FINAL REPORT

Environmentally Sound and Safe Military Munition Demilitarization

SERDP Project WP-2616

SEPTEMBER 2017

Allan Dokhan
Physical Sciences

SERDP
DOD ▪ EPA ▪ DOE

Page Intentionally Left Blank

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
25-09-2017	SERDP Final Report	2 May 2016 – 1 May 2017

4. TITLE AND SUBTITLE
Environmentally Sound and Safe Military Munition Demilitarization

5a. CONTRACT NUMBER
W912HQ-16-P-0009

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Dokhan, Allan and Ziemba, Lauren M.

5d. PROJECT NUMBER
WP-2616

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Physical Sciences Inc.
20 New England Business Center
Andover, MA 01810-1077

8. PERFORMING ORGANIZATION REPORT NUMBER
PSI-6735 Final

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
WP-2616

12. DISTRIBUTION / AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Physical Sciences Inc. (PSI) has conducted two green, low-cost, multi-cycled, closed-loop, environmental friendly, chemical demilitarization processes for pyrotechnic-smoke munitions. The developed demilitarization successfully recovered all components from the pyrotechnic-smoke compositions for commercial resale, as well as all solvents for recycling. The demilitarization process eliminated the environmental footprint of hazardous materials while simultaneously maximizing the reduction in operational costs. The two demilitarization processes segregated and recovered greater than 65% of all pyrotechnic-smoke materials from the bulk formulations. Simultaneously, all solvents were recovered and used in subsequent cycles of the green, closed-loop, environmentally friendly demilitarization process.

15. SUBJECT TERMS
Demilitarization, environmental, munitions, non-hazardous

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			ALLAN DOKHAN
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR	44	**19b. TELEPHONE NUMBER** *(include area code)* 978-738-0003

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Page Intentionally Left Blank

Table of Contents

List of Tables

List of Figures

List of Acronyms

Al	aluminum
Al_2O_3	aluminum oxide
CDD	capability development document
CDR	critical design review
CLEC	closed-loop, environmental friendly, chemical
CO_2	carbon dioxide
CS	2-chlorobenzalmalononitrile
CW	carbonated water
DI	deionized
H_2O	water
HC	hexachloroethane
ICP-OES	optical emission spectroscopy
$KClO_3$	potassium chlorate
KPP	key performance parameters
MeOH	methanol
$MgCO_3$	magnesium carbonate
NaOH	sodium hydroxide
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
OG	obscurant grenades
PSI	Physical Sciences Incorporated
RCG	riot control grenades
SERDP	Strategic Environmental Research and Development Program
SG	signal grenades
SON	statement of need
TGA	thermogravimetric analysis
ZnO	zinc oxide

Keywords

Demilitarization, environmental, munitions, non-hazardous

Acknowledgements

This material is based upon work supported by the Humphreys Engineer Center Support Activity under Contract Number W912HQ-16-P-0009. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Humphreys Engineer Center Support Activity.

Abstract

Objectives: Physical Sciences Inc. (PSI) has conducted two green, low-cost, multi-cycled, closed-loop, environmental friendly, chemical (CLEC) demilitarization processes for pyrotechnic-smoke munitions.

Three types of conventional pyrotechnic-smoke compositions have been demilitarized:

1. Obscurant grenade: 46.8 % wt. Hexachloroethane / 46.8 % wt. ZnO / 6.4 % wt. Al
2. Riot control grenades: 35% wt. CS / 30% wt. $KClO_3$ / 10% wt. MgCO3 / 25% wt. Sugar; and
3. Signal (obscurant) grenades: 35% wt. Red-Dye / 30% wt. $KClO_3$ / 10 % wt. $MgCO_3$ / 25% wt. Sugar

Technical Approach: The CLEC demilitarization Process A focused on recovering HC and ZnO, the processing byproduct Al_2O_3, $NaOH/H_2O$ and MeOH solvents. Process B focused on recovering CS or red-dye from the pyrotechnic kit ingredients, and regenerating the NMP and water solvents.

Results: Process A's objective was achieved with HC being recovered in 81% yield, the ZnO and Al_2O_3 being recovered in 62% yield with an 83% purity. For Process B, the recovery of each additive was achieved at greater than 85% for each additive, and 67% for the pyrotechnic kit. For both processes, all solvents were recovered and used in subsequent cycles of the demilitarization process.

Benefits: The CLEC demilitarization process developed by PSI successfully recovered all components from the pyrotechnic-smoke compositions for commercial resale, as well as all solvents for recycling. The CLEC process eliminated the environmental footprint of hazardous materials while simultaneously maximizing the reduction in operational costs.

Objective

Physical Sciences Incorporated (PSI) has successfully executed a Phase I program to design, develop, and demonstrate a multi-cycled, **c**losed-**l**oop, **e**nvironmental friendly, **c**hemical (CLEC) process to demilitarize three classes of pyrotechnic-smoke formulations: (1) Obscurant Grenades, (2) Riot Control Grenades, and (3) Signal (Obscurant or colored smoke) Grenades. The formulation and example munition of each grenade type is contained in Table 1.

Table 1: Grenade Formulations and Example Munition

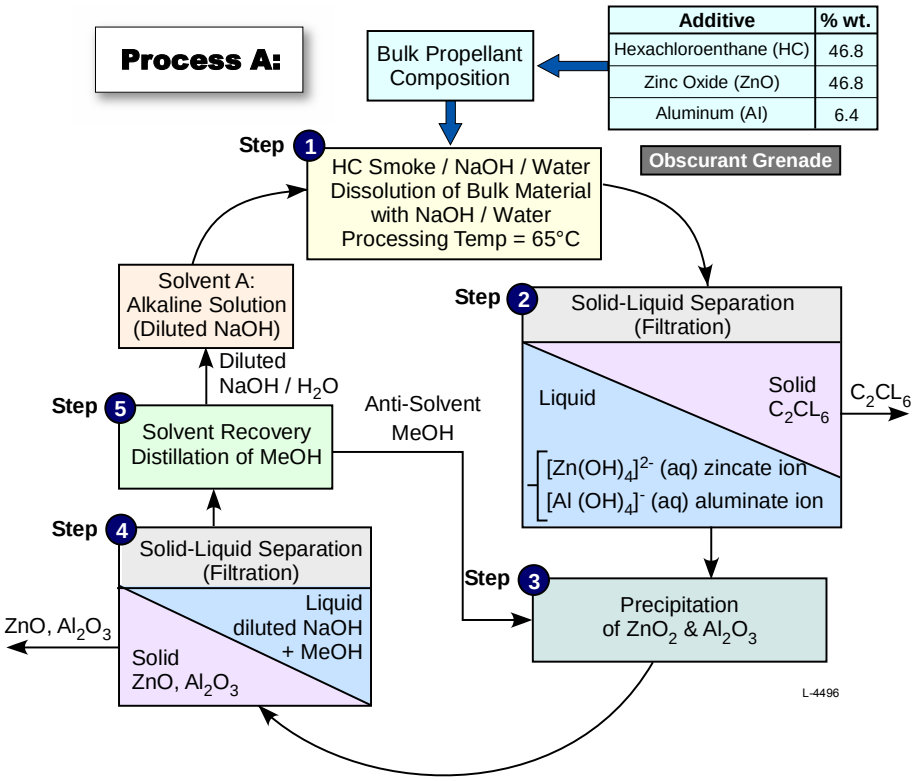
Formulation Component	Obscurant Grenade (Wt. %)	Riot Control Grenade (Wt. %)	Signal Grenade (Wt. %)
Hexachloroethane (HC)	46.5 – 47.5		
Zinc Oxide (ZnO)	46.5 – 47.5		
Aluminum (Al)	5 – 7		
Potassium Chlorate ($KClO_3$)		20 – 30	25 – 35
Sugar		15 – 25	20 – 30
Magnesium Carbonate ($MgCO_3$)		15 – 25	5 – 15
Dye / Coloring Agent			35 – 55
CS / Tear Gas		25 – 30	
NC/PVA Binder		1 - 3	1 – 3
Munition Examples:	AN-M8, M5, M4A2	M7A1-3, M6, M47, M25	M18, M84,E75, M62

The chemical demilitarization of munitions with energetic materials refers to safely segregating additives from the bulk material without the generation of dangerous byproducts while simultaneously maximizing commercial reuse of recovered materials.

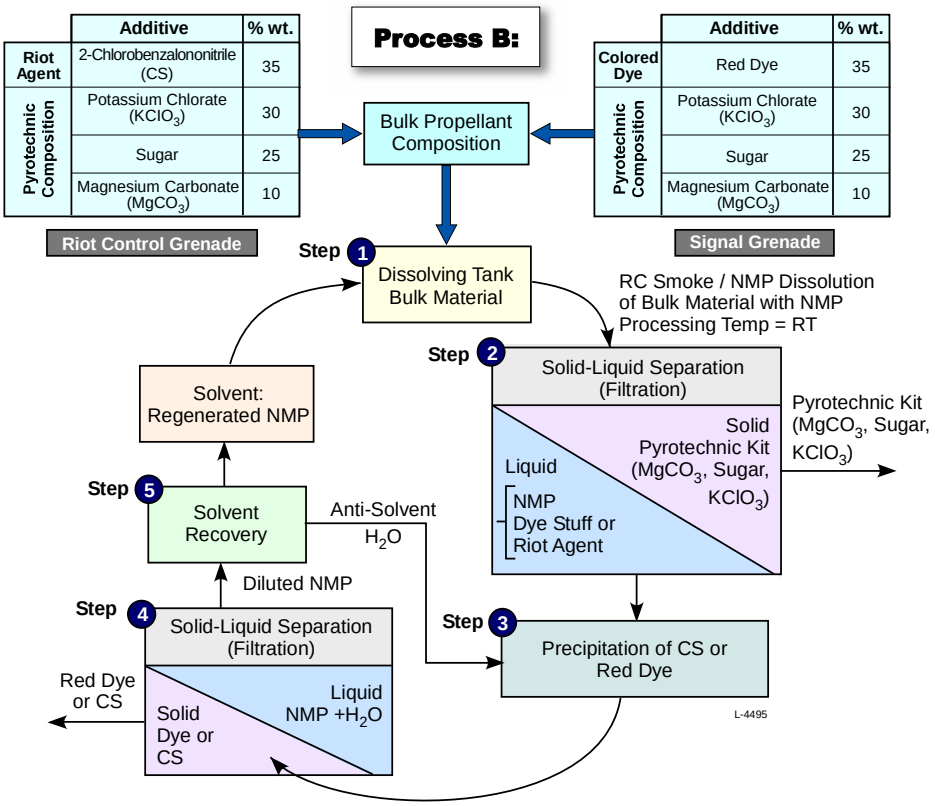
Background

Figure 1 illustrates the two developed CLEC demilitarization processes: ***Process A*** recovers hexachloroethane (HC), zinc oxide (ZnO), and aluminum (Al) from HC based obscurant grenades. ***Process B*** recovers 2-chlorobenzalmalononitrile (CS), red dye, and the pyrotechnic kit, from riot control and signal grenades.

Each step is based on established chemical processes to maximize risk reduction.



