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APPLICATIONS OF NEW CHEMICAL HEAT SOURCES
PHASE 2

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14. ABSTRACT

Report developed under "Small Business Innovative Research" contract.
This project developed a formulation for use in heating military field rations, particularly the Meal, Ready-To-Eat (MRE). The heater that was developed is in the form of one-eighth inch diameter pellets, packaged in a porous, water-permeable scrim. The heater is conveniently activated by the addition of water. A heater weighing two ounces, activated by one ounce of water, will heat the eight-ounce MRE by at least 100 degrees Fahrenheit (e.g. from 70 to 170 degrees F) under standard test conditions. This heater represents an improvement on current technology because it does not produce flammable hydrogen gas during operation. The product remaining after activation does not contain any hazardous materials. The production cost estimated for large quantities is $0.19 to $0.23 per two-ounce heater. During this project 2,000 heaters were provided to Natick RD&E Center for testing.

15. SUBJECT TERMS

RATIONS
SAFETY
CONVENIENT
DISPOSABLE
SELF HEATING
FIELD RATIONS
HEAT SOURCE
NON-FLAMMABLE
WATER ACTIVATED
NONHAZARDOUS WASTES
CHEMICAL HEATING
MRE(MEAL READY-TO-EAT)
MILITARY RATIONS
FIELD FEEDING
PORTABLE HEATERS
HEATING
COST-EFFECTIVE
RATION HEATERS
RATION HEATING
CHEMICAL HEATER

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Preface

This project, performed by TDA research under Small Business Innovative Research (SBIR) contract DAAK601-92-C-0030 examined one of two potentially useful heat-producing chemical reactions that were identified in Phase I. P_2O_5/CaO was selected as the most suitable. The Army's current ration heater, the Flameless Ration Heater (FRH) is a magnesium/water reaction that produces hydrogen gas as one of the bi-products. The goal was to develop a reaction that would produce the optimal amount of heat without producing hydrogen gas and reducing the cost of the heater. The final heater contains approximately seven cents worth of materials and can be produced for about 19 to 23 cents per unit.

Summary

In Phase I, TDA Research (TDA) identified two potentially useful heat-producing formulations: P_2O_5/CaO and $AlCl_3$/CaO. In Phase II tests, P_2O_5/CaO was selected as the more suitable. The primary challenge was developing means to control the rate of heat output. The goal is to produce heat only as fast as the target material can absorb the heat. TDA developed a method for controlling temperature by adding inert liquids that allowed the heater to produce heat over a period of 10-12 minutes, compatible with the intended food products.

Several different meals were investigated for use with the new heater during this project. Initial work focused on a heater for the Self-Heating Individual Meal (SHIM), which contained a 10-ounce meal in a plastic tray. We also considered heaters for the Self-Heating Group Ration (SHGR), which contains food for 18 people. At the direction of the COR, later work focused on the Army's primary individual field ration, the Meal, Ready-to-Eat (MRE). The Army currently offers a chemical heater for the MRE, the flameless ration heater (FRH). Yet, two improvements to the FRH were desirable: (1) eliminating production of flammable hydrogen gas, and (2) lowering the cost.

TDA demonstrated that its proprietary heater formulation performed well with the MRE. The materials required for the heater are low cost, and in this Phase II project TDA developed manufacturing techniques that should make it possible to produce an effective heater with increased feasibility and safety.

User safety has been a top priority throughout this project, and TDA has carried out several different evaluations to assure safety. A Product Regulatory Assessment was conducted by an independent contractor (Industrial Compliance, Golden, CO). This study covered the following areas: Resource Conservation and Recovery Act (RCRA); Hazardous Materials Transportation ACT (HMTA); Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); Clean Water Act (CWA); Toxic Substance Control Act (TSCA); Occupational Safety and Health Act (OSHA); and preparation of the Material Safety Data Sheet (MSDS). Each of these topics is treated separately in the section on safety, but the key results are as follows: (1) RCRA: independent laboratory tests of ignitability, corrosivity, reactivity, and toxicity confirm that the heaters after use are not hazardous wastes. The used heater may be disposed of through normal means, e.g. in sanitary landfills. (2) HMTA: the heaters are not hazardous materials as defined in CFR 49. (3) CERCLA: requires reporting of storage of more than 10,000 pounds of CaO to local agencies. (4) An MSDS has been prepared for the new heater.

Although development of production methods occupied the largest part of the effort in this project, the methods that we developed for preparing heaters suitable for use with the MRE are simple and use readily available equipment. The production steps can be summarized as follows: (1) Mix P_2O_5 and CaO, both available in bulk as powders, with the inert liquids. (2) Extrude the resulting wet solid into pellets of approximately ⅛ inch diameter. (3) Heat the materials for a short time to about 100°C; this step increases stability on storage. (4) Package the materials in a porous scrim. (5) Package the heater bag in a polymer film with suitably low water vapor transmission rate (any of several metallized films are satisfactory). The final heater weighs about two ounces and can be activated by addition of one ounce of water. The heater contains about seven cents worth of materials and can be produced for about 19 to 23 cents per unit.

APPLICATIONS FOR NEW CHEMICAL HEAT SOURCES, PHASE 2

1. Introduction

The Army now uses the Flameless Ration Heater (FRH) as a heat source for the Meal, Ready-to-Eat (MRE). The FRH contains a magnesium/iron (Mg/Fe) alloy, which reacts with water to produce heat; the other products are magnesium hydroxide ($Mg(OH)_2$) and hydrogen (H_2). The FRH is currently produced in large quantities, but improvements in two areas would be desirable: first, the FRH produces substantial quantities of hydrogen, a flammable gas, which is both an inconvenience to the user and a potential fire or explosion hazard. Elimination of hydrogen gas would be an important improvement to the safety of the users. Second, a heat source that costs less to produce than the FRH would be a significant advantage, especially given the large numbers of heaters in use. Thus, our objectives in this project were to retain the advantages of the FRH, while eliminating the hydrogen and lowering the cost.

The ideal portable heat source will be safe, convenient to use, low in cost, weight, and volume, efficient, stable on storage, and readily disposable after use. Many reactions have previously been considered for portable food heaters, but none has proven itself completely satisfactory. For example, the reaction of water with calcium oxide (CaO) is a cheap and effective heat source, but the weight and volume are too high for convenience.

A significant consumer market for a portable heat source would benefit the military by simplifying future procurements. It appears that such a consumer product will require an improved heater. Concern about product liability is likely to limit commercialization of the hydrogen-producing FRH.

1.1. Phase II Objectives

The overall objectives of the Phase II work were to prepare a heater formulation that was effective, safe, and inexpensive, and to prepare quantities of the heaters for tests by the U.S. Army Natick RD&E Center (Natick).

Supporting these overall objectives were the following specific objectives:

1. Determine the best formulation to produce heat at the desired rate.

2. Identify potential heater designs.

3. Prepare limited quantities of ration heaters for tests; refine the design based on test results.

4. Prepare large quantities of ration heaters for further testing: two thousand heaters were provided to Natick RD&E Center.

5. Conduct a systems analysis to estimate the manufacturing cost.

6. Conduct an ongoing systems safety analysis.

7. Prepare monthly progress, status and management reports, and this comprehensive final report.

1.2. Summary of Results

In Phase I, TDA identified two different heat-producing formulations: P_2O_5/CaO and $AlCl_3$/CaO. Both could produce the required amount of heat with acceptable weight, and both were low in cost. Tests showed that the P_2O_5/CaO formulation gave excellent performance, and avoided a potential odor problem with evolution of HCl gas associated with the $AlCl_3$/CaO formulation. Therefore, subsequent work focused on the P_2O_5/CaO material. The primary challenge was to develop a means to control the rate of heat output. The goal is to produce heat only as fast as the target material can absorb the heat. TDA developed a method for controlling temperature by adding inert liquids that allowed the heater to produce heat over a period of 10-12 minutes, compatible with the intended food products.

Several different meals were investigated for use with the new heater during this project. Initial work focused on a heater for the Self-Heating Individual Meal (SHIM), which contained a 10-ounce meal in a plastic tray. We also considered heaters for the Self-Heating Group Ration (SHGR), which contains food for 18 people. At the direction of the COR, later work focused on the Army's current primary field ration, the MRE.

TDA demonstrated that its proprietary heater formulation performed well with the MRE. The materials required for the heater are low in cost, and in this Phase II project we developed manufacturing techniques that should make it possible to produce the heaters at very attractive prices.

User safety has been a top priority throughout this project, and TDA has carried out several different evaluations to assure safety. A Product Regulatory Assessment was conducted by an independent contractor (Industrial Compliance, Golden, CO). This study covered the following areas: Resource Conservation and Recovery Act (RCRA); Hazardous Materials Transportation ACT (HMTA); Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); Clean Water Act (CWA); Toxic Substance Control Act (TSCA); Occupational Safety and Health Act (OSHA);; and preparation of the Material Safety Data Sheet (MSDS). Each of these topics is treated separately in the section on safety, but the key results are as follows: (1) RCRA: Independent laboratory tests of ignitability, corrosivity, reactivity, and toxicity confirm that the heaters after use are not hazardous wastes. The used heater may be disposed of through normal means, e.g. in sanitary landfills. (2) HMTA: The heaters are not hazardous materials as defined in CFR 49. (3) CERCLA: Requires reporting of storage of more than 10,000 pounds of CaO to local agencies. (4) An MSDS has been prepared for the new heater.

Although development of production methods occupied the largest part of the effort in this project, the methods that we developed for preparing heaters suitable for use with the MRE are simple and use readily available equipment. The production steps can be summarized as follows: (1) Mix P_2O_5 and CaO, both available in bulk as powders, with the inert liquids. (2) Extrude the resulting wet solid into pellets of about ⅛ inch diameter. (3) Heat the materials for a short time to about 100°C; this step increases stability on storage. (4) Package the materials in a porous scrim. (5) Package the heater bag in a polymer film with suitably low water vapor transmission rate (WVTR). Any of several metallized films have been satisfactory. The final heater weighs about two ounces and can be activated by addition of one ounce of water. The heater contains about seven cent worth of materials and can be produced for about 19 to 22 cents per unit.

1.3. Organization of the Report

In Section 2, we discuss the background to this project, including system requirements and reactions previously used in heaters. Section 3 contains results and discussion and Section 4 covers safety considerations. Section 5 contains the systems analysis, including manufacturing methods. Conclusions are summarized in Section 6.

In Phase II TDA investigated two formulations: P_2O_5/CaO and $AlCl_3$/CaO; P_2O_5/CaO proved to be superior and was used for the new heater. In Appendix A, we review other reactions that were investigated in Phase I. Appendix B contains the Product Regulatory Assessment conducted by an independent contractor, Industrial Compliance (Golden, CO). Appendix C contains the Material Safety Data Sheet prepared for the new heater.

2. Background

In this section, we review the reasons for using a portable energy source for heating food, the requirements for a portable heat source for food heating, and systems previously used for this purpose.

Large groups of soldiers can be well served by field kitchens; however, many situations arise where small groups or individuals need a hot meal. In such cases either a chemical heat source or a portable stove can be used. The weight of a stove need not be large, and the energy content of a hydrocarbon fuel (18,500 Btu/lb) is better than that of all but a few possible chemical reactions. For small groups, there will be a weight savings associated with using a chemical heat source for each meal, rather than a stove and fuel; with larger groups the stove is the lighter alternative. The main reason for using a chemical heater, however, is convenience. Those of us who have often cooked over camp stoves, in all weather conditions, know that it requires both time and energy. A portable, chemical heat source is much more convenient for the users, leaving them both well fed and rested, and ready for their next task.

2.1. Requirements for Portable Heat Source for Food

What are the requirements and desirable features of a portable heat source system? The following features are most important:

1. It must be safe for the user.
2. It must be conveniently activated.
3. It must be low in cost.
4. It should have minimal weight and volume for convenience in storage and transport.
5. The rate of heat output must be controllable, so the food/beverage is warmed in a short time, but without excessive elevation in

temperature, which could cause undesirable changes in food quality and taste.

6. The heater must transfer heat efficiently to the food container.

7. The heater must be stable in storage for an extended period of time, preferably more than 3 years.

8. The heaters should be readily disposable after use, with minimal environmental impact.

An important issue in the design of portable heat sources is the means of activation. A convenient means of activating the heater is addition of water (or a solution) to a solid. This has several advantages: first, the water aids in heat transfer from the heater to the food container, both by contact and by steam vaporizing from the hot mixture and condensing on the food container, there releasing the heat of vaporization (like the steam table in a cafeteria). If we use water to activate the heater, the water source could be locally available, and if it is only used for the heater, it need not be potable water.

In this project we have assumed that the water for activation will be provided by the user from a canteen or other container. It is also possible to include the water in the package with heater and food, and means to add water to heater by a pull strip are available. If the water is packaged with the heater, an anti-freeze may be desirable. In Phase I TDA found that calcium chloride ($CaCl_2$) made a suitable, inexpensive antifreeze. The Army does not plan on cooking frozen MREs, and the present heater has not been tested with an anti-freeze solution.

2.2. Heater Configurations

In this project, TDA initially focused on a heater for the Self-Heating Individual Meal (SHIM; Figure 2.0). This 10-ounce meal consists of a meat, starch, and vegetable in a plastic tray. The heater is contained in a separate tray below the food. The water for activation is shown packaged with the heater, the configuration most convenient for a single user, and probably closest to a consumer product. However, the SHIM was determined to be relatively expensive using current packaging techniques and is not now scheduled for large-scale production.

Another field feeding system considered was the Self-Heating Group Ration (SHGR; Figure 2.1), which contains food for 18 people. This system would be effective for squad-size groups, but, like the SHIM, is not in large-scale production.

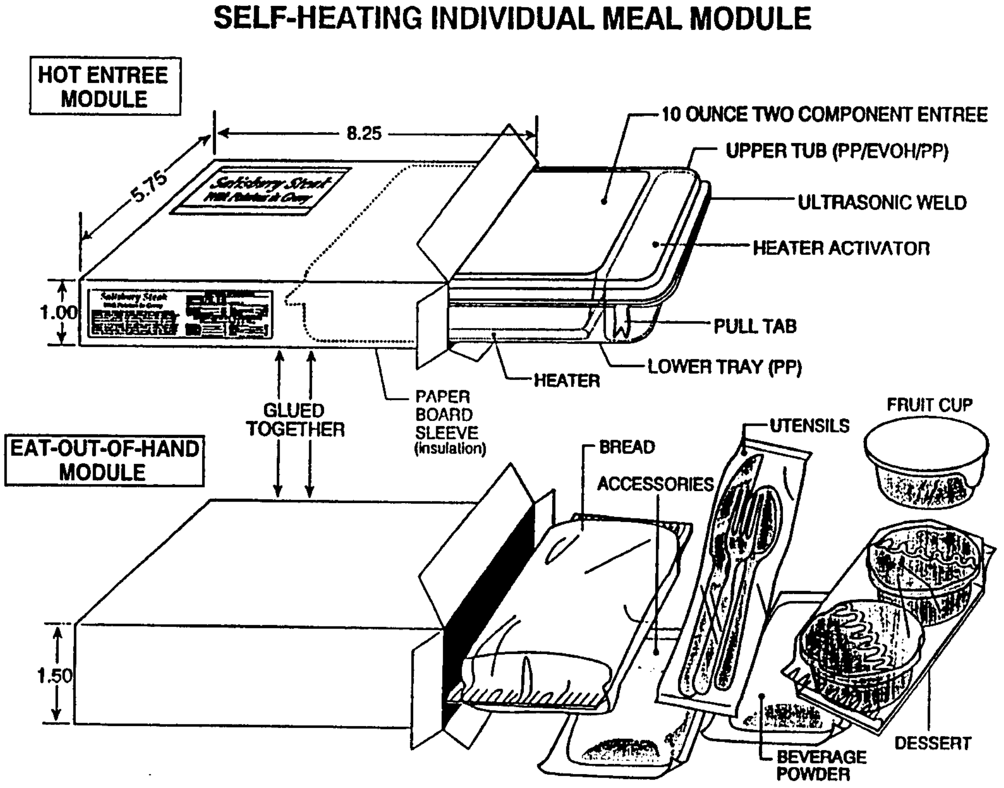


Figure 2.1 Self-Heating Individual Meal (courtesy of U.S. Army Natick RD&E Center).

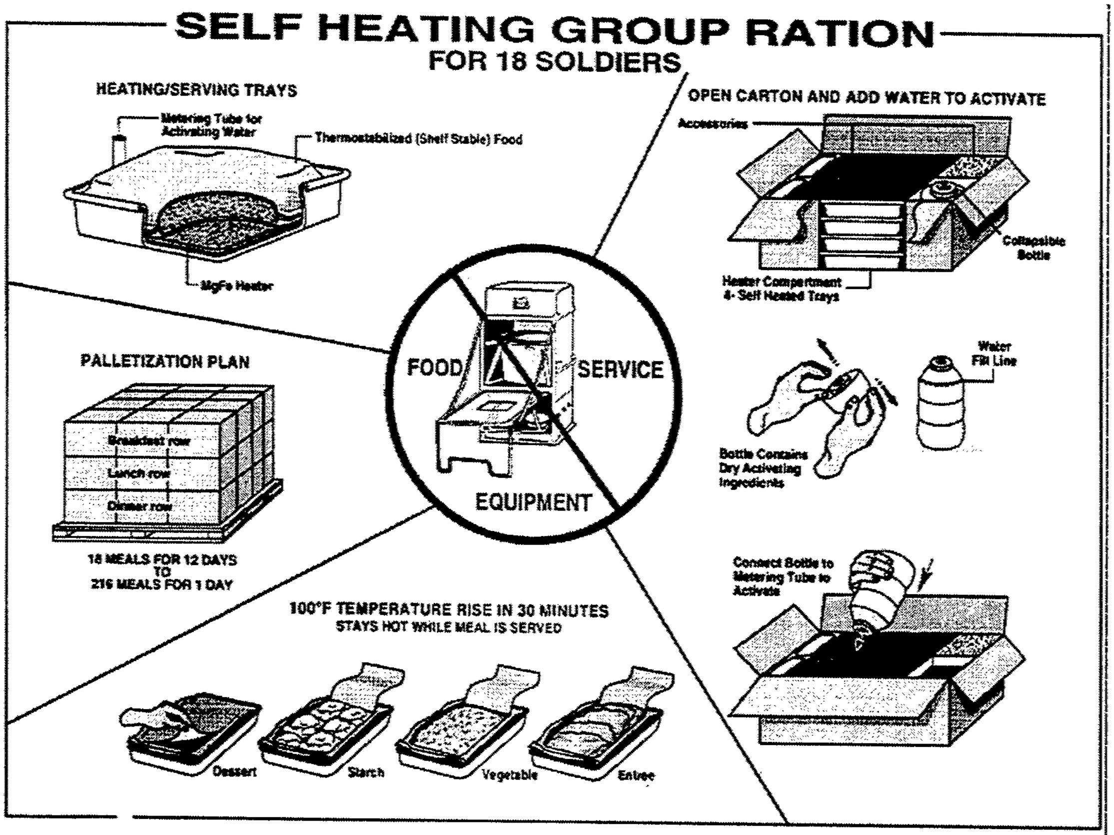


Figure 2.2 Self-Heating Group Ration; courtesy U.S. Army Natick RD&E Center.

The field ration currently in large-scale use is the MRE. This familiar 8-ounce pouch is very inexpensive to produce, and is conveniently heated by the FRH. As described earlier, the product developed in this project is designed to be a direct replacement for the FRH, for use with the MRE.

2.3. Previous Heater Formulations

In Phase I, TDA investigated a wide variety of reactions suitable for portable heat sources; this investigation is summarized in Appendix A. Much of the patent literature relates to the self-heating package, and lists only a few exothermic reactions, with no reason to prefer one over another.

The reaction used in many systems is the hydration of quicklime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

While the reactants are inexpensive and the reaction generally acknowledged to be quite safe, the heat output per weight is low (501

Btu/lb). Also, the powder density of calcium oxide is low, so that the volume of calcium oxide required for a given heat output is high. When the weight and volume of the activator solution is included, we have a heater that approaches the size of the food to be heated, a condition that is unacceptable.

The reaction of water with the magnesium/iron composition in the FRH has a much higher specific heat output, but the production of hydrogen is a potential hazard, which would be preferable to avoid. The production of hydrogen also means that the FRH is a hazardous material under CFR 49, which regulates interstate transportation. This classification can increase transportation, storage and manufacturing costs. TDA's heater is not classified as a hazardous material under CFR 49.

3. Results and Discussion

We begin this section with fundamental investigations and continue to tests that are more directly related to heater performance. We first discuss mathematical modeling carried out to determine the optimum rate of heat production for the SHIM. Next, we describe the chemical reactions involved in each of the two heater materials selected in Phase I, with the contribution of each reaction. We then discuss the methodology used in calorimetry and heater testing, and tests of heaters for the SHIM, SHGR, and MRE. Last, we describe methods used to prepare heaters, both as pads and as extrudates, and tests of shelf stability.

3.1. Mathematical Modeling

TDA developed a computer spreadsheet model that predicts the time-temperature profile of each component in the Self-Heating Individual Meal (SHIM). The model divides the food into 10 nodes, with the temperatures being calculated at each node. The average food temperature is thus the average of the temperatures at the ten nodes. Thermal conductivity and density of the food have been taken as the average values of pork over the temperature range of interest (40-212°F), based on the methods described by Toledo (1991).

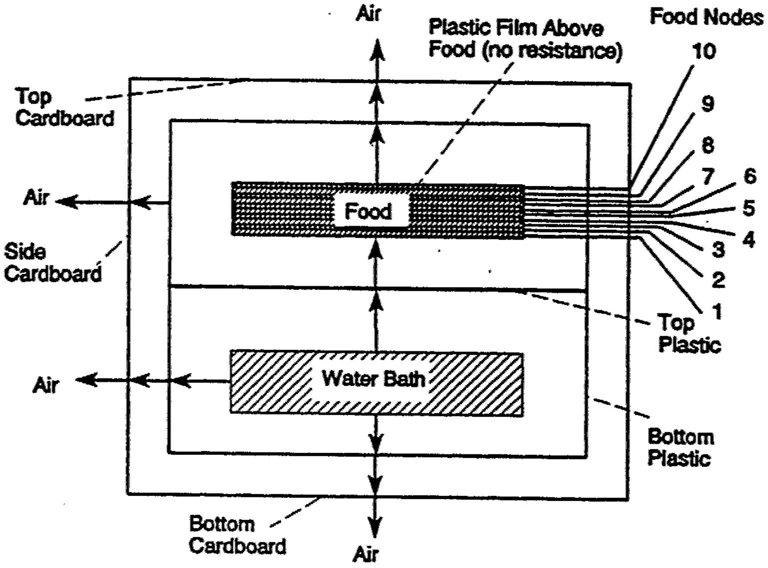


Figure 3.1 Schematic of self-heating ration assembly (exploded view).

Figure 3.1 presents a schematic of the mathematical model. The objectives of this model are to identify the quantity of heat required to operate at all design conditions and to optimize the heater design. The model requires as input a value or series of values for the heat generation rate. We developed an ideal heat generation profile for an initial temperature of 40°F, which heats the food to the design temperature of 140°F within 10 minutes (based on the food's average temperature). Another constraint is the need to avoid producing appreciable amounts of steam, which both wastes energy and could burn the fingers of users. A third constraint is to thaw all of the food in the coldest conditions, -25°F. The model used a heat generation curve that produced 115 Btu, or 29,000 cal, and assumed that 50 g of water was used to activate the heater (Figure 3.2).

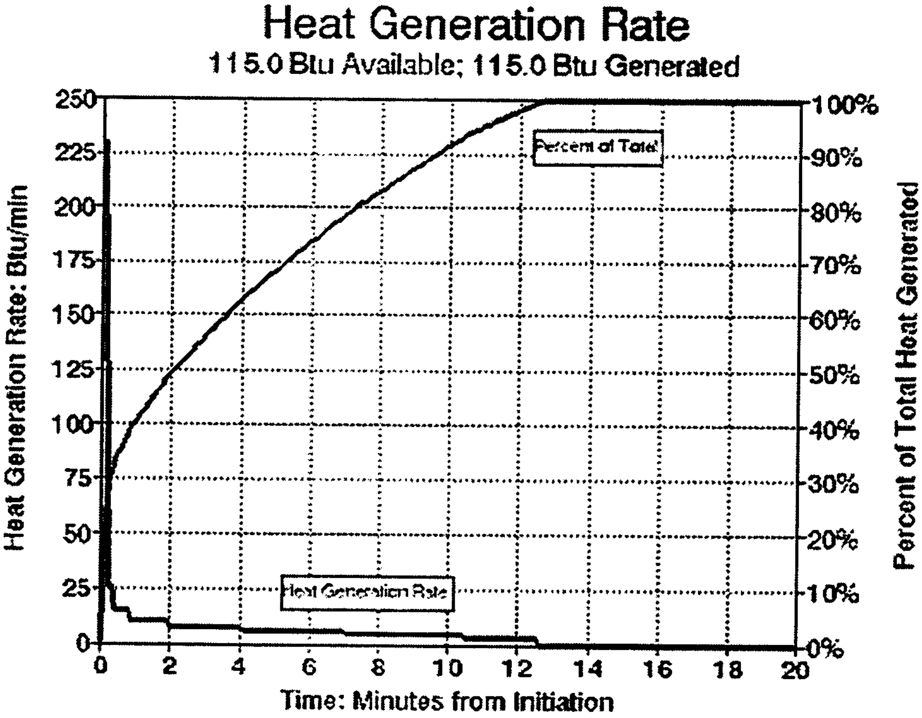


Figure 3.2 "Ideal" heat generation curve for 0.11 lb (50 g) of reactants.

