Use of JMP in the Development of High Performance Explosives

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The role of explosives in today's battlefield has become increasingly tailored for specific target sets. Requirements from recent urban warfare highlight the importance of minimizing collateral damage. With such tradeoffs comes a sacrifice in performance, which puts the solider and mission success at risk. Among the most important responses involving tradeoffs is between insensitivity (the ability of an explosive to resist unintentional initiation) and high energy (the amount of explosive energy delivered). Typically, these two responses are diametrically opposed; as an explosive possesses more energy content it becomes more sensitive, which has profound logistical consequences. Recently, however, certain Picatinny Arsenal Explosives (PAX) were formulated to maximize energy release but minimize hazard sensitivity. This presentation will share the use of JMP from concept and downselection of ingredients, thermodynamic modeling driven by mixture statistical design of experiments (DOE), experimental formulation utilizing the Custom DOE tool, and finally analysis of blast test results using various platforms. Certain test results, such as video of blast tests, sensitivity tests, and other related evaluations will be shared. In the end, a high powered explosive was developed that met all mission requirements while possessing excellent insensitivity.

1 Background

The development of new explosives involves synthesis and recrystallizaiton of organic crystalline solids, preparation of the solids into a usable formulation, and finally testing and evaluation. Due to the hazard class of these materials (Division 1), specific safety precautions and handling procedures are necessary. In practice, this limits resolution in any design of expeirments (DOE) when formulating, processing, and testing high explosives. Often, main effects are only afforded. In the concept and development phases, however, thermodynamic equilibrium codes can be used to identify realistic design space with proper input from formulators. This approach was used for the optimization of PAX-Si, a three-component formulation. Further details of this formulation can be found in the literature [1].

Aluminum (Al) is often used as an energetic additive to promote late term blast in military explosives [2]. The blast is due to its extremely high enthalpy (energy) of oxidation, which adds energy to the expanding products upon detonation. Depending on particle size and oxygen content in the formulation, the aluminum can react at very early, medium, or late time frames [3]. As early as 1943, however, the aluminum (Al) in aluminized explosives was recognized as a prime contributor to unacceptable response to hazard studies [4]. The investigators replaced Al in Minol with silicon to make "Silicominol". Responses obtained to bullet impact with 50-caliber ball ammunition resulted in nearly zero response in the siliconized version of Minol when compared to more violent reactions with the standard aluminized Minol. This early precedent showed silicon could possibly serve as an Insensitive

Munition (IM) fuel additive when compared to aluminum. In practice, the thermodynamic enthalpy of the oxide formation from elemental silicon versus aluminum is comparable on a per weight basis (15.2 kJ/g SiO_2 versus 16.6 kJ/g Al_2O_3). Further thermodynamic code calculations indicated early reaction of silicon in the detonation could be possible arising from silicon's unique depressed melt characteristics at high pressures and temperatures.

This paper provides an overview JMP's use in certain phases of explosive development. First, the mixture DOE platform was used for theoretical calculations using Cheetah thermodynamic code. The optimum formulation and trade-offs were conducted prior to actual testing. A formulation process DOE was then devised, adjusting silicon particle size along with 3 mixture factors (energetic solid, silicon amount, silicon particle size, and binder amount). The responses used for formulation optimization included detonation energy output from detonation calorimetry and shock sensitivity tests for safety. The optimum particle size was then used in pilot level production runs, and large scale detonation tests performed. The non-linear fit platform of JMP was used to identify the alpha term in the blast overpressure decay equation, which gives an indication of the blast perforance of the formulation.

2 Experimental

2.1 Mixture DOE – Thermodynamic Calculations

A screening mixture DOE was utilized with 3 factors (energetic, silicon, and binder amounts, Table 1. The binder was composed of two proprietary ingredients at the same ratio for each mixture. While Scheffe cubic designs were first explored for use in these simulations, often 2nd order interaction designs were sufficient to resolve curvature in the responses. Therefore, an I-optimal mixture design with 2nd-oder interactions was used for simulations. Additional points were added for verification (points 12 and 13) and were not included in the model fits, but were included in the prediction plots visually for verification purposes. The ternary plot is shown in Figure 1. The unusual constraints in the lower left arise because of formulation constraints associated with the ability to coat the solids particles.

Second order interactions were included which resulted in 11 runs for Cheetah thermodynamic code. The responses included Chapmen-Jouget pressure (detonation pressure, maximize), detonation velocity (the "speed" of the detonation front, $7.8 \leq$ value ≤ 8.3 km/s), cylinder expansion at 6.5 volume expansions (a measure of explosive power to drive fragments and metal, maximize), and density (higher is better for total energy density), and total volumetric energy associated with formulations (maximize).

Table 1. Design space for silicon formulations. The ingredients are in percent weight.

Component	Min	Max
Energetic	70	88
Silicon	4	24
Binder	6	12

For each response, a least squares regression prediction expression was generated. The profiler was then used to explore the theoretical design space (Figure 2). Since Cheetah is a deterministic code, the

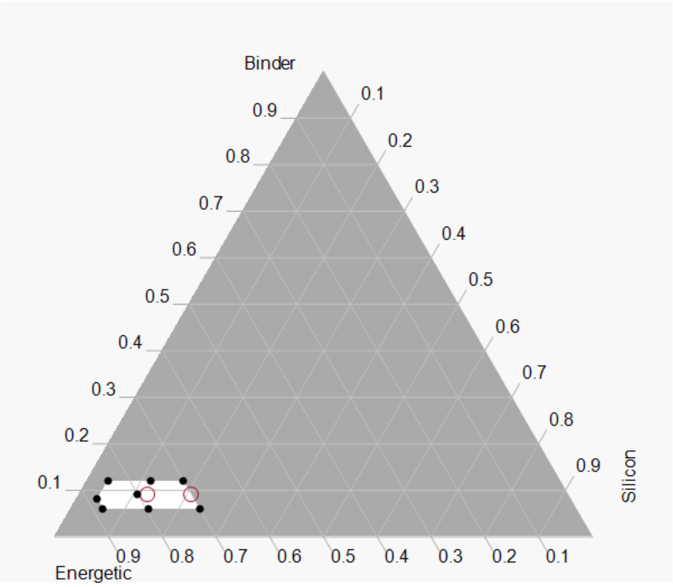


Figure 1. Ternary plot of the thermodynamic mixture DOE. Red circles were validation points.

