as was the case with the SC products). Active scrubbing was required to clean the previously uncontaminated surfaces.

In order to assess the effectiveness of more aggressive dissolution conditions on cleaning authentic scrap, the last grenade fragments containing thick deposits were placed in beakers containing either 75% SC/0.5% limewater or 50% aqueous acetone *without limewater*. Under either set of conditions, the fragments were completely cleaned within 48 hours. As in the previous tests, the SC did not dissolve all of the RDX in that time, but it did remove all of the CompB from the scrap. Both TNT and RDX were completely dissolved by the aqueous acetone; however, without added base, little of the TNT was transformed to polymeric products. The solution did turn the characteristic red color of the Meisenheimer anion since a small amount of acetone dissociates to form the enolate anion in aqueous solution. Furthermore, when 0.5% lime was mixed into this highly contaminated (3000mg/L TNT and 2300mg/L RDX), deeply colored solution, complete degradation of the TNT and RDX was accomplished in 24 hours as determined by HPLC. Precipitation began as soon as agitation ceased and proceeded for nearly two weeks when the decontamination solution was substantially decolorized (Appendix B, Figure 10).

SC is chemically stable as formulated at pH 10; however, its stability in limewater at pH 12.4 is unknown. There is reason to believe that the activity of SC/limewater may diminish over time since fatty acid methyl esters in the formulation can undergo saponification reactions at elevated pH. Indeed, a cleaning agent related to SC was rapidly converted to a white paste at pH 12. The long-term stability of SC/limewater formulations warrants further investigation.

Task 3. Biological treatment of decontamination solutions.

Under this additional task, two experiments were conducted to examine the potential for biological degradation of highly colored residual decontamination solutions. In the first experiment, 1mL aliquots of the 25% acetone/limewater and 25% SC/limewater decontamination solutions were added twice daily to flasks containing 2L of activated sludge "mixed liquor" from a local wastewater treatment facility. The sludge was aerated, agitated and fed with cat food kibbles to reproduce the conditions at the facility (they use dog food). A control batch of sludge was also maintained. After 10 days, 20mL of each solution had been added to the 2L of liquor - a 1:100 dilution ratio. The sludge was allowed to settle and the clarified supernatant was decanted from the solids. A 100mL aliquot of each supernatant was then passed through an activated carbon solid-phase extraction cartridge that retained remaining colored decontamination residuals. The retained color was eluted with 1mL of acetone, a 1:100 concentration, counteracting the previous 100-fold dilution. The resulting solutions were compared to the color of the original solutions and to the naturally occurring color in the control batch. Based on the optical density of the solutions at 650nm, 90% of the colored decontamination residuals were removed by the activated sludge (Appendix B, Figure 11). Considering the simplified experimental set-up used for this initial test, these results were very encouraging. The sludge cultures were not adversely affected by the decontamination solutions supplied at a reasonable rate and the color (degradation products) were largely removed.

The second experiment was performed with small portions of compost. Again, 20 mL of each solution was added daily in 1-mL aliquots to 250-mL beakers of compost. After 10 days, the compost was dried and extracted first with water, then with acetone. For both treatments and controls the extracts were highly colored green-brown solutions. The optical densities of the extracts were so large across the UV-visible range that it was not possible to determine quantitatively if the reddish color of the decontamination residuals was completely removed. However, qualitatively there was no discernible color difference between the controls and post-treatment extracts, indicating that the residuals were removed by the compost.

Although the results are very preliminary, they suggest that removal of soluble EM degradation products in decontamination formulations using biotreatment is a feasible approach to handling range scrap treatment waste. Additional study is needed to fully establish the viability of either biotreatment approach.

CONCLUSIONS

The objectives of this exploratory research program have been fully met. The experimental results are highly encouraging and point to two potential treatment schemes as candidates for full-scale decontamination of range scrap. A design for one possible embodiment of a pilot scale treatment system that can accommodate both schemes is included in Appendix B, Figure 12. Either treatment soak solution (SC/limewater or acetone) will remove thick deposits of CompB from multi-ton batches of range scrap in a day or two. The initial decontamination solution is then be transferred from the "soak" tank to the "storage" tank and the cleaned scrap rinsed with water and removed for recycling or disposal. The solutions in the holding and rinse tanks will be dischargeable to a compost or wastewater treatment system, pending further proof that no toxic products will occur in the final effluent or sludge. In the case of the acetone treatment scheme, limewater is added to the storage tank to effect hydrolysis of the dissolved energetics prior to discharge to the wastewater treatment system. The parameters to be considered in choosing between the two decontamination schemes are speed, cost, safety and regulatory approval. Each facility may have different requirements and restrictions that influence this choice. Briefly, the comparative factors are as follows:

	<u>Acetone/followed by limewater</u>	<u>SuperSolve/limewater</u>
Speed	1-2day soak, 1day hydrolysis 14 days to precipitate (if desired) ? day to add slowly to biotreatment process (depends on plant capacity)	2day soak no holding time ? day to add slowly to biotreatment process (depends on plant capacity)
Operating costs	\$2/gal acetone that may last for many batches \$3/1000gal of 0.5% aqueous lime	\$15/gal - may only last a few batches \$3/1000gal of 0.5% aqueous lime
Safety	neat acetone is flammable but dilute solutions are not (could be blended off-site)	non-flammable/non-toxic
Regulatory	Acetone is acceptable and amounts required on-site can remain below Reportable Quantity of 7000 gal. The discharge rate of acetone and colored polymers into a wastewater system will have to be negotiated.	SC is already approved for discharge. The regulatory issue will be with the colored polymers.

In addition to the decontaminant solution-related operational costs presented above, our preliminary cost estimate to setup a field-scale decontamination system as outlined in Appendix B, Figure 12 is less than \$50K. This includes the purchase and installation of 1000gal size tanks, an appropriately sized liquid transfer pump, mixers, and all other system hardware (pipes, valves, etc.). Existing equipment that is in place for handling range scrap can be used to transport materials to and from the treatment tanks. The process itself will require little electrical power - approximately 200 kWh/batch to run a 1.5-hp circulating/transfer pump. Electrical energy costs are estimated at less than \$20 per hr during continuous operation. If extremely rapid processing is required, large quantities of scrap can still be treated at low cost by simply adding more soaking tanks (at less than \$1000 per 1000-gal plastic tank). This contrasts markedly with hot gas or other treatment systems with orders of magnitude higher equipment costs; installation of multiple systems to speed throughput is cost prohibitive.

Additional cost advantages of our technology relate to maintenance and waste handling/disposal. Because the overall quantity of energetics on range scrap is expected to be modest, the decontamination formulations should have a long life in the tanks (i.e., they will not be depleted quickly). Acetone that is lost through evaporation can be replaced at just \$2 per gallon. At \$15 per gallon, a more significant cost increment will occur if the green cleaner is degraded at elevated pH.

