Characterization of Existing Stockpile and Development of Synthetic $CaSi_2$

Dr. Paul E. Anderson
Energetics and Warheads Division,
Explosives Research and Development
Picatinny Arsenal, NJ 07806

Abstract 7984, 2009 IMEM
paul.erik.anderson@us.army.mil, 973-724-2982

Team Members

Cerametec, Inc.
Dr. Raymond Cutler (Program Management, powder classification), Joe Hartvigsen (XRD).

Irvin Industries
Dr. Mark Hash (synthesis)

Crane Naval Warfare Center, Test Services Branch
David Southern, Dr. Doug Papenmeier, Louis Schwenk (ICP Analysis)

Picatinny Arsenal
Kerry Henry (PM Joint Services) and Jim Terhune (PM-MAS)
Dr. Ed Hochberg (AA Analysis); Henry Grau (thermal analysis, heat capacity); Deepak Kapoor, Darold Martin (XRD); Dr. Chris Haines (XRF); Gary Chen, Chris Fish, Jessica Martin (particle size analysis, SEM/EDX, thermal analysis)

Background

- Calcium Disilicide ($CaSi_2$) is a bimetallic compound used as an additive in many pyrotechnics and primary explosive compositions.
- Single point failure status due to dwindling stockpiles and non-specification material
- Commercial stockpiles of $CaSi_2$ vary in characteristics, and availability between lots and vendors. Thus, it was proposed to synthesize $CaSi_2$.
- MIL-C-324C contains outdated, tedious procedures for elemental composition. Newer techniques are needed to supplement current standard.
- To guide synthesis efforts, a thorough characterization of existing materials was undertaken.

GOTChA

Goal

Synthesize an economically feasible $CaSi_2$ product that is a drop-in replacement for existing product from coking process.

Objective

Eliminate single point failure of dwindling stockpile of $CaSi_2$ and variability between lots. Design and deliver 15 lbs of synthetic product for testing in M52A1 primer.

Tasks

- Characterize existing $CaSi_2$ materials
- Formulate DOE for synthetic material and identify commercial synthetic options.
- Perform synthesis runs ship to ARDEC and contractor for testing.
- Test, validate DOE model, document, update MIL-C-324C

Challenges

- Relatively unknown chemistry and physics of $CaSi_2$ in primers
- Need for scalable, robust technique for powder synthesis.

Approach

- Identify key attributes of existing $CaSi_2$
- Perform small scale tests for screening attributes
- Item scale tests for performance testing

