RESPONSE SURFACE OPTIMIZATION OF LEAD AZIDE FOR EXPLOSIVE DETONATORS

MAJ Ian McCulloh* and Dr. Darrell Massie
United States Military Academy
West Point, New York 10996

Emily Cordaro
Armament Research, Development and Engineering Center
Picatinny Arsenal, New Jersey 07806

ABSTRACT

The Armament Research, Development and Engineering Center, Picatinny (ARDEC) has been tasked with developing a new chemical process to produce lead azide, the key explosive ingredient in detonators. The new process is physically smaller than the traditional process, and incorporates newer technologies to improve process safety while reducing the costs of setting up new production. The new process has been shown to produce lead azide, but the process settings and operations have not yet been fully characterized. Chemical engineers at ARDEC, Picatinny were also unable to produce a lead azide that met military specifications. This, coupled with a shortage of lead azide, has placed the country's ability to manufacture detonators in jeopardy.

This research project used a statistically designed experiment and response surface methods to optimize the process settings. The objective is to discover the ideal process settings to produce a lead azide that meets military specifications and is similar to the lead azide produced by the original process. An optimum (minimum) number of process setting trials is required as a single experimental run can take over a week to fully analyze. Therefore, sequential and efficient experimentation is critical.

The execution and analysis of the experiment was completed with 10 experimental runs and two confirmation runs. The process was optimized across 12 separate responses. A modification was incorporated with the desirability function approach to multiple response optimization (Derringer and Suich, 1980) to incorporate military specification standards into the optimization equation.

This research problem has also been incorporated into the Mathematics curriculum at the U.S. Military Academy. The research is an excellent example of the usefulness of designed experiments and response surface optimization to real-world military problems.

1. INTRODUCTION

All detonators used in military ordinance contain an explosive known as lead azide. Historically, lead azide was produced in large vats, in a process that posed a safety risk to operators (necessitating expensive dedicated facilities), and involved chemicals harmful to the environment. US manufacturers discontinued production of lead azide in the 1970s, and the military has been relying on stockpiled material since that time. This stockpile is depleting and deteriorating and therefore new production must be initiated. Restarting the traditional production is not feasible, so the US must develop a new, safer, more economically and environmentally friendly means of producing this critical chemical. ARDEC has been tasked with developing this process. The procedure under investigation is physically smaller than what was previously used and incorporates newer technologies. The process settings and operations for this smaller system have not yet been fully characterized. A diagram of the process equipment, known as the "Blue Pig", is shown in Figure 1.

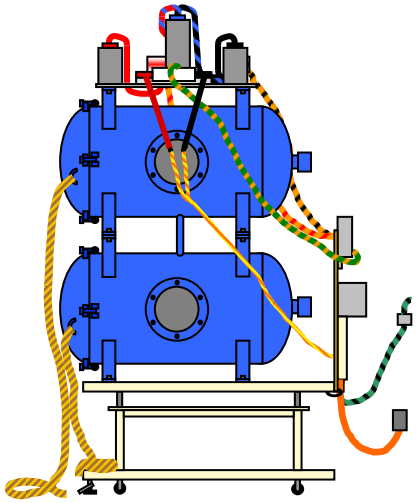

Figure 1. Lead Azide Production Process Setup

The objective of this research is to determine optimal factor settings and important environmental controls for

producing lead azide that meets MIL standard and is desirable according to the criteria set forth in section 3. Much of the consulting effort in this project has been to define desirability criteria for the lead azide. The desirabilities are set forth in section 3.

2. FACTORS, LEVELS, AND RANGE

2.1 Cause and Effect

Engineers from ARDEC and the principal investigators met to review the process under investigation and design an experiment to characterize the process. During this meeting, a cause and effect analysis was performed to identify all of the potential sources of variability that may affect the MIL-standard requirements of the lead azide. From this analysis, 24 sources of variability were identified: 6 experimental variables; 3 noise variables; 3 hold constant variables; and 9 control variables. Recommendations for the handling of each of these sources of variability are included.