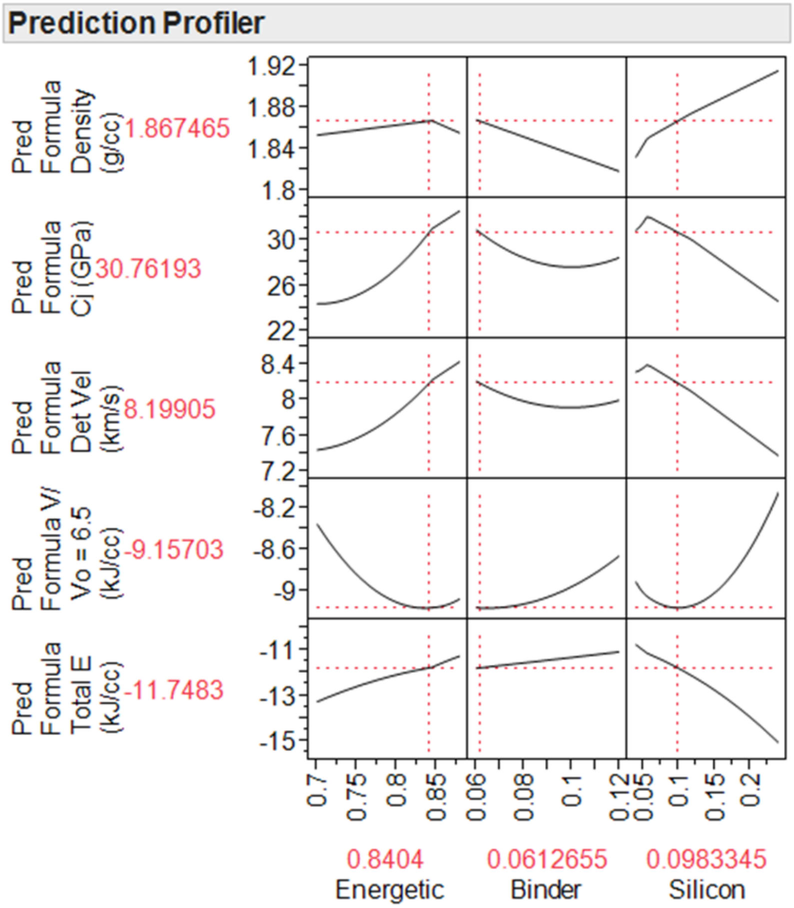


Figure 2. Final combined profiler generated from multiple prediction equations for each response of interest.

results from this study are viewed as the “ideal” performance possible. In reality, particularly with metalized explosives, the final results do not always match thermodynamic calculations. Therefore, initial calculations are used to understand trends and identify working design spaces. Figure 2 shows the combined profiler for all the responses. It also reveals a high amount of curvature associated with responses such as volume expansion energy. This inherently makes sense as the volumetric energy is related to the Gurney energy which scales as the inverse square root of the total energy of the system.

2.2 Mixture DOE – Physical mixtures

Based on results from thermodynamic calculations, the final DOE decided upon is shown in Figure 3. From a preliminary assessment, it would at the very least yield main effects information about the particle size and solids loading. At most it would yield evidence of a 2nd-order interaction between two components.

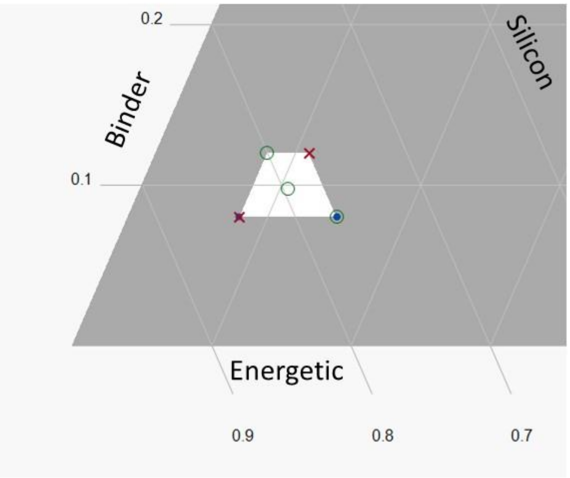


Figure 3 (left). The main factors contributing to sensitivity in this formulation. Silicon particle size (categorical; red X, green O, and blue O), amount of energetic solid (mixture), amount of silicon (mixture), and amount of binder (mixture). Due to schedule and budget constraints, only 7 experimental points were allowed.