Use statistical DOE to identify and track attributes

RDECOM

Characterization Tools

Not performed | Underway | Complete   P – Picatinny C – Crane Ce - Ceramatec

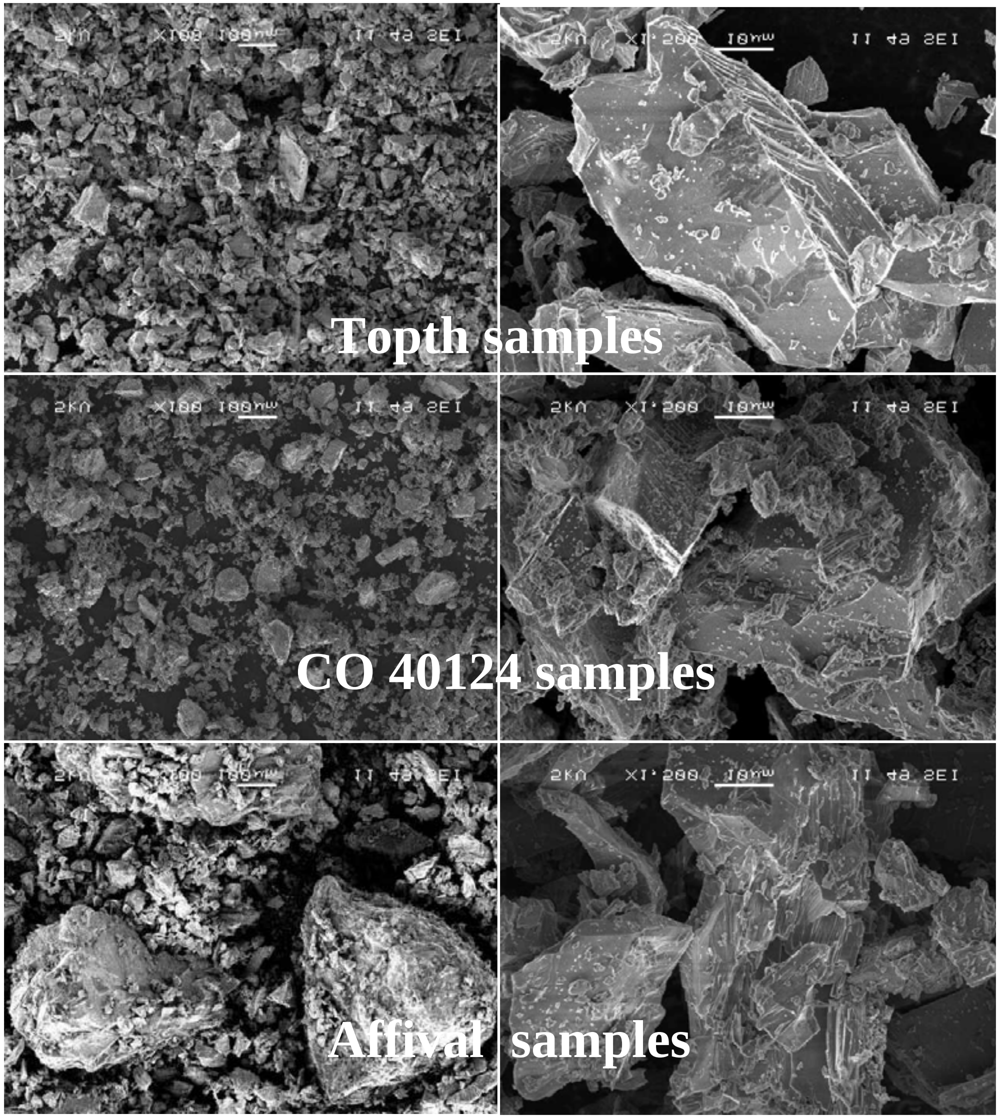
* Required for MILC-324C qualification

1	**THERMAL ANALYSIS (melting point, decomposition, phase changes)**
a.	**Thermogravimetric Analysis (TGA): moisture content, impurities (P)**
b.	**Differential Thermal Analysis (DTA): phase transformations, impurities (P)**
2	**SURFACE MORPHOLOGY (flowability, processing)**
a.	**Scanning Electron Microscopy (SEM): particle morphology and size (P)**
b.	**Surface Area Analysis: surface roughness and porosity (P, Ce)**
3	**CHEMICAL/STRUCTURAL ANALYSIS (composition, crystal structure)***
a.	**Energy Dispersive Spectroscopy (EDS): surface composition**
b.	**X-Ray Diffraction Analysis (XRD): identify and quantify compounds and impurities (P, Ce)**
c.	**Inductively Coupled Plasma-Atomic Absorption (ICP-AA): atomic composition (P, C)**

Characterization Tools

3.	**CHEMICAL/STRUCTURAL ANALYSIS cont'd***
d.	**X-ray Fluorescence: percent atomic species (P)**
4.	**MATERIAL CHARCTERISTICS (MILSPEC, particle size, density)**
a.	**Particle Size Analysis (PSA) (P)**
b.	**Tapped Density (P)**
c.	**Apparent Density (P)***
d.	**Sieve Analysis (P)***
5.	**THERMAL CHARCTERISTICS (heat flow, heat capacity)**
a.	**Thermal conductivity, effusivity, heat capacity (P)**

Example: SEM Results



Current commercial samples: Differences in morphology will affect flowability, packing density, and sieve results.

Elemental Composition Results

Description	Si (theo)	Si(XRF)	Si(ICP) ± 1.6%	Ca (theo)	Ca(XRF)	Ca (ICP) ± 2.6%	Fe (theo)	Fe (XRF)	Fe (ICP) ± 1.8%
Run 1	58.4	58.23	58.6	41.6	40.42	39.7	0.00	0.36	0.10
Run 2	64.3	64.79	64.9	35.7	34.21	34.3	0.00	0.32	0.20
Run 3	62.4	63.85	62.9	34.6	32.56	33.1	3.00	2.87	2.90
Run 4	60.5	56.72	59.3	33.5	35.78	31.6	6.00	6.71	6.00
Run 5	61.4	59.93	59.6	34.4	35.85	30.2	2.56	3.14	2.70
Run 3R	62.4	60.84	57.6	34.6	35.11	30.8	3.00	3.37	3.20
Affival		58.6	55.9		34.4	26.2		5.58	4.80
CO 40214 - production lot	, 59.8	59.8	58.1	, 29.6	33.3	26.6	, 2.95	4.77	4.20
Topth 1205		59.1	56.7		32.7	23.6		5.45	4.80
Topth 1129		58.9	55.2		33.4	24		5.1	4.70
Perkins -7		58.6	53.8		36.6	26.1		3.79	3.20
Perkins -140		59.4	55.1		34.7	24.3		3.54	3.50

