

GA-A24040

IODINE ON DEMAND

FINAL REPORT

**by
L.C. BROWN**

**Work supported by
U.S. Air Force through
the U.S. Department of the Interior
under Contract No. NBCHC010017**

AUGUST 2002

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**GENERAL ATOMICS PROJECT 30089
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EXECUTIVE SUMMARY

Iodine on Demand (IOD) is a concept that has the potential to drastically simplify iodine delivery to a Chemical Oxygen Iodine Laser (COIL), a promising addition to our military arsenal. If the potential is realized, the size and weight of the iodine supply system for COIL will be reduced by an order of magnitude. Ground support and logistics are also simplified with the IOD concept.

Present COIL systems require that a pressure vessel containing molten iodine be maintained at temperature for whenever the laser is on alert and available for firing. This requires that either the iodine delivery system be continuously online or that several hours of notice be given before the COIL is to be fired. Care must be taken when melting iodine due to large volume changes that can stress the containment vessel, also, line pluggage could occur if residual clumps of solid iodine were present on start-up. In addition, existing iodine systems are complex and operational availability may be an issue. Due to the unusually corrosive nature of iodine, the time that the iodine system is maintained in its ready state must be factored into the system maintenance schedule and will reduce the overall system availability.

The IOD system delivers iodine to the COIL cavity on short notice from an iodine pyrotechnic, a solid-solid chemical iodine gas generator. The line to the laser cavity is preheated by an iodine free pyrotechnic and, after the laser shot, the system is purged by another inert pyrotechnic.

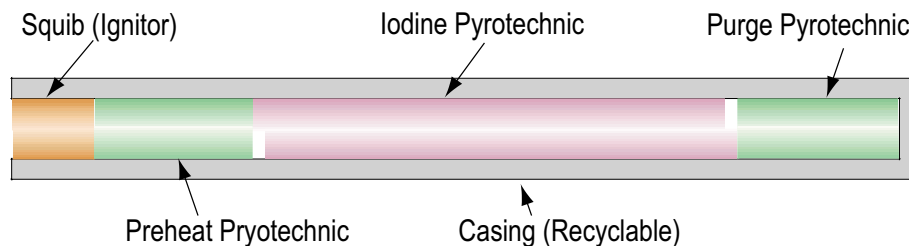


Diagram of Iodine-on-Demand cartridge. Iodine exits from the left end of the casing.

This work is the first phase of a proposed two-phase effort to demonstrate the basic feasibility of IOD. This basic feasibility demonstration is concerned only with the iodine pyrotechnic. The work scope was divided into three technical tasks, (1) screen potential fuel/oxidizer systems and systems for laboratory testing, (2) perform detailed safety analysis, and (3) perform burn test of selected fuel/oxidizer systems.

Forty solid-solid fuel/oxidizer systems were analyzed in terms of their potential to produce iodine vapor. The number of potential systems was kept low by only considering reactants that are catalog items or that can be readily made from catalog items. In

addition to the reaction products, the analysis included consideration of the adiabatic reaction temperature, T_a , the temperature of products the assuming the reactants were at room temperature. The promising reactions were tested for safety considerations for the purpose of eliminating unstable reactant systems. The performance of the chemical system in the safety tests also provided insight into the probable performance in an IOD system. Two systems, tetraiodoethylene/iodine pentoxide and tin/iodine pentoxide, were burn tested under conditions similar to that required for IOD operation. More testing is required but both systems performed adequately and, on the basis of present knowledge, either system could be used as the basis for a fieldable iodine supply system for a COIL weapon system. It is recommended that both systems be further examined in Phase 2 of this work.

1. INTRODUCTION

The Chemical Oxygen-Iodine Laser (COIL) is being developed by the U.S. Air Force into advanced weapon systems. Development of the COIL-based Air-Borne Laser (ABL) is well underway and work on the Advanced Tactical Laser (ATL) is scheduled to begin shortly. A COIL system can potentially be used in air, space, naval and land based weapons. This work is aimed at providing a small, simple and low-weight iodine delivery system to a COIL weapon.

The COIL has two input streams, one containing excited molecular oxygen, $O_2(^1\Delta)$, and the other containing iodine vapor. On first view, the oxygen stream seems the most complicated, but generation of $O_2(^1\Delta)$ has the advantage, when ultimately deployed, of being a low temperature all-fluid process. Iodine, however, is a solid at room temperature and requires a preheated system, both to liquefy and vaporize the iodine and then to prevent it from condensing and plugging the system.

The singlet delta oxygen generation feed system may require a fraction of a minute to reach operational status but existing iodine feed systems, based on molten iodine, require several hours to reach operational status. The ideal iodine source will be continuously online and instantaneously available when required. An iodine gas generator based on solid chemical reactants has the potential to meet this ideal. Such a system provides tremendous operational advantages for weapon system applications, including significantly reduced weight and volume, operational simplicity, reduced maintenance, enhanced safety, and rapid weapons readiness. These factors are critical for airborne applications.

Iodine-on-Demand (IOD) is a concept that meets the iodine supply needs of a COIL weapon system. IOD addresses the following concerns of related to current COIL iodine supply systems:

1. Present concepts for a weapons system, based on a COIL, require that the iodine delivery system be preheated to melt the iodine before the laser can be fired, which typically takes several hours. The system must be maintained at temperature for the laser to remain operational. The iodine in the iodine reservoir must be molten prior to operation. All piping exposed to iodine, up to the laser cavity, must be maintained at a temperature above the melting point of iodine (114°C) to prevent iodine condensation and line pluggage.
2. Existing iodine delivery systems are complex. They involve moving parts (valves), heat traced lines, precision orifices and temperature and pressure instrumentation. Measurement of pressure in iodine systems is particularly complicated because of the requirement that all passages exposed to iodine must be maintained above the melting point of iodine.

3. Existing iodine delivery systems are costly. Iodine is corrosive, requiring expensive materials of construction, e.g. Hastelloy C-276.
4. Valves in iodine systems must be operated hot and in the presence of iodine, providing a potential leak path. Any trace of the corrosive iodine must be kept away from electronic equipment and from oxide protected structural materials such as aluminum or titanium.
5. The laser run time is limited by the capacity of the iodine reservoir. The system must be shut down and cooled down to recharge the iodine reservoir, or provisions must be made for hot swapping or hot loading iodine reservoirs.
6. The carrier gas used to transport the iodine to the laser cavity must be heated to prevent condensation of the iodine vapors.

The IOD concept addresses these concerns by using a solid-solid chemical reaction to provide the iodine vapor feed to a COIL weapon system. The iodine pyrotechnic is contained in a cartridge (Fig. 1,) along with a preheat pyrotechnic, used to preheat the passages to the laser cavity and a purge pyrotechnic, used to remove traces of corrosive iodine from the system after firing. The iodine pyrotechnic will provide enough energy to heat the carrier gas, eliminating the necessity of providing a separate gas heating system. A loading mechanism (e.g., a revolver or other magazine) can provide for rapid cartridge replacement. Each cartridge will deliver iodine at a uniform flowrate for a fixed time into the COIL system. The iodine pyrotechnic is based on technology similar to that used in signal or warning flares. A solid oxidizer, a solid fuel and, perhaps, an inert solid (e.g., silica or iodine), are compounded into a solid rod within a recyclable casing. The cartridge is designed so that a chemical reaction proceeds at a constant rate down the length of the rod, producing gaseous products. The composition of the pyrotechnic is such that molecular iodine is a major constituent of the product stream and the minor gaseous constituents, e.g. carbon dioxide, do not interfere with the laser.

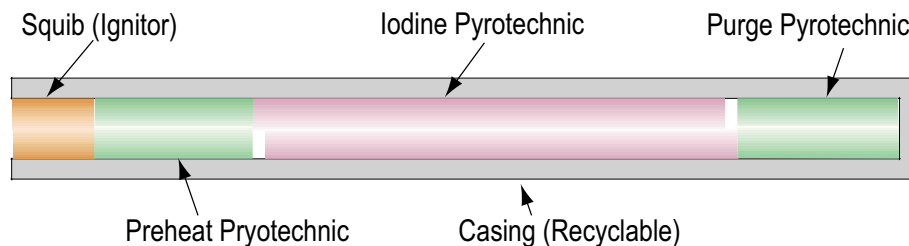


Fig. 1. Diagram of Iodine-on-Demand cartridge. Iodine exits from the left end of the casing.

The IOD concept answers the technical issues:

1. The cartridge iodine delivery system does not use a molten iodine source. The preheat pyrotechnic preheats the iodine transport line and the purge pyrotechnic cleans the residual iodine from the system.

2. The system is simple. Minimal instrumentation is required and no moving parts are in the iodine flow system.
3. Use of expensive materials of construction is minimized. Considering the low exposure time to iodine, inexpensive materials may completely replace expensive materials or the expensive materials may be used as thin liners.
4. Valves are functionally replaced by a cartridge insertion mechanism. This mechanism need not operate hot or in the presence of iodine.
5. Each cartridge is good for one shot. Cartridges can be shot one after the other with only minimal time between shots.
6. The exothermic reaction of the iodine generating reaction can eliminate the need of providing a carrier gas heating system.

Our approach is a two-phase feasibility demonstration of the IOD pyrotechnic. The first phase, the object of this report, is a proof of principle demonstration of the iodine gas generator. The second phase will be a demonstration of the operation of the IOD system on a COIL system at the Air Force Research Laboratory (AFRL) at Kirtland AFB, Albuquerque New Mexico. The objectives of Phase 1 are to demonstrate the feasibility of the IOD concept and to perform the preliminary system development.