2.2 Experimental Factors

There are six process variables that chemical engineers at ARDEC believe should affect the chemistry of lead azide formation. Two of the factors are the temperatures of the lead and the azide solutions before they are pumped into the process equipment. Pilot experiments indicated that temperature may be one of the more significant factors. The target temperature during the larger, original process was 30 °C. The factor levels are therefore set with a low level of 25 °C and a high level of 35 °C. This will allow adequate testing across the design space with a center point located at the original target temperature to detect a second order response surface.

Two other key factors in the process are the amount of an additive known as CMC that is added to the lead and/or azide solutions. The use of CMC in the old process dramatically reduced the probability of a detonation during lead azide formation; therefore all test trials used least a small amount of CMC. As the azide solution will be carrying all the CMC, a setting of 0% cannot be used. Instead a low factor level is set at 0.2%, and high level concentration of 0.8%.

Another experimental factor is the rate at which the pump meters the azide and lead solutions into the process equipment. The flow rate will be the same for both solutions, but it is adjustable. The current pump can operate with a minimum flow rate of approximately 200 ml/min (100 ml/min for each stream) to a maximum of about 400 ml/min (200 ml/min each). Factor levels for this experiment will be set at 20% away from the extreme settings to allow sufficient sampling across the design space and provide the ability for later response surface optimization. Therefore, the low factor level is 240 ml/min, and the high factor level is 360 ml/min.

The final experimental factor is the concentration of azide and lead in their respective solutions. The reaction stoichiometry dictates that two azide ions be present for each lead ion in the reacting solution. This proportion remains constant, while varying the concentration in the solutions. The maximum concentration possible, based on the solubility of the lead material is 0.83 M (Molar, moles/liter) with a corresponding azide concentration of 1.66 M. The minimum allowable setting for this factor is 0 M, however, a setting of 0 M is impractical, because the reacting streams would not contain any azide or lead, and no product can form. Instead, the low level tested will be half the high concentration: 0.415 M lead solution and 0.83 M azide. If this factor is determined to be non-significant, high concentrations are more desirable as they reduce the amount of waste.

2.3 Noise Variables

Three potential noise variables were identified for the process. These variables are beyond the control of the equipment, and may affect the system's output directly or indirectly. While these variables are not under control, engineers have closely monitored them, and where possible worked to mitigate their affects on the process.

The ambient room temperature is a significant noise variable. The relatively low room temperature can cause the azide and lead solutions to cool considerably as they pass through the process equipment before they are mixed. This change in temperature affects kinetics of the chemical reaction. Efforts undertaken by the engineers, including insulating the feed tubes and preheating them with water, may reduce the effect of room temperature, but can not be expected to eliminate it.

The relative humidity may also affect the process. Although the humidity is not likely to affect the chemistry occurring in an aqueous solution, it is possible that it affects the product as it dries. The relative humidity will be measured, recorded, and for safety the experiment will only be conducted while the relative humidity is between 50% and 60%.

The final noise variable is the batch production order. As multiple different batches are processed during a day, there is opportunity for a variety of subtle effects to impact the process. The batch number will be recorded, along with the date of production, and a normal residual versus run order check for correlation will be used to estimate any potential effect from production order.

2.4 Hold Constant Variables

There are several other variables in the process that were held constant during the experiments. The length of the experimental run may affect the performance of the final product. It was therefore held constant for these experiments. There are approximately 15 different static mixers that can be used in the process. Due to experimental constraints, only one type of static mixer was used during experimentation. The other static mixers may be tested at a later date. It is not anticipated that the choice of static mixer will significantly impact the performance of the explosive. Lastly, the choice of thermocouples will be held constant.

2.5 Controls

In a final effort to minimize the variability in the experiments, several controls were implemented. The process was automated and computer controlled. The only human control in the experiment occurs during the response testing.