- X-ray Fluorescence and ICP analysis
- Procedure developed and carried out by Crane Naval Warfare Center
- Within error, samples of interest still fall within elemental specifications of MIL-C-324C.
- ICP recommended as technique to augment MIL-C-324C

Calculated % weight components from XRF data

Sample	% weight Si	% weight $CaSi_2$	% weight $FeSi_2$
MIL-324C[1]	14.1	72.1	7.6
Affival	4.8	82.6	11.2
P CO40124	8.3	80.0	9.6
Topth 1205	7.8	78.5	10.9
Topth 1129	6.9	80.2	10.2
Alfa Aesar	6.8	80.5	10.1
Perkins R 7	3.5	87.9	7.6
Perkins R 140	7.2	83.3	7.1

Assumes calcium then iron reaction only with silicon.

[1] Calculated from MIL-C-324C minimum requirements for type II (60 Si /30 Ca/3.8 Fe)

Synthetic Routes of CaSi2

Route 1. $CaO + C + Si \rightarrow CaSi_2 + CO$ ~925°C (s)

Route 2. $SiO_2 + 2C \rightarrow Si + 2CO$ ~900°C (s)

$Fe + Si \rightarrow$ FeSi alloys

$CaCO_3 + 4C \rightarrow CaC_2 + 3CO$ ~1000°C

or

$CaCO_3 + \Delta H \rightarrow CaO + CO_2$ ~900°C

$CaO + 3C \rightarrow CaC_2 + CO$ ~1900°C (l)

$2SiO_2 + CaC_2 + 2C \rightarrow CaSi_2 + 4CO$ ~1800°C (l)

Route 3. $2\ Si\ (l) + Ca\ (l) \rightarrow CaSi_2$ ~1200°C

Which route would you choose?

Sample Runs and Design Logic

Irvin Industries

6 sample runs

1. Stoichiometric
2. Eutectic (free Si)
3. Eutectic + 3% Fe

3R. Repeat Run 3

4. Eutectic + 6% Fe
5. Blend commercial $CaSi_2$ + new Ca/Si

Constraints from MIL-C-324C, desire to understand effects of chemistry on performance (Fe content, CaSi ratio, free silicon)

Ceramatec

Milling

Portion of original sample was milled in SS media in SS vessel in hexanes. Products were air passivated.

Surface area, density (true, apparent, tap), heat capacity/effusivity

Particle size classification/blending

Milled samples were blended with original samples to make three products: low surface area (LSA), medium surface area (MSA), and high surface area (HSA).

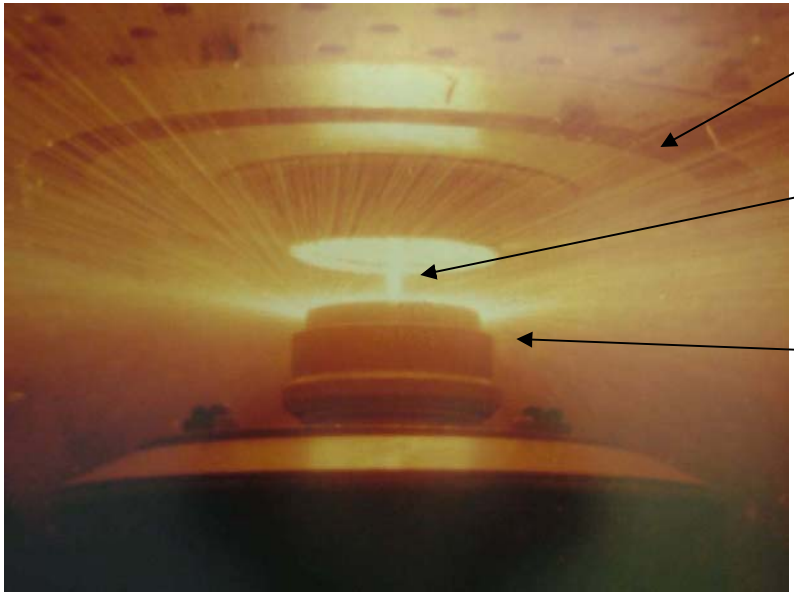
At least one product MIL compliant, others at extremes