Converting solid energetics residues to *solid* polymers may be a very cost-effective approach. At an estimated 100g/ton residue level, the net volume of waste generated from 10 tons of scrap will fit into a home canning type "Mason" jar. Costs for handling and disposing solid waste will be minimal, unless the polymers are found to be in some way hazardous in those quantities. However, the additional time required to generate the precipitate may be more costly than simply discharging the highly colored solution and suspended polymers to wastewater treatment. Additional work will be required to quantify these trade-offs.

Finally, an additional benefit of the proposed treatment technology is that monitoring the process will be facile. Future research with authentic range scrap will be required to determine how long the soaking will have to be to clean a worst-case mass of energetics that might be sent through our process. However, to ensure that HE degradation and polymerization is complete in actual practice, simple, low-cost field colorimetric methods for nitroaromatic and nitramine explosives can be performed on-site with samples collected from the tank(s).

TRANSITION PLAN

In order to transition our treatment technology to implementation on ranges, some further R&D and pilot-scale work needs to be conducted to validate the efficacy and safety of the process, and more accurately assess treatment issues and costs. Thus, a two-year follow-on program of advanced R&D is recommended with the following objectives:

Year One

(1) Determine the load-capacity and durability of SuperSolve and acetone limewater solutions. Investigate related cleaners and optimize formulation. Extend analysis to include other energetics - e.g., DNT, NG, HMX, PETN and metals.

(2) In collaboration with the ARA Bioremediation Group in Panama City, FL, determine the fate of nitroaromatic polymers and nitramine/nitrate ester ionic degradation products in aerobic, activated sludge. Investigate the potential toxicity of final effluent.

"GO/NO GO" Decision Point.

Year Two

(3) Scale-up to 55-gal drums to treat authentic range scrap of various materials such as metals (most important), rubber, and wood. Explore and evaluate processing options (bulk tanks, pressure washing, conveyors, etc) in the field on actual ranges. Use existing facility equipment, where possible.

(4) Perform a detailed cost analysis based on the best processing procedures.

(5) Seek regulatory approval for final disposal in wastewater treatment facility.

Successful completion of the program outlined above will bring the technology to the point of readiness for final validation/acceptance and initial full-scale implementation on ranges. The flexibility (applicability on different scales), simplicity and low costs associated with our decontamination technology render us confident that it will be welcomed by site personnel and transitioning to full-scale implementation on ranges will not prove difficult. The capability for handling LOD debris and chunk energetics will reduce the amount of hard-to-handle UXO that must be processed by site personnel, resulting in improved safety and lower disposal costs. The process could easily be automated (along with the range clearance activities) to reduce the current risks to personnel during handling and inspection of scrap materials. Furthermore, by dealing with the most contaminated materials, implementation of the new process is likely to reduce the need for wide-area decontamination, again reducing clean-up costs. The equipment will not be highly complex for operators and existing equipment that is in place for handling range-scrap can also be used to transport materials to and from the treatment tanks.

Site personnel will appreciate the flexibility of the technology. Small tanks can be carried to the clearance areas so that detonable residues can be "decomposed" before being transported to larger staging areas. If extremely rapid processing is required to decontaminate existing stockpiles, large quantities of scrap can be treated at low cost by simply adding more soaking tanks (at less than \$1000 per 1000-gal tank). This contrasts markedly with hot gas or other treatment systems with high equipment and operation costs - installing multiple systems to speed throughput is cost prohibitive. A final benefit of the new treatment technology is that monitoring the process will be facile and will not require highly trained analysts or equipment.

During the proposed follow-on program, our decontamination technology will be introduced at several ranges as the first step in transitioning the technology. It is expected that familiarity with the process and its performance will encourage those ranges to adopt the technology for full-scale remedial clean-ups and for the more extensive routine clearances that will be required once the LOD debris problem is fully recognized. Preliminary discussions have been held with remediation personnel at Camp Bonneville (WA), Fort Ord (CA), Camp Guernsey (WY), Massachusetts Military Reserve (MA), Dugway Proving Ground (UT), Nellis AFB (NV), Nevada Test Site (NV), Idaho National Engineering and Environmental Laboratory (INEEL), Los Alamos National Laboratory (NM), and the Canadian Department of National Defense. All have expressed interest in implementing the technology once developed.

ARA is well positioned to supply decontamination systems and support to end users such as those mentioned above. It is our intention to commercialize the technology through both the sale of systems and decontamination services. In this regard, we are already active in range characterization and cleanup with several EOD personnel on staff. We have recently conducted site characterizations at MMR, Dugway, and LANL and are currently in negotiations to provide test range characterization and clearance at Camp Bonneville and Fort Ord. In the New England Division we also provide manufacturing, training, and service for the All-terrain Remote Transport System (ARTS), a remotely controlled robotic vehicle used for range clearance and other applications (mine clearance, etc.). It is notable that the company also has a growing international business in the area of explosives manufacturing site characterization and remediation within the private sector using automated equipment we developed. If the scrap treatment technology proves safe and effective, we will solicit support from our industrial clients to adapt and implement the technology to meet their specific cleanup needs. While many of these needs relate to remediation of contaminated soil and groundwater, there are a large number of former private manufacturing sites worldwide that are being decommissioned. Treating dismantled building materials is closely related to treating range scrap. For safety and environmental reasons, it is becoming increasingly difficult to decontaminate former manufacturing buildings by burning and/or demolition. Decontamination processes that are gentle and complete are vitally needed at these sites.

RECOMMENDATIONS

In this preliminary laboratory R&D effort, we have established feasibility for timely and effective treatment of a variety of critical energetics residues on authentic range scrap. The new technology is an exceptionally low-cost alternative to other approaches and is suitable for implementation at DoD and DoE sites such as those listed above. Our recommendation is that additional work be conducted as outlined in the previous section of this report to bring the technology to full development and readiness for implementation. Thus, we anticipate applying for additional support from SERDP and ESTCP to conduct larger scale laboratory and field tests with more energetics samples. In collaboration with CRREL researchers (Tom Jenkins and co-workers) and other independent evaluators (e.g., ORNL scientists - Roger Jenkins and co-workers), field demonstrations and validations of the technology will be performed at sites such as those listed above. Researchers with the Department of National Defense, Canada have also expressed keen interest in this technology. It is notable that our company has a growing international business in the area of explosives manufacturing site characterization and remediation within the private sector. If the scrap treatment technology proves safe and effective, we will solicit support from our industrial clients to adapt and implement the technology to meet their specific cleanup needs. While many of these needs relate to remediation of contaminated soil and groundwater, there are a large number of former private manufacturing sites worldwide that are being decommissioned. Treating dismantled building materials is closely related to treating range scrap. For safety and environmental reasons, it is becoming increasingly difficult to decontaminate former manufacturing buildings by burning and/or demolition. Decontamination processes that are gentle and complete are vitally needed at these sites.

