AIR-ACTIVATED RATION HEATERS

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ABSTRACT

The current Mg-Fe flameless heater is based on the accelerated corrosive oxidation of magnesium resulting from dissimilar metals placed in contact with an electrolyte[1,2]. Water is used to activate the heater, and hydrogen is released as a by-product. RBC Technologies (RBC) and the Natick Soldier RDEC have developed a flameless heater technology based on the direct oxidation of a metal in air. The new heater technology requires no additional reactants, and has no undesired by-products.

1. INTRODUCTION

The standard operational ration for the Department of Defense is the Meal, Ready-to-Eat (MRE™). The MRE™ (Figure 1) includes a lightweight, low cost, easy-to-use chemical heater called the Flameless Ration Heater (FRH). The FRH consists of a magnesium/iron mixture sealed in a waterproof pouch. When one ounce of water is added to the FRH, it can raise the temperature of one MRE entree by 100°F in 12 minutes or less:

$$2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2 \quad \Delta H_f = -5.92 \text{ kcal/g Mg} \qquad (1)$$

The Army is investigating alternative chemistries that are entirely self-contained, so that the ration heater can be activated without the use of essential drinking water by individual Warfighters.

RBC Technologies, through work funded by the Small Business Innovation Research program, and in partnership with the Natick Soldier RDEC, has developed a self-contained air activated heater that can be integrated into packaging configurations to provide a ration heater for use with the MRE.

Figure 1. The MRE (left) utilizes the FRH (right) for heating the main entrée pouch

The heater is based on the exothermic oxidation reaction of Zinc (Zn):

$$2\ Zn + O_2 \rightarrow 2\ ZnO \quad \Delta H_f = -1.28 \text{ kcal/g Zn} \qquad (2)$$

This electrochemical reduction of oxygen readily takes place on activated carbon. To achieve the reaction, Zn powder and activated carbon are embedded into a flexible binder substrate. This substrate is then rolled into sheets which can be cut, wrapped or folded into the desired form.

Past work has identified several air activated reactions, but each candidate possessed drawbacks that made it difficult to apply to military rations. Air-activated reactions that utilize common metals, have been categorized as “difficult to control”, “produces extreme temperatures”, and “requires special handling procedures”. For these reasons, air-activated heaters have found niche markets at each end of the spectrum: slow reactions (hand warmers, medical heating pads) and very aggressive reactions (infrared countermeasures). No air-activated reactions have been demonstrated to operate safely, affordably, and fast enough to provide the time/temperature profile required for heating of the MRE. However, the application of this technology within combat rations extends far beyond only the MRE. The flexibility of the heater sheets provides for application to commercial beverages, soups, and other platforms. These applications as well as the heater design and results will be discussed.

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1. HEATER DESIGN

There is a narrow operating temperature range for chemical heaters for this specific application. The films, seals, and materials used in the packaging of the MRE entrée have an upper temperature limit that approaches 300°F. There is also a lower operating temperature limit due to the need to heat the entrée by a temperature difference of 100°F (56°C) within 12 minutes. This brings a unique heat transfer challenge to the Zn chemistry. Potential heater temperatures of over 400°F have been tempered by optimizing zinc, electrolyte, and binder percentages to control the reaction kinetics and keep the packaging and materials from being damaged.

1.1. Flexible Sheet Design

It had been demonstrated that the electrochemical oxidation of Zinc could be carried out in powder form to generate heat. By mixing the zinc powder with activated carbon, and applying potassium hydroxide (KOH) electrolyte, the reaction readily occurred in atmospheric conditions. However, spreading the powder uniformly around a water bag or MRE pouch proved to be difficult. Moving or handling of the bag led to redistribution, shifting, and clumping of the powder, which makes it difficult for the oxygen to access all the Zinc material. Also, a change in the powder redistribution can lead to an unpredictable performance, non-uniform heating, and hot spots that can affect package integrity. The need to produce the heater in sheets comes from these issues.

RBC Technologies created a process which involves mixing zinc metal powder, activated carbon, a binder, and a solvent within a mixer$_3$. The resulting 'cake' is passed through a set of heated rollers, which leads to fibrillation of the binder and formation of a flexible sheet that can be cut into desired shapes. These sheets are stable in air. The sheets are then treated with an electrolyte solution in an oxygen deficient atmosphere. These heater sheets are enclosed within a pouch with air access holes. A barrier sheet with a peelable seal is then applied over the access holes. The heater is activated by simply peeling off this sealing sheet. The heater does not require any other input by the Warfighter, and does not produce any undesirable byproducts, such as hydrogen. An exploded view of the heater assembly is shown in Figure 2.