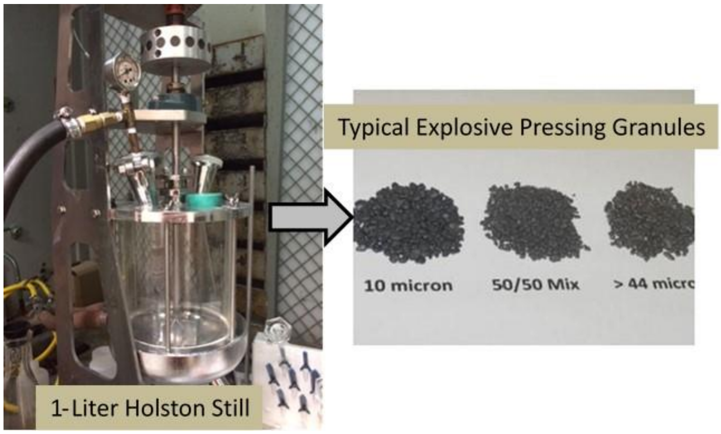


Figure 4 (right). Typical laboratory Holston still (left) used to formulation explosive pressing granules (right).

The high explosives were made using a slurry-type process in a standard Holston Still (Figure 4). The lacquer with dissolved binder was added to an aqueous solution of suspended solids (energetic and silicon). Upon lacquer addition, heat and vacuum were applied to remove the solvent and granular particles form. The solids were filtered, dried, and sieved if necessary. Particles were then pressed using standard single action press tooling to form pellets which were then used in various detonation tests.

2.3 Small scale testing and Analysis

Per standard operating procedures, small mixtures were first performed at the 5 and 10-gram level. Such tests serve as a prerequisite to ensure the formulated materials are safe to handle and process on the larger scale. The small mixtures (as well as later large production runs) were characterized using Bundesanstalt für Materialprufung (BAM) Friction, BAM Impact, Explosives Research Laboratory (ERL) impact, and Picatinny Electrostatic Discharge (ESD) instruments. The material thermal stability was tested using a Perkin Elmer 4000 Differential Scanning Calorimeter (DSC) operated at 5°C/min in dry nitrogen and Sapphire Thermal Gravimetric Analyzer (TGA) operated at 5°C/min in dry argon. The results will not be shared here, suffice to say that certain criteria must be met in order to proceed with scale up above 10 grams of material.

2.4 Detonation testing

2.4.1 Detonation calorimetry

Once sufficient material was formulated, detonation testing proceeded. For detonation calorimetry, the setup and operation is described in other publications [5]. In short, a 15-gram sample of the test explosive is detonated using a 5.0-gram C4 booster with an RP-80 exploding bridgewire (EBW) detonator (Figure 5). Confinement is ensured by bonding the sample with a ceramic adhesive in an alumina crucible having a 0.25-cm thick wall. Upon detonation in argon gas, all heat produced is absorbed by the surrounding water bath. The total change in water bath temperature is proportional to the energy liberated in the detonation. The calculation also corrects for any condensed water within the calorimeter. From knowledge of the theoretical energy output, one can estimate the extent of silicon reaction from the detonation event. Since no oxygen was present in the system, the energy obtained is from silicon reacting with only detonation products (anaerobic). The energies obtained were then compared with thermodynamic calculations using Cheetah, assuming both reactive silicon (100%) and unreactive silicon (0%) by equation 1:

$$\frac{(Actual\ Detonation\ energy) - (0\%\ Si\ Reaction\ Detonation\ Energy)_{calc}}{(100\%\ Si\ Reaction\ Detonation\ Energy)_{calc} - (0\%\ Si\ Reaction\ Detonation\ Energy)_{calc}} \times 100 \qquad (1)$$

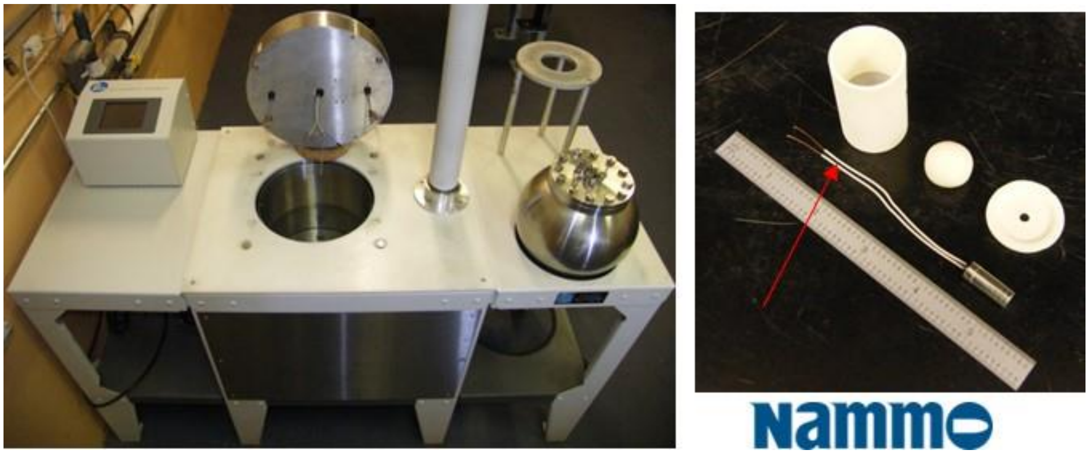


Figure 5. Detonation calorimeter used in these studies.

2.4.2 *Shock sensitivity*

Insensitive High Explosive (IHE) gap test enables one to determine the shock sensitivity of an explosive. This is the minimum shock pressure required to initiate a full detonation reaction in the test material. The shock input is controlled by the thickness of acrylic spacers, or “cards”, that attenuate the shock input from the donor (Figure 6). The acceptor, or test explosive, then undergoes a detonation (which leaves a dent in the witness plate) or no reaction, which leaves no damage. A 50% point is then calculated after a sufficient number of go’s and no-go’s is obtained, usually in 8-10 firings.