(a)



(b)

Figure 1: CLEC demilitarization process for: (a) Obscurant; and (b) Riot Control / Signal Grenades.

In this Phase I effort, the technical objectives were to demonstrate and quantify the operational feasibility of the chemical demilitarization process. Specifically:

1. Quantify:
   (a) A bulk propellant material-to-solvent solubility efficiency ≥ 200 grams per liter of green solvent in a single cycle;
   (b) Solvent recovery > 90 % wt.;
   (c) Additive recovery and purity ≥ 90% wt. from the bulk propellant.
2. Show a cyclic process to demilitarize ≥ 1000 grams of bulk propellant per liter of solvent in a multi-cycle process.
3. Establish a scalable manufacturing plan to encompass the full cycle of demilitarization process.

All Phase I Technical Objectives were achieved.

Overview of Developed Capability

In Phase I, two simple, low-cost, safe, multi-cycle, CLEC demilitarization processes with near identical operational efficiencies were successfully developed, demonstrated and quantified (Figure 1). Each process is comprised of five simple distinct steps to allow:

- Complete recovery and recycling of inexpensive solvents of sodium hydroxide (NaOH), methanol (MeOH), water, and *N*-methyl-2-pyrrolidone (NMP) to eliminate environmental hazards, while;
- Maximizing additive recovery and their processing byproducts from each pyrotechnic-smoke formulation of HC, CS, red-dye, ZnO, Al_2O_3, and the pyrotechnic kit for commercial resale and/or re-use in propellant compositions.

The Reader is encouraged to refer to "Results and Discussion" section for more details of Processes A and B.

Specifically:

1. Demonstrated a green, highly efficient, **three-cycled, CLEC Process A** to demilitarize *HC based obscurant grenades (OG)* with the following operational efficacies (Table 2a):
   - Dissolution of 815 grams of bulk propellant material per liter of NaOH / H_2O solvent
   - Average additive recovery of:
     i. ~ 81% wt. HC and ~ 62% wt. ZnO and Al_2O_3
     ii. ~100% vol. NaOH / H_2O and MeOH
   - Additive purity of ~83% wt. ZnO and Al_2O_3.

Table 2: Operational Efficacy: (a) Process A: HC Based Obscurant Grenades; and (b) Process B: CS Based RCG (c) Red-dye SG.

Process Capability Objectives			1 Cycle	Process Capability Results - 3 Cycles				
HC smoke grams / L solvent **(1 cycle)**	HC smoke grams / L solvent **(multiple cycles)**	Additive recovery efficiency (%)	HC smoke grams / L solvent (%)	Average HC smoke grams / L solvent	HC recovery (% wt.)	ZnO & Al_2O_3 (% wt.)	NaOH / H_2O solution recovery (% vol.)	Methanol recovery (% vol.)
300	1200	>90	272 (91%)	815 (68%) of multiple cycle target	80.7	62	100	100

L-4498

(a)

Process Capability Objectives			1 Cycle	Process Capability Results - 3 Cycles				
CS smoke grams / L solvent **(1 cycle)**	CS smoke grams / L solvent **(multiple cycles)**	Additive recovery efficiency (%)	CS smoke grams / L solvent	CS smoke grams / L solvent	CS riot agent recovery (% wt.)	CS pyro-kit removed	Solvent recovery (NMP) (% vol.)	Anti-solvent recovery (H_2O) (% vol.)
200	1000	>90	330 (150%) of the single cycle target	1000 (100%) of multiple cycle target	85	67.1%	97	99

L-4500

(b)

Process Capability Objectives			1 Cycle	Process Capability Results - 4 Cycles				
Red dye smoke grams / L solvent **(1 cycle)**	Red dye smoke grams / L solvent **(multiple cycles)**	Additive recovery efficiency (%)	Red smoke grams / L solvent	Red smoke grams / L solvent	Red dye recovery (% wt.)	Red dye pyro-kit removed	Solvent recovery (NMP) (% vol.)	Anti-solvent recovery (H_2O) (% vol.)
200	1000	>90	330 (165%) of the single cycle target	1330 (133%) of multiple cycle target	89.32	66.05%	96	98

L-4499

(c)

2. Demonstrated a highly efficient **<u>multi-cycled, CLEC Process B</u>** capable to demilitarize *CS based riot control grenades* (RCG, Table 2b) and *red-dye based signal grenades* (SG, Table 2c) with near identical operational efficacies of:
   - Dissolution of 1000 grams (RCG, 4-cycles) and 1330 grams (SG, 3-cycles) of bulk propellant material per liter of NMP solvent
   - Additive recovery of:
     i. ~ 85% wt. for CS and ~89% wt. for red-dye
     ii. ~ 67% wt. for the pyrotechnic kit
     iii. ~99% vol. NMP and water
     iv. Additive purity of: ~99% wt. for CS and red-dye.

3. Demonstrated operational refinements in the **CLEC Process B** to eliminate use of the NMP solvent with carbonated water (CW) to establish a **completely green process**. The use of CW:
   - Solubilizes all three constituents of the pyrotechnic-kit (i.e., sugar, $KClO_3$ and $MgCO_3$) followed by the filtration of the CS to reverse the processing activities of Step 1 and 2 as is illustrated in Figure 2; and
   - Significantly improved the recovery efficacy of CS to 97% wt. Similar processing efficacy is also expected for recovering red-dye.

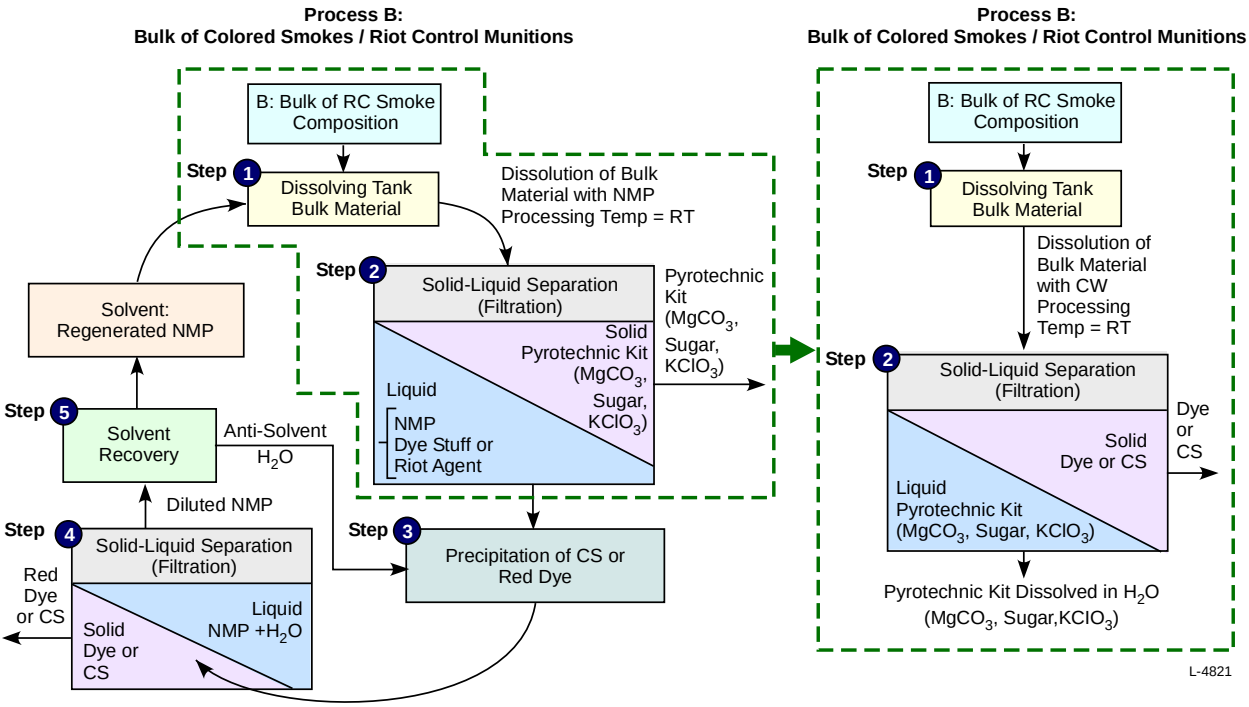


Figure 2: Operational refinements in Steps 1&2 of the CLEC Process B to replace use of NMP with CW.

4. Developed a low cost, green CLEC process to demilitarize multiple pyrotechnic-smoke compositions by off-setting material expenses through recycling of solvents and recovery of materials. A 1st order cost analysis based on recovered material showed a profitable CLEC process of:
   - >$0.42 per kg of HC/OG demilitarize
   - >$9.90 per kg of CS/RCG demilitarize
   - >$8.85 per kg of Red-dye/SG demilitarize

Table 3: Process Cost Analysis: (a) HC/OG; (b) CS/RCG; and (c) Red-dye/SG

	$ / kg
Processing Material	(4.58)
Recovered Material	1.24
Recycled	3.76
Overall Processing Efficacy	0.42

(a)

	$ / kg
Processing Material	(12.00)
Recovered Material	10.50
Recycled	11.40
Overall Processing Efficacy	9.90

(b)

	$ / kg
Processing Material	(12.00)
Recovered Material	9.45
Recycled	11.40
Overall Processing Efficacy	8.85

(c)

5. Successfully scaled-up the CLEC Process A to 20 grams and identified operational refinements to allow a 20kg production capability and demonstration in Phase II. Use of a jacketed reactor vessel and mechanical agitator showed to significantly improve the recovery efficiency of ZnO and Al_2O_3 from 62% wt. to 92.5% wt. Accordingly, a commercially available 100L cylindrical jacketed processing reactor with a covered jacketed vessel and mechanical agitator will allow reliable scale-up to maximize recovery of materials in shorter processing times.

Profit margins and recycling efficiencies are expected to increase during scale-up due to improvement in operational efficiencies.

The developed CLEC demilitarization process successfully achieved all of the Statement of Need (SON) objectives for WPSEED-16-02.

Results and Discussion

CLEC Demilitarization Process A

Figure 1a illustrates the CLEC demilitarization Process A. The process is comprised of five distinct steps:

***Step 1: Dissolution of Primary Components*:** A green solvent, 50% wt. NaOH / H_2O solution, is utilized to dissolve ZnO and Al additives. The high solubility of ZnO and Al in the concentrated basic solution creates an ionized solution of zincate and aluminate.[1] Figure 3 contains the balanced chemical equations for the conversion of ZnO and Al to zincate and aluminate ions, respectively. The solubility of ZnO as a function of the concentration of NaOH-to-H_2O is shown in Figure 4.[1] The experimental results show ZnO is highly soluble in a basic solution.

Specifically, increase in the concentration of NaOH from 25% wt. to 50% wt. provides a six-fold increase in the ZnO solubility (Figure 4).

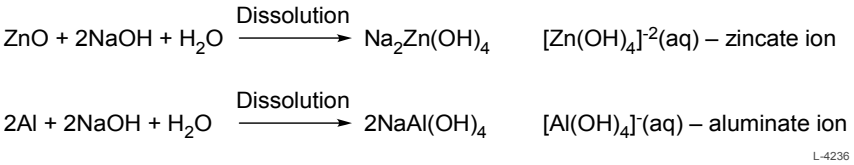


Figure 3: Dissolution of ZnO and Al to zincate and aluminate ions, respectfully, in an aqueous NaOH solution.

