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Active Range Restoration Via Caustic Hydrolysis of Explosively Contaminated Metal Parts

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Background

- Objective: Demonstrate an Active Ranges-Restoration Mobile Munitions & Metals Treatment Unit for the Neutralization of Explosive Residues.
- Scope: Scale up & ruggedize a two-stage Strategic Environmental Research and Development Program (SERDP) system
 - Caustic Decomposition/Hydrolysis (D/H)
 - Caustic hydrolysis
 - Catalytic Hydrothermal Conversion (CHTC)
 - 700°C catalyzed steam reformer
- Emergent CHTC Challenges
 - Exotic materials of construction required to accommodate 700°C
 - Concerns with power consumption and molten stack discharge
- Caustic hydrolysis alone meets non-hazardous criteria
- Resultant process modifications:
 - CHTC process eliminated
 - Modified Decomposition/Hydrolysis (MDH) instituted

Prior Caustic Hydrolysis Experience

- Caustic hydrolysis of energetic material has been extensively studied
- Selected technology for two U.S. chemical demilitarization facilities
- Primary Composition B (Comp B) hydrolysate components:
 - Acetate, Ammonia, Formate
 - Sodium Cyanide
 - Low concentration (40 ppm)
 - Well established mitigation options
- Primary Comp B off-gas components:
 - Ammonia, NOx
- Energetic neutralization with manageable products

System Requirements

- Treat explosive material [Trinitrotoluene (TNT) and Comp B] in chunks (cast/poured explosives) or adhering to ordnance fragments
- Treat a 10 kg batch of explosives and accommodate up to 100 kg of steel from mortars or artillery projectiles that have ruptured due to low order explosion
- Skid-mount on a trailer and ruggedize to be weatherproof and resist damage from short distance off-road transport
- Minimize liquid waste
- Handle hydrolysate whose composition is qualitatively similar to that generated during prior testing
- Include a cyanide oxidation process
- Include a liquid sampling capability and analytical methods for detection of cyanide and energetic material
- Include provisions for the safe management of hydrogen gas

Modified Decomposition/Hydrolysis

- Caustic hydrolysis neutralizes energetics
- Colorimetric analysis of liquid sample to verify energetics have been neutralized
- *In situ* sodium cyanide treatment (D/H Reactor)
 - Hydrogen peroxide (H_2O_2) oxidizes CN^- to CNO^-
- Analysis of liquid sample for sodium cyanide
- pH neutralization and hydrolysate thickening
 - Phosphoric acid (H_3PO_4) forms buffer
 - Resulting sodium phosphate thickens to paste

Lower Temperature/Lower Cost

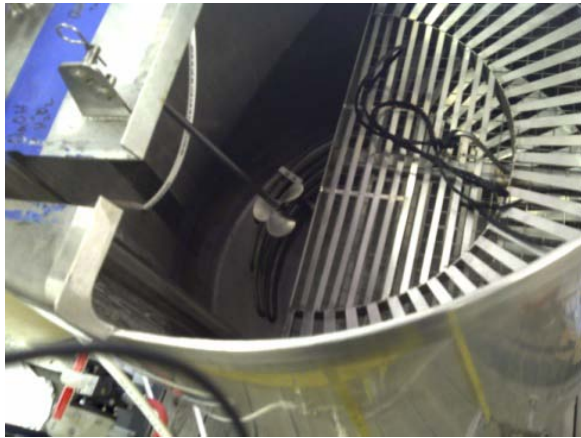
MDH System Description

- Mounted on a standard 40 foot flatbed trailer
- Can be brought directly to the contaminated scrap located on the range
- On-site treatment typically involves more flexible regulatory requirements than those associated with hazardous waste off site shipment and disposition
- 160 gallon stainless steel hydrolysis reactor vessel
- Controlled remotely from beyond the explosive stand-off distance
- 32% (w/w) sodium hydroxide (NaOH) feed supply
- 55-gallon gravity drain water tank available as emergency quench
- 1/4 gallon supply of hydrogen peroxide
- 275 gallon water storage tote
- 55-gallon drum mounted on a vibrating table receives a 3:1 mixture of 85% (w/w) H_3PO_4 and hydrolysate
- No liquid waste in the final material, simplifying disposal

