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# APPLICATIONS OF NEW CHEMICAL HEAT SOURCES

## PHASE 1

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Report developed under Small Business Innovative Research (SBIR) contract. This project has examined the application of new chemical heat sources, with emphasis on portable heaters for military field rations. We conducted a comprehensive literature survey, aided by a computerized search, and also generated a large number of candidate reactions from fundamental chemical principles. We also evaluated the reaction currently used in the Flameless Ration Heater (FRH) for purposes of comparison. A disadvantage of the FRH is that it produces flammable hydrogen gas. By a process of elimination, using data on materials costs, reaction rate studies, and calorimetry to measure heat output, we selected the best reactions for ration heaters. The best materials identified are the combination of aluminum chloride with calcium oxide (AICI3/CaO) and diphosphorous pentoxide with calcium oxide (P2O5/CaO). Either can provide the same heat as the FRH with a small increase in weight, and does not produce any hydrogen. Our overall conclusion is that the new materials here identified for ration heaters have the potential to produce a heater which is more convenient and less hazardous (by avoiding the production of hydrogen), while significantly lowering the cost.

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RATION HEATERS
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RATION HEATING
HEAT SOURCES
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## Preface

This project performed by TDA Research under contract # DAAK60-91-C-0054 examined ways in which the application of new chemical heat sources could benefit the military. We have specifically considered the use of portable heat sources for military field rations, since this is an important and high-volume application. Our evaluation began with a comprehensive literature survey, aided by a computerized search, and also generated a large number of candidate reactions from fundamental chemical principles. We also evaluated the reaction currently used in the Flameless Ration Heater (FRH) for purposes of comparison. By a process of elimination, using data on materials costs, reaction rate studies, and calorimetry to measure heat output, we selected the best reactions for ration heaters. We concluded that an opportunity exists to improve on the performance of the FRH in two ways: (a) by lowering the cost of the heater through use of new materials, and (b) eliminating the hydrogen produced by the FRH, which will increase user convenience and safety.

The best materials identified for a ration heater are the combination of aluminum chloride with calcium oxide ($AlCl_3/CaO$) and diphosphorus pentoxide with calcium oxide ($P_2O_5/CaO$). Either can provide the same heat as the FRH with a small increase in weight, and does not produce any hydrogen. The most convenient arrangement for the user is a Self-Heating Ration (SHR), including both the heat-producing solid and an activator solution; pulling a tab allows the activator solution to mix with the solid, producing heat when needed. The best choice for the activator solution, as determined by weight and cost analysis and by experiments, is water with calcium chloride ($CaCl_2$).

A systems analysis compared a Self-Heating Ration using one of the new materials we identified with one using the hydrogen-producing reaction in the FRH. With the new materials the SHR is 6.0% heavier and 2.4% larger in volume. We assigned a cost penalty of roughly one cent per unit for the additional weight and volume due to increased transport costs. The cost of materials is essentially the same for the new reactions and for the materials used in the FRH, but the fabrication costs should be much less for the new materials, resulting in a lower cost product. The new materials are self-neutralizing for safety, and the used material does not present a disposal problem.

Our overall conclusion is that the new materials here identified for ration heaters have the potential to produce a heater which is more convenient and less hazardous (by avoiding the production of hydrogen), while significantly lowering the cost.

# APPLICATIONS OF NEW CHEMICAL HEATERS

## Summary

We examined a large number of reactions which could potentially be used in portable heat sources. We considered reactions with substantial heat output, as calculated from thermodynamic heats of formation. Materials with obvious safety problems were not considered in this initial screening. We then calculated the weight of material required and selected reactions with the highest heat output per unit weight. Next we determined the costs of the materials used in each reaction, and selected those with satisfactory materials costs for further tests. We carried out experiments to determine which reactions occurred at a useful rate. We carried out calorimetry on the best reactions to measure their heat output. Using the heat output we calculated the weight and volume of heaters using the new reactions, and compared them to the current FRH. We also estimated transport and storage costs for self-heating rations using the new heaters.

We found that a heater using the reaction of water with either a mixture of aluminum chloride and calcium oxide ($AlCl_3/CaO$) or a mixture of diphosphorus pentoxide and calcium oxide ($P_2O_5/CaO$) has a weight and volume only slightly higher than a heater using the magnesium/water reaction of the FRH, and produces no hydrogen. From our estimates of costs for materials, processing, transport and storage, we find that the new heaters should be less expensive then heaters using the magnesium/iron reaction of the current FRH. We conclude that the new materials TDA has identified would be useful as a heater for the SHR. Compared to the current FRH, the new materials have a small increase in weight and volume, eliminate the venting of hydrogen (which increases user convenience and safety) and may have significantly lower cost.

Another energy source originally identified as potentially of value in portable heat sources is the aluminum-air battery. This battery uses the reaction of aluminum metal with oxygen from the air to produce electric power. The aluminum-air battery has a high energy density, and produces non-toxic end products. In our analysis of this battery for a ration heater, we determined that its power output is not sufficient to warm food in the required time. We concluded that the Al-air battery is desirable where electric power is essential, or for low-power heating applications (such as a boot heater), but would be too high in weight and volume, and probably too expensive for a ration heater.

We also found, in agreement with past practice, that the best mode of activation for a ration heater is the addition of water or an aqueous solution. This is a convenient way to initiate the reaction, using water or solution available locally or contained in the food package. The water serves to enhance heat transfer from the reacting materials to the food container, both by direct contact and by evaporation/condensation. If the activating liquid is to be packaged with the meal, it should contain an antifreeze so that it remains liquid at all temperatures (if the solution freezes, it cannot flow to mix with the other reactants and start the heater). We evaluated both propylene glycol and calcium chloride as antifreezes. Based on the cost of the antifreeze, the weight and volume of the solution, we found that calcium chloride was preferred. Materials evaluated in this project were tested both with water and with a calcium chloride solution. The calcium chloride worked well in all cases. It also produces a small increase in boiling point, which is useful in increasing the rate of heat transfer from the heat source to the food container.

## Introduction

Everyone likes a good, hot meal. As the level of stress a person experiences increases, so to does the benefit from a meal of familiar foods presented in a convenient way. The Army wants to provide hot meals to troops in the field to increase their physical and mental well-being and enhance their effectiveness. For large groups, meals are provided through field kitchens. For small groups or individuals, field kitchens are not feasible, and other means must be found. Camp stoves can be used to cook for small groups and individuals, but they are not as convenient as desired. Providing a fuel supply, getting the stove lit under all conditions, and cooking over the camp stove are all quite feasible, but require time and effort that detract from the soldiers' main mission: they are in the field to fight, not to cook.

The best solution from the soldier's point of view would be a meal that cooks itself when the soldier is ready to eat. To do this, a flameless heat source is needed which can easily be activated to warm the food. There have been a number of materials introduced over the years to provide such a portable heat source, and development of new products is continuing. The Army has used a flameless heat source for the Meal, Ready-to-Eat (MRE), and is now developing a new meal, the Self-Heating Ration (SHR) which will incorporate a flameless heat source. In this project, TDA Research, Inc. (TDA) has carried out analysis and experiments to determine the best heat source for the SHR.

The heater currently used for the MRE 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 ($H_2$). This product, the Flameless Ration Heater (FRH) is conveniently activated by the addition of water, and produces heat over 5-10 minutes, which is satisfactory for the intended use. The FRH is also light in weight and non-toxic. Its major technical disadvantage is that it produces substantial quantities of hydrogen, a flammable gas. This is both an inconvenience to the user and a potential fire or explosion hazard. A heat source which costs less to produce than the FRH would be a significant improvement, 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 cost, low 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.

No self-heating food packages are generally available in this country, although several are available and others under development in other countries, most notably in Japan. A commercial self-heating food package would benefit the military by simplifying future procurements. It appears that such a commercial product will require an improved heater. Particularly with the current concern about product liability, no company is likely to invest in commercialization of the hydrogen-producing FRH.

In Phase I, TDA carried out a systematic evaluation to identify reactions for use in a portable heat source. We started with a comprehensive literature review, aided by a computerized search, and also generated a large number of candidate reactions from fundamental chemical principles. By a process of elimination, using cost data, reaction rate studies, and heat production measurements, we arrived at two new materials for a ration heater. The new materials can eliminate the hydrogen produced by the FRH, and should be significantly less expensive to manufacture than the FRH. A systems analysis demonstrated that self-heating rations using the new materials would be only slightly higher in weight and volume. We concluded that the new materials have useful potential, and we propose to develop these materials in Phase II.

## Opportunity

An opportunity exists for the development of improved heat generating materials for a portable heater. The ideal portable heater would contain reactive materials which are easily activated to produce heat in a controlled manner, without the need for a stove, fire, or electrical power. The portable heaters could be used to heat food or beverages, to warm emergency supplies (such as blood plasma), to warm personal equipment in cold weather (such as boots or gloves), to maintain performance of portable electronic equipment in cold weather, or to serve as an infrared beacon, signal or decoy.

The Army would benefit from a portable heater for field rations which was lower in cost and which did not produce flammable hydrogen gas (as the current portable heater does). A significant opportunity also exists for the development of self-heating meals for civilian consumers. When such materials are developed and self-heating meals become readily available, this will simplify procurement for the military. It will also generate significant new business in the packaged foods industry. Once the materials for self-heating foods are developed and tested, they will likely be introduced to the U.S. market. Most of the current development in self-heating food packages is in Japan (Sacharow 1991). Thus, an opportunity exists to develop materials for self-heating foods and beverages before the Japanese or other international competitors have perfected the process.

## Phase I Objectives

The overall objectives of the Phase I work were to identify chemical reactions with useful energy output, identify problems which could be solved by the application of these reactions, and carry out an analysis of the effectiveness of each new chemical heat source in its best application.

1. Supporting these overall objectives were the following specific objectives:

2. Identify reactions with significant potential as heat sources and useful applications of the reactions.

3. Carry out systems analysis of the reaction/application to determine the feasibility of the process.

4. Carry out a system safety analysis to identify and assess potential hazards to the user in applications incorporating the new chemical heat sources.

The questions we answered in Phase I were:

1. What problems can be solved by application of new chemical heat sources?

2. How effective are these chemical heat sources?

3. What is the cost of the new technology relative to current devices?
4. What are the logistic and environmental impacts of the new heat sources?
5. What are potential hazards of the new heat sources?

## Organization of the Report

Following this introduction, we discuss the background to this project, including system requirements and reactions previously used in heaters. We discuss the approach used in our evaluation of new reactions, including selection criteria, apparatus and methods. Section 0 contains results and discussion. We discuss the systems analysis, including estimates of weight, volume and cost of self-heating rations and summarize conclusions.

## Background

In this section we review the reasons for using a chemical energy source for heating food, the requirements for a portable heat source for food or beverage heating, and reactions 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. Here portable stoves are often 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. The problems associated with carrying a fuel supply, and with filling and lighting the stove, are not severe. 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 can reduce that time because it is much more convenient for the users, leaving them both well fed and rested, and ready to be about their next task.

## Requirements for Portable Heat Source for Food

If we want to use a portable heat source to heat food or beverage, what are the desirable features for the system? We list the following features as the most important:

1. It must be safe for the user.
2. It must be conveniently activated.
3. It must be low 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 that the food or other item is warmed in a short time, but without elevated temperatures which could cause undesirable changes in the taste of the food.

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

7. The heater must be stable in storage for an extended period of time, preferably more than 2 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, it could be locally available, and if it is only used for heating, it need not be potable water. However, as we noted above, the reason for using the portable heat source is not primarily to save weight but for convenience. The most convenient arrangement for the user is to have the activator solution packaged with the food and heater. All the user needs to do is pull a tab or otherwise open the solution container, mix the solution and reactants, wait until the food is warm, and eat.

In our analysis we have assumed that the heater will include an activator solution. We have considered not only the weight of the reactants but the weight of water consumed in the reaction (if any), plus some additional water to aid in heat transfer. It is also clear that the activator solution must not freeze in cold weather. We have therefore considered antifreeze additives, which are discussed in Section 0.

### Previous Commercial and Military Systems

With the above criteria in mind, we now examine previously reported reactions for portable heaters. From a survey of the literature, aided by a computerized search, we identified the reactions shown in Table 1. We note that 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 cheap 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; this condition is unacceptable.