The Phase 1 tasks are summarized as follows:

1. Screen potential fuel/oxidizer systems and select several for laboratory testing. Include an investigation of chemical recovery and recycle in addition to operational considerations.
2. Perform laboratory testing of safety aspects of proposed fuel/oxidizer systems. The testing was intended to discover if the chemical reaction would be initiated upon mixing, when subjected to friction, upon compaction or upon impact. Samples were also to be tested for thermal ignition, both as mixed powders and as compacts. Finally, compacts were to be tested for stability upon storage.
3. Demonstrate fabrication of the iodine pyrotechnic cartridge components and initiate testing to measure the burn rate and verify product composition. Analyze the results of the tests to verify that the concept can meet the COIL requirements.
4. Provide progress reports and this Phase 1 final report.

2. INITIAL SCREENING

The initial screening had the primary goal of selecting chemical systems suitable for the iodine pyrotechnic of with the Iodine-on-Demand concept. A secondary goal was to emphasize the selection of systems for which chemical recycle was practical. These two goals were approached in tandem. The research into recycle concentrated on those systems for which IOD appeared practical and the search for practical systems tended to look for systems for which recycle seemed possible. The selection was further restricted to compounds that are available as catalog items. Finally, feedback from the AFRL as to the undesirability of water in the product led to a further reduction in the systems under consideration.

2.1. Thermodynamic Computations

One very useful tool, in the initial screening, was the computer program HSC Chemistry 4.1, from Outokumpu Research Oy, Finland. This program contains an extensive thermodynamic database, which allowed the potential reactivity and heat release from a chemical reaction to be easily estimated. Table 1 summarizes data for reactions that are of most interest. Table A-1, in Appendix A presents the full list of reactions investigated that will proceed in the direction indicated (negative ΔG). Most of the reactions are exothermic (negative ΔH) but a few are endothermic. HSC also permits the estimation of the adiabatic reaction temperature, T_a .

The value of T_a given by HSC is a useful screening tool. T_a is not expected to be accurate, particularly when the value is high, but it does provide insight into the amount of energy that will be available to heat the carrier gas. There are several reasons for inaccuracy in the T_a , calculated by HSC. (1) Much of the heat capacity data in HSC is only good for low temperatures. (2) The T_a calculation assumes that the reaction goes to completion and at high temperatures the equilibrium of exothermic reactions is shifted away from completion. And, (3) the calculation does not take into account the fact that iodine will be present as atomic iodine at high temperatures (above $\sim 1000^\circ\text{C}$).

At the time this work was originally proposed, chemical systems producing only gaseous reaction products were being considered. The most desirable systems, under this constraint, are systems with a high ratio of iodine to less desirable gaseous products, such as nitrogen, carbon dioxide and, especially, water. Thereafter, it was realized that some systems, which have solid reaction products, produce no gaseous reaction products except iodine.

TABLE 1
SUMMARY OF FUEL/OXIDIZER SYSTEM EXAMINED WITH HSC

Reaction	Notes ^(a)	ΔH (kJ/mole I ₂)	ΔG (kJ/mole I ₂)	T _a (°C)
10 Al + 3 I ₂ O ₅ + 5 SiO ₂ = 3 I ₂ (g) + 5 Al ₂ SiO ₅	(b)	-2740	-2787	5920
5 C + 2 I ₂ O ₅ = 2 I ₂ (g) + 5 CO ₂ (g)		-763	-962	4080
5 Cl ₄ + 2 I ₂ O ₅ = 12 I ₂ (g) + 5 CO ₂ (g)	(c)	-92.6	-162	1500
5 C ₂ I ₄ + 4 I ₂ O ₅ = 14 I ₂ (g) + 10 CO ₂ (g)	(d)	-199	-272	2380
5 MgI ₂ + Ca(IO ₃) ₂ = CaO + 5 MgO + 6 I ₂ (g)		-67.3	-150	804
5 CuI + I ₂ O ₅ = 7/2 I ₂ (g) + CuO		-18.5	-63.5	210
15 Fe + 4 I ₂ O ₅ = 4 I ₂ (g) + 5 Fe ₂ O ₄		-1177	-1245	3340
(C ₈ H ₈) _x + 4 I ₂ O ₅ = 4 I ₂ (g) + 8 CO ₂ (g) + 4 H ₂ O(g)	(e)	-834	-1044	4020
5 Mg + I ₂ O ₅ = I ₂ (g) + 5 MgO		-2785	-2820	6970
5 MgI ₂ + 2 NaIO ₃ + 6 SiO ₂ = 6 I ₂ (g) + 5 MgSiO ₃ + Na ₂ SiO ₃	(d)	-111	-153	730
5 Sn + 2 Ca(IO ₃) ₂ = 2 I ₂ (g) + 5 SnO ₂ + 2 CaO		-988	-1247	2930
5 Sn + 2 I ₂ O ₅ = 2 I ₂ (g) + 5 SnO ₂	(f)	-1224	-1265	4500
5 Sn + I ₂ O ₅ = I ₂ (g) + 5 SnO	(f)	-1183	-1235	3070
5 Sn + 2 Mg(IO ₃) ₂ = 2 I ₂ (g) + 5 SnO ₂ + 2 MgO	(g)	-1079	-1325	3060
5 Sn + 4 NaIO ₃ = 2 I ₂ (g) + 5 SnO ₂ + 2 Na ₂ O		-836	-853	2110
5 Zn + I ₂ O ₅ = I ₂ (g) + 5 ZnO		-1532	-1578	3880

^(a)All thermodynamic data from HSC Chemistry 4.1 except as noted. All material in solid phase except as noted.

^(b)Adding SiO₂ tends to decrease (make more negative) the ΔH and ΔG of the reaction but the added mass results in a decrease in the adiabatic reaction temperature.

^(c)Thermodynamic properties of Cl₄ estimated: $\Delta H_f = +41.84$ kJ/mole, $\Delta G_f = -28.39$ kJ/mole.

^(d)Thermodynamic properties of C₂I₄ estimated: $\Delta H_f = +41.84$ kJ/mole, $\Delta G_f = -42.86$ kJ/mole.

^(e)Polybutadiene approximated by butadiene(l).

^(f)Polystyrene approximated by styrene(l).

^(g)Thermodynamic properties of Mg(IO₃)₂ estimated: $\Delta H_f = -903.744$ kJ/mole, $\Delta G_f = -741.574$ kJ/mole.

The enthalpy of the chemical reaction can be used to heat the carrier gas, but if more heat is available than required, the iodine stream may be very hot. This may be desirable if the laser is designed to operate with atomic iodine, but contemporary COIL systems require a temperature under 160°C. The reaction temperature can be reduced by either adding inert material or by operating the chemical reaction off stoichiometric. Early on, iodine was considered as an inert additive that would also increase the iodine content of the offgases but, upon further consideration, iodine seems less desirable as an additive. The systems that have the highest adiabatic temperature rise tend to be those based on metal fuels and metal/iodine mixtures tend to be chemically unstable.

Operating with the fuel/oxidizer mixture off stoichiometry can be very effective in decreasing the reaction temperature, particularly if the reaction is run fuel lean as the iodine containing oxidizers all decompose endothermically. To examine the effects of cooling the reaction with the addition of extra oxidizer, a chemical process simulator, AspenPlus, was used to predict the adiabatic reaction temperature and product composition for four different fuels as a function of the amount of oxidizer incorporated in the cartridge. The adiabatic reaction temperature calculated by AspenPlus is expected to be reasonably accurate as both chemical equilibrium and the formation of atomic species are taken into consideration. The adiabatic reaction temperature is the maximum possible temperature that can be reached as in actuality, some of the enthalpy of reaction

will be conducted or radiated to the surroundings and will not be available to heat the reaction products.

Figures 2 through 5 show the temperature and product composition expected from cartridges composed of polystyrene (C_8H_8), tetraiodomethane (CI_4), tetraiodoethylene (C_2I_4), and tin (Sn) combined with varying amounts of iodine pentoxide (I_2O_5). The ordinate of each graph is the stoichiometric multiple of oxidizer to fuel in the cartridge (i.e., a “stoichiometric mixture” is 1) so lean burning is to the left and rich burning is to the right. The actual temperature and composition entering the laser cavity will, in addition, depend upon the conditions of the carrier gas.

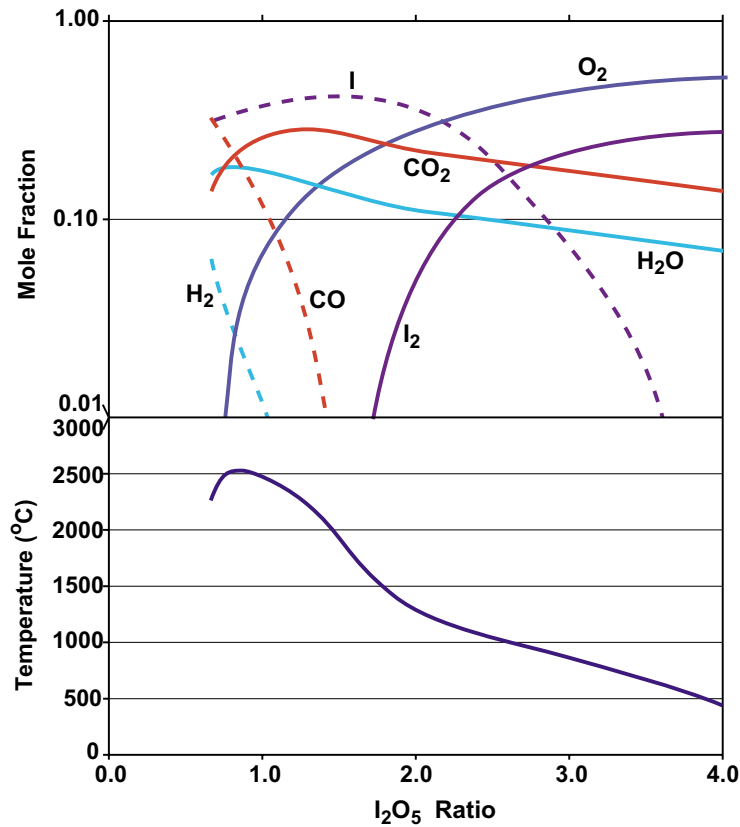


Fig. 2. Results for the system C_8H_8/I_2O_5 .

