DEMILITARIZATION OF M55 CHEMICAL MUNITION SYSTEMS: THE COMBUSTION OF SOLID FUEL-OXIDANT MIXTURES

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Picatinny Arsenal
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OCTOBER 1975

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**DEMISSION OF M55 CHEMICAL MUNITION SYSTEMS: THE COMBUSTION OF SOLID FUEL-OXIDANT MIXTURES**

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**Abstract**
The object of this study is to determine the feasibility of using coal as a fuel in demilitarizing M55 chemical munitions by burning. A clay soil trench was constructed to simulate the actual trenches in which these munitions are located at Dugway Proving Ground; canisters filled with oil were used to simulate the munitions. Coal beds consisting of alternate layers of coal and sodium nitrate were built up, and thermocouples were placed in the trench and canisters before each test. Kerosene was used as an igniter.
The factors investigated were (1) the type of coal, (2) the type of oxidant, and (3) the use of rhenium in addition to the fuel-oxidant mixture. The results show that a bed containing soft coal-coke-NaNO₃ or soft coal-coke-annel coal-NaNO₃ achieves the most satisfactory results. Temperatures as high as 2000°F can be achieved in the canister within 15 minutes of ignition and the bed remains above 800°F for 1 to 3 hours, depending on its depth. These temperatures are sufficiently high to melt the aluminum warhead and to assure the degradation of the chemical agents contained in the M55 munition.
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INTRODUCTION

The Pyrotechnics Branch of the Explosives Division at Picatinny Arsenal was presented with a problem involving the demilitarization of M55 chemical munitions systems at Dugway Proving Grounds. These munitions, which consist of aluminum canisters containing an explosive charge and a chemical agent, are presently located in trenches at the Proving Grounds. According to Dugway's test data, the chemical agent can be effectively destroyed if it is heated to 1000°F (538°C) for 0.1 second or to 800°F (427°C) for one second. This research program was undertaken to determine the feasibility of using a coal fire to heat the munitions to the required temperature.

Preliminary experiments indicated that it would be difficult to sustain a coal fire in a trench because of the inaccessibility of oxygen from the air. However, experiments also showed that if an inorganic oxidant was added to the bed of coal, virtually complete combustion would occur. The scope of this research program includes the design and construction of an experimental trench along with the associated instrumentation for measuring temperature, and the formulation and testing of various combinations of coal and other materials for use as best sources.

EXPERIMENTAL

An experimental trench was constructed from a metal box 46 inches long, 21 wide, and 36 inches deep. The box was filled with approximately one ton of clay soil in which was dug a trench 17 inches long, 11 inches wide, and 12 inches deep (Fig 1 and 2). The various heat source formulations which were investigated were layered in the trench in the form of beds. Chromel-alumel thermocouples sheathed in stainless steel were used to measure the temperature at various points in the bed and in the soil surrounding the trench. These temperatures were recorded on a multi-channel potentiometric recorder. The M55 chemical munitions canister was simulated by an aluminum flare case with an ogive (Fig 3). The simulated canisters were filled with SAE 30 motor oil, which has physical properties similar to the chemical agent. Although the flare case (5 inches long, 1.5 inches in diameter) is considerably smaller than the M55 canister (28.2 inches long, 3.87 inches diameter), its wall thickness (0.065 inch) is the same as that of the M55.

The following procedure was followed for each experiment:

1. Three canisters filled with motor oil were placed in the trench, the first was partially buried in the soil and protruded about 1/4 inch above the bottom of the trench, the second was placed horizontally on the bottom of the trench, and the third was placed upright in the trench.
2. One thermocouple was inserted inside the upright canister (A, Fig 4), and another was centered in the bottom of the trench (B).

3. A bed of fuel and oxidant 7 inches deep was laid in the bottom of the trench.

4. One thermocouple was inserted into the bed (C) and another was clamped about eight inches above the bed.

5. Other thermocouples were inserted into the soil at various distances from the surface of the trench (E, F, and G).

6. A flammable liquid (ethyl alcohol or kerosene) was poured over the top of the bed and ignited.

7. During the burning, temperatures were measured in the flame above the bed, in the bed, in a canister located in the bed, at the interface of the bed and the bottom of the trench, and in the soil at various locations and distances from the trench.