Table 1, Reported Reactions for Chemical Heaters

| Reference | Reactants | $\Delta H^{o}_{rxn}$ kcal/mol | Heat output Btu/lb * | Comments |
|---|---|---|---|---|
| Charvin, 1989 and others | $CaO + H_2O$ | -15.95 | 501 | commonly used, low cost; high weight and bulk |
| Labrousse, 1988 | $SrO + H_2O$ | -21.78 | 322 | no advantage over CaO reaction |
| " | $BaO + H_2O$ | -52.92 | 302 | no advantage over CaO reaction |
| " | $KOH + H_2O$ | -13.77 | 442 | strong base |
| " | $NaOH + HCl$ | -23.99 | 565 | strong acid and base |
| " | $Mg(OH)_2 + HCl$ | -27.22 | 373 | strong acid |
| " | $CaO + HCl$ | -50.00 | 411 | strong acid |
| " | $Fe + O_2$ | -197.0 | 3,169 | difficult to control |
| Yukawa, 1988 | $MgCl_2 + H_2O$ | -38.13 | 721 | no strong acid or base |
| Benmussa, 1985 | $H_3PO_4 + KOH$ | -80.99 | 644 | strong acid and base |
| Okamoto, 1989 | $Fe + KMnO_4$ | -131.80 | 554 | No water req'd; $T_{max} > 1000°C$ |
| Ryan and Reed, 1963 | $Al/KClO_3/CaSO_4$ | --- | 1,058 | several reactions possible |
| Kuhn *et al.*, 1985 (Current FRH) | $Mg + H_2O$ | -84.88 | 5,643 | Produces hydrogen gas |

* weight of water not included

## Survey of Heater Reactions

Many of the 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.

## Metal-Air Heaters

The reaction of a metal with air produces large amounts of energy, and has seen practical application in hand-warmers (Labrousse 1988; $Fe + O_2$). Here a metal (such as iron) reacts with oxygen from the air to produce heat. The main difficulties with these materials are control of the rate of reaction and control of the maximum temperature reached. The rate of reaction depends on the surface area of the metal. This is at a maximum initially, and decreases as the reaction continues. Unless there is some provision to provide new surface area, the reaction rate will decrease steadily, when we would prefer a constant rate. A metal-oxygen heater also suffers from inefficient heat transfer from the heater to the food container. The only mechanism available for heat transfer is conduction through the porous solid and convection. Neither of these is likely to be satisfactory for the quantities of heat required to be transferred in a ration heater (150 Btu in <10 minutes).

A more serious difficulty which would be encountered with the $Fe + O_2$ or similar reactions, however, is controlling the maximum temperature achieved. If the temperature of the heater exceeds the melting point of the polypropylene tray containing the food at any point, then the heater will melt a hole in the tray, and the contents of the heater will mix with the food. This is not an acceptable circumstance. Given the quantities of heat involved, we believe it would be difficult if not impossible to avoid accidentally melting the container in some cases, unless water is provided to limit the temperature. With water present, the temperature cannot exceed 100°C (or slightly higher in the cases of a salt solution), assuring that the tray is not damaged by high temperatures. However, the metal-air reactions will not work if the metal is wet. Thus we do not believe that metal-air reactions will be practical for a ration heater given the quantity of heat required, the surface area and time available for its transfer to the food container, and the polypropylene construction of the container. Instead, we have focused on reactions which are activated by water, with the water both aiding in heat transfer and limiting the maximum temperature achieved.

## 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, we could easily exceed the lower explosion limit of hydrogen in air, 4.1% (Sax and Lewis 1987). Any spark could then produce fire or an explosion

The FRH is also relatively expensive at about $0.50/unit. Since the materials costs for a heater producing 150 Btu and using the magnesium/iron alloy of the FRH are only about $0.07/unit, it is clear that a large proportion of the cost is in materials processing. A system which required less complicated processing could result in a heater at substantially lower cost.

In summary, our review of the previous systems indicates that there is 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.

## Analytical Approach, Apparatus and Methods

To identify new reactions useful as portable heat sources and evaluate their potential, we first generated a large number of candidate reactions, and then carried out a selection process to choose the best candidates. The process had the following steps:

1. Consider the requirements of a chemical heat source to establish criteria for selection.
2. Review the literature to identify reported reactions.
3. Identify other reactions from fundamental chemical considerations; calculate the heat output based on thermodynamic heats of formation of the reactants and products. Reactants which were clearly unsafe were eliminated at this stage.
4. Select reactions with the highest heat output for further consideration.
5. Carry out cost analysis for the materials in each reaction. We used material cost data from manufacturer or published sources, and calculated the cost of materials for a given heat output. We selected the reactions with the lowest materials cost for further evaluation.
6. Measure reaction rates to determine whether the reaction occurs fast enough to be useful for a ration heater. This was done in a simple apparatus where the reactants were activated by addition of water or a solution, and the temperature was measured over time. We chose reactions which proceeded at a useful rate for further evaluation.
7. Measure reaction heat output to allow direct determination of the amounts required for a given heat output. This was done using a Parr solution calorimeter, in both water and calcium chloride solution.
8. Carry out systems analysis to estimate the weight and volume, storage and transportation costs, and materials and processing costs of heaters using the new reactions.

The apparatus and method used to measure the reaction rates and heat output are discussed below. The conclusions at each stage are described in Section 0, Results and Discussion.

### Reaction Rate Measurements

To estimate reaction rates, TDA assembled a simple apparatus to measure the reaction temperature *vs*. time. We called this an air calorimeter, since the reaction container was insulated by being surrounded by air (rather then vacuum, as in the Dewar used in a normal calorimeter). In this simple apparatus we could run reactions on a moderate scale, and get a good idea of what was working and what was not. The air calorimeter is shown in Figure 1.

For safety reasons, the initial experiment with each reaction set was carried out with a small quantity of material in a large test tube, situated behind a blast shield. The solid was placed in the test tube, and water was carefully added. Because of the possibility of an explosion, the water or solution was added while the experimenter was wearing heavy gloves. If the reaction looked satisfactory on this small scale, it was repeated on a larger scale using the air calorimeter.

The reaction mixture was placed in a round-bottom flask, and water or solution was added to start the reaction. For safety, we kept the calorimeter behind a blast shield at all times. We used amounts of solid and solution calculated to produce a 10 Btu output (where heating an MRE requires 125-150 Btu). In order to control the maximum temperature, approximately 175 g of glass beads (6-mm diameter) were added on top of the solid, to absorb much of the heat produced. The beads also acted to condense the steam that formed during the reaction, returning it to the solution in the calorimeter. The temperature was monitored with three thermocouples, which were recorded using a data acquisition program, *Control EG*, currently in use in several experiments at TDA. These three thermocouples monitored the temperature at the bottom of the calorimeter (in contact with the reactants, at the top of the glass beads, and outside the reactor for an ambient measurement. This allowed us to follow the change of temperature *vs.* time for all of these tests.

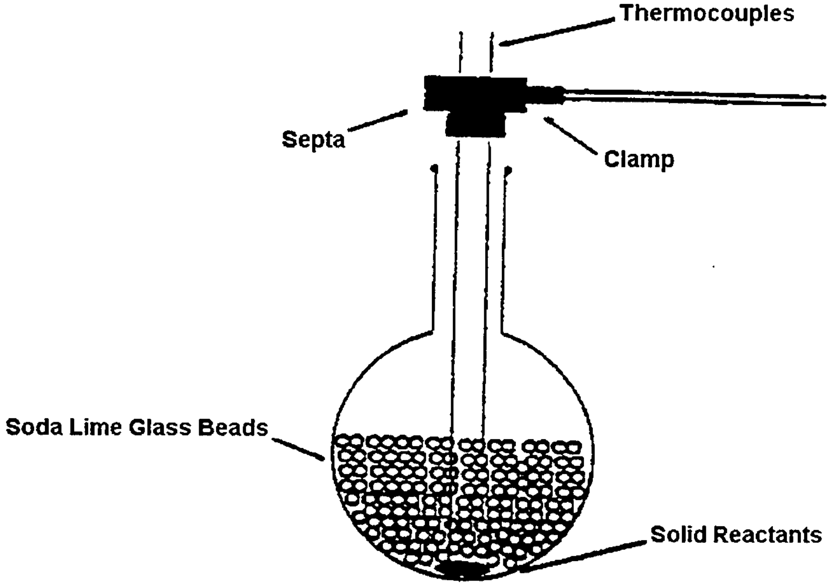


Figure 1, Schematic of air calorimeter used in reaction temperature measurements

Excess water, two to five times beyond that which is stoichiometrically necessary, was added to start the reaction as well as to assist in heat transfer. The stoichiometric amount of water in these experiments was typically less than 1.0 mL. When this amount of water was added there was a very limited reaction. It took a significant amount more to reduce or eliminate crust formation and get an adequate reaction. Therefore, the amount over and above the stoichiometric value was not kept constant, as the needs for the different reactions varied significantly. Some had limited crust formation with small quantities of water, and others required 2-4 mL, a significant excess.

Reactions that did not seem to produce heat, or which produced only a small amount, were not tried in the air calorimeter as they did not seem to be feasible reactions for a portable heat source. It was assumed that these reactions had kinetic limitations, even though they were thermodynamically favored. Reactions that were successful at this stage were evaluated by solution calorimetry, described below.

## Reaction Heat Output by Calorimetry

For these measurements, TDA purchased a Parr 1455 Solution Calorimeter. This instrument is used to measure the heats of solution or reaction for the systems under investigation. The Parr 1455 provides temperature data in digital form, and allows for computerized data acquisition. The calorimeter was interfaced to a Intel 80286-based IBM compatible computer. The 0-10V output from the thermistor was digitzed using a RTI-820 A/D-D/A board, and a STB-HL02 high level board, both manufactured by Analog Devices. The data acquisition program used was *Control EG* (Quinn-Curtis). Temperature data were taken at 1-second intervals and stored for further analysis. The data were then transferred into the Borland spreadsheet *Quattro* to determine net temperature change. The time-temperature curves could be printed from *Quattro* or from the Lotus graphics package *Freelance*, using a Hewlett-Packard LaserJet printer. A photograph of the calorimeter and computer is shown in Figure 2.

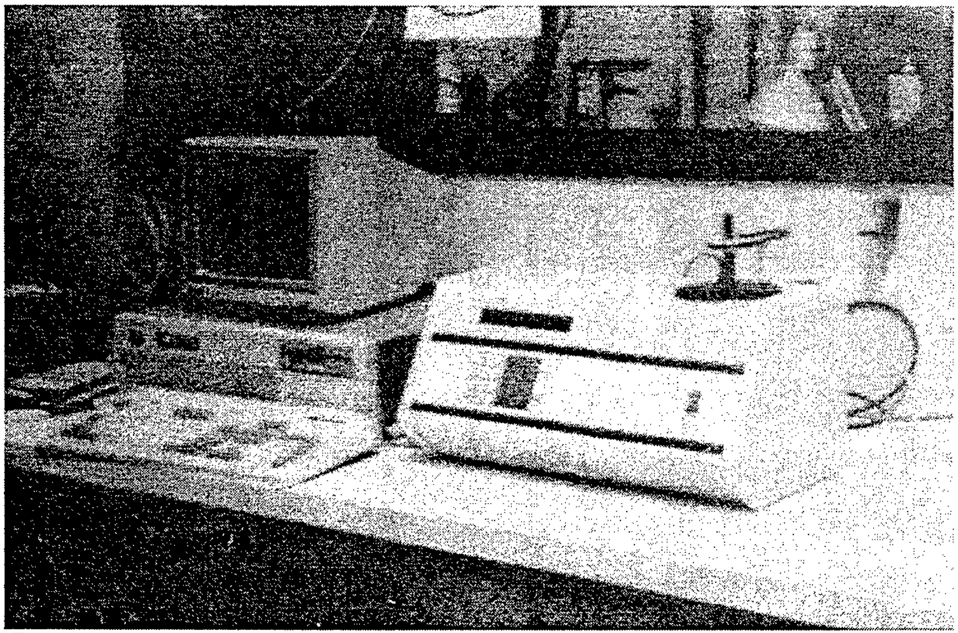


Figure 2, Solution Calorimeter with Computer for Data Acquisition

The Parr 1455 solution calorimeter was calibrated according to the manufacturer's procedure using the reaction of the base TRIS (tris(hydroxymethyl)aminomethane) with 0.1 N HCl solution. To determine the point in the time-temperature curve at which the temperature rise due to the reaction ($\Delta T_c$) should be measured, we used the method of Gunn (1971). From the digitized data on a spreadsheet, we calculated the area above and below the curve in the region of interest. At the point where the two areas are equal we measured $\Delta T_c$ as the separation between the extrapolated curves before and after mixing. This procedure offers improved precision compared to the graphical technique recommended in the manual. From this point, the calculations to determine the heat capacity of the calorimeter are the same as in the Parr manual.

Calorimetry was done both in water and in 28% calcium chloride solution, since previous analysis indicated that this solution would be a useful antifreeze. The data reduction to obtain the temperature change was first done graphically, and later by spreadsheet analysis of the digitized data. The spreadsheet analysis gave improved precision in the determination of $\Delta T_c$. The heat capacity of the empty calorimeter, determined in the calibration, is 25.475 $cal^{-1}$ $K^{-1}$. The heat capacity at 25°C for water is 0.99893 cal $g^{-1}$ $K^{-1}$ and for the 28% calcium chloride solution is 0.6775 cal $g^{-1}$ $K^{-1}$ (Dean 1985; Perry *et al.* 1984). We determined the range of results in each experiment performed in duplicate. We expressed those numbers as the percent deviation from the average value and determined their standard deviation to be 1.15%. Using two standard deviations for the confidence interval, we estimate the precision of the measurements as ±2.3% of the reported value.

