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# **Development History of Fe/KClO<sub>4</sub> Heat Powders at Sandia and Related Aging Issues for Thermal Batteries**

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### **Abstract**

Pelletized pyrotechnic discs ("heat pellet") are used in thermally activated ("thermal") batteries for nuclear weapons for the Department of Energy (DOE) as well as in a large variety of missiles for the Department of Defense. Thermal batteries provide the primary power for these applications and depend on a molten-salt electrolyte. The batteries deliver power upon melting of the electrolyte caused by the heat released during burning of heat pellets in the battery stack. Prior to the use of heat pellets, a heat paper based on Zr/BaCrO<sub>4</sub> was used as the heat source in thermal batteries. This material had a number of disadvantages, including static and shock sensitivity and forming highly resistive reaction products that would not allow for intercell connection of cells in a stack. This report describes the history of the development of pelletized pyrotechnics at Sandia National Laboratories for the DOE's nuclear weapons. The final chemistry selected was Fe/KClO<sub>4</sub>, since it met all of the desired qualities for the anticipated applications. This report also provides relevant historical aging data for this material, as well as related data generated as part of a stockpile surveillance program.

## **Acknowledgments**

The author wishes to acknowledge the efforts of a number of individuals who contributed to this report. The anion analyses were performed by Sandra Klassen and Elaine Boespflug, Org. 2552. The inert-gas fusion analyses were done by Jeff Reich, Org. 1822. The calorific output measurements were conducted by Sandra Klassen and Tom Massis, Org. 2552. Frederick Reinhardt, Org. 2522, assisted with some of the accelerated aging tests.

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# Development History of Fe/KClO<sub>4</sub> Heat Powders at Sandia and Related Aging Issues for Thermal Batteries

## INTRODUCTION

The purpose of this report is to provide a history and perspective on the development of Fe/KClO<sub>4</sub> pyrotechnic powders at Sandia National Laboratories. These materials are used as a heat source in nuclear weapons and in all thermal batteries. Data on aging of these materials that were generated in the development process are included for information purposes. Aging issues that relate to the performance of the pyrotechnics used in thermal batteries are also discussed.

## UNIDYNAMICS' DEVELOPMENT WORK

All of the DOE thermal batteries use the Fe/KClO<sub>4</sub> pellet technology, which evolved out of development work at Unidynamics/Phoenix Inc. (UPI) (now Pacific Scientific), in Phoenix, AZ under contract to Sandia.<sup>1-5</sup> This pellet technology was originally developed as a pyrotechnic source for thermal batteries. This same technology was subsequently used to develop a heat source for nuclear-weapons applications as well.

In the early 1960s, Sandia contracted with Unidynamics/Phoenix Inc. (UPI), Phoenix, AZ, to develop a gasless pelletized heat source that could be used to replace the Zr/BaCrO<sub>4</sub> heat paper that was then being used in the Department of Energy (DOE) thermal batteries.<sup>1</sup> This heat paper is extremely shock and static sensitive, which makes handling of this material hazardous. A number of performance metrics were used to characterize potential heat sources. These included:

- Physical strength of the heat pellets
- Calorific output
- Gas evolution
- Ignitability by 360-cal/g heat paper
- Relative ignition sensitivity
- Linear burn rate
- Electrical conductivity
- Combustion temperature
- Dimensional stability

The ideal heat source would have good physical strength, high gravimetric heat output (over 200 cal/g), be easily ignited, have a minimum linear (one-dimensional) burn rate of >0.5 in/s, be dimensionally stable after ignition (i.e., no warpage), and produce little or no gas during burning. In addition, the material must be chemically stable over long storage periods (>25 years) and very reproducible in its burn characteristics.

In earlier related work, heat generation by intermetallic alloy formation and thermites was examined, as well as various metal-oxidant combinations. The list was narrowed down to the systems Fe/KClO<sub>4</sub>, Fe/Ag<sub>2</sub>O, and Fe/CuO. The latter system was dropped early in the study due to poor ignition sensitivity. Similar problems were encountered with the Fe/Ag<sub>2</sub>O system. This, along with the high cost due to the silver content, forced further testing of this material to be discontinued. The primary focus of the work then became the Fe/KClO<sub>4</sub> system. A total of 21 commercial suppliers of Fe powder were contacted during this work, with the list being narrowed to a final number of 13.

Initial work was centered on a 90% Fe/10% KClO<sub>4</sub> composition, based on earlier known characteristics of this composition. One Fe material from C. K. Williams and several from Glidden Co. showed great promise and additional compositions using these Fe sources were examined. In addition, the supplemental use of Zr powder was evaluated. The addition of Zr greatly increased the ignition sensitivity and burn rate but at the expense of somewhat erratic electrical properties, which was deemed unacceptable for thermal-battery use, since the burned heat pellets serve as intercell connectors in a battery stack.

Characterization Methods – The burn rate of the heat pellets was measured with the use of two photocells to start and stop a counter to measure the time for the flame front to travel a known distance. Three methods of ignition sensitivity were evaluated. One was only semiquantitative and involved the use of a strip of Zr/BaCrO<sub>4</sub> heat paper. A second measured the autoignition temperature with a heating apparatus. A third used a resistance heater (bridgewire) imbedded in a pile of the heat powder. The minimum current required to ignite the powder after 10 s was used as the metric. The fourth method for measuring ignition sensitivity used a dc arc from a charged capacitor bank (i.e., capacitive discharge, or CD, technique). A tungsten electrode with a ball-shaped tip was used as the arc-generating electrode. The energy needed to ignite a heat pellet was recorded in joules. The precision of this method, however, was less than desired, but was still superior to the other methods examined at the time. The peak combustion temperature was recorded with a Type K thermocouple placed in contact with the heat pellet.

Density effects were also noted during the work. Pellet ignition required a higher energy when the pellet density increased. This had also been observed in subsequent related work at Sandia involving burn-rate measurements. At high densities (>80% of theoretical), the high thermal conductivity of the excess Fe present resulted in quenching of the burn front, so that combustion could be sustained. Sandia typically uses a heat-pellet density of 50%-55% of theoretical in its thermal batteries.

The best source of Fe powder was the I-68 material from C. K. Williams. The morphology of this material was responsible for its high pellet strength and ease of ignition of the Fe/KClO<sub>4</sub> heat pellets.

## **FOLLOW-ON WORK AT UNIDYNAMICS**

Additives – A follow-on contract was placed with UPI to improve the ignition sensitivity of the Fe/KClO<sub>4</sub> pyrotechnic that was developed under the initial contract.<sup>2</sup> The new work



built on the information gathered in the initial development efforts. The Fe used in the study was C. W. Williams I-68. The original work used an experimental lot; in the follow-on work, a 5,000-pound lot of this same material was procured. There were some differences in the properties of the two lots that resulted in some difficulties. A number of additives were examined to increase the ignition sensitivity, including  $\text{CuCrO}_2$ ,  $\text{Pb}_3\text{O}_4$ , and  $\text{KClO}_3$ . Only the last one, at levels of 2% to 4% was effective with the 90/10 composition and densities of 50 – 55%.. Blends based on 88% Fe actually required more energy and produced a lower calorific output when  $\text{KClO}_3$  was added.

Alternative Pyrotechnic Compositions – In a continuation of the work on pelletized heat sources, UPI pursued other pyrotechnic compositions, as well as a new source of Fe powder from Pfizer.<sup>3</sup> Some compositions substituted Ni for Fe. One reason for this was to reduce the tendency for oxidation of the Fe in heat pellets in a somewhat humid environment. Mixes of Fe-S and Ni-S were also examined. Eight experimental Fe powders from Pfizer were characterized. This material was the Fe formerly designated as I-68 from C. K. Williams. As part of this program, a list of possible Fe suppliers was compiled and totaled 116. Only 30 of these were in a position to provide the type of Fe needed for the pyrotechnic application.

This work was further extended with an additional contract with UPI where alternative metal-oxidizer combinations were evaluated for Sandia's applications.<sup>4</sup> It was during this portion of the work that the designation NX-1000 was given to Pfizer's experimental Fe powder. Metal fuels that were evaluated included Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Pb, Mo, and W. Oxidizers included S,  $\text{KClO}_4$ ,  $\text{KClO}_3$ ,  $\text{KBrO}_3$ ,  $\text{KIO}_3$ ,  $\text{KIO}_4$ ,  $\text{K}_2\text{CrO}_7$ ,  $\text{CuO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbCrO}_4$ , and  $\text{Ca}(\text{IO}_3)_2$ . While many of the various combinations did function as pyrotechnics, there were a number of problems. Some could not be consolidated into pellets, even at high pressures, and some lacked dimensional stability after ignition, while others could not be easily ignited. Some mixes had low calorific outputs on a per-gram basis and some generated unacceptable levels of gas or burned violently and came apart. Several compositions were not stable during long-term storage at room temperature. The combustion products for a number of compositions were very resistive and thus unsuitable for use as intercell connectors between cells in a thermal-battery stack.

In the end, the favored material was a mix with Pfizer's experimental Fe, designated NX-1000, with  $\text{KClO}_4$ . This is the genesis of the current heat powders used in Sandia's thermal batteries and nuclear-weapon applications. In order to specify qualification and testing of the new Fe/ $\text{KClO}_4$  heat powders, Sandia placed another contract with UPI to develop the necessary procedures, specification, and documentation for these tasks.<sup>5</sup> It was during this work that the effects of particle size on the burn characteristics were determined. The particle size of  $\text{KClO}_4$  had little or no effect on the pellet breaking strength or gas evolution, but it did impact the burn rate and ignition sensitivity. Both of these parameters reflect the kinetic effects of solid-state chemical reactions, which one would expect to be influenced by reactant particle size. The smaller particle size resulted in higher burn rate and lower ignition sensitivity.

It was also during this work that the use of a laser for ignition-sensitivity measurements was developed to replace the previous CD unit. A minimum in ignition sensitivity was observed near a pellet density of 3.5 g/cc, which is slightly higher than the nominal value called out for Sandia's thermal batteries.

## **SANDIA'S CHARACTERIZATION EFFORTS**

The effects of a number of physical parameters of Fe/KClO<sub>4</sub> heat pellets on the combustion characteristics were examined as part of a characterization effort reported in a memorandum written in late 1976.<sup>6</sup> The effects of composition, pellet density, temperature, and stack pressure were examined as part of a partial-factorial screening study. It was found that the burn rate showed a maximum at a composition of 86% Fe/14% KClO<sub>4</sub> (relative to the 88/12 and 84/16 compositions) and a maximum in burn rate with density near 3.40 g/cc [54.2% of theoretical density (TD)]. There was no effect due to pellet thickness or pressure.