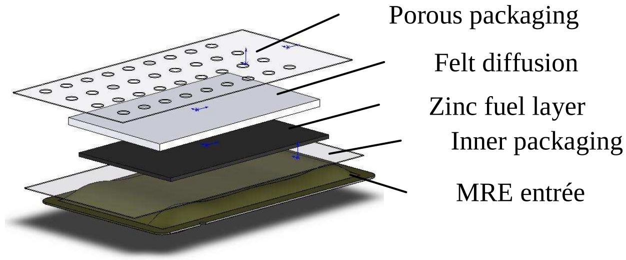

Figure 2. Exploded and assembly views of Zinc-Air ration heater

The advantage of the heater sheet design is the robust nature of its application. The sheets can be used to heat irregular surfaces (MRE entrée, water pouches), flat surfaces (polymeric trays), and cylindrical surfaces (soup cans, coffee cups) Figure 3 demonstrates the flexible nature of these heater sheets.

Figure 3. Flexible zinc composite heater sheets

1.2. Heater Sheet Thickness

Heater thickness can also be adjusted to optimize heating based on the application. For the application of the MRE, the goal is a 100°F temperature rise. To design a heating profile that meets this goal requires a tradeoff between the speed of the reaction, the weight of the reactants, and the maximum temperature reached by the heater. The thickness of the heater sheet directly impacts each of these properties. Heating profiles of varied thickness heater sheets were measured, and the results are presented in Figure 4. As shown, there is a clear correlation between the thickness and the temperature profile. However, heaters at 20 and 30 mils still had a 100°F temperature rise.

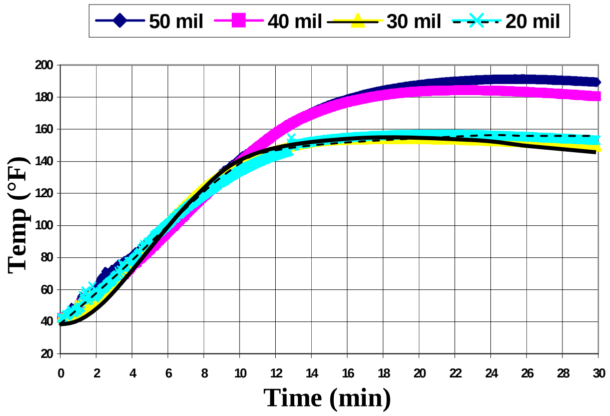

Figure 4. Heating profile for different heater thicknesses, ranging from 20 to 50 mil.

2. HEATING PERFORMANCE

In order to meet operational requirements, any heater designed for use with the MRE must be capable of heating one 8 oz. (230g) entrée pouch from 40°F to 140°F within 12 minutes. To accomplish this heating, several assumptions must be made: the heat capacity of food is equivalent to that of water (4.18 kJ/kg·K), and the entrée pouch is assumed to be a two-dimensional plane wall. In practice, the heat capacity of food stuffs is slightly lower than that of water, and so is the thermal conductivity.

2.1. Current Heat Transfer Mechanism

The current FRH heats the MRE entrée through two heating mechanisms: thermal conduction and latent heat of steam condensation. The first mechanism is through direct conduction on one side of the MRE entrée pouch. The FRH acts as a plane wall with uniform heat generation, and conduction in only one direction. Since the reaction is fueled by water, it is controlled by the boiling point of water, and remains at approximately 212°F for the length of the reaction. The second mechanism, steam condensation, provides for steam produced in the reaction to condense on the available surface area of the MRE entrée.

A heater containing 8g Mg powder, theoretically produces 198 kJ of heat, about twice the energy needed to heat an MRE entrée by 100°F, 94 kJ. Empirical data shows that a heater containing 8g Mg will actually raise the temperature by over 110°F, This leads to the conclusion more than 1/3 of the heat of reaction is lost to the environment through convective heat transfer and mass transfer in the form of steam. A byproduct of this reaction, hydrogen gas, contributes to this mass transfer phenomenon by acting as a carrier for the steam.