Trailer-Mounted MDH System



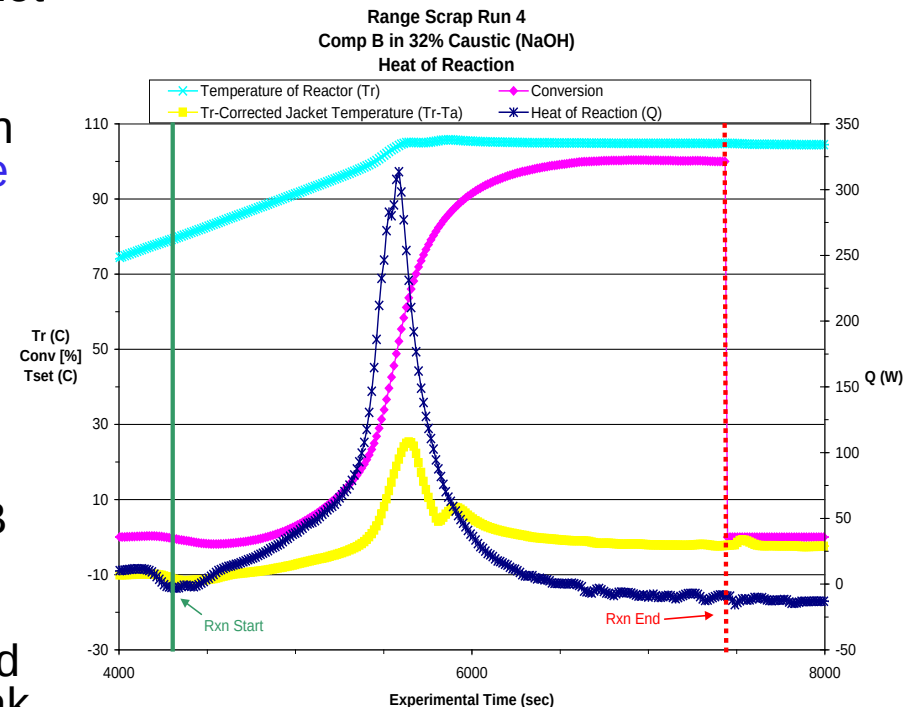
MDH Reactor Configuration



- Atmospheric pressure
- Operating temperature up to 120°C
- Complete submersion of 100 kg steel and 10kg of energetic material
- Nominal 100 gallon liquid volume
- Manual top loading and unloading of metal scrap/energetics
- Agitation comparable to that during the calorimeter testing demonstrations
- Heating capability, automatic temperature control
- Automatic level control
- Visual observation from a remote location – Lexan or other clear top
- Liquid contact with all scrap metal and energetic material surfaces

Basis of Design (BOD) Calorimeter Testing

- Batch hydrolysis using sodium hydroxide effectively treats TNT and Comp B, but not C4. The MDH feed will be limited to TNT and Comp B.
- Complete neutralization requires reaction temperatures in excess of 100°C. Single caustic batch feed rather than dosing to maintain b.p. > 100°C.
- 32% wt. NaOH concentration
- Approximate 30 minute reaction time
- Foaming requires head space equal to liquid volume
- Total heat of reaction for 90 g of Comp B was 132 kJ, with a peak heat generation rate of 325 watts.
- Total heat of reaction for 90 g of TNT and 44 g of aluminum was 754 kJ, with a peak heat generation rate of 550 watts.
- Heat load is conservatively estimated as 754 kJ/90 g and 550 watts/90 grams of energetic