## Systems Analysis

In this systems analysis, we first describe the construction and operation of a self-heating ration using a solid reactant activated by the addition of water (Section 0). We assume that the required heat output is 150 Btu; the flameless ration heater used for MREs produces about 130 Btu. The actual heating requirement will depend on the heat capacity of the food, heater and package, and on any heat losses (such as steam vented). The 150 Btu value is a conservative assumption, in that the actual demand may be somewhat less; if so, the heater can be proportionally smaller. We compared heaters using the new materials with the current FRH (using the Mg/Fe + $H_2O$ reaction). We determined heater weights and volumes (Section 0), and estimated transport and storage costs (Section 0). We also considered production costs for heaters using the new materials (Section 0). The safety analysis is described in Section 0.

### Design of New Ration Heater

The design of the Self-Heating Ration (SHR) is as shown in Figure 5.1. We have assumed there will be a 10-ounce entree' in a polypropylene tub. The tub will also contain the heater and activator solution. The heater will be located below the food for the most efficient heat transfer. To start the heater, a soldier will pull a tab which lets the activator solution mix with the solid heater materials. The heat produced by the reaction is transferred to the food container by direct contact and by the vaporization and condensation of water.

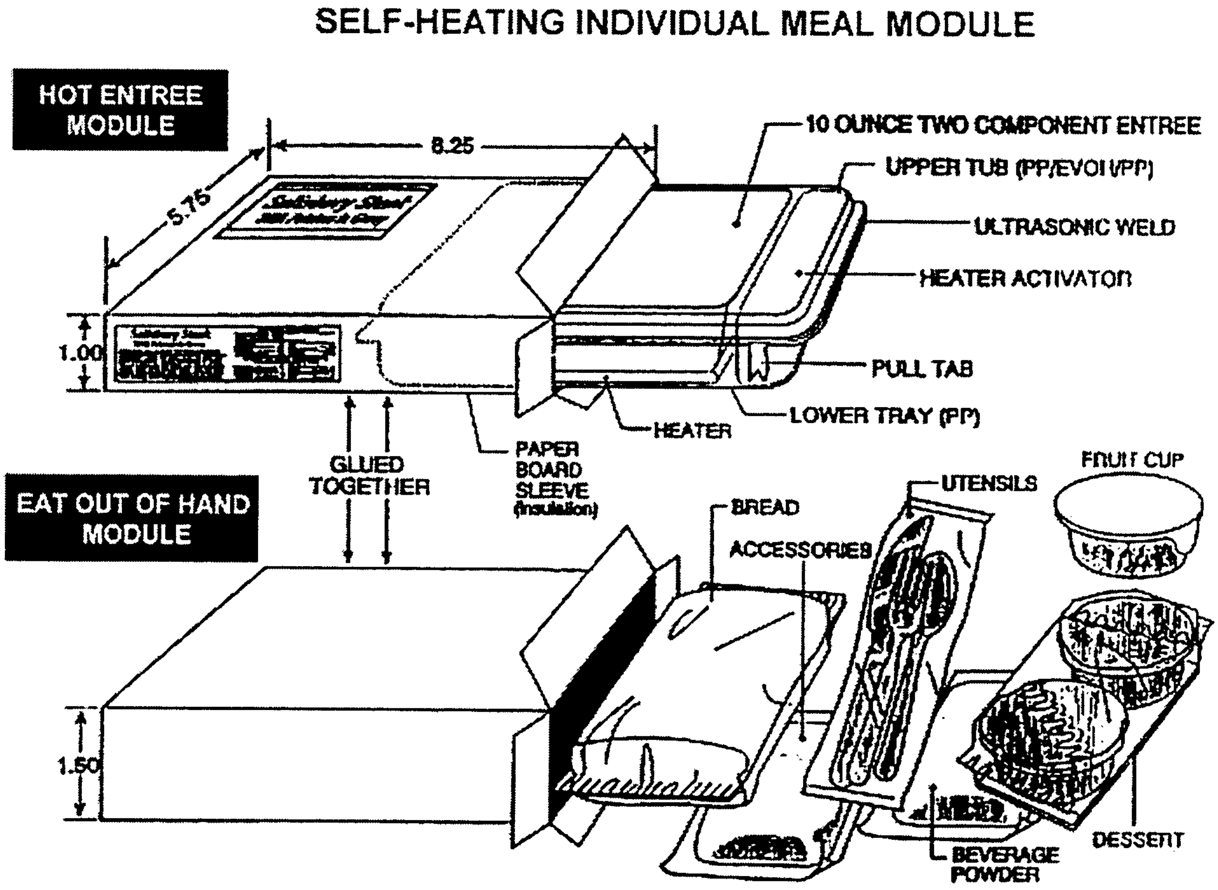


Figure 3, Self-Heating Ration (courtesy of U.S. Army TROSCOM, Natick RD&E Center)

## Weight and Volume of New Ration Heater

Previous analysis has shown that the systems considered here have materials costs comparable to those of the current flameless ration heater (FRH), using a Mg/Fe/HDPE formulation. We have determined, from experimental data and thermodynamic calculations, the comparative weights and volumes of the heaters under consideration, assuming a standard heat output (150 Btu). We then used this information to estimate costs associated with storage and transport of self-heating rations using these heaters.

We analyzed a self-heating ration (SHR) consisting of two modules: a hot entree module, containing a 10-oz. two-component entree, with ration heater and solution to activate the heater, and an eat-out-of-hand module, containing bread, fruit, dessert, *etc*. The nominal dimensions of the SHR are 8.25 x 5.75 x 2.5 inch.

For the chemical ration heater we considered three different reactions:

1. The magnesium/iron/HDPE composition used in the current flameless ration heater (FRH)

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

2. The chemical heater using the reaction of aluminum chloride with calcium oxide

   $2AlCl_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaCl_2$

3. The chemical heater using the reaction of diphosphorus pentoxide with calcium oxide

   $3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$

We first determined the relative weight and volume of each system for the following assumptions:

- heat output = 150 Btu
- amount of water required is the amount consumed in the reaction (stoichiometric amount) plus 30 g of water to assist in heat transfer.
- water was provided as a 28% $CaCl_2$ solution, since this has good antifreeze properties, and our experiments have shown it works well with all three of the chemical heaters listed here. This solution has a density of 1.27 g/mL and a freezing point of -38°F.

The weight of the FRH is taken from data on the current product, extrapolated from the current 133 Btu output to the baseline 150 Btu output. The weights for the other two systems are taken from the calorimetry measurements shown in Table 13. We then measured the powder densities shown below in order to determine the volume of each system:

| Component | Powder density ($g/cm^3$) |
|---|---|
| Mg (granules) | 1.0 |
| Mg/Fe/HDPE (FRH) | 0.51 |
| $AlCl_3$ | 1.23 |
| $CaO$ | 0.58 |
| $P_2O_5$ | 1.23 |

Using these values, we arrived at the conclusions on heater weights and volume shown in Table 2.

Table 2, Weight and volume of chemical heaters.

| Heater composition | Mg/Fe/HDPE (FRH) | | $AlCl_3/CaO$ | | $P_2O_5/CaO$ | |
|---|---|---|---|---|---|---|
| Heat output, Btu | 150 | | 150 | | 150 | |
| Hydrogen produced, L at STP | 10 | | 0 | | 0 | |
| Calculated or experimental data | Calc | Exptl | Calc | Exptl | Calc | Exptl |
| Weight of solid, g | 11 | 23 | 64 | 85 | 66 | 97 |
| Volume of solid, $cm^3$ | 11 | 45 | 75 | 100 | 86 | 126 |
| Weight of water consumed in reaction, g | 16 | | 8 | | 0 | |
| Weight of water to aid in heat transfer, g | 30 | | 30 | | 30 | |
| Total weight of water, g | 46 | | 38 | | 30 | |
| Weight of $CaCl_2$ solution, g | 56 | | 46 | | 37 | |
| Volume of $CaCl_2$ solution, $cm^3$ | 44 | | 36 | | 29 | |
| Total heater weight, solid + solution, g (oz.) | 67 (2.4) | 79 (2.8) | 110 (3.9) | 131 (4.6) | 103 (3.6) | 134 (4.7) |
| Total heater volume, $cm^3$ (fl. oz.) | 55 (1.9) | 89 (3.0) | 111 (3.8) | 136 (4.6) | 115 (3.9) | 155 (5.2) |

## Transport and Storage Costs of New Ration Heater

We next carried out an analysis to determine the additional costs, if any, associated with the increase in weight and volume for a SHR using one of the new reactions. Based on experimental data and the calculations in Table 1, we assumed that the Mg/Fe heater would have a weight of 79 g and a volume of 89 $cm^3$, and that a heater using the $CaO/AlCl_3$ reaction would have a weight of 131 g and a volume of 136 $cm^3$. The difference in weight is 52 g (1.8 oz.) and the difference in volume is 47 $cm^3$ (1.6 fl. oz.). These differences could have an effect on both storage and transportation costs. For storage costs, we consider first the difference in volume. To account for the difference in volume of 47 $cm^3$, a SHR using the Mg/Fe heater could be 0.060-inch thinner. Assuming that a SHR using the $CaO/AlCl_3$ heater has dimensions of 8.25 x 5.75 x 2.5 inch, a SHR using the Mg/Fe heater could have dimensions of 8.25 x 5.75 x 2.44 inch, a difference in volume of 2.4%.

We assume that the SHR meals will be stored and transported on standard 4 ft. x 4 ft. pallets. If they are laid out in rows of five wide by eight deep (40 meals per layer), then they will probably be stacked about 25 layers deep. (Assuming the pallet weighs 50 lbs., this gives us a palletized load weighing about 2050 lbs.) Assuming the pallet is 6-inches thick, the height is 68.5 in. with the thicker package and 67.0 inches with the lower volume heater. Considering how the pallets are likely to be moved and stacked, we conclude that this difference of 1.5 inch is of no practical significance. We therefore assign no cost penalty for the 2.4% higher volume of the SHR with the $CaO/AlCl_3$ heater.

The difference in weight between the two heaters has no effect on storage costs, but will affect transportation costs. We considered three different transportation scenarios:

1. Ground transport: Denver to New York: full 45 ft. trailer (22 standard pallets), piggyback on railroad car.
2. Sea transport: Houston to London: full 40 ft. shipping container (20 standard pallets).
3. Air transport: Dallas to Newark: full 60 x 61.5 x 64 inch container.

We again assumed that the meals would be shipped on pallets, for ground or sea transport, with the pallet weighing 50 lbs. and the palletized load weighing 2,000-2,200 lbs.; smaller pallets are used for air transport. We used values for the overall SHR weight in the range suggested by the COR, and values for the heater weights from Table 2. We assumed that a SHR using the Mg/Fe FRH weighed 30.2 oz. and a SHR using the $AlCl_3$/CaO heater weighed 32 oz. The results of the comparison are shown in Table 3.

Table 3, Costs to transport Self-Heating Rations with two types of heater.

| Transport | Ground | | Sea | | Air | |
|---|---|---|---|---|---|---|
| Load weight, lbs | 46,500 | | 45,000 | | 3,500 | |
| Cost | $1560 | | $2270 | | $255 | |
| Heater type | Mg/Fe | CaO/$AlCl_3$ | Mg/Fe | CaO/$AlCl_3$ | Mg/Fe | CaO/$AlCl_3$ |
| Meals per load | 24,040 | 22,700 | 23,290 | 22,000 | 1,705 | 1,610 |
| Shipping cost per meal | $0.0649 | $0.0687 | $0.0975 | $0.1032 | $0.1496 | $0.1534 |
| Cost difference | $0.0038 | | $0.0057 | | $0.0088 | |

From this we conclude that the additional cost in shipping the heavier meal is between 0.4 and 0.9 cents per meal, depending on the method of transport chosen. We consider that, on the average, each meal will be shipped more than once after it is manufactured. Assuming that a typical SHR is transported two times by ground and once by sea, we assign a cost penalty of 1.4 cents per unit for the heavier heater.

The results of the systems analysis to this point are that chemical heaters using the new reactions developed by TDA can provide the same heat output as a heater using the Mg/Fe FRH, while eliminating the flammable hydrogen gas produced by the FRH. The new chemical heaters should have a slightly higher volume and a small (6%) increase in the weight of the self-heating ration. While it is clear from this analysis that the new heaters are attractive, due to the elimination of hydrogen gas at only a small weight penalty, the new systems would clearly be more valuable if we find that they could also be produced for lower cost.