2.2. Conduction Only Heat Transfer Mechanism

Due to the oxygen activated nature of the Zinc based heater, water is no longer a reactant, and steam can no longer be used as a highly efficient heat transfer mechanism. Additionally, the absence of water eliminates the self-regulating temperature, which is an important attribute of the Mg-based heater. Conductive heat transfer remains as the sole heat transfer method between the Zinc sheet, and the entrée pouch.

Because linear conduction is the only heat transfer method the Zn heater uses, it is important to maximize the surface area for heat transfer. Surface area is optimized by placing Zn heating sheets on both sides of the MRE entrée. Another advantage of the air-activated heater is that physical orientation is not an issue during operation. Water activated systems require orientation, which hinders military operations that require heat on-the-move.

A heater containing 42g Zn powder, within a flexible substrate, produces about 225 kJ of heat, slightly more than twice which is needed to heat an MRE entrée by 100°F, 96 kJ. As expected, these empirical results show that conduction alone is slightly less efficient than conduction combined with the latent heat of condensation. Due to the absence of steam, the heater operates at a temperature of approximately 350°F. Theoretically, approximately 17g Zn is needed for heating, which confirms these numbers.

In Figure 5, heating profiles are shown for each heating mechanism. Both mechanisms display a typical first order response, but the conduction only mechanism is slightly more dampened than when steam is present. It is also apparent that the steam provides moderation and provides a smooth temperature rise.

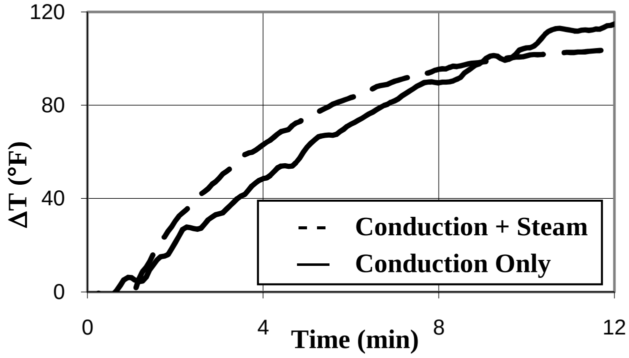

Figure 5. Comparison of Heat Transfer Mechanisms

3. PACKAGING

For an air-activated heater, the design of the package is no less important than the heating element itself. The material between the heater and the MRE entrée must maintain its physical integrity during active heating. For both the outer and the inner packaging, good stability and oxygen barrier properties are needed to maintain the heating properties of the zinc for at least 3 years. Additionally, good vapor barrier properties are needed to keep moisture from entering or escaping the pouch. The electrolyte, KOH, is at a set concentration for optimized heating. If moisture were to enter or escape through the packaging, heating profiles could be significantly changed.

3.1. Pouch Materials

Based on several experiments, 2.2 mil, 4-layer metalized film storage bags, designed for food, serve as excellent candidates. The film provides excellent oxygen and water vapor barrier properties, was used in the prototype heater pouches, and provided excellent seals. Although the metalized film worked very well, it has a highly reflective surface, which makes it unsuitable for military operations (Figure 6). Consequently, the film needed to be replaced by a non-reflective material.

Curlam® Grade 1834-K protective packaging film has been identified as a film suitable for making heater pouches and peelable seals (Figure 6). This material is coextruded film with a polyester layer, an adhesive layer and an EVOH EZ Peel® EVA layer. The material provides an oxygen barrier property of < 0.2 CC O_2/100in^2/24 hrs @ 73°F and 0% RH, and water vapor transmission rate of < 1g H_2O /100in^2/24 hrs at 100°F and 90% RH.

Figure 6. Prototypes of air-activated heaters using a 4-layer metalized film (left) and Curlam® Grade 1834-K protective packaging film (right)

3.2. Activation

A peelable seal formed using the identified film, provides the barrier properties discussed, and is strong enough to maintain integrity during shipping, while still being peelable by the end user. Nylon was identified as an excellent barrier film, but it can only be heat sealed on one side. Consequently, the material must be reoriented for each seal, which significantly slows the assembly process. EVOH has also been identified as an excellent barrier material for oxygen sensitive applications. The Curlam® material has the barrier properties of EVOH, but the EVA provides additional flexibility and peelable properties. This material can be sealed on both sides, and does not need to be reoriented. Short term storage studies have confirmed that the Curlam film seals well to form an oxygen barrier while maintaining good peel properties. Long term storage studies are being conducted.