In a second phase of this work, more-detailed experiments were carried out with fewer variables.<sup>7</sup> The main effects were due to composition, density, and temperature. The burn rate increased with temperature. There was also an interaction between composition and density. More-detailed interactions were outlined in a memorandum concerning the subsequent Phase 3 work.<sup>8</sup>

The results of this early heat-pellet characterization work agree reasonably well with those of D. McCarthy *et al.*<sup>9</sup> and similar but more-detailed work at Mound at a later date.<sup>10,11</sup> The Mound work examined the three standard compositions and parameters such as density, substrate effects, pellet thickness, and temperature. It substantiated the fact that pellet thickness had no effect on the burn rate. The lack of correlation of burn rate to thickness (size) of the pyrotechnic part is important from both the perspective of thermal-battery use as well as a reliable heat source for nuclear-weapons applications.

### **Sandia Heat-Powder Task Force**

In 1981, Sandia established a Battery Ignition Task Force to more fully characterize the properties and parameters that impact the combustion of Fe/KClO<sub>4</sub> heat pellets in terms of thermal-battery activation. The team members were D. K. McCarthy (Org. 2522), R. W. Dietzel and W. B. Leslie (Org. 2513). The team met with Ken Grothaus and R. D. Wehrle (manager) of the thermal-battery group, and J. E. Kennedy (Org. 2513), and P. D. Wilcox (Org. 2515), to present their recommendations. The objectives of the Task Force were to develop a program for improved ignition of thermal batteries by developing a better understanding of ignition characteristics, to eliminate heat paper, determine and evaluate alternate methods of ignition (e.g., laser), develop an igniter-battery interface tester, define a reliable ignition system, and to publish a battery-designer's handbook.

Objectives – Some of the Task Force objectives were not easily attainable and were abandoned. For example, it was not possible to measure the caloric output of an igniter with a bomb calorimeter. High-speed photography was proposed for capturing burn characteristics of igniters. (Work along these lines was done sometime later, using a Cu-vapor laser at Mound.<sup>12</sup>) The use of an IR microscope was pursued, however, and the

initiation of ignition by laser, such as the unit used by UPI, was explored in detail. The use of laser ignition raises a number of questions, however, such as repeatability, since the spot size varied and there were hot spots within the beam. The actual energy deposited onto the target was not known with certainty, nor was the effect of atmospheric oxygen defined. The use of a standoff device for characterization of igniters with heat pellets was again suggested for center-hole-fired batteries. Subsequent to this meeting, a number of reports were generated to address many of the concerns of the Task Force.

Ignition Sensitivity – An effort was made to assess factors affecting ignition sensitivity and pellet breaking strength in late 1981.<sup>13</sup> All of the data in the memorandum related to ignition sensitivity are questionable, however. There were functional problems with the laser that was used and the data were not correctly analyzed by the Bruceton procedure, as acknowledged by the author. There were also inconsistencies in the data that were reported. The data for breaking strength are also statistically questionable, given that the correlation coefficients ( $r^2$ ) were only 0.407 to 0.614. However, the trend for increased breaking strength with pellet density corroborated earlier work.<sup>14</sup> That work reported little difference in strengths between the 86/14 and 84/16 compositions but both had slightly higher strengths than the 88/12 blend. A linear dependency between pellet density and breaking strength for all compositions was noted.

Some success was realized using the IR microscope with high-speed photography to capture the ignition and burning process.<sup>15,16</sup> Peak pellet temperatures of 1,100°C were recorded. Some difficulty in clearly recording the complete combustion process was encountered due to the plume of KCl that evolved. Still, the experiments provided much useful information previously unknown concerning the initiation and burning of the heat pellets.

As an outgrowth of recommendations to the Battery Ignition Task Force, a contract was placed with UPI to develop a stand-off test fixture for characterization of the ignition of heat pellets by two Sandia-designed igniters.<sup>17</sup> These igniters (100 total) were to be constructed at UPI. The test fixture was to then be used with the heat pellets to determine the ignition characteristics using the standard Bruceton method. Very erratic pellet-ignition responses were obtained that could not be treated in a satisfactory statistical manner. Plugging of the center hole by igniter debris complicated the process as well. The main problem was that the igniters were so powerful that the limits of the test fixture were exceeded. Additional tests were then performed under an argon atmosphere with one of the igniters. These tests showed that this igniter would reliably ignite either 88/12 or 84/16 heat pellets at a distance of 8" at a reliability of 97.6% at a 95% confidence level. The reliability dropped to 96.2% at a distance of 12". The distance for reliable ignition in air was about twice that in argon of a typical thermal-battery match (the MC2943). It is not clear if such data can be extrapolated to the closed volume of a thermal-battery environment, however.

Humidity Effects – The concern of humidity effects on the ignition and burning properties of Fe/KClO<sub>4</sub> heat pellets resulted in a contract being issued to UPI by Los Alamos National Laboratory to study this in detail.<sup>18</sup> Pellets pressed to 3.47 g/cc (55.3% TD) were exposed to relative humidities of between 23% and 52% for times ranging between four hours to six months, with the highest humidities having the shorter exposure times. Only the 88/12

composition was examined. No weight-change measurements were recorded, however, so that the extent of oxidation of Fe is not known. The metrics measured for the effects of humidity on heat pellets were calorific output, ignition sensitivity, burn rate, and ignition sensitivity. The test results are summarized in Table 1. A 1-J ruby laser with optical-density filters was used for ignition.

Table 1. Summary of Results of Humidity Tests with 88/12 Fe/KClO<sub>4</sub> Heat Pellets.

<u>Relative Humidity, %</u>	<u>Exposure Time</u>	<u>Effect on Calorific Output</u>	<u>Comments</u>
23	6 months	No change	No ignition failures
33	7 days	6.2% reduction	No ignition failures
42	16 hours	4.5% reduction	Some ignitions failures
42	2 days	12.4% reduction	Some ignitions failures
52	4 hours	1.6% reduction	No ignition failures
52	1 day	5.1% reduction	3 out of 5 ignition failures

Environmental Storage Effects – The effects of environmental storage conditions were also explored with this same material. The test results are summarized in Table 2. There was no change in the calorific output after storage at 50°C for 37 months. However, storage at 75°C for the same time resulted in a 3% decrease in calorific output, which put the material out of specification. No ignition failures were observed for these two groups of pellets.

The exposure of heat pellets to a relative humidity of 33% or greater severely impacted the ignition sensitivity and dramatically reduced the burn rate. This would have serious adverse effects on the function time of both a thermal battery as well as the heat source for nuclear weapons. Storage at elevated temperatures for prolonged periods also desensitized the heat pellets, so much so that the thermally treated samples in Table 2 would have failed the specifications for this material.

*The bottom line is that improperly stored heat pellets can suffer severe degradation in their burning characteristics to compromise the applications that depend on them.* The presence of moisture is of primary concern as is long-term storage at elevated temperatures. While the data presented are only for the 88/12 composition, there is no reason to expect that these effects would not be equally pertinent for the 86/14 and 84/16 heat pellets.

### **Fe Characterization**

The NX-1000 Fe from Pfizer ended up being the material of choice for the heat powder used as a heat source in Sandia's thermal batteries and nuclear weapons. An extensive effort was spent in detailed characterization of the properties of this Fe powder.

In the 1980s, parallel Fe-characterization work was carried out at General Electric Neutron Devices (GEND), at its Pinellas, FL facility.<sup>19</sup> This involved chemical analysis of the NX-

Table 2. Summary of Results of Ignition-Sensitivity Measurements of Moisture-Exposed and Thermally-Aged 88/12 Fe/KClO<sub>4</sub> Heat Pellets.

<u>Environment</u>	<u>Exposure Time</u>	<u>Effect on Required Ignition Energy</u>	<u>Effect on Burn Rate</u>
23% RH	30 days	No effect	No effect
23% RH	6 months	Poss. increase	No effect
33% RH	2 days	50% increase	30% decrease
33% RH	7 days	50% increase	50% decrease
42% RH	16 hours	88% increase	42% decrease
42% RH	2 days	667% increase	83% decrease*
52% RH	4 hours	27% increase	14% decrease
52% RH	1 day	114% increase	47% decrease
Ambient	Control	0.51 J mean	-----
50°C	37 months	29.4% increase	8.5% higher
75°C	37 months	59% increase	3.2% lower

\* 14 of 25 pellets failed to ignite.

1000 for impurities, elemental-Fe content, oxide level, surface area, and particle-size distribution. Metallic impurities in the heat powder can have an adverse impact on performance. Various metal oxides have been shown to catalyze the decomposition of KClO<sub>4</sub>.<sup>20</sup> The elemental-Fe content ranged from 89.0% to 93.9% for three lots that were sampled. The corresponding total Fe ranged from 97.9% to 98.6%. The oxygen content ranged from 1.56% to 1.52%. The median particle sizes as determined by a Sedigraph 5000 sedimentation technique using an x-ray beam were 11.6, 16.5, and 20 micrometers. The corresponding BET surface areas were 0.76, 0.50, and 0.76 m<sup>2</sup>/g.

The *elemental-Fe* content of the heat powder determines the *fuel* content of the pyrotechnic mixture. This parameter appears to be quite variable. In related work, the content of elemental Fe was found to be 83.7% for one lot of material<sup>21</sup> and only 80.4% for another lot.<sup>22</sup> In an attempt to improve the burning characteristics of the heat powders, GEND embarked on a program in the early 1980s to develop their own Fe powder. Bill Welbon led this effort and was successful in reduction of Fe salts in an aqueous environment using an autoclave.<sup>23-25</sup> As a follow-up to this work, a contract was placed by Sandia with UPI to prepare heat powder using the GEND Fe powder.<sup>26</sup> Batches of 88/12 and 84/16 heat powders of 1-kg each were prepared with this material. The materials appeared to function as desired, except that the ignition sensitivity was reduced and the burn rates were slightly less than those for blends with NX-1000.