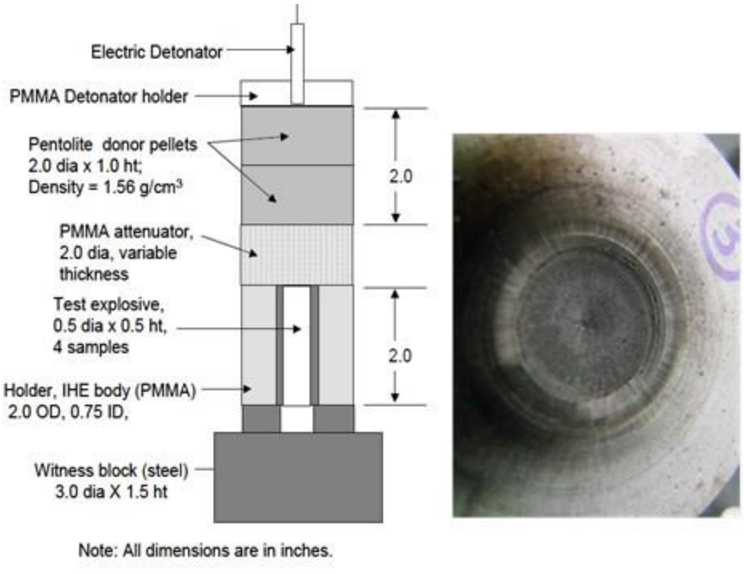


Figure 6. Insensitive High Explosive (IHE) gap test. Setup is on the left, and a typical dent from a "go" is on the right.

2.4.3 *Blast testing*

After optimization from these two tests among others, large amounts of explosive were made, pressed into warheads, and blast overpressure tests performed. A typical setup of blast overpressure is shown in

Figure 7, and consists of piezo pressure gauges at certain distances and heights from the event. High speed video was also taken. A typical trace from one of the pressure gauges is shown in Figure 8. From the pressure measurements, further analysis can ensue, such as shockwave speed, Mach number, peak pressure, and impulse. Note that the detected peak overpressure p_0 is not the actual peak pressure; the instrument response time cannot react to determine the actual peak overpressure. Therefore, peak overpressure must be extrapolated from the decay curve to obtain the true value for p_0, which is imperative for later calculations.

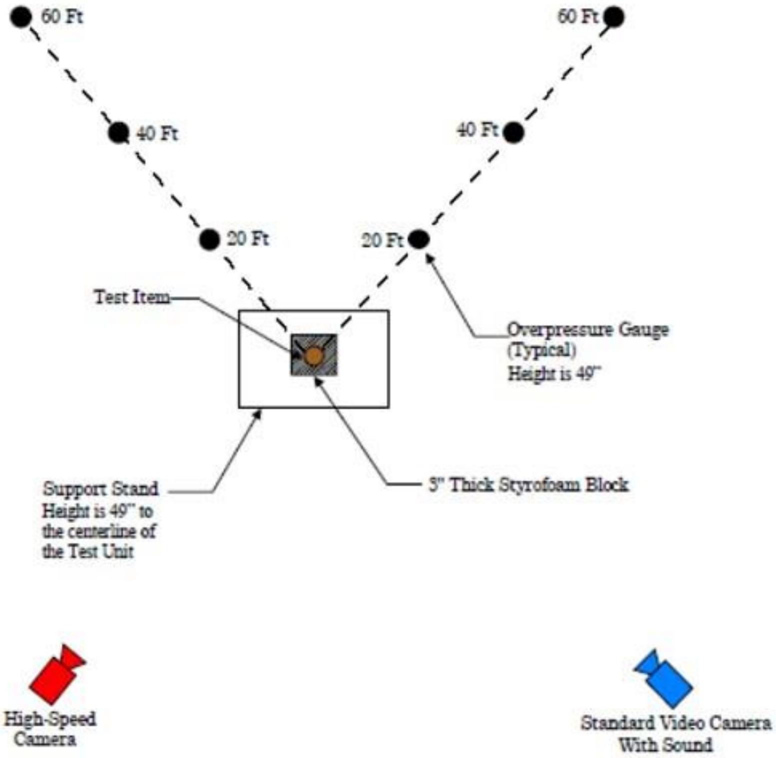


Figure 7. Typical blast overpressure test setup.

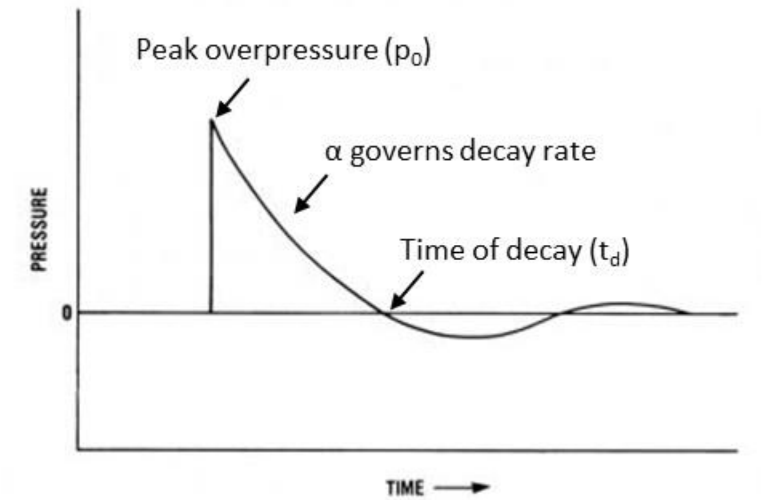


Figure 8. Typical blast wave decay curve obtained from a pressure gauge in Figure 5.