For the first three cases (Fig. 2 through 4), as the amount of I_2O_5 is increased beyond stoichiometric into the fuel-lean regime, the adiabatic reaction temperature decreases. Note the ratio of atomic iodine to molecular iodine decreases as well.

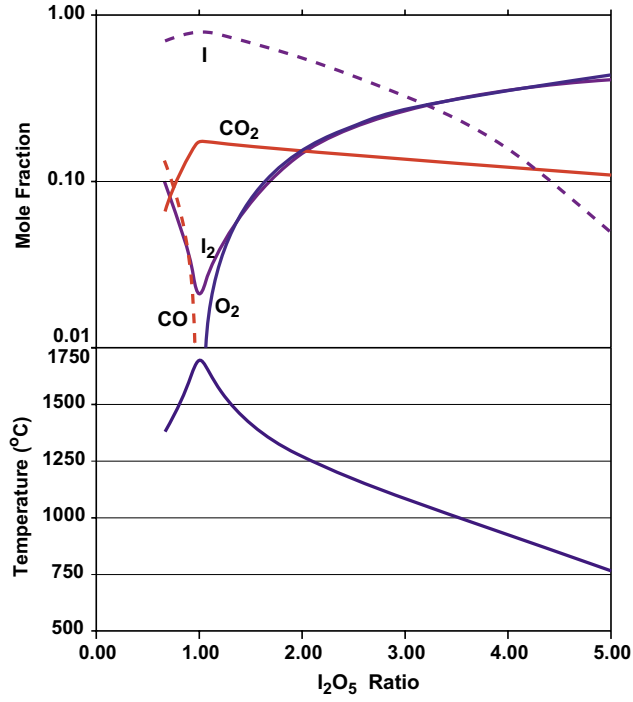


Fig. 3. Results for the system Cl_4/I_2O_5 .

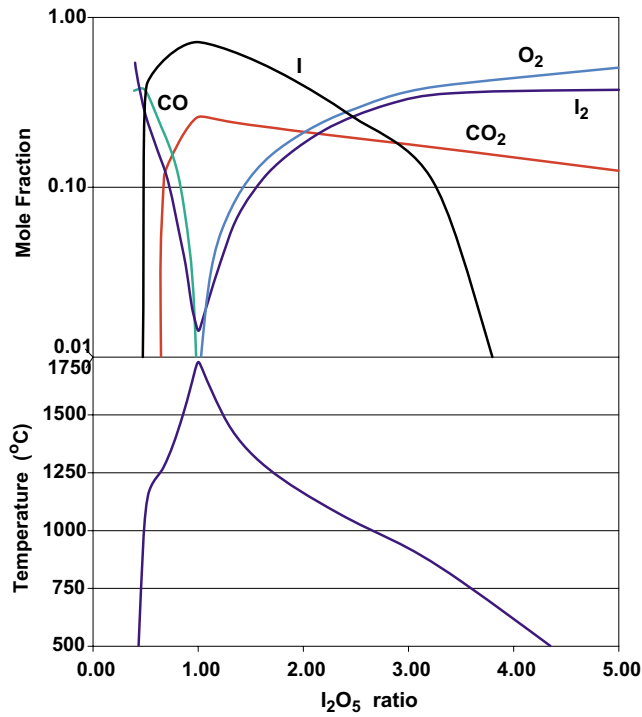


Fig. 4. Results for the system C_2I_4/I_2O_5 .

The tin case (Fig. 5) is qualitatively quite different in that the peak temperature holds reasonably constant for an I_2O_5 ratio of 0.25 to 2 and the concentration of tin does not go to zero at an I_2O_5 ratio of one as might be expected. Note that the mole fractions in the condensed phase (Sn , SnO_2) are independent from the gas phase (I_2 , I , O_2) so the mole fractions sum to 2. According to Le Chatelier's principle, if stress is applied to a system at equilibrium, the system readjusts so that the stress is reduced. Thus, for an exothermic chemical reaction such as the reaction being considered, high temperature favors the reverse reaction. The calculated adiabatic temperature for the stoichiometric reaction is $4500^\circ C$ but, as shown in Fig. 5, the temperature is constant near $2000^\circ C$ for an I_2O_5 ratio between 0.25 to 2. Once this temperature is reached, additional Sn cannot react unless there is a means of taking up the heat. Since the decomposition of I_2O_5 to iodine and oxygen is endothermic both the oxidation of tin and the decomposition of I_2O_5 take place simultaneously as additional I_2O_5 is added. Additionally, part of the heat is used in forming atomic iodine. After all the tin is consumed, additional I_2O_5 continues to lower the temperature until atomic iodine is not formed.

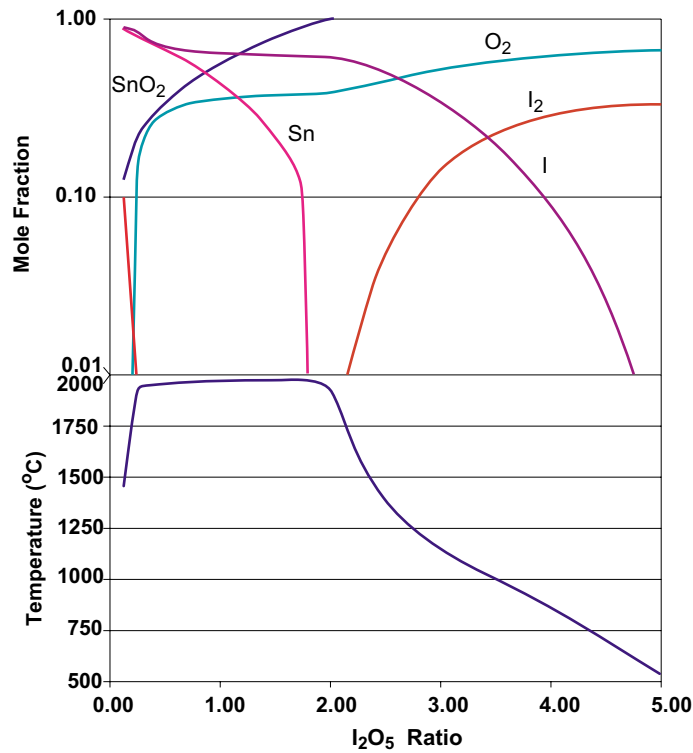


Fig. 5. Results for the system S_n/I_2O_5 .

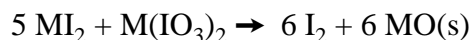
The HSC and AspenPlus calculations were important in determining which fuel/oxidizer combinations should be subjected to experimental examination. The calculations continued throughout the whole of Phase 1. As new systems were considered for experimentation, additional calculations were made to investigate feasibility. The calculations also played a part in determining which systems should be considered for recycle.

2.2. Recycle

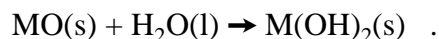
There is a real logistical benefit if the waste products of an IOD system can be recycled into the chemicals require to make the IOD pyrotechnic devices. Obviously, the waste products can be recycled back to the manufacturers of the original chemicals. While this can, and does, make sense while in a peace time training mode, the real logistical benefits of recycle would be if the recycle could be done in the battlefield, or at least at forward bases. Our analysis concentrated on recycle at a forward base. Besides the material being recycled, only the chemicals required to support $O_2(^1\Delta)$ generation are assumed to be available. The compounds assumed present to support $O_2(^1\Delta)$ are hydrogen peroxide, chlorine, and the basic hydroxides and their mixtures. We also assume that electrical energy and heat are available.

The more promising fuel/oxidizer systems identified by the thermodynamic calculations were examined for reaction products that could be recycled. In addition to iodine, the primary materials available for recycle are metal oxides and silicates. Carbon dioxide would also be available but its recycle was not seriously considered.

The only systems that lend themselves to recycle are the alkaline earth metal iodides and iodates, MgI_2 , CaI_2 , $Mg(IO_3)_2$, and $Ca(IO_3)_2$. The fuel/oxidizer reaction consuming them is:



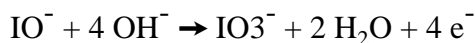
where, M = Ca or Mg. Note that a recycle system will need to make five times as much iodide as iodate. Reacting the alkaline earth oxide (MO) with water produces the hydroxide:



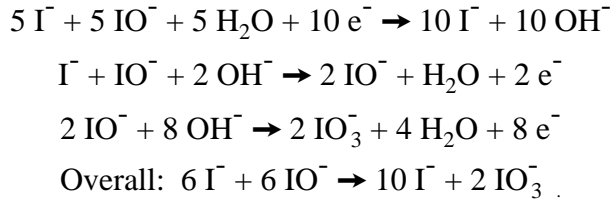
Dissolution of iodine in the alkaline earth hydroxide rapidly forms iodide (I^-) and hypoiodite (IO^-) ions at 50°C (Kirk-Othmer, 1995):



The hypoiodite can be oxidized to iodate in an electrolytic cell. The electrolytic oxidation, represented by the half-cell reaction:



has a standard potential of 0.56 Volts in a basic solution, (CRC, 1979). The complete electrolytic cell is shown in Fig. 6. The electrolysis must be performed batchwise as a two step reaction occurs in the anode compartment. Since the iodide: iodate ratio must be 5:1, the reduction compartment must contain five times the volume of the anode compartment:



The cell is operated at constant current and the voltage is monitored to indicate the end point. When the reaction is complete, both compartments are emptied and the resulting solutions are processed in separate evaporators to eliminate water.