The formulations tested included various mixtures of soft coal, cannel coal, and coke as fuels, and sodium nitrate and potassium perchlorate as sources of oxygen. Experiments were also performed in which a layer of thermite (powered aluminum and ferric oxide) was placed on the bottom of the trench beneath the fuel and oxidant bed. The soft coal used was obtained from the Picatinny Arsenal power plant and consisted of particles ranging in size from dust to walnut-sized lumps. The cannel coal, obtained from a local fuel dealer in the form of large chunks, was broken into lemon-sized pieces. The coke, from Koppers Corporation, ranged from pea-sized to walnut-sized particles. The sodium nitrate and potassium perchlorate were technical grade materials.

RESULTS

A series of trials were performed in which the main objective was to determine the conditions most conducive to feeding heat to the bottom of the trench. Initial testing indicated that the use of coal alone was unsatisfactory because it was difficult to ignite and difficult to burn without a forced draft of air.

These ignition and combustion problems could be overcome by piping air or oxygen into the bottom of the trench and forcing the gases up through the coal bed. This approach, however, is hazardous and costly, since it requires placing a grill type arrangement at the bottom of the trench and using air compressors, compressed air, or oxygen to provide adequate gas flow. A simpler approach is to use an inexpensive
material such as sodium nitrate for the oxygen supply during the initial phases of combustion. A coal-sodium nitrate mixture is relatively easy to ignite and the coal is consumed at a much faster rate than coal burning in air. The coal undergoes combustion with the oxygen produced by the decomposition of the oxidant according to the reactions:

\[
\begin{align*}
\text{NaNO}_3 & \rightarrow \text{NaNO}_2 + \frac{1}{2} \text{O}_2 \\
2\text{NaNO}_2 & \rightarrow \text{Na}_2\text{O} + \text{N}_2 + 3/2 \text{O}_2 \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2
\end{align*}
\]  

The reaction illustrated in Equation (3) can produce a temperature in excess of 3000°F. Undoubtedly the combustion reaction is more complex; the vigorous combustion is accompanied by a flame which is indicative of a flame reaction between coal volatiles and oxygen.

In the initial tests, the sodium nitrate was mixed with soft coal, the mixture was soaked with kerosene, and the kerosene was ignited. As expected, the burning kerosene readily ignited the mixture of coal and sodium nitrate. However, the combustion diminished after only a few minutes, apparently because the sodium nitrate had been consumed; the coal remaining in the bed did not undergo further combustion. It was necessary, consequently, to consider a different approach in which the combustible bed was built up with alternate layers of coal and oxidant. Kerosene was again poured over the bed and ignited. This arrangement produced a quiet burning of the kerosene at first, followed by vigorous burning caused by the combustion of the coal with the decomposition products of the oxidant. The combustion continued for approximately 30 minutes before subsiding, leaving a bed of glowing embers.

Because the heat generated during the vigorous stage of combustion appears to be sufficiently intense to permit sustained combustion of the coal bed, the use of coal-oxidant layers appears most desirable. Based on this assumption, a series of trials were performed to determine:

1. The most suitable type of coal
2. The most suitable oxidant
3. The required quantity of coal and oxidant

The performance of the materials tested is shown in Table 1.
In this test, the bed was built up with alternate layers of coal and sodium nitrate. After the initial quantity of sodium nitrate was consumed, further additions were made at periodic intervals to maintain the oxygen supply at a high level and to assure that the coal was completely consumed. The initial construction of the bed, sequentially from the bottom of the trench up, was as follows:

5 layers, alternating NaNO$_3$ (750 g per layer) and soft coal (1200 g per layer), beginning with NaNO$_3$

1 layer (2600 g) of cannel coal

1 layer (750 g) of NaNO$_3$

1 layer (1200 g) of soft coal powder

The cannel coal was used in this array because it appears to sustain combustion somewhat more easily than in the soft coal; the soft coal powder was used for ignition.