For this study, the JMP non-linear fit platform was used to determine the peak pressure (p_0) time of positive phase (t_d), and the decay constant (α) in Equation 2, which describes blast wave decay [6]:

$$p = p_0 \left[1 - \frac{t}{t_d}\right] e^{-\alpha \frac{t}{t_d}} \qquad (2)$$

Once determined, these quantities were used to determine the impulse of the positive phase blast wave from the integrated form of Equation 2:

$$Impulse = \int_0^{t_d} p dt = p_0\, t_d \left[\frac{1}{\alpha} - \frac{1}{\alpha^2}(1 - e^{-\alpha})\right] \qquad (3)$$

Therefore, it is important to obtain the implicit variable α from equation 2 before using equation 3.

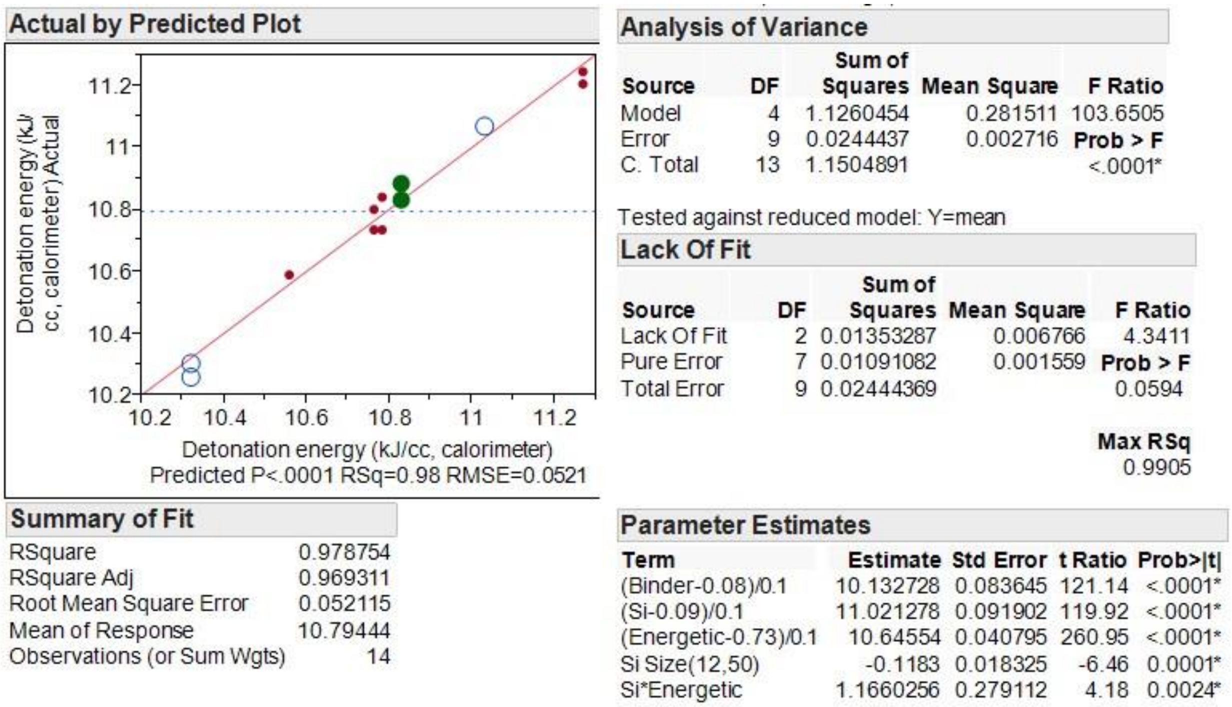
3 Results

3.1 Detonation calorimetry

The results from the DOE least squares regression fit in the detonation calorimeter, in units of detonation energy (kJ/cc), is shown in Figure 9. An acceptable model was generated, with some possible lack of fit detected. Each formulation was shot in duplicate. One misfired and the calorimeter lost the data. According to the model and parameter estimates, note that all components of the energetic contributed to the detonation energy, which meant that the silicon did indeed participate at early timeframes. This was one of the goals of this study. The silicon size, however, had a negative parameter estimate, which means that as the particle size increased, the detonation energy decreased. This is consistent with particle reaction kinetics where smaller particles react kinetically faster than larger particles. Finally, the detonation energy of these fills all outperformed PBXN-9, despite the formulations having volumetrically less energetic solids.

3.2 Shock sensitivity

The shock sensitivity least squares regression and ANOVA is shown in Figure 10. Note the very large parameter estimates associated with the first order formulation components. In this very non-linear response of shock sensitivity, logistic analysis and modeling is further warranted but was beyond the scope of this initial study. The model was developed by the closest “go” and “no go” data points. Hence the duplicate measurements for each formulation. Suffice to say, even when dealing with a logistic response, the goal of obtaining an engineering solution with the least shock sensitive explosive was met. Additionally, evidence of a second order interaction indicated that the silicon-energetic interaction plays some small role in helping to decrease the shock sensitivity. The shock sensitivity of the final formulation was in the 165-170 card range, which is significantly less shock sensitive than traditional high energy explosives such as PBXN-9 and PBXN-5 which is around 190-200 cards.