This process will not work if silica is added to the reactant mixture in the iodine generator. Adding silica in the iodine generator increases the negative free energy and enthalpy of reaction in the iodine generator because the alkaline earth silicates are more stable than the alkaline earth oxides but this added stability prevents the silicates from reacting with water and iodine.

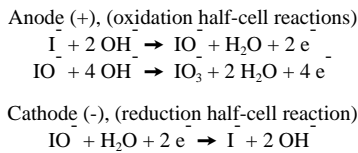
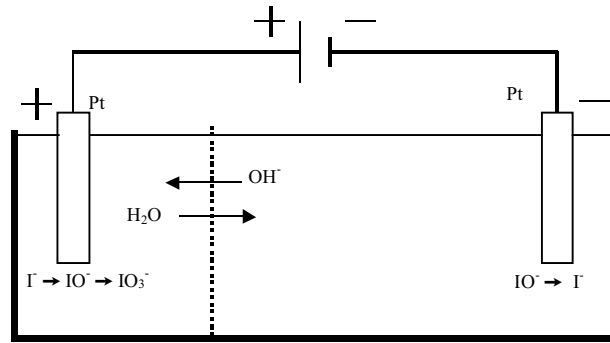
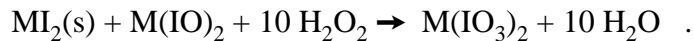
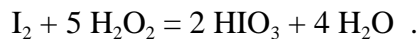


Fig. 6. Depiction of an electrolytic cell transforming iodine ions back into starting materials.

If only the iodate is to be produced, the electrolytic cell can generate hydrogen in the cathode compartment. Alternatively the alkaline earth iodide hypoiodite mixture can be directly oxidized to the iodate using hydrogen peroxide.



Recycle of I₂ to I₂O₅ cannot be performed electrolytically due to the low solubility of iodine in water but iodine can be oxidized using hydrogen peroxide:



The water can be evaporated to produce solid HIO_3 , and the HIO_3 can then be further heated to 200°C , where it decomposes into I_2O_5 . If the I_2O_5 is overheated it will decompose into iodine and oxygen but this does not occur until about 300°C .

Elemental iodine was originally considered a candidate for direct recycle. Iodine can be incorporated into the fuel/oxidizer mixture to both reduce the adiabatic temperature rise and increase the iodine content of the product stream. Iodine melts at 114°C and has a significant vapor pressure at lower temperatures so, as previously indicated, addition of iodine to the mixture is no longer being considered.

All other recycle schemes require chemicals not present in the logistical tail for COIL or require extensive processing and are not deemed practical.

3. LABORATORY SAFETY TESTING

The initial screening effort provided thermodynamic data on a number of fuel/oxidizer systems that had the potential for generating iodine and a shorter list of chemicals, which might be recycled at a forward support position. Before proceeding to develop an iodine pyrotechnic it was necessary to demonstrate, in small-scale laboratory tests, that the chemical mixtures could be safely handled and fabricated into compacts. Fuel/oxidizer systems were chosen, for safety testing, from those presented in Table 1. The systems containing alkaline earth iodides and iodates were given more emphasis than otherwise indicated because of their potential for recycle. This work was begun before the decision was made to exclude system that would produce water in the product gases. As a side benefit, the tests also gave indications as to suitability of the solid-solid mixture in an iodine gas generator for the COIL. The fuel/oxidizer systems chosen for safety analysis are the same as were presented in Table 1. The sources of each compound are given in Appendix A, Table A-2.

3.1. Safety Testing Scheme

A seven-step testing program was designed to verify that a fuel/oxidizer mixture could be safely handled through the processing steps necessary to fabricate iodine pyrotechnics. The tests, designed to delineate the regions of safe handling of the fuel/oxidizer mixtures and to eliminate systems that are unstable, are listed in Table 2. The tests for each system were performed in the order indicated. If a mixture failed a test, subsequent tests were not performed with that mixture.

At General Atomics, any work involving hazardous materials or hazardous operations must be performed in accordance with a formal safety document, the Hazardous Work Authorization (HWA). The HWA was prepared by the experimenters to address the specific issues involved in the experimental program and was reviewed and approved by the cognizant safety committee. In accordance with the HWA, all tests were performed in a fume hood behind a laboratory safety shield and, with the exception of the second test, all were initiated remotely. For the remotely initiated experiments, the calculated energy release was limited to 500 Joules. For Test 2, in which the experimenter is hand working the fuel/oxidizer mixture behind the safety shield, the limit was 20 Joules. The limits are conservatively calculated assuming a stoichiometric fuel/oxidizer mixture yielding gaseous room temperature products. For all the tests, the reactants were combined according to their stoichiometric ratio so as to have the maximum probability of initiating a reaction.

TABLE 2
SAFETY ANALYSIS TESTS

Test	Function
1. Mixing	The components are mixed in a small plastic V-blender (Fig. 7) to check for reaction initiation upon mixing. The fuel and oxidizer are loaded into separate legs of the inverted V. The 30-RPM motor is started remotely and the materials are blended.
2. Friction	A small sample of components is subjected to vigorous hand grinding in a 1-in. carborundum mortar and pestle (Fig. 8) to check for ignition due to friction. The experimenter, wearing chemical goggles and gloves, grinds the sample behind the safety shield in the hood.
3. Thermal ignition of powder sample	A blended sample is heated slowly in a cavity in a stainless steel block (Fig. 9). The block is instrumented (Fig. 10) to make it into a robust differential thermal analysis apparatus. Exotherms and endotherms can be seen in the sign and magnitude of the signal from the differential thermocouple. Detonation would have been indicated by the sound produced.
4. Compression	A blended sample is compressed in a 1/4 in. diameter hardened steel pellet die (Fig. 11) in a hydraulic press (Fig. 12) to a pressure of 20,000 psi, far exceeding the pressure to be used in fabricating IOD cartridges. Detonation would have been indicated by the sound produced and by observation of the residue.
5. Pellet impact	A pellet is placed between an anvil and a pin in a stainless steel die. A 1.5-kilogram mass (Fig. 13) falls 0.7 meters to impact the pin and shock the pellet. The mass is guided to the die by a plastic pipe strapped to the side of the hydraulic press (Fig. 12). Detonation would be indicated by the sound produced and by observation of the residue.
6. Thermal ignition of a pellet	A pellet is prepared with an embedded thermocouple. This thermocouple forms half of a differential thermocouple pair of the DTA apparatus (Figs. 9 and 10). Exotherms and endotherms can be seen in the sign and magnitude of the signal from the differential thermocouple. Detonation would have been indicated by the sound produced.
7. Pellet long term stability	Each pellet from a compression test was visually examined and, if the pellet was not discarded due to short-term degradation, it was labeled and stored. After several months of storage the pellet was reexamined and any changes noted.



Fig. 7. V-mixer used in mixing tests.



Fig. 8. Friction test using mortar and pestle.



Fig. 9. Thermal ignition apparatus.

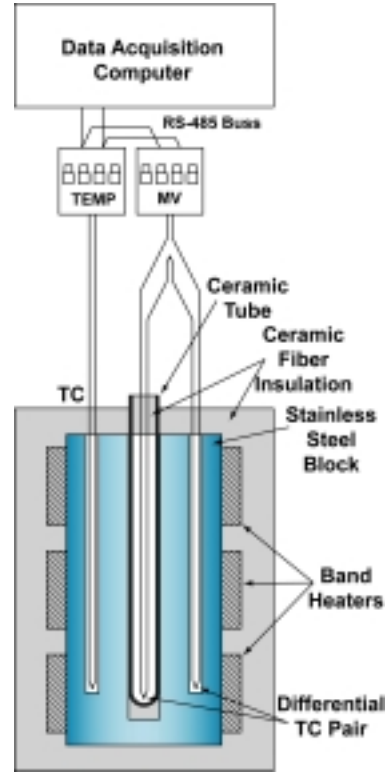


Fig. 10. Thermal ignition instrumentation.



Fig. 11. Pellet die.

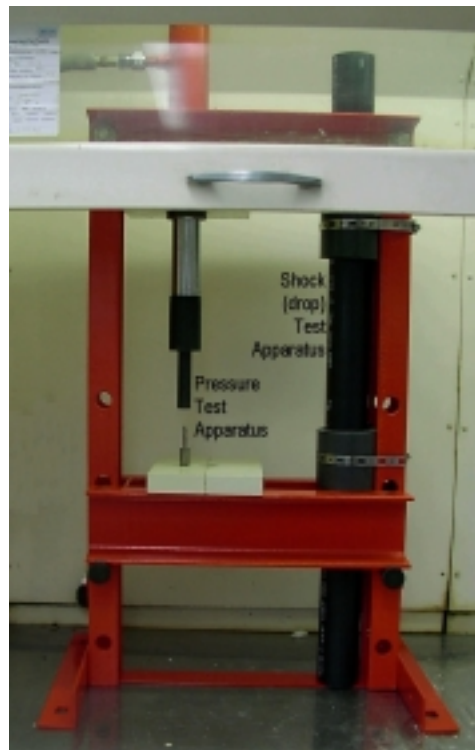


Fig. 12. Pressure and shock test apparatus.