## Materials and Production Costs for New Ration Heater

The raw materials costs for the old and new systems are comparable, at about 7 cents per unit for each type. This includes the magnesium, iron and high-density polyethylene in the FRH, the anhydrous aluminum chloride and calcium oxide in one of the new materials, and the phosphorus pentoxide and calcium in the other new material. The new design is estimated to cost roughly 1 cent per unit more than the old design to transport, and to have essentially identical storage costs. The key issue remaining is the processing cost of the competing systems. Since we know that the current FRH costs roughly 50 cents per unit, with a materials cost of around 7 cents, processing is clearly an important factor in production costs, and therefore overall system cost.

To compare processing costs, we considered the steps in assembling a heater of both types. The current FRH uses a Mg/Fe alloy produced by high energy metallurgical milling techniques. This alloy is then subjected to a pressureless sintering process with high-density polyethylene for 20 minutes at 168°C (Kuhn *et al.* 1985). A heater using a reaction such as the $CaO/AlCl_3$ heater would not require either of these steps. The major operation in assembling a heater with this reaction would be to fill the container with measured amounts of both reactants. The reactants may first be pressed into granular or pellet form to reduce surface and thereby lower the reaction rate to a more convenient value. A small amount of a porous material may also be added to separate the two solid components, also to slow the reaction rate. The conclusion from this comparison is that the new designs have the potential to be significantly lower in cost because the manufacturing process is considerably more simple and less expensive.

## Safety Analysis of New Ration Heater

The safety aspects of the ration heater have been addressed in an ongoing effort throughout this project. Many reactions that would otherwise have been attractive on a heat-per-weight basis were not considered at all due to obvious safety limitations. For example, compounds containing highly toxic beryllium were eliminated from consideration. A Preliminary Hazard Analysis Report has been prepared in accordance with MIL-STD-882B. This report is included as Appendix A, and the conclusions are summarized below.

The solid materials described above undergo a reaction with water which produce roughly 150 Btu of heat from 64-97 g of solid. The heat produces temperatures sufficient to boil water, and will produce some steam. 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 ($AlCl_3$ and $P_2O_5$) 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) which 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 the new 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.

The calcium chloride used in the activator solution is described as an irritant, and users are instructed to avoid contact with eyes, skin and clothing (MSDS). It is also taken internally as an electrolyte replacement (Budavari 1989).

We identified three categories of hazards: (1) burns from steam or hot surfaces, (2) toxic effects which may be produced by the heater material or activator solution if swallowed, inhaled or exposed to skin and (3) a hazard of steam explosion if the heater is activated in a confined space. These are discussed in order below.

1. <u>Burn</u> Personnel will normally handle the hot tray, 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. Burn hazard should be minimized by design, so that (a) the SHR can be handled without burning the fingers of the user, and (b) by arranging the vents for steam so that the steam does not vent toward the user. Warning signs will also be provided.

2. <u>Toxicity</u> Personnel will not be exposed to the reactive solid material or the activator solution during normal operation, but may be exposed to the contents by skin contact or inhalation in the event a package is accidentally ruptured in transport or in use. Personnel could potentially swallow the solid heater material or activator solution by accident. The materials used in the heater, taken individually, are harmful if inhaled, swallowed or absorbed through the skin. Safety considerations have directed the choice of materials for the heater so that they are self-neutralizing, which should minimize the toxicity hazard to personnel. Materials will be formulated to minimize dust which could be inhaled by the user if a package is ruptured. Warning signs will tell the user not to eat the heater material or drink the activator solution.

3. <u>Reactivity</u> The heater materials are normally activated by water, and a hazard exists that the reactive materials will be accidentally exposed to water, activating the heat-producing reaction. If reaction occurs in a confined space, pressure will build up and an explosion could result. Signs will tell users that the heater produces steam and should not be operated in a closed container.

The overall conclusion of the system safety analysis is that the materials should be safe in manufacturing, transportation and normal operation. Studies to quantify the safety aspects of the new materials will be part of the Phase II effort.

## Results and Discussion

In this section we first describe the reactions we identified as potentially useful for portable heat sources, and how we narrowed the field based on the calculated heat output. We then describe the materials cost analysis, and the reactions that were acceptable on that basis. Then we describe the results of reaction rate measurements. Heat output measured by solution calorimetry is summarized in the Section entitled "Reaction Heat Output by Calorimetry". The selection of an antifreeze for the activator solution is discussed in the same section, and the evaluation of the aluminum-air battery as a portable heater is discussed in the following section. Results are summarized in the summary of results. The results of this work were used in a systems analysis which estimated the weight, cost, safety, and commercial potential of heaters using the new reactions (see systems analysis).

### 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 4-8. 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 which produce hydrogen were considered in the proposal, they are excluded from this report since there is no reason to prefer any of these over the magnesium/water reaction of the FRH.

Table 4 presents replacement reactions with ionic salts. Of the reactions considered, those with magnesium have higher energy densities than those with aluminum.

Table 4, Metal Ion Replacement Reactions

| Metal | Salt | Products | Heat Output Btu/lb* | Comments |
|---|---|---|---|---|
| Al | $CuCl_2$ | $AlCl_3 \bullet 6\ H_2O$ + Cu | 1,240 | Releases HCl |
| Al | $Cu(C_2H_3O_2)_2$ | $Al(C_2H_3O_2)_3$ (aq) + Cu | 931 | |
| Mg | $CuCl_2$ | $MgCl_2 \bullet 6\ H_2O$ + 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 5 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 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 5, 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. | | | | |

Table 6 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 6 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 ($NaBO_3 \bullet 4H_2O$). These materials have the effect of storing oxidizing power equivalent to hydrogen peroxide in a solid form.

Table 6, 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 |

Table 7 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 7, 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) + ½ $O_2$ | 621 | |
| $CaSO_4 \bullet \frac{1}{2}H_2O$ | $CaSO_4 \bullet 2H_2O$ | 51 | |
| $CaSO_4$ | $CaSO_4 \bullet 2H_2O$ | 53 | |

*Weight of water not included.

Table 8 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, by 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)], we have a heat-producing reaction which gives us neutral products. Furthermore, we realize the heat of hydration of both components, as well as the heat of the neutralization reaction. This means that the combination is not only safer, but has a higher energy output. The advantages of this approach do not appear to have been recognized in previous work on portable heat sources.

Table 8, 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 |
| $AlCl_3 \bullet 6H_2O$ | $Na_2O$ | $Al(OH)_3$ + NaCl (aq) | 617 |
| $NaHCO_3$ | $Na_2O$ | $Na_2CO_3$(aq) | 538 |
| $FeCO_3$ | $Na_2O$ | $Na_2CO_3$(aq) + FeO | 647 |
| $FeCl_3 \bullet 6H_2O$ | $Na_2O$ | $Fe(OH)_3$+ 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 have a heat output high enough to be of interest, and there are 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) + $NaBO_3 \bullet 4H_2O$ | 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. A general comment for all of the reactions is that some development will be required to produce a formulation which releases 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 which would not be of interest given their heat release.

For one example above (reaction of $AlCl_3$ with CaO), TDA carried out a comparison of heat output of the new system with the magnesium/water reaction, based on dry weight, weight of water consumed in the reaction, and weight of excess water (required for forming a solution, for heat transfer, and for controlling temperature). The relevant equation for the magnesium/water reaction is:

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

The equation for the aluminum chloride/calcium oxide reaction is:

$$2AlCl_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaCl_2$$

The heat output per weight, based on no water, the stoichiometric amount of water, and an excess of water (30 g) are shown in Table 9 below.

Table 9, Heater weight with varying water content in package

| Amount of water in package | Reaction: $Mg/H_2O$ weight of reactant 11 g | | Reaction: $CaO/AlCl_3$ weight of reactant 64 g | |
|---|---|---|---|---|
| | water weight, g | total weight, g | water weight, g | total weight, g |
| none | 0 | 11 | 0 | 64 |
| required for reaction | 16 | 27 | 8 | 72 |
| required + 30 g for heat transfer, *etc.* | 46 | 57 | 38 | 102 |

This analysis illustrates the dependence of heater weight on reaction heat output. If the product is a stand-alone heater, like the FRH, and we supply water from a local source, then the dry weight of the reactant is critical. If we package water (or solution) with the reactants, then we should consider the overall system weight. While the $Mg/H_2O$ reaction is still lighter, the difference is roughly 1.5 ounces out of a package weight of around 2 pounds. This may prove to be a desirable trade-off, if the new materials result in improved convenience and lower cost.

Note that the $CaO/H_2O$ reaction, which has been used in many heaters, requires reaction of 136 g of CaO to produce 150 Btu. With 44 g of water consumed in the reaction and an additional 30g of water for heat transfer, the total weight would be 210 g (7.4 ounces). At this point, the heater weighs almost as much as the food; this does not appear to be an acceptable trade-off. We concluded that the heater weight (reactant plus activator solution) should not exceed 150 g (5 ounces), and that this target was achievable with several of the reactions identified in the study.

## Cost Analysis

For each system, TDA determined the materials cost for 150 Btu output, using data from the Chemical Marketing Reporter (CMR) or from the manufacturer. The material, price, source, and specifications are shown in Table 10. We note that any material that is practical for this application must be available in bulk. If we require 1 million SHR units with chemical heaters, and each heater contains 0.1 pound of reactant, then the reactant weight is 50 tons. Any material not readily available in large quantities will not be practical.

Table 10, Reactant costs

| Reactant | Price ($/lb) | Source, comments |
|---|---|---|
| Mg | 2.10 | Rossborough, powder, ton |
| Al | 1.66 | Reynolds Metal, truckload |
| $CaO_2$ | 1.65 | Interox, 50 kg drum<br>85% purity |
| $NaIO_3$ | 7.60 | Ajay Chemicals |
| $NaBO_3 \bullet H_2O$ | 0.69 | Interox, 900 kg |
| $NaBO_3 \bullet 4H_2O$ | 0.40 | Browning, 2100lb |
| CuO | 1.64 | CMR, 40,000 lb |
| $CuCl_2$ | 2.37 | CMR, anyhd., 1-5 ton |
| MgO | 0.143 | Baymag, truckload<br>96% purity |
| $B_2O_3$ | 1.29 | US Borax, $2585/ton |
| $P_2O_5$ | 1.08 | CMR, drum |
| $AlCl_3$ | 0.76 | Gulbrandsen, drum,<br>anhydrous |
| $FeCl_3$ | 0.49 | CMR, drum, anhyd. |
| CaO | 0.026 | CMR, ton |
| $Na_2O$ | 25.00 | Atomergic Chemetals,<br>1100 lb |

One result of the cost analysis was the unexpectedly high price of sodium oxide ($Na_2O$). The cost analysis of the aluminum chloride/sodium oxide reaction is shown; other reaction sets using sodium oxide produced similarly high costs. This led us to reject all the reaction sets involving this material on a cost basis. The cost analysis is shown in Table 11.

From cost considerations, two reactions were eliminated:

Table 11, Cost analysis and weight of reactants

| Reaction | Cost, \$ per 150 Btu | Dry weight, lb | Weight with water, lb |
|---|---|---|---|
| $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ | 0.06 | 0.027 | 0.066 |
| $3Mg + NaIO_3 + 3H_2O \rightarrow 3Mg(OH)_2 + NaI$ | 0.33 | 0.055 | 0.065 |
| $3\,CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ | 0.074 | 0.145 | 0.145 |
| $2AlCl_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaCl_2$ | 0.07 | 0.142 | 0.159 |
| $2AlCl_3 + Na_2O + 3H_2O \rightarrow 2Al(OH)_3 + 6NaCl$ | 1.12 | 0.105 | 0.118 |
| $2Al + 3CaO_2 + 6H_2O \rightarrow 2Al(OH)_3 + Ca(OH)_2$ | 0.085 | 0.051 | 0.072 |
| $Mg + CaO_2 + 2H_2O \rightarrow Mg(OH)_2 + Ca(OH)_2$ | 0.09 | 0.049 | 0.068 |
| $2Al + 3NaBO_3 \bullet 4H_2O \rightarrow 2Al(OH)_3 + 3NaBO_2 + 9H_2O$ | 0.05 | 0.098 | 0.098 |
| $NaBO_3 \bullet 4H_2O + Mg \rightarrow Mg(OH)_2 + NaBO_2 + 3H_2O$ | 0.06 | 0.091 | 0.091 |
| $2Al + NaIO_3 + 3H_2O \rightarrow 2Al(OH)_3 + NaI$ | 0.67 | 0.27 | 0.346 |
| $2Al + 3NaBO_3 \bullet H_2O \rightarrow 2Al(OH)_3 + 3NaBO_2$ | 0.06 | 0.067 | 0.062 |
| $Mg + NaBO_3 \bullet H_2O \rightarrow Mg(OH)_2 + NaBO_2$ | 0.061 | 0.063 | 0.063 |
| $2AlCl_3 + 3MgO + 3H_2O \rightarrow 2Al(OH)_3 + 3MgCl_2$ | 0.09 | 0.15 | 0.171 |
| $2AlCl_3 + 3Mg + 6H_2O \rightarrow 2Al(OH)_3 + 3MgCl_2 + 3H_2$ | 0.07 | 0.064 | 0.095 |
| $Mg + CuCl_2 \cdot + 6H_2O \rightarrow MgCl_2 \bullet 6H_2O + Cu$ | 0.23 | 0.10 | 0.165 |
| $CaO + H_2O \rightarrow Ca(OH)_2$ | 0.008 | 0.298 | 0.393 |

$2AlCl_3 + Na_2O + 3H_2O \rightarrow 2Al(OH)_3 + 6NaCl$ and

$2Al + NaIO_3 + 3H_2O \rightarrow 2Al(OH)_3 + NaI$

The remaining reactions were further evaluated by experiments to determine the reaction rates on activation with water.

