Recovery and Reuse of Core Ingredients from Decommissioned/Obsolete Gun Propellant

Foster-Miller, Inc. and Gradient Technology

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This research was initiated through the Army’s Small Business Innovative Research (SBIR) Program and is currently under the sponsorship of the Product Manager for Demilitarization with technical management and supervision by the Armament Research, Development and Engineering Center at Picatinny Arsenal.
Presentation Overview

- Description of the problem
- Brief overview of R³ demilitarization
- The demil process
- Process kinetics
- Pilot-plant demonstration
Description of the Problem

- DOD stockpiles of obsolete, excess, and off-spec munitions
  - Significant quantities of multi-base gun propellant exist, some as bulk material, some in yet-to-be demilled rounds
  - Stockpiles may continue to grow as ammunition in the currently active inventory is decommissioned
  - OB/OD disposal is costly and environmentally unfriendly
- Currently no domestic source of nitroguanidine (NQ)
- \( R^3 \)-type recovery process desired for gun propellant formulations
Resource Recovery and Reuse (R³)

- Requirements for explosive wastes processing
  - Safety
  - Recover valuable energetic materials for reuse and/or produce high value by-products
  - No discharge of toxic-materials to the environment
  - Cost-effective
  - Capable of high throughput for bulk processing
The Solution

- Develop a cost-effective and safe process for NQ, NC, and NG recovery from waste gun propellants and design a commercial-scale operation that can supply products to both the government and private sectors.
The Solution
R³ Products

- Nitroguanidine (NQ) suitable for reuse by the military
- Nitrocellulose (NC) in a form useful for industrial and biomedical applications
- Nitroglycerin (NG) suitable as a feedstock for the pharmaceutical and blasting industries
The Solution

Simplified Process Schematic

M30A1
NG, NQ, NC

Unit Op 1
NG
to purification or hydrolysis

Unit Op 2
NQ, NC

NC to reuse

NQ
to purification/crystallization

NG, NQ, NC
Advantages of the Solution

- Safety
- Benign processing conditions
- Non-aggressive reactants
- Operator-friendly
- Recovery of valuable products from hazardous wastes
## Gun Propellant Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>M30A1</th>
<th>M31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitroguanidine, NQ</td>
<td>47</td>
<td>54</td>
</tr>
<tr>
<td>Nitrocellulose, NC</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td>Nitroglycerine, NG</td>
<td>22.5</td>
<td>19</td>
</tr>
<tr>
<td>Ethyl centralite, CNT</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>Dibutylphthalate, DBP</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>2-Nitrodiphenylamine, NDP</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Potassium nitrate, KNO₃</td>
<td>1.85</td>
<td>-</td>
</tr>
<tr>
<td>Potassium sulfate, K₂SO₄</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.15</td>
<td>-</td>
</tr>
</tbody>
</table>

Chemical structures:
- [Nitroguanidine](#)
- [Nitrocellulose](#)
- [Nitroglycerine](#)
- [Ethyl centralite](#)
- [Dibutylphthalate](#)
- [2-Nitrodiphenylamine](#)
- [Potassium nitrate](#)
- [Potassium sulfate](#)
- [Graphite](#)
Nitroguanidine Recovery

- Military is target market (NQ is currently imported; sole source of supply is undesirable situation)

- Optionally, NQ also has potential as a commercially viable product for propellant manufacture

- Post-processing of NQ for purification and re-crystallization
Nitroguanidine Characterization
NQ Crystals From Commercial Sources
Nitrocellulose Recovery

- Recover NC as a commercially-viable product
- Products currently under target industry evaluation
- Potential markets include biomedical and coating industries
Recovered Nitrocellulose Coating Industry Market

Evaluated as a coating ingredient

1. Replacement for high-cost component
   • No adverse effects on performance

2. Additive to existing formulation
   • Significantly increased hardness

Post-processing

1. Cross-link with diisocyanate

2. Adjust viscosity with selected solvents
Nitroglycerine Recovery

- Recover NG as a commercially-viable product or hydrolyze and discharge

- Commercial markets not yet established

- Potential markets include explosives, medical and organic chemical industries
Progress During the Past Year