In the testing of measured responses (further described in section 3), there is room for variability as the tester performs the actual test. The same individual conducted all the tests of a single type. A single process set-up was used for all experiments to eliminate the potential for different systems to be calibrated differently, or have slight variations. In addition, the process tubing was insulated and pre-heated with water. This significantly reduced the heat transfer in the azide and lead solutions as the solution moved from the heated source to the inner chamber of the process equipment as a result of the ambient room temperature and the temperature of the tubing.

The final concern in the experimental control was the different sources for each of the three raw materials: the azide, lead, and additive (CMC). Each of the raw materials used must meet strict purity requirements, and, where possible, solutions should be prepared from the same stock material. It is believed that the materials will all be similar and have negligible effects on the performance of the final product. Experimental resources will not be expended studying the effects raw materials have on the process.

3. RESPONSES

The process involves 12 multiple responses. These 12 responses will be measured for every experimental run and combined in a desirability function. This desirability function will be used to determine the optimality of various design points. The measuring of these responses can be extremely time consuming. In some cases it has taken over a week to complete all response measurements. Therefore, the number of experiments must be kept to a minimum.

Most of the responses were pass/fail. There were five responses, however, that could be used to evaluate optimal batches of lead azide.

Dent in Disk after Detonation: A sample of the lead azide is loaded into a detonator, which is detonated on a metal disk ¼ inch thick. The depth of the resulting hole in the metal disk is then measured as the dent. The minimum response is 0 inches and the maximum response would be 0.25 inches, meaning that the hole passed though the disk. This response is the primary performance measure of the lead azide and large values are better. This response is most heavily weighted in determining overall optimality of a lead azide compound.

Microscopy: The microscopy test is complex and is the result of several smaller sub-tests. The resulting value is a desirability score ranging from 0 to 2. The microscopy is a key measure of the stability and shelf life of a lead azide batch. This is the second most important response and is heavily weighted in determining overall optimality of a lead azide batch.

Purity: After the lead azide is formed, some of the CMC additive often remains in the compound. The purity measures what percentage of the substance is actually lead azide. A compound that is less than 95% purity is deemed unacceptable. The acceptable range for purity is therefore 95%-100%. This response has medium weight in determining overall optimality of a lead azide batch.

Bulk Density: The bulk density has a specification requirement to be between 0.9 and 1.3. A larger bulk density is better; as lower values may cause problems in automated loading equipment. Therefore bulk densities that do not fall within the requirements of 0.9 to 1.3 are unacceptable. This response has mild importance and weight in determining the overall optimality of a lead azide batch.

Additive Remaining in Compound: This response will be highly correlated with the purity, and is defined as the concentration of CMC additive remaining in the final compound. No more than 1.2% CMC by weight can remain in the product. This response has the lowest importance and weight in determining the overall optimality of a lead azide batch.

The remaining responses are pass or fail. Their requirements for passing are outlined below.

Detonator Function Test: For this test, a sample of lead azide is loaded into detonators and initiated. If all detonate, it passes. Otherwise, it fails.

Ball Drop: The standard Ball Drop test uses a 1 oz. steel ball that is dropped onto a sample of lead azide spread on a test block. The first height tested is chosen by the technician based on his previous experience. The drop height is then increased until a reaction occurs (which proves the material is reactive), and then decreased incrementally. The drop test is repeated at each test height until a reaction occurs, and then the drop height is decreased one inch. The test ends when, for a given drop height, no reactions occur in a predetermined number of trials (usually 20, but sometimes reduced to 10 for time considerations). Acceptable results for a lead azide compound are 7 to 12 inches.

pH Level: The pH level of a lead azide batch is required to be between 5.5 and 7.5.

Solubility in H_2O: The solubility of a lead azide batch must be less than 1% to be considered acceptable. Otherwise it is unacceptable and fails.

Digital Scanning Calorimetry (DSC): When tested lead azide must cause a DSC exotherm at more than 300 °C. Therefore, any lead azide with a DSC exotherm at less than 300 °C must be considered unacceptable.