The thermocouples used in Trial A were located:

1. In the bottom of the trench

2. In an oil-filled canister buried in coal

3. At the side of the trench, 2 inches from the trench wall and 3 inches from the bottom, and

4. Two inches below the trench floor.

The results of the test are summarized in Figure 5. Within 15 minutes of ignition, the temperatures at the bottom of the trench and inside the canister rose above 1400°F and remained above 800°F for almost two hours. The temperature inside the canister was maintained above 1000°F for about three hours by the periodic addition of NaNO$_3$ and a mixture of coal and NaNO$_3$, as shown in Figure 5. The temperature at the side of the trench rose to over 350°F. The low temperature recorded in the soil was probably due to moisture, the low thermal conductivity of the soil, and the large heat sink surrounding the bed.
Trial B

The only difference between Trial A and Trial B is the time at which the NaNO₃ was added to the bed. In Trial A, NaNO₃ was added periodically (every 15 minutes), while in Trial B, NaNO₃ was added as required, that is, when the fire became quiescent. The temperature at the bottom of the trench and inside the canister reached a maximum between 1300° and 1500°F, and remained above 800°F for over two hours (Fig 6). The side of the trench reached 300°F in this case, and the temperature 2 inches below the floor of the trench reached 200°F.

Although the concept proved feasible, this line of testing was discontinued because of the hazards involved in adding oxidant to the fuel bed during the burning process.

Trial C

The main objective of this test was to determine the temperature rise in and around a trench containing a coal-oxidant bed which was not re-fueled during burning. For this trial, the bed was built up essentially the same as for Trial A, except that about 4000 g of cannel coal mixed with 750 g of NaNO₃ was used instead of 2600 g of cannel coal alone. About 750 g of NaNO₃ was also mixed with the coal powder that was sprinkled on top of the bed. The placement of the thermocouples was the same as for Trial A with an additional thermocouple placed one inch below the top of the coal bed.

The temperature in and around the burning coal-oxidant bed is shown in Figure 7. After eight minutes the temperature in the canister rose rapidly to over 1400°F, then dropped, at first rapidly and then more gradually. The temperature remained above 800°F for 30 minutes; the coals about one inch from the top of the bed retained a temperature of over 800°F for about one hour and burned for about three hours with gradual diminution in temperature.

The canisters as they appeared after the trial are shown in Figure 8. The canister partially covered with dirt(A,Fig 8) remained intact, although the oil it contained was partially decomposed. The canister lying on its side (B) was partially melted, and the upright canister (C) was almost totally melted and the oil consumed.

Trial D

The objective of this trial was to determine the feasibility of using coke in conjunction with soft coal. The bed was constructed from the bottom of the trench up, as follows:
5 layers, alternating NaNO$_3$ (1500 g per layer) and soft coal (1200 g per layer),
beginning with NaNO$_3$.

6 layers, alternating coke (100 g per layer) and NaNO$_3$ (750 g per layer)

1 layer of a mixture of soft coal powder (100 g) and NaNO$_3$ (750 g)

The bed was 7 inches deep. The thermocouple sites and canister arrangement were
the same as in Trial C.

This trial was conducted in two phases D$_1$ and D$_2$. The D$_1$ trial consisted of the
aforementioned mixture while the D$_2$ trial, instead of using coke, a 50-50 mixture of
cannel coal and coke was used. During Trial D$_1$, shown in Figure 9, the temperature in
the upright canister and one inch below the surface of the coal bed rose to approximately
2000°F about 15 to 20 minutes after ignition and remained above 800°F for about one
hour. The temperature at the bottom of the trench reached a maximum of 1500°F and
remained above 800°F for about two hours. The test clearly shows that the bed con-
structed of soft coal-coke-NaNO$_3$ performed better than the formulation previously
tested. The results of the test using 50-50 cannel coal-coke mixture (Trial D$_2$) instead of
coke (Trial D$_1$) shown in Figure 10 resulted in a 25% higher temperature after 2 hours
while the burning time was about the same.

The condition of the canisters after Trial D$_1$ is shown in Figure 11. The canister
partially covered with dirt (A) was charred but intact. The canister lying on its side (B)
was almost completely melted, and the upright canister (C) was destroyed.