Although this proposed project is directed toward treating segregated range scrap, the technology should have much wider application. First, the current practice segregating scrap with visible signs of energetics residues or hidden recesses and treating it as UXO could be eliminated by simply treating *all* scrap (non-UXO) in the decontamination tanks. The process could easily be automated (along with the range clearance activities) to reduce the current risks to personnel during handling and inspection of scrap materials. ARA has considerable experience in automation and remote control operations for handling hazardous materials - the military now uses remotely controlled ARA equipment to clear ranges. We are also under contract to provide remote-controlled site investigation services to a private international customer that has numerous explosives manufacturing facilities scheduled for remediation and decommissioning. As noted above, D&D of former manufacturing structures is another major potential application for the new technology.

APPENDIX A Technical Publications

Published Technical Abstracts

P. G. Thorne, "Removal, Degradation, and Recovery of Energetics Residues from Range Scrap," Partners in Environmental Technology Symposium, Washington, DC, Nov 27-29, 2001.

Figure 1. One low order fragment can contaminate one acre-foot of water. Range clean-ups may need to become more thorough.

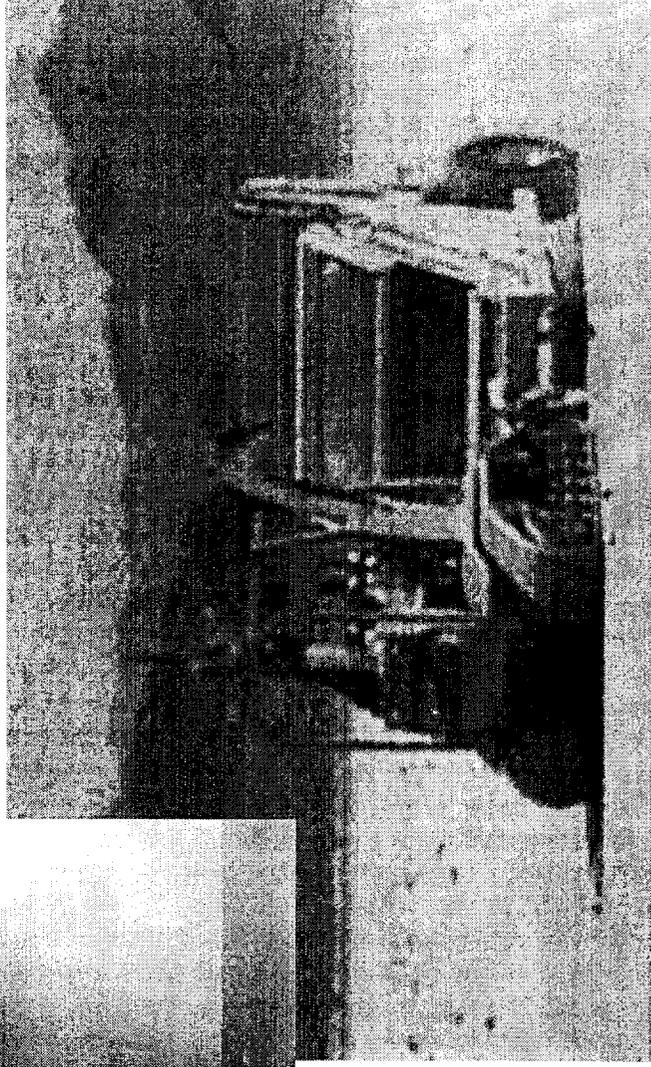
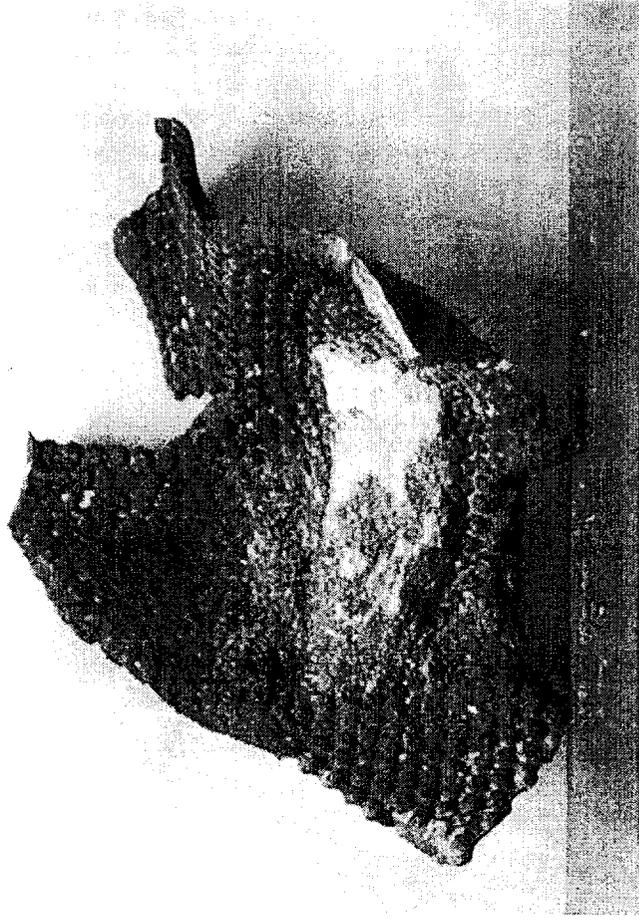
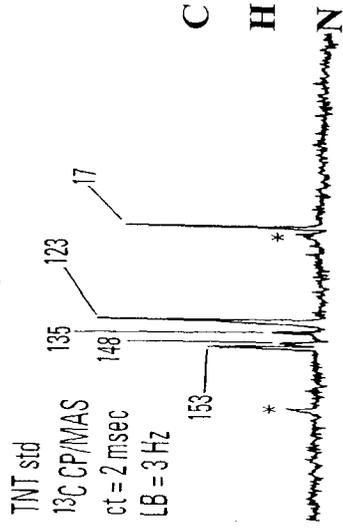
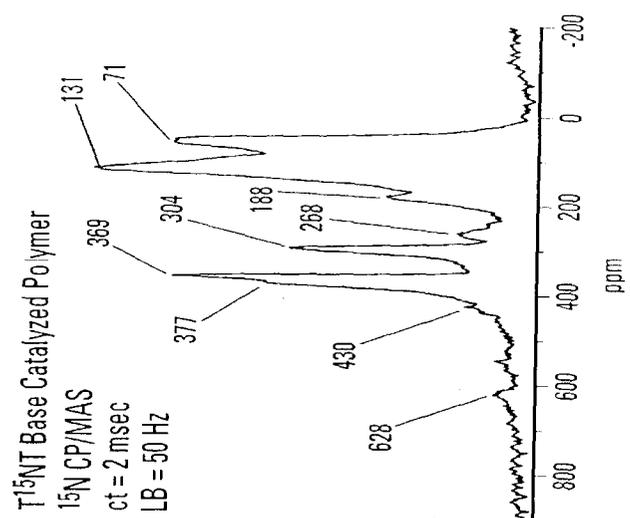
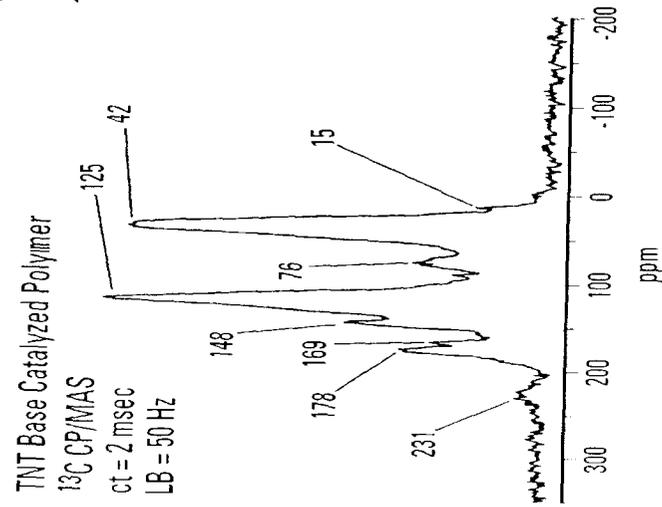
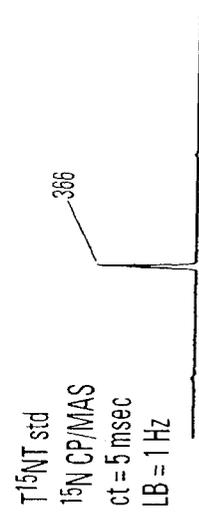