Photographs taken by a scanning electron microscope (SEM) are shown in Figures 1 and 2 for a representative sample of Pfizer NX-1000 Fe powder. This unique morphology and

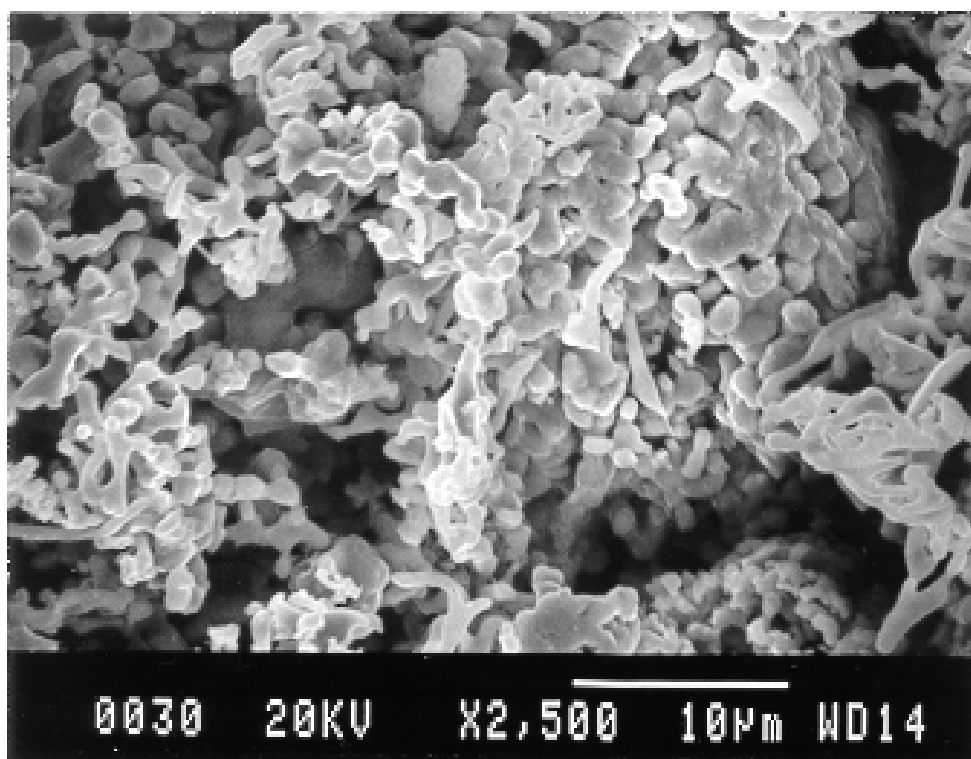


Figure 1. SEM Photomicrograph of Pfizer's NX-1000 Fe Powder.

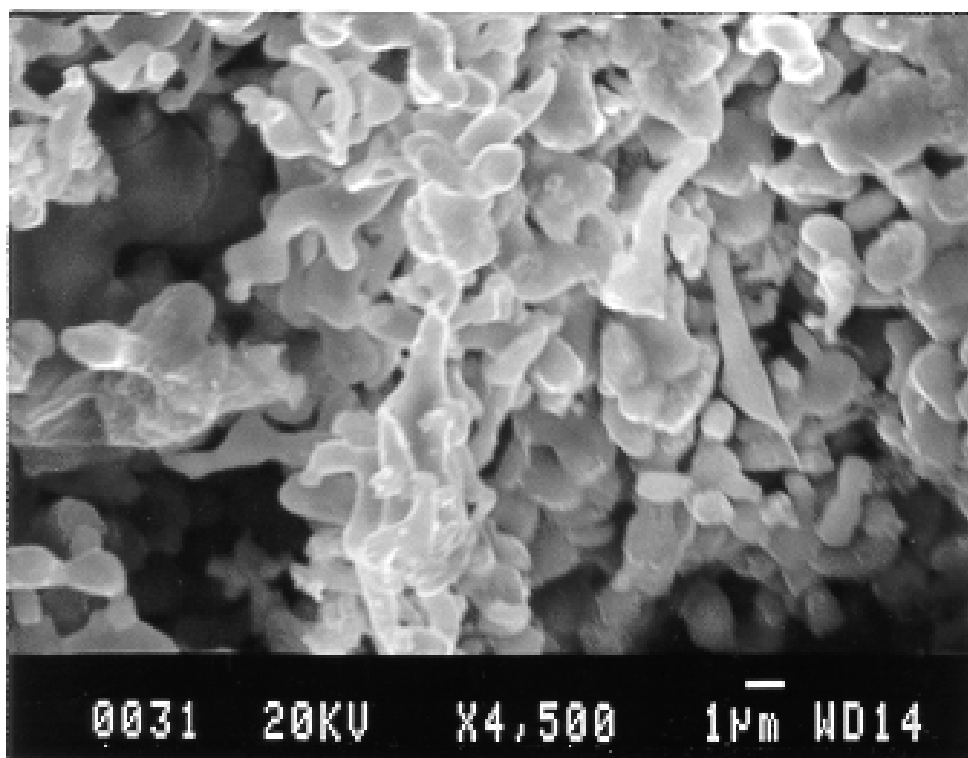


Figure 2. Higher Magnification SEM Photomicrograph of Pfizer NX-1000 Fe Powder.

high surface area are the major reasons for its excellent behavior as a fuel in the Fe/KClO<sub>4</sub> pyrotechnic mixtures.

GEND also examined ways to improve ignition-sensitivity measurements.<sup>27</sup> Only two compositions of Fe/KClO<sub>4</sub> heat pellets were examined: 88/12 and 84/16. These were pressed from UPI heat powder based on Pfizer NX-1000 Fe. The test unit consisted of a 250 μF capacitor that was discharged across the heat pellet through spring-loaded Ni-plated electrodes. An adjustable voltage source was used to charge the capacitor to higher voltages until ignition took place. The data were generated using a standard Bruceton method. The effects of pellet density on ignition sensitivity were examined and it was found that both compositions showed a minimum in ignition sensitivity near 3.4 – 3.5 g/cc. The highest densities required higher energies for ignition in all cases. All of Sandia's heat pellets for thermal batteries are pressed to a density of 3.35 g/cc, which corresponds to 53.4%, 55.3%, and 57.2% theoretical density for compositions of 88/12, 86/14, and 84/16, respectively. These GEND data indicate that the current pellet densities now being used are ideal for minimizing ignition sensitivity of our heat pellets.

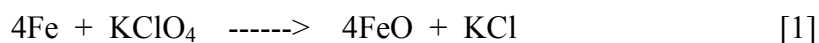
Some work was also done at GEND using a stand-off test setup, where a row of heat pellets were suspended on a rod and the distance for ignition of heat pellets was determined for various igniters. The results of that work were not formally documented, however, as far as can be determined.

There are two reports that document some of the thermal properties of heat pellets in detail. Some work in this area was done at Mound in the early 1980s.<sup>28</sup> A memorandum was generated for some thermal tests done at Sandia in early 1985.<sup>29</sup> This information would be useful for modelling purposes.

## AGING EFFECTS

Documenting the impact of various aging processes on the performance of Fe/KClO<sub>4</sub> heat pellets is a secondary purpose of this report. The history presented above should give a better feeling for how Sandia arrived at where it is today with these materials. One concern is the effects of long-term storage on the performance of nuclear-weapons components that use these pyrotechnics. To study this in detail, an aging study was developed as part of a nuclear-weapons stockpile surveillance program. As part of this effort, heat pellets were removed for characterization from Ca/CaCrO<sub>4</sub> batteries that were more than 18 years old.

The heat pellets were subjected to calorific-output measurements and, in some cases, oxygen analysis of the Fe portion of the pyrotechnic. Chloride analysis of the heat pellets was performed, since chloride would be a reaction product from the solid-state reaction of Fe with KClO<sub>4</sub>, as shown in equation 1:



[It was during characterization work at GEND that the primary products of combustion of Fe/KClO<sub>4</sub> heat pellets were clearly defined.<sup>30</sup> In the past, reference has been made to Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> (magnetite) as the main combustion phases. In reality, the primary product is FeO, as defined by equation 1.]

By comparing typical chloride levels in fresh, unaged blends of heat powder to those in heat pellets taken from stockpile batteries of various ages, one may be able to determine whether there are any aging effects. This was the methodology used in the surveillance study. Originally, measurement of ignition sensitivity using a small portable laser with a fiber-optic coupling was planned. However, chronic failure and malfunction of the unit precluded its use during the project, so no data of that type were generated.

An important factor that must be considered when dealing with such heat pellets is that the oxidant and fuel are in intimate contact and subjected to thermal cycling over the storage lifetime of the weapon. The rate of this solid-state reaction under the hottest storage conditions (typically, up to 85°C) could be substantial enough that after 30 years, some loss in calorific output could result. It is highly unlikely, however, that the battery would ever see such a temperature extreme on a sustained basis over its storage lifetime. Even if the loss in calorific output is not great (e.g., <5%), such a loss could result in the battery stack temperature being reduced enough to impact lifetime or other performance parameters. The temperature of the battery stack determines the ultimate fate of the battery during discharge. In the case of the Ca/CaCrO<sub>4</sub> system, the chemical reactions that occur generate additional heat that is taken into account when a battery is being designed. The mass of the heat pellets used in the battery stack is determined through empirical testing over a range of values until the desired “heat balance” is obtained.

### **Calorific Output**

The calorific output of the heat pellets was first examined using a new instrument from Parr that was microprocessor controlled. A Parr Model 1261 isoperibollic calorimeter was used in conjunction with a Parr Model 1107 Semimicro oxygen bomb. The samples were loaded in a glovebox under argon to avoid any oxidation errors by residual oxygen in the bomb. Samples were tested both in the form of powder and as pellets. Typically, 4 – 5 g of sample was used per run. The results obtained for unaged powder of 88/12 composition were somewhat lower than the specification value of  $221 \pm 2$  cal/g, averaging 219.3 cal/g (lot # 88041). Periodically, the calorimeter’s microprocessor would generate an error that would cause loss of the data for a run. Repeated calls to Parr failed to resolve these difficulties. Consequently, alternative sources for the heat-pellet calorimetry were examined. The bulk of the calorimetric analyses were performed at Eagle Picher Technologies (EPT), Joplin, MO, using an older adiabatic-type of Parr calorimeter. Supplemental data were also obtained using a similar calorimeter in the Explosive Materials/Subsystems group (Org. 2552).

In an attempt to eliminate experimental errors associated with calorific measurements at one particular facility, a number of samples of heat powder were analyzed at both SNL and EPT and served as controls for comparison to data obtained with aged heat pellets from stockpile batteries. The results of those tests are summarized in Table A-1 (Appendix A). The heat



powders in the comparison study were taken from the stockpile of the Thermal Battery Group and were over 20 years old and procured from UPI. These materials had been stored under a controller thermal environment all of this time. One lot of material was only several years old and had been procured from a new supplier, Pyrotechnic Specialties, Byron, GA. This 86/14 material (lot number 988010-001) was purchased to the product specification of  $259 \pm 2$  cal/g. The measured calorific value was lower than that by as much as 2.2%, which meant that this material did not meet the product specification.

The agreement between SNL and EPT of measured calorific values was very good on both of the replicate samples, with low standard deviations (0.2% or less). Similar trends were observed with the UPI 86/14 heat powder (lot number 86043). All measured values for the calorific output were lower than the product specification. Comparable results were obtained when the UPI 84/16 heat powders were analyzed. Calorific values ranged from 2.1% to 2.6% lower than the product specification, which placed these materials out of specification. Again, the agreement between duplicate samples taken from different cans of the master lot of material was very good. For example, 290.4 cal/g was measured for the first sample vs. 291.8 cal/g for the second one when analyzed at SNL. The same samples analyzed at EPT gave 291.7 and 291.3 cal/g, respectively.