Operating Temperature

- 103°C setpoint based on calorimeter testing
- Mixing 50% NaOH and water to produce 32% NaOH will raise temperature to approximately 60°C
- 32 kW electric heater to reach 103°C
- Exothermic reaction begins at approximately 80°C
- 65 kW peak heat load for 10 kg energetic batch
- 2.5°C/min rise to 117°F boiling point in approximately 6 minutes
- Boiling point serves as upper temperature limit
- Maximum 10 gallon boil off for 10 kg energetic batch
- Automatic makeup water feed
- Low level alarm initiates fail safe water quench

BOD - Safety

- Handling and processing explosive materials
- Use of hazardous chemicals, including sodium hydroxide, hydrogen peroxide, phosphoric acid
- Exothermic chemical reactions
- High temperature operations/hot surfaces
- Hydrogen gas generation resulting from accidental introduction of aluminum
- Low level production of sodium cyanide
- Electrical shock hazards
- Compressed air
- Rotating equipment
- Lifting operations
- Working at heights
- Heat stress associated with wearing personal protective equipment (PPE)
- Proximity to artillery range operations
- Outdoor conditions, including cold weather lightning, and wildlife

Explosion-Proof Components

- Reaction of aluminum with sodium hydroxide will produce hydrogen gas
- Scrap metal will be magnetically screened prior to loading
- Highly unlikely that hydrogen will be produced
- However, electrical components will be located at least 15 feet from the reactor where possible
- Pneumatic pumps, valves and agitators will be used to minimize the number of electrical motors
- A bleed stream from the air compressor will be positioned to dilute reactor vapors
- Electrical components which must be located within 15 feet of the reactor will comply with National Electrical Manufacturers Association (NEMA) Class 1, Div 2

BOD - Environmental

- Air Emissions
 - No specific emission criteria
 - Primary components are ammonia and oxides of nitrogen with some trace organics
 - These constitute only nuisance emissions provided the system is located at least a quarter mile from the installation boundary
 - Ammonia and nitrous oxides are both precursors of PM-2.5
 - U.S. Environmental Protection Agency (EPA) has proposed PM 2.5 nonattainment designations for many areas
 - The field demonstration installation should not be located in one of these areas to simplify the any regulatory requirements
- Secondary Containment
 - Sodium Hydroxide, Hydrogen Peroxide, Phosphoric Acid

BOD - Process Development Demonstrations

- Energetic Detection Analytical Method
- Hydrolysate Characterization
- Cyanide Detection Method Demonstration
- Cyanide Oxidation Demonstration
- pH Neutralization/Hydrolysate Thickening

BOD - Process Development

Energetic Analytical Method

- EnSys® TNT & RDX Test Kit, Strategic Diagnostics, Inc.
- Colorimetric screening method using solid phase extraction
- 2 liter hydrolysate sample passed through two membrane stack to concentrate TNT & RDX
- Acetone elutes & reacts with energetics
- Hach DR2000/2010 spectrophotometer detects color change
 - RDX absorbance at 510 nanometers
 - TNT absorbance at 540 nanometers
- Quantitative detection within 30 to 60 minutes

BOD - Process Development

Hydrolysate Characterization

- Calorimeter testing hydrolysate was characterized for comparison with composition found in the literature

Hydrolysate Component	ACWA Concentration	HERLA Concentration	Unit
Acetate	3,680.00	708.00	mg/l
Ammonia	1,380.00	923.00	mg/l
Cyanide	40.00	N.D.	mg/l
Formate	27,600.00	6,625.00	mg/l
TIC	1,917.50	10,000.00	mg/l
TOC	21,190.00	20,300.00	mg/l
COD	56,000.00	62,800.00	mg/l
Total Suspended Solids	170.00	520.00	mg/l
Total Dissolved Solids	176,000.00	1,040,000.00	mg/l
Normality as NaOH	1.15	9.73	N

- Only noticeable differences were higher TIC, TSS, TDS, and normality
- Cyanide non-detect due to matrix interference
- Some batch specific variability to be expected