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	1.1260454	0.281511	103.6505
Error	9	0.0244437	0.002716	**Prob > F**
C. Total	13	1.1504891		<.0001*

Tested against reduced model: Y=mean

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	2	0.01353287	0.006766	4.3411
Pure Error	7	0.01091082	0.001559	**Prob > F**
Total Error	9	0.02444369		0.0594
				Max RSq
				0.9905

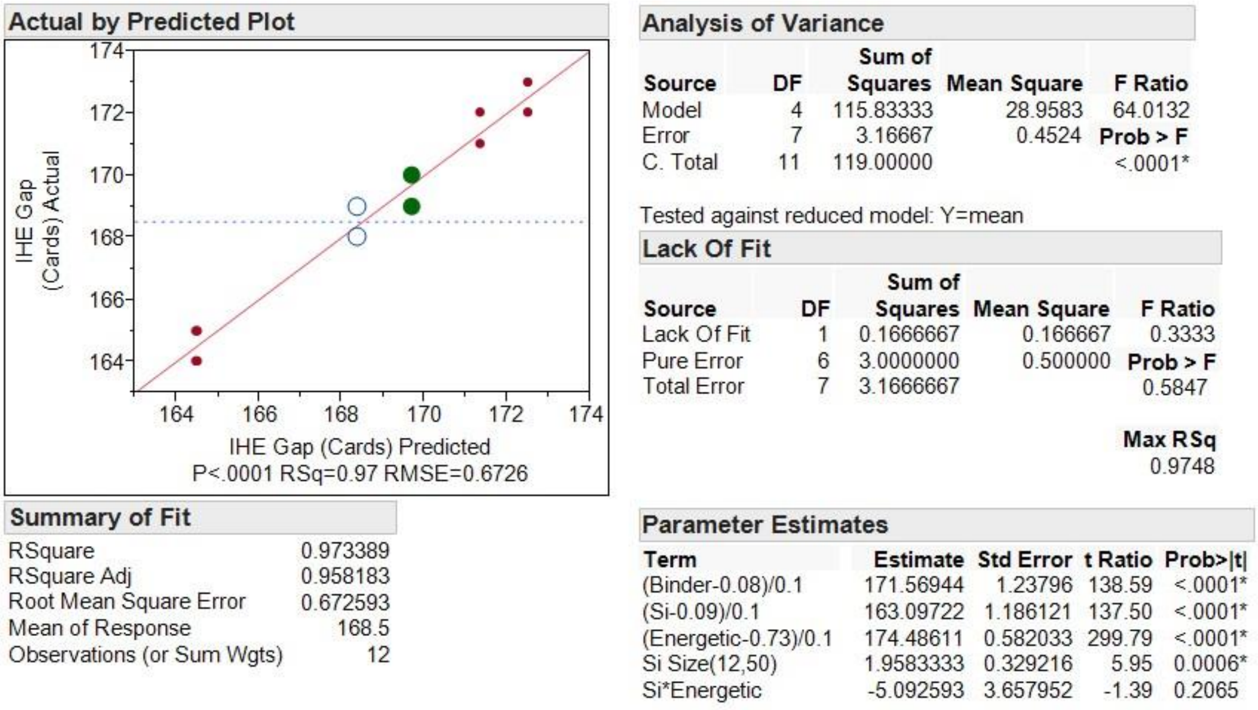
Summary of Fit

RSquare	0.978754
RSquare Adj	0.969311
Root Mean Square Error	0.052115
Mean of Response	10.79444
Observations (or Sum Wgts)	14

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
(Binder-0.08)/0.1	10.132728	0.083645	121.14	<.0001*
(Si-0.09)/0.1	11.021278	0.091902	119.92	<.0001*
(Energetic-0.73)/0.1	10.64554	0.040795	260.95	<.0001*
Si Size(12,50)	-0.1183	0.018325	-6.46	0.0001*
Si*Energetic	1.1660256	0.279112	4.18	0.0024*

Figure 9. Detonation calorimeter results. Note negative parameter estimate associated with silicon particle size.



Summary of Fit

RSquare	0.973389
RSquare Adj	0.958183
Root Mean Square Error	0.672593
Mean of Response	168.5
Observations (or Sum Wgts)	12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	115.83333	28.9583	64.0132
Error	7	3.16667	0.4524	**Prob > F**
C. Total	11	119.00000		<.0001*

Tested against reduced model: Y=mean

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	1	0.1666667	0.166667	0.3333
Pure Error	6	3.0000000	0.500000	**Prob > F**
Total Error	7	3.1666667		0.5847
				Max RSq
				0.9748