Fig. 13. Drop weight and shock die.

3.2. Safety Analysis Results and Discussion

A summary of the individual safety tests is presented in Table 3, following this the thermal ignition tests are discussed in more detail. All the fuel/oxidizer systems examined passed the friction and blending tests, so these results are not included in the table and will not be mentioned further. The order of tests was kept the same, starting with friction and blending tests, then moving on to the powder ignition tests. If the powder ignition test resulted in removal of the particular fuel/oxidizer system from further consideration the remaining tests were generally suspended for that system. Generally, a system was removed from consideration because of processing or stability considerations, and not because of safety concerns. In fact, only one system was dropped from consideration because of safety concerns. Long term stability testing was undertaken only if a system passed all the other safety tests, and is presented later in this section.

TABLE 3
RESULTS OF SAFETY ANALYSIS TESTING

Mixture	Test	Result
Cl ₄ , I ₂ O ₅	Powder ignition [†]	Exothermic reaction initiated at 82°C [‡] in lean system and 87°C in rich mixture. Lean system showed endotherm, probably due to I ₂ O ₅ decomposition.
	Compression	No detonation but liquid [†] bled from compact. Color of pellet almost black, compared to initial reddish brown powder.
	Pellet impact	Slight deformation of compact.
	Pellet ignition	Exothermic reaction initiated at 89°C. Two endothermic reactions, a minor event at 117°C and major event at 186°C, probably due to I ₂ O ₅ decomposition.
C ₂ I ₄ , I ₂ O ₅	Powder ignition	Strong exothermic reaction initiated at 191°C in rich mixture.
	Compression	No significant alterations of color in rich mixture compact.
	Pellet impact	No significant alteration to compact.
	Pellet ignition	Strong exothermic reaction initiated at 167°C in stoichiometric mixture. Two more minor exothermic reactions at 213°C and 272°C. Probably from incomplete ignition of pellet.
Al, I ₂ O ₅ , SiO ₂	Powder ignition	No exothermic reaction evident. Small endothermic reaction occurred at 380°C.
	Compression	No test performed.
	Pellet impact	No test performed.
	Pellet ignition	No test performed.
Fe, I ₂ O ₅	Powder ignition	No exothermic reaction evident. Large endothermic reaction initiated at 380°C.
	Compression	Iron rapidly oxidized after compaction but without ignition.
	Pellet impact	Slight deformation of compact.
	Pellet ignition	No test performed.
MgI ₂ , Ca(IO ₃) ₂	Powder ignition [‡]	No definitive reactions initiated. Vapor evolution was evident throughout the test, from 150°-350°C.
	Compression	No test performed.
	Pellet impact	No test performed.
	Pellet ignition	No test performed.
MgI ₂ , I ₂ O ₅	Powder ignition	Exothermic reaction initiated at 71°C. A following endothermic reaction occurred at 189°C. Vapor evident through both reactions.
	Compression	Color of compact (reddish-orange) darker than original powder.
	Pellet impact	No significant alteration from initial shape.
	Pellet ignition	No test performed.

MgI ₂ , Na(IO ₃), SiO ₂	Powder ignition	No significant exothermic reaction. Two endothermic reactions initiated at 133°C at 250°C. Slight vapor evolution at 370°C.
	Compression	No significant alteration in color.
	Pellet impact Pellet ignition	Test fractured half the compact into powder. No test performed.
(C ₈ H ₈) _x . I ₂ O ₅	Powder ignition	Sharp, well-defined exothermic reaction at 230°C.
	Compression	Compact had red "specks" evident on surface. Compression resulted in a very thin pellet.
	Pellet impact Pellet ignition	Slight deformation of compact. No test performed.
Sn, I ₂ O ₅ to Sn(II), Sn(IV)	Powder ignition	Sn(II): Vigorous exothermic reaction initiated at 308°C. Sn(IV): Extremely vigorous exothermic reaction initiated at 306°C. The heat release melted the K-type thermocouple utilized for the differential temperature measurement (resulting in the chaotic readings after ignition).
	Compression	Both mixtures formed a hard shiny pellet.
	Pellet impact Pellet ignition	Slightly fractured both pellets. No formal test was performed but pellets were ignited as part of the pyrotechnic development task.
Zn, I ₂ O ₅	Powder ignition	Exothermic reaction initiated at 373°C.
	Compression	Formed a pellet with a shiny surface. Slightly fractured pellet.
Pellet impact	Pellet ignition	Exothermic reaction initiated at 383°C, ten degrees higher than the powder ignition. Additionally, a larger increase in temperature was recorded than in the powder test.
C, I ₂ O ₅	Powder ignition	Exothermic reaction initiated at 206°C. A following exothermic reaction occurred at 349°C. The initial reaction blew some material up and out of the tube (C powder was very fine).
	Compression	A pellet could not be formed.
	Pellet impact Pellet ignition	No test performed. No test performed.
CuI, I ₂ O ₅	Powder ignition	No significant exothermic reaction. Iodine vapor constantly wafting out of tube from ~200°C to 400°C.
	Compression	No obvious chemical change in forming pellet from powder.
	Pellet impact Pellet ignition	No test performed. No test performed.
Sn, Ca(IO ₃) ₂	Powder ignition	Vigorous exothermic reaction initiated at 420°C.
	Compression	No obvious chemical change in forming pellet from powder.
	Pellet impact Pellet ignition	Slightly fractured pellet. Exothermic reaction initiated at 302°C, ~100°C cooler than powder. Thermocouple may have been damaged in the powder test.
Sn, Mg(IO ₃) ₂	Powder ignition	Exothermic reaction initiated at 273°C. Vigorous ignition resulted in a sound resembling a burning match.
	Compression	No obvious chemical change in forming pellet from powder.
	Pellet impact Pellet ignition	Slight deformation of pellet. Exothermic reaction initiated at 271°C.
Sn, NaIO ₃	Powder ignition	Exothermic reaction initiated at 431°C but no iodine observed.
	Compression	No obvious chemical change in forming pellet from powder.
	Pellet impact Pellet ignition	Slight deformation of pellet. No test performed.

[†]Ignition test performed in air, all others in argon.

[‡]Temperatures quoted are that of the block. The temperature of the sample is probably 2°-3°C lower.

*The temperature was below the melting point of iodine and the color was more red-brown than purple. The color was similar to that of the I₃⁻ ion formed when iodine is dissolved in a solution of iodide salts.

Data for the thermal ignition tests is presented below in Fig. 14 through 24. The ordinate is the temperature of the fuel/oxidizer system, while the abscissa is the recorded voltage. This format enables interpretation of results between thermal tests by standardizing the time scales for each. Raw data graphs of separate temperature and voltage versus time for each of these tests is available in Appendix A.

The thermal ignition temperatures of $\text{Cl}_4/\text{I}_2\text{O}_5$ and $\text{MgI}_2/\text{I}_2\text{O}_5$ (Figs. 14, 15, and 16) are so low, $<90^\circ\text{C}$ and 71°C respectively, that fielding of these systems would require special storage and handling considerations. Additionally, since chemical changes are seen during the compression tests for these two mixtures, they were eliminated from further consideration.

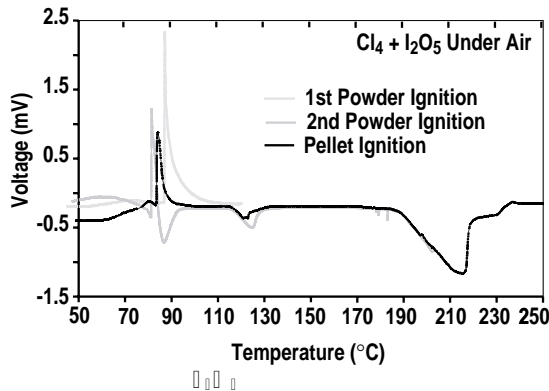


Fig. 14. $\text{Cl}_4/\text{I}_2\text{O}_5$ ignites at less than 90°C .

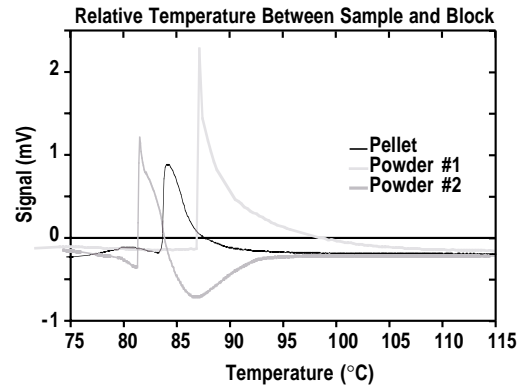


Fig. 15. Detail of $\text{Cl}_4/\text{I}_2\text{O}_5$ ignition.

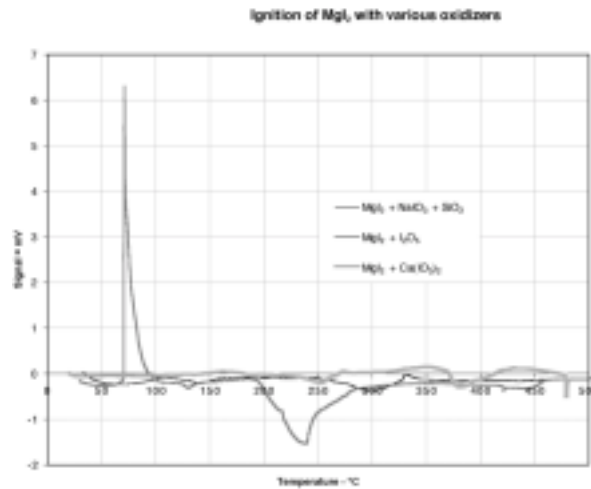


Fig. 16. $\text{MgI}_2/\text{I}_2\text{O}_5$ ignites at 71°C , $\text{MgI}_2/\text{NaIO}_3$ and $\text{MgI}_2/\text{Ca}(\text{IO}_3)_2$ fail to ignite.