## Reaction Rates

Experiments were carried out to determine whether a reaction would proceed fast enough to be useful in a ration heater. In these experiments we reacted small quantities of solid with water or calcium chloride solution, and measured the temperature change with time. (The calcium chloride was selected as an antifreeze, as noted earlier and discussed in the 'Selection of Anti-freeze for Activator Solution section). The "air calorimeter" apparatus and detailed experimental procedure are described in Section 3.1 (above).

The data obtained for the Mg/Fe FRH and for the aluminum chloride/calcium oxide reaction are shown in Figures 4, 5 and 6. Table 12 summarizes the reactions and the results.

In all of these experiments the water or solution was added at $t$ = 1.0 minute. The temperature curve labeled "bottom" is the temperature of a thermocouple at the bottom of the air calorimeter and is measuring the temperature of the reacting mixture. The curve labeled "top" is the temperature in the glass beads in the air calorimeter. This material is analogous to the food in that it is heated partially by conduction from the solution and partially by condensation of water vapor produced by the reaction. The ambient curve is the measured temperature of the surrounding air. In the case of the Mg/Fe alloy, the reaction displays an induction period; that is, there is a delay before the heat production reaches a maximum. This delay is increased slightly when calcium chloride solution is used as the activator rather than water. This can be seen by comparing the two curves in Figure 4. In the case of the aluminum chloride plus calcium oxide reaction, the reaction is immediate on addition of either water or calcium chloride solution. This is seen in Figure 5. In Figure 5 (top) we have compared the temperatures of the Mg/Fe FRH on activation with water and calcium chloride, and it is now more clearly seen that this reaction proceeds slower in calcium chloride solution. Figure 5 (bottom) shows that there is no difference in the rate of the aluminum chloride/calcium oxide reaction, whether activated with water or with calcium chloride solution.

Table 12, Reaction and comments

| Reaction | Comments |
|---|---|
| $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$ | 2x4 cm piece tested; heat as expected* |
| $3Mg + NaIO_3 + 3H_2O \rightarrow 3Mg(OH)_2 + NaI$ | No reaction observed |
| $3\ CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ | Reaction immediate, vigorous* |
| $2AlCl_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaCl_2$ | Reaction immediate; crust formed; vapor observed* |
| $2AlCl_3 + Na_2O + 3H_2O \rightarrow 2Al(OH)_3 + 6NaCl$ | Rejected on cost basis |
| $2Al + 3CaO_2 + 6H_2O \rightarrow 2Al(OH)_3 + Ca(OH)_2$ | Grey foam, some heat |
| $Mg + CaO_2 + 2H_2O \rightarrow Mg(OH)_2 + Ca(OH)_2$ | No reaction observed |
| $2Al + 3NaBO_3 \bullet 4H_2O \rightarrow 2Al(OH)_3 + 3NaBO_2 + 9H_2O$ | No reaction observed |
| $NaBO_3 \bullet 4H_2O + Mg \rightarrow Mg(OH)_2 + NaBO_2 + 3H_2O$ | No reaction observed |
| $2Al + NaIO_3 + 3H_2O \rightarrow 2Al(OH)_3 + NaI$ | Rejected on cost basis |
| $2Al + 3NaBO_3 \bullet H_2O \rightarrow 2Al(OH)_3 + 3NaBO_2$ | Some heat, solid formed |
| $Mg + NaBO_3 \bullet H_2O \rightarrow Mg(OH)_2 + NaBO_2$ | No reaction observed |
| $2AlCl_3 + 3MgO + 3H_2O \rightarrow 2Al(OH)_3 + 3MgCl_2$ | No advantage over CaO rxn. |
| $2AlCl_3 + 3Mg + 6H_2O \rightarrow 2Al(OH)_3 + 3MgCl_2 + 3H_2$ | Immediate reaction; gas evolved* |
| $Mg + CuCl_2 + 6H_2O \rightarrow MgCl_2{*}6H_2O + Cu$ | Solution turned green, Cu formed. Some gas evolved. * |
| $CaO + H_2O \rightarrow Ca(OH)_2$ | Reaction immediate, some crust formed* |
| * Also tested with 28% $CaCl_2$ solution | |

Another feature apparent in comparing the reactions with water to the reactions with calcium chloride solution is the higher temperature reached with calcium chloride. While the boiling point of water in Wheat Ridge, CO, is 94.5°C, higher temperatures were observed in the calcium chloride solution because the high salt concentration raises the boiling point of the reaction mixture. This is potentially an advantage for us, since the higher temperature (110-120°C) will increase the rate of heat transfer to the food in our SHR package without raising the temperature to a point where the food taste is affected or the packaging is damaged.

The sharp spike in temperature observed with the aluminum chloride/calcium oxide reaction indicates that the reaction is essentially immediate on adding water. This is not desirable, since it leads to loss of heat as steam, where a slower, more controlled reaction would transfer more of the heat to the food. Fortunately, we note that a reaction that proceeds too rapidly can be fairly readily controlled, for example by increasing the particle size of the reactants or by slowing the rate at which the reactants can mix. in general, slowing a reaction which is too fast represents a straightforward engineering problem, where increasing the rate of a slow reaction may be impractical.