BOD - Process Development

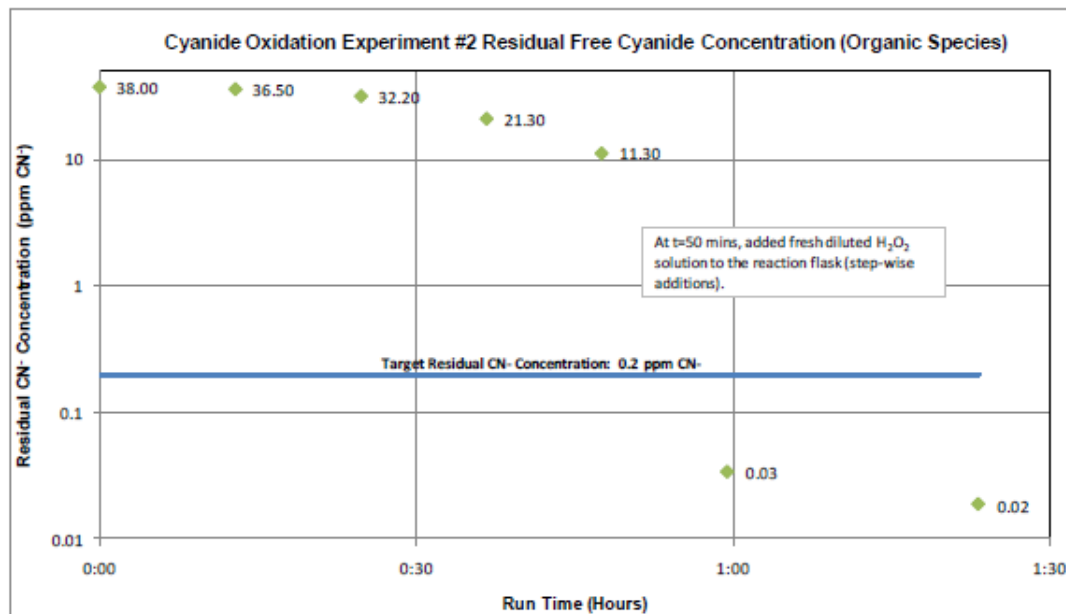
Cyanide Detection Method

- Cyantesmo® Paper method
- Green test paper turns blue in presence of cyanide
- Concentrated sulfuric acid added to a 10 mL sample converts free cyanide into HCN
- 2 – 25 minutes for concentrations >1 mg CN⁻/L
- 0.2 mg/L sensitivity
- Cyantesmo performance confirmed via quantitative Thermo Orion AQUAfast Cyanide Free Test

BOD - Process Development

Cyanide Oxidation Demonstration

- Hydrogen peroxide commonly used to oxidize low level cyanide
- H_2O_2 oxidizes cyanide (CN^-) to cyanate (CNO^-)
- CNO^- hydrolyzes to ammonia and carbonate
- Demonstrated process both with surrogate and “calorimeter” hydrolysate.
- 1 – 2 hours required for neutralization