Initially, sequential experiments were conducted to test the components solubility (Table 4). Through this series of experimentation, the optimized processing parameters were determined to be using an amount of 50 wt. % NaOH solution equal to four times the stoichiometric amount necessary for dissolution at a processing temperature of 65°C. These parameters allowed for full dissolution of the Al and ZnO in a reasonable amount of time, and lowered the amount of HC sublimation.

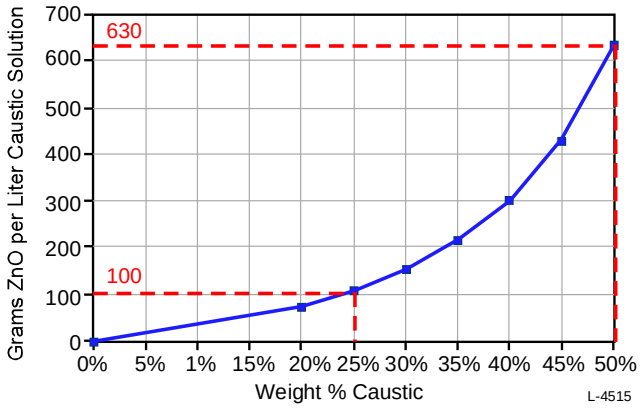


Figure 4: Solubility of ZnO in basic solution at varying concentrations of aqueous NaOH

Table 4: Dissolution Experiment Components

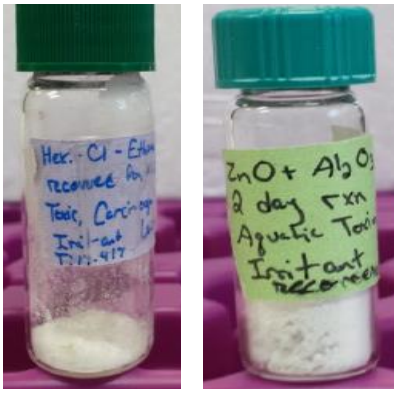
ZnO (g)	Al (g)	HC (g)	Processing Temp (°C)	NaOH / H_2O (g (mL))	Comment
25			100	65 (45)	Dissolved
22	3		100	65 (45)	Clumping of Al
22	3		100	260 (173.3)	Dissolved
22	3	22	100	260 (173.3)	HC partially sublimes
22	3	22	65	260 (173.3)	Dissolved / Dispersed

Step 2: Filtration of HC: Filtration separates the water soluble components from the solid HC. The $NaOH/H_2O$ solution provides the processing advantage of using excess water to reduce solution viscosity for faster vacuum filtration without the risk of precipitation of the ions due to a reduction in the basic solution. No evidence existed of the precipitation of ZnO and Al_2O_3 from the diluted $NaOH/H_2O$. The recovered HC was dried at 65°C and its purity is characterized using ICP-OES (Figure 5a).

Step 3: Precipitation of ZnO and Al_2O_3: Methanol (MeOH) is used to precipitate ZnO and Al_2O_3 from the ionized $NaOH/H_2O$ solution through an anti-solvent technique. The balanced equation for the conversion of zincate and aluminate ions to ZnO and Al_2O_3, respectively, are as follows:

$ZnO\ (s)$: $2\ Na_2Zn(OH)_4 \rightarrow 2\ ZnO + 4\ NaOH + 2\ H_2O$
$Al_2O_3(s)$: $2\ Na_2Al(OH)_4 \rightarrow Al_2O_3 + 2NaOH + 3\ H_2O$

This activity is conducted on ice to avoid excessive vaporization of the MeOH. The amount of precipitation is dependent on the amount of MeOH used. As a general rule, a volume of MeOH equivalent to five times that of the NaOH solution is used.



(a) **(b)**

Figure 5: Recovered: (a) HC; and (b) ZnO and Al_2O_3.

Step 4: Filtration of ZnO and Al_2O_3: The ZnO and Al_2O_3 is separated from the $NaOH/H_2O$/MeOH solution through vacuum filtration, dried at 105°C and characterized for its purity using TGA and ICP-OES. [2,3,4] TGA examines the weight loss based on the inorganic-to-organic ratio of the recovered ZnO and Al_2O_3. In this context, the organic material will evaporate/pyrolize during the temperature ramp. The results (Figure 6) showed four distinct mass loss events: (1) Water; (2) Residual HC; (3) and (4) Metal oxide surface hydroxyl groups. Approximately 2% of the total weight loss of the sample was due to dehydration of surface hydroxyl groups. This phenomenon is commonly seen in the TGA of metal oxides.

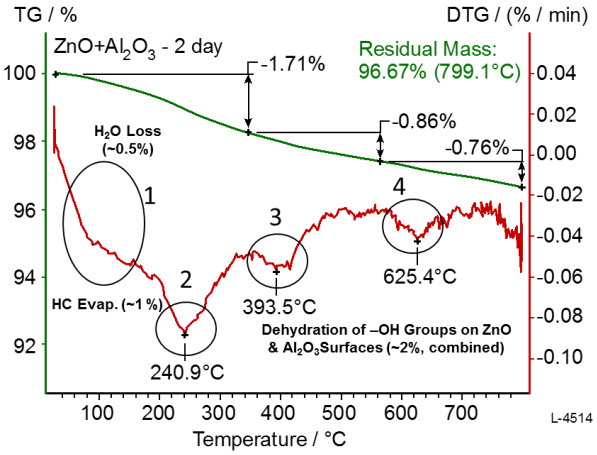


Figure 6: TGA of recovered ZnO and Al_2O_3, green = weight loss, brown = rate of weight loss

Step 5: Solvent Recovery: Recovery of MeOH from the $NaOH/H_2O$/MeOH is through simple distillation. The remaining diluted $NaOH/H_2O$ due to use of water during the filtration process in Step 2 is characterized for its purity using ICP-OES and regenerated accordingly by distillation.

Table 5 summarizes the measured processing efficacy of each step as a function of the number of cycles. It should be noted: (1) 50% wt. $NaOH/H_2O$ solution was initially used in the 1st cycle but subsequent regeneration to ~20-25% wt. $NaOH/H_2O$ in proceeding cycles was found to be sufficient to ensure similar processing efficiencies of the recovered materials; and (2) Approximately 100% wt. of the solvent was recovered to eliminate the environmental footprint while simultaneously maximizing the reduction in operational costs.

Table 5: Overview of Processing Efficacy of Process A

	Step 1			Step 2		Step 3	Step 4			Step 5		
Cycle	Temp °C	Time (Hr)	mL Lye / g HC smoke (mL)	mL H_20 / mL Lye Step 1 (mL)	Recovered HC (%)	mL MeOH / mL Lye Step 2 (mL)	Recovered ($ZnO+Al_2O_3$) / Theoretical ($ZnO+Al_2O_3$) (%)	Purity of ZnO & $Al_2O^{(*)}$		Recovered MeOH (vol %)	Recovered Lye* (vol %) (NaOH % wt.)	Regenerated Lye* (vol %) (NaOH % wt.)
								ZnO & Al_2O_3 (%)	$Na_2Zn(OH)_4$ & $NaAl(OH)_4$ (%)			
1	65	48	3.7	1.9	67	4	53.3	82.2	17.3	100	100	
1	65	48	3.7	1.9	90	4	63.4 Ice Cooling	85.0	15.0	100	100 (11.7)	100 (19.1)
2	65	72	3.7	1.9	82	4	68.0 Ice Cooling	84.9	15.1	100	100 (12.0)	100 (23.3)
3	65	72	3.7	1.9	70	4	54.3 Ice Cooling	80.4	19.6	100	100 (7.8)	100 (25.0)

L-4506

Based on the market value of the raw materials used and recovered from the CLEC demilitarization Process A, the developed process would allow for a minimum positive offset of $0.42 USD per kg of HC/OG demilitarized (Table 3a and Table 6).*

Table 6: 1st Order Cost Analysis as a Function of Processing Steps in Process A.†,‡

Step 1		Step 2		Step 3		Step 4				Step 5			
NaOH / HC Smoke		Recovered HC / HC Smoke		MeOH / HC Smoke		Recovered ZnO / HC Smoke		Recovered Al_2O_3 / HC Smoke		Recovered MeOH / HC Smoke		Recovered NaOH / HC Smoke	
WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost
2.75	(1.38)	0.38	0.57	4.00	(3.20)	0.31	0.62	0.054	0.054	3.6	2.88	1.75	0.875
NaOH		HC		MeOH		ZnO		Al_2O_3		MeOH		NaOH	

L-4508

CLEC Demilitarization Process B

A similar processing methodology to Process A was followed for Process B. Figure 1b illustrates the CLEC demilitarization Process B with NMP as the solvent. This process is also comprised of five distinct steps:

***Step 1: Dissolution of Primary Components*:** Initially, NMP solvent was utilized to dissolve the CS and red-dye at room temperature. The dissolution process was stirred for one hour for the CS or red-dye to fully dissolve. The solution forms a viscous solution. The use of sulfolane as a solvent was also attempted, but it gave poor results and its usage ceased.

Step 2: Filtration of Pyrotechnic Composition: Filtration separated the soluble CS or red-dye from the precipitated $KClO_3$, sugar, and $MgCO_3$ of the pyrotechnic kit. During the vacuum filtration, the filter would routinely clog due to the particle size of the $MgCO_3$. Filter papers with larger pores would have increased the risk of pyrotechnic kit flow-through and the contamination of the CS or red-dye solution. As a result, for faster and reliable filtration a centrifugation was

* NaOH: $0.5/kg; HC: $1.5/kg; MeOH: $0.8/kg; ZnO: $2/kg; Al_2O_3: $1/kg

† WR refers to the weight ratio of ingredients in the process (i.e., solvent), in the bulk material, and recovered.

‡ Red color refers to an expense or cost. Green color refers to profit through re-sale at market value

used to separate the aqueous solution from the pyrotechnic composition. The solid pyrotechnic kit remained while the soluble CS or red-dye was poured off.

Step 3: Precipitation of CS and Red-Dye: Water is added to the NMP solution to precipitate the dissolved CS or red-dye through an anti-solvent technique. This activity is conducted on ice to maximize precipitation and recover of the CS and red-dye by lowering their partial solubility in water.

Step 4: Filtration of CS and Red-Dye: The precipitated CS or red-dye (Figure 7) was separated from the NMP/water mixture through vacuum filtration, dried at 105°C, then characterized for purity using NMR, and TGA. Figure 8 illustrates the TGA results of the weight loss of the recovered red-dye. The results show the weight loss occurs in a signal event during the temperature ramp up to 800°C. Specifically, the demonstrated total weight loss of 99.69% at 800°C suggests a high purity of the recovered red-dye.

Initial NMR results indicated a small amount of sugar remaining in the red-dye. In subsequent filtration steps for both the red-dye and the CS, the remaining sugar was removed with a hot water wash of the collected solids. This method fully removed the sugar (Figure 9). Later results show definitive evidence of successfully isolating each additive with high purity.