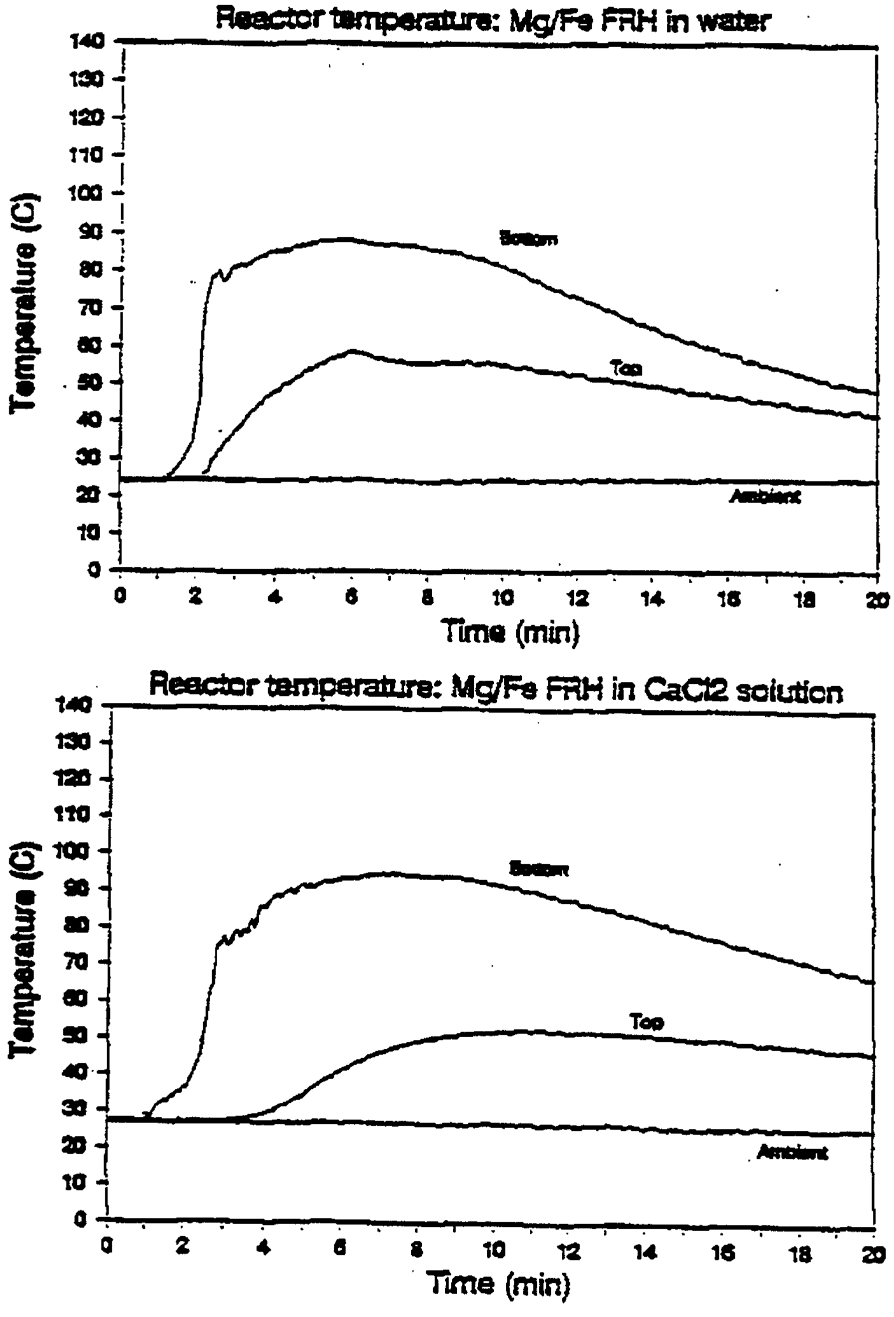


Figure 4, Reaction of Mg/Fe FRH with water and with calcium chloride solution

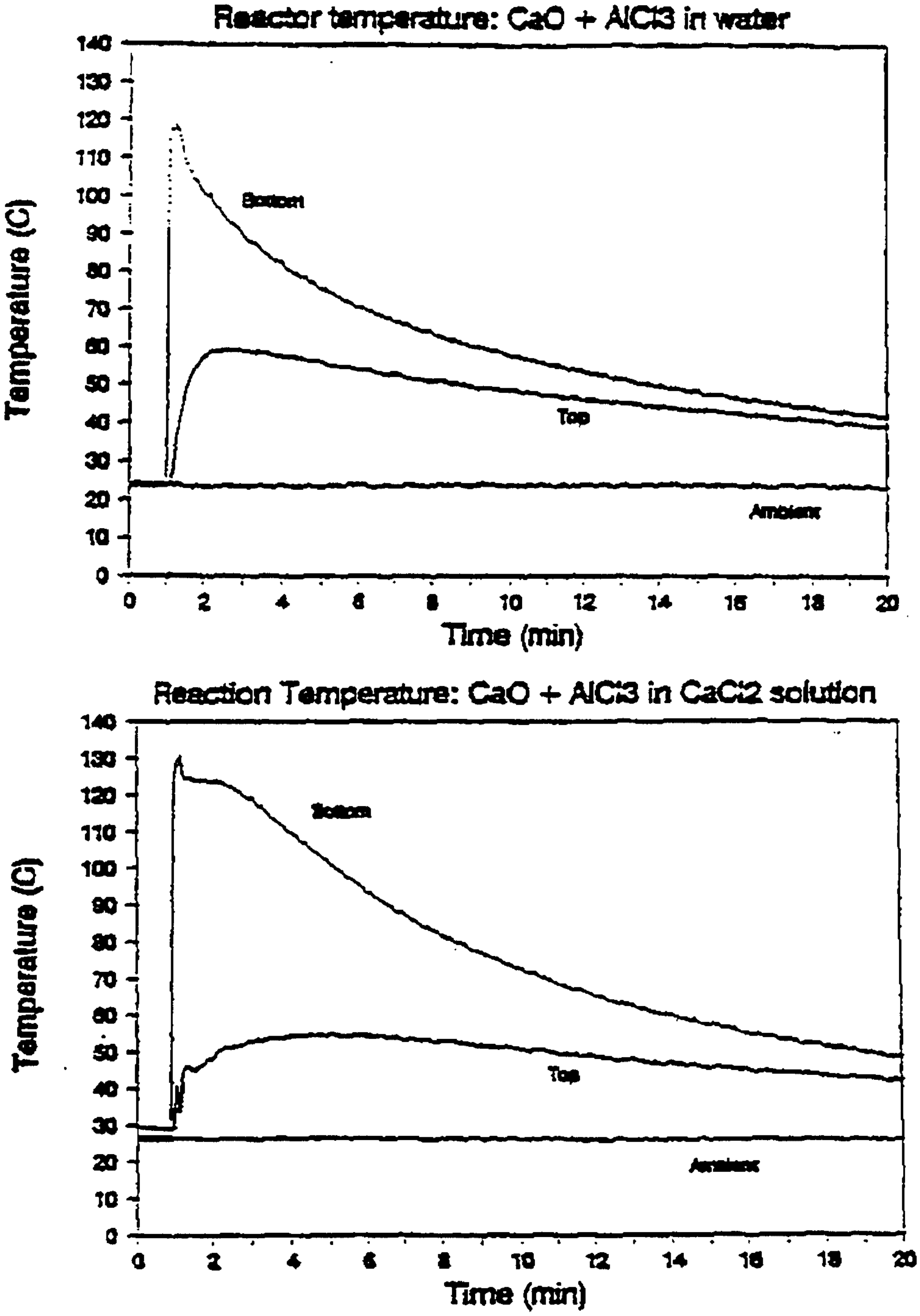
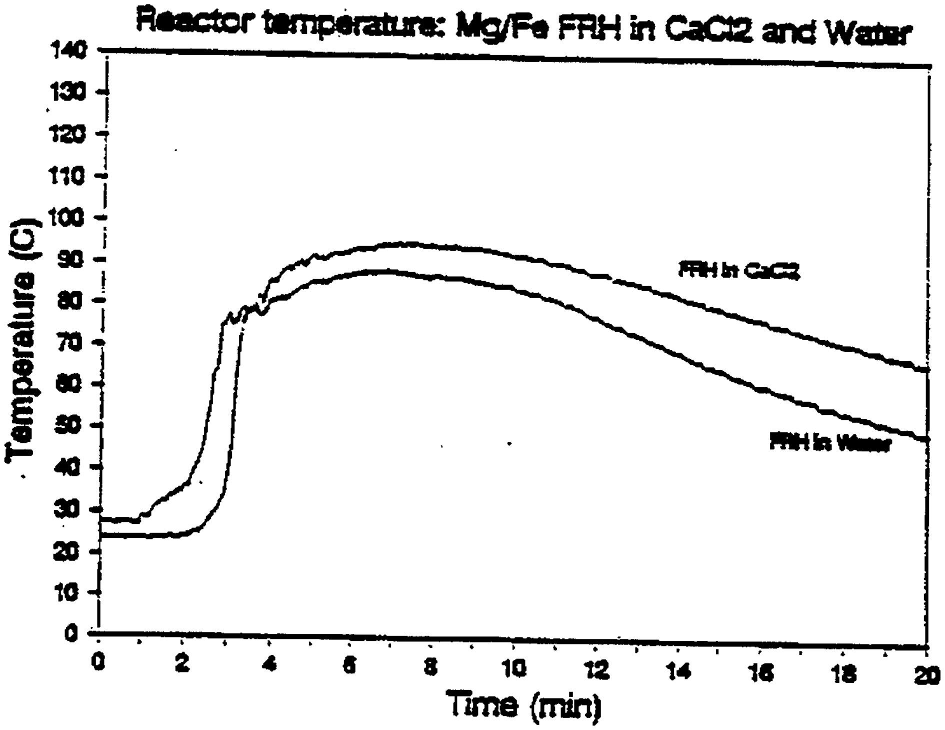


Figure 5, Reaction of aluminum chloride and calcium oxide with water and with calcium-chloride solution



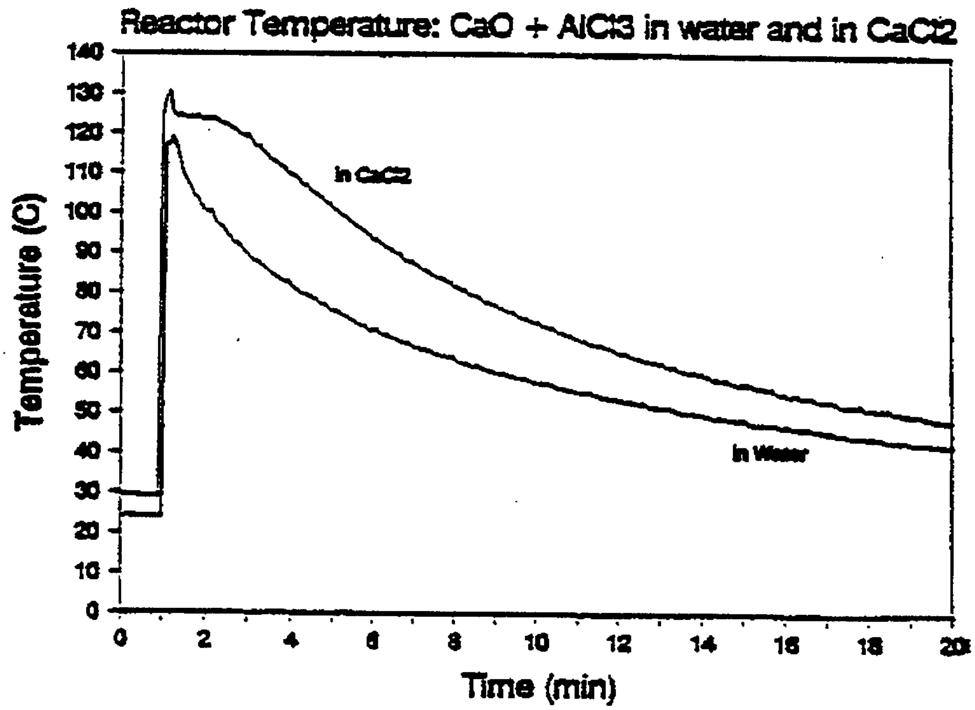


Figure 6, Comparison of reaction temperatures with water and with calcium chloride solution

We arrived at two conclusions from these reaction temperature measurements:

1. As tested, the reactions of magnesium or aluminum powders with an oxidant were all too slow. However, the reaction rate of these materials depends on, among other quantities, the particle size and the thickness of oxide coating on the metal surface. It is possible to increase the reaction rate by using smaller particles and by surface treatment (or possibly by using material which has been more recently produced). These metal/oxidant combinations may yet prove useful, but are now clearly less encouraging.

2. The reactions of a basic anhydride (calcium oxide, CaO) with an acidic anhydride (aluminum chloride, $AlCl_3$, or diphosphorus pentoxide, $P_2O_5$) produced heat immediately on addition of water, as expected. A slower rate would be preferable, and TDA has outlined simple methods to decrease the reaction rate. Slowing a fast reaction is inherently easier than speeding up a reaction that is too slow. Thus, we selected these two reactions for further investigation:

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$

$$2AlCl_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaCl_2$$

**Reaction Heat Output by Calorimetry**

Accurate calorimetry experiments were essential to determine the heat output of each reaction directly. The data from these experiments were used in our calculation of system weight and volume (described in the systems analysis). In these experiments we reacted a solid with water or a solution in the Parr 1455 calorimeter. The calorimeter is insulated, so that heat loss to the surroundings is minimal. The method for determining the temperature change due to the reaction is described in Reaction Heat Output by Calorimetry (above). Knowing the temperature change, and also knowing the heat capacity of the calorimeter and the contents, we can calculate how much heat is produced by the reaction.

TDA carried out calorimetry on calcium oxide, aluminum chloride, and diphosphorus pentoxide reacting with water individually, and on calcium oxide/aluminum chloride and calcium oxide/diphosphorus pentoxide mixtures reacting with water. A time-temperature profile from a typical calorimetry experiment is shown in Figure 7. Calorimetry was done both in water and in 28% calcium chloride solution, since previous analysis indicated that this solution would be a useful antifreeze. The results are summarized in Table 13.

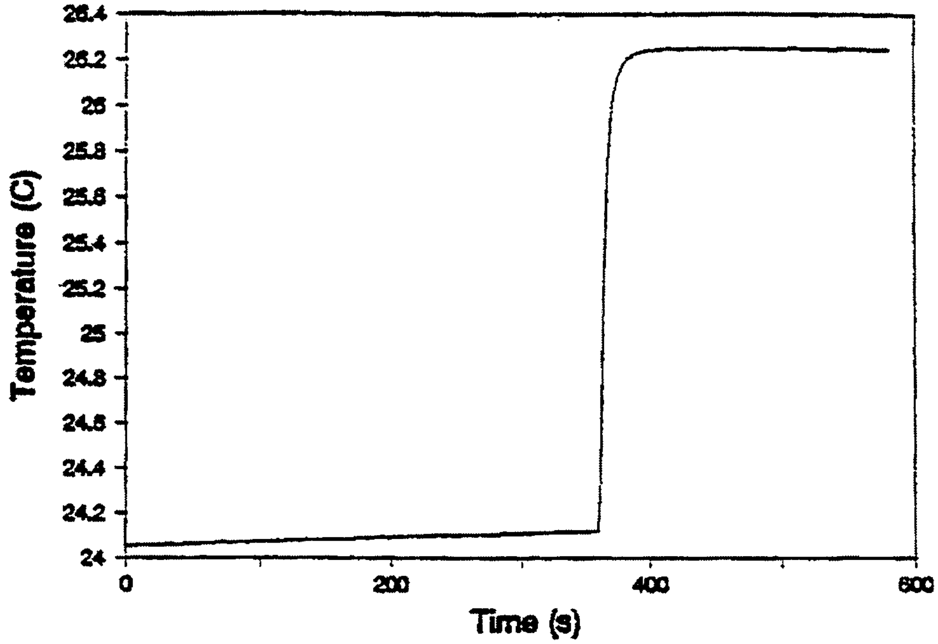


Figure 7, Time-temperature profile for aluminum chloride in water

The results obtained with calcium oxide and aluminum chloride in water are identical to the predicted values within experimental error. Slightly lower values are obtained for both materials in calcium chloride solution. However, the combination reaction we propose to use in the ration heater, CaO + $AlCl_3$, produces significantly less heat in both water and calcium chloride solution, producing only 75% of the expected heat output. We tentatively attribute this discrepancy to the reaction of the materials with water from the atmosphere as the samples are transferred to the calorimeter. We note that reaction of water with aluminum chloride produces HCl, which can react with the calcium oxide even in the absence of liquid water. The small samples used here (0.25 to 0.4 g) make the absorption of water from the air much more noticeable than it would be with the larger quantities we are proposing for a ration heater. Experiments to test whether water absorption is the cause of this difference would be relatively straightforward, involving preparation of the sample in a controlled atmosphere (dry box). These experiments are proposed as part of Phase II work to develop these ration heaters.

Table 13, Heat output measured by calorimetry

| Material | Expected $\Delta H$ Btu/lb | $\Delta H$ in water Btu/lb | $\Delta H$ in 28% $CaCl_2$, Btu/lb |
|---|---|---|---|
| $CaO$ | 501 | 500 | 472 |
| $AlCl_3$ | 1061 | 1062 | 958 |
| $CaO + AlCl_3$ | 1060 | 792 | 806 |
| $P_2O_5$ | 684 | 540 | 504 |
| $CaO + P_2O_5$ | 1035 | 756 | 707 |

If the difference between the expected and measured values for the $CaO + AlCl_3$ reaction is in fact due to reaction with water vapor from the air, then this could be fairly easily dealt with in production work (for example, by operating in a humidity-controlled environment). In fact, simply operating with the needed quantities of these materials may reduce the relative weight of water absorbed on transfer to a negligible value. In further analysis, we have used the experimental values shown in Table 13. If the heat output can be increased to the expected value, then the relative performance would be better than our analysis has shown.

The situation with reactions involving diphosphorus pentoxide ($P_2O_5$) is somewhat different. Here we find that all the reaction heats are less than expected, averaging about 74% of the expected value. There is no clear difference in the behavior of $P_2O_5$ by itself and with CaO. We conclude that the $P_2O_5$ has picked up water, either in storage or on handling, decreasing the heat output. We calculated that addition of 20 mg water to a 0.3 g sample, typical of those used in calorimetry, would reduce the heat output to about 77% of the expected value. Again, this may not be a significant problem when dealing with production of a large number of heaters.

## Selection of Anti-freeze for Activator Solution

The activator solution for the portable heat source must remain liquid to function. Therefore, for the system to function in all environments, it must include some antifreeze. When we are evaluating new reactions for chemical heaters, we should also assess performance when activated by an antifreeze solution as well as water, so that any potential problems can be identified as early as possible. Accordingly, we examined two potential antifreeze additives for the activator solution.

The commonly used antifreeze materials are either inorganic salts or organic polyalcohols (used to minimize corrosion in metal systems). The salt most commonly used as an antifreeze is calcium chloride, $CaCl_2$. For an organic antifreeze, the best choice by virtue of its very low toxicity is propylene glycol (PG). We recognized that while $CaCl_2$ is a solid, PG is a liquid, and so can contribute to heat transfer by liquid contact. PG does not contribute significantly to heat transfer by vaporization/condensation due to its high boiling point (370°F). Since the relative contribution to heat transfer by contact and by vaporization/condensation is a system design parameter that has not been established for the SHR, we evaluated antifreeze materials considering only the weight of water in the solution. We also considered that it would be useful to have one of the reactants act as the antifreeze material; however, no examples of this approach have yet been identified.