Figure 3.3 shows the calculated time-temperature profiles for the base case, heating from an initial temperature of 40°F. Figure 3.4 and Figure 3.5 show the corresponding curves for initial temperatures of 110°F and -25°F, respectively. The results for the 95°F and 17°F (35°C and -8°C) cases are similar and are not limiting conditions. The overall conclusion from the modeling study was that, for the SHIM, heating times of 10 to 12 minutes are feasible, and the heater should be designed to produce heat no faster than the rate indicated by the model. Heat produced at a faster rate cannot be transferred to the food and is lost (for example, as steam). The result will be different for other meals (such as the MRE) that can be heated at different rates, but the same principles apply.

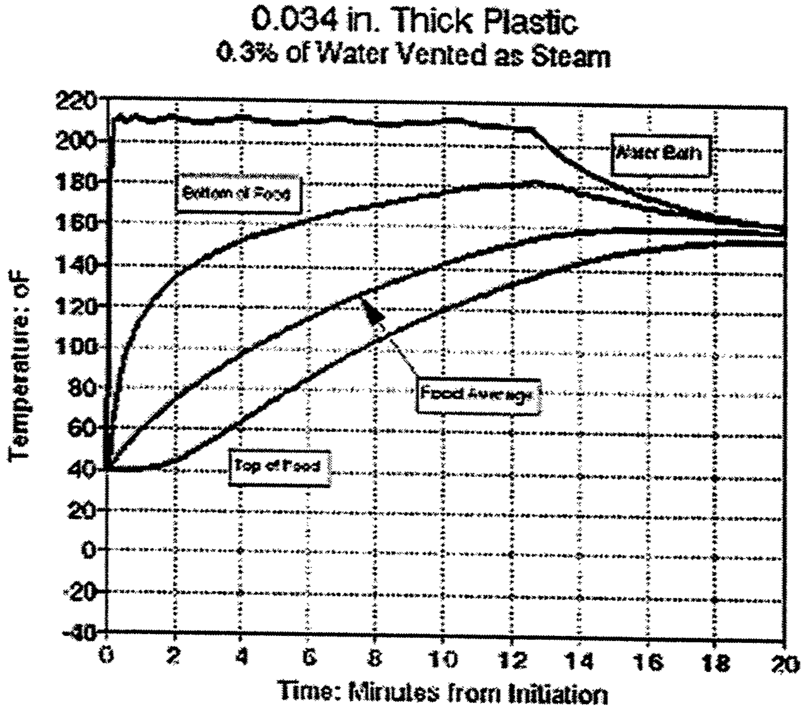


Figure 3.3 Time-temperature profiles for water bath and various sections of food; 40°F initial temperature.

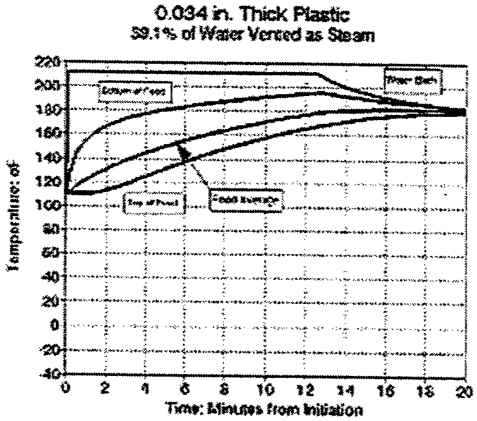


Figure 3.4 Time-temperature profiles for water bath and various sections of food; 110°F initial temperature.

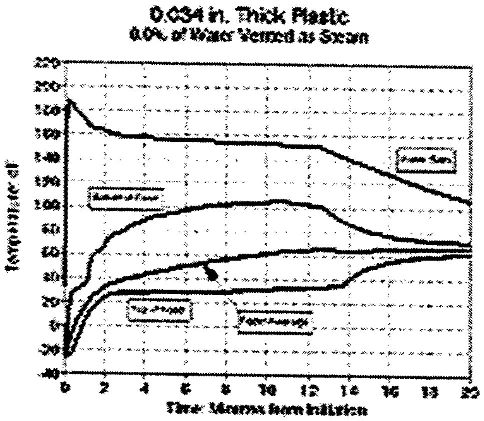


Figure 3.5 Time-temperature profiles for water bath and various sections of food; -25°F initial temperature.

3.2. Heat Production in CaO/P_2O_5 and $AlCl_3/CaO$

Reactions of P_2O_5, and CaO with H_2O

We considered this reaction in more detail, in order to better understand our previous results. Phosphoric acid dissociates in three steps as shown below:

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	$K_1 = 2.3 \times 10^{-2}$	pK = 1.64
$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$	$K_2 = 7.5 \times 10^{-3}$	pK = 2.12
$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$	$K_3 = 6.23 \times 10^{-6}$	pK = 7.21

These ions could participate in the reaction with $Ca(OH)_2$.

The following equations describe reactions that may occur in a heater using P_2O_5 and CaO and their associated heat production (here and below, the subscripts (s), (l), and (aq) denote solid, liquid, and aqueous solution, respectively, while ΔH denotes reaction enthalpy):

Hydration of the acidic anhydride:

$$P_2O_{5(s)} + 3H_2O_{(l)} \rightarrow 2H_3PO_{4(aq)} \qquad \Delta H = -55.7 \text{ kcal/mole } P_2O_{5(aq)} \quad (1)$$

Hydration of the basic anhydride:

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \qquad \Delta H = -15.6 \text{ kcal/mole } CaO_{(s)} \quad (2)$$

The following neutralization reactions are possible:

$$2H_3PO_{4(aq)} + 3Ca(OH)_{2(s)} \rightarrow Ca_3(PO_4)_{2(s)} + 6H_2O_{(l)} \Delta H = -77.1 \text{ kcal/mole } Ca_3(PO_4)_{2(s)} \quad (3)$$

$$H_3PO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow CaHPO_4 \bullet 2H_2O_{(s)} \Delta H = -32.8 \text{ kcal/mole } CaHPO_4 \bullet 2H_2O_{(s)} \quad (4)$$

Therefore, the following overall reactions are possible:

$$P_2O_{5(s)} + 3CaO_{(s)} \rightarrow Ca_3(PO_4)_{2(s)} \qquad \Delta H = -179.6 \text{ kcal/mole } Ca_3PO_{4(s)} \quad (5)$$

$$P_2O_{5(s)} + 2CaO_{(s)} + 5H_2O_{(l)} \rightarrow 2CaHPO_4 \bullet 2H_2O_{(s)}$$
$$\Delta H = -152.4 \text{ kcal/2 moles } CaHPO_4 \bullet 2H_2O_{(s)} \quad (6)$$

When the process follows the course shown by reaction (5), the individual reaction contributions are as shown in Table 3.1. When the process follows the course shown by reaction (6), the individual reaction contributions are as shown in Table 3.2. As the two tables above make clear, all three of the component reactions (hydration of acidic anhydride, hydration of basic anhydride, and neutralization) make substantial contributions to the overall heat production. The exact nature of the neutralization reaction (i.e., reaction (5), (6), related reactions, or some combination thereof) does not greatly affect the overall heat production as a function of the weight of reactants.

Table 3.1 Heat contributions of different steps when $Ca_3(PO_4)_2$ is the product.

Reaction	ΔH, kcal/mole	% of total
(1) 2 moles $H_3PO_{4(aq)}$ formed	55.7	31.0
(2) 3 moles $Ca(OH)_{2(s)}$ formed	46.8	26.0
(3) 1 mole $Ca_3(PO_4)_{2(s)}$ formed	77.1	43.0
(5) overall reaction	179.6	100.0
Heat production of stoichiometric reaction: 1043 btu/lb		

The formation of a hydrate, such as $CaHPO_4 \bullet 2H_2O$, has two advantages. First, the water used for activation is taken up by the heater formulation, yielding a final product that is solid rather than liquid. A solid product is cleaner and more convenient to dispose, and has minimal environmental impact. A second advantage of water present in the used heater in the form a hydrate is that, in the event that the heater reaches an excessive temperature, the water of hydration will be driven off, producing a cooling effect. For example, if a portable heater prepared by other methods is activated in the absence of a suitable heat sink, the adiabatic temperature can be high enough to present a fire hazard, or to cause undesirable fumes or odors from the heater or packaging material.

Table 3.2 Heat contributions of different steps when Ca_3HPO_4 is the product.

Reaction	ΔH, kcal/mole	% of total
(1) 2 moles $H_3PO_{4(aq)}$ formed	55.7	36.5
(2) 2 moles $Ca(OH)_{2(s)}$ formed	31.2	20.5
(4) 2 moles $CaHPO_4 \bullet 2H_2O_{(s)}$ formed	65.6	43.0
(6) overall reaction	152.5	100.0
Heat production of stoichiometric reaction: 1080 btu/lb		

Reaction of $AlCl_3$ with CaO

The following reactions occur in a heater using $AlCl_3$ and CaO:

Hydration of the acidic salt:

$AlCl_{3(s)} + 6H_20 \rightarrow AlCl_3{\bullet}6H_2O_{(s)}$ $\Delta H = -78.35$ kcal/mole $AlCl_{3(aq)}$ (7)

Hydration of the basic anhydride:

$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)}$ $\Delta H = -15.6$ kcal/mole $CaO_{(s)}$ (2)

Neutralization:

$2\ AlCl_{3(aq)} + 3\ Ca(OH)_{2(s)} \rightarrow 3\ CaCl_{2(aq)} + 2\ Al(OH)_{3(s)}$

$\Delta H = -42.4$ kcal/3 mole $CaCl_{2(aq)}$ (8)

The overall reaction is as follows:

$2\ AlCl_{3(s)} + 3\ CaO_{(s)} + 3\ H_2O_{(l)} \rightarrow 3\ CaCl_{2(aq)} + 2\ Al(OH)_{3(s)}$

$\Delta H = -245.8$ kcal/3 moles $CaCl_{2(aq)}$ (9)

If the process follows the course shown by reaction (5), the individual reaction contributions are as shown in Table 3.3.

Table 3.3 Heat contributions of different steps in the reaction of $AlCl_3$ and CaO.

Reaction	ΔH, kcal/mole	% of total
(7) 2 moles $AlCl_{3(aq)}$ formed	156.7	63.7
(2) 3 moles CaO formed	46.8	19.0
(8) 3 moles $CaCl_{2(aq)}$ formed	42.4	17.3
(9) overall reaction	245.9	100.0
Heat production of stoichiometric reaction: 1017 Btu/lb.		

3.3. Test Methods

3.3.1. Sub-Scale Testing

In the course of this project, TDA used several test methods to evaluate heaters under development. The Parr 1455 Solution Calorimeter was used in Phase I and in the early stages of Phase II to measure heat output of different materials when they were completely hydrated. In the first part of Phase II we constructed a microscale calorimeter, which could measure the amount of heat evolved when water was introduced to small samples (1-5 g) of heater compositions. This calorimeter consisted of two cylindrical blocks of copper; the lower block held the material to be tested in a glass cup, and the upper block had six vertical holes, through which water could be added and gas could escape. The two blocks were in good thermal contact. This microscale calorimeter was constructed so that any steam produced would be condensed in the upper copper block of the calorimeter, and so the heat output could be accurately measured by a thermocouple placed a well in the upper copper block.

TDA also constructed a subscale (one-sixth scale) calorimeter, which could measure the heat output from samples of 5-10 g size. A schematic of this subscale calorimeter is shown in Figure 3.6. This calorimeter provided a quantitative measure of heat generation, sacrificing some precision for an arrangement much closer to the final design.

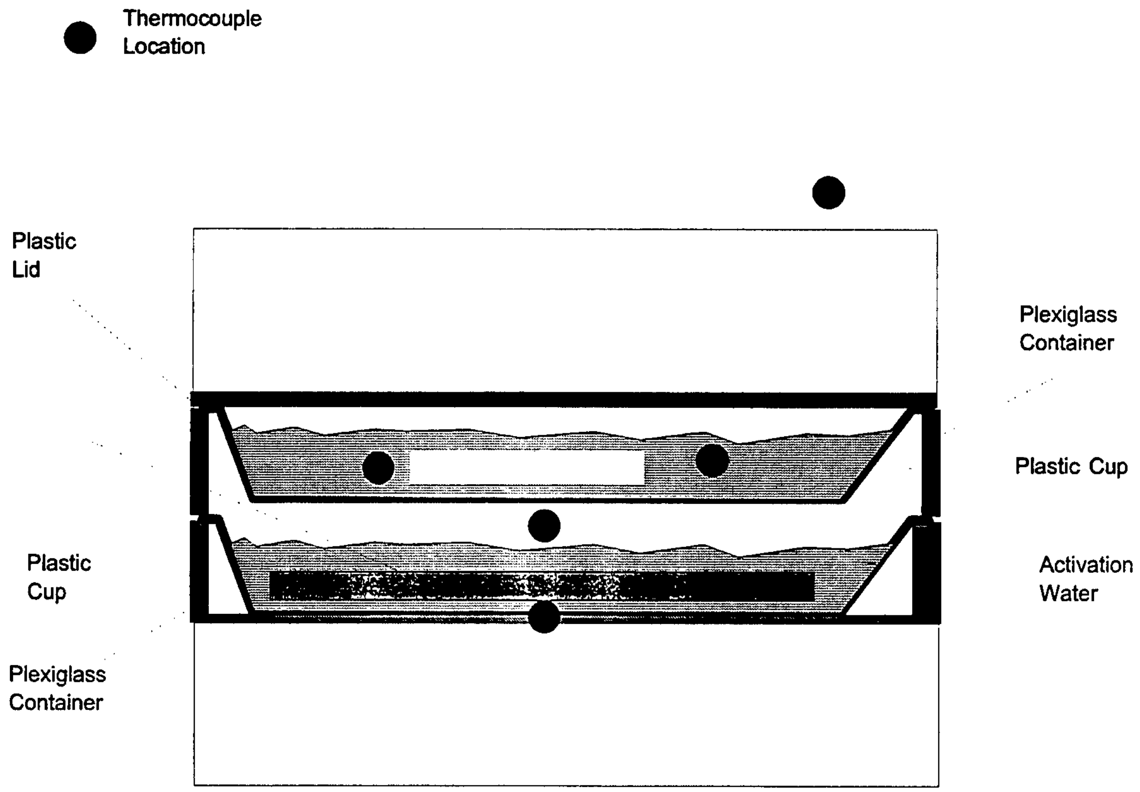
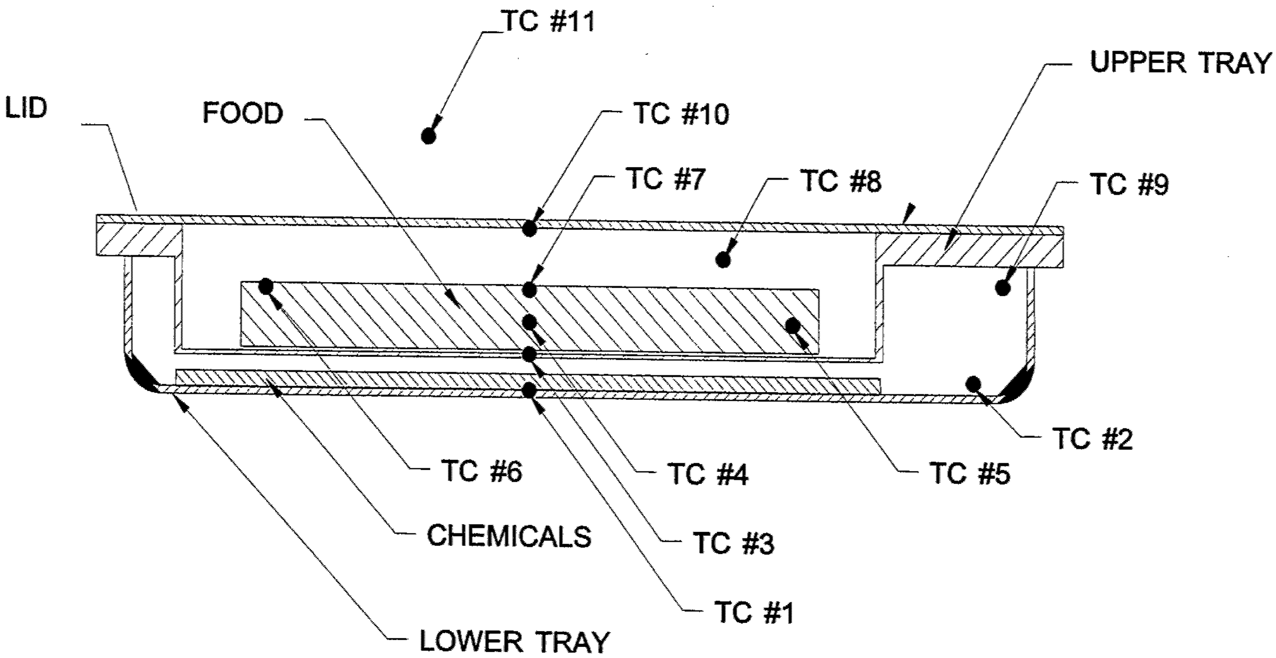


Figure 3.6 Schematic of sub-scale calorimeter.

3.3.2. Full Scale Testing of SHIM

TDA constructed a test rig utilizing a hydrated bentonite (clay) to simulate food, and whose dimensions were identical to those of the proposed Self-Heating Individual Meal. A schematic of this ration calorimeter is shown in Figure 3.7. This calorimeter used multiple thermocouples to measure the time-temperature profiles at different points in the simulated food. For this and other experiments, the time-temperature data were recorded on a computer disk for later display and analysis. A comparison of the FRH and TDA's pad heater in the ration calorimeter is shown in Figure 3.8.



TC #	DESCRIPTION
1	BETWEEN LOWER TRAY AND CHEMICALS
2	IN LOWER TRAY WATER
3	BETWEEN UPPER TRAY AND FOOD
4	IN THE MIDDLE OF THE FOOD
5	IN THE EDGE OF THE FOOD
6	ON THE TOP EDGE OF THE FOOD
7	ON THE TOP CENTER OF THE FOOD
8	IN THE UPPER TRAY AIR
9	IN THE LOWER TRAY STEAM
10	ON THE OUTSIDE LID SURFACE
11	SURROUNDING AIR

Figure 3.7 Schematic of Ration Calorimeter T/C locations.

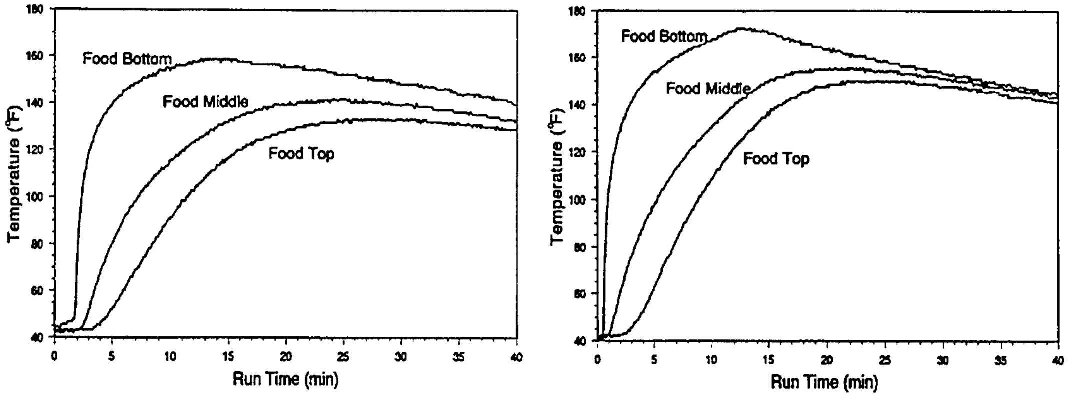


Figure 3.8 Comparison of the FRH (left) and TDA's pad heater (right) in the ration calorimeter.

3.3.3. Full Scale Testing of MRE Heaters

Both heaters for the Meal, Ready-to-Eat were tested according to the methods specified in MIL-R-44398A. The heater was placed in a plastic tray 7.5 inches long, 4.75 inches wide, and 1.75 inches deep. An MRE pouch was filled with 8 ounces of water, at a temperature between 35°F and 45°F, and fitted internally with a thermocouple. This pouch was placed on the heater, and a quantity of water (usually 30 to 60 g) at a temperature below 72°F was added. A lid was placed on the tray and the time and temperature rise recorded for at least 15 minutes. In these tests, we considered a temperature rise of 100°F acceptable, as specified in MIL-R-44398A. In addition, we tested MRE heaters by activating them in the HDPE bag that is normally supplied with the FRH.

3.4. Development of Heaters for the Self-Heating Individual Meal

In this section we describe production of heaters for the Self-Heating Individual Meal (SHIM). Early work investigated heaters formed by pressing the ingredients into pads, similar in dimension to the FRH pad. To form the pads, inert liquids were mixed with the CaO and P_2O_5 and the mixture pressed in a mold. The specific inert liquids were the object of extensive investigation. TDA found that a surface-active agent (surfactant), in combination with oils, waxes, or polymers, was effective in forming the heater materials into pads, and in controlling the reaction rate. For pad heaters, one effective arrangement consisted of two compositions that produced heat at different rates: the bottom layer produced heat rapidly, and the top layer produced heat more slowly. We also demonstrated that a single-layer pad, which would be simpler to produce, was effective with the SHIM. Later work investigated heater configurations in which the active materials were in the form of aggregates contained in a porous scrim, like a tea bag. The latter arrangement would avoid the pressing step.

3.4.1. Pad Heaters for the Self-Heating Individual Meal

For the pad heaters, TDA used a Stenhoj 110 ton press capable of pressing a full size (3.5"x5") ration heater in a single step. The tests described here used either Paranox or Brij 30 as the surfactant, with varying amounts of oil and wax. Results described later (in the section on heaters for MREs) showed superior performance from the Acrafos surfactant, and we believe that the SHIM results could be improved upon with a different formulation. However, the project focus subsequently shifted to the MRE, and the results reported in this section for the SHIM were not repeated with the newer formulations.

<u>One or Two Layer Pad Heaters</u>

Early results had shown that it was difficult to obtain a satisfactory heating profile with a single layer heater. The material tended to react too rapidly (wasting heat that was vented as steam) or too slowly. Observations showed that the primary difficulty was initiating the reaction: once the heater material was at the temperature of boiling water, the reactions generally proceeded well. Therefore we developed a heater with two layers, one that reacted rapidly to start the reaction, and one that reacted more slowly, producing

heat over the required period. A schematic of the two layer pad design is shown in Figure 3.9. These heaters were produced by placing one layer of scrim in the die, adding one composition, leveling the materials, adding a second layer of scrim, pressing to 10,000 psi, adding the second formulation and the top layer of scrim, and pressing again.

Use of Channels in Pad Heaters

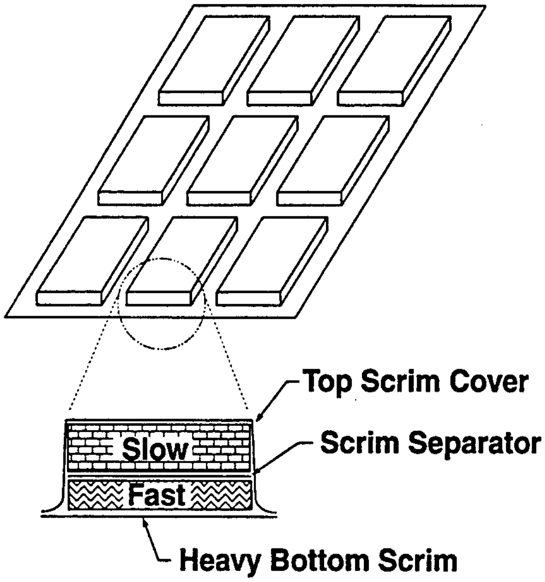


Figure 3.9 Two layer pad, in nine squares.

A heater consisting of a single solid piece does not produce all available heat because water does not reach all parts of the pad to activate the heater. Because the heater is in direct contact with the food tray, water can only enter the pad through its edges. This problem could be solved by arranging the pad into squares with water channels between them. Each heater square must be secured firmly in its proper position so that it will not shift during subsequent shipping and handling. Such a pad could be molded into the appropriate number of squares during the actual pressing step. A nine-square heater is illustrated in Figure 3.9. Such heaters could be produced as sheets of squares with the reactant mixtures contained entirely within the polyethylene scrims. The squares would be integrally bound together with the bottom (thicker) scrim sheet during pressing. In addition to providing superior reactant containment, this type of design is quite flexible and could easily be adapted to different types of SHIM designs by simply adjusting the number or size of the squares.

Full scale testing was performed to determine the optimum number of squares to use in the heater pad. During this investigation, it was discovered that the heater performance is closely related to the channel spacing between the squares as well as the number of squares. Earlier testing had revealed that pads composed of four squares were unsatisfactory no matter what size of water channels were used. This problem was traced to the inability of water to adequately penetrate into the interior area of the squares when the heater pad was pressed securely between the bottom tray and food tray of the SHIM. When pressed between the trays, nine squares was the minimum number found to produce acceptable results. Additional tests were performed, with squares ranging in size from 1.16"x1.67" (the 9 square pad) to 0.7"x0.9" (a 20 square pad). For squares in this size range tested in the SHIM, the performance is coupled to both the number of squares and the spacing between them.