No significant exothermic reaction was observed for $\text{MgI}_2/\text{NaIO}_3$, or $\text{MgI}_2/\text{Ca}(\text{IO}_3)_2$ (Fig. 16). These two systems have the lowest predicted adiabatic reaction temperatures of any of the systems tested.

C_2I_4/I_2O_5 and polystyrene/ I_2O_5 (Figs. 17 and 18) have sharp exothermic reactions at temperatures of 160°C and 240°C respectively. Both systems appear suitable for IOD from an ignition temperature standpoint, but polystyrene produces water as a product, which is undesirable.

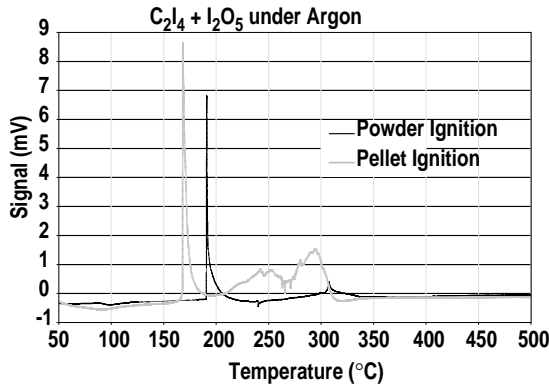


Fig. 17. C_2I_4/I_2O_5 ignites above 150°C.

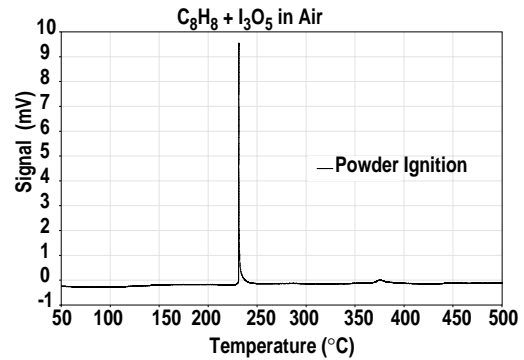


Fig. 18. Polystyrene/ I_2O_5 ignites above 200°C.

No significant exothermic reaction was observed for Fe/ I_2O_5 or Al/ I_2O_5/SiO_2 (Fig. 19). In these two cases, all the I_2O_5 thermally decomposed at between 370°C and 450°C: the reaction was never initiated and the unreacted fuel was found in the crucible after the test. The endothermic decomposition of the I_2O_5 can be seen in the two traces. We were surprised at this result since iron and aluminum have the highest adiabatic temperature rises and should react very vigorously. It is noted that the fuel tends to melt before the I_2O_5 decomposes for systems that react. Iron and aluminum should be usable if they can be rapidly ignited using a high temperature ignition system or if more finely divided metal powders were employed.

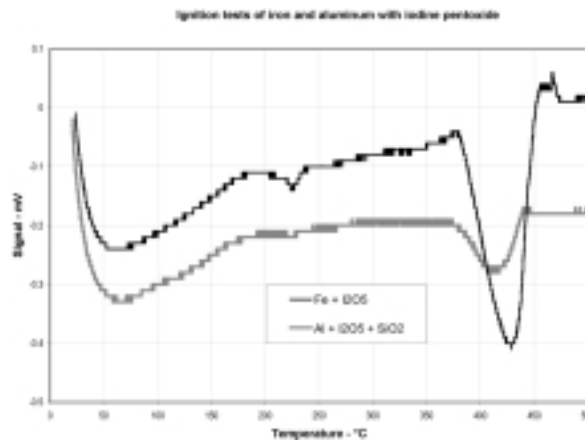


Fig. 19. Al and Fe/ I_2O_5 do not ignite below decomposition temperature of I_2O_5 .

Tin and zinc melt at or below the decomposition temperature of I_2O_5 and they gave strong exotherms in the vicinity of their melting point. The exotherm of Sn/ I_2O_5 (Fig. 20)

occurs very sharply at 300°C when forming either Sn(II) or Sn(IV). The reaction forming Sn(IV), with a calculated adiabatic reaction temperature of 4500°C, was hot enough to melt the K-type thermocouple used to measure the ignition temperature as seen by the erratic temperature reading after ignition. The ignition temperature of Zn/I₂O₅ (Fig. 21) is slightly higher at 373°C, possibly reflecting the different melting points of Sn versus Zn, 231°C and 419°C respectively.

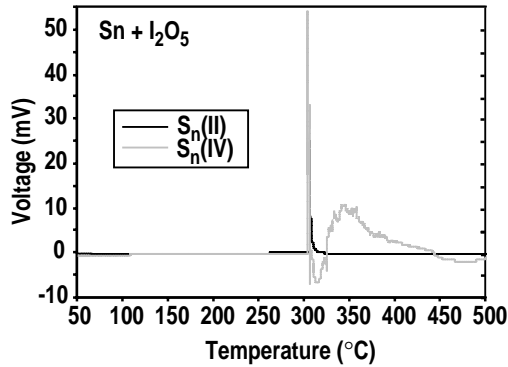
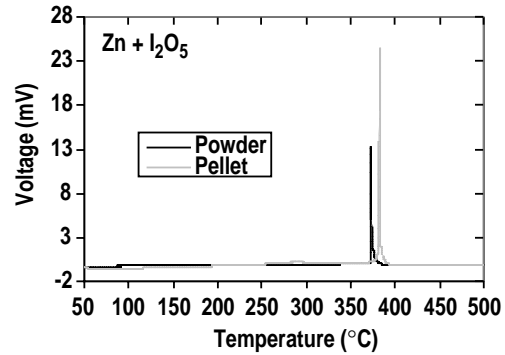


Fig. 20. Sn/I₂O₅ to Sn(II),Sn(IV) (powder).



Powder Fig. 21. Zn/I₂O₅.

Pellet

Tin was also reacted with various iodates, Ca(IO₃)₂, Mg(IO₃)₂, and NaIO₃, (Fig. 22) resulting in ignition temperatures of 273°C, 420°C, and 431°C. Use of metal iodates in place of iodine pentoxide both reduces the adiabatic reaction temperature and lowers the melting point of the solid reaction products. If the solid reaction products form large aggregates it will be easier to prevent them from entering the iodine stream.

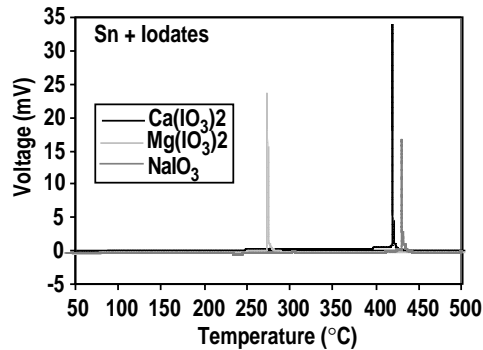


Fig. 22. Sn with various iodates (powder).

The system C/I₂O₅ (Fig. 23) resulted in an ignition temperature of 207°C, but this system would not form a solid pellet in the compression testing. CuI/I₂O₅ (Fig. 24) was also examined, but did not demonstrate an ignition up to 500°C. Additionally, CuI/I₂O₅ demonstrated an endothermic reaction releasing iodine starting at 200°C up to 400°C.

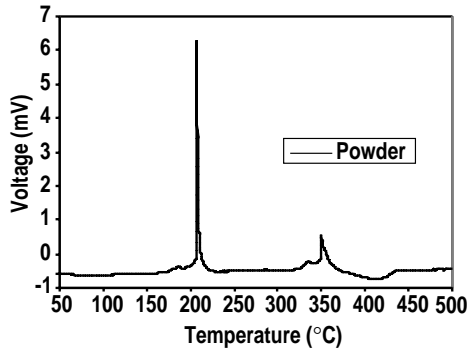


Fig. 23. C/I₂O₅.

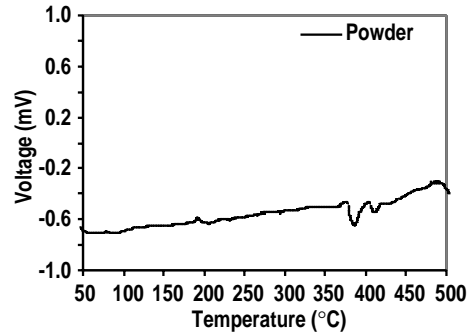


Fig. 24. Cu/I₂O₅.

3.3. Conclusions of Safety Analysis

The safety analysis found no safety concerns in any of the tests. The only indication of any safety issue was with the system Al/I₂O₅/SiO₂. After pressing and extruding the pellet used in the ignition tests, the pin was stuck in the die. While driving the pin out with a hammer a loud bang was heard: aluminum was eliminated from consideration as a primary fuel.

The end result of the safety analysis was a down-selection to two systems that would undergo scale-up. Only the fuel aluminum was eliminated from consideration for any safety consideration, the safety testing did produce much information to guide the choice of chemical systems from which a fieldable IOD system can be developed. The criteria used to reduce the number of chemical system under consideration to two main systems are listed in Table 4.