The only heat powder analyzed that was within its product specification with respect to calorific output was the UPI 88/12 materials (lot number 88041). This material is of the same vintage as the 84/16 material. The sample from one can was within specification, but the sample from a second can showed a slightly lower calorific output that was just below the minimum called out in the product specification. (This assumes that representative samples were obtained from each can for analysis.) The original UPI data (Table B-1, Appendix B) shows that this material was well within product specifications at the time of manufacture. These data indicate a possible nonhomogeneity in the master lot, which is usually made in 100-pound batches. After receipt at Sandia, this material is partitioned into 10-pound cans for storage and use.

The low values observed with the control heat powders is somewhat disturbing in that these materials were certified by the manufacturers to meet Sandia's product specifications. What could be the possible causes for these discrepancies? One possibility is the calorific values were in error when the powders were made. A second possibility is the current calorific values are wrong or low because of experimental errors during analysis. A third possibility is the powder showed some loss in output with time during storage. Or, it could be a result of several of these factors in combination.

The loss of calorific output during long-term storage is not likely, since not all of the heat powders showed this effect. This is more likely in the case of pellets, where the fuel and oxidant are in intimate physical contact. It does not appear reasonable, however, for a loosely packed powder blend stored at  $20^{\circ} - 25^{\circ}\text{C}$ . As noted above, the 88/12 UPI heat powder still met the product specification—at least for one of the cans analyzed.

The heat powders that Sandia uses in its thermal batteries are bought to a manufacturer's certification and are not normally checked independently after receipt at Sandia. This is one

of the few materials used in DOE thermal batteries whose properties are not verified or qualified prior to use. The starting halide salts used in the electrolytes (e.g., LiCl and KCl) are purchased to a Reagent-Grade purity but are not analyzed for impurities because it is not deemed necessary. The same cannot be said to be true for the heat powder, since the performance of the thermal battery is intimately tied directly to the calorific output. Qualification of Fe/KClO<sub>4</sub> heat powders has generally not been an issue when used in thermal batteries. The battery engineer normally uses a specific weight of heat pellet for a given application and then tests the battery design empirically until he obtains satisfactory performance. He then specifies that weight of pellet and composition for his final design, without ever knowing the actual calorific output of the heat powder. Since the heat powders are made in such large lots, this generally has not caused any problems. The only time that this approach could lead to problems is if a different lot of heat powder is used that, although in specification, differs measurably from the one used during development. A lower calorific output could lead to a lower battery temperature with a reduction in voltage during a pulse or a lower battery life. Since thermal batteries are intrinsically very robust, the performance effects are usually minimal unless the original battery design was marginal.

Analysis of some historical data can provide some perspective on this issue. The calorific output of a lot of 88/12 heat powder that was 13.2 years old was analyzed at GEND in 1992 as part of a shelf-life study of several Li(Si)/FeS<sub>2</sub> thermal batteries. The measured output was 221.0 cal/g, which compares favorably with the UPI value of 222.4 cal/g at the time of manufacture. However, when a larger population of samples was taken, the results were cause for concern. The calorific outputs of 22 lots of 88/12 heat powder were measured for conformance to the product specification. Seven lots of 86/14 heat powder were similarly analyzed. The test results are listed in Table A-2 (Appendix A). Fifty-nine percent of the 88/12 heat powders were out of specification and over 71% of the 86/14 heat powders were out of specification. In all but one instance, the calorific output was higher than the upper limit of the product specifications. The validity of the GEND data can perhaps be questioned but since GEND used heat-powder standards traceable to the National Bureau of Standards (now National Institute for Standards and Technology), the likelihood of inaccuracies in these data is believed to be low.

The low calorific values noted for the control samples (powders) were also evident for heat pellets taken from a number of the stockpile batteries for the surveillance program. The calorific data are shown in Table B-1 (Appendix B), along with analyses for chloride and chlorate. (See next section for detailed description of the anion results.) All the calorific measurements were performed at EPT and the anion analyses were done at SNL. Pellets were randomly taken from each battery stack and were crushed into a powder so that approximately 8 – 10 g of material were available per replicate tests. The samples were stored in a dry room at EPT prior to calorimetric analysis, to avoid possible oxidation of the Fe by water vapor.

The average age of the thermal batteries surveyed was 17 years to slightly over 20 years. All the calorific measurements for the 88/12 heat pellets (from a low-voltage thermal battery) were lower than called out in the product specification, ranging from 1.27% to 1.48% low. Similar results were noted for other low-voltage thermal batteries from an

earlier weapon system, whose ages ranged from 19.0 years to 29.3 years. Both of these batteries used the same heat-pellet composition. The lowest average calorific output was for the pellets from the oldest battery, but that was probably a coincidence. This value had a much higher standard deviation, as well.

A different medium-voltage thermal battery used heat blocks to heat the stack externally, rather than heat pellets in each cell of the stack. The calorific values for the 84/16 heat blocks from these batteries were likewise lower than called out in the product specification—especially for two of the three units evaluated. The magnitude of the reduced calorific output was greater than that for the 88/12 heat pellets. The medium-voltage thermal battery from an earlier weapon system also used heat blocks but of 86/14 composition. All of the batteries evaluated were between 18.1 and 18.9 years old. The calorific outputs were all less than the product specification and, again, more than the differences observed for the 88/12 heat pellets.

There was one notable exception to the out-of-specification calorific output and that was for one of the heat-source pellets of 84/16 composition. This material was still within product specification, although the actual age of the samples was not available. The lack of any loss in calorific output for this particular material may just be fortuitous and coincidental.

The consistent low calorific output for both the control heat powders and battery heat pellets differs from the GEND data that indicated the calorific output of these materials was actually higher than the maximum value allowed by the product specification. As mentioned above, the real impact on the performance of the thermal batteries may not be significant because of how the batteries are designed. However, it is cause for alarm for the heat source used in nuclear weapons, where loss of thermal output could compromise its function.

The contradictory nature of the two data sets makes resolution of this issue difficult. There are no ready answers at this time. If both sets of data are indeed correct, this would mean that both the controls and battery heat pellets have suffered significant loss in calorific output after manufacture. The more likely answer may lie with the accuracies of the instrumentation used at the various facilities for measurement of calorific output. One way to address this would be to have UPI analyze some of the same heat powders that were characterized at SNL and EPT during this work. Also, additional samples of the heat source used in nuclear weapons should be procured and characterized for calorific output. The history (ages) of the samples should be known in order to discern any trend in output with age.

### **Anion Analyses**

Samples of unaged heat powders and heat pellets from stockpile batteries were leached with deoxygenated distilled water to remove soluble salts. The slurry was then quickly filtered and washed with acetone and air dried. The filtrate was used for anion analysis by ion chromatography using a Dionex DX100. The anion of primary interest was chloride, but nitrate, chlorate, and sulfate were also analyzed at the same time. The Fe remaining was

analyzed for oxygen by inert-gas fusion (IGF) and fast-neutron activation analysis (FNAA).

The chloride and chlorate data of Table B-1 (Appendix B) were analyzed as a function of age of the various heat pellets, to see if any obvious trend was apparent. The data are plotted in Figure 3. There is no correlation between the chloride content and the age of the heat pellets.

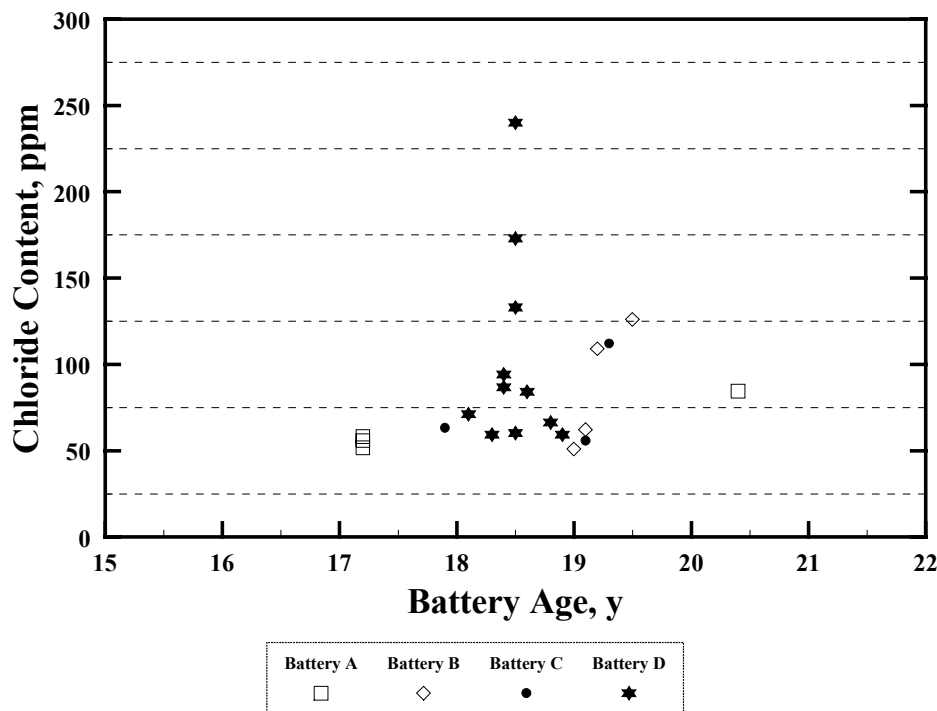


Figure 3. Chloride Content of Heat Pellets from Stockpile Thermal Batteries as a Function of Age.

The chloride and chlorate content of heat pellets taken from the stockpile batteries are plotted as a function of the calorific output in Figures 4 and 5. There was no correlation between the calorific outputs and the anion impurities tested. Similar results were noted in a GEND report for 12 lots of 88/12 heat powder.<sup>32</sup> The chloride content ranged between 48 ppm to 81 ppm and only two of the lots had calorific outputs that were below the specification.

Data from GEND for some shelf-life studies of a number of  $\text{Li(Si)/LiCl-KCl/FeS}_2$  thermal batteries in the early 1990s were examined for possible corroboration of the data in this work. Figure 6 shows the calorific output vs. chloride content for unaged 88/12 heat powders. Similar data for the 86/14 and 84/16 powders are presented in Figures 7 and 8, respectively. Except for one lot of 84/16 heat powder, all the lots were within the product specifications for calorific output, which would validate the original UPI data at the time of manufacture. This could indicate that the EPT data of Appendix B may be intrinsically low

because of inaccuracies in analysis or instrumentation. More work would be needed to verify this unequivocally.