Figure 3.10 shows two runs for pads with 20 squares. The narrow channel heater (a 70 g heater using 40 g of water) had square spacings of approximately 1/16" inch. Because of the narrow spacing, the simulated food was heated only to 150°F instead of the normal 160°F. The second test illustrates a 20 square heater with wider, 3/16" channels. In order to accommodate the wider channels, the heater was trimmed from 70 to 59 g and the run was completed using 34 g of water. (In each run the amount of water used was 57% of the pad weight.) Note that in this second run, the final food temperature reached a respectable 140°F even though the pad contained 15% less heat (89.7 vs. 105.5 Btu). This demonstrates how important it is to maintain a temperature profile that follows closely the ideal heating curve as previously calculated by TDA. The composition of the heaters is shown in Table 3.4.

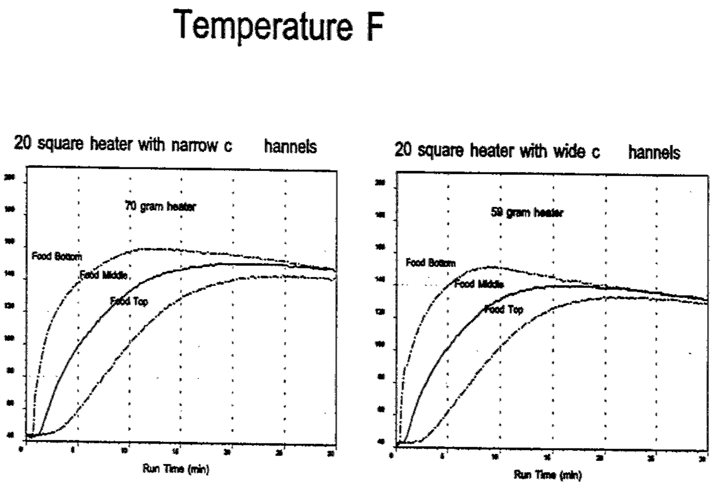


Figure 3.10 Effect of channel width on performance.

For this particular reactant formulation, the wider water channels provide the necessary water access and heat transfer rates required to obtain optimal heating. It is also worth noting that this reduced weight pad was capable of heating the food to 140°F (ΔT of 100°F) which meets the target for the current SHIM. The conclusion from this test is that the wider channel was

Table 3.4 Pad heater, pressed at 12,500 psi.

Component	Fast layer (45% of pad)	Slow layer (55% of pad)
CaO	43.75%	43.75%
P_2O_5	43.75%	43.75%
Brij 30 surfactant	1.67%	6.25%
Mineral oil	8.33%	4.37%
Paraffin wax	--	1.88%
Polyethylene beads	2.50%	--

significantly more effective in realizing the heating potential available in a pad.

From these experiments we have concluded that heater squares of approximately 3/4" to 1-1/2" square (or rectangular) will perform well when used in conjunction with water channels 3/16-1/4" in width and waters amounts that are about 50% of the pad weight. These experiments also indicate that smaller squares may be beneficial when using low water levels. With smaller squares, all parts of the heater pad can be evenly exposed to the water before it becomes permanently hydrated into the reactants.

Later experiments showed that an arrangement of three strips worked as well as nine squares, and would potentially be simpler to produce. We believe that the critical feature is that no part of the heater be more than a certain distance from the outside (i.e., the part of the heater that has access to water). This effect can be accomplished with multiple squares or with thin strips.

3.4.2. Pouch Heaters for the Self-Heating Individual Meal

To simplify production and improve performance, TDA tested other configurations other than the pad heater. We found that a scrim pouch containing heater compositions as loose agglomerates, powders, or a mixture of pad and powder and pad, was effective for heating the SHIM. Such an arrangement would be an alternative to the two-layer pad, and poses another potential means to simplify production. The scrim material could also be a porous weave such as tea bag paper, and we sometimes referred to heaters of this type as tea bag heaters. The time-temperature profiles for a tea bag heater are shown in Figure 3.11. This particular composition consisted of three components: bare CaO + P2O5, a powder of 10% oil and 90% $CaO + P_2O_5$), and a pressed pad of 10% Paranox, oil, and wax and 90% $CaO + P_2O_5$.

The most important conclusions from these tests with the SHIM are that either pads or pouch heaters can be effective. The pad heater requires that provision be made for access of water to the heater, so the heater pad should be in the form of squares or strips, with channels of about ¼ inch width to admit water.

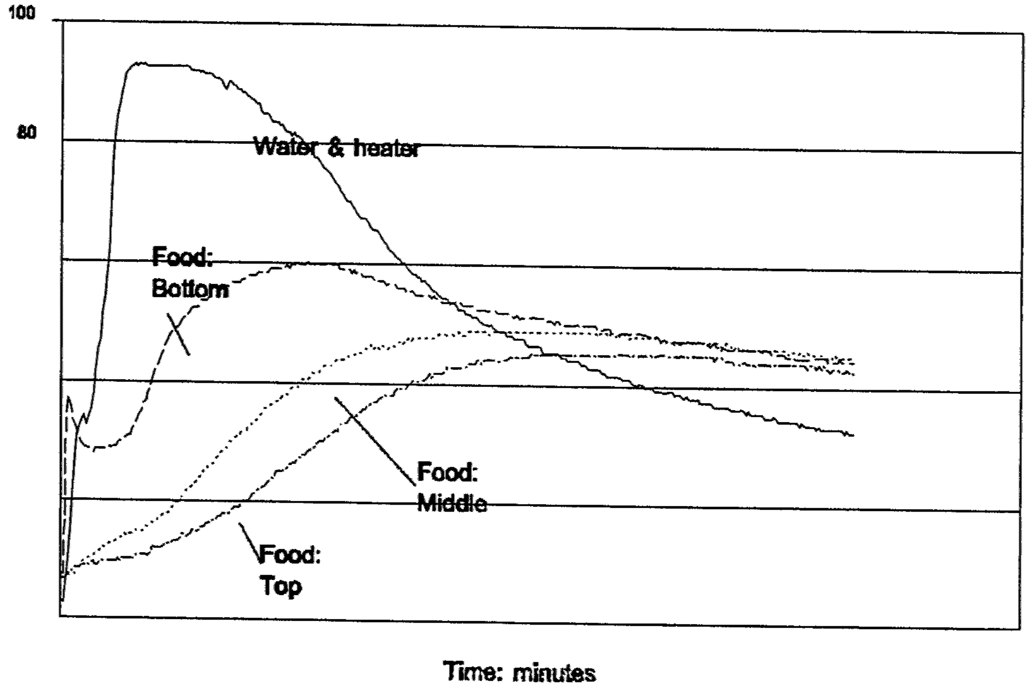


Figure 3.11 Test of pouch heater in ration calorimeter; data from thermocouples

3.5. Heaters for the Self-Heating Group Ration

TDA tested both the FRH and the new heat source in the SHGR tray supplied by Natick, using a sealed bag containing 6.6 pounds of water to simulate the food. TDA's tests used seven of the FRH pads, without the pasteboard sleeves, weighing a total of 140g. To test the new heat source, we used strips of dimensions similar to those used in the SHIM, 5.0 x 0.7 x 0.23 inch, for a total weight of 480 g. (In the SHIM test TDA's heater weighed 70 g, compared to 20 g for the FRH pad without sleeve; the weights used in the SHGR test kept the weight ratio constant.) The results are shown in Figure 3.12 and Figure 3.13. The new heat source raises the temperature of the food bag from room temperature to 145°F in ten minutes and sustains heating for over thirty minutes. In these preliminary SHGR tests, we found that the new heat source performs better if the food bag is not resting directly on the heater surface at the initiation of the reaction.

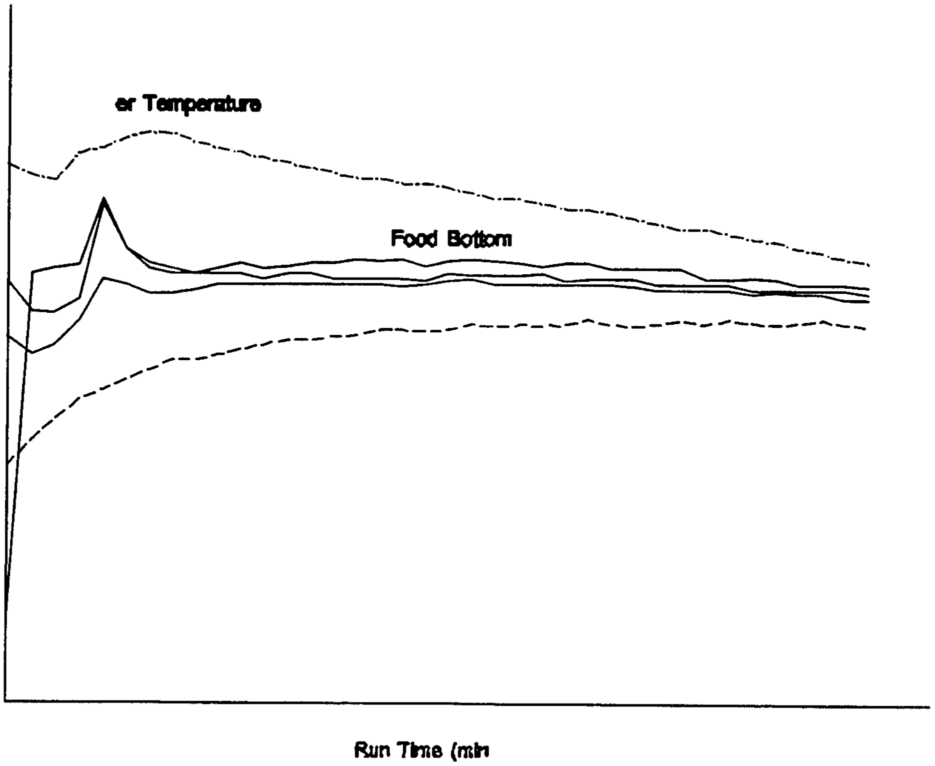


Figure 3.12 Temperature trajectories for the SHGR heated by the FRH.

The food bag weight appears to slow water uptake into the heater pad and in some cases full heat output is not observed. For best performance with this heater configuration, the food bag should be supported above the heater. This could be done with spacers pressed into the bottom of the thermoformed tray, similar to those that are used in the current tray to allow water to access the bottom of the pad. The objective of these SHGR tests was to assess the effectiveness of the new heater formula. Significant additional testing would be required to define the optimal heater formulation and design, and to assure proper and safe performance in the range of expected conditions.

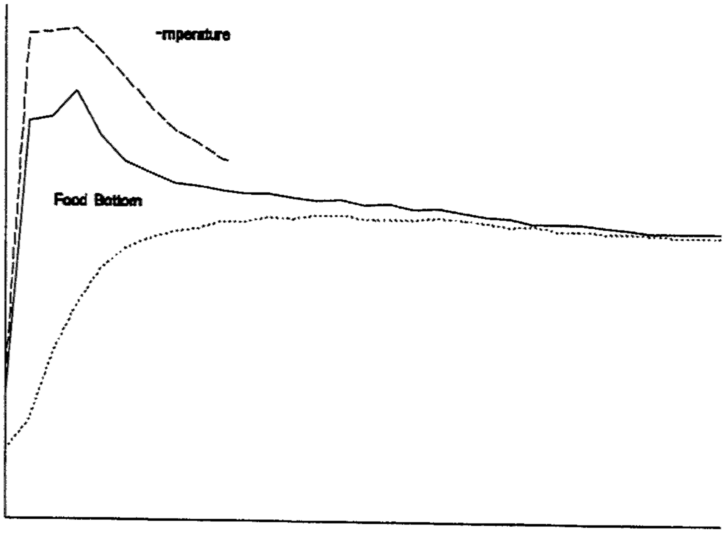


Figure 3.13 Temperature trajectories for the SHGR heated by TDA's heat source.

3.6. Heaters for the Meal, Ready-to-Eat (MRE)

A fundamental difference between heaters used for the SHIM and those for the MRE is that the SHIM heaters must be flat pads. Because they are packaged with the food tray, the SHIM heaters can have a top and bottom that differ in composition and rate of heat production. As described above, TDA prepared such two-layer heaters and demonstrated their effectiveness. Because the MRE and heater are packed separately, and combined for use, the heater must be usable in either orientation. Therefore, TDA developed a single formulation heater for the MRE.

Additionally, we found that the single-formulation heater could be produced not only as a flat pad but also as spherical agglomerates or cylindrical pellets. (Loose powders were also investigated but did not produce the desired sustained heat release. The agglomerates or pellets could be contained in a porous scrim bag, an approach that was inherently more amenable to continuous production than the flat pad, and should be lower in cost. TDA developed two methods to produce particles for the MRE heaters: (1) agglomeration, and (2) extrusion/pelletizing. These methods are discussed in separate subsections below.

In both cases P_2O_5 and CaO were mixed in 1:1 weight ratios. This ratio gave a slight stoichiometric excess of CaO, which was intended to assure that the final pH was neutral or slightly basic. The particular inert materials used were critical to the result. TDA investigated a number of different surfactants, the most successful being Brij 30 and Actrafos 216. We also tested compositions that included either mineral oil, paraffin wax, or both.

3.6.1. Heaters Prepared by Agglomeration

In preparing heater materials, we noticed that on mixing in the surfactant and other inert ingredients, the powder tended to form aggregates or agglomerates. As the heater material was being agitated by the mixer, it formed into rough spheres of a range of sizes. Some of these agglomerates had good mechanical stability, with dimensions on the order of ⅛ inch. To test the heat production of these materials, we used a set of standard sieves to separate pellets of different sizes. These agglomerated pellets worked to heat the MRE.

If we could prepare the heater materials by this process on a large scale it should be even cheaper than extrusion. The equipment would consist of a disc pelletizer (essentially a rotating inclined disc), such as is used to prepare material like fertilizer pellets. We found that the larger pellets reacted somewhat slower than the smaller ones, as would be expected because of the higher surface/volume ratio of the smaller pellets. Temperature curves for two different size pellets are shown in Figure 3.14, and the temperature data are tabulated in Table 3.5 and Table 3.6. These pellets were prepared with the surfactant Actrafos, which had been identified from screening experiments as having the necessary solubility in mineral oil and an ability to slow the rate of heat production.

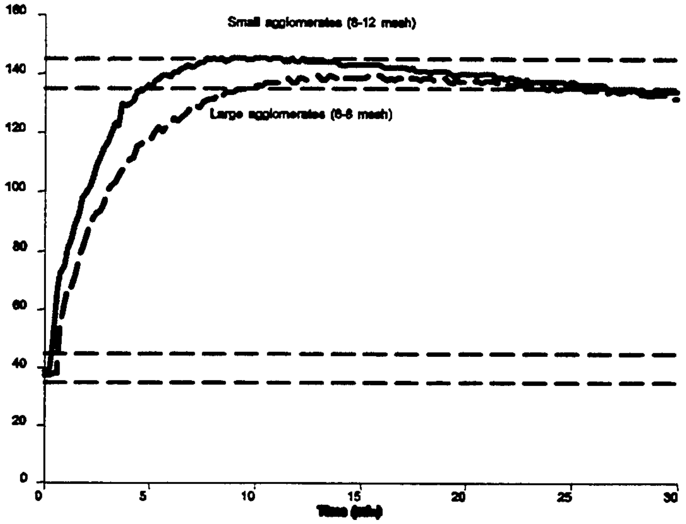


Figure 3.14 Agglomerates with Actrafos, two different sizes.

The major problem with agglomeration was that not all of the material was agglomerated, with a substantial fraction remaining as unusable fines. In production, of course, essentially all of the material must be used. Analysis showed that the largest sized agglomerates contained the greatest proportion of inerts, with the amounts decreasing with decreasing sieve mesh size. Although the difference in the proportion of inerts between the largest and smallest diameter agglomerates was not dramatic, we know from previous work that small differences in some inerts can make a large difference in activity. Therefore, we tested different mixing and processing techniques to increase the uniformity of distribution of the inerts. We had previously been adding all of the CaO/P_2O_5 into the inert liquids and mixing with a whisk-type mixer. Simply by adding the CaO/P_2O_5 slowly to the inerts, we obtained a higher yield in +12-6 agglomerates (73+% vs. 62%). This result suggests that the inerts are more evenly distributed with the slower addition. With quantities of several hundred grams, the addition was complete in less than five minutes. Further tests would be required to determine the rate of addition appropriate for larger quantities, and whether this rate would be acceptable in large-scale production.

TDA investigated this process in a series of tests using a 16-inch disk pelletizer. The disk angle and speed of rotation were varied, as was the point at which the material was introduced. Although materials of the appropriate particle size performed very well, the yields of materials in the necessary size range remained too low to be of interest. We abandoned this method in favor of extrusion, as discussed below.

Table 3.5 Agglomerates with Actrafos (6-8 mesh).

Del(T) at 8 Min.	94°F
Del(T) at 12 Min.	101°F
Del(T) at 15 Min.	101°F
Max. Del(T)	102°F
Time to reach Max. Del(T)	12.93 min

Table 3.6 Agglomerates with Actrafos (8-12 mesh).

Del(T) at 8 Min.	106°F
Del(T) at 12 Min.	105°F
Del(T) at 15 Min.	104°F
Max. Del(T)	106°F
Time to reach Max. Del(T)	7.72 min

3.6.2. Heaters Prepared by Extrusion

The tests with agglomerates described above had demonstrated that heater particles with dimensions on the order of ⅛ inch performed well. Extrusion is an inexpensive processing technique, and could be used to produce heater particles in a continuous process. The challenge for us was to find a formulation that extruded well and then produced heat at the necessary rate. Many formulations we tested extruded well but contained so many inert liquids that they produced heat much too slowly. When the amount of inerts was decreased to improve heating, the formulations would be too dry to extrude and would jam in the extruder. TDA carried out most of the early extrusion tests with a ram extruder, consisting of a 7-inch stainless steel cylinder and piston, with the extrusion orifice in the bottom. The cylinder is 1.0 inch i.d. and rated to 60,000 p.s.i. The orifice through which the material was extruded was constructed of mild steel and was 0.1 to 0.1875 inch in diameter, with most extrusions done at ⅛ (0.125) inch. Pressure was applied to the piston with a 25-ton hydraulic press.

In extrusion of most materials the liquid used is water, and sufficient water is added to facilitate extrusion. If this yields a material too wet for the intended purpose, then the extrudate is dried. Obviously we could not use water, and we also did not pursue the alternative of adding a non-aqueous solvent to facilitate extrusion that could later be removed by evaporation. Any such solvent would necessarily be an organic material, and in addition to cost factors, would introduce a significant fire hazard.

The extruded heater pellets were mechanically the strongest we prepared. Although there was still a relatively narrow range of inert concentrations that gave both facile extrusion and good performance, we were able to show that ⅛-inch extrudates prepared with only Actrafos and mineral oil gave good performance (Figure 3.15).

Previous work with both extrusions and agglomerates has shown that smaller particles produced heat at a faster rate. To increase the range of sizes that could be prepared by extrusion, we tested 0.10-inch extrudates both as-formed and broken up to smaller sizes. The broken extrudates were sieved to two different size ranges.

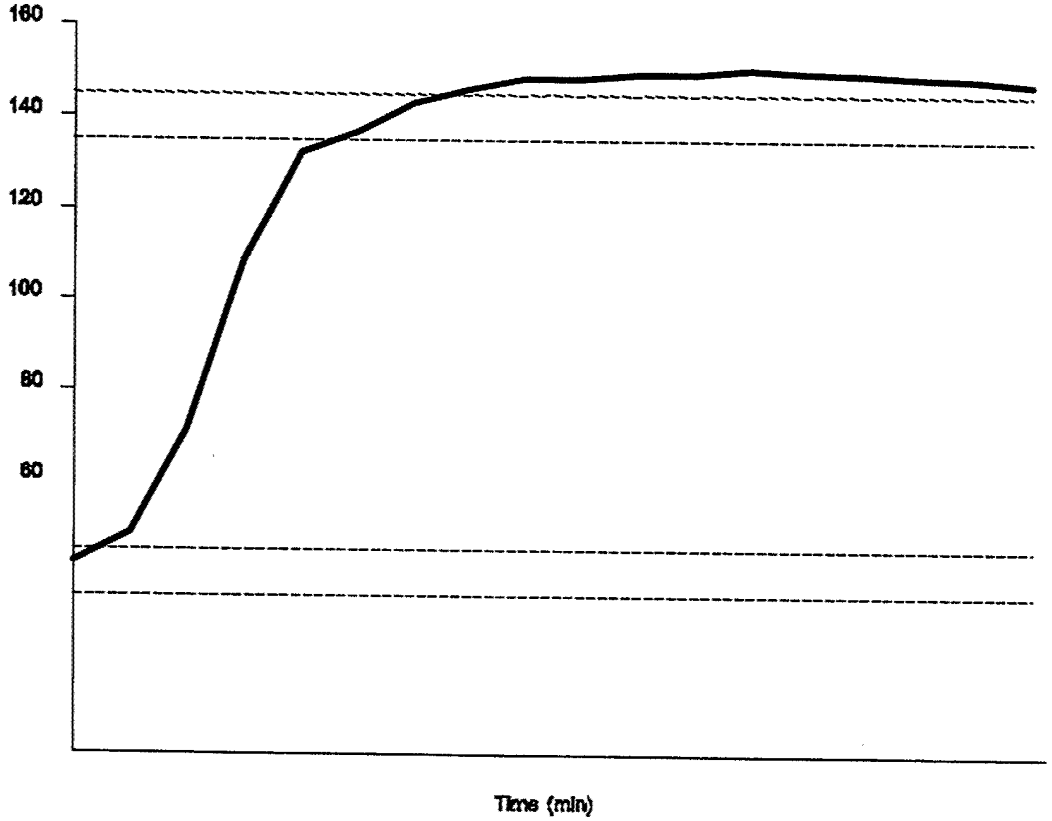


Figure 3.15 Heat production rate of extrudate pellets with MRE (ram extruder, Actrafos surfactant).

As shown in Figure 3.16, the intact extrudates have the slowest rate of heat production, and both of the broken extrudates are faster. (These materials were from an unsuccessful formulation, and none of the materials produced the target amount of heat, but the trend within the three samples nevertheless represents a useful comparison.) By extruding, and then breaking up the extrudates into smaller particles, we can combine the best features of both the agglomerates and extrudates (i.e., high strength with a more controlled reaction and high surface to volume ratio). While adding one step would add to the processing cost, size reduction is a relatively inexpensive process. As later events showed, this step does not appear to be necessary.

3.6.3. Heaters Prepared by Pelletization

Another process for aggregation of solids that has been particularly effective with materials that are too dry to be extruded readily is pellet milling. A screw extruder uses a longer path to form the extrudate, where the pellet mill has a circular die and rollers with a shorter path. A schematic of a pellet mill is shown in Figure 3.17. The shorter path lowers the working pressure for extrusion. This method proved to be the best procedure for preparing extruded heaters, and was used for the 2,000 heaters delivered to Natick for field tests. The pelletizer used was a California Pellet Mill Model CL-3, with a ⅛-inch die. We prepared heaters using Actrafos and oil, varying the amount of inerts. This combination was used because experiments had shown that mineral oil alone was not effective in producing controlled heat release, but that mineral oil with a surfactant was effective. Actrafos was the best of the surfactants tested.

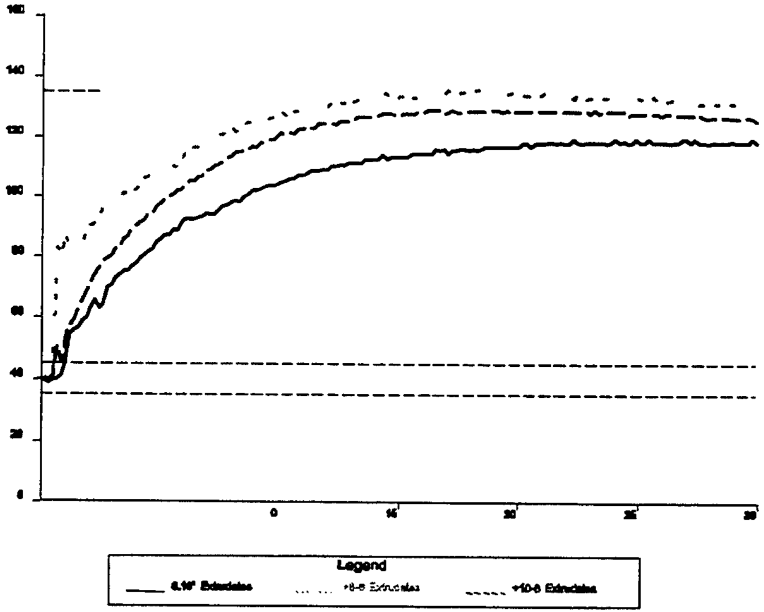


Figure 3.16 Heat production rate, comparing extrusions with broken extrusions of the same composition in two different sizes. Corrected to same starting temperature.

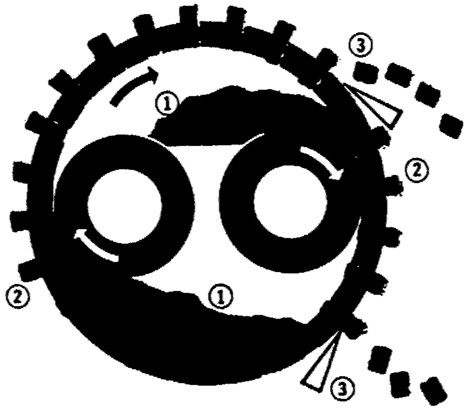


Figure 3.17 Schematic of a pellet mill: as the die and rollers rotate, the powdered feed (1) is extruded through a die (2) and cut to length (3).