Particle Size Classification and Surface Area

Atomizer Run	Surface area, m2/g	Batch surface area notation	Type II compliant?
1	0.117	LSA	PASS
	0.681	MSA	PASS
	1.112	HSA	FAIL
2	0.148	LSA	PASS
	0.723	MSA	PASS
	1.28	HSA	FAIL
3	0.127	LSA	PASS
	0.713	MSA	PASS
	1.215	HSA	FAIL
4	0.106	LSA	PASS
	0.618	MSA	PASS
	1.028	HSA	FAIL
5	0.122	LSA	PASS
	0.723	MSA	PASS
	1.159	HSA	FAIL
3R	0.131	LSA	PASS
	0.703	MSA	PASS
	1.096	HSA	FAIL

Type II powders successfully obtained. Surface area effectively controlled at values $<0.8 m^2/g$ by reblending powders.

Synthesis Effort



Vacuum chamber

Molten sample

High speed rotary atomizer

Variables include rpm of atomizer, temperature, flow rate of material, density of material

- Led by Raymond Cutler (Ceramatec, Inc.)
- Synthesis on Rotary Atomizer at Irvin Industries, Inc.
- Production quantities up to 45 kgs per run to 200 kgs per run (production).

Loaded Induction Furnace

Ceramatec, Presentation at Salt Lake City

Induction Furnace & Tundish

Ceramatec, Presentation at Salt Lake City

Placing Vessel Lid

Ceramatec, Presentation at Salt Lake City

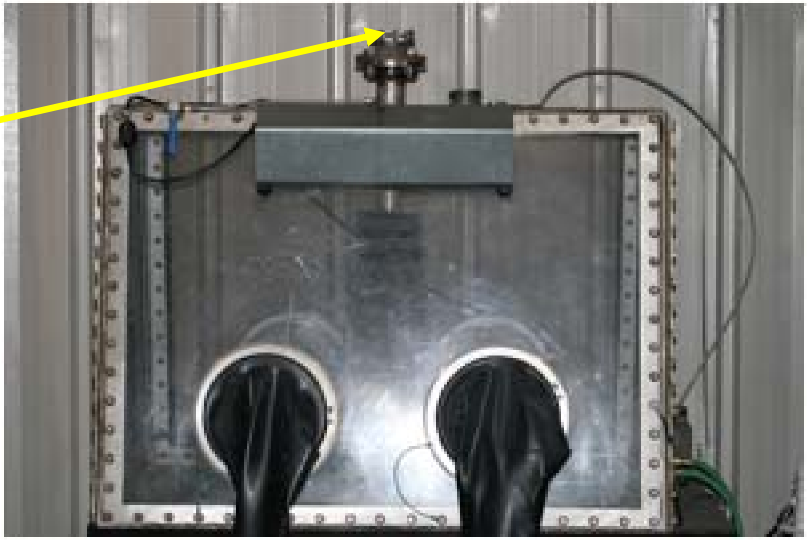
Ready For Atomization

Ceramatec, Presentation at Salt Lake City

Post-Run Powder Collection and Handling

Base of atomization chamber

Powders are transferred directly to purged glove box atmosphere for sampling, screening, and packaging



Powder collection canister with mating valve to rig and glove box

Yields

Run #	Amount Melted (kg)	Amount Shipped (kg)	Ervin Yield %	Ceramatec Yield/Overall Yield (%) Type II LSA	Type II MSA	Type I HSA
1	22.7	7.3	32	43/14	100/32	99/32
2	22.7	17.7	78	64/50	100/78	100/78
3	22.7	18.2	80	58/47	100/80	100/80
3R	22.7	19.5	86	52/45	100/86	100/86
4	22.7	15.5	67	14/10	41/28	99/67
5	22.7	17.7	78	67/52	100/78	100/78