(a) **(b)**

Figure 7: Recovered: (a) Red-dye; and (b) CS.

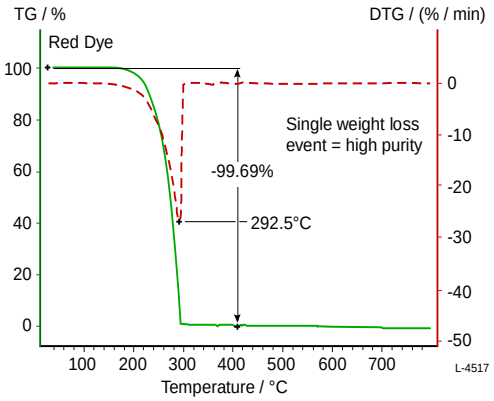
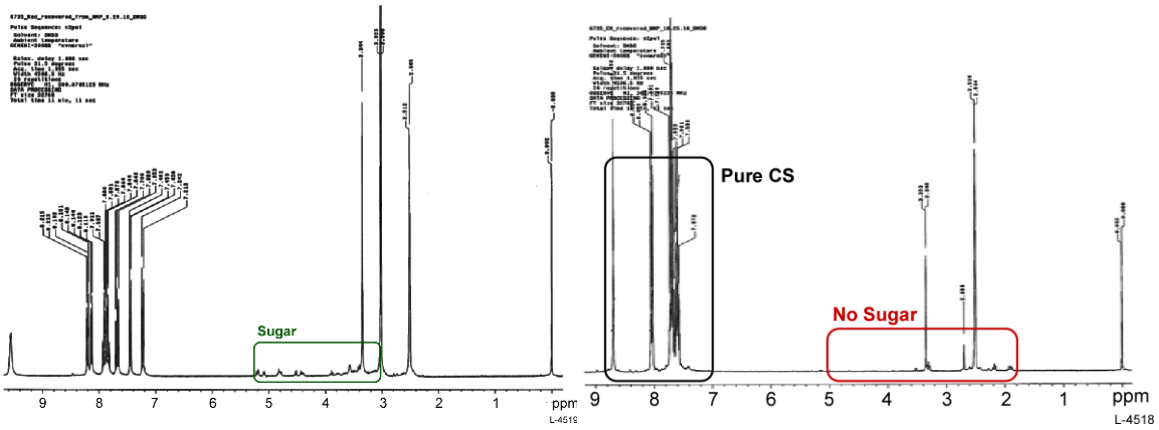


Figure 8: TGA of recovered red-dye.



(a) **(b)**

Figure 9: NMR spectrum of recovered: (a) Red-dye; and (b) CS using NMP.

Step 5: Solvent Recovery: Recovery of the NMP solvent from the NMP/H_2O was through simple distillation of the water.

Table 7 summarizes the measured processing efficacy of each step as a function of the number of cycles for red-dye and CS. Similar to Process A, ~100% wt. of the solvent was recovered to simultaneously maximize the reduction in operational costs. Based on the market value of the raw materials used and recovered from the CLEC demilitarization Process B, the developed process would allow for a minimum positive offset of $8.84 per kg of Red-dye/SG and $9.90 per kg of CS/RCG demilitarized (Table 3b, c and Table 7).

Table 7: Overview of Processing Efficacy of Process B for: (a) Red-dye; and (b) CS

	Step 1			Step 2		Step 3	Step 4	Step 5	
Cycle	Temp °C	Time (Hr)	mL NMP / g Red smoke	mL NMP / mL NMP (step 1)	Recovered Pyro Comp (% wt.)	mL H_2O / mL Solvent	Recovered Red Dye (% wt.)	Recovered NMP (% vol.)	Recovered H_2O (% vol.)
1	RT	4	2	4	70.5	4	80.0	95	100
1	RT	4	2	4	68.2	4	88.6 Ice cooling	98	100
2	RT	4	2	4	65.3	4	85.7 Ice cooling	95	98
3	RT	4	2	4	66	4	93.0 Ice cooling	95	98.5
4	RT	4	2	4	64.7	4	90.0 Ice cooling	94.5	96

L-4507

(a)

	Step 1			Step 2		Step 3	Step 4	Step 5	
Cycle	Temp °C	Time (Hr)	mL NMP / g CS smoke	mL NMP / mL NMP (step 1)	Recovered Pyro kit (% wt.)	mL H_2O / mL Solvent (step 2)	Recovered CS (% wt.)	Recovered NMP (% vol.)	Recovered H_2O (% vol.)
1	RT	4			64.5	4	81.0		
1	RT	4	2	4	68.4	4	83.0 Ice cooling	98.2	100
2	RT	4	2	4	67	4	87.0 Ice cooling	97.9	99.3
3	RT	4	2	4	65.8	4	84.0 Ice cooling	96	98.5

L-4510

(b)

CLEC Demilitarization Process B Modification: In an effort to eliminate NMP from the CLEC Process B, carbonated water was used to effectively solubilize all components of the pyrotechnic kit. This allowed vacuum filtration recovery of the solid red-dye or CS (Figure 1b and Figure 2) instead of recovery of the pyrotechnic kit, as described in Figure 10. Recovery of the pyrotechnic kit will be done by distillation or drying.

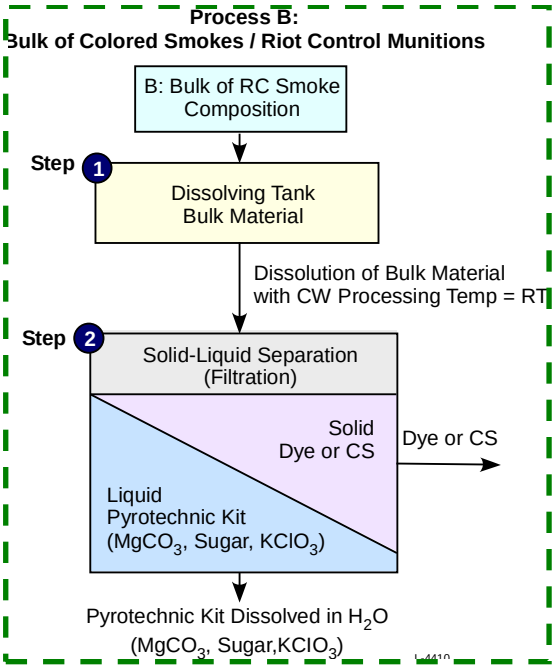


Figure 10: Modified Process B using CW.

Additionally, solubilizing the pyrotechnic kit improves the explosive safety of Process B. By wetting and dissolving the pyrotechnic kit, energetic capability is removed from the pyrotechnic kit mixture. During recovery of the pyrotechnic kit mixture, allowing the mixture to remain wetted vastly improves handling safety and reduces operator exposure.

This capability was demonstrated on the CS/RCG composition. The NMR results showed the recovered CS samples had identical purity to those recovered using NMP with no evidence of sugar (Figure 11). Simultaneously, the recovery efficiencies improved significantly, from ~85% wt. to ~97% wt.

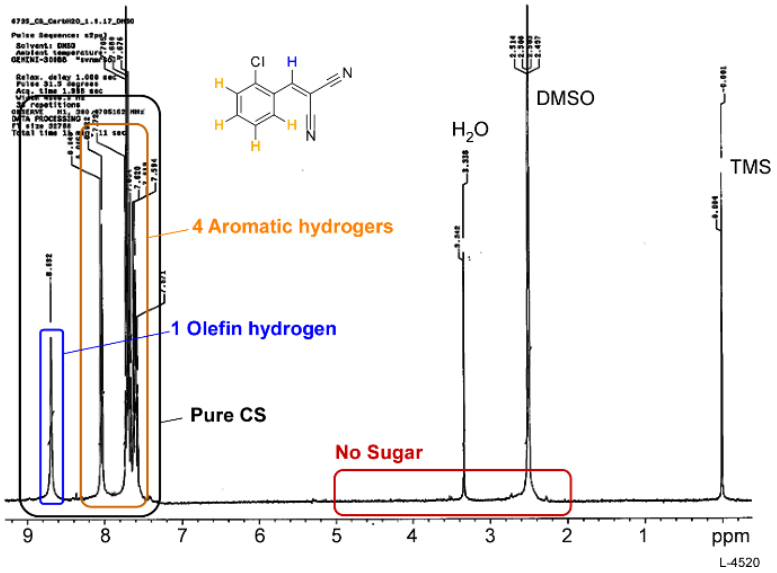


Figure 11: NMR spectrum of the recovered CS using CW.

The use of CW in the modified CLEC Process B establishes a completely green process by removing toxicity and waste treatment concerns associated with the use of NMP.

Scale-Up of the CLEC Demilitarization Process A

Process A was scaled-up linearly from 5g to 20g (a factor of 4) in order to identify operational refinements and equipment types needed to achieve reliable production demonstration in Phase II.

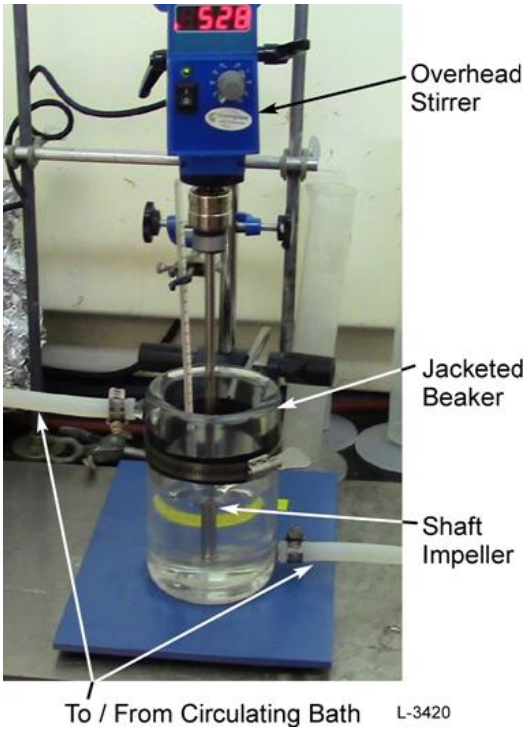


Figure 12: Scale-up processing using a jacketed vessel and mechanical agitator.

At the five gram scale, it was identified two main areas of improvement to improve upon the additive recovery during the dissolving and precipitation step: (1) Greater control of the thermal environment; and (2) Agitator type and speed. As a result, a jacketed reaction vessel combined with a digitally-controlled overhead mechanical stirrer and a 2″ four blade impeller (Figure 12) showed to significantly improve the recovery of ZnO and Al_2O_3 from 62 % wt. to 92.5% wt. This represented a 50% improvement in recovery efficiency. Unfortunately, the recovered HC had reduced to 49.1% wt. This was due to use of an uncovered jacketed beaker that allowed greater than expected sublimation of HC, preventing complete recovery. Accordingly, use of covered jacketed vessel will provide recovery efficiencies greater than 81%wt. as seen at the 5g scale.