Figure 2. NMR and elemental analysis of insoluble red TNT-polymers



Elemental analysis-% of total

	TNT	Polymer	Polymer Polymer-Ashfree
C	37	27.4	36.1
H	2.2	2.6	3.4
N	18.5	8.3	11
O	42.3	37.5	49
Ash(Ca)	0	24.2	---

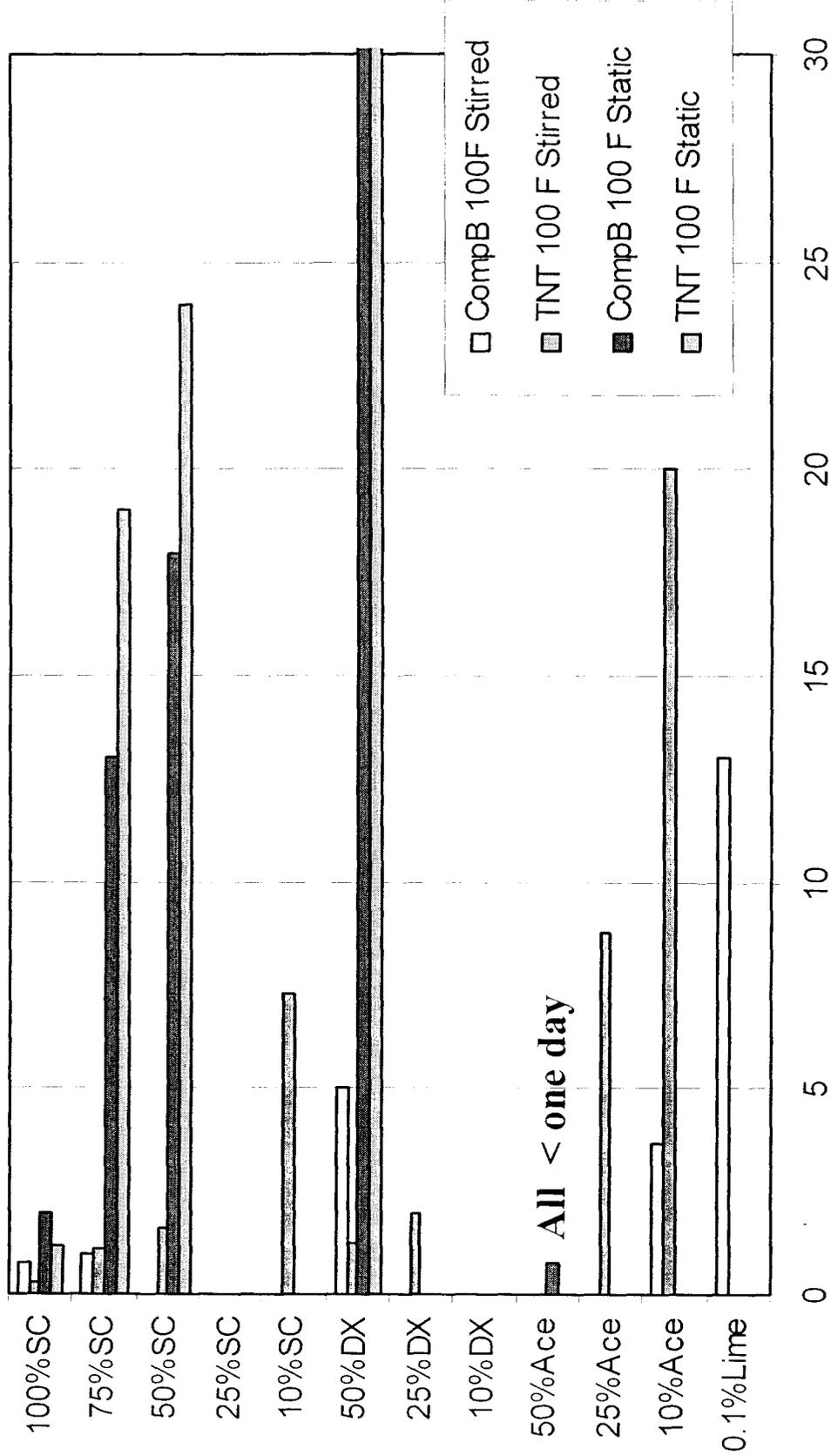


NMR Assignments

- methyl carbon gone-17ppm
- methylene, alcohol/ether-42,76ppm
- carbonyl carbons-160-200ppm
- aminodinitrotoluene, ammonia, hydroxylamine, condensations with catechol, hydroquinone-71-304ppm
- residual nitros-369,377ppm
- nitrosophenol-431ppm