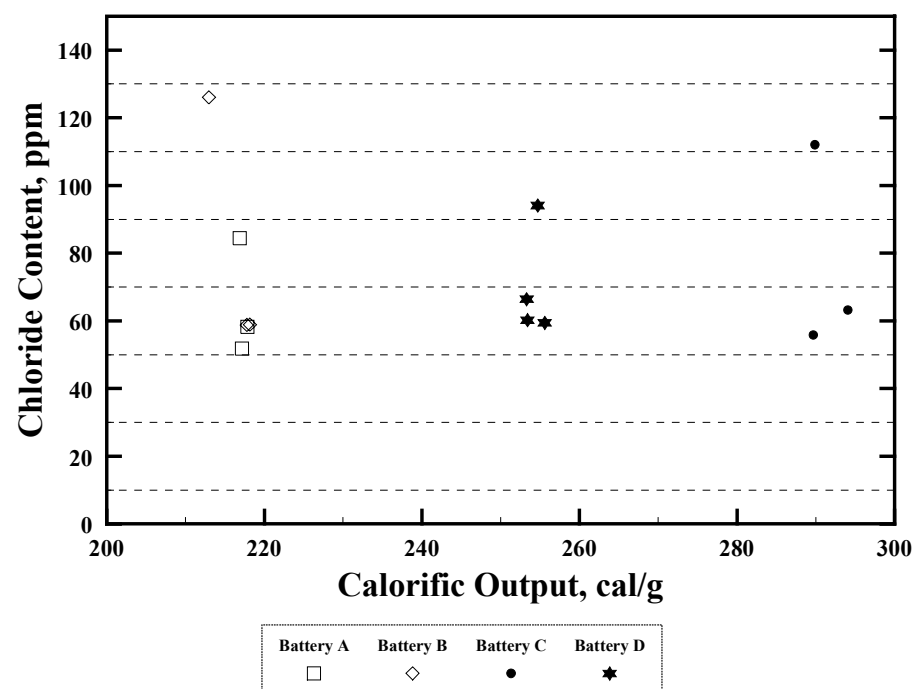


Figure 4. Chloride Content of Heat Pellets from Stockpile Thermal Batteries as a Function of Calorific Output.

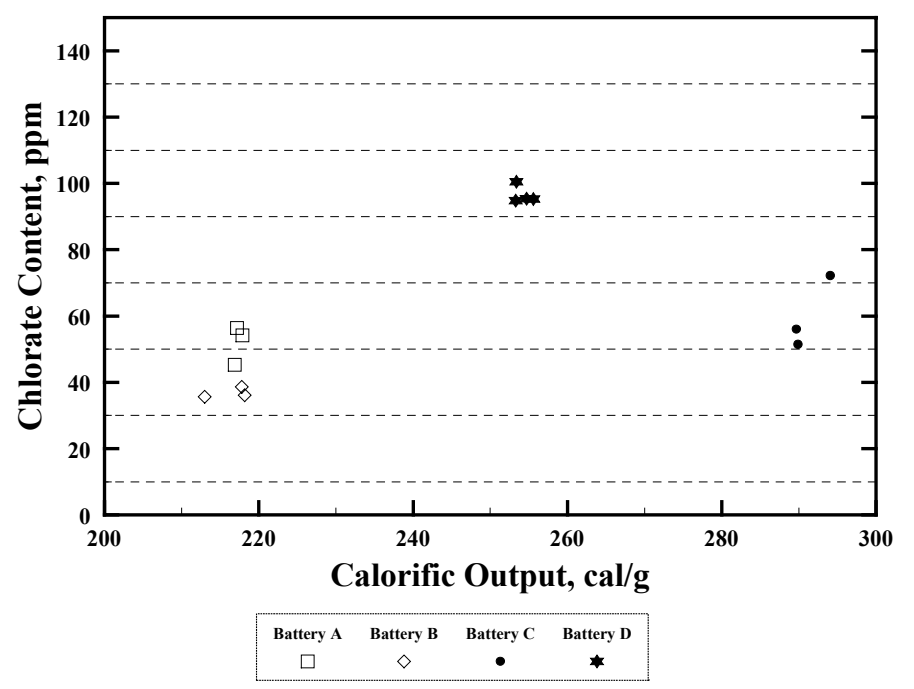


Figure 5. Chlorate Content of Heat Pellets from Stockpile Thermal Batteries as a Function of Calorific Output.

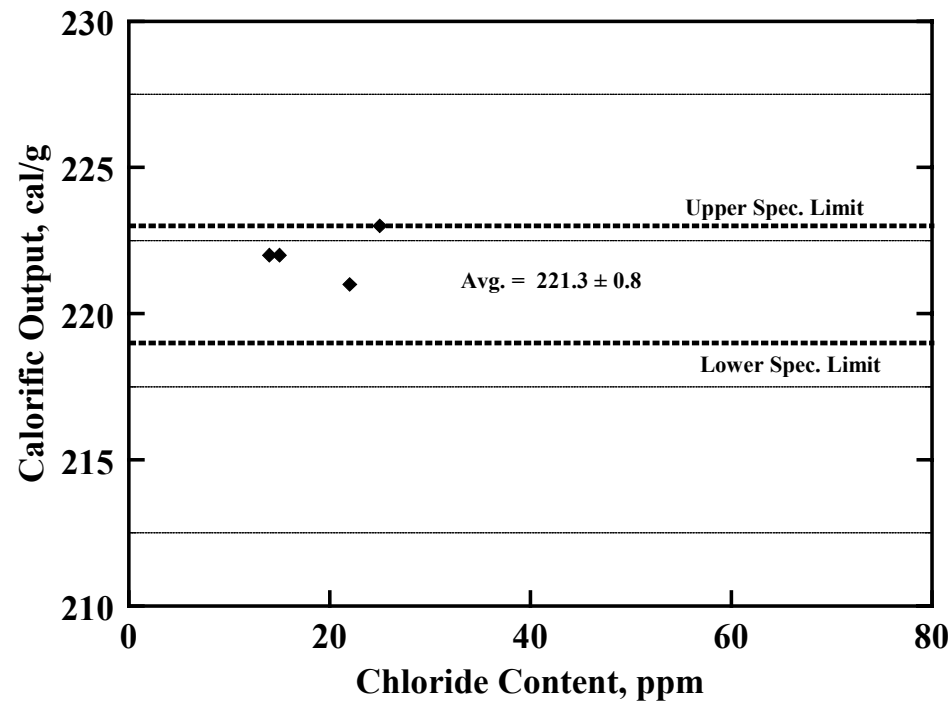


Figure 6. Calorific Output vs. Chloride Content for Unaged 88/12 Heat Powder. (The Dotted Lines are the Specification Limits for this Material.)

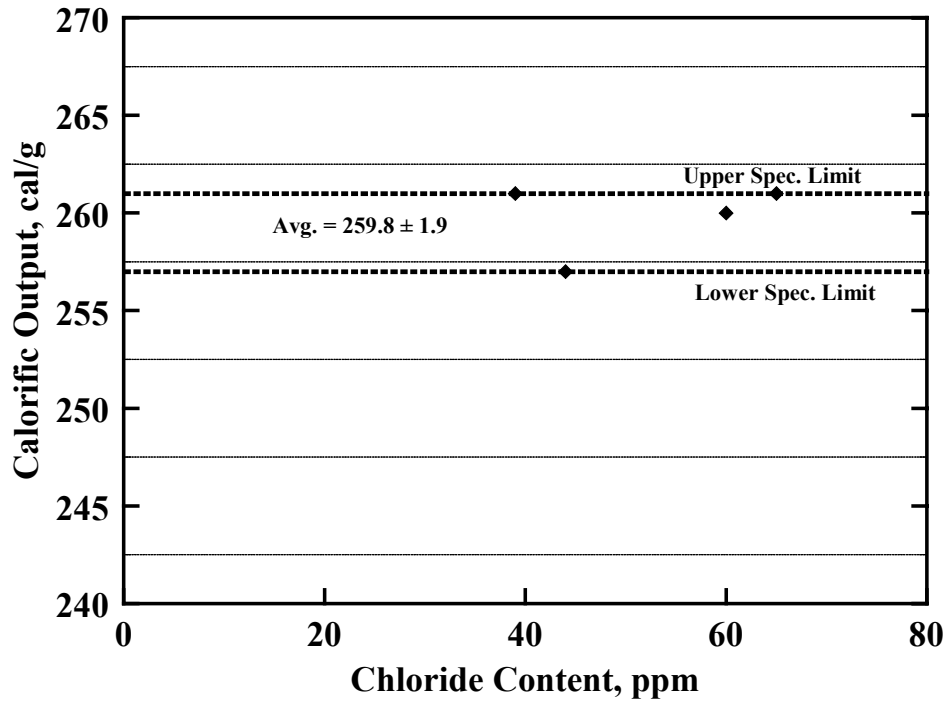


Figure7. Calorific Output vs. Chloride Content for Unaged 86/14 Heat Powder.

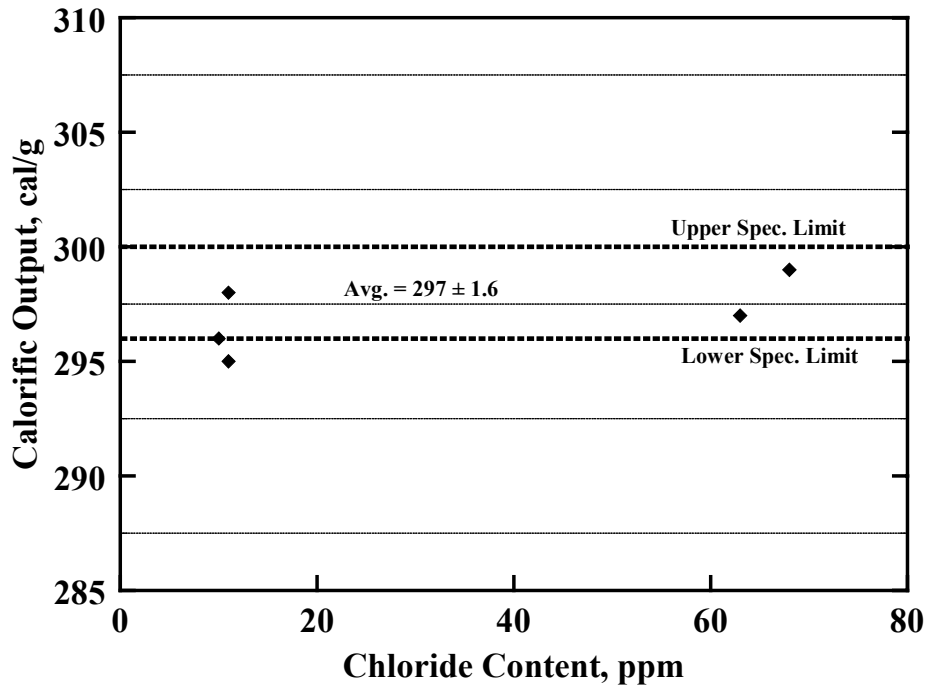


Figure 8. Calorific Output vs. Chloride Content for Unaged 84/16 Heat Powder.