Conclusions and Implications for Future Research

PSI has successfully executed a Phase I program to design, develop, and demonstrate a multi-cycled, CLEC process to demilitarize three classes of pyrotechnic-smoke formulations: (1) Obscurant Grenades, (2) Riot Control Grenades, and (3) Signal (obscurant or colored smoke) Grenades. This effort was divided between two 5-step processes. The developed CLEC demilitarization process successfully achieved all of the criteria required of the Statement of Need for WPSEED-16-02.

CLEC Process A successfully isolated highly pure HC in an average yield of 81% from ZnO and Al. The ZnO and Al were recovered as a mixture of ZnO and Al_2O_3 in an average yield of 62% with an average purity of 83% by weight. All solvents used in this process were recovered or regenerated in 100% yield. Using these recovery yields, it was estimated an average of 815 g of HC smoke could be processed using a single liter of solvent.

CELC Process B was used to isolate CS and red dye from their respective pyrotechnic smoke formulation. Using this method, highly pure (~99%) red dye and CS were recovered at yields of 89% and 85%, respectively. The pyrotechnic kit, consisting of a mixture of $MgCO_3$, $KClO_3$, and sugar, was recovered in an approximately 67% yield. Using these recovery yields, it was estimated 1 kg of CS-based Riot Control Grenade formulation, and 1.33 kg of Signal Grenade formulation

could be demilitarized per one liter of solvent. Due to the toxicity concerns surrounding the use of NMP as the primary solvent for Process B, the process was modified to substitute carbonated water for the NMP. The modification of Process B allows for higher yields (~99 wt. %) of CS or red dye, the most valuable and easily recyclable component of the RCA and SG formulations.

These methods were shown to allow the offset of processing expenses by the resale of recovered materials, and recycling solvents. The first order cost analysis of the CELC processes shows a profitable offset of $0.42 per kg of HC/OG, $9.90 per kg of CS/RCG, and $8.85 per kg of the Red-dye/SG demilitarization efforts.

Future work in this area would be a continuation of the successful Phase I results. The Phase II development of the green, highly efficient, multi-cycled, CLEC demilitarization process would continue in two interlinked parts to ensure a successful technology development phase and transition to production scale in Phase III. They are the:

(1) Manufacturing scale-up of the CLEC process to 20 kg using commercially-off-the-shelf (COTS) components. Validation of the processing efficacy, recovered materials and their purity through systematic evaluation of each processing step to ensure a reliable performance measurements (Figure 13); and
(2) Demonstration of the CLEC demilitarization performance as a function of recycling process and life cycle cost to ensure a commercial viable solution.

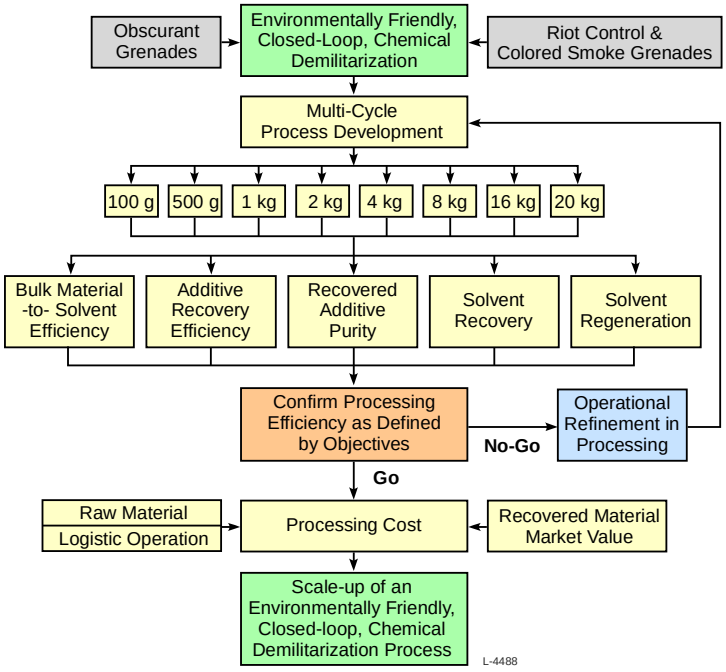


Figure 13: Overview of proposed scale up of the CLEC demilitarization process.

This two-tier approach continues development of the CLEC processing modalities while simultaneously maturing the manufacturing readiness level (MRL) to +5. It is envisioned at the end of a Phase II effort, the scaled-up CLEC demilitarization process will have been developed and quantified for each incremental step to ensure reproducibility. This will provide the basis to establish a detailed cost analysis / model based on the end-to-end value stream map including cost targets allocated for each processing step, the off-set of recycling materials, and the commercial resale of recovered materials.

The developed technology and results are summarized in a PowerPoint presentation in Appendix A.

Literature Cited

1. Frenay J., Hissel J. and Ferlay S. (1985). *Recovery of Lead and Zinc from Electric Steelmaking Dusts by the Cebedeau Process*. Taylor P., Sohn H.Y. and Jarret N. eds.: Recycle and Secondary Recovery of Metals, TMS, Fort Lauderdale, Fl, Dec 1-4, pp. 195-201
2. Laurin, M., Paspek , S., US Patent # 2013/0064743 A1 "Process for Purifying Zinc Oxide," Mar. 14, 2013
3. Lemaire, G., US Patent # 4005061A, "Method for recovering potassium hydroxide and zinc oxide from potassium zincate solutions,", Jan 25,1977
4. Mellor, Inorganic and Theoretical Chemistry, Longmans Green & Co., vol. II (1922) pp. 757, 758, vol. IV (1929) pp. 528, 529.

Appendix A

Physical Sciences Inc.

6735-FinalBrief

Environmentally Sound and Safe Military Munition Demilitarization

Final Brief

(16 WPSEED02-009 / WP-2616)

January 18, 2017

Allan Dokhan, Lauren Ziemba, and Lucian Stoenescu

Acknowledgement of Support and Disclaimer

This material is based upon work supported by the Humphreys Engineer Center Support Activity under Contract Number W912HQ-16-P-0009. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Humphreys Engineer Center Support Activity.

Physical Sciences Inc. 20 New England Business Center Andover, MA 01810

Outline

Physical Sciences Inc.

6735-FinalBrief-1

- **Program Funding and Partners**
- **Overall Capability to be Developed**
- **Targeted Pyrotechnic Smoke Formulations**
- **Exit Performance Parameters**
- **Critical Results, Processing Efficacy and Costing**
- **Scale-up Approach in Phase II**

Program and Funding

Physical Sciences Inc.

6735-FinalBrief-2

- **SEED SON WPSEED-16-02**: ***"Environmentally Sound and Safe Military Munition Demilitarization"***
- **Title:** ***Environmentally Sound and Safe Military Munition Demilitarization***
- **Technology Areas**: Weapon Systems and Platforms (WP)
- Program Managed by Strategic Environmental Research and Development Program (SERDP)
  - **TPOC**
    Dr. Robin Nissan
    Program Manager for Weapons Systems and Platforms
  - Funded $149,846
  - Technical Period of Performance:
    - 12 Months
  - **Start Date**:05/02/2016
  - **End Date**: 05/01/2017

SERDP
DOD ▪ EPA ▪ DOE

Solicitation Requirements

Physical Sciences Inc.

6735-FinalBrief-3

- **OBJECTIVE**
  - Alternative technologies are sought for open burn/open detonation of munitions that have:
    - Environmentally acceptable demilitarization methodologies, and
    - Who's waste treatment has re-use e.g., explosive components, metal additives, etc.
- **GOAL**
  - Develop innovative approaches and new technologies
    - Recycle, reuse or otherwise demilitarize in an environmentally sound and safe manner excess, obsolete, and unserviceable conventional ammunition
- **METRICS**
  - New technologies are sought:
    - Maximizes recycling and reuse
    - Minimize operator exposure
    - Enhance explosive safety
    - Reduce life-cycle costs

Overall Capability Being Developed

Physical Sciences Inc.

6735-FinalBrief-4

Develop an environmentally friendly, closed loop, chemical process that enables the re-use / recycling of solvents for the demilitarization of munitions with pyrotechnic-smoke compositions

↓

Demilitarization refers to:
Segregation of additives from the bulk energetic materials

- **Three classes of pyrotechnic-smoke formulations are targeted for demonstration**
  1. **Obscurant Grenade**
     - Hexachloroethane (HC) / ZnO / Al based formulation
  2. **Riot Control Grenades**
     - 2-Chlorobenzalmalononitrile (CS) / $KClO_3$ / $MgCO_3$ / Sugar based formulation
  3. **Signal (Obscurant) Grenades**
     - Red-Dye / $KClO_3$ / $MgCO_3$ / Sugar based formulation

Pyrotechnic-Smoke Formulations

Physical Sciences Inc.

6735-FinalBrief-5

Obscurant Grenade Formulations

Additive	% wt.
HC	46.8
ZnO	46.8
Al	6.4

	Additive	% wt.
Colored Dye	Red Dye	35
Pyrotechnic Composition	$KClO_3$	30
	Sugar	25
	$MgCO_3$	10

Riot Control Grenade Formulations

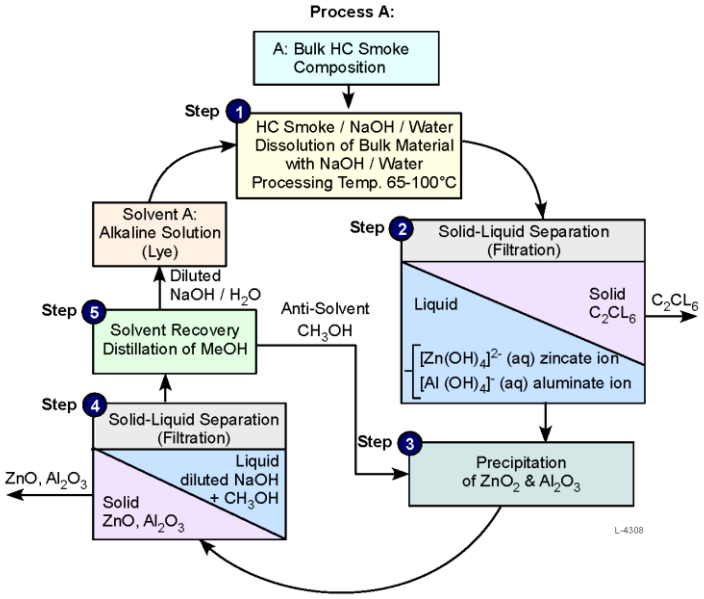
	Additive	% wt.
Riot Agent	CS	35
Pyrotechnic Composition	$KClO_3$	30
	Sugar	25
	$MgCO_3$	10

Technology Solution: Demilitarization Process

Physical Sciences Inc.