We show performance (using the MRE test procedure) for two batches of material processed in the pellet mill, with 15.4% and 13.4% inerts concentration respectively. In these tests the inerts consisted of 26% Actrafos and 74% mineral oil, a ration that had previously shown good performance. Varying the ratio of Acrtrafos and mineral oil would have expanded the number of experiments significantly and was not considered necessary. Both batches were successfully extruded at well below the recommended maximum power draw, indicating that we still have some leeway to reduce inert concentration. More important, while both batches produced pellets that reached the desired temperature change in 12 minutes, the material with lower (13.4%) inerts showed an increased temperature profile, similar strength, and less tendency to stick together, (a problem we had noted with some other formulations). A comparison of the two materials, with different heat treating times/temperatures, is shown in Figure 3.18 and Table 3.7.

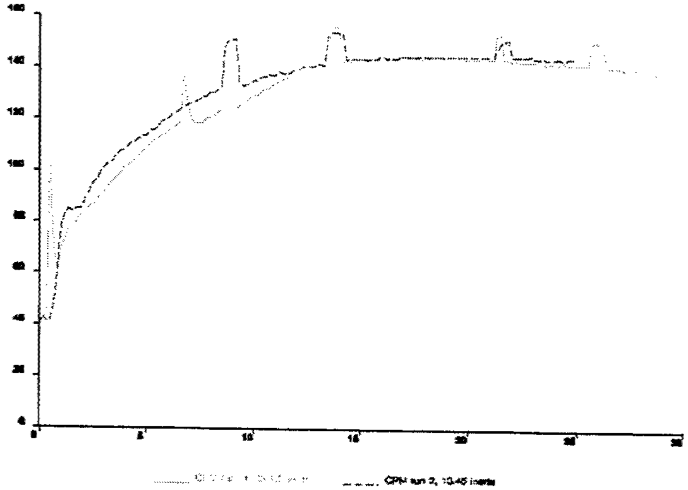


Figure 3.18 Comparison of batch #1 (15.4% inerts) and batch #2 (13.4% inerts).

Use of Compartments in Heater Pouch

Table 3.7 Comparison of batch #1 (15.4% inerts) and batch #2 (13.4% inerts).

Batch/Cut Temp/Time	1 / 3 Unheated	1 / 3 D / 2Hr	2 / 2 Unheated	2 / 2 80C / 3Hr
Del(T)12 (Top)	98.5	99.7	101.2	98.4
Max Del(T) (Bottom)	117.0	113.8	108.3	113.0

Another issue that was addressed in tests was that the scrim bag, containing either extrudates or agglomerates, tended to swell into a round shape when activated, particularly if packed tightly. The MRE pouches have a similar shape, and we thought that some efficiency in heat transfer might be lost by having two convex surfaces. We tested several configurations to see whether an arrangement that produced a flatter or concave surface in the heater would improve heat transfer by increasing the area of contact. The scrim pouch was cut to 7 x 3.5 inch dimensions and heat-sealed to provide a bag that enclosed the heater materials, yet allows water to penetrate. In addition, the heater pouch may easily be divided into sections by heat-sealing an additional seam, e.g. lengthwise through the middle.

These tests used a series of same weight, same lot extrudate heaters with a fixed amount of activation water. The variation came from different containment setups in the scrim bag. By adding channels into the scrim, the pellets were more densely packed into the smaller sections of the various heater pouches, all having the same overall size. (None of these test materials produced the target amount of heat, but the amount of heat produced was sufficient to test the effect of the different configurations.) By being more densely packed, the pellets would have a more restricted movement and therefore be less susceptible to shifting during transport. A bag with no channels was run first to get a baseline measurement. Following this we tested several heaters using two or three strips of material (sealed in the scrim) to compare temperature profiles with the original arrangement. However, we added more material to the outside strips in the three-strip setup in an effort to make the heater conform to the shape of the MRE pouch. These pouches were 7 inches long; all but one were 3.5 inches wide; the exception was 4 inches wide (listed as "2 strips, wider" in the figure).

As shown in Figure 3.19, the three configurations were essentially identical in their heat transfer. We conclude from these experiments that the heaters should have two channels running lengthwise, with equal amounts of heater material in both, to decrease the possibility that the heater material will shift to one side or another during transport. A three-channel heater could be used but did not appear to offer any advantage. Later tests showed that when the heater and MRE were dropped into a pouch together, the heater material tended to settle at the bottom of the pouch. In the 2,000 heaters that were supplied to Natick, we therefore added an additional seam across the middle (at right angles to the first seam), so the heater was divided into four equal compartments.

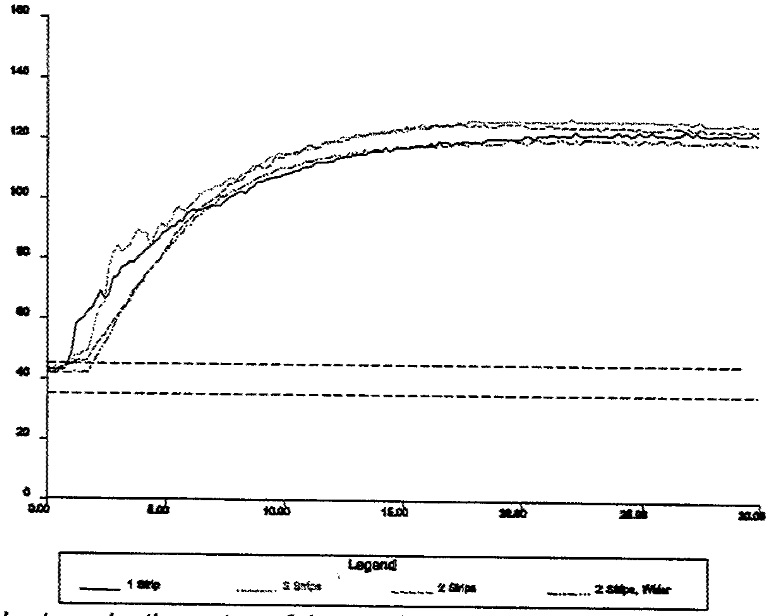


Figure 3.19 Heat production rates of three different heater configurations.

Tests of Heat Treatment to Stabilize Heaters

Experiments showed that the activity of agglomerated or extruded heaters decreased over time. Tests of as-prepared heaters would show good heat production, where heaters stored in a dry environment for several weeks would show a significant decline in performance. We found that heating for a short period of time to a temperature of 60°C to 120°C would stabilize performance. Both heating and aging are accompanied by a color change of the heater materials from light gray to dark brown. We believe that this change results from a chemical reaction of the inert ingredients. Though the mechanism of this reaction is not known, the Product Regulatory Assessment did not identify it as a hazard.

The first set of experiments entailed heating the agglomerates at 60°C for 3 hours with a varied mixture of agglomerate sizes. One set was heated on day two after production, the other set was heated on day 14 after production. These results are summarized in Figure 3.20 and Table 3.8 below. The heating produces a small decrease in performance for this formulation, but stabilizes heat output to avoid the slow decrease over time that had been a problem before. These tests used the MRE test pouches supplied by Natick to TDA, which have a type T thermocouple sealed into the pouch. The position of the thermocouple can vary, so all measurements are taken from the top of the MRE bag (which should be the coldest region) to assure an accurate comparison between test heaters. Humps in

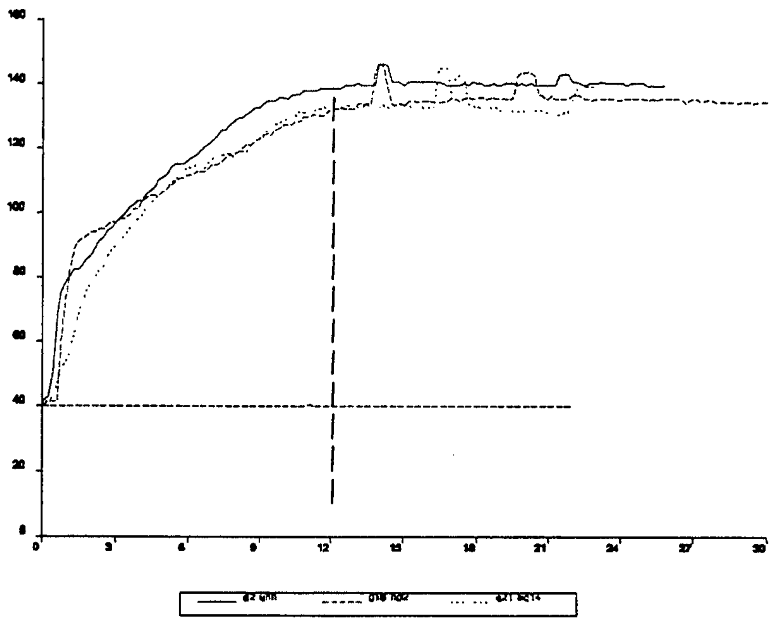


Figure 3.20 Effect of heat treating in stabilizing heater performance.

the heat profile curve indicate manually placing the TC at the bottom of the MRE bag, where the temperature should be the hottest, to help estimate the value in the mid region.

Further tests were carried out to determine the minimum heating time, which would be important to lower the capital and energy cost of the ovens in production. Therefore, we heated extruded pellets (from batch #2 in figure 3.20, with 13.4% inerts) at varying times and temperatures, hoping to find an optimal balance between temperature and time. We heated test samples to 100°-110°C, and 120°-130°C, for 0.5 hour, 1 hour, 1.5 hours, and 2 hours. The pellets were stirred every ten minutes to assure the interior of the pellet mass would reach the desired temperature. (This also explains the wide temperature range, from opening the oven door every ten minutes.) Stirring the pellets also simulates heating the pellets in a rotary kiln, which would probably be used in production and provides slow agitation to the pellet mass. While some fines were generated, these levels were small.

By increasing the temperature of stabilization to >100°C, the heat profile of the pellets is improved, as shown in Figure 3.21 and Table 3.9. We believe that at these elevated temperatures, some of the mineral oil is volatilized out of the pellet,

Table 3.8 Evaluation of heaters stabilized by brief heat treatment: test results with different times and different particle size distributions.

Heater Composition (weight, mesh)	40 g 12-8 20 g 16-12			30 g 12-10 20 g 16-12 10 g 20-16		30g 12-10 30g 16-12		60 g 12-10	
Day heated: Day reacted:	n/a 2	2 16	14 21	2 16	14 17	2 16	14 24	2 16	14 24
Del(T)12:(□F) Top of Bag	98.7	91.7	87.2	100.9	88.5	94.4	92.7	94.3	96.8
Max del(T):(□F)	106.2	106.5	101.5	114.0	99.7	108.6	105.0	107.5	117.9

increasing its porosity and decreasing the inert concentration. At elevated temperatures the pellets turn a dark brown - black color, and a distinct odor is noticeable in the furnace used. There is a slight odor associated with activation of the untreated TDA heater, which is similar to the odor detected during the stabilization step. The heat-stabilized pellets produce almost no discernable odor in normal use.

Table 3.9 Heat stabilization tests using shorter times at higher temperatures.

Temp. (C) Duration	Unheated	110 1 Hr.	110 1.5 Hr.	110 2 Hr.	130 0.5 Hr	130 1 Hr.	130 1.5 Hr.
Del(T) 12 (Top)	96.1	107.5	107.2	107.2	106.8	99.3	109.8
Max Del(T) (Bottom)	111.2	117.9	111.2	114.2	118.5	110.4	118.8

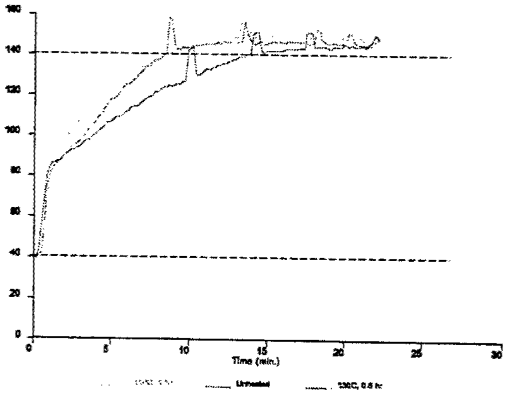


Figure 3.21 Effect of varying stabilization temperature on heater pellets (batch CPM #2, 13.4% inerts).

3.7. Production of Heaters for Field Tests

In this subsection, we summarize the methods used to prepare the 2,000 heater provided to Natick for field tests. The rationale for the particular materials and methods was discussed in previous sections. The most critical process was production of the heater pellets. The formulation used P_2O_5 and CaO in a 1:1 weight ratio, with 13.4% inerts, consisting of 74% white mineral oil and 26% surfactant Actrafos 216.

In production of this material, caution must be exercised that the mixed CaO and P_2O_5 powders do not contact water. If this occurs, localized heating may be sufficient to melt some of the P_2O_5. The molten P_2O_5 can react with CaO, and a highly exothermic reaction can occur that consumes an entire batch of material. Very high temperatures (we estimate in excess of 500°C) are reached, and could cause a fire. Once the inert materials have been mixed, the material is much easier and safer to handle. However, on one instance we observed that when a small quantity of water reached the mixed powders (with inerts), enough heat was evolved to ignite the inert liquids. The pen cup flash point of Actrafos is listed in the MSDS as 300°F. Sax and Lewis (1987) list the open cup flash point of mineral oil as 444°F. This result was not consistent with other experience with the same composition and could not be explained, but is reported here in the interest of safety.

A Hobart mixer with a stainless steel container of about 5 gallon capacity and a wire whisk mixing paddle was used to mix the CaO and P_2O_5 powders. All materials were pelletized on the same day that they were mixed. Mixing was done in several batches due to the limited capacity of the mixing container. The mixed material was stored in closed containers until all of the material for a given batch was mixed. Mixing and pelletizing could have been done simultaneously, but this would have required more staff. In large scale production, of course, a continuous mixer that feeds the pellet mill directly would be used. The Actrafos and mineral oil were first mixed in the correct proportions. Separate batches of CaO and P_2O_5 were weighed out into plastic bags; e.g., 1.5 lb of CaO to be combined with 1.5 lb of P_2O_5. The dry CaO and P_2O_5 were combined and mixed in a large plastic bag and then immediately added to the mixing container, and the appropriate amount of inert liquid was added with mixing. In this way the time that a mixture of CaO and P_2O_5 was present without inerts was minimized. Because this dry mixture without inerts is very sensitive to water, this procedure increased safety.

The mixed powders were introduced into a California Pellet Mill (Model CL-3, as described in Section 3.6.2) and extruded through a ⅛-inch die. The pellets were chopped to lengths of ⅛ to ¼ inch and then heated to a temperature of about 100°C for one-half hour to stabilize performance. After heating, the materials were passed over an 8 mesh sieve to remove fines; very little fines were collected in this step.

A 3.5x5 inch heater pouch was prepared using Fischer Robertson polyester scrim. This material was sealed on three sides to form the pouch. The sealer used was a TEW Electric Heating Equipment Co. Ltd. Model TISH-300, rated at 430 W maximum power. This sealer applied heat and pressure to a strip ⅛-inch wide through teflon-coated jaws. The temperature, pressure, and duration were determined by experiment. Firm pressure was applied with one hand. A temperature setting of about 3 (out of 8 maximum) and a duration of 1-2 seconds were used. After conditions were determined by TDA, the scrim heater pouches for preparing the lot of 2,000 heaters delivered to Natick were prepared (cut and sealed on three sides) by Adams Industries of Westminster, CO, an enterprise that hires developmentally disadvantaged people. The pouch was filled with 60 g of material at TDA and sealed closed. All of the scrim seals were made with the ⅛-inch flat heat sealer. The filled pouch was sealed across the middle on both the long and short sides, forming a cross that divided the pouch into four equal compartments.

A heater storage bag was made of Schaar Industries 2 mil black polyolefin to 48 gauge aluminized polyester laminate film. This film is not a stock item but was run to TDA's specifications. Adams Industries again sealed the bag on three sides, and labels were applied. TDA loaded the heater pouches into the bags and sealed them closed. All of these seals were made with a Clamco Model 241B sealer with ¾-inch serrated jaws. This sealer had a maximum power of 550 W. Again the temperature, pressure, and duration were determined by experiment. Pressure was applied by a foot pedal, which allowed both hands to be used for holding the film. The power-regulating knob was not calibrated, but the temperature of the jaws was shown by a thermometer on the sealer. A power setting that gave a jaw temperature of about 300°F was used. A duration of 1-2 seconds was sufficient to produce a strong seal. In preparing these bags we observed that it was difficult to avoid having a fold of the film material caught by the sealing jaws, which in turn could lead to pinhole leaks. In Phase II it was necessary to seal the pouches and bags by hand due to the small quantity. It larger scale production, automated equipment would not only operate faster but provide more reliable seals.

To determine the best operating conditions for these heaters, TDA carried out tests in which the amount of water used to activate the heater was varied. One ounce of water (30 ml) is optimal, and less heat is produced if 1/3 ounce (10 ml) or if 3.5 ounces (100 ml) are used. An advantage of the heater is that even with 3.5 ounces of water, only a small amount (ca. 3 ml) of liquid waste remains. The amount of dissolved solids in the liquid waste is less than 0.15 g per 100 g solution. This low concentration minimizes safety concerns about the liquid waste. We also activated the heater without a food pouch present to serve as heat sink, using both 1 ounce and 1/3 ounce of water. Even in these off-design conditions, the maximum temperature reached was below 400°F (200°C). Limiting the amount of water to activate the heater limits the extent of heat production, as expected; in addition, this result indicates that the water present in the used heater (as the hydrate $CaHPO_4 \bullet 2H_2O$) can be lost to provide an additional cooling effect.

3.8. Shelf Stability and Packaging Materials

A requirement for any portable heat source is storage stability. For military applications, this requirement is particularly rigorous, with a three-year shelf life required. Consumer products would tolerate a shorter shelf life, since most products are sold and used within six months. TDA's heater contains materials that can absorb water from the air, which can render the heater inactive. Packaging that can keep out atmospheric moisture is essential.

We carried out a fairly large number of tests of shelf life at ambient temperature and either ambient humidity (30-60%) or 100% humidity. We measured the weight gain of the heaters to see how much water had been absorbed, and tested the performance to monitor any changes. From these tests, we concluded that the heaters could tolerate about a 3% weight gain from absorption of atmospheric water without a significant decrease in performance. We caution that this 3% value is drawn from earlier formulations, and may not be valid for the final heater composition. This composition was arrived at close to the end of the project, and there was not time for additional shelf life tests on these materials. However, previous tests had shown no reason to believe that the final composition was any more sensitive to water uptake; if anything, it appeared more resistant to deactivation by water absorption.

We also found that the bag currently used for the FRH does not have adequate water vapor barrier properties for TDA's heater. We investigated a number of other materials, and found that the lowest values of water vapor transmission rate (WVTR) were available with aluminized films. We first investigated DuPont MC2 aluminized Mylar; tests of heaters packaged in Mylar, prepared by extrusion and agglomeration using a variety of formulations, gave the results shown in Figure 3.22. The calculated shelf life is shown in Table 3.4.

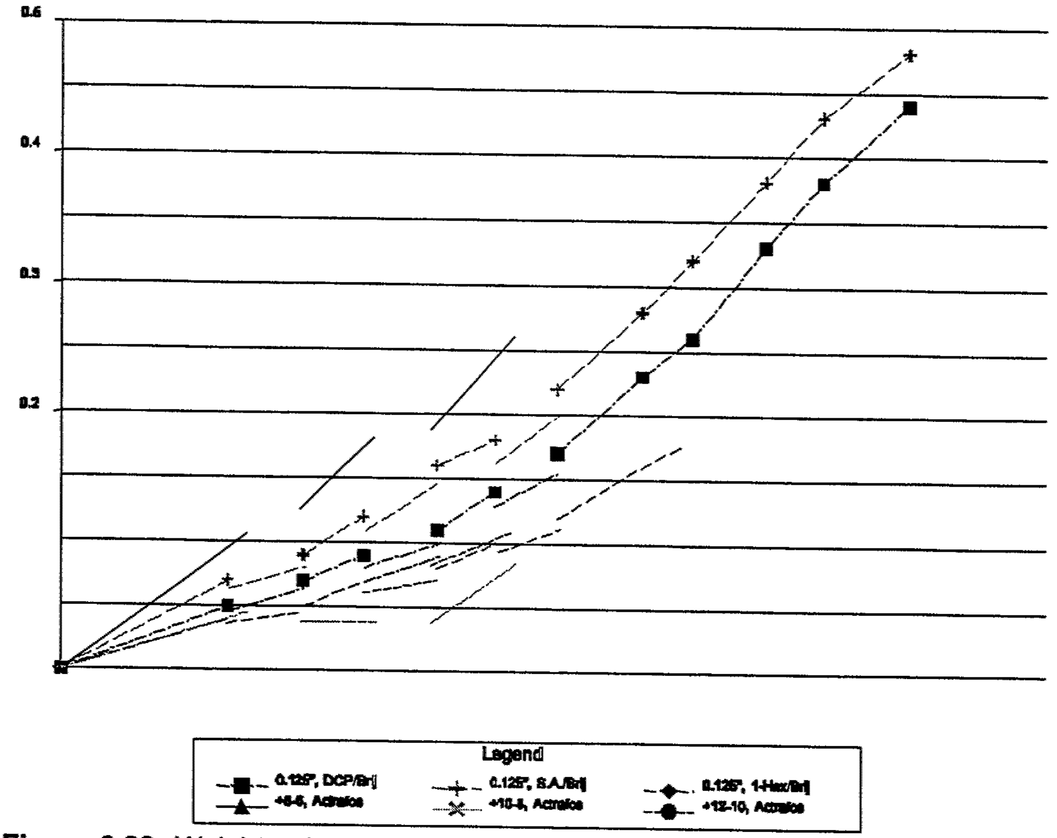


Figure 3.22 Weight gain over time of heaters packaged in Mylar and exposed to indoor ambient temperature and humidity.

We later found that a product from Schaar Industries offered better specifications at a lower price, while providing improved tear resistance. The WVTR for the DuPont MC2 100 gauge aluminized Mylar is 0.04 g/100 in^2/day; the Schaar Industries 2 mil black polyolefin to 48 gauge aluminized polyester laminate has a WVTR 0.033 g/100 in^2/day under the same conditions. Assuming the heater pouch is 6 in x 8 in, 2 sides, for 96 in^2/heater bag, the DuPont product, at $5.25/lb and 19,800 in^2/lb, costs 2.52¢/heater. The Schaar product, at $2.45/lb and 10,512 in^2/lb, costs 2.23¢/heater. The Schaar film was used to package the 2,000 heaters supplied to Natick.

A significant but not immediately apparent complication in the shelf life studies was the difficulty of obtaining good, reproducible seals with manual sealers. We used a heat sealer that gave a ¾-inch flat seam to seal the heater bags. This heat sealer worked well on the scrim pouches, but did not give satisfactory results with the aluminized Mylar. We discovered this by testing several identical heaters and finding significant variations, which proved to be due to defective seals. We then obtained a heat sealer that gave a ⅛-inch serrated seal (similar to those on potato chip bags). This sealer provided much better results, and was used to seal the 2,000 heaters provided to Natick. These heaters were sealed by hand, and more reliable results would be obtained on an automated packaging line.

Table 3.10 Shelf life tests with extrusions and agglomerates (sealed in Mylar, exposed to ambient indoor temperature and humidity).

Pellet Form, Inerts	Calculated Shelf Life (Months)
0.125" Extrusions, DCP/Brij.	20
0.125" Extrusions, S.A./Brij.	19
0.125" Extrusions, Hex./Brij.	28
+8-6 Agglomerates, Actrafos	17
+10-8 Agglomerates, Actrafos	53
+12-10 Agglomerates, Actrafos	38

4. Safety

Data relating to the safety of the materials was taken from the Material Safety Data Sheets (MSDSs) provided by the manufacturers, and from Sax and Lewis (1987, 1988), Budavari (1989), and Bretherick (1990). The specific materials investigated in detail by TDA are all strong desiccants (drying agents), and taken individually each is harmful if swallowed, inhaled or absorbed through the skin. Part of the innovation introduced by TDA is to package the acidic material ($AlCl_3$ or P_2O_5) with the basic material (CaO). This results in an increase in heat output, due to the neutralization of the acid and the base. It also results in a product (after the heating reaction is complete) that is neutral and may be safely disposed of. The effect of combining the two materials will also increase the safety of personnel exposed to accidental spills, since the mixture will react, with self-neutralization, on any exposure to water. This includes situations in which solid dust could come in contact with people's skin or mucous membranes. While each of these materials taken individually (including quicklime, commonly used in previous food heaters) is an irritant and is toxic, nevertheless, all of these materials are articles of commerce, and are routinely handled in large quantities.

We consider here two categories of hazards: (1) burns from steam or hot surfaces, and (2) toxic effects that may be produced by accidental exposure to or ingestion of the heater material. These are discussed in order below.

1. <u>Burn</u> Personnel will normally handle the hot heater, and may be burned by the hot surface or by escaping steam. This will occur occasionally, but should only result in minor injury: people will let go of the package if it gets too hot, and no one should suffer more than a minor burn.

2. <u>Toxicity</u> Personnel will not be exposed to the heater material during normal operation, but may be exposed to the contents by skin contact in the event a package is accidentally ruptured in transport or in use. Heater toxicity was investigated as part of a separate Health Hazard Assessment by the Office of the Surgeon General. The conclusion of this study was that the heater should have warning signs on the package informing users not to eat the heater and to avoid direct contact of the heater material with the eyes and skin. With this provision, there were no major hazards that would prevent the Army from using the heater as intended.

The overall conclusion of the system safety analysis is that the materials should be safe in manufacturing, transportation and normal operation.