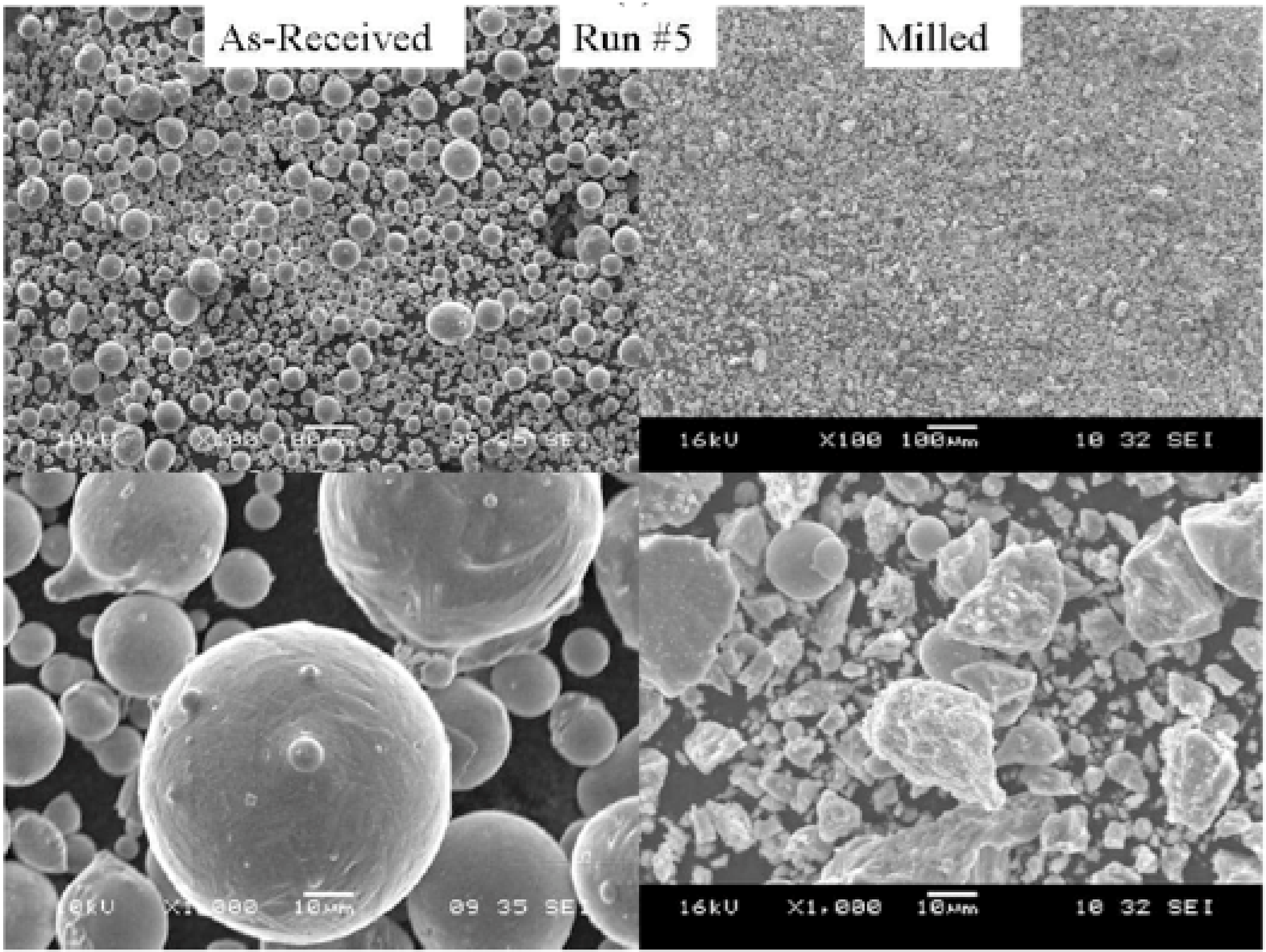
From Phase 1 Report, Ceramatec

18 Samples for Phase I

Run	Surface Area (m^2/g)	Particle Size (μm)					
Type II Low Surface Area (LSA)		d_{10}	d_{50}	d_{90}	Mean	Min	Max
1 (RC15-125A)	0.1168±0.0009	2.2	15.0	56.8	23.1	≈0.05	≈100
2 (RC15-125C)	0.1483±0.0015	3.4	15.6	51.4	21.3	≈0.05	≈100
3 (RC15-125E)	0.1271±0.0008	4.0	18.4	73.8	33.3	≈0.05	≈310
3R (RC15-126E)	0.1305±0.0009	4.9	20.4	66.7	28.8	≈0.05	≈110
4 (RC15-126A)	0.1063±0.0006	4.3	20.0	71.8	33.5	≈0.05	≈310
5 (RC15-126C)	0.1224±0.0016	3.7	17.2	59.5	27.0	≈0.05	≈310
Type II Medium Surface Area (MSA)							
1 (RC15-125B)	0.6806±0.0057	1.6	15.5	53.7	21.8	≈0.05	82
2 (RC15-125D)	0.7231±0.0081	0.9	10.2	28.8	13.9	≈0.05	100
3 (RC15-125F)	0.7130±0.0074	1.2	11.8	50.8	20.4	≈0.05	210
3R (RC15-126F)	0.7034±0.0074	1.5	13.0	53.2	20.2	≈0.05	180
4 (RC15-126B)	0.6183±0.0068	1.3	12.2	63.9	23.5	≈0.05	220
5 (RC15-126D)	0.7232±0.0075	2.0	17.7	68.9	27.6	≈0.05	180
Type I High Surface Area (HAS)							
1 (RC15-124E)	1.1128±0.0113	0.4	5.0	19.9	7.8	≈0.04	50
2 (RC15-124C)	1.2799±0.0123	0.2	4.2	17.7	6.6	≈0.04	40
3 (RC15-124A)	1.2147±0.0113	0.5	6.9	18.9	8.6	≈0.05	45
3R (RC15-124B)	1.0956±0.0117	0.7	7.3	19.3	8.9	≈0.05	45
4 (RC15-122C)	1.0280±0.0108	0.3	4.7	17.0	6.9	≈0.04	45
5 (RC15-124D)	1.1597±0.0114	0.3	4.3	16.5	6.5	≈0.04	40