6735-FinalBrief-6

Obscurant Grenade Formulation

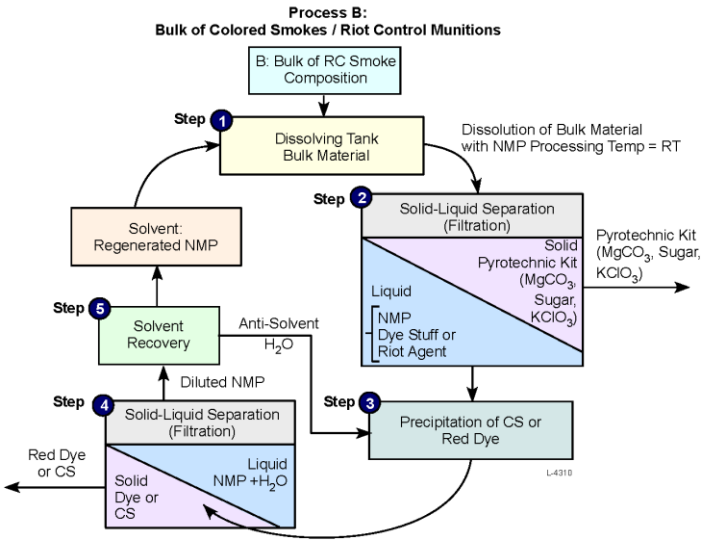


Technology Solution: Demilitarization Process

Physical Sciences Inc.

6735-FinalBrief-7

Riot Control & Signal Grenade Formulations



Exit Performance Parameters

Physical Sciences Inc.

6735-FinalBrief-8

1. **Ensure a consistent batch-to-batch repeatability of a closed loop chemical process for demilitarizing pyrotechnic-smoke formulations with the following metrics:**
   - **Green Solvent**
     - → **Recovery Efficiency > 90 %**
       - ***Obscurant Formulation***
         - NaOH / Water / MeOH (anti-solvent) / Water (viscosity reduction)
       - ***Riot Control Formulation***
         - NMP / Water (anti-solvent)
   - **Recovery of Additives > 50%**
   - **Bulk Material-to-Solvent Efficiency**
     - → **Greater than 200 grams / Liter of Solvent**
2. **Establish a scalable manufacturing plan to encompass the full cycle of demilitarization process**

Physical Sciences Inc.

6735-FinalBrief-9

Obscurant Smoke Formulation

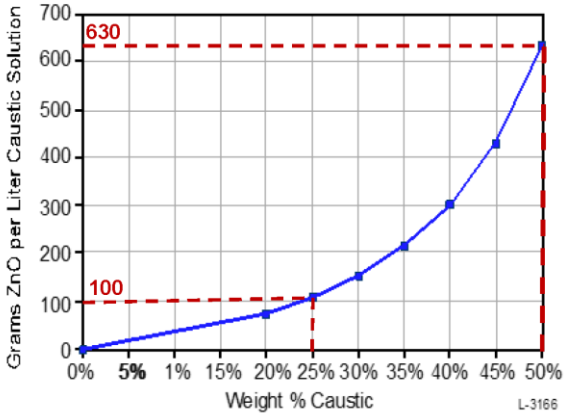
Process A

Critical Technology Solution: Dissolution of Metal / Metal Oxides in a Basic Solution

Physical Sciences Inc.

6735-FinalBrief-10

- **Segregation of the additives from the bulk material relies on dissolving the ZnO and Al in a basic solution**
- **ZnO is highly soluble in a basic solution**
  - Increase in the concentration of basic solution from 25% to 50 %wt.
    - Six fold increase in ZnO solubility
- **Dissolving ZnO and Al in a basic solution of NaOH / H_2O will produce an ionized solution of:**
  - Zincate ion
  - Aluminate ion
- **Use of a basic solution provides processing simplicity when water is added**
  - Reduce the viscosity of the ionized solution for faster filtration
  - Prevents precipitation of ions due to reduction in basic concentration; Zinc and Al



$$ZnO + 2NaOH + H_2O \rightarrow Na_2Zn(OH)_4 \qquad [Zn(OH)_4]^{-2}(aq) - \text{zincate ion}$$

$$2Al + 2NaOH + H_2O \rightarrow 2NaAl(OH)_4 \qquad [Al(OH)_4]^{-}(aq) - \text{aluminate ion}$$

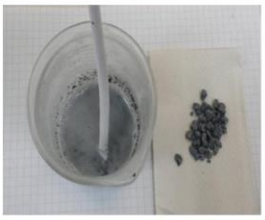
Dissolution of ZnO, Al, and Dispersion of HC

(Step 1)

Physical Sciences Inc.

6735-FinalBrief-11

- **Exploratory study was initially conducted to identify the operational specification of the chemical process. Specifically, identify:**
  - Dissolution and dispersion of the primary additives as a function of:
    - Concentration; and
    - Processing temperature in **50% wt. NaOH / 50% wt. H_2O solvent**
  - **All materials were added as a powdered material at equivalent wt. ratios to the bulk material**



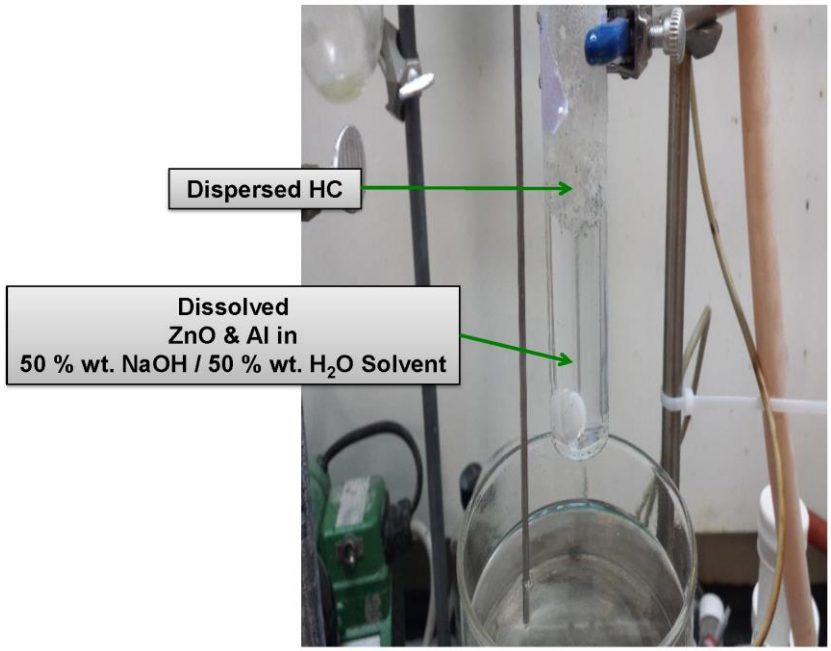
ZnO (g)	Al (g)	HC (g)	Processing Temp (°C)	NaOH / H_2O g (mL)	Comment
25			100	65 (45)	Dissolved
22	3		100	65 (45)	Clumping of Al
22	3		100	260 (173.3)	Dissolved
22	3	22	100	260 (173.3)	HC partially sublimes
22	3	22	65	260 (173.3)	Dissolved / Dispersed

Dissolution of ZnO, Al, and Dispersion of HC (Cont.)

(Step 1)

Physical Sciences Inc.

6735-FinalBrief-12



Filtration of HC from Ionized Solvent and Precipitation of ZnO / Al_2O_3

(Step 2 and Step 3)

Physical Sciences Inc.

6735-FinalBrief-13

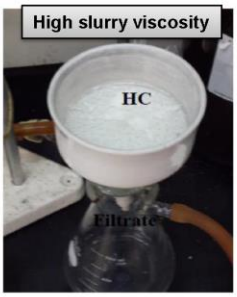
- **Separation of HC from the ionized solvent was accomplished using vacuum filtration**
  - ***Issue***: Filtration of the HC was limited due to slurry's viscosity
  - ***Solution***: Water was added to the ionized NaOH/water solvent to reduce the viscosity of the slurry and speed-up filtration process
    - As expected, no evidence of precipitation of ZnO and Al_2O_3
- **Precipitation of ZnO and Al_2O_3 from the ionized NaOH / water solvent was accomplished with the use of an anti-solvent Methanol (MeOH)**

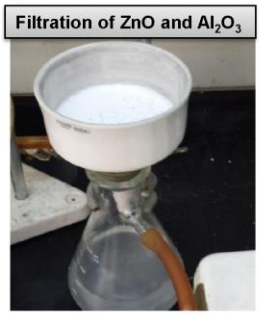
$$2Na_2Zn(OH)_4 \xrightarrow[\text{Methanol}]{\text{Anti-Solvent}} 2ZnO + 4\,NaOH + 2H_2O$$ ZnO (s) - zinc oxide

$$2NaAl(OH)_4 \xrightarrow[\text{Methanol}]{\text{Anti-Solvent}} Al_2O_3 + 2\,NaOH + 3\,H_2O$$ Al_2O_3 (s) - Aluminum oxide

L-4237

  - ***Process***:
    - Solution was stirred on ice for ~30 minutes
    - ZnO / Al_2O_3 was separated from the NaOH / water / MeOH solution using vacuum filtration

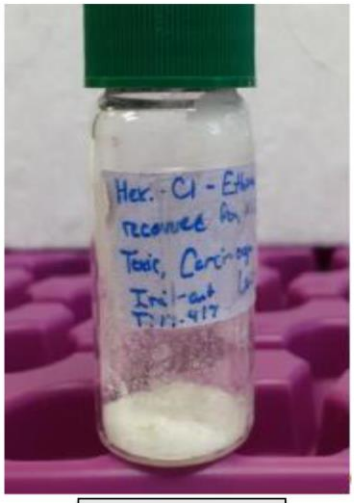




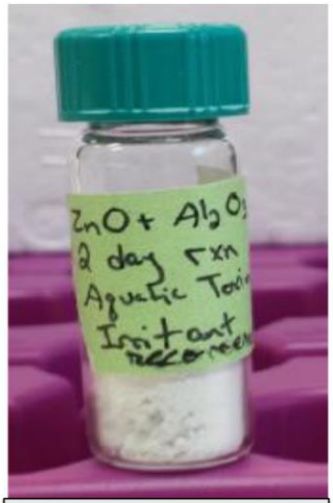
Recovered HC, ZnO and Al_2O_3

Physical Sciences Inc.

6735-FinalBrief-14



Recovered HC



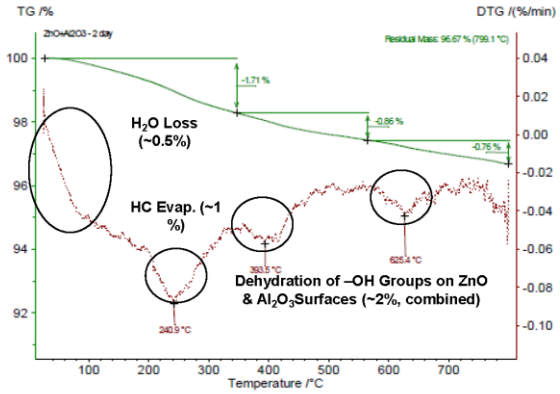
Recovered ZnO & Al_2O_3

Purity of the Recovered ZnO and Al_2O_3

Physical Sciences Inc.