4.1. Regulatory Assessment

A Product Regulatory Assessment was conducted by an independent contractor (Industrial Compliance, Golden, CO). Their report is included as Appendix B. This section reviews their findings and recommendations, with TDA's actions and the outcomes.

The study by Industrial Compliance covered the following areas:

- Resource Conservation and Recovery Act (RCRA);
- Hazardous Materials Transportation ACT (HMTA);
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA);
- Clean Water Act (CWA);
- Toxic Substance Control Act (TSCA);
- Occupational Safety and Health Act (OSHA);
- Preparation of MSDS.

4.1.1. Resource Conservation & Recovery Act (RCRA)

- Regulates ongoing generation, transportation, storage, and disposal of hazardous wastes.
- Classifies materials as hazardous waste based on characteristics of ignitability, corrosivity, reactivity, or toxicity.
- TDA's heater and/or its constituents are not listed hazardous wastes.
- Reactive hazardous waste includes any material that "..reacts violently with water."
- The heater may be classified as a reactive hazardous waste if disposed of in its normal state, before use.
- After use, the material is benign and does not present any problem in disposal.

Recommendations

IC recommends that, when manufacture begins, TDA has analysis for ignitability, corrosivity, reactivity, and toxicity as defined under RCRA performed by an accredited independent laboratory.

Action

Hazen Research, Inc. of Golden, Colorado tested the heater material for ignitability, corrosivity, reactivity, and toxicity as defined under RCRA. All tests performed gave a result within the safe range. These analyses demonstrate that the reacted heaters can be disposed of without special requirements or procedures. Table 4.5 and Table 4.5 summarize the results of the toxicity testing.

Table 4.1 Report of analysis

Parameter	Result	Detection Limit	EPA Limit
Flash Point (□F)	>200	45	140
Reactive cyanide as HCN (mg/kg)	<0.05	0.05	250
Reactive sulfide as H_2S (mg/kg)	<1	1	500
Corrosivity by pH	5.1	0.1	>2 & <12

Table 4.5 Toxicity Characteristics of Leaching Procedure (TCLP).

Parameter	Result (mg/l)	Detection Limit	TCLP Limit (mg/l)
Arsenic	<0.2	0.2	5.0
Barium	<0.5	0.5	100
Cadmium	0.03	0.03	1.0
Chromium	0.30	0.05	5.0
Lead	<0.3	0.3	5.0
Mercury	<0.001	0.001	0.2
Selenium	<0.03	0.03	1.0
Silver	0.05	0.05	5.0

4.1.2. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

- EPA through CERCLA, regulates releases to the environment of hazardous substances, or pollutants.
- Under CERCLA, the Superfund Amendments and Reauthorization Act (SARA) imposes emergency planning and notification requirements.
- Industrial facilities that "use, process, or manufacture" a toxic chemical in amounts above the threshold quantity report releases of the toxic chemicals to the environment.
- "Spills" of more than one pound of P_2O_5 must be reported to the EPA.

- Storage of more than ten pounds of P_2O_5 must be reported to local agencies.
- Storage of more than 10,000 pounds of CaO must be reported to local agencies.

Recommendations

IC recommends that, when manufacture begins, TDA evaluate materials management practices and develop procedures to ensure compliance with CERCLA and SARA Title III reporting requirements.

Action

During Phase II the appropriate agencies were notified of the quantities of P_2O_5 and CaO being stored. In addition, the local fire department reviewed and approved TDA's procedures for storage and handling of the heater components. No problems were encountered, and the procedures used should not be unduly expensive to implement on large scale production. On May 7, 1996, EPA removed P_2O_5 from the "extremely hazardous" list, which will remove some restrictions on the use of P_2O_5. The decision was recorded in the Federal Register of the same date.

4.1.3. Clean Water Act (CWA)

- CWA establishes water quality standards and regulates waste water discharge.
- The heaters are not regulated under the CWA.
- Heater manufacture may require an agreement/permit for waste water discharges to the sanitary sewer system.

Recommendations

IC recommends evaluation of process when manufacturing begins to identify required permits. No additional testing is required at this time.

Action

TDA's facilities comply with local regulations for waste water discharge. No further action was required.

4.1.4. Toxic Substance Control Act (TSCA)

- TSCA regulates new and existing chemicals in commerce.

- No new chemicals are involved in the heaters.
- The heaters do not appear to constitute a "significant new use" of the materials involved, but EPA must make this determination.

Recommendations

IC recommends TDA contact EPA to verify that the heaters do not constitute a significant new use of the materials involved.

Action

TDA contacted the EPA and discussed the Significant New Use Rules (SNURs). As expected, a very significant body of material exists on the uses of CaO and P_2O_5 that must be reviewed before making the case that the ration heater does or does not constitute a significant new use of the materials. It would be appropriate to carry out this review and determination at a later date, for example when preparing a detailed plan for a production facility.

4.1.5. Occupational Safety and Health Act (OSHA)

- OSHA regulates the manufacturing practices used to produce the heaters.
- With the materials used, general safe manufacturing procedures should be followed; no unusual hazards or reporting requirements were identified.

Recommendations

IC suggests a number of standard procedures, including use of safety equipment, employee training, and process hazard analysis, to assure worker safety.

Action

Standard safety procedures were satisfactory in producing several hundred pounds of material for Phase II tests.

4.1.6. Hazardous Materials Transportation Act (HMTA)

- Department of Transportation (DOT) regulates commerce in hazardous materials
- DOT lists CaO, P_2O_5, and $AlCl_3$ as corrosive materials.
- Proposed DOT shipping name for CaO/P_2O_5 heater material: Corrosive solids, n.o.s., 8, PG II, UN 1759 (calcium oxide & phosphorus pentoxide).
- Without further testing, the heater materials would have to be shipped as hazardous materials.

- With further testing, heaters should be identified as non-hazardous because the reaction is controlled and products are benign. The heater material is not corrosive as CaO and P_2O_5 alone are because the reaction is self-neutralizing.
- Materials with similar heat evolution (e.g., $MgCl_2$) are not identified as hazardous materials.

Recommendations

IC recommends that when heater manufacture begins, TDA contact DOT to determine labeling and packaging requirements for transport, and testing required to determine that heaters do not have to be transported as corrosive solids.

Action

In normal use TDA's heater is activated by adding water, and no liquid water remains. When an excess of water is added, the resulting liquid solution has a pH in the range from 5 to 9 (typically about 6.5) and contains no hazardous substances.

The heater is a single formulation manufactured from multiple components, in such a way that the individual components cannot be accidentally separated, and the components would be very difficult to separate intentionally. One of the components of the heater is listed as a corrosive solid in CFR 49, §172.101. However, the heater as manufactured has different properties than the components, and does not produce a corrosive product on activation. TDA has tested the heater as described in CFR 49, §173.136, and determined that the heater is not a corrosive material as defined in that section. The details of the test procedure are shown below. Therefore, the heater is not classified as a hazardous material as defined in CFR 49. TDA has communicated this result to DOT.

4.1.7. Material Safety Data Sheet (MSDS)

- Manufacturer required to provide MSDS with any chemical product.
- If a mixture has not been tested as a whole, it is assumed to have the same health hazards as its constituents.
- The complete ration heater should be tested to determine properties for the MSDS.
- Animal testing would not yield useful knowledge and is not required.
- A heater pad taken into the mouth would burn the mouth, but is not likely to be kept in the mouth long or to be ingested.

Recommendations

Tests to be performed for the MSDS, preferably by an independent laboratory, include:

Reactivity
Solubility in Water
Solubility in Other Solvents
pH
Appearance/Color/Form
Density/Specific Gravity
Melting Point/Boiling Point
Autoignition Temperature
Specific Heat
Heat of Combustion
Odor
Decomposition Products
Decomposition Temperature

Action

TDA has prepared an MSDS, which is included as Appendix C.

4.2. Supplementary Data on Heater Safety

TDA prepared a Supplementary Report on Heater Safety to provide additional information to representatives of the Office of the Surgeon General. These comments are provided from that report.

1. Uniformity and Stability of Heater

The two active ingredients, calcium oxide (CaO) and phosphorus pentoxide (P_2O_5) are both supplied as fine powders. In producing the heater, the two powders are intimately mixed and combined with the inert liquids; the mixture is then formed into pellets. The pellets are typically cylindrical with both diameter and length on the order of ⅛ inch. For both the calcium oxide and phosphorus pentoxide, 90% of the material will pass a 100 mesh screen, indicating a particle size less than 0.149 mm (0.0059 inch). In each ⅛-inch pellet there are equal weights of CaO and P_2O_5, and roughly equal numbers of particles of each component: about 5,000 particles of each type in every pellet. Given the small size and intimate mixing of the particles, and their combination in a mechanically robust pellet, the two ingredients cannot become separated accidentally. In principle, it would be possible to separate the components of this mixture, as of any physical mixture, but no practical method for such a separation exists to the best of our knowledge. Separation of a solid mixture typically begins with addition of a liquid to dissolve one or more of the components, but addition of water to the heater simply begins the intended reaction. Other solvents such as alcohol would have a similar effect. In summary, each heater pellet contains an intimate mixture of both components that cannot separate accidentally and would be very difficult to separate intentionally.

2. Heater pH

As the heat producing reaction proceeds, the phosphorus pentoxide combines with water to make phosphoric acid (or polyphosphoric acid), while the calcium oxide combines with water to make the base calcium hydroxide. The acid and base then combine to make a salt, giving a final product of neutral pH. Regions of high local concentration of acid or base should be no larger than the size of an individual particle (less than 0.149 mm or 0.0059 inch). The phosphoric acid is soluble in water, but the calcium hydroxide is only slightly soluble. While the heater is active, the surface of a pellet will typically be acidic (pH about 4) due to the greater mobility of the acidic component. When the reaction is complete the pH is normally about 6.5.

3. Wetting Agent

The wetting agent used in TDA's heater is an organic phosphate ester. According to information supplied to TDA in a telephone conversation with the manufacturer, the wetting agent is on the list of materials Generally Recognized as Safe (GRAS). No further information except the MSDS was available from the manufacturer. The MSDS for Actrafos states that the material is not considered carcinogenic, that it may cause skin and eye irritation, and that prolonged contact with skin should be avoided.

4. Residual Water

The heater is typically activated by adding an amount of water equal to ½ the heater weight. When an excess amount of water is used, the heater can consume up to 1.7 times its weight in water after 15 minutes, and up to 2.6 times its weight in water after 18 hours, without any liquid water being present.

5. End Products

The initial product of the neutralization reaction is calcium hydrogen phosphate, $CaHPO_4$, which occurs in nature as the mineral *monetite*. When the heater is completely reacted, the majority of the calcium hydrogen phosphate is in the form of the dihydrate, $CaPO_4 \bullet 2H_2O$; this material also occurs in nature as the mineral *brushite*. These materials are used in fertilizer and as a dietary calcium supplement. The relative amounts of the hydrate and anhydrous calcium hydrogen phosphate will depend on the amount of water used to activate the heater. Small amounts of calcium phosphate [$Ca_3(PO_4)_2$; bone ash] and monocalcium phosphate [$Ca(H_2PO_4)_2$; used in baking powder] may also be present, along with some calcium hydroxide. A small amount of calcium hydroxide remains unaltered due to its low solubility in water.

The solution obtained after mixing heater material and water (in a 1:4 weight ratio) contains less than 1 g of solute per 100 g of water. The pH of this solution is in the range of 5-9. The identity of the solute has not been determined but the solution logically contains a mixture of calcium ions (Ca^{+2}) and phosphate ions ($H_2PO_4^{-1}$, HPO_4^{-2} and PO_4^{-3}). The exact proportion of these ions in solution will depend on the temperature and pH.

4.3. Corrosion Test

TDA has tested the heater to verify that it heater is not a corrosive material. TDA carried out tests according to NACE Standard TM-01-69, Laboratory Corrosion Testing of Metals for the Process Industries, as specified in CFR 49, §173.136. Standard test coupons were obtained from Metal Samples Company Inc. and measured 4"x1"x$^{1}/_{8}$" with a mounting hole of $^{5}/_{16}$" on one end. Materials were purchased with a mill finish and final polish was done in house. Metal composition with physical properties for both the 1020 steel and 7075-T6 aluminum are presented in Table 4.3 and Table 4.4. A summary of experimental procedures follows.

Table 4.6 Chemical and physical properties of SAE 1020 steel lot # K857.

Element	%	Element	%	Element	%	Element	%
Carbon	0.180	Aluminum	0.048	Silica	0.010	Phosphorus	0.008
Sulfur	0.005	Manganese	0.410	Iron	Balance		
Physical Hardness: HB68.6				Metal Density: (g/cm^3)7.86			

Table 4.7 Chemical and physical properties of 7075-T6 aluminum lot # L173.

Element	%	Element	%	Element	%	Element	%
Magnesium	2.540	Aluminum	Balance	Iron	0.270	Titanium	0.020
Chromium	0.190	Manganese	0.040	Silica	0.080	Copper	1.600
Zinc	5.720						
Metal Density (g/cm^3) 2.73							

Metal samples were first sanded with a 50 grit sandpaper to remove the surface layer, then polished with 150 grit paper. This step is to eliminate variations in the condition of the original metallic surface. Following polishing, the samples were sonicated in an acetone bath for 5 minutes to remove any surface oils that may have existed. The metal coupons were then allowed to air dry and were weighted and measured (2). Following specimen preparation, the samples were suspended in ration heater waste water: 500 g TDA's ration heater in 3000 ml distilled water. This mixture was allowed to sit overnight, the ration heater pellets were removed and the remaining liquid was gravity filtered through a #4 filter paper (Note: A tear was later found in the paper resulting in some suspended hydrated ration heater in the liquid waste.) The final liquid residual water contained approximately 1.5 g/L dissolved solids from the heater and ~0.6 g/L suspended solids (calcium hydrogen phosphate) and a pH of 4.45. (Note: this pH value is far lower then we normally see in similar circumstances when the final pH of residual water is 6-6.5, but we assumed this was a worst case scenario and proceeded.) The two test metal coupons of steel were then suspended on a piece of tygon tubing and immersed in 1,000 - 1250 ml of the waste water solution. When these samples were finished, the test was repeated with the T6 aluminum. A diagram of the testing apparatus is included in Figure 4.2. The temperature was raised to 55°C (+/- 5°C) and allowed to sit for a period of 1 week (168 hrs.) At the beginning of the test we experienced some difficulty in regulating the temperature, allowing for a temperature value of up to 70°C to be attained, but the majority of the test was conducted within the above parameters.

At the end of one week, the samples were removed from the solution, which was then refiltered through a #4 filter paper to measure suspended solids. The pH was measured at 4.0-4.2 and the remaining solution discarded. The steel samples were then cleaned in a bath of cold concentrated HCl with 20 g/L $SnCl_2$ and 20 g/L Sb_2O_3 for 6 hours, followed by 7 min of sonication in acetone and reweighed. The aluminum was immersed in 70% HNO_3 for 5 min. and lightly washed in tap water, followed by sonication in acetone for 5 min. per side. During testing the steel samples were touching on one plane and in this area the corrosion was more severe. The rest of the samples and all the aluminum surfaces were essentially unchanged except for some minor discoloration in the steel in a couple of localized spots (noted in Figure 4.1). Despite these areas of attack at this interface, which would simulate an artificially high corrosion rate, the numbers attained were still extremely low. A summary of results follows.

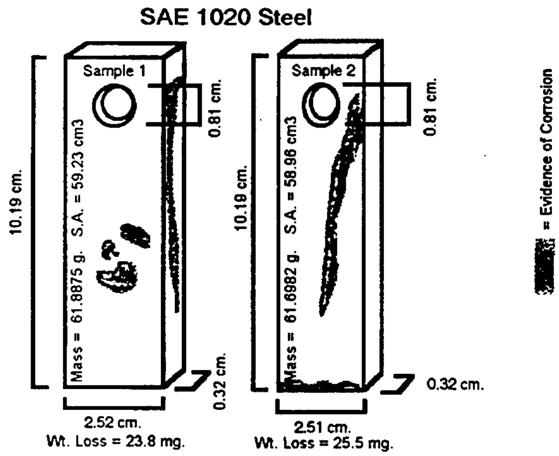


Figure 4.1 Corrosion test samples

Measurements for the two steel metal samples are shown in Figure 4.1; the aluminum is the same general shape and area (not shown). Corrosion is stated in millimeters/yr (mmpy) and calculated using the formula: wt. loss (g) x 87.6 / surface area (cm^2) x time (hr) x metal density (g/cm^3). The results for our two samples on SAE1020 steel are 0.026 and 0.029 mmpy, for an average of 0.0275 mmpy. The corrosion in mmpy for the T6 aluminum is even lower with values of 0.0006 and 0.0003 mmpy and an average of 0.00045 mmpy. According to DOT §173.136 Class 8-Definitions a.2, "A liquid is considered to have a severe corrosion rate if its corrosion rate exceeds 6.25 mm (0.246 inches) a year on steel (SAE1020) or aluminum (nonclad 7075-T6 at a test temperature of 55□C (131°F). An acceptable test is described in NACE Standard TM-01-69)." It is shown that our ration heater has a value far below this threshold value and as such should not be considered as a severe corrosive. It should therefore not be assigned to Packing Group III.

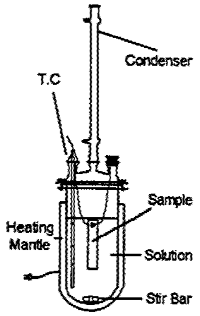


Figure 4.2 Corrosion Test Apparatus

4.4. Tests Related to Heater Safety and MSDS

Additional tests were performed to identify various properties of the TDA heater for the MSDS. These included pH, solubility, flashpoint, hydrated weight gain, and hydrated density. A 30.16 g heater (about half normal size) was placed in 119.75 g water and the mixture allowed to stand overnight. The large quantity of water is needed to have residual water left to take pH and solubility measurements. When a two-ounce heater is activated with less than three ounces of water there is essentially no free liquid waste. (Recall that one ounce of water is the recommended amount to activate the heater.) The next day, the heater was removed and allowed to dry. The residual water was collected and filtered, the pH was taken, and the water was evaporated to dryness to determine the residual solids. The results can be summarized as follows: pH of the residual water was 6-7, total solids content of the residual water was less than 0.15 g/100 g H_2O. Table 4.7 summarizes the weight and volume changes on heaters prepared using the California Pellet Mill.

Table 4.8 Weight and volume change on activation, heaters prepared on pellet mill.

	Before Use	After Use
Weight, g	60	69.5
Volume, cm^3	66	110
Bulk density, g/cm^3	1.1	0.63

An unactivated heater was placed on a melting point apparatus to determine an □ignition temperature. At 180°-200°C the material started smoking, which we assume to be the mineral oil burning off, but the material never ignited even at temperatures > 300°C. Based on these tests, the heater produces minimal liquid waste under normal conditions, and the liquid that is produced when an excess of water is used is neutral and contains minimal solids.

Reacting a 60 g heater with 10-100 ml activation water yielded a worst case of only 3 ml residual water after a 25 min. test, indicating that even if the soldier adds over 3 times the recommended water to activate, the environmental impact from liquid waste is minimal. Heat profiles from test where the amount of water was varied are shown in Figure 4.2. All temperature measurements were taken at the top of the food pouch (i.e., the minimum food temperature). As is shown, even with 2-3 times the recommended activation water, the heat profile is not severely reduced. With a large excess of water the food temperature falls below the target, as would be predicted, but the heater would still produce a palatable meal.

The temperature change at 12 minutes and the residual water measurements from these profiles are summarized in Table 4.9. All heaters were 60 g and equal parts +10-8, +12-10, +16-12, and +20-16 mesh agglomerates with two 1.5" channels encased in a 4.5" x 3" scrim.

Table 4.9 Amount of liquid waste formed with varying amounts of activation water (temperature curves shown in Figure 4.2).

Activation Water (ml)	10	30	60	100
Del(T) 12 min. (F)	56.1	98.3	93.6	87.2
Residual H_2O (ml)	0	0	3	3

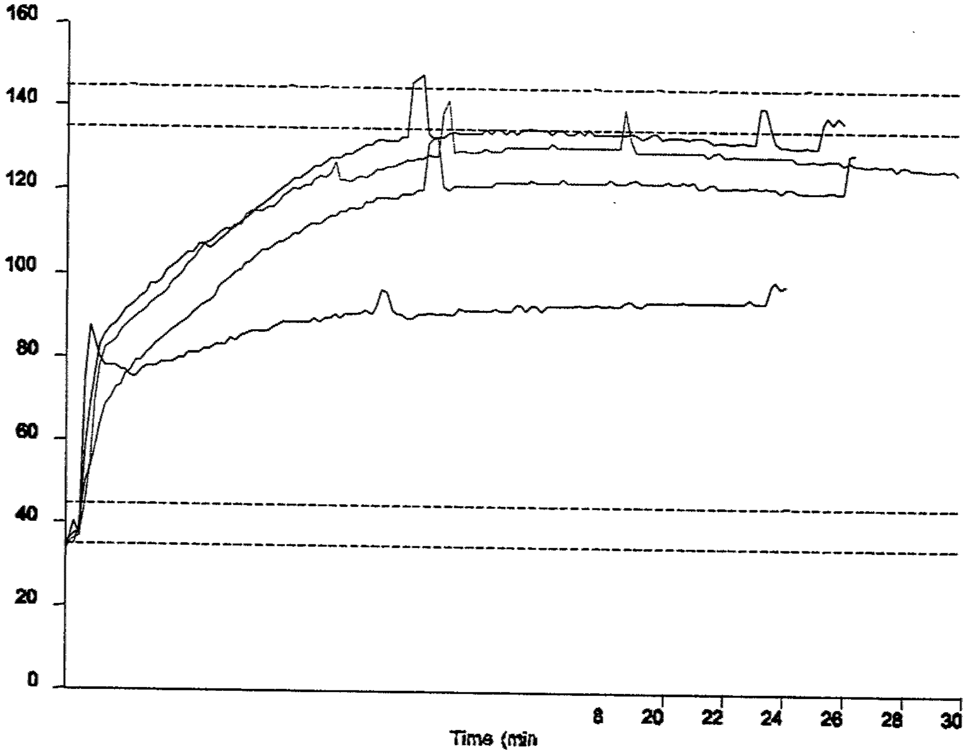


Figure 4.3 Effects of various amounts of activation water on heater performance. Top curve: activation with 30 ml water; next two lower curves: activation with 60 and 90 ml water respectively; lowest curve: 10 ml water.

We also carried out tests to assure that the heater would not produce a safety hazard if activated without the MRE present to provide a heat sink. These experiments entailed placing thermocouples on the top, middle, and bottom of the heater pad, activating with either 30 ml water (recommended amount) or 10 ml water (a condition to encourage overheating due to not enough water to carry away the heat produced) without the simulated MRE on top. This experiment is detailed in Figure 4.3 and Figure 4.5, again with equal parts +10-8, +12-10, +16-12, +20-16 agglomerates in a 60 g, 2 channel scrim configuration. As shown, the top TC in both cases reaches similar maximum temperatures, which may be due to similar residence times of the water poured on top to activate. A summary of the data from Figure 4.3 and Figure 4.5 is included in Table 4.9.

The bottom layer of the heater activated with 10 mL reached a higher temperature than the 30 ml activated heater, as would be expected since there is less water to carry away the heat produced. Even in this deliberately constructed worst case scenario, the maximum temperature reached by the TDA heater never exceeded 400°F.

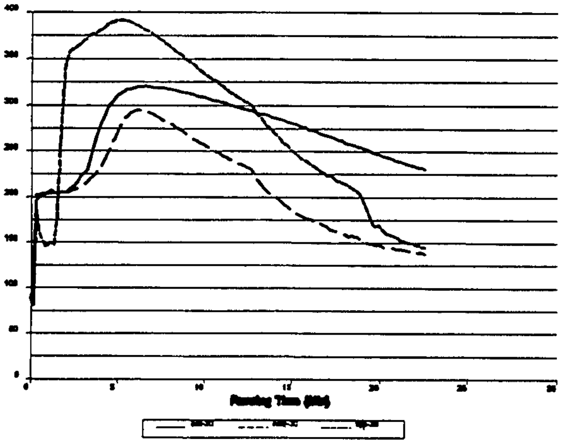


Figure 4.4 Heater activated with 30 ml water (normal amount), and no heat sink. The apparent drop at the beginning of one curve is an artifact: the TC slipped and was returned to the correct location.

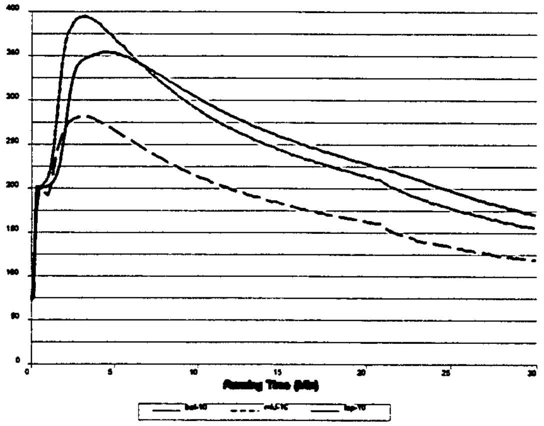


Figure 4.5 Heater activated with 10 ml water (1/3 the normal amount), and no heat sink.

Table 4.10 Heater activated with 10 and 30 mL water, no heat sink.