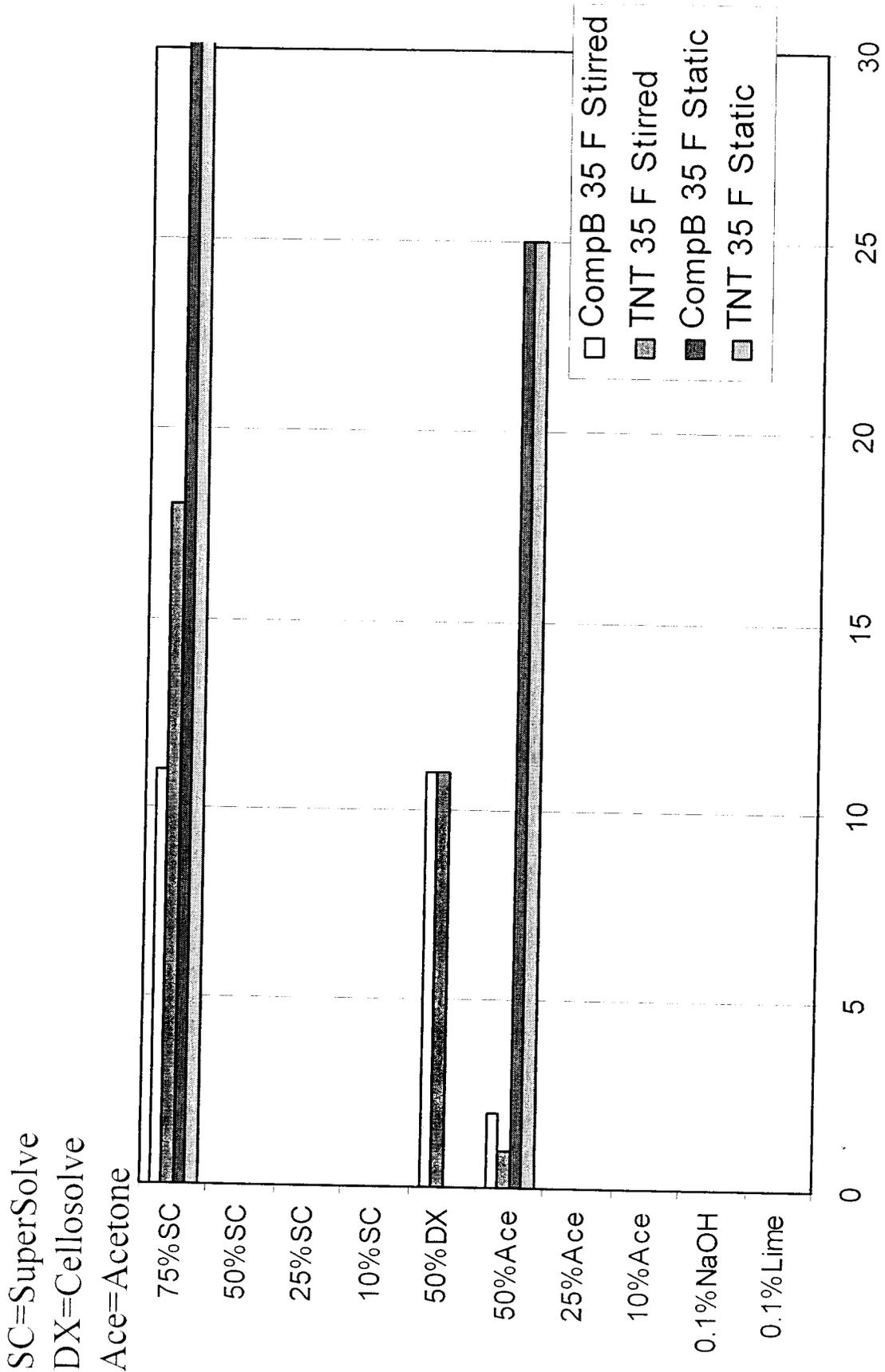
Figure 3. Days to dissolve 5mg chips CompB and TNT @ 100°F

SC=SuperSolve
 DX=Cellosolve
 Ace=Acetone



(intact chips @60 Days NOT charted)

Figure 4. Days to dissolve 5mg chips CompB and TNT @35°F



(intact chips @60 Days NOT charted)

Figure 5. TNT and RDX in Limewater, polymerization begins with dimers and continues in acetone until an insoluble precipitate forms. In SuperSolve, the polymer remains in solution.