BOD - Process Development

pH Neutralization & Hydrolysate Thickening Demonstration

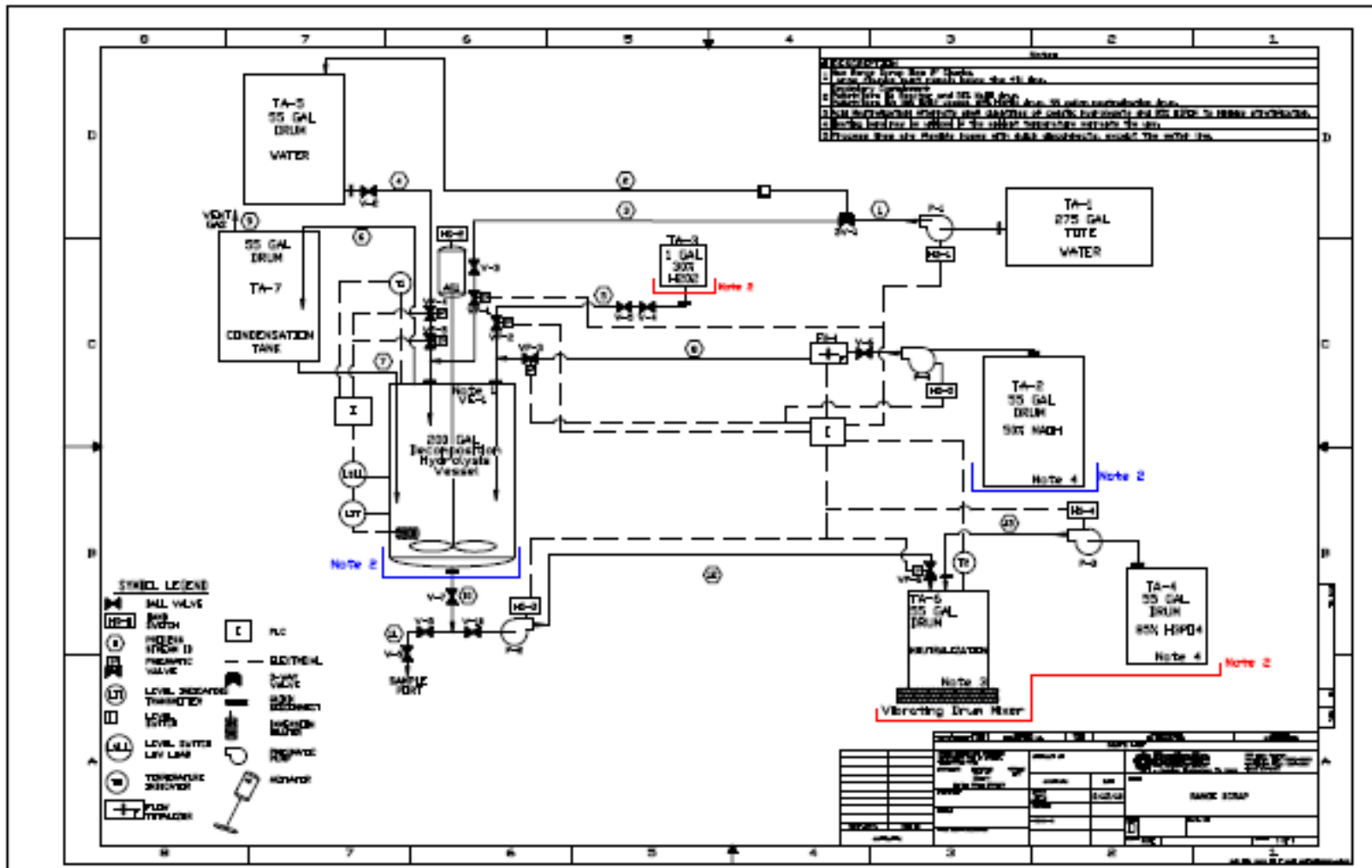
- Alkaline hydrolysate neutralized by 85% phosphoric acid
- Forms buffered solution at pH 7.0 – 8.0
- Solution reaches 60°C



Sodium phosphate forms a 12 hydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), thickening solution to a paste – mixing is critical



Piping & Instrumentation Diagram



Field Demonstration Assumptions

- Energetic material will be handled only by qualified Explosive Ordnance Disposal (EOD) personnel
- EOD personnel will screen all energetic materials to assure only TNT and/or Comp B will be processed.
- Magnetic screening of all scrap metal will be performed to assure it does not include aluminum
- Reduced energetic loads will be processed during initial field test batches to verify the system performs as designed
- The system will be operable within the boundaries of permitted test and training range and is therefore exempt from Resource Conservation and Recovery Act (RCRA) regulations
- Processing rate is not a test criterion

Opportunities for Further Study

- Better quantification of gaseous products
- Develop suitable PM-2.5 emission controls
- Hydrogen mitigation measures to allow for the processing of aluminum parts
- Demonstrating the neutralization of explosives other than TNT and Comp B
- Reduced batch cycle time
- Increased automation



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