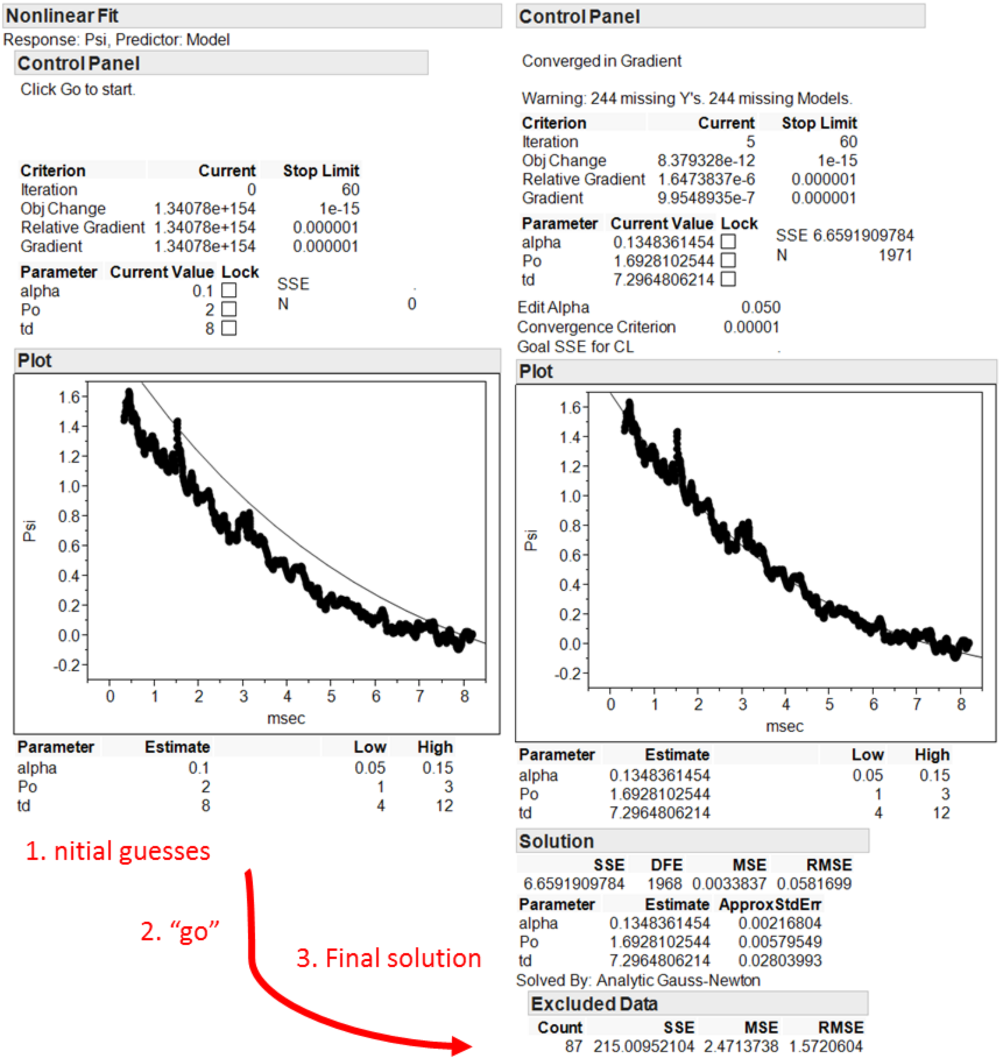
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
(Binder-0.08)/0.1	171.56944	1.23796	138.59	<.0001*
(Si-0.09)/0.1	163.09722	1.186121	137.50	<.0001*
(Energetic-0.73)/0.1	174.48611	0.582033	299.79	<.0001*
Si Size(12,50)	1.9583333	0.329216	5.95	0.0006*
Si*Energetic	-5.092593	3.657952	-1.39	0.2065

Figure 10. Results of model generation for shock sensitivity. Note again contribution by all factors under parameter estimates, with the silicon-energetic interaction showing a negative effect, which is beneficial for this test.

3.3 Blast Overpressure

A final formulation was chosen based on tradeoffs between shock sensitivity and calorimetric energy. 6-pound charges were fabricated into test fixtures and detonated in the setup shown in Figure 7. A non-linear fit model was developed to rapidly assess the parameters in equation 2. Figure 11 shows a screen grab from the non-linear model. First, some data leading to the highest peak pressure was excluded, which were easily excluded manually or by scripting. They cannot be part of the equation because the initial points need to be near the peak pressure for more accurate estimates of actual p_0. The parameters set in the "Model" column included peak pressure p_0, alpha, and total positive wave time t_d. Equation 2 was written into the formula field for the "Model" column. An additional column was made to perform the same duties as the non-linear fit platform but manually. Initial guesses were made in the model (left side of Figure 11). Upon hitting "go" the model yielded a p_0 = 1.69 psi, α = 0.135, and t_d = 7.29 milliseconds for this particular pressure trace.



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Nonlinear Fit
Response: Psi, Predictor: Model
  Control Panel
  Click Go to start.

  Criterion                Current    Stop Limit
  Iteration                      0            60
  Obj Change          1.34078e+154         1e-15
  Relative Gradient   1.34078e+154      0.000001
  Gradient            1.34078e+154      0.000001
  Parameter  Current Value  Lock
  alpha                0.1  ☐      SSE                .
  Po                     2  ☐      N                  0
  td                     8  ☐
  Plot
  Parameter   Estimate            Low     High
  alpha            0.1           0.05     0.15
  Po                 2              1        3
  td                 8              4       12
```

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Control Panel

 Converged in Gradient

 Warning: 244 missing Y's. 244 missing Models.
 Criterion                 Current   Stop Limit
 Iteration                       5           60
 Obj Change           8.379328e-12        1e-15
 Relative Gradient    1.6473837e-6     0.000001
 Gradient             9.9548935e-7     0.000001
 Parameter  Current Value  Lock
 alpha      0.1348361454 ☐     SSE 6.6591909784
 Po         1.6928102544 ☐     N           1971
 td         7.2964806214 ☐
Edit Alpha                     0.050
Convergence Criterion        0.00001
Goal SSE for CL                    .
Plot
Parameter    Estimate                    Low    High
alpha        0.1348361454               0.05    0.15
Po           1.6928102544                  1       3
td           7.2964806214                  4      12
Solution
          SSE    DFE        MSE       RMSE
 6.6591909784   1968  0.0033837  0.0581699
Parameter    Estimate      ApproxStdErr
alpha        0.1348361454    0.00216804
Po           1.6928102544    0.00579549
td           7.2964806214    0.02803993
Solved By: Analytic Gauss-Newton
 Excluded Data
   Count          SSE        MSE       RMSE
      87 215.00952104  2.4713738  1.5720604
```

1. nitial guesses

2. “go”

3. Final solution

Figure 11. Use of the non-linear fit analysis tool in JMP to identify blast wave decay parameters. Left is prior to running the model and right is after the model fit.