The chloride data from GEND agree with similar data from the surveillance study that there is no correlation between the chloride content and the calorific output. It is not possible to make any statement as to whether the chloride content increased during long-term storage in

the weapons stockpile, since this parameter was never measured at the time of blending of the heat powders. The variability observed in the chloride data very likely reflect differences in the chloride contents of the different lots of  $\text{KClO}_4$  that were used.

### **Oxygen Analysis of Fe**

The oxygen data for Fe are summarized in Table B-2 (Appendix B) for water-leached heat powders and heat pellets from stockpile thermal batteries. The oxygen levels in pellets from three batteries that ranged from 17.1 to 20.3 years old ranged from 0.53% to as high as 2.12%. This was lower than what was found for three unaged heat powders, where values as high as 3.5% were noted. The agreement between the FNAA and IGF methods was very good. A representative sample of NX-1000 Fe which is used in these heat powders had a relatively low oxygen level that was about half of that for Fe obtained from SCM (now OMG Americas), Westlake, OH, a secondary source of Fe for heat powders.

While some of these oxygen levels for the Fe may appear high, examination of historical data shows that there have been much higher values in the Fe used in some of the earlier lots of heat powder. As mentioned earlier, the elemental Fe content has been found to be as low as 80.4% in some cases.<sup>22</sup> Since the oxygen content of the Fe used in the starting heat powder is generally not known, it is not possible to determine how much oxygen buildup occurred during the long-term storage of heat pellets; i.e., whether there was any significant oxygen contribution from a solid-state reaction.

### **Accelerated Aging**

Heat Pellets — Several sources of data related to the accelerated aging of  $\text{Fe/KClO}_4$  heat pellets were available for evaluation and have relevance for this report. One source was the shelf-life studies conducted in the early 1990s. Calorific data for 88/12 and 86/14 heat pellets stored at 70°C for 12 months are shown in Figure 9. These data are from shelf-life studies for several new  $\text{Li(Si)/FeS}_2$  thermal batteries that were going into weapon systems. The calorific output for a particular lot of heat pellets for a given battery did not show a statistically significant change (decrease) over the 12-month storage period. This shows that the loss of calorific output over long storage times is not likely to occur if the upper temperatures are not extreme. There was a measurable increase in the chloride level relative to the starting concentration, but as the data of Figure 9 show, no correlation was possible with the large amount of scatter in the data.



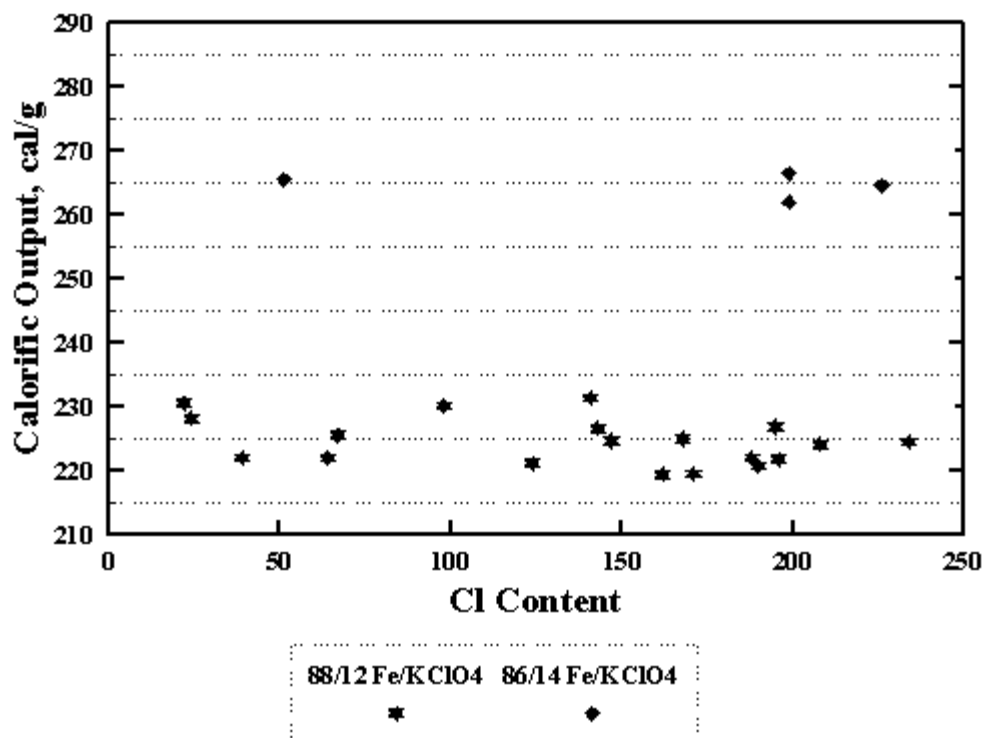


Figure 9. Calorific Output vs. Chloride Content of 88/12 and 86/14 Heat Pellets from Various Batteries that were Stored at 70°C for 12 Months.

On the other hand, if heat powders are subjected to severe accelerated aging by heating at 130°C for a month, one does observe product degradation. Representative data for a lot of 84/16 heat powder that experienced this environment are shown in Figure 10. The calorific values dropped to 254.6 cal/g and lower and the chloride levels climbed to as high as 728 ppm—an order of magnitude increase—but there still was no correlation of the chloride level with the drop in calorific output. One interesting feature of these data is that the chloride content was much lower when the heat pellets were stored in a 5% hydrogen/argon atmosphere with essentially no moisture (<1 ppm), instead of in dry-room air, which has a relative humidity of <3%.

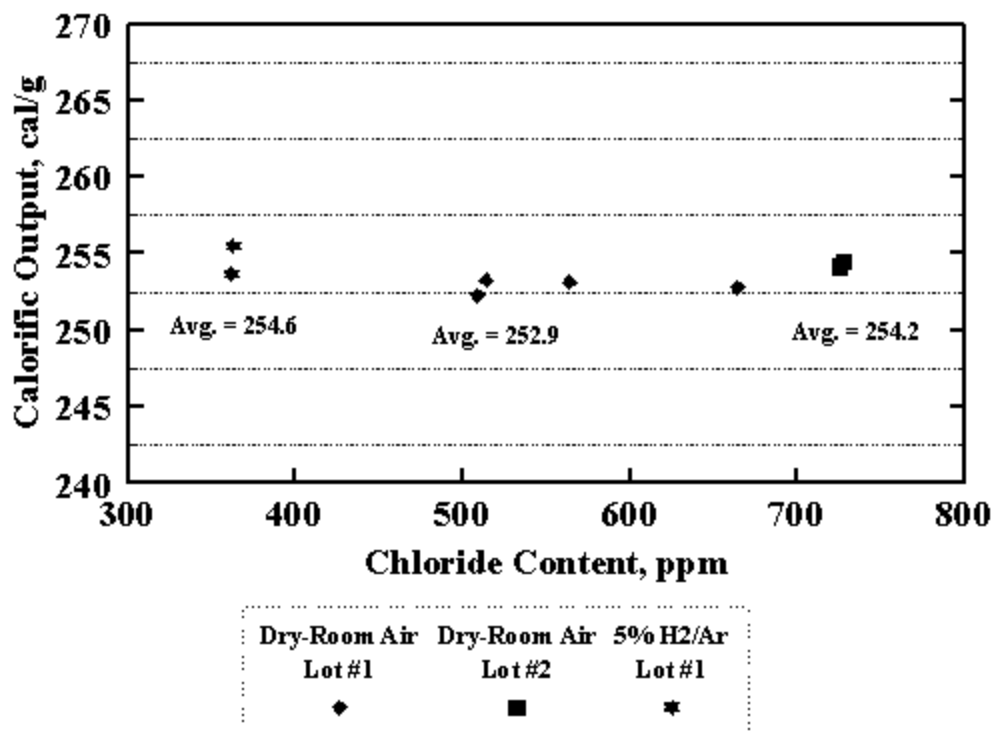


Figure 10. Calorific Output vs. Chloride Content of 86/14 Heat Pellets after Storage at 130°C for One Month.

To simulate accelerated aging of heat pellets due to oxidation of the Fe by ingress of moisture into the battery environment, pellets were subjected to exposure of moisture under closely controlled conditions. The intent of these tests was to prepare samples for use in subsequent ignition-sensitivity studies using a laser. The pellets were placed into a homemade humidistat where the air was constantly being circulated by a small fan. The relative humidity was controlled by the use of specific saturated salt solutions placed into the chamber and allowed to equilibrate. The pellets were weighed on a regular basis to monitor the weight gain associated with Fe oxidation. Attempts to use a thermogravimetric analysis (TGA) setup to do this automatically, while flowing a moisture-laden stream of argon through the apparatus, were not successful. The data that was obtained was unreliable and erratic.

A relative humidity of 40% was selected since previous work at Unidynamics had shown that the rate of oxidation (rusting) becomes significant at this RH.<sup>17</sup> (A saturated solution of potassium acetate at room temperature was used for these tests.) The rate of oxidation of Fe was comparable for all three heat-pellet compositions. Figure 11 presents the data normalized to the Fe content of the Fe/KClO<sub>4</sub> heat pellets. Initially the rate of weight gain was linear, but as the reaction progressed, the rate slowed due to limited access to the interior of the pellets. At that point, the rate became parabolic, with a  $t^{0.5}$  dependency, which is typically observed for diffusion-limited processes.

Unfortunately, data for ignition sensitivity and burn rate are not available for any of these aged samples due to malfunctioning of the test laser. This is also true for all of the shelf-life

studies that involved accelerated aging. Those types of data are important for monitoring functioning time of devices that use such pyrotechnics.