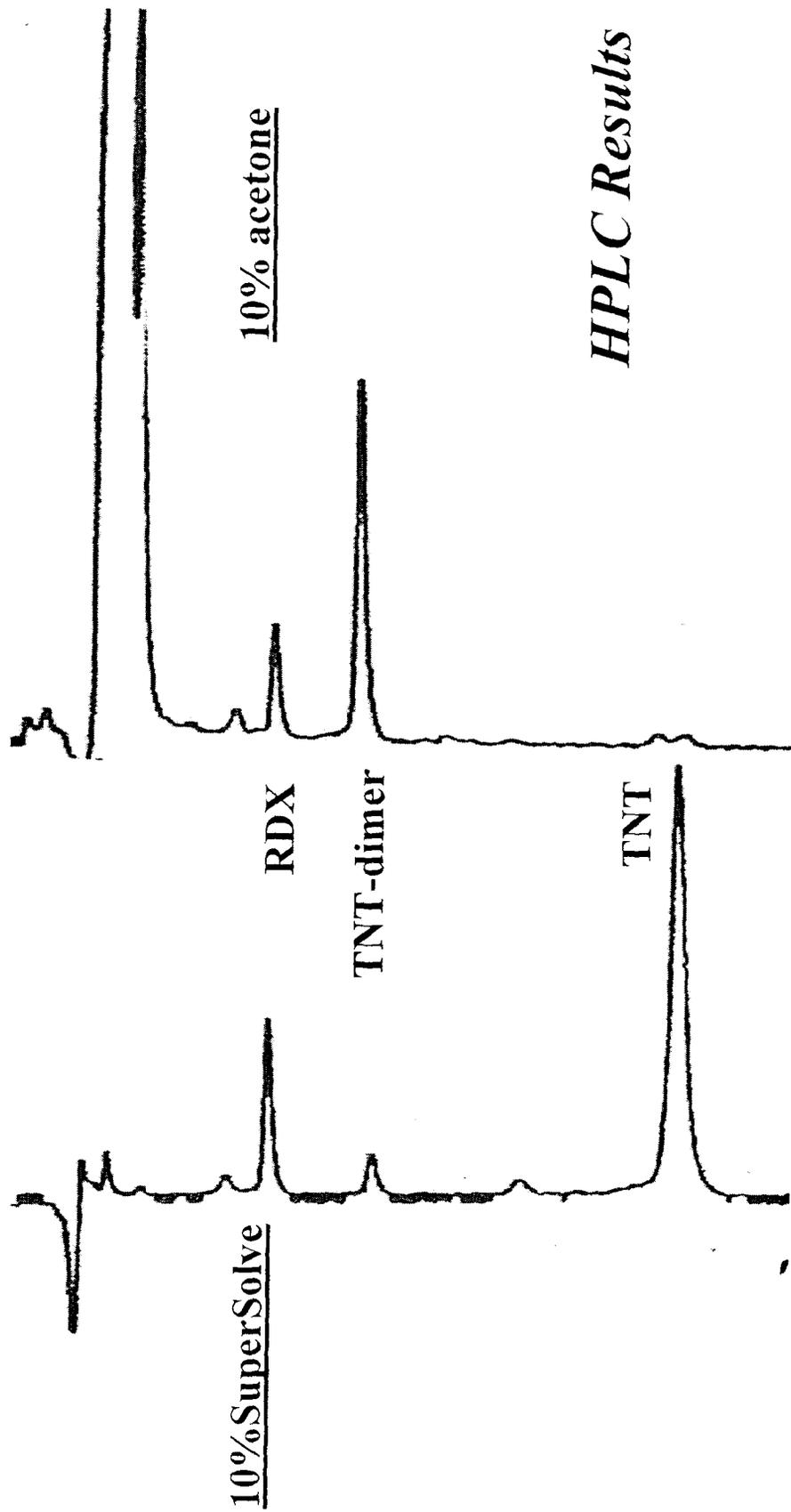
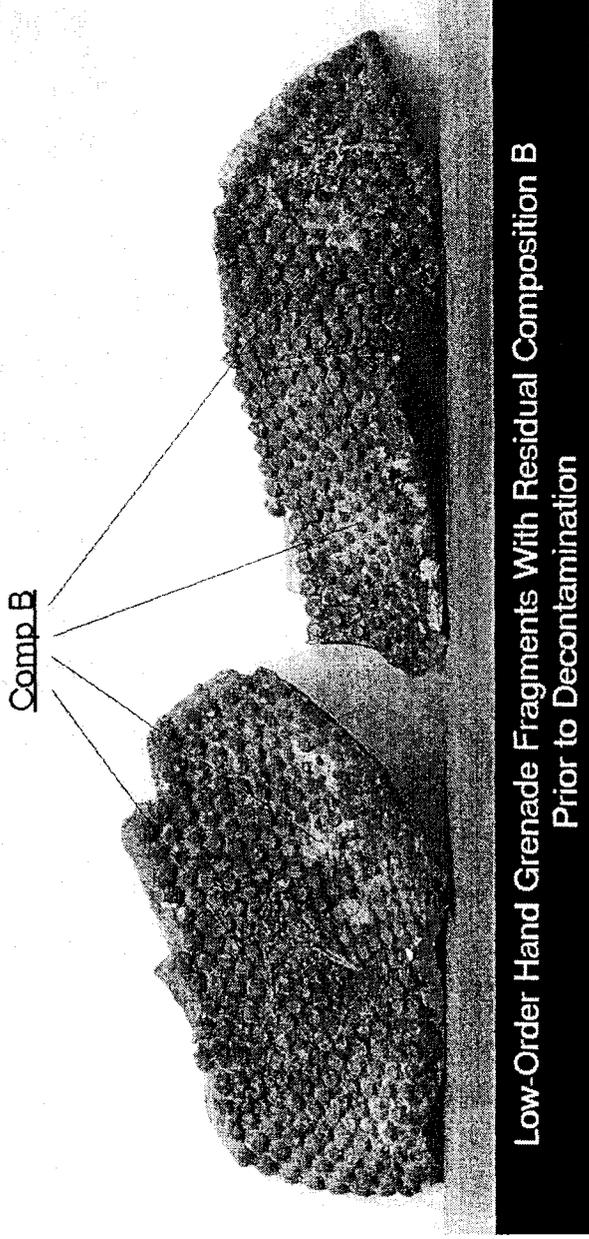
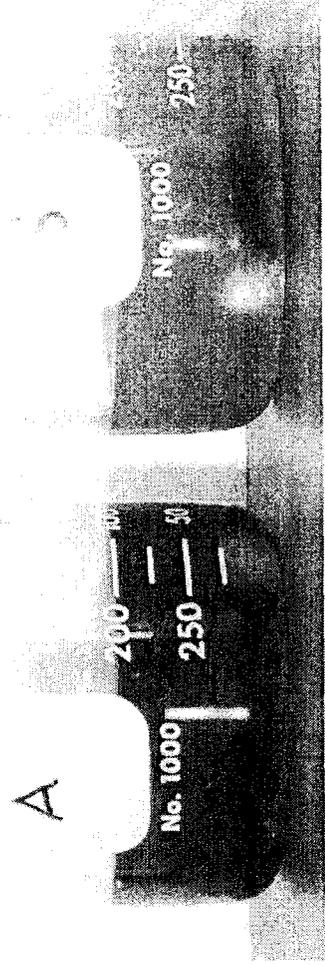


Figure 6. Successful cleaning of low order fragment with a thin layer of residual energetics.



CLEAN

Fragment after
14 days in
25% SuperSolve
(or 25% Acetone)



Grenade Fragments soaked for 24 hrs
25% Acetone/CaO 25% SuperSolve₆/CaO

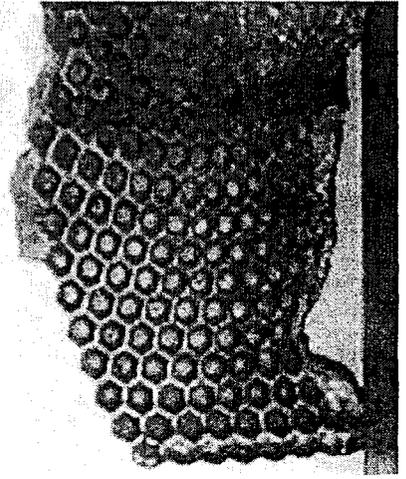


Figure 7. CompB is RDX crystal within a TNT matrix.