TC Location	Bottom	Middle	Top	Bottom	Middle	Top
Activation Water (ml.)	10	10	10	30	30	30
Max Temp. (F)	354.5	281.7	394.8	320.4	295.0	391.1
Time to Max. Temp (min)	4.5	3.1	3.2	6.2	6.2	5.0

5. Systems Analysis

In this section, we estimate the cost of an MRE heater produced using the materials and methods that TDA has developed in Phase II. We consider the materials and production costs separately. The materials costs are based on values provided by the manufacturers for the actual materials used in the 2,000 heaters provided to Natick. The heater materials reflect bulk pricing, and the packaging materials reflect estimates of bulk costs based on the quantities used in Phase II. In the case of the packaging materials, revisions as the heater development continues may result in some cost savings. The materials costs are shown in Table 5.1.

Table 5.1 Heater materials costs.

Material	lb/heater	cost/lb	cost/heater
P_2O_5	0.0565	$0.90	$0.0508
CaO	0.0565	$0.15	$0.0085
Surfactant	0.0005	$1.68	$0.0083
mineral oil	0.0143	$0.35	$0.00050
scrim (40 in^2)			$0.0095
packaging (aluminized polyolefin, 96 in^2)			$0.0210
		Total	$0.1032

To estimate production costs, we made the following assumptions: First, we assumed that large scale production uses mixing and pelletizing equipment analogous to that used in Phase II production. The heater weight is taken as two ounces, or eight heaters to the pound, also as in Phase II. Process equipment has a capacity of 500 lb/hr, 90% utilization factor, operating 2,000 hours per year (one shift). The equipment included transport from bulk storage to mixer, mixer, pellet mill, rotary tube kiln, shaker table to remove fines, equipment for collection of fines and product, desiccant wheel to maintain dry atmosphere, and fork lift to move drums of raw materials and product. Annual output of the production line in single shift operation is 900,000 lbs or 7.2 million heaters. We estimated costs for production quantities of either 7.2 or 14.4 million heaters/year; for the larger production quantity, we assumed that the production line is operated for two shifts daily. Smaller production quantities do not realize satisfactory economies of scale. The current production of FRHs is more than 15 million units per year.

The capital equipment prices were determined by vendor quotes or estimated from catalog process. For capital equipment, we considered two scenarios, one in which all the equipment is purchased at new cost ($225,000), and one in which the equipment is purchased used, at a cost averaging 40% of new ($90,000). When pellet mills are used to pelletize alfalfa for animal feed, a significant part of the operating cost of the mill is replacement of the perforated drum. In our case it will not be possible to get a realistic estimate of drum life until production begins. Nevertheless, information provided by the manufacturer suggests that on a large scale machine (⅛-inch pellets, 16 inch drum) we could expect a lifetime of not less 2,000 tons (4 million pounds, or roughly 32 million heaters). This calculation demonstrates that in our scenario, assuming a drum cost in the range of $5,000 to $8,000, drum replacement should add less than 0.025 cents to the heater cost.

We assumed a 3 year payback on capital equipment, and an interest rate of 12%. The facility was sized by assuming (1) the production equipment occupies 600 ft^2, and (2) storage of 950 ft^2 is needed for one month (75,000 lbs in the smaller production scenario) of either raw materials or finished heater pellets. The heater pellets could be stored in drums and shipped to a different location for packaging. The total facility is estimated at 2,000 to 3,000 ft^2, at a cost of $30,0000/year for the lower production levels, or $45,000/year for the higher production level.

Table 5.2 Production cost of ration heaters.

	7.2 million heaters/yr		14.4 million heaters/yr	
equipment new or used	new	used	new	used
equipment cost	$225,000	$90,000	$225,000	$90,000
installation	$675,000	$675,000	$675,000	$675,000
total capital cost	$900,000	$765,000	$900,000	$765,000
annual cost of capital	$374,714	$318,507	$374,714	$318,507
labor	$150,000	$150,000	$270,000	$270,000
overhead	$150,000	$150,000	$270,000	$270,000
facility cost	$30,000	$30,000	$45,000	$45,000
total labor and facility	$330,000	$330,000	$585,000	$585,000
unit cost, capital	$0.0520	$0.0442	$0.0260	$0.0221
unit cost, labor and facility	$0.0458	$0.0458	$0.0406	$0.0406
unit cost, all materials	$0.1032	$0.1032	$0.1032	$0.1032
unit packaging cost	$0.0250	$0.0250	$0.0250	$0.0250
total unit cost	$0.2260	$0.2182	$0.1948	$0.1909

An important consideration is the cost of installation of equipment. This factor, called the Lang factor, can vary from 2.6 to 3.5 (Ulrich 1984). We assumed a value of 3.0, that is, that installation costs three times as much as the (new) cost of the equipment. This factor allows for the cost of work to assure that, for example, the mixer, pellet mill, shaker table, and other parts of the line all function together. The labor cost assumes (in each shift) 3 operators at $25,000/year and 1 supervisor at $45,000/year. Overhead was taken to be 100% of direct labor. An additional $30,000 per year direct cost was included for regulatory compliance, and was the same for both production quantities. We assumed that packaging would cost $0.025 per unit (an annual cost of $180,000 for 7.2 million heaters), including the cost of printing any needed instructions and cost of transport to a separate packaging facility. The results are shown in Table 5.2.

A few comments on these results are in order. The materials cost, which is the largest single factor, has the least uncertainty. The prices are provided by vendors of the same material that was used in preparing the heaters delivered to Natick in Phase II, and are bulk prices. The installed cost of capital equipment has the highest level of uncertainty, but if amortized over a sufficiently large number of units this uncertainly does not greatly affect the final unit cost. The production labor cost also has a moderate level of uncertainty, since it will not be possible to determine the exact number of operators until the plant is operating. Overhead rates can also vary over considerable range, but the values we have assumed are typical. The next step toward production would be to prepare a detailed design for the production facility, which would allow much more accurate estimation of the associated costs.

6. Conclusions

TDA arrived at the following specific conclusions:

1. From the two alternatives identified in Phase I, P_2O_5/CaO was selected as the best formulation for the new ration heater.

2. TDA developed methods to control the rate of heat production, and used these methods to produce a heater that generates heat at the rate at which it can be efficiently absorbed by the food.

3. The best production method was to mix the active and inert components of the heater, extrude pellets of about ⅛-inch diameter, and heat the pellets briefly to 80-100°C to stabilize performance. Heaters prepared in this manner worked well to heat the MRE under standard test conditions. When a two-ounce (56 to 60 g) heater was activated with about 1 ounce (30 ml) of water, a temperature change of more than 100°F was observed for the MRE.

4. The safety of the new heater was evaluated with reference to the relevant regulations, with the assistance of an independent contractor in regulatory assessment. Necessary tests were carried out, either at TDA or independent laboratories. A Material Safety Data Sheet (MSDS) was prepared. To the best of our knowledge, there are no safety issues that would preclude the intended use of the new heater, or unduly complicate its manufacture, transportation, or disposal.

5. TDA carried out an engineering analysis of the materials and production methods for the new heater. The materials cost is less than seven cents per unit for the two-ounce heater suitable for the MRE. The production methods include standard mixing devices and a pelletizer such as the California Pellet Mill. The estimated production costs were 19 to 23 cents per unit. This value compares very favorably with the current FRH.

7. References

ACGIH (American Conference of Government Industrial Hygienists) (1987) *TLVs: Threshold Limit Values and Biological Exposure Indices*. ACGIH: Cincinnati, OH.

Bretherick, L. (1990). *Handbook of Reactive Chemical Hazards*, 4th ed. London, England: Butterworths.

Budavari, S. (1989). *Merck Index*, 11th ed. Rahway, NJ: Merck & Co.

Dean, J.A. (1985). *Lange's Handbook of Chemistry*, Thirteenth edition. New York: McGraw-Hill.

Gunn, Stuart R. (1971). "On the calculation of the corrected temperature rise in isoperibol calorimetry. Modifications to the Dickinson extrapolation method and treatment of thermistor-thermometer resistance values" *J. Chem. Thermodynamics* **3**, 19-34.

Kuhn, W.E., K.H. Hu and S.A. Black (1985). *Flexible Electrochemical Heater*, U.S. Patent No. 4,522,190.

Labrousse, B.L.P.E. (1988). *Single-use Heat Transfer Packaging for Drinks, Foodstuffs and Medicaments*, U.S. Patent No. 4,753,085.

Okamoto, T., T. Sunagawa and S. Sato (1989). *Self-Heating Container*, U.S. Patent No. 4,819,612.

Perry, R.H., D.W. Green and J.O. Maloney (1984) *Perry's Chemical Engineers Handbook*, Sixth Edition. New York: McGraw-Hill.

Ryan, E.C. and R.E. Reed (1963). *Heating Device*, United States Patent No. 3,7079,911.

Sax, N. I. and R. J. Lewis (1987). *Hazardous Chemicals Desk Reference*. NY: Van Nostrand Reinhold.

Sax, N.I. and R.J. Lewis (1988). *Dangerous Properties of Industrial Materials*, 7th ed. NY: Van Nostrand Reinhold.

Toledo, R.T. (1991). *Fundamentals of Food Process Engineering, 2nd ed.* New York: Van Nostrand Reinhold.

Ulrich, G.D. (1984). *A Guide to Chemical Engineering Process Design and Economics*. New York: Wiley.

Yukawa, H. (1988). *Container for Self-heating or Self-cooling of Drinks or Foodstuffs by an Exothermic or Endothermic Reaction*, U.S. Patent No. 4,751,119.

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Appendix A: Heat Producing Reactions Identified in Phase I

Heat-Producing Reactions Identified in Phase I

The oldest reaction reported for use in a portable heat source is the hydration of quicklime (CaO). This reaction suffers from the relatively low heat output per weight of CaO, and its low powder density. This combination means that a CaO-based heat source may be heavier and larger in volume than the food or beverage it is intended to heat. Many of the other reported reactants [such as the hydration of strontium oxide (SrO) or barium oxide (BaO)] are inferior to calcium oxide in both weight and cost. Several of the reactions also use either strong acid (HCl), strong base, ($NaOH$, KOH) or both; this is undesirable from a safety standpoint. One (Okamoto et al., 1989) is a pyrotechnic mixture used for heating the Japanese beverage sake. With the high temperatures (>1000°C) reached, the metal container can melt if not continuously cooled by vaporizing liquid. This system does not appear to be either safe or useful for our purpose.

A patent by Ryan and Reed (1963) describes a mixture of aluminum potassium chlorate and calcium sulfate. For the composition stated, that mixture releases only 1,058 Btu/lb without hydrogen release. If all of the aluminum reacts, it releases large quantities of H_2 but produces 4,675 Btu/lb. The latter reaction is similar to the super-corroding magnesium/iron now in production and thus represents no improvement, since both produce similar quantities of H_2. Without the H_2, the excess materials required to control the reaction make that formulation reactively uninteresting.

The hydration of magnesium chloride (Yukawa 1988) is initially encouraging, but when the weight of water is included this system is again no better on a weight basis than calcium oxide.

Magnesium-Iron Alloy Flameless Ration Heater

The best system developed to date is that of Kuhn et al. (1985). This system, used in the current flameless ration heater (FRH), uses the following reaction:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

The heat output of this reaction is 5,643 Btu/lb (dry weight), or roughly 1170 Btu/lb when the weight of water is included. This system uses a magnesium/iron alloy, in a matrix of high-density polyethylene (HDPE). The iron is required to increase the rate of reaction with water; normally magnesium reacts very slowly with water, due to the presence of an oxide coating on the surface, which prevents further reaction. The major problem with this system is the production of hydrogen gas. The FRH produces 9-10 L of hydrogen (at standard temperature and pressure) when used to heat one MRE. This volume of gas, which must be vented along with some of the steam produced by the heater, is an inconvenience for the user. While it is also a potential fire or explosion hazard, the FRH has been used safely in the field with minimal precautions.

The hydrogen production is, however, enough to discourage a company from producing a self-heating meal for the consumer market with the magnesium + water reaction. Consider what would happen if a functioning heater were placed in a microwave oven. [This seems likely to happen if millions of self-heating meals were sold in stores. Using the "more is better" logic, a consumer is likely to believe that if one heat source (the chemical heater) is good, then two heat sources are better.] Since the internal volume of a typical microwave oven is 0.8 ft^3 (23 L) and since the hydrogen produced is about 9 L, this could easily produce an explosive mixture: the lower explosive limit of hydrogen in air is 4.1% and the upper explosive limit is 74.1% (Sax and Lewis 1987). Any spark could then produce fire or an explosion.

In summary, our review of the previous systems indicated that there was potential for improvement in the reaction used in portable heat sources. A useful improvement would be similar in system weight to the magnesium + water reaction of the FRH, while reducing or eliminating hydrogen production, increasing user convenience, and reducing cost.

Identification of Reactions with Useful Heat Output

TDA screened a number of reactions for potential use as chemical heaters. We calculated the heat output based on thermodynamic heats of formation of the reactants and products. A usable reaction must also be satisfactory in terms of cost, safety, and other considerations, but the heat output was chosen for the initial screening, with further analysis to follow for the most interesting new exothermic reactions.

The screening initially calculated the heat output considering only the dry weight of reactant(s). This is the critical feature if the water used to activate the reaction comes from a local resource, and is not included in the package weight, as is the case with the current Mg-Fe alloy FRH. However, for reasons of user convenience, it is desirable to combine food, chemical heater and water in a single package; this is the configuration of the self-heating ration currently under development. The water is highly desirable to aid in heat transfer and to limit the temperature reached in the reacting mixture to the boiling point of water; it may also be a reactant in the chemical heater. For a comparison of heat output based on dry weight, the Mg/Fe reactant in the current FRH produces 5,643 Btu/lb. The hydration of calcium oxide, which has been used in a number of self-heating packages, produces 501 Btu/lb; the weight and bulk of calcium oxide required for a given heat output make it uninteresting for further development. To be of interest to us in this analysis, a reaction must have a substantially higher heat output, based on dry weight, than calcium oxide. Systems identified as interesting based on a heat output greater than 1,000 Btu/lb were examined in more detail; comparisons with the Mg/Fe alloy FRH, based on the weight of required water, were carried out for some promising new reaction systems.

The new systems are organized into five groups according to reaction type, and the results are shown in Tables A.1-A.5. In the first group, we considered reactions in which an active metal replaces a less active metal ion from solution. Second, we examined the solid phase reaction of an active metal with a less active metal oxide; the thermite reaction is an example of this process. In the third group are oxidation-reduction reactions; peroxides and other oxidizing agents were considered, with active metals or organic compounds as the reducing agents. The fourth group is the reaction of metal salts with water; while no hydrogen is produced, the heat output is typically lower than other reaction types. The last group is acid-base reactions; the best systems here have both acid and base present as a salt or oxide, i.e., an acidic or basic anhydride. Each group of reactions is discussed in order below. Note that although reactions that produce hydrogen were considered, they are excluded here because there is no reason to prefer any of these over the magnesium/water reaction of the FRH.

Table A.1 presents replacement reactions with ionic salts. Of the reactions considered, those with magnesium have higher energy densities than those with aluminum.

Table A.1 Metal ion replacement reactions.

Metal	Salt	Products	Heat Output Btu/lb*	Comments
Al	$CuCl_2$	$AlCl_3 \cdot 6\,H_2O$ + Cu	1,240	Releases HCl
Al	$Cu(C_2H_3O_2)_2$	$Al(C_2H_3O_2)_3$ (aq) + Cu	931	
Mg	$CuCl_2$	$MgCl_2 \cdot 6\,H_2O$ + Cu	1,569	Side reactions
Mg	$CuCl_2$	$MgCl_2$ (aq) + Cu	1,614	
Mg	$CuCl_2$	$MgCl_2$ (s) + Cu	1,182	
Mg	$Cu(C_2H_3O_2)_3$	$Mg(C_2H_3O_2)_3$ (aq) + Cu	1,112	
Mg	CuO + $CuCl_2$ + $Cu(C_2H_3O_2)_3$	$Mg(OH)_2$ (aq) + Cu + $MgCl_2$ (aq) + $Mg(C_2H_3O_2)_3$ (aq)	1,400	pH controlled to minimize H_2 evolution

*Weight of water not included.

Table A.2 presents thermite-type reactions with various oxides. Although these reactions are very energetic, they are difficult to control once initiated. Potentially the oxides could be used as a hydrogen scrubber where the hydrogen is produced by the reaction of magnesium or aluminum with water. As a separate reactor, the hydrogen would be reducing the oxide at a temperature around 100°C (212°F). At this temperature, hydrogen will not reduce iron, but will reduce copper oxide to the base metal, and will reduce

Table A.2 Thermite reactions.

Metal	Oxide	Products	Heat Release Btu/lb*	Comments
Al	CuO	Al_2O_3 + Cu	3,077	All thermite type reactions may be difficult to control
Al	Fe_2O_3	Al_2O_3 + Fe	1,491	
Al	MnO_2	Al_2O_3 + Mn	2,075	
Al	MnO_2	Al_2O_3 + MnO	1,784	
Mg	CuO	MgO + Cu	1,836	
Mg	CuO	$Mg(OH)_2$ + Cu	1,963	
Mg	NiO	MgO + Ni	1,573	

*Weight of water not included.

manganese to the monoxide (MnO), not the metal. However, the hydrogen reduction reactions are difficult to activate at the temperatures of interest. Thus, while such hydrogen-consuming reactions are thermodynamically favored, they would be very difficult to make work in practice.

Table A.3 presents oxidation-reduction reactions. There are a number of interesting reactions in this group. The oxidation of a magnesium or aluminum liberates large quantities of heat and the iodate, chlorate, and peroxides are efficient oxygen storage agents. The central issue is rate of reaction: it must be high enough to be useful, but explosion hazards must be avoided. Table A.3 indicates that hydrogen peroxide produces highly energetic systems, but the storage life of H_2O_2 is too short. This problem may be avoided by use of solid compounds containing active oxygen, such as calcium peroxide (CaO_2) and sodium perborate ($NaBO_3$ $4H_2O$). These materials have the effect of

Table A.3 Oxidation-reduction reactions.

Metal or organic	Oxidant (dry solid)	Products	Heat released Btu/lb.	Comments
Al	$NaIO_3$	$Al_2O_3 + NaI$	2,342	
Al	H_2O_2	$Al_2O_3 + H_2O$	4,713	Storage life
Al	KO_2	$KOH + Al_2O_3$	4,291	Vents H_2 & O_2
Al	$Na_2O_2 + AlCl_3$	$Al(OH)_3 + NaCl(aq)$	2,283	
Al	CaO_2	$Al(OH)_3 + Ca(OH)_2$	2,927	H_2 release
Al	$NaHCO_3 + Na_2O_2$	$Na_2CO_3 + Al(OH)_3$	1,237	H_2 release
Al	$KClO_3$	$Al(OH)_3 + KCl\ (aq)$	4,224	Explosion hazard
Al	Na_2CO_3 $1.5H_2O_2$	$Al(OH)_3 + H_2O + Na_2CO_3$	2,345	
Al	$NaBO_3$ $4H_2O$	$NaBO_2 + Al(OH)_3 + H_2O$	1,533	Water included
N.A.	H_2O_2	$O_2 + H_2O$	1,241	Storage life
CH_3OH	KO_2	$K_2CO_3 + H_2O$	2,358	Side reactions, explosion
C_2H_5OH	$Na_2O_2 + AlCl_3$	$Na_2CO_3(aq) + NACl(aq) + H_2O$	1,727	Side reactions, explosion
$HC_2H_3O_2 + 2\ H_2C_2O_4$	Na_2O_2	$Na_2CO_3 + H_2O$	1,769	Oxalic acid toxic
Mg	$NaIO_3$	$Mg(OH)_2 + NaI$	2,758	
Mg	$Na_2O_2 + AlCl_3$	$Mg(OH)_2 + Al(OH)_3$ $NaCl\ (aq)$	2,302	
Mg	BaO_2	$Ba(OH)_2 + Mg(OH)_2$	2,039	Barium toxic
Mg	CaO_2	$Ca(OH)_2 + Mg(OH)_2$	3,040	
Mg	$CaO_2 + 4\ H_2O$	$Ca(OH)_2 + Mg(OH)_2 + 2\ H_2O$	1,742	Water included
Mg	$NaBO_3$ $4H_2O$	$NaBO_2 + Mg(OH)_2 + 3H_2O$	1,643	Water included

storing oxidizing power equivalent to hydrogen peroxide in a solid form.

Table A.4 presents reactions of metal salts with water. These hydration reactions have been used in previous self-heating food containers, but their generally moderate heat release produces a food heater which is rather bulky and heavy.

Table A.5 presents acid-base neutralization reactions. Several compounds show promise of delivering reasonable quantities of heat. While acid-base reactions have previously been considered for food heaters, there is an inherent safety hazard in storing and transporting strong acids and bases. We recognized that this hazard could be minimized by using materials which are not strong acids or bases, but compounds which react with water to produce acidic and basic solutions. These solutions could then react with one another, yielding a neutral and non-hazardous product. For example, combining an acidic anhydride or salt [such as diphosphorus pentoxide (P_2O_5) or aluminum chloride ($AlCl_3$)] with a basic anhydride [such as calcium oxide (CaO)], yields a heat-producing reaction with neutral products. Heat is produced by the heat of hydration of both components, as well as the heat of the neutralization reaction. Thus the combination is not only safer, but has a higher energy output. The advantages of this approach have not been recognized in previous work on portable heat sources.

Table A.4 Reactions of metal salts with water.

Starting Reactants	Products	Heat Release Btu/lb*	Comments
CaO	$Ca(OH)_2$	501	
$AlCl_3$	$AlCl_3(aq)$	875	Releases HCl
$FeCl_3$	$FeCl_3(aq)$	345	
$MgCl_2$	$MgCl_2(aq)$	681	
$NaOH$	$NaOH(aq)$	463	Caustic NaOH
Na_2O	$NaOH(aq)$	1,650	
Na_2O_2	$NaOH(aq)$ + □ O_2	621	
$CaSO_4 \cdot ½ H_2O$	$CaSO_4 \cdot 2H_2O$	51	
$CaSO_4$	$CaSO_4 \cdot 2H_2O$	53	

*Weight of water not included.

Table A.5 Acid-base neutralization reactions.

Acid	Base	Products	Heat Release Btu/lb*
$AlCl_3$	$NaOH$	$Al(OH)_3 + NaCl$ (aq)	890
$AlCl_3$	MgO	$Al(OH)_3 + MgCl_2$(aq)	1,010
$FeCl_3$	MgO	$Fe(OH)_3 + MgCl_2$ (aq)	630
P_2O_5	MgO	$Mg_3 (PO_4)_2$ (s)	846
$AlCl_3$	Na_2O	$Al(OH)_3 + NaCl$ (aq)	1,678
$AlCl_3 \cdot 6H_2O$	Na_2O	$Al(OH)_3 + NaCl$ (aq)	617
$NaHCO_3$	Na_2O	Na_2CO_3(aq)	538
$FeCO_3$	Na_2O	Na_2CO_3(aq) + FeO	647
$FeCl_3 \cdot 6H_2O$	Na_2O	$Fe(OH)_3 + NaCl$(aq) + H_2O	1,004
$HC_2H_3O_2$	Na_2O	$NaC_2H_3O_2$(aq) + H_2O	1,125
B_2O_3	Na_2O	$NaBO_2$(aq)	1,165
B_2O_3	Na_2O	$Na_2B_4O_7$(c)	876
P_2O_5	Na_2O	Na_3PO_4(aq)	1,683
P_2O_5	Na_2O	Na_2HPO_4(aq)	1,554
$(CH_3CO)_2O$	Na_2O	$NaC_2H_3O_2$(aq)	1,080
P_2O_5	CaO	$Ca_3(PO_4)_2$(s)	1,035
$FeCl_3$	CaO	$Fe(OH)_3 + CaCl_2$ (aq)	625
$AlCl_3$	CaO	$Al(OH)_3 + CaCl_2$(aq)	1,016
$C_4H_4O_3$	CaO	$CaC_4H_2O_3$	759
$H_2C_2O_4$	CaO	$CaC_2H_2O_4$(aq) + H_2O	629
$(CH_3CO)_2O$	CaO	$Ca(C_2H_3O_2)_2$(aq)	696

*Weight of water not included.

Conclusions. An initial screening of potential reactions for chemical heaters identified several systems of interest. The reactions selected for further investigation had a heat output high enough to be of interest, and no obvious insurmountable problems with toxicity, reactive hazards, or cost. These materials may present attractive alternatives to the present magnesium-iron alloy ration heater if they increase user convenience and safety (by eliminating hydrogen production) with acceptable cost, weight and other properties. The reactions are listed below.

		Heat Released Btu/lb	
1.	Oxidation-reduction reactions		
	Mg (or Al) + CaO_2	3,040	(2,927)
	Mg (or Al) + $NaIO_3$	2,758	(2,342)
	Mg (or Al) + $NaBO_3 \cdot 4H_2O$	1,643	(1,533)
2.	Metal ion replacement reactions		
	Mg + $CuO/CuCl_2/Cu(C_2H_3O_2)_2$	1,400	
3.	Acid-base reactions		
	$B_2O_3 + Na_2O$	1,165	
	$P_2O_5 + Na_2O$	1,683	
	$AlCl_3 + Na_2O$	1,678	
	$FeCl_3 + Na_2O$	1,004	
	$AlCl_3 + CaO$	1,016	
	$P_2O_5 + CaO$	1,035	

All of these reactions would be activated by adding water or a solution to a solid. It was not apparent that any of these materials could be used to produce a formulation that released heat in the desired 10-minute time frame (and not too fast or too slow). This initial screening was intended to eliminate those compounds and reactions that would not be of interest given their heat release. Of the reactions listed above, those involving Na_2O and $NaIO_3$ were eliminated by a cost analysis. In Phase I, based on further analysis and experiments, TDA identified the formulations P_2O_5/CaO and $AlCl_3/CaO$ as the most promising. In Phase II both of these reactions were investigated, with P_2O_5/CaO proving to be preferable. Heaters were successfully prepared using this material.