The comparison of calcium chloride and propylene glycol antifreeze solutions effective down to -37°F is summarized in Table 14. In this comparison it is clear that for a given weight of water calcium chloride is lighter, lower in volume, and less expensive. For this reason, the reaction rate and calorimetry tests were conducted both with water and with calcium chloride solution.

Table 14, Composition and cost of antifreeze solutions

| Material | Calcium chloride | Propylene glycol |
|---|---|---|
| Freezing point | -37.8°F | -37°F |
| Composition (wt. %) | 28.0% | 54% |
| Specific gravity at 60°F | 1.27 | 1.045 |
| Material cost, \$/lb anti-freeze | 0.056 | 0.59 |
| Solution containing 1 lb water | 1 lb $H_2O$ + 0.389 lb $CaCl_2$ | 1 lb $H_2O$ + 1.17 lb Propylene glycol |
| Volume of solution for 1 lb water, mL | 497 | 943 |
| Cost of antifreeze, \$ per lb water in solution | 0.022 | 0.69 |

## Evaluation of Aluminum-Air Battery for Ration Heater

The large amount of energy available from the reaction of aluminum with oxygen makes this process attractive from a standpoint of energy density. The ease of fabrication and low cost of aluminum have led to its development as a primary battery for electric power applications, for example, in electric vehicles (Maimoni and Cooper, 1988) and as an emergency power supply (Budevski *et al.*, 1988). There are two basic configurations of aluminum-air battery: (1) the alkaline battery, proposed for electric vehicles, and (2) the saline battery, as used in special applications such as portable or emergency power supplies. The aluminum-air battery has the following cell reaction:

$$Al + 3/2\ H_2O + 3/4\ O_2 \rightarrow Al(OH)_3$$

The cell has an aluminum anode and an air cathode (carbon plus a catalyst). The battery has an infinite shelf-life in the inactivated state, and is conveniently activated by adding the electrolyte solution. As a heat source, the aluminum air battery produces 844 kJ/mole Al (13,400 Btu/pound Al). This is very attractive compared to oxidation of other metals and compares favorably with fossil fuels (18,500 Btu/lb).

To determine whether we could use this high energy density in a ration heater, we evaluated aluminum-air batteries as a heat source. In this evaluation TDA collaborated with Alupower, Inc., of Warren, NJ, the recognized leader in this field. We considered aluminum-air batteries for food heating and related applications in discussions with Dr. Bhaskara Rao and Dr. Bob Hamlen of Alupower. Alupower provided data on two types of aluminum-air batteries: alkaline batteries (electrolyte is sodium or potassium hydroxide) and saline batteries (electrolyte is sodium chloride). In both cases the energy is provided by the reaction of aluminum metal with oxygen from the air. The performance data supplied for both types are shown in table15.

Table 15, Aluminum-air battery performance data

| | Alkaline battery | Saline battery |
|---|---|---|
| Voltage | 0.8 V | 0.8 V |
| Current density | 150 mA/cm$^2$ | 30 mA/cm$^2$ |
| Electrical energy per volume | 150 Wh$_e$/L | 100 Wh$_e$/L |
| Electrical energy per weight | 150 Wh$_e$/kg | 120 Wh$_e$/kg |
| Total energy per volume | 300 Wh/L | 172 Wh/L |
| Total energy per weight | 300 Wh/kg | 206 Wh/kg |

Note that the battery produces both electrical energy (designated by a subscript e) and heat. The electrical energy can be converted to heat through resistance heaters at any location, potentially increasing the efficiency of heat transfer to the food. The data in Table 15 includes the weight of electrolyte needed, but not the weight of a resistance heater.

TDA analyzed a ration heater producing 150 Btu, using both of these aluminum-air battery conformations. The configuration examined assumed that the aluminum-air battery was a flat, rectangular plate; the length and width are roughly those of the proposed self-heating ration, and the thickness is the minimum required for a given energy output. We assumed that the anode is a flat aluminum plate, dimensions 20 × 15 cm, in contact with the bottom of the tray containing the food. (The aluminum anode could also potentially form the bottom of the food tray itself, with some savings in weight and increase in heat transfer efficiency, but this was not taken into account.) The other electrode, the air cathode, was assumed to be the bottom of the package, and thus to have the same length and width as the aluminum anode. The results are shown in Table 16.

Based on this evaluation for a particular configuration, neither type of aluminum-air battery is suitable for a ration heater. The weight of the aluminum-air battery is greater than the weight of simple chemical heaters, and the low power output (limited by the current density) is such that the heat is delivered over too long a time. Other configurations are possible, including those in which the cell is internally shorted to increase the rate of heat production. However, the critical feature for metal-air batteries in applications requiring a high power output is the current density at the air cathode. Since attainable current densities typically limit the power output, higher power requires a larger air cathode, which in turn increases weight. This also increases cost, since the air cathode is typically the most expensive component of metal-air batteries. Thus, we conclude that aluminum-air batteries are not suitable for ration heaters. They are potentially useful to the Army in applications which specifically require electrical energy, or which need a lower power output than used in the ration heater.

Table 16, Comparison of ration heaters using aluminum-air battery and chemical heater

| | Alkaline battery | Saline battery | Chemical heater ($AlCl_3/CaO$) |
|---|---|---|---|
| Total heat output | 150 Btu = 44 Wh | 150 Btu = 44 Wh | 150 Btu |
| Electrical energy output | 22 $Wh_e$ | 25.6 $Wh_e$ | --- |
| Dimensions | 20 × 15 × 0.5 cm (7.9 × 5.9 × 0.2 in) | 20 × 15 × 0.85 cm (7.9 × 5.9 × 0.34 in) | 20 × 15 × 0.25 cm (7.9 × 5.9 × 0.14 in) |
| Volume | 150 $cm^3$ | 255 $cm^3$ | 75 $cm^3$ |
| Weight | 150 g (0.33 lb) | 214 g (0.56 lb) | 64 g (0.15 lb) |
| Electrode surface area | 300 $cm^2$ | 300 $cm^2$ | --- |
| Electrical power output | 36 $W_e$ | 7.2 $W_e$ | --- |
| Rate of heat production | 72 W | 12.4 W | --- |
| Time to produce 44 Wh total heat output | 37 min | 213 min | <5 min |

## Summary of Results

From the work described above, we can make the following conclusions:

1. There is room for improvement in portable heat sources, specifically in new materials which would increase user convenience and lower cost.

2. The aluminum-air battery is not suitable as a ration heater due to its low power density, and probably also due to high cost.

3. The most effective approach to activating the heater is addition of water or a solution to a solid reactant material.

4. The best material for an antifreeze for the activator solution is calcium chloride, which has minimal weight and cost for a given amount of water.

5. The best materials for a solid reactant, based on materials cost, safety, reaction rate and heat output, are the $AlCl_3$/CaO and $P_2O_5$/CaO reactions, activated by addition of water.

## Conclusions

The focus of this project has been ways in which the application of new chemical heat sources could benefit the military. We have specifically considered the use of portable heat sources for military field rations, since this is an important and high-volume application. Our evaluation began with a comprehensive literature survey, aided by a computerized search, and also generated a large number of candidate reactions from fundamental chemical principles. We also evaluated the reaction currently used in the Flameless Ration Heater (FRH) for purposes of comparison. By a process of elimination, using data on materials costs, reaction rate studies, and calorimetry to measure heat output, we selected the best reactions for ration heaters. We arrived at the following specific conclusions:

1. An opportunity exists to improve on the performance of the FRH in two ways: (a) by lowering the cost of the heater through use of new materials, and (b) eliminating the hydrogen produced by the FRH, which will increase user convenience and safety.

2. The best materials identified are the combination of aluminum chloride with calcium oxide ($AlCl_3/CaO$) and diphosphorus pentoxide with calcium oxide ($P_2O_5/CaO$). Either can provide the same heat as the FRH with a small increase in weight, and does not produce any hydrogen.

3. The aluminum-air battery was investigated as a portable heat source, and was rejected on the basis of weight and cost for high-power applications such as ration heaters; it may well be suitable for lower-power applications such as boot and glove warmers.

4. For ration heaters which incorporate an activator solution, the best antifreeze, as determined by weight and cost analysis and by experiments, is calcium chloride ($CaCl_2$).

5. We conducted a systems analysis for a Self-Heating Ration (SHR) using one of the new reactions we identified, compared with one using the hydrogen-producing reaction in the FRH. We found that with the new reaction, the SHR is 6.0% heavier and 2.4% larger in volume. We assigned a cost penalty of roughly one cent per unit for the additional weight due to increased transport costs. The cost of materials is essentially the same for the new reactions and for the materials used in the FRH, but the fabrication costs should be much less for the new materials, resulting in a lower cost product. The new materials are self-neutralizing for safety, and the used material does not present a disposal problem.

Our overall conclusion is that the new materials here identified for ration heaters have the potential to produce a heater which is more convenient and less hazardous (by avoiding the production of hydrogen), while significantly lowering the cost. TDA has completed an Invention Disclosure describing the new reactions for a portable heater and their advantages over previous technology. We believe that this new process has patentable novelty. A copy of the Invention Disclosure is attached to this Final Report as Appendix B. The further development and testing of these materials is the subject of the Phase II proposal.

This document reports research undertaken at the U.S. Army Soldier and Biological Chemical Command, Soldier Systems Center, and has been assigned No. NATICK/TR-01/004 in a series of reports approved for publication.

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# APPENDIX A: PRELIMINARY HAZARD ANALYSIS REPORT

# Appendix A: Preliminary Hazard Analysis Report

## Preliminary Hazard Analysis Report

| | |
|---|---|
| **CDRL Number:** | A003<br>"System Safety Hazard Analysis Report" |
| **Project Title:** | Applications of New Chemical Heat Sources |
| **Contractor:** | TDA Research, Inc<br>12421 W. 49th Avenue<br>Wheat Ridge, CO 80033<br>(303) 422-7819 |
| **Principal Investigator:** | Dr. William L. Bell |
| **Sponsor:** | U.S. Army Natick RD&E Center<br>Natick Contracts Operation Division<br>ATTN: AMSTR-ANA<br>Natick, Massachusetts 01760-5011 |
| **Contract No.:** | DAAK60-91-C-0054 |
| **Contracting Officer's Representative** | Donald Pickard<br>STRNC-WAE<br>U.S. Army Troop Support Command<br>Natick RD&E Center<br>Natick, MA 01760-5011 |
| **Reporting Period:** | May 1-September 30, 1991 |
| **Security Classification:** | Unclassified |

**Objective:**

This report describes the Preliminary Hazard Analysis for new materials for ration heaters, developed in the course of the above-referenced contract. The format and heading are as given in MIL-STD-882B, Task 202.

### 10.3.1 System Description

The system is a military field ration incorporating a heater for part of the food. The heater is incorporated into a plastic tray or tub containing the food to be heated. The heater consists of a solid material, and an activator solution which is used to start the heater. The heater is in a compartment of the tray or tub adjacent to the food to be heated. The heater and activator solution never come in contact with the food. The estimated weight of the food is 10-12 ounces, and the heater and activator solution is 3-5 ounces. During storage, the activator solution is kept separate from the solid. In use, the activator solution is mixed with the solid, and a reaction occurs, producing heat. This heat then warms the food (or thaws the food if frozen).

The system is described in detail in the report *Applications of New Chemical Heat Sources, Final Report*, prepared by Dr. William L. Bell, Dr. Robert J. Copeland, and Amy L. Schultz for the U.S. Army Troop Support Command, Natick Research, Development and Engineering Center, under SBIR Phase I Contract No. DAAK60-91-C-0054, November 1991. The materials identified in the final report as being useful for the ration heater are: (1) for the heat-producing solid, either a combination of aluminum chloride and calcium oxide ($AlCl_3/CaO$) or a combination of diphosphorus pentoxide and calcium oxide ($P_2O_5/CaO$); (2) for the activator solution, either water or an antifreeze solution consisting of calcium chloride ($CaCl_2$) in water, at a concentration of up to 28%. Details of experiments with these materials, including the rate of reaction and heat output, are found in the above-referenced report.

A related system currently in use by the U.S. Army is the Flameless Ration Heater (FRH), used to heat the Meal, Ready-to-Eat (MRE). The materials used in the FRH are described by Kuhn *et al* (1985).

### 10.3.2 Data

The solid materials described above undergo a reaction with water which produce roughly 150 Btu of heat from 64-97 g of solid. The heat produces temperatures sufficient to boil water, and will produce some steam. 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), ACGIH (1987), 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 ($AlCl_3$ and $P_2O_5$) with the basic material (CaO). This results in an increase in heat output due to the neutralization reaction between the acid and the base. It also results in a product (after the heating reaction is complete) which 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. This includes situations in which solid dust could come in contact with people's skin or mucous membranes. Studies to quantify the safety aspects of this mixture will be part of the Phase II effort. At this point, we know that each of the new materials (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 with suitable precautions.