Friction Test: Various size weights are placed at specific positions along a bar to set it for various loads. A sample is placed on a ceramic tile on the test stage and the machine drags a ceramic test piece across the sample. As with the Ball Drop, the first test load is selected by the technician. Once a reaction occurs the load is reduced to the next setting. The test is repeated, reducing the load after each reaction, until no reactions occur for a predetermined number of trials (usually 20) or the lowest setting is reached. Lead azide typically reacts at the lowest setting, so the test is repeated at this setting to calculate the probability of reaction. Anything less than a 100% probability of reaction at the lowest setting is acceptable.

Electrostatic Discharge Test: In the electrostatic discharge test, a static charge is passed through a sample of lead azide. The initial energy setting is selected by the technician, and after a reaction the test is repeated at a lower energy setting. The test concludes when a predetermined number of trials yield no reaction (20 trials) or the lowest setting is reached. Results in the 0.001 to 0.009 J range are acceptable.

4. MULTIPLE RESPONSE OPTIMIZATION CRITERIA

Ten of the 12 responses will be used to evaluate the optimality of different lead azide batches. The procedure used to determine overall optimality of a batch makes use of a desirability function (Derringer and Suich, 1980). First, each response is converted into an individual desirability function, d_i, that varies over the range $0 \le d_i \le 1$, where if the response is at its goal or target, then $d_i = 1$. If, however, the response is an unacceptable value, $d_i = 0$. The process variables are then chosen to maximize the overall desirability, $D = (d_1 d_2 \cdots d_m)^{1/m}$, where there are m responses. In this case m = 12. The primary advantage of using a weighted geometric mean over an arithmetic mean is the ability for any unacceptable individual response to drive the overall desirability to 0. The following paragraphs describe the desirability function for each response.

Dent in Disk After Detonation: The desirability of the lead azide increases with this response. The desirability function is therefore given by,

$$d_1 = \left(\frac{y}{0.25} \right)^5$$

where y is the observed value of the response, and the exponent places a larger weight on this response, since it is the most important and primary measure of performance.

Microscopy: The microscopy test is complex and is the result of several smaller sub-tests. Ideal detonator material would be dissimilar (visually) in shape and "potato like." Quantification of "potato like" is difficult, making a pass-fail classification difficult. Sharp edges, needle shaped crystals and fine crystalline structures are all undesirable linear features that are safety hazards. Future classification may be aided using a general spatial directional filtering of the crystals to check for linear features and a general image classification using an unsupervised Euclidian-type classifier. At this stage in the project, visual verification by counting the number of occurrences of fines, needles, etc. is used.

Purity: The desirability of the lead azide increases with the response and a batch that is less than 95% purity is deemed unacceptable. The individual desirability function is therefore given by,

$$d_3 = \begin{cases} 0 & y < 0.95 \\ \left(\dfrac{y - 0.95}{0.05} \right)^3 & 0.95 \le y \le 1 \end{cases}$$

where y is the observed value of the response, and the exponent places a medium weight on this response, since it is of medium importance.

Bulk Density: The bulk density has a regulatory requirement to be between 0.9 and 1.3. Within this range, however, the desirability of the lead- azide increases with the response. The desirability function is therefore given by,

$$d_4 = \begin{cases} 0 & y < 0.9 \\ \left(\dfrac{y-0.9}{0.4}\right)^2 & 0.9 \le y \le 1.3 \\ 0 & y > 1.3 \end{cases}$$

where y is the observed value of the response, and the exponent places mild weight on this response.

Additive Remaining in Compound: Ideally there will be no CMC additive remaining in a lead azide batch. The desirability therefore decreases with an increase in the response. The desirability function is therefore given by,

$$d_5 = \begin{cases} \dfrac{1.2-y}{1.2} & y \le 1.2 \\ 0 & y > 1.2 \end{cases}$$

where y is the observed value of the response. There is no weight for this response.