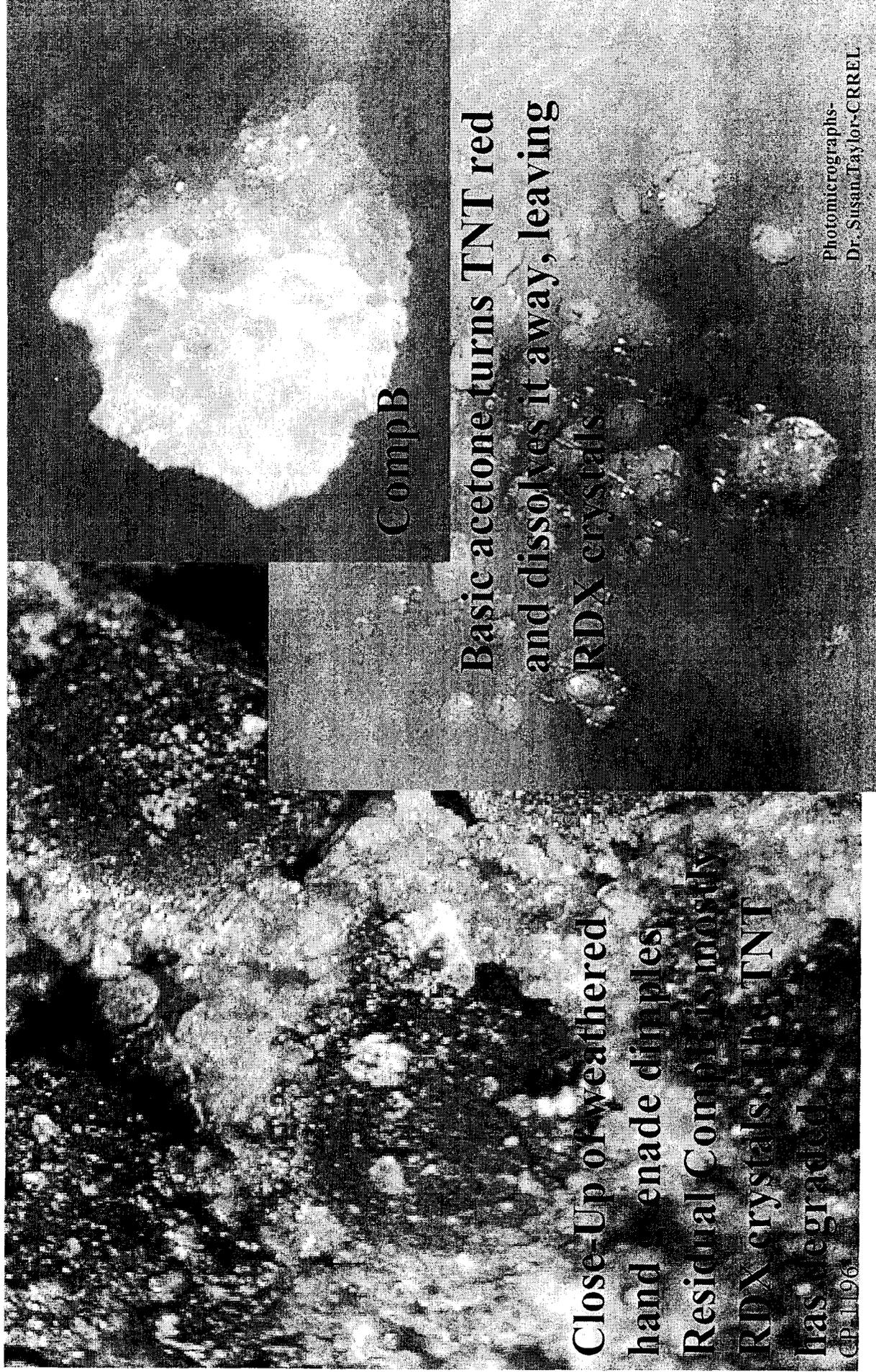


Figure 8. Decontamination of fragments with thick layers of energetics.

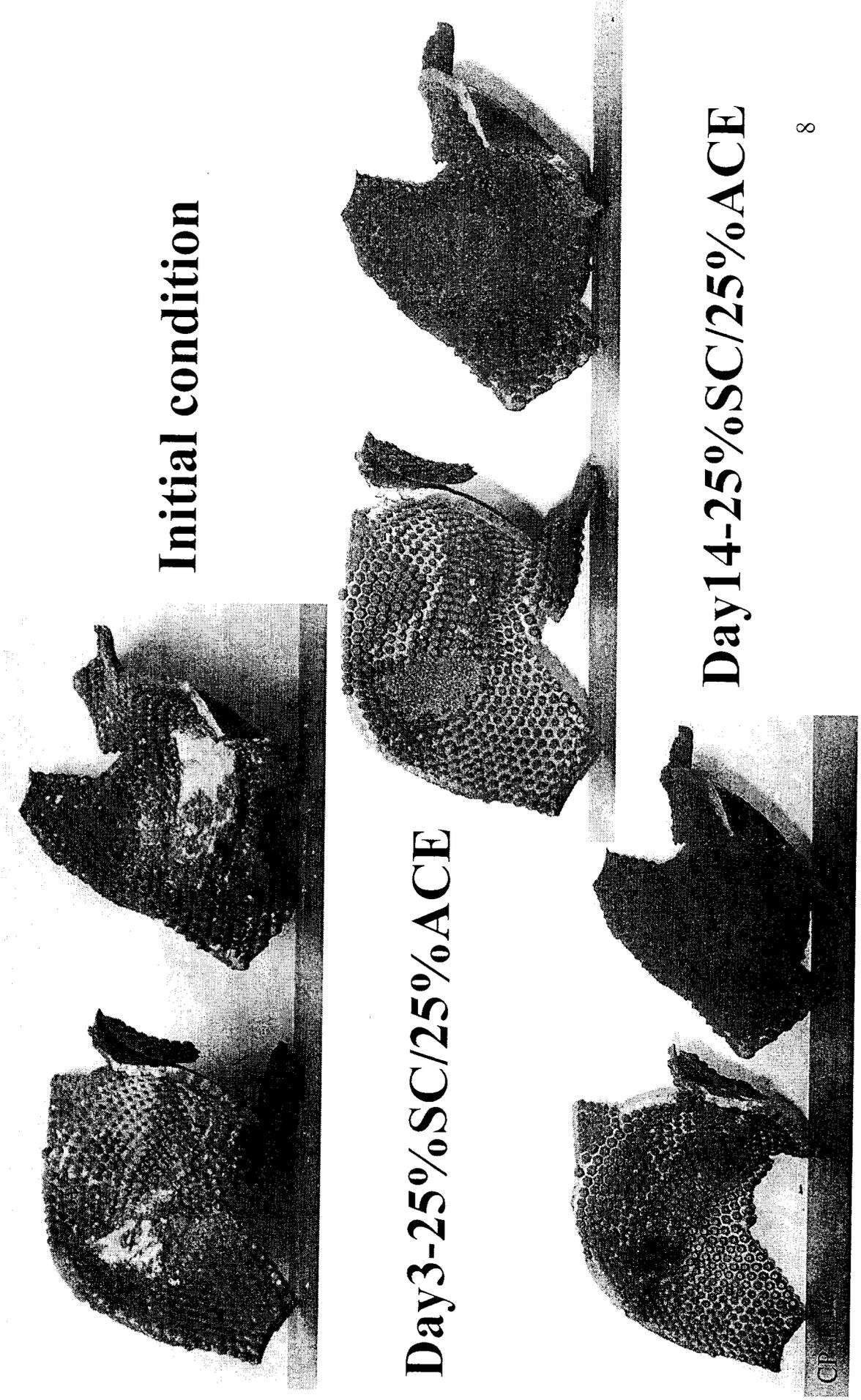
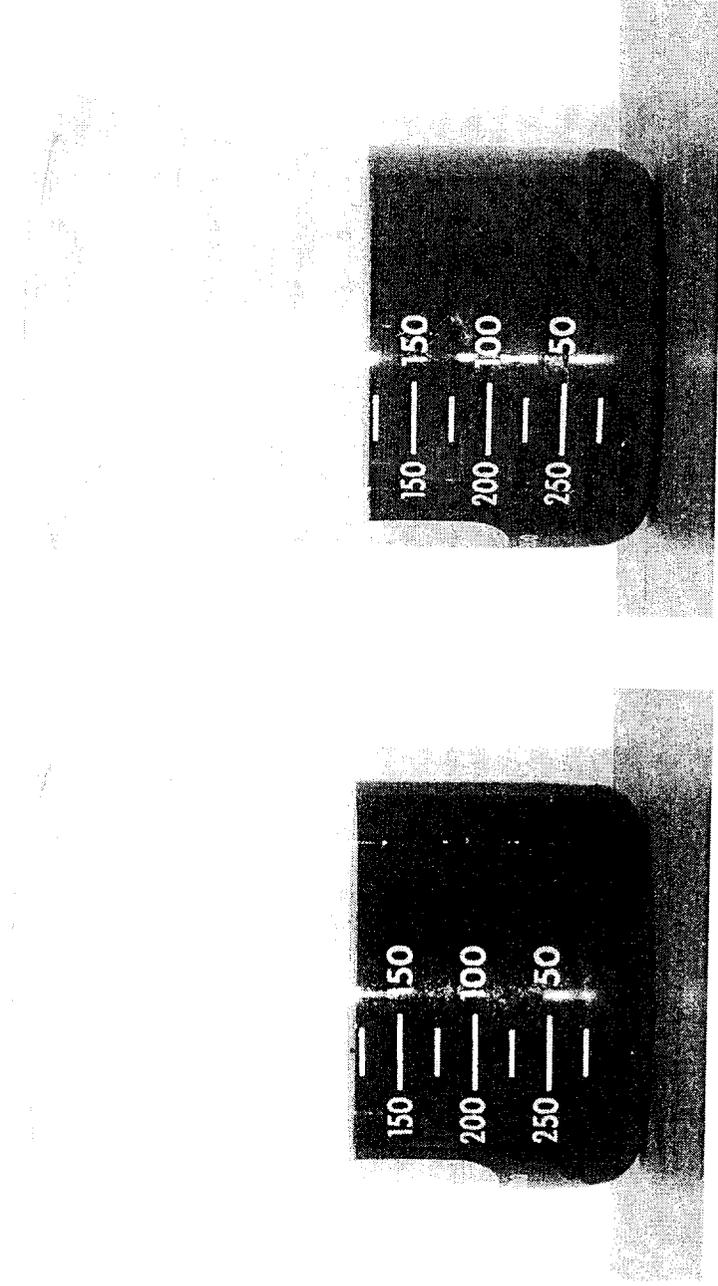