Miscellaneous Trials

Tests were also performed to determine if the transfer of heat to the bottom of the
trench could be improved by the use of different compositions. In one test, Trial E,
potassium perchlorate (KClO$_4$), was substituted for sodium nitrate; in another Trial F,
a thermite-type mixture (Fe$_2$O$_3$-A$1$) was placed at the bottom of the coal-NaNO$_3$ bed.
In both instances, the results were less satisfactory than in previous trials. The
temperature-time traces for Trials E and F are shown in Figures 12 and 13.

CONCLUSIONS AND RECOMMENDATIONS

The use of a bed of coal and inorganic oxidant appears to provide the heat neces-
sary to demilitarize M55 chemical munition systems by burning, if the canisters are in
direct contact with the burning coals. However, canisters completely covered with soil
will not be heated to a high enough temperature to insure destruction. For this reason,
it is recommended that all canisters be uncovered if this method is used.
The formulation which generated the most heat for the longest period of time is the mixture of cannel coal and coke with sodium nitrate as the oxygen source. A layer of coarse soft coal mixed with sodium nitrate on the bottom of the bed, and a layer of fine soft coal mixed with sodium nitrate on top of the bed is suggested to promote ignition of the main bed. Field tests should be performed using scaled-up quantities of the recommended formulation. In the tests reported here, each layer of fuel was about 3/4 inch thick while the oxidant layer was about 1/4 inch thick. The adequacy of this thickness should be determined during the field tests.

Consideration should also be given to the sequence of events that may occur if burning is used to demilitarize the M55 munition. Heating the munition will cause it to explode. The explosion will destroy the bed and cause fragments and chemical agent to be ejected from the trench. For these reasons it is suggested that a blast mat be placed over the trench and gas burners be used to maintain a curtain of flame over the top of the blast mat. These features should trap flying fragments and prevent the escape of the chemical agent into the atmosphere.
Table 1
Performance of coal-oxidant mixtures

<table>
<thead>
<tr>
<th>Trial</th>
<th>Mixture</th>
<th>Maximum temperature (°F)</th>
<th>Time above Al melting point (hr)</th>
<th>Time above 800°F (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Soft coal-cannel coal-NaNO₃</td>
<td>1450</td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td>B</td>
<td>Soft coal-cannel coal-NaNO₃</td>
<td>1450</td>
<td>0.25</td>
<td>2.5</td>
</tr>
<tr>
<td>C</td>
<td>Soft coal-cannel coal-NaNO₃</td>
<td>1600</td>
<td>0.2</td>
<td>0.5 to 1.0</td>
</tr>
<tr>
<td>D₁</td>
<td>Soft coal-coke-NaNO₃</td>
<td>~2000</td>
<td>0.5</td>
<td>1.0 to 1.5</td>
</tr>
<tr>
<td>D₂</td>
<td>Soft coal-cannel coal-coke</td>
<td>~2000</td>
<td>0.5</td>
<td>1.5 to 3.0</td>
</tr>
<tr>
<td>E</td>
<td>Soft coal-cannel coal-KC₁₀₄</td>
<td>1600</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>F</td>
<td>Soft coal-cannel coal-NaNO₃</td>
<td>2000</td>
<td>0.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

---
a. NaNO₃ added at 15-min. intervals.
b. NaNO₃ added as needed.
c. In canister sitting upright in coal bed.
Fig 1 Instrumented experimental trench

Fig 2 Coal bed in trench with two thermocouples extending from bed
Fig 3 Simulated M55 munition system
Fig 4 Location of thermocouples in experimental trench
Fig 5 Temperature-time trace of Trial A
Fig 6 Temperature-time trace of Trial B
\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Temperature-time trace of Trial C}
\end{figure}
Fig 8 Canisters recovered from Trial C
Fig 9 Temperature-time trace of Trial D₁
Fig 10 Temperature-time trace of Trial D₂
Fig 11 Canisters recovered from Trial D
Fig 12: Temperature-time trace of Trial E
Fig 13 Temperature-time trace of Trial F