After assessing all of the data in this way (6 total shots, 9 pressure gauges for each shot, so 54 data sets, each about 2000 lines long), the shots could be integrated and impulse compared. The final comparison of impulse (psi-millisecond) is shown in Figure 12. Both PAXSi formulation show dramatic increases in blast overpressure over the traditional PBXN-9 formulation, which actually possesses more energetic solids than do the PAXSi formulations.

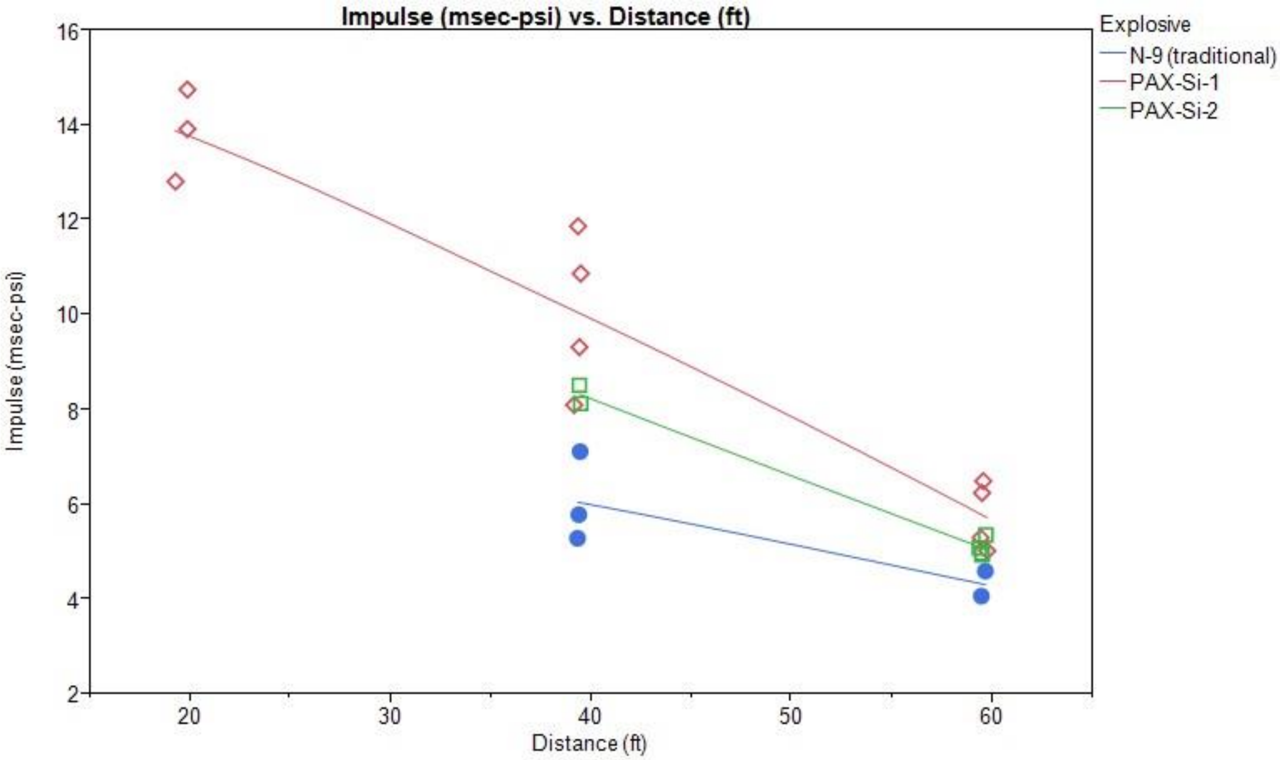

Figure 12. Comparison of blast overpressure at various distances for two "optimized" PAXSi fomulations and a traditional PBXN-9 formulation.

4 Conclusions

JMP has become a key tool in the development of explosive, pyrotechnic, and propellant items for the United State Department of Defense. The US Army is utilizing the software in many aspects of research and development, from deterministic thermodynamic models to actual formulations and testing. This study showed the utility of using JMP and the DOE approach to optimize a 3-component mixture design with an additional continuous factor. The final formulations were safer (by shock sensitivity standards) and more powerful (from blast overpressure and detonation calorimeter studies) than traditional explosives that contain *more* explosive solids.

5 Acknowledgements

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6 References

[1] Paul E. Anderson, Paula Cook, Andy Davis, Kyle Mychajlonka, Melissa Mileham. “Silicon Fuel in High Performance Explosives”. *Propellants Explosives, and Pyrotechnics.* 2014, **39**, 74 – 78.

[2] W. A. Trzcinski, S. Cudzilo, J. Paszula, Studies of Free Field and Confined Explosions of Aluminum Enriched RDX Compositions, *Propellants, Explosives, and Pyrotechnics*. 2007, **32**, 502.

[3] M. N. Makov, M. F. Gogulya, A. Y. Dolgoborodov, M. A. Brazhnikov, V. I. Arkhipov, V. I. Pepekin, “Acceleration Ability and Heat of Explosive Decomposition of Aluminized Explosives”. *Combustion, Explosions, and Shock Waves,* 2004, **40**, 458.

[4] Sensitivity of Explosives to Projectile Impact, Appendix A, OSRD 3156, 1944.

[5] A.R. Davis, K. Mychajlonka, S. Hall. “Detonation Calorimeter: Application and Operation for Thermobaric Explosive Characterization and Evaluation.” *Proceedings of the 36th North American Thermal Analysis Society*, Atlanta, GA,USA, August 17 – 20, 2008.

[6] Kinney, G.F. “Explosive Shocks in Air”, New York: Macmillan, 1962.