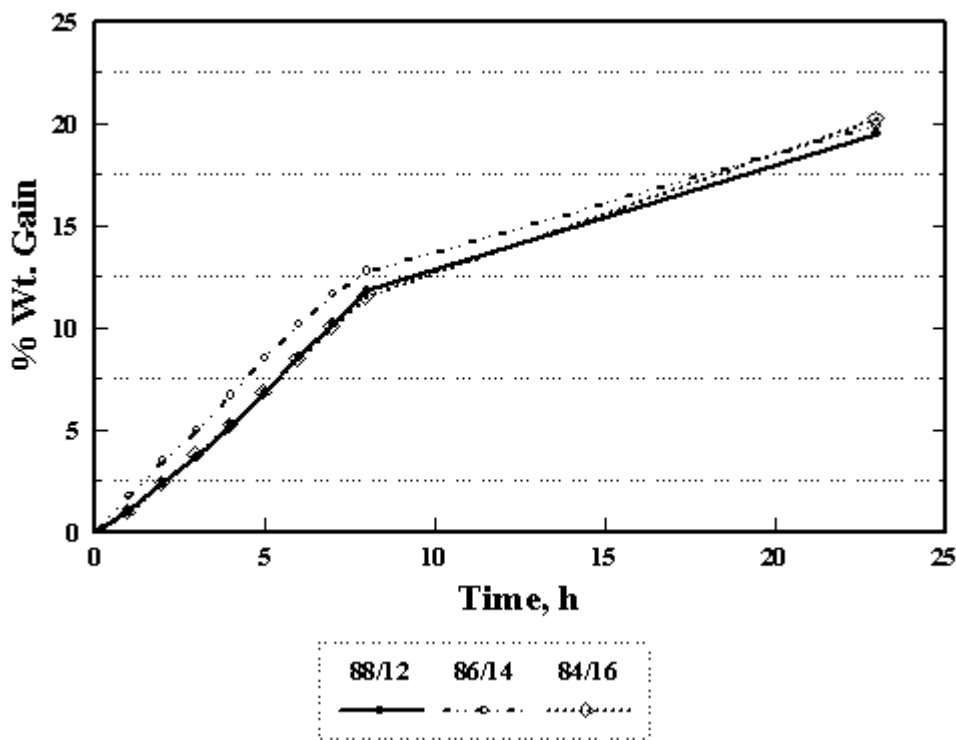


Figure 11. Weight Gain of Fe/KClO<sub>4</sub> Heat Pellets Exposed to a Relative Humidity of 40%.

The rate of oxidation observed in the current tests at 40% RH would obviously not apply to the heat pellets that are hermetically sealed in a thermal battery or other container. Such a scenario is not possible under normal storage conditions in the weapons in the stockpile. In principle, a crack in a glass-to-metal seal could develop in a thermal-battery header. (None were found in all of the stockpile batteries examined in the surveillance work.) Given that there will be secondary containment in the weapon, in addition to the hermetic primary containment, the probability of having a sufficiently large leak develop in the primary container over the storage lifetime of the weapon, causing significant oxidation of the heat pellets, is very close to zero.

Heat Paper — The effects of limited accelerated aging on the calorific output and burn characteristics of Zr/BaCrO<sub>4</sub> heat paper are summarized in Figures 12 and 13, respectively. The degradation of the Fe/KClO<sub>4</sub> heat pellets was small when compared to that observed when the Zr/BaCrO<sub>4</sub> heat paper (fuse) was subjected to temperatures of 150°C or more for various times. At 110°C, the drop in calorific output was slight, even after 20 days (Figure 12). However, at 150°C the drop in calorific output became substantial. By 200°C, the decrease was dramatic, with the output dropping by 25% after only 7 days. Similar effects were evident in the burn rate (Figure 13).

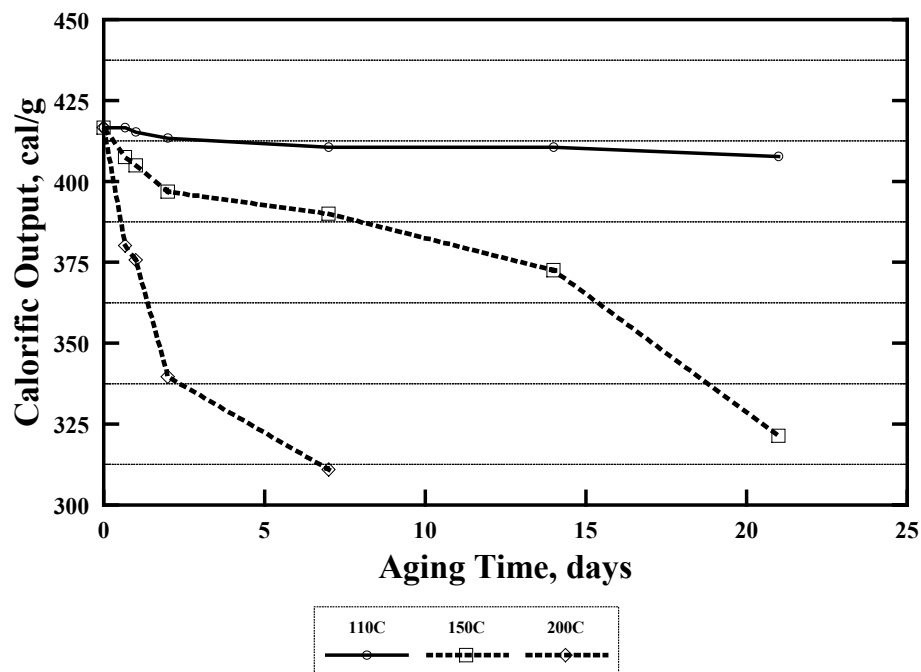


Figure 12. Calorific Output of Zr/BaCrO<sub>4</sub> Heat Paper as a Function of Aging Time at Three Different Temperatures.

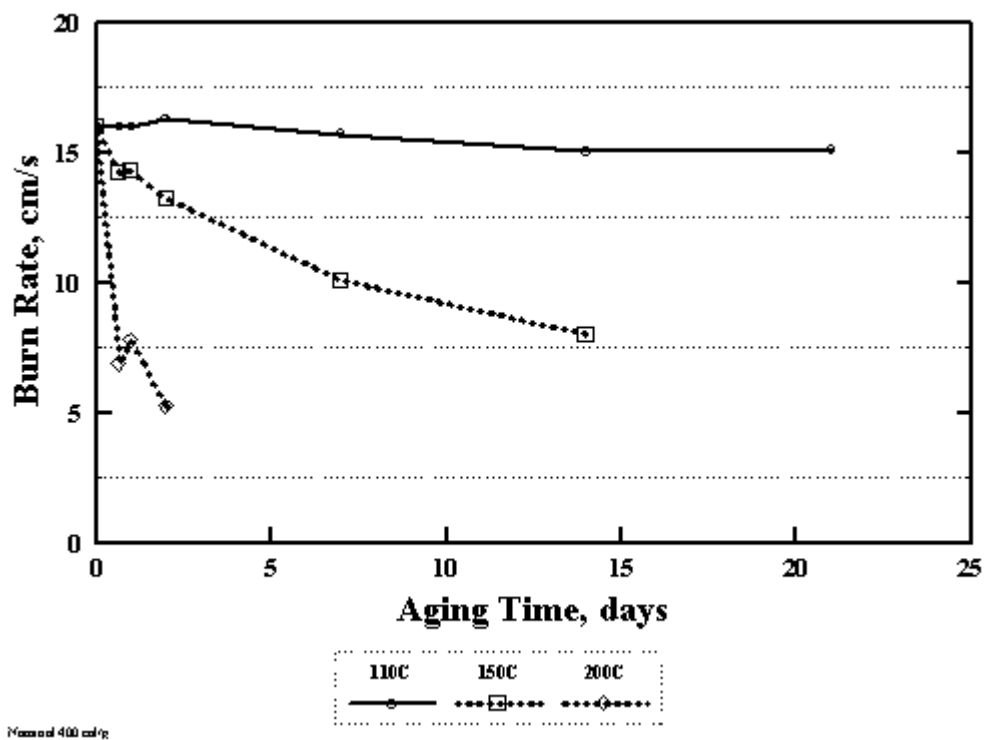


Figure 13. Burn Rate of Zr/BaCrO<sub>4</sub> Heat Paper as a Function of Aging Time at Three Different Temperatures.

## CONCLUSIONS

The paper has presented a historical perspective on the development of pelletized heat sources for use in thermal batteries and nuclear weapons by the DOE, with the primary focus on the Fe/KClO<sub>4</sub> system. Examination of early historical data and published performance data for this system, along with related stockpile-surveillance data for heat pellets leads to a number of general and specific conclusions, which are summarized below.

- ◆ Although there are apparent discrepancies in the absolute values of calorific output of heat pellets taken from stockpile thermal batteries, there are no indications of degradation of output with age of the heat pellets.
- ◆ Earlier UPI data indicate that heat pellets show an onset of performance degradation at relative humidities of 33% and higher, with an increase in ignition energy (decreased ignition sensitivity), reduction in burn rate and loss of calorific output. The extent of the oxidation was not quantified, however.
- ◆ Storage at 75°C for over three years also had adverse affects on the performance of the heat pellets. Again, no quantification of the extent of oxidation was made.
- ◆ In the normal dry environment that the heat sources will see in nuclear weapons, the Fe in the heat pellets is not susceptible to oxidation. Long-term storage at temperatures of 75°C is extremely unlikely, so that the impact of the performance of the heat pellets is not expected to be significant.
- ◆ The lack of historical data for the virgin heat powders prevents correlation of the chloride and oxygen content in aged or stockpile materials with the measured calorific output. The historical data for these parameters indicate that there is no correlation over the nominal range found in typical heat powders. Deliberate accelerated aging of heat pellets does result in a dramatic increase in the chloride content (over several hundred parts per million) but there was still no correlation to the calorific output.
- ◆ There is a dearth of information on the ignition sensitivity of the various Fe/KClO<sub>4</sub> heat powders as a function of aging and oxide-impurity content. This is the one area that should receive further attention.
- ◆ Aging of Zr/BaCrO<sub>4</sub> heat paper at temperatures above 150°C results in significant degradation of both calorific output and burn rate.

## FUTURE WORK

There is a need for supplemental work to better define the effects of aging and oxide content of the ignition sensitivity of Fe/KClO<sub>4</sub> heat pellets. While some work was done at UPI in this area, the tests were not conducted in a systematic and comprehensive manner. The laser that was used at the time was overpowered and required the use of filters to attenuate the power. However, not enough energy levels were used in the Bruceton analyses to determine the 50% and 90% fire levels accurately. In addition, when the samples were aged or exposed to high temperatures and relative humidities, the effects on the chloride and oxide contents were not measured. This is needed if one is to make meaningful correlations. The effect of Fe source and particle size of the Fe and KClO<sub>4</sub> should also be included in such a study. This is increasingly important as we use additional commercial sources of heat

powders with component materials from different sources. These new sources are only qualified for calorific output. The type of Fe can dramatically affect the ignition sensitivity and this needs to be accurately documented and correlated with sample morphology and purity. This information is important for battery engineers for future applications, as this can affect the rise times (functioning times) of devices that use heat pellets. A proposed statement of work that addresses all of these concerns is provided in Appendix D.

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**Appendix A. Summary of a Number of Calorimetric Measurements of Heat Powders Done at EPT, SNL, and GEND.**



Table A-1. Comparison of Calorific Measurements of Control Fe/KClO<sub>4</sub> Heat Powders Done at EPT and SNL.