References

Bretherick, L. (1990). *Handbook of Reactive Chemical Hazards*, 4th ed. London, England: Butterworths.

Budavari, S. (1989). *Merck Index*, 11th ed. Rahway, NJ: Merck & Co.

Dean, J.A. (1985). *Lange's Handbook of Chemistry*, Thirteenth edition. New York: McGraw-Hill.

Kuhn, W.E., K.H. Hu and S.A. Black (1985). *Flexible Electrochemical Heater*, U.S. Patent No. 4,522,190.

Labrousse, B.L.P.E. (1988). *Single-use Heat Transfer Packaging for Drinks, Foodstuffs and Medicaments*, U.S. Patent No. 4,753,085.

Okamoto, T., T. Sunagawa and S. Sato (1989). *Self-Heating Container*, U.S. Patent No. 4,819,612.

Perry, R.H., D.W. Green and J.O. Maloney (1984) *Perry's Chemical Engineers Handbook*, Sixth Edition. New York: McGraw-Hill.

Ryan, E.C. and R.E. Reed (1963). *Heating Device*, United States Patent No. 3,7079,911.

Sax, N. I. and R. J. Lewis (1987). *Hazardous Chemicals Desk Reference*. NY: Van Nostrand Reinhold.

Sax, N.I. and R.J. Lewis (1988). *Dangerous Properties of Industrial Materials*, 7th ed. NY: Van Nostrand Reinhold.

Yukawa, H. (1988). *Container for Self-heating or Self-cooling of Drinks or Foodstuffs by an Exothermic or Endothermic Reaction*, U.S. Patent No. 4,751,119.

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Appendix B: Product Regulatory Assessment

PRODUCT REGULATORY ASSESSMENT

IC Project No. 06104556

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INTRODUCTION

TDA Research, Inc. (TDA) contracted Industrial Compliance (IC) to conduct a regulatory assessment and assist in the preparation of a Material Safety Data Sheet (MSDS) for a product that TDA is currently developing. The purpose of this assessment is to identify the potential regulations that may regulate the product and to provide information to TDA concerning development of a MSDS for the product.

The product that TDA is currently developing is an improved heat source to be used for heating military rations. TDA provided IC with two possible formulations for the heat source. Both formulations pair a basic anhydride (calcium oxide) with an acidic material (either aluminum chloride or phosphorus pentoxide). The calcium oxide, aluminum chloride, and phosphorus pentoxide all react exothermically with water; consequently, the heat source is designed to be activated by water. Additionally, based on information provided by TDA, other materials including a surfactant (Paranox 100, Exxon Paramines Division) and a polymer (Pulplus from DuPont) may be added to control the rate of heat production.

SCOPE OF WORK

The purpose of this investigation is to conduct a regulatory assessment and assist in the preparation of a MSDS for the chemical heating source used in the product.

IC performed the following services for this assessment:

*Review of the following federal regulations:

-Resource Conservation and Recovery Act (RCRA);
-Hazardous Materials Transportation ACT (HMTA);
-Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA);

- Clean Water Act (CWA);
- Toxic Substance Control Act (TSCA); and the
- Occupational Safety and Health Act (OSHA).

Individual state regulations that may be more stringent than the above listed federal regulations may pertain to the product. This assessment does not include an analysis and/or review of these potential specific state regulatory requirements.

* Assistance in the preparation of a MSDS for the product with respect to regulatory requirements including analytical testing requirements.

LIMITATIONS

This report is prepared for the exclusive use of TDA and/or their assignees to aid in the assessment of the above mentioned product. IC performed services in a manner consistent with the level of care and expertise exercised by members of the environmental auditing/risk assessment profession. No warranties, expressed or implied, are made except as stated herein and in accordance with the scope of work presented above.

IC's assessment is limited strictly to identifying potential regulatory requirements and assistance in the preparation of a MSDS for the heating source product in accordance with the Scope of Work presented above.

Results are based on the analysis and review of the above listed federal regulations by IC personnel. All conclusions and recommendations regarding the potential regulatory requirements of the heating source represent the professional opinions of the IC personnel involved with the project, and the results of this report should not be considered a legal interpretation of existing environmental regulations. IC assumes no responsibility or liability for errors in the information provided by TDA, any public data utilized, statements from sources outside of IC, or developments resulting from situations outside the scope of this project.

REGULATORY ASSESSMENT

IC reviewed federal environmental regulations to evaluate the potential regulatory requirements that may regulate the chemical heating source. The federal regulations reviewed include the Resource Conservation and Recovery Act (RCRA); the Clean Water Act (CWA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); the Toxic Substance Control Act (TSCA); Hazardous Materials Transportation Act (HMTA); and the Occupational Safety and Health Act (OSHA).

Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA), promulgated in 1976, regulates ongoing generation, transportation, storage, and disposal of hazardous wastes; and regulates storage of non-hazardous material in underground storage tanks (USTs). RCRA lists specific hazardous wastes and defines the processes for which waste may be classified as hazardous based on the characteristics of ignitability, corrosivity, reactivity, or toxicity. Facilities generating hazardous wastes are required to notify the Environmental Protection Agency (EPA), handle wastes properly, maintain records of wastes produced or shipped, and dispose of wastes at a RCRA-permitted treatment, storage, or disposal (TSD) facility. RCRA regulations are codified in Title 40 of the Code of Federal Regulations Parts 261 through 280 (40 CFR Parts 261-280).

A waste may be classified as a hazardous waste if it is a listed hazardous waste as identified in 40 CFR Part 261 Subpart D or meets the criteria for a characteristic hazardous waste as identified in 40 CFR Part 261 Subpart C. Based on review of the chemical constituents of the heating source, the heating source and/or its constituents are not listed as hazardous wastes. RCRA's definition of a characteristic reactive hazardous waste includes any material that "..reacts violently with water." It is currently unknown if the heating source is classified as a characteristic reactive hazardous waste, either before or after use. If the heating source is classified as a characteristic reactive hazardous waste for disposal purposes, the heating source will have to be handled and disposed of as a hazardous waste in accordance with RCRA. Based on the water reactive nature of the chemicals in the heating source, the heating source has the potential to be classified as a characteristic reactive hazardous waste if disposed of in its normal state, before use.

Recommendation

IC recommends that the heating source be analyzed in its normal state before use, and after use, to determine if at the time of disposal the heating source would be classified as a characteristic hazardous waste under RCRA. This would include submitting a sample of the heating source to an accredited laboratory that would analyze the sample for ignitability, corrosivity, reactivity, and toxicity as defined under RCRA.

Clean Water Act

The Clean Water Act (CWA) establishes water quality standards, waste water effluent standards, facility operations requirements, and waste water discharge permit requirements to protect wetlands and waters of the United States. Waste water discharges to waters of the United States are permitted under the National Pollutant Discharge Elimination System (NPDES). The Safe Drinking Water Act (SDWA) amendments to the CWA establishes primary and secondary drinking water standards to protect existing and potential beneficial use of ground waters.

The individual heating sources do not appear to be regulated under the CWA. However, the manufacturing process for the sources may have waste water discharges that may be regulated under CWA. The manufacturing process for the sources is currently unknown; however, the process may require a discharge contribution agreement, for waste water discharges to the sanitary sewer system NPDES waste water discharge permit, and/or stormwater discharge permit.

Recommendations

IC recommends that at the time of manufacturing, the manufacturer should evaluate the manufacturing process to determine if any discharge agreements and/or permits are required under the CWA. Currently, the heat source is not being manufactured, and no additional testing is required at this time.

Toxic Substance Control Act

The Toxic Substances Control Act (TSCA) regulates new and existing chemicals in commerce. The Act provides for premanufacture review of new chemicals prior to production, development of product data and risk assessment information to evaluate chemical toxicity, and establishment of recordkeeping and reporting systems to monitor distribution of chemicals in commerce. Additionally, the Act regulates "Significant New Uses" of existing chemicals to evaluate potential new risk assessment information. Additionally, TSCA regulates the management and disposal of a variety of chemicals that pose an imminent hazard to human health and the environment, the most notable of which include polychlorinated biphenyls (PCBs) and asbestos. TSCA regulations are codified in 40 CFR Parts 700-end.

Review of the chemicals involved in the possible formulations of the heating source indicates that there are no new chemicals involved in the heating source. Additionally, the use of the chemicals involved in the heating source does not appear to constitute a significant new use of the chemicals involved. However, it is required that the EPA make this determination.

Recommendations

To ensure compliance with TSCA, IC recommends TDA, as developer of the product, contact the EPA to verify that the heating source does not constitute a significant new use of the chemicals involved.

Comprehensive Environmental Response, Compensation, and Liability Act

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) provides regulatory authority to the EPA to investigate and remediate releases to the environment of oil, hazardous substances, pollutants, or contaminants, which may present an imminent or substantial danger to public health or welfare. The National Oil and Hazardous Substances Pollution Contingency Plan (NCP) under CERCLA establishes the regulatory framework and responsibilities for efficient, coordinated, and effective response to releases of oil, hazardous substances, pollutants, or contaminants. CERCLA regulations are codified in 40 CFR Parts 300-399.

The Superfund Amendments and Reauthorization Act of 1986 (SARA), also known as the Emergency Planning and Community Right-to-Know Act, revises and extends the authorities established under CERCLA of 1980. SARA Title III regulations, codified in Title 40 CFR Parts 350 - 372, impose requirements for emergency planning and emergency notification reporting upon facilities that have "extremely hazardous substances" present on site above "threshold planning quantities". Industrial facilities that "use, process, or manufacture" a toxic chemical in amounts above the threshold quantity must submit reports documenting releases of the toxic chemicals to the environment.

Review of the regulations indicates that under CERCLA, phosphorus pentoxide is considered an extremely hazardous substance with a reportable quantity (RQ) of one pound. In the event a sufficient quantity of the heating sources to equal one pound or greater of phosphorous pentoxide are "spilled", the spill must be reported as a release of phosphorous pentoxide to the environment. Additionally, phosphorus pentoxide has a threshold planning quantity of ten pounds; therefore, if ten pounds or more of phosphorus pentoxide are stored at a facility, the facility is subject to the emergency planning notification and inventory reporting requirements of SARA Title III. These requirements include notifying the Local Emergency Planning Commission (LEPC), and the State Emergency Response Commission (SERC). There are no Form R reporting requirements for phosphorous pentoxide.

Additionally, calcium oxide is a listed chemical on the OSHA Hazard Communications listing of chemicals. There is no reportable quantity or threshold planning quantity for calcium oxide; therefore, it is not subject to release or emergency planning notification. However, if the quantity of calcium oxide stored on site exceeds 10,000 pounds, calcium oxide is subject to the inventory reporting requirements of the Community Right-to-Know Act, which includes notifying the LEPC and SERC. There are no Form R reporting requirement for calcium oxide.

Recommendations

Upon manufacture of the heating source, IC recommends that TDA evaluate its materials management practices and develop procedures to ensure compliance with CERCLA and SARA Title III reporting requirements.

Hazardous Materials Transportation Act

The Hazardous Materials Transportation Act (HMTA) provides standards for transportation of hazardous materials in commerce to protect public health and safety of property. "In commerce" extends to all activities that affect interstate transportation. The HMTA regulations, codified in Title 49 CFR Parts 171 - 179, cover all modes of transportation (highway, railroad, air, and water) and require, among other things, proper marking, containerization, storage, shipping papers, and placarding. The HMTA regulations are administered by the U.S. Department of Transportation (DOT). The two formulations and their potential status under HMTA regulations are presented below.

Calcium Oxide and Phosphorus Pentoxide Formulation

The DOT lists both calcium oxide and phosphorus pentoxide as hazardous materials. Each of these chemicals have their own particular DOT shipping name. Because the heating element contains both of these chemicals as a mixture, the DOT shipping names for calcium oxide and phosphorus pentoxide cannot be used. A shipping name must be used that describes the hazardous component that comprise the heating element. The most appropriate DOT shipping name is:

Corrosive solids, n.o.s., 8, PG II, UN 1759 (calcium oxide & phosphorus pentoxide)

Another alternative to consider when establishing a shipping name for this product, is how the product will be packaged and shipped. Regulations codified in 49 CFR Subpart A Part 173.4, Exemptions for Small Quantities, lists the criteria for exempt hazardous materials. The exemptions state that small quantities of class 3, division 4.1, division 5.1, and division 5.2 materials; class 8, Division 6.1 materials; class 7 materials; and class 9 materials that also meet the definition of one or more of these hazard classes, are not subject to any other requirements of this subchapter.

The calcium oxide and phosphorus pentoxide are class 8 materials. If the maximum quantity of material per inner receptacle is limited to thirty (30) grams (i.e., 1 ounce) for authorized solids, other than Division 6.1 Packing Group I, materials; the material may be shipped as a non-regulated material. The product would also have to meet the other packaging requirement set forth under the exemptions for small quantities.

Calcium Oxide and Aluminum Chloride Formulation

Both chemicals in this formulation are DOT corrosive materials. The proper DOT shipping name is:

Corrosive solids, n.o.s., 8, PG III, UN 1759 (calcium oxide & aluminum chloride)

The small quantity exemption (discussed in detail in the previous formulation) can also be applied to this formulation.

Recommendations

Upon manufacture of the heating source, IC recommends that TDA contact the DOT to confirm the labeling and packaging requirements for transporting the heating sources.

Occupational Safety and Health Act

The TDA formulation includes two possible acid-base reactions. Manufacturing operations can vary widely depending on the number and the nature of the specific processes, materials, equipment involved and facility design. Accordingly, numerous different OSHA General Industry Standards may be applicable. Since the product produced involves two combinations of three different starting materials that are all corrosive and toxic, some of the general safe manufacturing requirements would include the following:

* Minimize contact between the employees and the chemicals through enclosures or isolation of the processes.
* If manufacturing activities result in generation of airborne particulates or vapors, provide local exhaust ventilation equipped with suitable filters.
* Store bulk chemicals in the original or other appropriate containers separate from incompatible materials. Storage areas should be cool, dry, and well ventilated.
* Keep containers tightly sealed and away from moisture and inspect periodically. Follow chemical manufacturer's recommendations for shelf life of bulk chemicals.
* Employees should avoid breathing dusts and contact with these materials without wearing appropriate protective clothing and other personal protective equipment. This would include eye and face protection, gloves, coveralls or aprons, and foot protection. If there is a high probability of skin contact, impervious clothing should be worn.
* Contaminated clothing should be removed immediately and decontaminated.
* Employees should wash thoroughly after handling these materials.

- Work areas should be decontaminated periodically to avoid accumulation of materials on equipment, surfaces, etc.
- Quick drench or safety showers and eyewashes should be located in proximity to the workplace operations.
- Employees should be thoroughly trained in handling of these materials and in the usage of personal protective equipment. All personal protective equipment should be maintained in a sanitary and reliable condition.
- A process hazard analysis should be performed.
- Standard operating procedures should be developed and available at the workplace.
- Employees should be trained in accident prevention.
- Employees should be trained in spill containment and other control measures and responding to leaks, fires, equipment failure, etc. A written hazard communication program would need to be developed and implemented to comply with all requirements of 29 CFR 1910.1200.
- When effective engineering controls for controlling airborne occupational exposures are not feasible, or while they are in the process of being instituted, appropriate and approved respiratory protection is required. A written respiratory protection program would need to be developed and implemented to comply with all requirements in 29 CFR 1910.134.
- Employees should be monitored initially and periodically to evaluate potential occupational exposures.

Additionally, the general safety requirements would include a thorough inspection and evaluation of the following equipment, processes, and work areas for compliance with OSHA Standards:

- Loading areas and docks
- Exits and other wall openings
- Stairs, ramps, walkways, platforms and floors
- Material storage areas
- Electrical wiring and equipment grounding
- Illumination
- Human factors
- Mechanical material handling equipment
- Heating, ventilation, and air conditioning systems
- Boilers, pipes, tanks and other pressure equipment
- Fire control and suppression systems
- Machine safety guarding
- Waste disposal
- Machinery and tools

MATERIAL SAFETY DATA SHEET ASSESSMENT

In accordance with the OSHA Hazard Communication Standard, codified in 29 CFR Part 1910.1200, a manufacturer of a chemical product is required to provide a Material Safety Data Sheet (MSDS) for any chemical product that it manufactures. OSHA provides minimum requirements and guidelines for what information must be included in the MSDS. IC reviewed the MSDS's for the chemical constituents of the heating source and reviewed the chemical reactions involved to evaluate what further information is needed to satisfy the MSDS requirements of the Hazard Communication Standard for the heating source.

Pursuant to 29 CFR Part 1910.1200 (d) and (g), if a mixture has not been tested as a whole, the mixture is assumed to exhibit the same health hazards as its constituents. Therefore, since the heating source has not been tested as a whole to determine the specific health hazards, the heating source is assumed to exhibit the same health hazards as its constituents (i.e., phosphorus oxide, aluminum chloride, calcium oxide). As noted above, IC reviewed the MSDSs for the constituents which were provided by TDA. Below is additional and updated information for the products.

Aluminum Chloride - $AlCl_3$

Synonyms. Aluminum trichloride, trichloroaluminum

Composition/Information on Ingredients

Component	Aluminum chloride
CAS Number	7446-70-0
OSHA PEL	*2 mg/M^3 8 Hr.TWA
ACGIH TLV	*2 mg/M^3 8 Hr. TWA

*The Permissible Exposure Limit (PEL) and the Threshold Limit Value (TLV) are based on exposure limits established for the soluble salts of aluminum as Al.

Concentrations that are Immediately Dangerous to Life or Health (IDLH) have not been determined.

Hazards Identification

Aluminum chloride is a highly corrosive material and is an irritant to the eyes, skin, and respiratory system. Routes of entry into the body include inhalation, ingestion, and contact. Target organs include respiratory system, skin and eyes. Exposure to respiratory system may result in severe irritation and lung injury. Ingestion can result in cramping, vomiting, and hemorrhagic gastroenteritis. Contact with skin may result in severe skin irritation and burns. Eye exposures may produce irritation and burns. This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be immediately irrigated with large amounts of water for at least 30 minutes, occasionally lifting the upper and lower lids. An ophthalmologic consultation should be obtained immediately.

Skin Exposure. Remove clothing contaminated with material. Irrigate affected skin areas with large amounts of water for at least 15 minutes or longer depending on the concentration, quantity, and duration of exposures. Get medical attention if irritation persists. Rapid removal of the material from the skin is very important to lessen the possibility of injury.

Inhalation. Move victim to fresh air and, if breathing difficult, or irritation continues, get medical attention immediately.

Ingestion. Medical attention should be obtained immediately.

Fire Fighting Measures

Fire may produce highly toxic hydrogen chloride gas.

Aluminum chloride is a non-flammable solid but will react violently with water. For small fires, use dry chemical or CO_2. For large fires, flood fire area with water from a distance. Apply cooling water to sides of containers exposed to flames. Do not direct a solid stream of water onto the spilled material or in container. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be worn before entering area.

Accidental Release Measures

Do not touch or walk through spilled material. For small dry spills, shovel material into a clean, dry container and cover loosely. Fully encapsulating, vapor protective clothing should be worn for spills and leaks with no fire. Use water spray to reduce vapor. Do not put water directly on a leak, spill area, or inside container. Cleanup only under supervision of trained personnel.

Handling and Storage

Handling. Avoid breathing dust and do not get into eyes, skin, or clothing. Protective clothing should be worn if there is any possibility of skin or eye contact. Avoid contact with water and other incompatible materials.

Workers should wash affected areas immediately if skin becomes contaminated with material. Non-impervious clothing should be removed immediately if contaminated. Workers should change clothing after work if there is any reasonable probability that clothing has become contaminated.

Dust on equipment surfaces and floors should be collected by industrial vacuum systems designed for use with this material. Refer to personal protective equipment section. Eyewashes and quick drench facilities or safety showers should be provided in proximity to workplace operations.

Storage. Material should be stored in a cool, dry area and protected from moisture, rain and direct sunshine. Material containers should be tightly closed. Storage in buildings equipped with sprinkler fire protection systems is not recommended.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers. Air contaminated dust should be passed through appropriately designed pollution control equipment before being discharged to the atmosphere. Laboratory usage should be performed in fume hoods.

Eye Protection. Safety goggles and/or faceshields should be worn if there is any probability of eye or facial contact.

Hand and Body. Chemically resistant gloves, protective clothing, and footwear should be worn if there is any probability of skin contact. If exhaust ventilation or engineering controls do not eliminate dusty atmospheres, full protective clothing should be worn in dusty atmospheres.

Respiratory protection. Airborne concentrations should be maintained below exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	White granular crystals
Molecular Weight	133.34
Odor:	Strong odor of hydrogen chloride
Boiling Point:	183°C
Melting Point:	190°C at 2.5 ATM
Density/Specific Gravity:	2.44
Heat of Combustion:	No data
Heat of Vaporization	No data
LEL/UEL	N/A
Vapor Pressure:	1 mm Hg at 100°C
Solubility in Water:	Freely soluble in water
Solubilities:	Some organic solvents and alcohols
pH:	No data
Flash Point:	Non-flammable solid

Stability

Material will absorb moisture from air.

Reactivity

Material will react violently with water with liberation of heat and hydrogen chloride.
The material is incompatible with alcohols, alkali hydroxides, carbonates, borax, and lime.

No hazardous polymerization will occur.

Calcium Chloride - $CaCl_2$

Synonyms. Calcium dichloride

Composition/Information on Ingredients

Component	Calcium chloride
CAS Number	10043-52-4
OSHA PEL	*15 mg/M^3 8 Hr.TWA
ACGIH TLV	*10 mg/M^3 8 Hr. TWA

* A PEL and TLV have not been established for this substance. The concentrations listed are for particulates not otherwise classified (PNOC) or regulated, total dust fraction.

IDLH concentrations have not been determined.

Hazards Identification

Routes of entry into the body include inhalation, ingestion, and contact. Inhalation can result in irritation, cough, tachypnea, and wheezing. Ingestion can result in nausea, vomiting, diarrhea, irritation and hemorrhage. Contact with skin or eyes may cause swelling, redness and pain.

This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be irrigated promptly with large amounts of water. Get medical attention if any irritation continues.

Skin Exposure. Dust off affected skin areas promptly and flush areas with water.

Ingestion. Medical attention should be obtained promptly.

Inhalation. Move victim to fresh air and, if breathing is difficult, or irritation continues get medical attention immediately.

Fire Fighting Measures

No data on hazardous combustion or decomposition products.

Calcium chloride is a non-flammable solid. Use water, dry chemical, carbon dioxide, or foam to extinguish fires. Cool fire-exposed containers with water. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be worn before entering area.

Accidental Release Measures

Isolate area and deny entry to unnecessary or unprotected personnel. Contain leak or spill and shovel material into clean, dry container and cover. Avoid creating dust in spill-affected areas.

Handling and Storage

Handling. Avoid breathing dust and do not get into eyes, skin, or clothing. Protective clothing should be worn if there is any possibility of skin or eye contact.

Workers should wash affected areas promptly if skin becomes contaminated with material.

Workers should change clothing after work if there is any reasonable probability that clothing has become contaminated.

Dust on equipment surfaces and floors should be collected by industrial vacuum systems designed for use with this material. Refer to personal protective equipment section. Eyewashes and quick drench facilities or safety showers should be provided in proximity to workplace operations.

Storage. Material should be stored in sealed containers and in a well ventilated space.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers. Air contaminated with dust should be passed through appropriately designed pollution control equipment before being emitted to the atmosphere. Laboratory usage should be performed in fume hoods.

Eye Protection. Safety glasses, goggles, or face shield should be worn if there is any probability of eye contact.

Hand and Body. Rubber gloves should be worn when handling any calcium chloride product. Coveralls or rubber raincoat and rubber or well oiled shoes should be worn if there is any probability of skin contact.

Respiratory protection. Airborne concentrations should be maintained below exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	Colorless granules, flakes, or powder
Molecular Weight	110.99
Odor:	None
Boiling Point:	1935°C
Melting Point:	772°C
Density/Specific Gravity:	2.152 at 15°C
Heat of Combustion:	No data
Heat of Vaporization	235.1 kJ/mole
LEL/UEL	N/A
Vapor Pressure:	No data
Solubility in Water:	Freely soluble in water
Solubilities:	Acetone, alcohol, and acetic acid
pH:	8.0 to 9.0 aqueous solution
Flash Point:	Non-flammable solid

Stability

The material will absorb moisture from air.

Reactivity

The material reacts violently with water and generation of heat.

The material forms flammable gases and evolves hydrogen when reacted with zinc.

The material reacts violently with bromine trifluoride.

The material is incompatible with furan-2-peroxycarboxylic acid.

Violent polymerization occurs when the material is mixed with methyl vinyl ether.

Calcium Hydrogen Phosphate - $CaHPO_4$

Synonyms. Bicalcium phosphate, calcium acid phosphate, calcium hydrogen orthophosphate, calcium monohydrogen phosphate, calcium phosphate, dicalcium orthophosphate, monocalcium acid phosphate, monocalcium orthophosphate, phosphoric acid, calcium salt

Composition/Information on Ingredients

Component	Calcium hydrogen phosphate
CAS Number	7757-93-9
OSHA PEL	*15 mg/M^3 8 Hr.TWA
ACGIH TLV	*10 mg/M^3 8 Hr. TWA

* A PEL and TLV have not been established for this substance. The concentrations listed are for particulates not otherwise classified (PNOC) or regulated, total dust fraction.

IDLH concentrations have not been determined.