Other Responses: The other five responses used to determine overall optimality, are binary pass/fail responses. The desirability functions for these responses are given by,

$$d_i = \begin{cases} 0 & y = fail \\ 1 & y = pass \end{cases}$$

where y is the observed value of the response. Notice that if the lead azide batch does not pass these five tests for acceptability, the overall desirability will be 0, regardless of how well it is evaluated in terms of the other responses.

5. EXPERIMENTATION

5.1 Experimental Design

A major concern in the design of these experiments is the time required to perform response testing. If each combination of the six factors was tested using only two settings each, it would require 64 experiments. With typical response testing requiring a week, this study would take well over a year. Furthermore, with only two levels for each factor, there would be no insight into potential second and third order models of the process. Efficient experimental design must be leveraged in this application. The initial design is a six factor one-eighth fraction factorial experiment with two centers to estimate pure error. This requires 10 experiments including centers. The eight design points are a subset of the 64 potential combinations. If all six factors are significant in the process, then the other 56 experiments will still need to be run. If, however, some of the factors are not significant in affecting the response, those factors can be screened and fewer experiments will need to be conducted. This represents a major potential saving of time. The factor levels were set as previously discussed in section 2. The design matrix for the initial experiment is shown in Table 5.1.

Table 5.1. Design Matrix, Initial Screening Experiment.

Lead Azide Mixture Process Design Matrix							
		Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Std	Run	A:Azide Temperature	B:Lead Temperature	C:Additive to Azide	D:Additive to Lead	E:Flow Rate	F:Azide-(2x Lead)
Ord	Ord	Degrees C	Degrees C	% Concentration	% Concentration	ml/min	M Azide
6	1	35	25	0.8	0.2	240	0.83
3	2	25	35	0.2	0.2	240	1.66
8	3	35	35	0.8	0.5	360	1.245
7	4	25	35	0.8	0.8	240	0.83
2	5	35	25	0.2	0.8	240	0.83
10	6	30	30	0.5	0.2	300	0.83
5	7	25	25	0.8	0.2	360	1.66
9	8	30	30	0.5	0.5	300	1.245
1	9	25	25	0.2	0.8	360	1.66
4	10	35	35	0.2	0.8	360	1.66

5.2 Performing the Experiment

The experiment was conducted with only minor problems. The initial experiments took over four months to complete. The temperature settings for the lead and the azide were very difficult to control and therefore the experimenters did not achieve the targeted high and low settings for most of the runs. This necessitated the use of multiple linear regression to analyze certain process variables. In addition, not all responses were evaluated for the confirmation runs. The confirmation runs only focused on responses that did not meet MIL standards. Initial experiments indicated problems in maintaining CMC solubility in the lead solution, so for remaining experiments no CMC was added to the lead stream.

5.3 Statistical Analysis

After the 10 experiments had been conducted and the responses measured, two of the responses had an individual desirability of 0; purity and bulk density. The statistical analysis was therefore focused on those two problem responses. The other 10 responses met MIL-standard and therefore were not preventing acceptable production of lead azide. Furthermore, there was a definite problem with achieving the targeted temperature settings for the lead and the azide. This made two-sample testing infeasible and so multiple linear regression of both of these responses was performed. The resulting ANOVA tables are shown in Tables 5.2 and 5.3.

Table 5.2. ANOVA for Purity (MLR)

Predictor	Coef	SE	T	P
Constant	97.2729	0.7907	123.02	0.000
Additive to Azide	-1.5481	0.4560	-3.39	0.015
Flow Rate	0.00638	0.0027	2.33	0.058
Concentration	-0.2447	0.1818	-1.35	0.227

Purity = 97.25 – 1.14 * *Additive* + 0.006 * *Flow Rate* – 0.35 * *Concentration.*

Table 5.3. ANOVA for Purity (Effects)

Source	Sum Sq	DF	MS	F	P-Value
Model	2.06	3	0.69	26.13	0.0018
Additive	0.93	1	0.93	35.37	0.0019
Flow R	0.85	1	0.85	32.13	0.0024
Conc.	0.75	1	0.75	28.49	0.0031
Curve	0.055	1	0.055	2.10	0.2070
Residual	0.13	5	0.026		
Cor Tot	2.25	9			

The bulk density is affected by only one of the factors; the flow rate. The half normal plot for the bulk density is shown in Figure 5.3. It can be seen from the figure that the flow rate significantly affects the bulk density, while the others do not. The ANOVA table shows that there is no significant curvature.