- **Dissolution Kinetics**
  - Laboratory study
  - Relative extraction and reaction rate of each component
  - Amount and temperature of solvents

- **Planning and designing pilot plant**
  - Process 500 pounds of propellant per day
  - Generate mil-spec NQ

- **Markets for each component**
  - Income source
  - Reduced costs
Some Important Features of Aspen Plus

- Rigorous Electrolyte Simulation
- Solids Handling
- Petroleum Handling
- Data Regression
- Data Fit
- Optimization
- User Routines
What is the composition of stream PRODUCT?

To solve this problem, we need:

- Material balances
- Energy balances
- Thermodynamic and kinetic data
Ideal Solubility

\[ x_i^{\text{Ideal}} = \frac{\Delta S_{\text{fusion}}}{R} \left(1 - \frac{T_{\text{melt}}}{T}\right) \]

- Predicts identical solubility for all solvents
- \( x_i \): Mole fraction of component \( i \) in solution
- \( \Delta S_{\text{fusion}} \): Entropy change of \( i \) on freezing
- \( R \): Gas constant
- \( T \): Solution temperature
- \( T_{\text{melt}} \): Melting point of \( i \)
# ASPEN-PLUS

## Solubility Modeling

### Pure-Component Solubility Parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{melt}$ (K)</th>
<th>$\Delta H_{\text{fusion}}$ (kJ/mol)</th>
<th>$\Delta S_{\text{fusion}}/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG$^1$</td>
<td>286</td>
<td>26.6</td>
<td>11.2</td>
</tr>
<tr>
<td>NQ$^2$</td>
<td>400</td>
<td>34.6</td>
<td>10.4</td>
</tr>
<tr>
<td>NC$^2$</td>
<td>424</td>
<td>37.2</td>
<td>10.5</td>
</tr>
<tr>
<td>CNT$^2$</td>
<td>900</td>
<td>50.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

$^1$ Data  
$^2$ Estimated values
**ASPEN-PLUS**

*Solubility Modeling*

Actual solubility

\[ x_{i}^{Actual} = x_{i}^{Ideal} \gamma_{i} \]

\( \gamma_{i} \): Activity coefficient of \( i \) in solvent of interest
The NRTL model calculates liquid activity coefficients.

- It is recommended for highly non-ideal chemical systems, and can be used for VLE and LLE applications. The equation for the NRTL model is:

\[ \ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left( \tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \]

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Solubility Modeling

Solute - Solvent Mutual Solubility

Temperature (°C)

Weight % Solute
Dissolution Kinetics

Objectives

- Determine the effect on reaction and separation rate of
  - Amount of solvent (slurry concentration)
  - Temperature of solvent
  - Stirring rate
  - Alternative solvents

- Determine relative rates of dissolution
  - NQ losses in NG solvent, etc.

- Product recovery
  - Dissolution time - recovery trade off
Dissolution Kinetics

Conclusions

- Virtually all the NG is recovered with less than 5% NQ loss
- NG can be effectively recovered in a single batch.
- More than 98% of the NQ remaining is recovered
- NG can be effectively obtained.
- Stirring rate has little effect on recovery rate in range investigated (not $\Delta C$ limited)
Scale-Up

- The process was originally developed using 1g quantities of gun propellant
- Recovery of energetic materials in the laboratory has been successfully demonstrated on 10g and 75g batches of gun propellant
- Process demonstrated using 10 pounds batches
- Process will be demonstrated in a 1/10th scale pilot plant
- Commercial scale development to follow
The Approach

Laboratory Scale
- Product Isolation
- Pilot Plant
  - Design, construct, run
- Environmental Controls
  - Reagent recovery
  - Post-processing
- Process Optimization
  - Economic analysis
  - Flow sheet mods

Pilot Scale
- Product Purification
- Process Evaluation
- Full-scale Prototype Plant Design

The Approach