Hazards Identification

Routes of entry into the body are inhalation and ingestion. Inhalation of dust may result in irritation of the upper respiratory tract. Acute single ingestion of calcium salts may produce mild gastrointestinal distress. Solid particles may cause transient eye irritation.

This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be irrigated promptly with large amounts of water. Get medical attention if any irritation continues.

Skin Exposure. Dust off affected skin areas promptly and flush areas with water.

Ingestion. Medical attention should be obtained promptly.

Inhalation. Move victim to fresh air and, if breathing difficult, or irritation continues, get medical attention immediately.

Fire Fighting Measures

No data on hazardous combustion or decomposition products.

Calcium hydrogen phosphate is a non-flammable solid. Extinguish fire with any agent suitable for the type of surrounding fire. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be donned before entering area.

Accidental Release Measures

Do not walk through spilled material. Shovel material into clean, dry container and cover.

Handling and Storage

Container should be kept closed when not in use. Dusty operations may require exhaust ventilation to minimize airborne concentrations.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers to minimize airborne concentration levels. Air contaminated with dust should be passed through appropriately designed pollution control equipment before being emitted to the atmosphere. Laboratory usage should be performed in fume hoods.

Eye Protection. Use safety glasses with side shields. Use goggles if eye contact is likely.

Hand and Body. For brief contact, no precautions other than clean clothing should be needed.

Respiratory protection. Airborne concentrations should be maintained below exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only a NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	White crystalline powder
Molecular Weight	136.06
Odor:	None
Boiling Point:	No data
Melting Point:	No data
Density/Specific Gravity:	2.31
Heat of Combustion:	No data
Heat of Vaporization	No data
LEL/UEL	N/A
Vapor Pressure:	No data
Solubility in Water:	Practically insoluble
Solubilities:	Soluble in dilute HCl, HNO_3, and acetic acids
pH:	No data
Flash Point	Non-flammable solid

Stability and Reactivity

The material is stable under normal conditions.

Hazardous polymerization will not occur.

No data is presently available on the reactivity.

Aluminum Hydroxide - $Al(OH)_3$

Synonyms. Alpha-alumina trihydrate, alumigel, alumina hydrate, alumina trihydrate, aluminum hydrate, aluminum oxide hydrate, aluminum oxide trihydrate, aluminum trihydrate.

Composition/Information on Ingredients

Component	Aluminum hydroxide
CAS Number	21645-51-2
OSHA PEL	*15 mg/M^3 8 Hr.TWA
ACGIH TLV	*10 mg/M^3 8 Hr. TWA

* A PEL and TLV have not been established for this substance. The concentrations listed are for particulates not otherwise classified (PNOC) or regulated, total dust fraction.

IDLH concentrations have not been determined.

Hazards Identification

Routes of entry into the body are by inhalation and ingestion. Inhalation of dust may result in irritation of the upper respiratory tract. Ingestion of large amounts can result in diarrhea, constipation, distention and/or obstruction with perforation such as that observed with prolonged or excessive antacid administration. Prolonged contact with material may irritate skin.

This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be irrigated promptly with large amounts of water. Get medical attention if any irritation continues.

Skin Exposure. Dust off affected skin areas promptly and flush areas with water.

Ingestion. Medical attention should be obtained promptly.

Inhalation. Move victim to fresh air and, if breathing difficult, or irritation continues, get medical attention immediately.

Fire Fighting Measures

No data on hazardous combustion or decomposition products.

Aluminum hydroxide is a non-flammable solid. Extinguish fire with any agent suitable for the type of surrounding fire. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be donned before entering area.

Accidental Release Measures

Do not walk through spilled material. Shovel material into clean, dry container and cover.

Handling and Storage

Container should be kept closed when not in use. Dusty operations may require exhaust ventilation to minimize airborne concentrations.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers. Air contaminated with dust should be passed through appropriately designed pollution control equipment before being emitted to the atmosphere. Laboratory usage should be performed in fume hoods.

Eye Protection. Use safety glasses with side shields. Use goggles if eye contact is likely.

Hand and Body. Coveralls or aprons and chemically resistant gloves should be worn if skin contact is probable.

Respiratory protection. Airborne concentrations should be maintained below exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	White powder, balls, or granules
Molecular Weight	77.99
Odor:	None
Boiling Point:	No data
Melting Point:	300°C
Density/Specific Gravity:	2.42
Heat of Combustion:	No data
Heat of Vaporization	No data
LEL/UEL	N/A
Vapor Pressure:	No data
Solubility in Water:	Practically insoluble
Solubilities:	Alkaline solutions, HCl, H_2SO_4, other strong acids
pH:	No data
Flash Point:	Non-flammable solid

Stability

Material will form gel on prolonged contact with water. Absorbs acids and carbon dioxide.

Reactivity

The material is spontaneously flammable in air at 170 to 210 °C when coprecipitated with bismuth hydroxide and reduced by hydrogen.

Hazardous polymerization will not occur.

Calcium Oxide - CaO

Lime, Calcium Monoxide, Calxyl, Calx, Calcia, Quicklime, Unslaked Lime.

Composition/Information on Ingredients

Component	Calcium Oxide
CAS Number	1305-78-8
OSHA PEL	5 mg/M^3 8 Hr. TWA
ACGIH TLV	2 mg/M^3 8 Hr. TWA

IDLH concentrations have not been determined.

Hazards Identification

Calcium oxide is a highly caustic material and is an irritant to the eyes, skin and respiratory system.

Routes of entry into the body include inhalation, ingestion, and contact. Target organs include respiratory system, skin, and eyes. Exposure to respiratory system may result in breathing harshness due to a pulmonary obstruction (stridor), difficulty in breathing (dyspnea), and pulmonary edema. Oral ingestion may result in burns to the lips, tongue, oral mucosa, and esophagus. Gastrointestinal exposures may produce spontaneous emesis, abdominal pain and difficulty in swallowing (dysphagia). Contact with skin may result in severe skin irritation, burns and dermatitis. Direct contact with the eye may result in severe eye injury (such as distortion of cellular membranes, the loss of corneal, conjunctival and lens epithelium and loss of endothelium of the cornea and blood vessels).

This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be immediately irrigated with copious amounts of water for at least 30 minutes. An ophthalmologic consultation should be obtained.

Skin Exposure. Remove clothing contaminated with material. Irrigate affected skin areas with copious amounts of water for at least 15 minutes or longer depending on the concentration, quantity, and duration of exposures.

Ingestion. Medical attention should be obtained immediately.

Inhalation. Move victim to fresh air and if breathing is difficult or irritation continues get medical attention immediately.

Fire Fighting Measures

No data on hazardous combustion or decomposition products.

Calcium oxide is a non-flammable solid. For small fires use dry chemical, CO_2, halon, water spray, or standard foam. For large fires use water spray, fog, or standard foam as recommended. If water is used, flood area with large amounts to absorb the heat generated. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be donned before entering area.

Accidental Release Measures

Do not touch spilled material without proper protective equipment. Avoid generating dust. For small dry spills, shovel material into clean, dry container and cover. For small liquid spills, use sand or other noncombustible absorbent material and place into containers for later disposal. For large liquid spills, contain material with dikes, dams, etc. far ahead of spill for later disposal. All spill areas should be ventilated and washed after cleanup.

Handling and Storage

Handling. Avoid breathing dust and do not get into eyes, skin, or clothing. Protective clothing should be worn if there is any possibility of skin or eye contact. Avoid contact with water and other incompatible materials.

Workers should wash affected areas promptly if skin becomes contaminated with material. Non-impervious clothing should be removed immediately if contaminated. Workers should change clothing after work if there is any reasonable probability that clothing has been contaminated.

Dust on equipment surfaces and floors should be collected by industrial vacuum cleaners. Refer to personal protective equipment section. Eyewashes and quick drench facilities or safety showers should be provided.

Storage. Material should be stored in tightly closed containers to avoid absorbing carbon dioxide and water from air or surrounding operations. Containers should be stored in a dry and well ventilated area away from acids and other incompatible materials and inspected periodically.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers. Air contaminated with lime dust should be passed through cyclones, filters, or scrubbers before emitted to the atmosphere. Laboratory use should be performed in fume hoods.

Eye protection. Safety goggles should be worn if there is any probability of eye contact.

Hand and body. Chemically resistant gloves, protective clothing, and footwear should be worn if there is any probability of skin contact. If exhaust ventilation or engineering controls do not eliminate dusty atmospheres, full protective clothing should be worn in dusty atmospheres.

Respiratory protection. Airborne concentrations should be maintained below exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	White or grayish white lumps or granular powder
Molecular Weight	56.08
Odor:	None
Boiling Point:	2850° C
Melting Point:	2572° C
Density/Specific Gravity:	3.32-3.35
Heat of Combustion:	No data
Heat of Vaporization	No data
LEL/UEL	N/A
Vapor Pressure:	No appreciable vapor pressure
Solubility in Water:	1 gram in 840 ml water
Solubilities:	Acids, glycerol, sugar solution
pH:	Saturated water solution is about 12.5
Flash Point:	Non-flammable solid

Stability

Calcium oxide readily absorbs carbon dioxide and water from air becoming airslaked.

Calcium oxide crumbles on exposure to moist air.

Reactivity

Calcium oxide will form calcium hydroxide in water and generate large quantities of heat.

Calcium oxide reacts violently with phosphorus pentoxide when initiated by local heating.

Calcium oxide reacts violently with liquid hydrofluoric acid.

Calcium oxide reacts with chlorine trifluoride and fluorine.

Material swells after contact with water and may burst containers.

No data is presently available on polymerization reactions.

Phosphorus Pentoxide - P_2O_5

Synonyms. Diphosphorus pentaoxide, diphosphorus pentoxide, phosphoric acid anhydride, phosphoric acid, anhydrous, phosphoric oxide, phosphorus oxide

Composition/Information on Ingredients

Component	Phosphorus pentoxide
CAS Number	1314-56-3
OSHA PEL	Not listed
ACGIH TLV	Not listed

AIHA Hygienic Standard for permissible exposure is 1 mg/M^3.

IDLH concentrations have not been determined.

Hazards Identification

Phosphorus pentoxide is a highly corrosive material due to its dehydrating action and is an irritant to the eyes, skin, and respiratory system.

Routes of entry into the body are inhalation, ingestion, and contact. Target organs include respiratory system, skin, and eyes. Exposure to respiratory system may result in irritation, pulmonary edema, and lung injury. Oral ingestion may result in burns to the mouth, throat, esophagus, and stomach. Gastrointestinal exposures may produce nausea, vomiting, abdominal pain, bloody diarrhea, acidosis, and shock. Contact with skin may result in severe skin irritation, burns, and dermatitis. Eye exposures may produce irritation and burns of the lids and eyelid linings.

This material is not regulated by OSHA or listed by IARC or NTP as a carcinogen.

First Aid Measures

Eye Exposure. The exposed eyes should be immediately irrigated with copious amounts of water for at least 30 minutes, occasionally lifting the upper and lower lids. An ophthalmologic consultation should be obtained immediately.

Skin Exposure. Remove clothing contaminated with material. Irrigate affected skin areas with large amounts of water for at least 15 minutes or longer depending on the concentration, quantity and duration of exposures. Get medical attention if irritation persists.

Ingestion. Medical attention should be obtained immediately.

Inhalation. Move victim to fresh air and, if breathing difficult or irritation continues get medical attention immediately.

Fire Fighting Measures

No data on hazardous combustion or decomposition products.

Phosphorus pentoxide is a nonflammable material and does not support combustion, but will react violently with water. For small fires use dry chemical or CO_2. For large fires flood fire area with water from a distance. If large quantities of combustibles are involved, use flooding quantities of water as spray or fog. Do not get solid stream of water on the spilled material. Only properly trained personnel should engage in fire suppression techniques. Appropriate personal protective equipment and clothing must be donned before entering area.

Accidental Release Measures

Do not touch or walk through spilled material without proper protective equipment. For small spills, shovel material into clean, dry container and tightly seal. Avoid generating any dust or contact with water. Material may be neutralized with crushed limestone, soda ash, or lime. Fully encapsulating impermeable clothing should be worn for large spills with no fire. Do not use water directly on material itself. Cleanup of large spills should only be performed under the supervision of trained personnel.

Handling and Storage

Handling. Avoid breathing dust and do not get into eyes, on skin, or clothing. Protective clothing should be worn if there is any possibility of skin or eye contact. Avoid contact with water and other incompatible materials.

Workers should wash affected areas immediately if skin becomes contaminated with material. Non-impervious clothing should be removed immediately if contaminated. Workers should change clothing after work if there is any reasonable probability that clothing has been contaminated.

Dust on equipment surfaces and floors should be collected by industrial vacuum systems designed for use with this material. Refer to personal protective equipment section. Eyewashes and quick drench facilities or safety showers should be located close to workplace operations.

Storage. Phosphorus pentoxide must be stored in a tightly sealed container and a waterproof building. The building should be elevated and separated from other storage areas. The building should conform to the construction requirements for hydrogen storage. The building should be well ventilated, cool, and kept dry.

Exposure Controls/Personal Protection

Dusty operations should be enclosed and equipped with local exhaust ventilation or isolated from workers to minimize airborne concentration levels. Air contaminated with dust should be passed through appropriately designed pollution control equipment before being discharged to the atmosphere. Laboratory usage should be performed in fume hoods.

Eye protection. Safety goggles and/or faceshields should be worn if there is any probability of eye or facial contact.

Hand and body. Chemically resistant gloves, protective clothing and footwear should be worn if there is any probability of skin contact. If exhaust ventilation or engineering controls do not eliminate dusty atmospheres, full protective clothing should be worn.

Respiratory protection. Airborne concentrations should be maintained below occupational exposure limits through safe work practices or exhaust ventilation. When respiratory protection is required for certain operations, use only NIOSH/MSHA approved full facepiece respirator if air concentrations exceed the allowable or recommended exposure limits or when working in areas with limited ventilation. The selection of respirator type will depend upon maximum use concentrations required.

Physical and Chemical Properties

Physical Form:	White powder
Molecular Weight	141.96
Odor:	No data
Boiling Point:	Sublimes at 360° C
Melting Point:	340° C
Density/Specific Gravity:	2.39
Heat of Combustion:	No data
Heat of Vaporization	No data
LEL/UEL	N/A
Vapor Pressure:	1 mm Hg at 384°C
Solubility in Water:	Very soluble in water
Solubilities:	Sulfuric acid
pH:	No data
Flash Point:	Non-flammable solid

Stability

The material absorbs moisture from air to form phosphoric acid.

Reactivity

Phosphorus pentoxide reacts violently with calcium oxide or sodium hydroxide when initiated by local heating.

The material reacts violently with water and alcohols to evolve heat.

Reaction of phosphorus pentoxide and sodium carbonate ignited by local heating can generate high temperatures.

Chlorine trifluoride produces a violent reaction without flame in the presence of phosphorus pentoxide.

May produce anhydrous perchloric acid from either its salts or its aqueous solution by heating with high boiling acids and dehydrating agents such as phosphorus pentoxide.

The material reacts with ammonia, hydrogen fluoride, oxygen difluoride, potassium, sodium, perchloric acid and chloroform solution.

The material may react with phosphorus trichloride and water.

No data is presently available on polymerization reactions.

ACRONYMS

CAS	Chemical Abstract Services
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
ACGIH	American Conference of Governmental Industrial Hygienists
TLV	Threshold Limit Value
IDLH	Immediately Dangerous to Life or Health
NIOSH	National Institute for Occupational Safety and Health
MSHA	Mine Safety and Health Administration
IARC	International Agency for Research on Cancer
NTP	National Toxicology Program
AIHA	American Industrial Hygiene Association
TWA	Time Weighted Average

Recommendations

When the final formulation has been determined, IC recommends that TDA further evaluate the toxic characteristics of the heating source, and conduct tests of the chemical and physical properties of the heating source to complete information for the MSDS. The chemical and physical properties testing should be conducted by an accredited analytical laboratory.

Toxicity Testing

Animal tests are a legitimate source of information concerning the possible toxic effects of a chemical or mixture of chemicals in humans. However, in the case of TDA's proposed product, there is little additional knowledge that could be gained from animal testing. In particular, it is unnecessary to test the toxicity of a chemical in animals when adequate human data exist to evaluate the toxicity of a chemical to humans. For example, it is already known that the chemical byproducts of the reacted product have little toxic potential in humans. Aluminum hydroxide is a common constituent of antacids and relatively large doses of aluminum are tolerated over chronic time periods. Although calcium chloride is known to be somewhat irritating to the human gastrointestinal tract, oral doses have been recommended in treating persons with hypocalcemia (low blood calcium) (Goodman and Gilman's *The Pharmacological Basis of Therapeutics*, 6th edition). Thus, there is no useful knowledge to be gained from animal tests of the reaction byproducts.

The unreacted product could cause physical injury if misused. For example, an individual attempting to ingest the unreacted product would probably burn the inside of the mouth as the material reacted with moisture in a typical acid base type reaction liberating heat. However, the likelihood that an individual would accidentally ingest the material and retain the material in the mouth until the reaction is complete seems highly unlikely. We are unaware of animal testing methods that have been designed or used to examine such a problem. It may be possible to determine the amount of tissue injury resulting from the complete reaction of the material in the mouth by measuring the BTUs produced from the reaction and measuring the amount of thermal energy that would be transmitted to the tissue.

Physical/Chemical Testing

In order to complete information for the MSDS, the following chemical and physical properties of the heating source should be evaluated.

Reactivity
Solubility in Water
Solubility in Other Solvents
pH
Appearance/Color/Form
Odor
Density/Specific Gravity
Decomposition Products
Autoignition Temperature
Melting Point/Boiling Point/Decomposition Temperature/Sublimation Temperature
Specific Heat
Heat of Combustion

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Appendix C: Material Safety Data Sheet

MATERIAL SAFETY DATA SHEET

Name:
TDA Ration Heater

Effective Date: December 6, 1995
Supersedes:

TDA Research, Inc.
12345 West 52nd Avenue, Wheat Ridge, CO 80033-1916
(303) 422-7819; fax (303) 422-7763

Section 1. IDENTIFICATION

Product Name: TDA Ration Heater
Primary Components: Phosphoric anhydride (phosphorus pentoxide, P_2O_5)
Calcium oxide (quicklime, CaO)
inert ingredients (trade secret)

Section 2. INGREDIENTS AND ASSOCIATED HAZARDS

Component	CAS #	Weight %
Phosphoric Anhydride	1314-58-3	25-50
Calcium Oxide	1305-78-8	25-50
Inert materials	--	2-20

- This product is irritating to the eyes, skin and mucus membranes.
- Risk of serious damage to eyes. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- Danger! Causes Burns. Reacts with water to generate heat and phosphoric acid.
- Reaction with water can generate sufficient heat to ignite materials that burn.
- Avoid breathing dust.

The following table provides NFPA data for the two active ingredients and the highest value found in each category for any of the inert materials.

National Fire Protection Association Hazardous Materials Identification System			
	P_2O_5	CaO	Inert materials
Health	3	1	1
Fire	0	0	1
Reactivity	2	1	1
Special	~~W~~		
4 = Extreme/Severe 3 = High/Serious	1 = Slight 0 = Minimum		

National Fire Protection Association Hazardous Materials Identification System			
	P_2O_5	CaO	Inert materials
2 = Moderate		~~W~~ = Water Reactive	

The only component of the TDA ration heater listed under the Superfund Amendments and Reauthorization Act (SARA) is P_2O_5.

SARA Title III Hazard Classification	
Acute Health	Yes
Chronic Health	No
Fire	No
Sudden release of Pressure	No
Reactive	Yes

SECTION 3. **PHYSICAL AND CHEMICAL PROPERTIES**

Appearance and Odor: Light to dark brown pellet or spheroid. Mild Odor.

Specific Gravity: approx. 2.6
Solubility in Water: <1
(g/100 g H_2O, for solution obtained after mixing heater material and water in 1:4 weight ratio)
pH @ 25°C 5-9
(for solution obtained after mixing heater material and water in 1:4 weight ratio)
Vapor Pressure (mm Hg): <1
Volatile by Weight % <1

SECTION 4. **FIRE-FIGHTING MEASURES**

Flash point (°C) >180 (inert materials); noncombustible (active ingredients)
Flammable Limits in Air Lower: No data Upper: No Data
Autoignition Temperature (°C)>180

Extinguishing Media: Carbon dioxide, foam, or dry chemicals are recommended.

Wear self-contained breathing apparatus (SCBA) and complete personal protective equipment when potential for exposure to vapor or products of combustion exist. Some dense smoke may be generated while burning. Carbon monoxide, carbon dioxide and other oxides may be generated as products of combustion.

Special firefighting procedures:

Heat generated by water contact can ignite nearby combustibles and generate frothing. If water must be used, the amount should be large enough to overcome heat buildup. Water may be used to cool nearby containers exposed to heat or flame.

Unusual fire and explosion hazards: Materials may form some phosphoric acid; phosphoric acid in contact with common metals may generate flammable and explosive hydrogen gas.

SECTION 5. **HEALTH HAZARD DATA/FIRST AID INFORMATION**

TOXICITY: No toxicity data available.

CARCINOGENICITY: This product does not contain any ingredient designated by IARC, ACGIH, or OSHA as a probable human carcinogen.

If ingested, this product may cause severe burns of the mouth, throat, esophagus, and digestive tract. Skin contact may cause burns, and irritation to the skin. Inhalation may cause irritation of the respiratory tract, and may be damaging to the mucus membrane of the upper respiratory tract. Eye contact may cause burns and irritation.

MEDICAL CONDITIONS THAT MAY BE AGGRAVATED: Skin irritation in persons with existing skin lesions. Breathing of dust may aggravate acute or chronic asthma or other chronic pulmonary disease.

EMERGENCY FIRST AID PROCEDURES:

Eyes: In case of eye contact, immediately flush eyes with copious amounts of water, including under the lids for at least 15 minutes. **GET IMMEDIATE MEDICAL ATTENTION**. If no physician is immediately available, flush for an additional 15 minutes.

Skin: In case of skin contact, wipe away excess material with a dry cloth, wash skin with soap and plenty of water for at least 15 minutes. **Get medical attention**.

Inhalation: If inhaled, remove patient to fresh air. If not breathing, administer cardiopulmonary resuscitation or artificial respiration. If breathing is difficult or irritation develops, administer oxygen. **Get Medical Attention**.

Ingestion: If swallowed, if victim is conscious and alert, give two or more glasses of milk or water. Do not induce vomiting. If vomiting does occur, give fluids again. Since swallowing is painful, flushing the mouth with water is often the only and best immediate therapy. NEVER give anything by mouth to an unconscious or convulsing patient. **GET IMMEDIATE MEDICAL**

ATTENTION.

SECTION 6. STABILITY AND REACTIVITY

The heater is designed to produce heat when activated by water. Reaction with water can generate sufficient heat to ignite materials that burn. Can react violently generating heat, phosphoric acid, and steam with explosive force. The inert components of the heater are incompatible with strong oxidizing agents.

Materials to Avoid: barium sulfide, formic acid, hydrogen fluoride, iodides, methyl hydroperoxide, oxygen difluoride, 3-propynol, boric oxide, and fluorine.

Hazardous combustion or decomposition products: CO, CO_2, H_3PO_4

Hazardous Polymerization: Will not occur.

SECTION 7. ACCIDENTAL RELEASE/DISPOSAL MEASURES

Accidental Release: Persons involved in clean up should wear appropriate protective equipment. Ventilate spill area if possible. Always wear respiratory and skin protection when handling spilled material. To the extent possible, clean up spillage, using shovels, or sweeping. Avoid generating dust. Place material in appropriate covered disposal container. Flush residual material to drain with plenty of water. Small amounts may be disposed of by adding slowly to a large excess of stirred water. Neutralize, collect solids residue and flush liquid to drain.

Disposal: The heater must be activated before disposal. After activation with water, the heater does not contain any materials that are classified as hazardous waste based on characteristics of ignitability, corrosivity, reactivity, or toxicity. After activation the heaters are suitable for disposal in a sanitary landfill. Dispose of in accordance with local, state, and federal regulations.

SECTION 8. HANDLING AND STORAGE

Store material in sealed containers, in a cool, dry place. Keep containers away from flammable materials and exercise caution to protect containers from physical damage. Avoid prolonged contact with skin. Avoid exposure to strong oxidizing agents and water.

SECTION 9. EXPOSURE CONTROLS/PERSONAL PROTECTION

Appropriate protective equipment should be used during the following procedures:

- Manufacture or formulation of this product.
- Repair and maintenance of contaminated equipment.
- Clean up of leaks and spills.
- Any activity with potential for hazardous overexposure.

Respiratory protection: Provide ventilation and local exhaust. When dusty conditions exist, an approved NIOSH/MSHA dust/mist respirator may be needed. Always wear a self-contained breathing apparatus in an emergency situation.

Protective clothing: During cleanup of accidental spills, wear full-body protective clothing, rubber gloves and boots.

Eye protection: Face shield with chemical worker goggles.

Other: Work area should have a sink, safety shower and eyewash fountain.

SECTION 10. **TRANSPORT INFORMATION**

These heaters contain materials that are classified by the U.S. Department of Transportation as corrosive solids and whose transportation is regulated. No regulatory classification has been assigned by the Department of Transportation at this time.

SECTION 11. **REGULATORY INFORMATION**

No regulatory information is available for this heater. Some components are regulated under the Toxic Substances Control Act (TSCA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Superfund Amendments and Reauthorization Act (SARA).

SECTION 12. **OTHER INFORMATION**

The above information is believed to be correct, but does not purport to be all inclusive and shall be used only as a guide. TDA Research, Inc., shall not be held liable for any damage resulting from handling or from contact with the above product when used other than as intended.