Figure 9. Polymerization of TNT in CompB soaked in 25% Acetone/Limewater



CompB with piece chipped off to reveal depth of TNT-polymerization. Such thick residues become more resistant to decontamination.

Figure 10. Decontamination of scrap using 50% Acetone without lime, followed by lime addition and 14 days of polymerization and precipitation.



Lime added-Day 1

Lime added-Day 14

Figure 11. Activated sludge treatment of limewater effluents.

A=25%Acetone (pre and post)
C=Control (no solvents or Lime)
S=25%SuperSolve (pre and post)

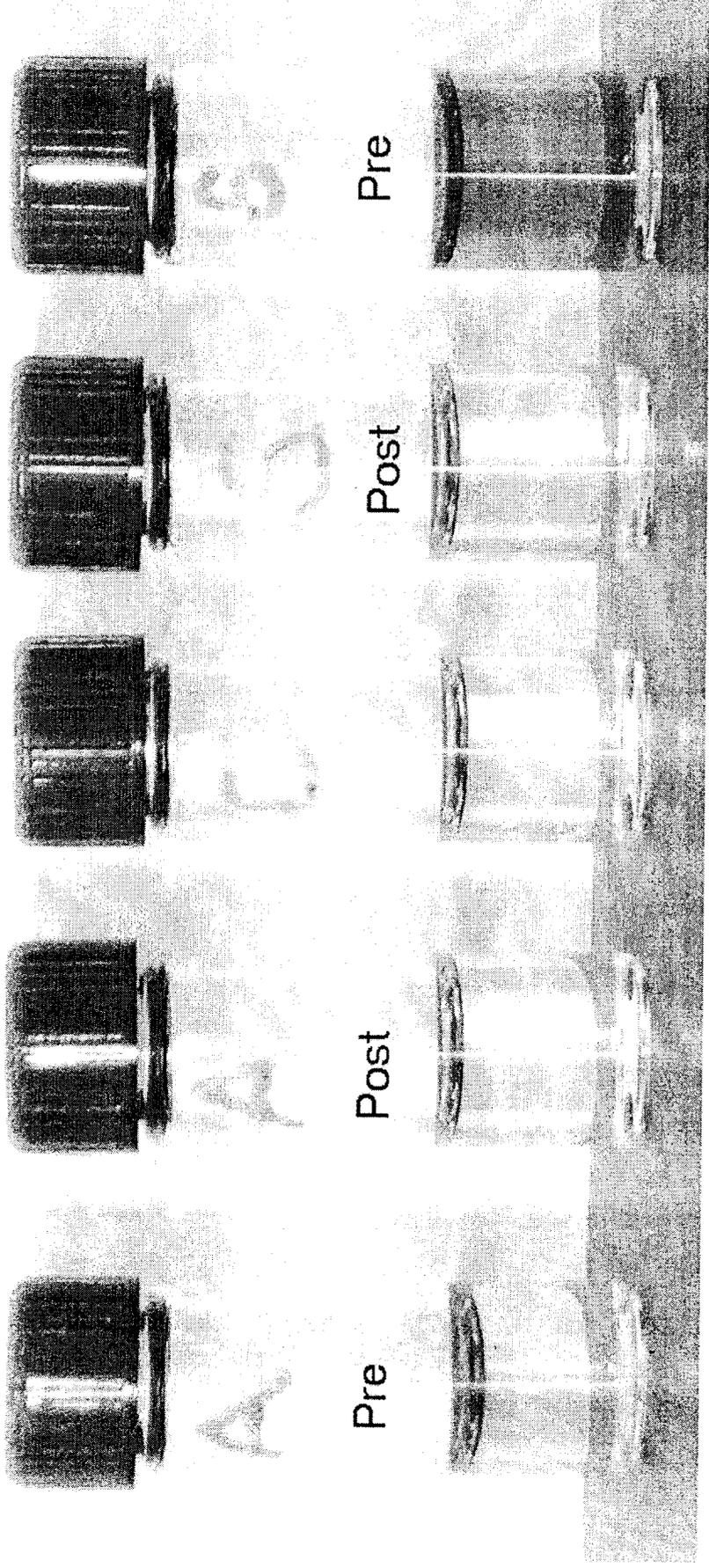


Figure 12. Proposed treatment system for 4-ton (5 yd³) batches of range scrap.

System consists of three, 1000-gal open-top plastic tanks containing “scrap soak,” “storage” and rinse solutions. A single pump/manifold performs all liquid transfers.

75% SuperSolve/0.5% Lime

50% Acetone/no Lime

Re-circulate for several days.

Pump supernate to 2nd tank.

Rinse scrap with water and pump to 3rd tank.

Add 0.5% Lime to 50% Acetone

Slowly drain to wastewater

treatment while new batch

soaks in 1st tank. Remove TNT polymer precipitate from Acetone solution.

Third tank is optional if water rinse can

be discharged directly to wastewater

REMOVE CLEAN SCRAP