TABLE 4
CRITERIA FOR ADVANCEMENT TO CARTRIDGE DEVELOPMENT AND TESTING

The system must pass all of the required safety testing.
The system has an ignition temperature higher than nominal aircraft and tarmac temperatures, generally designated as 100°C, in order to prevent accidental ignition while in storage.
The pelletized mixtures do not exhibit any change in chemical or physical properties over time.
The chemical system's adiabatic temperature is not excessive, or can be moderated by composition or with additives.
The reaction products do not include water.
The chemical system exhibits good reaction propagation when chains of pellets are ignited in propagation tests.

The first system chosen is C₂I₄/I₂O₅. When mixed stoichiometrically this system produces only the gases I₂ and CO₂. The major design parameter, the ratio of C₂I₄ to I₂O₅, determines the composition and temperature of the product gases. Excess I₂O₅ can be added to reduce the potential for producing traces of CO, but it adds O₂ to the product mix and reduces the adiabatic temperature rise. If additional heat is required to heat the carrier gas, powdered carbon can be added along with the I₂O₅ required to oxidize it.

The second system identified for further testing consists of the metal powders tin and zinc mixed with iodine containing oxidizers (I_2O_5 and/or metal iodates). For this system the only gases are iodine and if excess oxidizer is used, oxygen. The major concern this system is the preventing the entrainment of solids in the offgases. Filtration can be employed but the most effective means of solids trapping is expected to be in choosing a formulation that produces consolidated solids rather than fluffy powders. The consistency of the solids can be modified by adding “inert” materials such as SiO_2 or Al_2O_3 to the mix, which also will reduce the adiabatic temperature rise. Adding silicon or aluminum to the mix, along with the inerts, will let the adiabatic temperature rise be adjusted while controlling the solid consistency.

4. CARTRIDGE DEVELOPMENT AND TESTING

Cartridge development and testing had three steps. The first step was to develop electric cartridge ignition. Next the propagation of the ignition front from pellet to pellet was investigated using small diameter pellets and finally, the investigation was scaled-up to larger sizes.

4.1. Pellet Ignition

The ignition system developed was based on embedding wire in a fuel/oxidizer pellet and passing a current through the wire. Sn/I₂O₅ and Zn/I₂O₅ fuel/oxidizer pellets were tested first. Two different approaches to initiating the reaction were explored. The first approach attempted to use a reactive wire and make it part of the fuel in the pellet. The second approach was to use an inert wire. Use of a reactive wire was unsuccessful. A zinc wire, embedded in a zinc/I₂O₅ pellet, melted before it provided enough heat to ignite the bulk of the pellet. The thermal ignition tests seemed to indicate that ignition is associated with melting of one of the reactants but apparently the surface area of the molten zinc was insufficient to provide heat of chemical reaction faster than heat was transferred into the bulk of the pellet. Attempts to use other reactive wires were no more successful.

Copper, niobium, and tantalum wire were all tested for use as inert wires. Copper wire failed to ignite either of the two pellet systems tested (Zn or Sn plus I₂O₅). While hot enough (copper wire melts at 1084°C), the wire was too thin to impart a significant amount of heat to the pellet. Thicker copper wire was considered, but the current required to heat thicker wire was in excess of available equipment. Niobium and tantalum wires were examined next, since both these wires have high melting points, 2477°C and 3017°C respectively. However, both wires oxidized rapidly in ambient air, and while ignition of a Sn/I₂O₅ pellet with niobium wire was accomplished, it was the only successful test out of five using these wires.

Stainless steel and platinum/rhodium wires were tested next. These materials melt at ~1400°C and 1800°C respectively and readily ignited both tin and zinc based pellets without oxidation. Because of the high cost of the platinum/rhodium, stainless steel wire was chosen for use in the cartridge development test program. Table 5 summarizes results of the ignition wire testing, and a picture of the successful ignition of a Sn/I₂O₅ pellet is provided in Fig. 25. Subsequently it was found that pellets would ignite if the wire were pressed against the pellet instead of being embedded in it. Only stainless steel wire was used to ignite C₂I₄/I₂O₅ pellets. All the pellet ignition testing used 1/4 in. diameter pellets.

TABLE 5
SUMMARY OF IGNITION WIRE TESTING

Wire	Diam. (mm)	Pellet System	Ignition Voltage	Ignition Time (s)	Result
Cu	0.24	Zn/I ₂ O ₅	8	NA	Did not ignite pellet before melting.
Cu	0.24	Sn/ I ₂ O ₅	8	NA	Did not ignite pellet before melting.
SS	0.635	Zn/ I ₂ O ₅	12 to 15	4 to 6	Pellet ignition in all tests.
SS	0.635	Sn/ I ₂ O ₅	15	4	Fast and vigorous pellet ignition. White flame evident from test apparatus.
Pt/10% Rh	0.381	Zn/ I ₂ O ₅	12	5	Pellet ignition.
Pt/10% Rh	0.381	Sn/ I ₂ O ₅	12	2	Fast and vigorous pellet ignition. White flame evident from test apparatus.
Nb	0.432	Zn/ I ₂ O ₅	13 to 16	NA	Wire melted before ignition.
Nb	0.432	Sn/ I ₂ O ₅	17	2	Fast and vigorous ignition. White flame evident from test apparatus.
Ta	0.432	na	4 to 5	NA	Discontinued use. Wire oxidized quickly upon heating in air.



Fig. 25. Electrical ignition of Sn pellet during wire ignition testing.

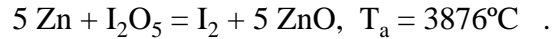
4.2. Burn Propagation

Propagation of the reaction from pellet to pellet through a stack of pellets was investigated next. A number of factors dictate whether a system will have good propagation ability, however, the major factors are the system's adiabatic reaction temperature and the rate of heat loss to the surroundings. If the reaction temperature is not high enough the reaction will not propagate through the pellet. Additionally, the propagation ability of a particular system had to be robust enough to overcome the small gaps between pellets for each gap encountered.

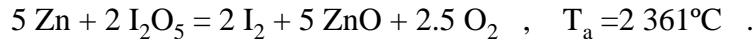
The propagation testing for each system is discussed separately.

4.2.1. Zn and I₂O₅

The stoichiometric reaction is:



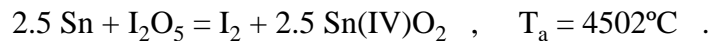
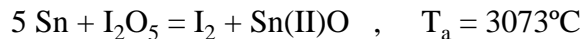
The ignition temperature of this mixture is ~380°C, well above the minimum safety ignition temperature of 100°C. Pelletized mixtures of this system do not exhibit any changes over the time observed. If desired, I₂O₅ can be increased above the stoichiometric amount to reduce the adiabatic reaction temperature, T_a, and increase the amount of iodine, but with the addition of O₂ to the gaseous products:



T_a is further reduced by additional I₂O₅, down to 1964°C and 1337°C for 3 and 4 times stoichiometric I₂O₅ respectively, but this reduction must be weighed against the loss of propagation ability through multiple pellets. As T_a is reduced, the system becomes more sensitive to heat losses that may hinder propagation from one pellet to another. As the pellet diameter increases, from the initial 0.25 in., propagation should be less of a problem. The additive SiO₂ was added to this system in a separate test, in order to study agglomeration effects with the metal oxide product. The silica does not significantly alter the ignition temperature or T_a, and did result in an increase in particle size through formation of zinc silicate. Silica can be added to any of the metal containing chemical systems under investigation, with similar results expected. Aluminum oxide or boron oxides might also be helpful in agglomerating the slag.

4.2.2. Sn and I₂O₅

The stoichiometric reactions, to tin (II) and tin(IV) are:



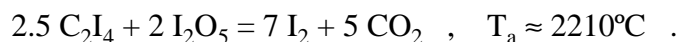
The reaction forming Sn(IV)O₂ has the highest T_a and SnO₂ was used as the basis all the analyses. As with zinc, I₂O₅ can be increased above stoichiometric amounts to reduce T_a, but will add O₂ to the gaseous products.

The ignition temperature of either mixture forming Sn(II)O or Sn(IV)O is ≈ 307°C, well above our minimum temperature of 100°C, and pelletized mixtures do not exhibit changes over the times investigated.

Pellets formed with stoichiometric composition to produce Sn(IV)O₂ demonstrated vigorous reaction propagation in a chain of pellets. Additional tests utilizing pellets with increasing amounts of I₂O₅, to 2, 2.5, and 3 times stoichiometric, were also performed. Propagation was evident up to 2.5 times I₂O₅, but not with 3 times. However, as described later, propagation at higher I₂O₅ ratios was possible with larger diameter pellets. Benefits of the added I₂O₅ include not only decreased T_a as mentioned previously, but also increase the amount of I₂ vapor in the product stream.

4.2.3. C₂I₄ Mixed With I₂O₅

The stoichiometric reaction is:



The ignition temperature of this mixture is $\approx 180^\circ\text{C}$, above the minimum temperature of 100°C , and pelletized mixtures do not visibly change over the times investigated. A benefit of this system is all the reactants are transformed into gaseous products. A reaction propagation test, utilizing a chain of 0.25 in. diameter pellets, with increasing I₂O₅ fraction, was performed. The test utilized pellets with increasing amounts of I₂O₅, from stoichiometric to 2 and 3 times stoichiometric. Propagation was evident up to 2 times I₂O₅, but not with 3 times. A picture of the components and of the I₂ vapor exiting the ceramic test apparatus during this test are displayed in Figs. 25 and 26.

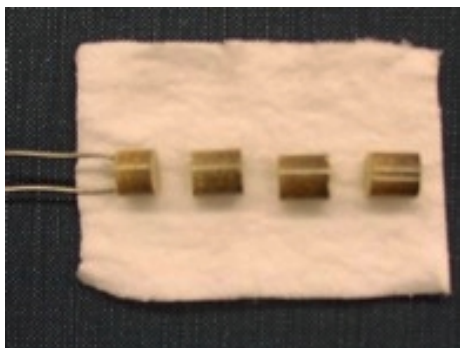


Fig. 26. C₂I₄/I₂O₅ propagation test components.