6735-FinalBrief-15

- **Multiple analytical techniques were used to quantify the purity of the recovered ZnO and Al_2O_3**
- **% wt. of inorganic-to-organic**
  - **Thermogravimetric Analysis (TGA)**
    - Organic materials will evaporate / pyrolize during temperature ramp
    - Results showed weight losses in 4 events:
      - water, residual HC, and expected loss of metal oxide surface hydroxyl groups



Green - % weight loss
Brown – rate of % weight loss

  - 96.67% (<4% weight loss @ 800°C)
    - **Recovered metal oxides have high purity (~99%)**
  - Optical Emission Spectroscopy (ICP-OES)
    - Samples were dissolved by acid or base, then ionized in an argon plasma. Spectrophotometer, is used to characterize concentration

Processing Efficacy

Physical Sciences Inc.

6735-FinalBrief-16

Cycle	Step 1			Step 2		Step 3	Step 4			Step 5		
	Temp °C	Time (Hr)	mL Lye / g HC smoke (mL)	mL H_2O / mL Lye Step 1 (mL)	Recovered HC (%)	mL MeOH / mL Lye Step 2 (mL)	Recovered ($ZnO+Al_2O_3$) / Theoretical ($ZnO+Al_2O_3$) (%)	Purity of ZnO & $Al_2O^{(*)}$		Recovered MeOH (vol %)	Recovered Lye* vol. % (NaOH % wt.)	Regen. Lye* vol.% (NaOH % wt)
								ZnO & Al_2O_3 (%)	$Na_2Zn(OH)_4$ & $NaAl(OH)_4$ (%)			
1	65	48	3.7	1.9	67	4	53.3	82.2	17.3	100	100	
1	65	48	3.7	1.9	90	4	63.4 Ice cooling	85.0	15.0	100	100 (11.7)	100 (19.1)
2	65	72	3.7	1.9	82	4	68.0 Ice cooling	84.9	15.1	100	100 (12.0)	100 (23.3)
3	65	72	3.7	1.9	70	4	54.3 Ice cooling	80.4	19.6	100	100 (7.8)	100 (25.0)

*ICP-OES analysis

Process capability objectives			1 cycle	Process capability results- 3 cycles				
HC smoke grams / L solvent (1 cycle)	HC smoke grams / L solvent (Multiple Cycles)	Process recovery efficiency (%)	HC smoke grams / L solvent (%)	Avg. HC smoke grams / L solvent	HC recovery (wt. %)	ZnO & Al_2O_3 (wt. %)	NaOH / H_2O solution recovery (Vol. %)	Methanol recovery (Vol.%)
300	1200	> 90	272 (91%)	815 (68%) of multiple Cycle target	80.7	62	100	100

1st Order Process Cost Analysis of HC Smoke

Physical Sciences Inc.

6735-FinalBrief-17

	Step 1 NaOH / HC Smoke		Step 2 Recovered HC / HC Smoke		Step 3 MeOH / HC Smoke		Step 4 Recovered ZnO / HC Smoke		Step 4 Recovered Al_2O_3 / HC Smoke		Step 5 Recovered MeOH / HC Smoke		Step 5 Recovered NaOH / HC Smoke	
	WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost	WR	Cost
NaOH	2.75	(1.38)											1.75	0.875
HC			0.38	0.57										
MeOH					4.00	(3.20)					3.6	2.88		
ZnO							0.31	0.62						
Al_2O_3									0.054	0.054				

Raw Material	Bulk Cost ($) per kg
NaOH	0.5
HC	1.5
MeOH	0.8
ZnO	2.0
Al_2O_3	1.0

	$ / kg
Processing Material	(4.58)
Recovered Material	1.24
Recycled	3.76
Overall Processing Efficacy	0.42 √

The developed process allows for a positive offset of 42 cents per kg of HC smoke demilitarized

Physical Sciences Inc.

6735-FinalBrief-18

Riot Control & Signal Smoke Formulations

Process B

Dissolution of CS or Red-Dye and Dispersion of Pyrotechnic Kit *(Step 1)*

Physical Sciences Inc.

6735-FinalBrief-19

- **A similar processing methodology was followed for demilitarizing riot control smoke composition**
- **Exploratory study was initially conducted to identify the operational specification of the chemical process. Specifically, identify:**
  - Dissolution and dispersion of the primary additives as a function of:
    - Concentration; and
    - Solvent type: **NMP and Sulfolane**
      - Material recovered from sulfolane had poor purity, NMP was the preferred solvent
  - **All materials were added as a powdered material at equivalent wt. ratios to the bulk material**

Red Dye (g)	CS (g)	Pyrotechnic Composition (g)	Sulfolane (mL)	NMP (ml)	Comment
1.75		3.25	10		Dissolved
1.75		3.25		10	Dissolved
	1.75	3.25	10		Dissolved
	1.75	3.25		10	Dissolved

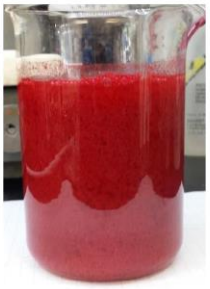
Filtration of Pyrotechnic Composition Solvent and Precipitation of CS / Red-Dye *(Step 2 and Step 3)*

Physical Sciences Inc.

6735-FinalBrief-20

- **Separation of pyrotechnic composition from the solvent was accomplished using a vacuum filtration**
  - ***Issue***: Filtration of the pyrotechnic composition from the solvent was limited due to the particle size of the $MgCO_3$ relative to porosity of filtration paper
    - Filter paper with larger pores increased the risk of contaminating the solvent
  - ***Solution***: Centrifuge was used to improve the filtration of the pyrotechnic composition from the solvent

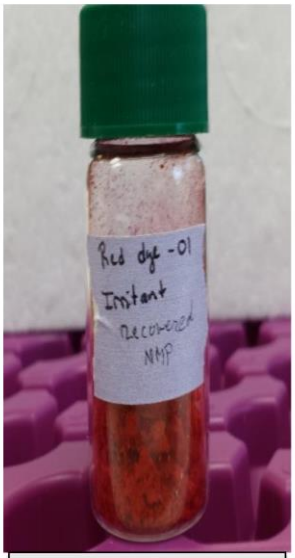
- **Precipitation of CS and red dye from the solvent was accomplished with the use of an anti-solvent water**
  - ***Process***:
    - Solution was stirred on ice for ~30 minutes
    - CS or red dye was separated from the NMP or Sulfolane using a centrifuge



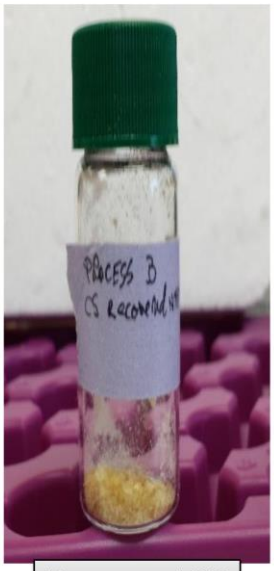
Recovered Red Dye and CS

Physical Sciences Inc.

6735-FinalBrief-21



Recovered Red Dye



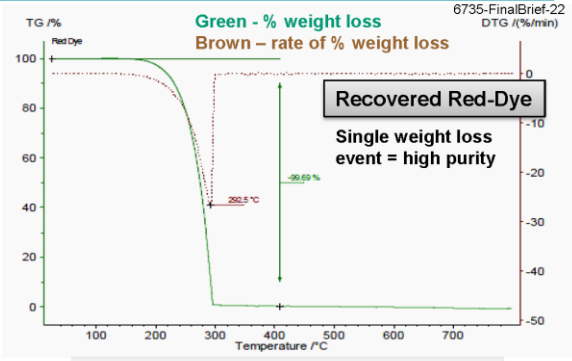
Recovered CS

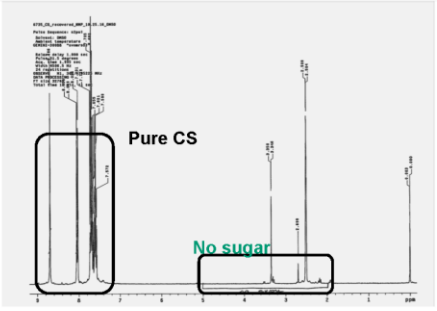
Purity of the Recovered Red-Dye and CS

Physical Sciences Inc.

6735-FinalBrief-22

- **Multiple analytical techniques were also used to quantify the purity of the recovered red-dye and CS**
- **TGA analysis of the recovered red-dye from NMP indicated a high purity**
  - Weight loss occurs in a single event during temp ramp up to ~800°C
    - Weight Loss: 99.69%
- **NMR spectrum of the recovered CS showed a high purity**
  - Isolation of CS was successful
- **NMR spectrum of the recovered red dye showed small amount of residual sugar.**
  - ~10% of sample was sugar
    - Amount too small alter the weight loss % in TGA
  - Sugar residue will be removed in future cycles by hot water wash





ITAR or Export Controlled

Processing Efficacy of the Red-Dye Smoke

Physical Sciences Inc.

6735-FinalBrief-23

Cycle	Step 1				Step 2			Step 3	Step 4	Step 5		
	Temp °C	Time Hours	mL Sulfolane / g Red smoke	mL NMP / g Red smoke	mL Sulfolane / mL Sulfolane (step 1)	mL NMP / mL NMP (step 1)	Recovered Pyro Comp (% wt.)	mL H_2O / mL Solvent	Recovered Red dye (% wt.)	Recov. Sulfolane (% vol.)	Recov. NMP (% vol.)	Recov. H_2O (% vol.)
1	RT	4	2		4		65	4	41.0	90		100
1	RT	4		2		4	70.5	4	80.0		95	100
1	RT	4		2		4	68.2	4	88.6 Ice cooling		98	100
2	RT	4		2		4	65.3	4	85.7 Ice cooling		95	98
3	RT	4		2		4	66	4	93.0 Ice cooling		95	98.5
4	RT	4		2		4	64.7	4	90.0 Ice cooling		94.5	96

Process capability objectives			1 Cycle	Process capability results- 4 cycles			
Red smoke grams/ L solvent (1 Cycle)	Red-Dye smoke grams/ L solvent (Multiple Cycles)	Process recovery efficiency (%)	Red smoke grams / L solvent	Red smoke grams/ L solvent	Red dye recovery (%)	Solvent recovery (NMP) (%)	Anti-solvent recovery (H_2O) (%)
200	1000	>90	330 (165%) of the single cycle target	1330 (133%) of multiple Cycle target	89.32	96	98

1st Order Process Cost Analysis of Red-Dye Smoke

Physical Sciences Inc.

6735-FinalBrief-24

	Step 1 & 2 NMP / Red-Dye Smoke		Step 4 Recovered Red Dye / Red-Dye Smoke		Step 5 Recovered NMP / Red-Dye Smoke	
	WR	Cost	WR	Cost	WR	Cost
NMP	6	(12)			5.70	11.40
Red Dye			0.32	9.45		

Raw Material	Bulk Cost ($) per kg
NMP	2.00
Red Dye	30.00

	$ / kg
Processing Material	(12.00)
Recovered Material	9.45
Recycled	11.40
Overall Processing Efficacy	8.85 √

The developed process allows for a positive offset of $8.85 per kg of Red-Dye smoke demilitarized

Processing Efficacy of the CS Smoke

Physical Sciences Inc.