<u>Lot #</u>	<u>Mfg. Date</u>	<u>Test Date</u>	<u>Fe/KClO<sub>4</sub> Wt. Ratio</u>	<u>Age, yr</u>	<u>Output, cal/g</u>	<u>Std. Dev.</u>	<u>% Difference from Specification</u>	<u>Tested At</u>
<i>Spec. = 259 +/- 2</i>								
988001-001	8/1/98	10/16/99	86/14	1.21	254.7	0.17	-1.7	SNL
988001-001	8/1/98	10/4/99	86/14	1.18	253.4	0.49	-2.2	EPT
988001-001	8/1/98	10/16/99	86/14	1.21	254.4	0	-1.8	SNL
988001-001	8/1/98	10/4/99	86/14	1.18	253.7	0.52	-2.0	EPT
86043	??	10/16/99	86/14	>20	255.7	0.14	-1.3	SNL
86043	??	10/4/99	86/14	>20	253.3	0.08	-2.2	EPT
86043	??	10/16/99	86/14	>20	254.0	0.28	-1.9	SNL
86043	??	10/4/99	86/14	>20	254.2	0.56	-1.9	EPT
<i>Spec. = 298 +/- 2</i>								
84026	??	10/16/99	84/16	>20	290.4	0	-2.6	SNL
84026	??	10/4/99	84/16	>20	291.7	0.34	-2.1	EPT
84026	??	10/16/99	84/16	>20	291.8	0	-2.1	SNL
84026	??	10/16/99	84/16	>20	291.3	0.32	-2.2	EPT

Table A-1 (Cont'd.). Comparison of Calorific Measurements of Control Fe/KClO<sub>4</sub> Heat Powders Done at EPT and SNL.

<u>Lot #</u>	<u>Mfg. Date</u>	<u>Test Date</u>	<u>Fe/KClO<sub>4</sub> Wt. Ratio</u>	<u>Age, yr</u>	<u>Output, cal/g</u>	<u>Std. Dev.</u>	<u>% Difference from Specification</u>	<u>Tested At</u>
				<i>Spec. = 221 +/- 2</i>				
88041	4/21/86	10/16/99	88/12	13.2	218.8	0.21	-0.5	SNL
88041	4/21/86	10/4/99	88/12	13.2	220.4	0.52	0.2	EPT
88041	4/21/86	10/16/99	88/12	13.2	217.2	0.49	-1.3	SNL
88041	4/21/86	10/4/99	88/12	13.2	216.4	0.98	-1.6	EPT
<b>88041</b>	<b>4/21/86</b>	<b>4/21/86</b>	<b>88/12</b>	<b>0</b>	<b>222.3</b>	<b>0.29</b>	<b>Mfgr. data</b>	<b>UPI</b>

Table A-2. Comparison of Calorific Measurements of Various Lots of Fe/KClO<sub>4</sub> Heat Powders Done at GEND and UPI.

<b><u>Measured Output, cal/g</u></b>	<b><u>Batches Out of Spec.</u></b>	<b><u>Specification, cal/g</u></b>	<b><u>Composition</u></b>
218.0	*	219 - 223	88/12
222.2			
224.2	*		
227.0	*		
221.9			
221.3			
222.2			
220.8			
219.7			
221.0			
219.5			
226.7	*		
231.5	*		
230.3	*		
222.1			
228.3	*		
230.7	*		
224.6	*		
224.8	*		
225.1	*		
225.5	*		
225.7	*		
	13 out of 22 (59%)		
259.7		258 - 262	86/14
266.6	*		
264.8	*		
262.1	*		
264.4	*		
261.6			
265.7	*		
	5 out of 7 (71.4%)		

**Appendix B. Summary of Characterization Tests with Fe/KClO<sub>4</sub> Heat Pellets taken from Stockpile Ca/CaCrO<sub>4</sub> Thermal Batteries. (Calorific Measurements done at EPT; Anion and Most Oxygen Analyses done at SNL).**

Table B-1. Calorific Measurements and Anion Analyses of Fe/KClO<sub>4</sub> Heat Pellets taken from W76 and W68 Thermal Batteries.

<u>Battery</u>	<u>Serial No.</u>	<u>Mfg.</u>	<u>Test Date</u>	<u>Fe/KClO<sub>4</sub> Compn.</u>	<u>Age, yr</u>	<u>Avg. Calorific Output, cal/g</u>	<u>Std. Dev.</u>	<u>% Diff. from Spec.</u>	<u>Cl, ppm</u>	<u>ClO<sub>3</sub>, ppm</u>
						<i>Spec=221 +/- 2</i>				
A	4537	11/1/79	6/15/99	88/12	19.6	217.2	1.14	-1.27		
A	3869	8/1/79	6/15/99	88/12	19.9	217.2	0.23	-1.27		
A	9933	4/1/82	6/15/99	88/12	17.2	217.2	1.48	-1.27	51.7	56.4
A	2780	2/1/79	4/15/99	88/12	20.2	216.9	0.49	-1.41	84.4	45.3
A	9867	4/1/82	4/15/99	88/12	17.0	217.9	0.84	-0.95	58.2	54.2
A	9758	4/1/82	6/18/99	88/12	17.2	N.A.			55.8	51.8
B	4200	5/1/80	6/15/99	88/12	19.1	217.8	0.26	-1.00	58.7	38.6
B	4183	5/1/80	6/15/99	88/12	19.1	218.2	0.42	-0.82	58.8	36.1
B	2828	1/1/70	4/15/99	88/12	29.3	213.0	2.35	-3.18	126	35.6
B	3588	4/1/80	6/18/99	88/12	19.2	N.A.			109	37.1
B	4594	6/1/80	6/18/99	88/12	19.1	N.A.			62.2	34.8
B	4967	7/1/80	6/18/99	88/12	19.0	N.A.			51.0	39.6
						<i>Spec=259 +/- 2</i>				
C	3526	9/1/80	6/17/99	86/14	18.8	253.3	N.A.	-2.2	66.4	94.8
C	3108	8/1/80	6/17/99	86/14	18.9	255.6	N.A.	-1.3	59.4	95.3
C	4826	2/1/81	6/17/99	86/14	18.4	254.7	N.A.	-1.7	94.1	95.4
C	4523	1/1/81	6/17/99	86/14	18.5	253.4	N.A.	-2.2	60.2	100.5
C	4310	12/1/80	6/18/99	86/14	18.6	N.A.			84.1	90.8
C	4465	1/1/81	6/18/99	86/14	18.5	N.A.			240	94.4
C	4470	1/1/81	6/18/99	86/14	18.5	N.A.			173	98.8
C	4533	1/1/81	6/18/99	86/14	18.5	N.A.			133	84.8
C	4718	2/1/81	6/18/99	86/14	18.4	N.A.			86.7	95.2

Table B-1 (Cont'd.). Calorific Measurements and Anion Analyses of Fe/KClO<sub>4</sub> Heat Pellets taken from W76 and W68 Thermal Batteries.

		<u>Mfg.</u>	<u>Test Date</u>	<u>Fe/KClO<sub>4</sub> Wt. Ratio</u>	<u>Age, yr</u>	<u>Avg. Calorific Output, cal/g</u> <i>Spec=259 +/- 2</i>	<u>Std. Dev.</u>	<u>% Diff. from Spec.</u>	<u>Cl, ppm</u>	<u>ClO<sub>3</sub>, Ppm</u>
C	4842	2/1/81	6/18/99	86/14	18.4	N.A.			471	98.2
C	5026	3/1/81	6/18/99	86/14	18.3	N.A.			59.4	97.9
C	5750	5/1/81	6/18/99	86/14	18.1	N.A.			71.1	96.3
						<i>Spec=298 +/- 2</i>				
D	3504	6/1/80	6/17/99	84/16	19.1	289.7		-2.8	55.8	56.0
D	3258	3/1/80	6/17/99	84/16	19.3	289.9		-2.7	112	51.4
D	6227	8/1/81	6/17/99	84/16	17.9	294.1		-1.3	63.2	72.2
Heat source	84033	?	6/18/99	84/16	?	298.3	14.2	0.1		

Table B-2. Summary of Oxygen Analyses of Fe in Heat Pellets and Heat Powders.

<u>Material</u>	<u>Anal. Method</u>	<u>% O</u>	<u>Battery</u>	<u>S/N</u>	<u>Build Date</u>	<u>Age, yr</u>	<u>History</u>
Fe	Inert gas fusion	2.12 +/- 0.31	MC2323	2828	Jan-70	29.3	Heat pellet
Fe	Inert gas fusion	0.527 +/- 0.047	MC2936	2780	Feb-79	20.2	Heat pellet
Fe	Inert gas fusion	0.932 +/- 0.054	MC2936	9867	Apr-82	17.1	Heat pellet
Fe	NAA	2.256	N.A.	N.A.	N.A.	>20	Unaged 88/12 heat powder (lot 88041)
Fe	NAA	3.482	N.A.	N.A.	N.A.	>20	Unaged 86/14 heat powder (lot 86043)
Fe	NAA	1.902	N.A.	N.A.	N.A.	>20	Unaged 84/16 heat powder (lot 84026)
Fe	Inert gas fusion	2.35	N.A.	N.A.	N.A.	>20	Unaged 88/12 heat powder (lot 88041)
Fe	Inert gas fusion	3.46	N.A.	N.A.	N.A.	>20	Unaged 86/14 heat powder (lot 86043)
Fe	Inert gas fusion	1.90	N.A.	N.A.	N.A.	>20	Unaged 84/16 heat powder (lot 84026)
Fe	Inert gas fusion	0.659	N.A.	N.A.	N.A.	N.A.	Analyzed as is (NX-1000)
Fe	Inert gas fusion	1.206	N.A.	N.A.	N.A.	N.A.	Analyzed as is (SCM)

## Appendix C. Proposed Future Work for Ignition-Sensitivity Studies with Fe/KClO<sub>4</sub> Heat Pellets.

The intent of this work is to document the ignition sensitivity of Fe/KClO<sub>4</sub> heat pellets after being artificially aged under various conditions to simulate long-term storage in the stockpile. Three compositions of heat pellets will be included in the study: 88/12, 86/14, and 84/16. The pellets will be exposed under controlled conditions to a relative humidity and temperature region where oxidation of the Fe will occur. The degree of oxidation will be carefully monitored.

The test parameters will include:

- ◆ Degree of oxidation, which will depend on the oxidation temperature and relative humidity
- ◆ Heat-pellet composition
- ◆ Heat-pellet density
- ◆ Heat-pellet temperature
- ◆ Concentration of iron oxide (a common impurity in these materials)

The work will require the use of a stable *laser* system fabricated from a solid-state laser diode and a constant-current power supply. (This approach is preferred to the earlier one that used a high-voltage power supply and flash tube for pulsing the laser.) The effect of Fe particle size and source would be examined, as well, as these can have a dramatic impact on the pyrotechnic performance.

The experimental setup would also provide valuable data on the burn rate of the pellets under these conditions.



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