3.3. Air Diffuser

The air diffuser is the layer between the porous layer and the heater sheet. The porous layer is made from the same material as the heater pouch, and has openings punched in it. The number and size of the openings determines the rate and amount of air/oxygen reaching the heater sheet. To further control the rate and amount of air/oxygen, an air diffuser layer is used. It diffuses air/oxygen across the thickness as well as laterally, and is light and inexpensive. In addition to distributing air to all parts of the heater sheet, this layer also acts as an insulator and helps in reducing heat loss from the heater to the environment.

The air diffuser is in contact with the heater sheet and therefore the material must not react with the KOH electrolyte. After testing various materials, air filter media initially was found to be satisfactory. Later experiments showed that the material slowly reacted with the electrolyte and fell apart, losing the “open” structure. Shelf life deteriorated to about 8 weeks.

To find a replacement, initial experiments focused on separator materials that are currently used in alkaline batteries. Materials that are treated to be hydrophobic or are naturally hydrophobic were tried first. It was found that a simple polymer felt acts as a good diffuser and has the added advantage of providing insulation properties.

4. SAFETY

For any ration heater, it is necessary to address the hazards and environmental issues including the characteristics of the materials which are present in the sheets before activation (zinc, carbon, and Teflon binder and potassium hydroxide solution) and after reaction (zinc oxide).

4.1. User Safety

In the heater sheet, fibrillated solid material is present as a binder, and KOH is absorbed in the pores of the sheet. As there is no free KOH electrolyte present on the surface, the hazard associated with coming in contact with the skin and causing chemical burn is eliminated.

Similarly, zinc powder and carbon in the non-reacted heater and zinc oxide in the reacted heater are bound in a matrix and are immobilized. This reduces/eliminates the hazard associated with powder being able to get airborne and thereby getting into eyes, coming in contact with the skin, being inhaled or ingested.

The air-activated heater also poses an inherent hazard of a skin burn if touched when hot. Such a hazard is reduced by the air diffuser layer on the outside of the heater sheet, which prevents contact with the skin. This layer helps in directing the heat towards the item to be heated. Additionally, diffusion of oxygen towards the heater acts as a natural heat barrier. This aids in preventing extreme temperatures from coming in contact with the user. In tests, the highest temperature measured on the exterior of the heater was approximately 160°F, well within the limits of heaters of this type.

4.2. Regulatory Issues

The major components of the heater system are zinc powder, carbon black, binder fibers, potassium hydroxide solution, plastic films and polymeric felt. The zinc powder, carbon black, and binder are not regulated for transportation by the Department of Transportation (DOT) and can therefore be shipped using normal means. Potassium hydroxide solution *does* have DOT shipment regulations as this is a caustic liquid that is spillable. However, in the fabricated heater sheet there is no free liquid KOH, because it is completely absorbed within the heater structure and can't be spilled. The plastic film and plastic felt materials are completely inert and also are not regulated for transportation by the DOT.

During the manufacturing of the heater sheet there are no chemical changes effected on any of the individual components that would cause them to be reclassified or regulated. After use, the product of the heating reaction is zinc oxide, an inert chemical used in many different products such as sunscreen, creams for diaper rash, and paint pigments. This material is also not regulated for transportation by the DOT and not regulated for disposal by the EPA.

5. OTHER APPLICATIONS

The Unitized Group Ration – Express (UGR-E), utilizes the Mg-based heating technology at the group ration level (Figure 7). The UGR-E heats 4 polymeric heat and serve trays in 30-45 minutes. Four 300ml saline pouches contained within the UGR-E are used to activate the Mg-based heaters located under each polymeric tray. Application of the air-activated heater to the UGR-E would allow for the elimination of Hydrogen by-products, remove regulatory restrictions, reduce packaging, and eliminate the need for the four heating trays to hold the saline pouches and activated heaters. This reduction in weight, packaging, volume, and in turn cost, would lead to improved military logistics.

Figure 7. UGR-E in operation (left) and its contents displayed (right)

6. CONCLUSIONS

An air-activated, flameless ration heater that harnesses the energy of oxidation of Zinc to heat an MRE entrée pouch in a reasonably simple, practical and cost-effective way has been achieved. The electrochemical heater is entirely self-contained, requiring only exposing the heater pouch to air. The rate of reaction or "cooking" time has been adjusted by controlling air permeation and heater configuration. The heater meets the Army specification of increasing the temperature of an eight ounce water pouch from 40 °F to 140 °F (+100 °F) in less than 12 minutes.

7. ACKNOWLEDGMENTS

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