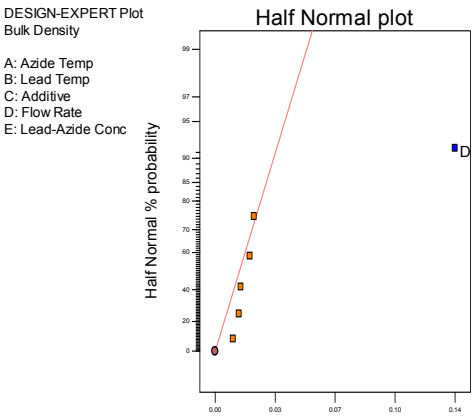

Figure 5.3. Half Normal Plot for Bulk Density.

Table 5.4. ANOVA for Bulk Density

Source	Sum Sq	DF	MS	F	P-Value
Model	0.015	1	0.015	73.55	0.0004
Flow R	0.014	1	0.014	70.63	0.0004
Curve	0.0002	1	0.0002	1.04	0.3538
Residual	0.001	5	0.0002		
Cor Tot	0.016	7			

The mathematical model for bulk density is therefore given by,

Bulk Density = 0.829 – 0.000855 * *Flow Rate.*

Notice the conflict in desireablility between purity and bulk density. An increase in the flow rate increases the purtity, however, it reduces the bulk density.

5.4 Process Improvement

The optimization of the purity and bulk density are at odds. An increase in the flow rate increases the purity, however, it reduces the bulk density. The advantage that exists is in the fact that there are other factors that contribute to the purity. A multiple response optimization looks at the compromise between these competing responses.

Before a multiple response optimization is performed, however, take a close look at the model for bulk density. If the flow rate were set at its lowest possible level of 200 ml/min, the maximum possible bulk density is 0.658, which is well below required 0.9 g/cm^3. Therefore, a setting that focuses on the bulk density is extremely important.

It is possible that the process may not be capable of meeting the bulk density requirement. The chemical engineers at ARDEC were directed to conduct two model validation experiments, where the flow rate was set at 200 ml/min and the additive and concentration was set at the low levels described earlier. The only responses to be investigated were the bulk density and the purity. The flow rate was higher than expected from the model, 0.732, however, it was still not near the 0.9 standard.

6. FUTURE DIRECTION

The chemical process was not capable of producing an acceptable batch of lead azide in accordance with MIL-standards. This left chemical engineers with three alternatives; make significant changes to their process, develop a new chemical process, or change the lead azide loading specifications for detonators. After the conclusion of this effort, the chemical engineers identified a raw material change that improved the product. This change made significant improvements to the lead azide bulk density without a negative effect on other responses.

Although response surface methods did not discover optimal settings for the process equipment, it did provide a major contribution to the project. This design and analysis of experiments enabled chemical engineers to discover that the process was not capable in a time span of less than three months. Otherwise, the engineers would have spent over a year and a half to reach the same conclusion. Furthermore, the desirability function defined in Section 4 provides a measure of overall lead azide quality.

7. CADET DEVELOPMENT

This project was a classic example of the power of Applied Statistics to further scientific research and development. Students taking Applied Statistics at the U.S. Military Academy during the Fall 2005 semester visited the lead azide process at Picatinny Arsenal. This project provided the cadets with an excellent contextual example in which lesson objectives were learned. The cadets conducted a course project where they developed an experimental design for the project. Almost all of the cadets felt that participation in a real-world project such as the lead azide process was one of the most educationally beneficial experiences they had at the Academy. Hopefully, future cadets enrolled in Applied Statistics will have similar opportunities to apply their knowledge of course material to real-world Army problems.

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