From Phase 1 Report, Ceramatec

Synthesized Products



ICP results

Description	Si (theo)	Si(XRF)	Si(ICP) ± 1.6%	Ca (theo)	Ca(XRF)	Ca (ICP) ± 2.6%	Fe (theo)	Fe (XRF)	Fe (ICP) ± 1.8%
Run 1	58.4	58.23	58.6	41.6	40.42	39.7	0.00	0.36	0.10
Run 2	64.3	64.79	64.9	35.7	34.21	34.3	0.00	0.32	0.20
Run 3	62.4	63.85	62.9	34.6	32.56	33.1	3.00	2.87	2.90
Run 4	60.5	56.72	59.3	33.5	35.78	31.6	6.00	6.71	6.00
Run 5	61.4	59.93	59.6	34.4	35.85	30.2	2.56	3.14	2.70
Run 3R	62.4	60.84	57.6	34.6	35.11	30.8	3.00	3.37	3.20
Affival		58.6	55.9		34.4	26.2		5.58	4.80
CO 40214 - production lot	, 59.8	59.8	58.1	, 29.6	33.3	26.6	, 2.95	4.77	4.20
Topth 1205		59.1	56.7		32.7	23.6		5.45	4.80
Topth 1129		58.9	55.2		33.4	24		5.1	4.70
Perkins -7		58.6	53.8		36.6	26.1		3.79	3.20
Perkins -140		59.4	55.1		34.7	24.3		3.54	3.50

- Procedure developed and carried out by Crane Naval Warfare Center
- Within error, samples of interest still fall within MILC-324C elemental specifications.
- ICP recommended as technique to supplant/augment MIL-C-324C

RDECOM

DOE for Testing Synthesized $CaSi_2$

Screening DOE (10 runs + 2 standards)		
Primer mix	**Milling**	**Sample**
1	standard mix	
2	Y	1
3	N	3
4	Y	2
5	Y	4
6	N	2
7	N	1
8	N	4
9	Y	3
10	Y	3*
11	N	3*
12	standard mix	

- DOE resolves 3 independent, non-interacting factors: effect of milling (SA), silicon content, and iron content.
- Samples
  - 1 $CaSi_2$ Stoichiometric
  - 2 $CaSi_2$ eutectic (~5% excess Si)
  - 3 3% free iron
  - 4 6% free iron
- Milling
  - N Sieved to MILSTD Type II, SA < $1 m^2/g$
  - Y Milled and sieved to MILSTD Type II, SA > $1 m^2/g$
- * denotes no TNR pretreatment
- Primers will be fired and performance gauged by pressure-time, impulse, and sensitivity data.
- Full cartridge tests to be performed with downselected candidates.

Conclusions

- Existing calcium disilicide fully characterized in an effort to understand chemistry
- Calcium disilicide synthesized successfully using rotary atomization from downselected characteristics of commercial lots
- Varying compositions delivered for primer assembly; variables to be tracked using statistical DOE
- LSA and MSA 3% and 6% Fe showed equivalent small scale sensitivity to production lot.

Path Forward

- Carry out primer testing at ARDEC – sensitivity, performance by end 4Q09
- Integrate ICP procedure developed by Crane Naval Surface Warfare Center into MIL-C-324C by end 4Q09
- Further investigate role of passivation layer in $CaSi_2$ based systems
- Chemistry of calcium disilicide in primers will (perhaps) be understood!