The calcium chloride used in the activator is described as an irritant, and users are instructed to avoid contact with eyes, skin and clothing (MSDS). It is also taken internally as an electrolyte replacement (Budavari 1989).

### 10.3.3.a Summary of Results

We identified three categories of hazards: (1) burns from steam or hot surfaces, (2) toxic effects which may be produced by the heater material or activator solution if swallowed, inhaled or exposed to skin, and (3) a hazard of high pressure steam generation if the heater is activated in a confined space.

### 10.3.3.b(1) System/Subsystem/Unit

The portable heat source is a subsystem of the Self-Heating Ration (SHR) under development by the U.S. Army Natick RD&E center.

### 10.3.3.b(5) System Event(s) Phase

This analysis considers hazards encountered during either of two conditions: (1) when the heater is in use, and (2) when the heater is being stored or transported.

### 10.3.3.b(7)(a) Hazard Description

The following hazards may be encountered:

1. Burn Personnel will normally handle the hot tray, and may be burned by the hot surface or by escaping steam.

2. Toxicity Personnel will not be exposed to the reactive solid material or the activator solution during normal operation, but may be exposed to the contents by skin contact or inhalation in the event a package is accidentally ruptured in transport or in use. Personnel may also swallow the solid heater material or activator by accident.

3. Reactivity The heater materials are normally activated by water, and a hazard exists that the reactive materials will be accidentally exposed to water, activating the heat-producing reaction. If reaction occurs in a confined space, pressure will build up and a rupture of the containment vessel could result.

### 10.3.3.b(9) Effect on System

1. Burn A burn will occur occasionally, but should be minimized by proper package design. It should at most 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. Toxicity The heater will be designed so that the user will not be exposed to any of the reactive materials. In the event that a container is accidentally ruptured, personnel may be exposed to the materials. The materials used in the heater, taken individually, are harmful if inhaled, swallowed or absorbed through the skin. Safety considerations have directed the choice of materials for the heater so that they are self-neutralizing which should minimize the toxicity hazard to personnel.

3. Reactivity The materials are reactive when exposed to water. The materials will be fabricated so that the release of heat is controlled. Tests planned in further work will verify an accidental activation of the heater (as, for example, if a number of SHRs are crushed by a weight) cannot result in a fire. If the vapor produced by the heating cannot escape, a steam rupture of the package can result. The resulting steam would generate a high velocity stream and could produce minor burns (see *Burn* above). The package will be designed to fail at a predetermined spot to prevent an explosive release of steam.

10.3.3.b(10) Risk Assessment

The risk assessment, with hazards, description, severity, and probability of occurrence, is shown in Table A-1 below.

**Table A-1** Risk assessment.

| Hazard | Description | Severity | Probability |
|---|---|---|---|
| Burn | contact with steam or hot surface | III (minor injury) | B (probable) |
| Toxicity | Skin contact with activator solution | IV (negligible) | C (occasional) |
|  | Ingestion of activator solution | III (minor illness) | D (remote) |
|  | Skin contact with reactive solid | III (minor injury) | C (occasional) |
|  | Ingestion of reactive solid | II (severe illness) | D (remote) |
|  | Inhalation of dust from reactive solid | III (minor injury) | C (occasional) |
| Reactivity | Heater activated by accident | III (minor injury) | D (remote) |

10.3.3.b(11) Recommended Action

and

10.3.3.b(12) Effect of Recommended Action

Recommended actions and anticipated effects are described below.

1. <u>Burn</u> Burn hazard should be minimized by design, so that (a) the SHR can be transported without burning the fingers of the user, and (b) by arranging the vents for steam so that the steam does not vent toward the user. Warning signs will also be provided.

2. <u>Toxicity</u> Materials will be formulated to minimize dust which could be inhaled by user if a package is ruptured. Warning signs will tell user not to eat the heater material or drink the activator solution.

3. <u>Reactivity</u> Signs will tell users that the heater produces steam and should not be operated in a closed container.

10.3.3.b(13) Remarks

None of the materials used in the new heaters are flammable. This represents an improvement over the magnesium/iron/high-density polyethylene formulation of the FRH, which is flammable. Also, the $Mg + H_2O$ reaction in the FRH produces hydrogen, which is flammable and can form explosive mixtures with air.

10.3.3.b(14) Status

No further action is anticipated in Phase I of this project.

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Report Preparer

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Certification of Technical Data Conformity

The Contractor, TDA Research, Inc., hereby certifies that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. DAAK60-91-C-0054 is complete, accurate, and complies with all requirements of the contract.

William L. Bell, Principal Scientist Date

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# APPENDIX B: INVENTION DISCLOSURE

# Energetic Materials for Portable Heat Source

Invention Disclosure

## Introduction

This invention relates to materials which can be used to produce heat in a portable heater, to warm food, beverage or other supplies without the need for a stove, fire, or electrical power. The major advantage of such a chemical heater is its simplicity of operation. The heater can be stored until needed, packaged separately or with the food or other supplies to be heated. When warm food is desired, the heater is activated and the food is heated, ideally over a period not exceeding 5-10 minutes. The hazard associated with fire or flame, and the weight and inconvenience of having both a stove and fuel to warm a limited amount of food, are thereby avoided.

The desirable features of such a chemical heater are:

1. It must be safe for the user.
2. It must be conveniently activated.
3. It must be low 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 that the food or other item is warmed in a short time, but without elevated temperatures which could cause undesirable changes.
6. The heater must transport heat efficiently to the food container.
7. The heater must be stable in storage for an extended period of time, preferably more than two years.
8. The heaters should be readily disposable after use, with minimal environmental impact.

## Background

Chemical heaters have been known for some time, and previously reported chemical reactions are summarized in Table B-1.

## Approach

A desirable method for activating a chemical heater is the mixing of water (or an aqueous solution) with a solid. The water or solution may be packaged with the heater or separately. The package must incorporate means for mixing the two components. Since these heaters may be used in cold environments, the activator solution must be kept from freezing. For this purpose, calcium chloride is a well-known anti-freeze which may be added to the water or solution for this purpose. The use of water or an aqueous solution has two specific advantages. First, it limits the temperatures which are attained by the heater, thereby avoiding over-heating of the food. Second, the vaporization and condensation of water provides an effective means of transferring heat from the heater to the food container.

**Table B-1** Reported reactions for chemical heaters

| Reference | Reactants | $\Delta H^{\circ}_{rxn}$ kcal/mol | Heat output Btu/lb* | Comments |
|---|---|---|---|---|
| Kuhn *et al.*, 1985 | $Mg + H_2O$ | -84.88 | 5,643 | Produces hydrogen gas |
| Charvin, 1989 and others | $CaO + H_2O$ | -15.95 | 501 | commonly used, low cost; high weight and bulk |
| Labrousse, 1988 | $SrO + H_2O$ | -21.78 | 322 | no advantage over CaO rxn |
| " | $BaO + H_2O$ | -52.92 | 302 | no advantage over CaO rxn |
| " | $KOH + H_2O$ | -13.77 | 442 | strong base |
| " | $NaOH + HCl$ | -23.99 | 565 | strong base |
| " | $Mg(OH)_2 + HCl$ | -27.22 | 373 | strong acid |
| " | $CaO + HCl$ | -50.00 | 411 | strong acid |
| Yukawa, 1988 | $MgCl_2 + H_2O$ | -38.13 | 721 | no strong acid or base; weight of water req'd high |
| Benmussa, 1985 | $H_3PO_4 + KOH$ | -80.99 | 644 | strong acid and base |
| Okamoto, 1989 | $Fe + KMnO_4$ | -131.80 | 554 | No water req'd; $T_{max} > 1000°C$ |

* weight of water not included

### Description of the Invention

The current invention is comprised of a solid which contains two components, one which reacts with water to produce an acid or an acidic solution, and one which reacts with water to produce a base or basic solution. The said acid or acidic solution, and the said base or basic solution then may react with one another in a neutralization reaction. In a preferred embodiment of the invention, the solid which reacts with water to produce an acid or acidic solution is anhydrous aluminum chloride ($AlCl_3$) or diphosphorus pentoxide ($P_2O_5$), or a combination thereof, and the solid which reacts with water to produce an base or basic solution is calcium oxide (CaO). The reaction of either solid, or both, with water may be exothermic, and the neutralization reaction is also exothermic.

The operation and advantages of this invention are summarized below.

1. The heater is safe for the user since it avoids toxic materials, highly reactive combinations which may produce excessive temperatures or the hazard of explosion, and strong acids or bases. The acidic and basic materials in the current invention react immediately with one another to give a product which is so close to neutral that it is inherently safe and readily disposable.

2. The heater is conveniently activated by the addition of water or a calcium chloride solution.

3. The heater is low cost. The materials described in the preferred embodiment are not expensive, and extensive processing is not required to give a rapidly reacting solid. The combination of the two dry powders reacts rapidly on addition of water.

4. Based on the reactions described in the preferred embodiment, the heater is lower in weight and volume than many previously used systems; in particular, it is both lighter and smaller than a heater based on the commonly used reaction of calcium oxide with water. The reactions described in the preferred embodiment and their heat production are:

| Reaction | Heat released Btu/lb dry weight |
|---|---|
| $2AlCl_3 + 3CaO + 3H_2O \longrightarrow 2Al(OH)_3 + 3CaCl_2$ | 1,061 |
| $P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2$ | 1,035 |

The weight and volume of a heater producing 150 Btu, using the above reactions activated by a calcium chloride solution, are shown in Table B-2

5. The rate of heat output may be controlled by arranging the two solid components so that the water or solution contacts both components at once (as in the case of an intimate mixture of the two solid powders), or contacts one component first, with some heat evolution, and then contacts the second solid component, producing more heat. The two components may be intimately mixed, or separated by a porous barrier, with or without further materials to affect the rate of uptake of water or solution. The rate of heat output may be controlled by adjusting the particle size of the solid; larger particles will react at lower rates. Control over the reaction rate is desirable to assure that the food is warmed in a reasonable time, while avoiding production of heat much faster than the heat can be transferred to the food container, which would lead to the loss of heat as steam. Loss of heat as steam would be inefficient and require the heater to be unnecessarily large.

6. The heater transports heat efficiently to the food both by conduction and by the vaporization and condensation of water. To the extent that heat transfer occurs by direct contact of the food container with the reacting mixture, the use of calcium chloride solution is advantageous, since it produces a highly concentrated solution with an elevated boiling point. This in turn increases the rate of heat transfer to the food, without reaching temperatures so high as to have undesirable effects on the food.

7. The heater is stable to storage for an extended period since it contains only simple compounds which are unaffected by oxygen. The solid components of the heater must

only be protected from reaction with water until the heater is activated.

**Table B-2** Heater weight and volume

| Heater composition | $AlCl_3/CaO$ | $P_2O_5/CaO$ |
|---|---|---|
| Heat output, Btu | 150 | 150 |
| Weight of solid, g | 64 | 66 |
| Volume of solid, $cm^3$ | 75 | 86 |
| Weight of water consumed in reaction, g | 8 | 0 |
| Weight of water to aid in heat transfer, g | 30 | 30 |
| Total weight of water, g | 38 | 30 |
| Weight of $CaCl_2$ solution, g | 46 | 37 |
| Volume of $CaCl_2$ solution, $cm^3$ | 36 | 29 |
| Total heater weight, solid + $CaCl_2$ solution, g (oz.) | 110 (3.9) | 103 (3.6) |
| Total heater volume, $cm^3$ (fl. oz.) | 111 (3.8) | 115 (3.9) |

8. The heater reaction products are readily disposed of after use, since the products are a neutral or almost neutral mixture of salts.

## Claims for the Invention

We claim a novel energetic material for a portable heat source, comprised of a solid containing two components, one which reacts with water to produce an acid or an acidic solution, and one which reacts with water to produce a base or basic solution. The said acid or acidic solution, and the said base or basic solution may then react with one another in a neutralization reaction. In a preferred embodiment of the invention, the solid which reacts with water to produce an acid or acidic solution is anhydrous aluminum chloride or diphosphorus pentoxide, or a combination thereof, and the solid which reacts with water to produce an base or basic solution is calcium oxide. The reaction of both solids with water can be exothermic, as in the preferred embodiment, and the neutralization reaction is also exothermic. We further claim a method for controlling the rate of heat production in said portable heaters, wherein the water or solution introduced to activate the heater either contacts both components at once (as in the case of an intimate mixture of the two solid powders), or contacts one component first, with some heat evolution, and then contacts the second solid component, producing more heat. The two components may be intimately mixed, or separated by a porous barrier, with or without further materials to affect the rate of uptake of water or solution.