6735-FinalBrief-25

Cycle	Step 1				Step 2			Step 3	Step 4	Step 5		
	Temp °C	Time Hours	mL Sulfolane / g CS smoke	mL NMP / g CS smoke	mL Sulfolane / mL Sulfolane (Step 1)	mL NMP / mL NMP (Step 1)	Recovered Pyro kit %	mL H_2O / mL Solvent Step 2	Recov. CS (% wt.)	Recov. Sulfolane (% vol)	Recov. NMP (% vol)	Recov. H_2O (% vol)
1	RT	4	2		4		64.5	4	81.0	90		
1	RT	4		2		4	68.4	4	83.0 Ice cooling		98.2	100
2	RT	4		2		4	67	4	87.0 Ice cooling		97.9	99.3
3	RT	4		2		4	65.8	4	84.0 Ice cooling		96	98.5

Process capability objectives			1 Cycle	Process capability results- 3 cycles			
CS smoke grams / L solvent (1 Cycle)	CS smoke grams/ L solvent (Multiple Cycle)	Process recovery efficiency (%)	CS smoke grams / L solvent	CS smoke grams / L solvent	CS riot agent recovery (% wt.)	Solvent recovery (NMP) (% vol.)	Anti-solvent recovery (H_2O) (% vol.)
200	1000	>90	330 (150%) of a single cycle target	1000 (100%) of a multiple cycle target	85	97	99

1st Order Process Cost Analysis of CS Smoke

Physical Sciences Inc.

6735-FinalBrief-26

	Step 1 & 2 NMP / CS Smoke		Step 4 Recovered Red Dye / CS Smoke		Step 5 Recovered NMP / CS Smoke	
	WR	Cost	WR	Cost	WR	Cost
NMP	6	(12)			5.70	11.40
CS			0.33	10.50		

Raw Material	Bulk Cost ($) per kg
NMP	2.00
CS	35.00

	$ / kg
Processing Material	(12.00)
Recovered Material	10.50
Recycled	11.40
Overall Processing Efficacy	9.90 √

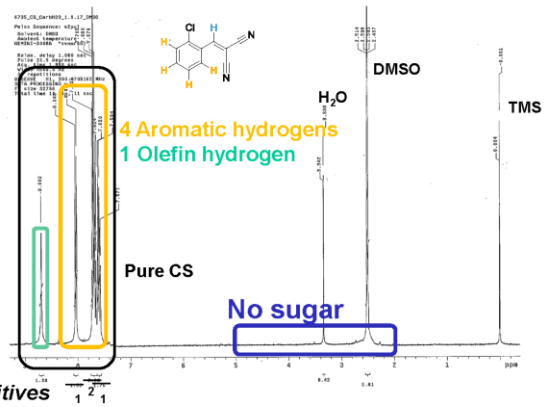
The developed process allows for a positive offset of $9.90 per kg of CS smoke demilitarized

Use of Carbonated Water (CW) to Replace NMP

Physical Sciences Inc.

6735-FinalBrief-27

- **Use of NMP offers challenges to its use at the manufacturing scale due to its toxicity**
- **CW was considered as an alternative solvent to ensure green processing**
  - Water dissolves Sugar and $KClO_3$ but not the $MgCO_3$ of the pyrotechnic kit
  - However, CW dissolves all three components of the pyrotechnic kit
- **Feasibility of using CW to replace NMP was demonstrated on the CS smoke formulation**
  - Step 2 of the demilitarization processing was modified: Specifically, ***Filtration of Additives***
    - NMP solubilizes CS→ Pyrotechnic kit is filtered
    - CW solubilizes Pyrotechnic kit → CS is filtered



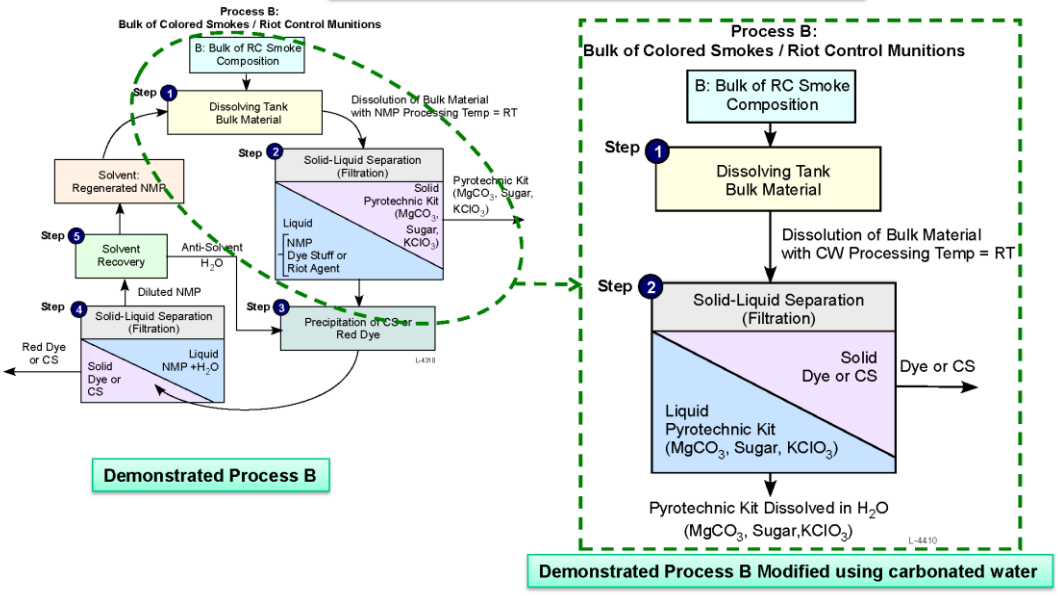
- **NMR spectrum of CW showed a greater efficacy compared to use of NMP**
  - **Recovered CS showed a high purity i.e., no presence of sugar and a greater recovery efficacy of 97% wt. compared to ~85% wt.**
  - **Isolation of CS was successful using CW**

Technology Solution: Revised Demilitarization Process

Physical Sciences Inc.

6735-FinalBrief-28

Riot Control & Signal Grenade Formulations



Scale-up of Processing Efficacy of HC Smoke

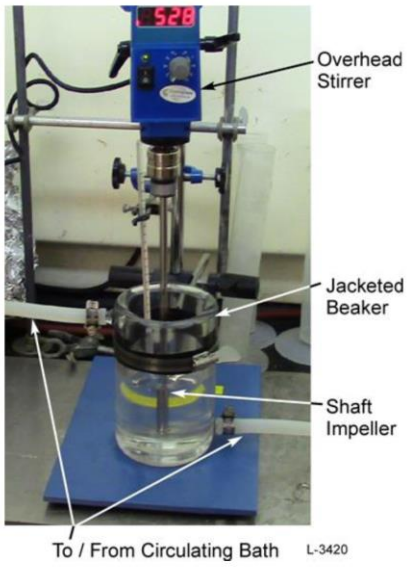
Physical Sciences Inc.

6735-FinalBrief-29

- **Scale-up process from 5g to 20g was evaluated to identify operational refinements needed for reliable production**
  - Greater control is needed of:
    - Thermal environment during dissolving and precipitation
    - RPM of the agitator; mechanical vs. magnetic stirrer
  - Processing parameters were scaled linearly (by a factor of 4) from 5g to 20g
- **Results showed:**
  - Recovered HC: 4.32 g (49.1% wt.)
    - Lower recovered HC was due to use of an uncovered jacketed beaker. This prevented adequate recovery of the subliming HC

      → Use of a lid will provide greater recovery efficiency >70% wt. (similar to the 5g scale)
    - Jacketed beaker provided superior temperature control
  - Recovered ZnO_2/Al_2O_3:
    - 10.24 g (92.5%)

      → Purity of 81.1% by ICP



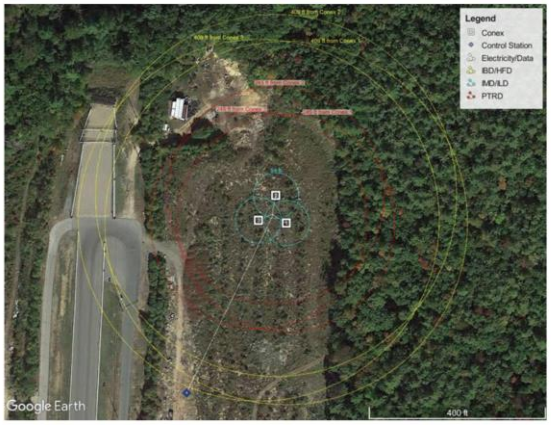
- **Similar results are expected for demilitarization of Red-Dye and CS smoke formulations**

Scale-Up Process to 20 kg in Phase II

Physical Sciences Inc.

6735-FinalBrief-30

- Scale-up chemical demilitarization process for demonstration in Phase II
- A systematic and incremental scale-up is needed for a reliable increase in production scale with similar processing efficacy demonstrated up to 20g
  - Use of a covered, jacketed reaction vessel with an overhead stirrer is needed
    - 100L size allows for scale-up by 1000x to achieve 20 kg batches



100L Cylindrical Jacketed Processing Reactor

- PSI's new remote test facility for explosive processing and testing ensures reliable development and demonstration in Phase II

Summary of Results

Physical Sciences Inc.

6735-FinalBrief-31

- Successfully developed and demonstrated a simple closed loop, chemical process that enabled the re-use / recycling of solvents for the demilitarization of three types of munitions using pyrotechnic-smoke composition
  1. Obscurant Grenade
     - Hexachloroethane (HC) / ZnO / Al based formulation
  2. Riot Control Grenades
     - 2-Chlorobenzalmalononitrile (CS) / $KClO_3$ / $MgCO_3$ / Sugar based formulation
  3. Signal (Obscurant) Grenades
     - Red-Dye / $KClO_3$ / $MgCO_3$ / Sugar based formulation
- Successfully demonstrated a multi-cycle, closed loop, chemical process with high processing efficacy for each pyrotechnic-smoke composition
  - Bulk material-to-Solvent: ~0.9 - 1.3 kg / L (in 3 to 4 cycles)
  - Solvent Recovery: ~ 97 - 100 %
  - Average Additive Recovery:
    - CS ~ 85% wt. / Red-Dye ~ 89% wt. / Pyrotechnic Composition ~ 66% wt.
    - HC ~ 81% wt. / ZnO and Al_2O_3 ~ 62% wt.
  - Positive offset: HC: $0.42 Red-Dye: $8.85 CS: $9.90

Summary of Results (cont.)

Physical Sciences Inc.

6735-FinalBrief-32

- **Successfully identified carbonated water (CW) as a solvent to replace NMP for demilitarization of Red-Dye and CS smoke formulations**
  - CW process showed higher recovery of the CS
    - **97% wt. versus ~85 % wt.**
- **Successfully scaled-up the developed process to 20g with equivalent processing efficacy to that established for 5g**
- **Identified a path to scale-up the process to 20 kg using commercially of the shelf equipment that will provide greater processing control to augment recovery of the additives and solvents**

Physical Sciences Inc.

6735-FinalBrief-33

Questions