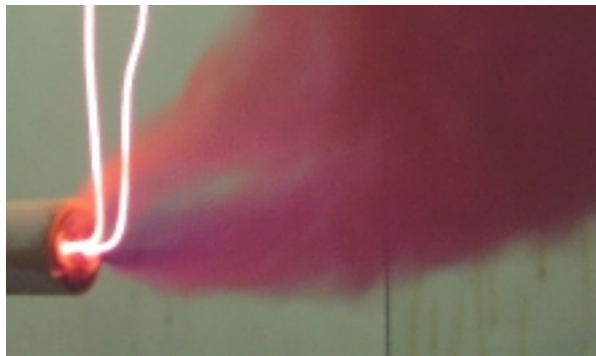


Fig. 27. C₂I₄/I₂O₅ propagation ignition test.

4.3. Cartridge Development

The goal of the cartridge development effort was to generate approximately 8-10 millimole/s of I₂ for up to 30 seconds in a helium flow of 1.14 mole/s. This is the generation rate required for the Phase 2 testing at AFRL. Considerable equipment was required for this scale-up effort so that the offgases of the system could be examined. Also, this amount of iodine is a high load for the activated charcoal trap on the hood offgas system to handle.

4.3.1. Scale-Up Test Equipment

The scale-up testing was performed using a test apparatus, illustrated in Figs. 28 and 29.

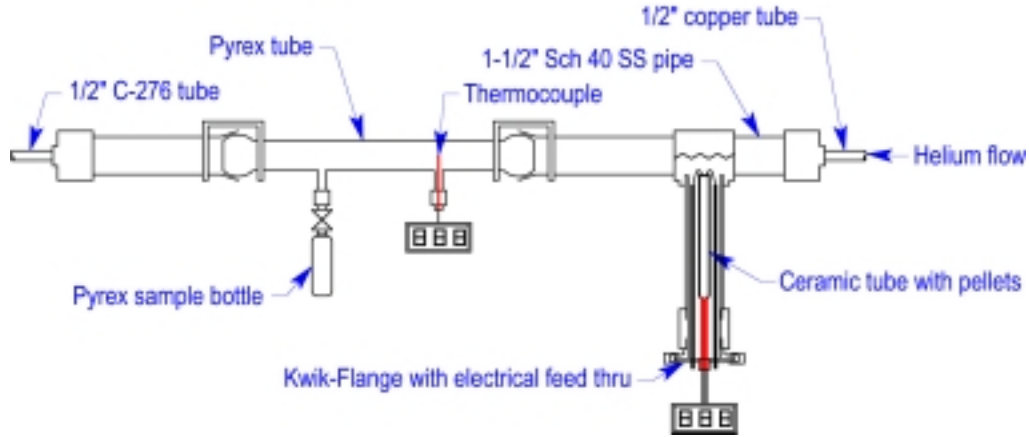


Fig. 28. Diagram of burn test apparatus.

Ignition takes place inside the ceramic (mullite) tube placed inside a 1.5 in. SS pipe. The reaction is initiated by the wire embedded in the igniter pellet at the top of the stack of pellets, or in later tests, resting against the top pellet. The bottom of the chamber consists of an electrical feedthrough, through which data signals and power for ignition will be routed. The mullite tube is wrapped in FiberFrax ceramic paper in order to reduce heat loss from the reacting pellets to the surroundings.

The apparatus employs a Pyrex tube for viewing of burn tests in progress. The Pyrex tube will have two ports for gas sampling and/or thermocouple insertion. The helium carrier gas enters the apparatus from the right side. Later, a low-flow helium purge was added to the bottom of the reaction chamber. Heating tape was wrapped around the entire apparatus to minimize iodine plate-out on the walls of the reaction chamber and viewtube. Figure 30 shows the experimental apparatus set-up in the hood. To the left is located a caustic scrubber, used to scrub iodine from the offgas stream.

The caustic scrubber was designed to reduce iodine to less than 0.01% of the stream. The scrubber outlet then passed to the activated charcoal hood offgas treatment system.

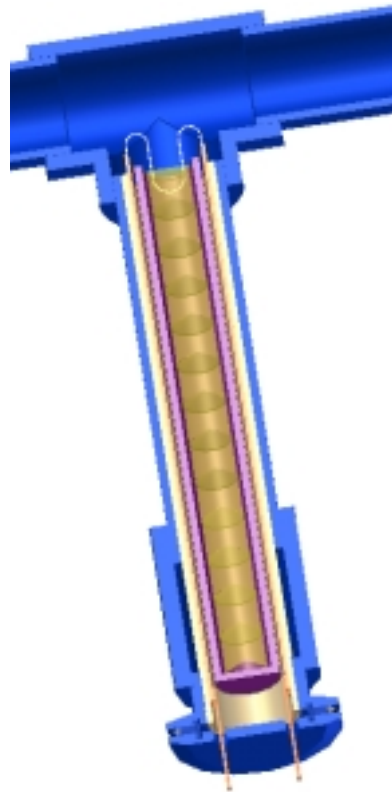


Fig. 29. Cut-away of reaction chamber.

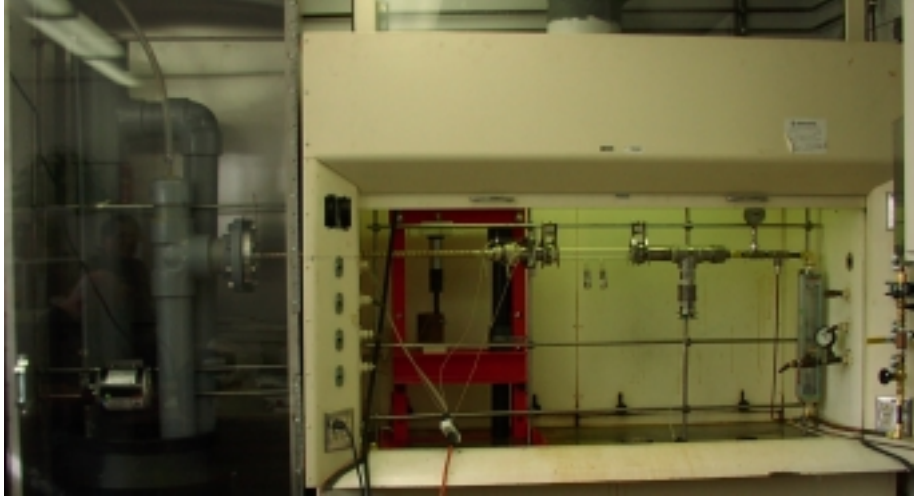


Fig. 30. Experimental set up depicting burn test apparatus and the caustic scrubber.

In response to a laboratory incident involving a detonation/deflagration event, while in the process of ejecting a completed pellet from the pressing apparatus, steel safety shields were installed around the pelletizing and burn test apparatus, pictured in Figs. 31 and 32. Both systems were designed to withstand detonations of considerable larger energy release than was theoretically possible, and consisted of telescoping, concentric steel pipes. The incident and resultant analysis are discussed later.



Fig. 31. Press shielding.



Fig. 32. Burn test shielding.

4.3.2. Cartridge Scale-Up Testing

The scale-up testing was performed in accordance with the Hazardous Work Authorization. The HWA stipulated that the scale-up factor between successful runs was to be by less than a factor of four in energy release. We chose to be on the conservative side. Our initial tests had been designed to produce less than 500 joules energy release. The pellet size for these tests was 1/4 in. diameter and the length was dictated by the energy release. Then, we scaled the length up to 1/4 in. long, which was less than a factor of four. For mixtures with low energy density, we never got to the 500-joule scale, as there was not enough room in the die to make a 500-joule pellet. We further limited the amount of material such that the final pellet length was not significantly more than the diameter so as to maintain uniform density in the compacted pellet. After scaling from one pellet to a four-pellet stack, we were ready to scale up to larger diameter pellets. Since the reaction propagation was expected to be easier at larger diameters, we reapplied the factor of four based on a single pellet. Assuming we maintained an L/D of 1, we could scale up the diameter by $4^{1/3}$. We decided to scale by a little less and chose to scale from 1/4 in. pellets to 3/8 in. pellets and then to 1/2 in. pellets. When it came time to actually fabricate the pellets the L/D ratio of 1 could not be maintained as there was not room in the die for the powders and the pellet length was maintained at about 1/4 in. A summary of all the scale-up test data is in Table A-3 of Appendix A.

4.3.3. Flow Test 1

The primary focus of the first test was to examine the operation of the flow test apparatus, a secondary focus, of course, was to examine results of the ignition the fuel/oxidizer system. The 3/8 in. diameter igniter pellet contained a twice-stoichiometric mixture of Sn and I_2O_5 with an embedded stainless steel wire for electrical ignition. The other three pellets in the chain also contained twice the stoichiometric I_2O_5 . At ignition, a wave of gaseous I_2 was witnessed flowing through the view tube, until plating of the cooling iodine on the walls of the view tube prevented viewing. It took several minutes of purging for the deposit to be removed from the viewing tube walls. After the run there were gray deposits on the tube wall and the mullite tube holding the pellets was found to contain liquid in addition to the whitish gray granular product formed from the reaction. It was subsequently determined that there was a slight down slope of the flow tube from scrubber back to the test apparatus. The angle of the tube was corrected, the end or outlet of the flow tube into the scrubber was modified to reduce the chance of droplets of scrubber liquid getting into the tube and thereafter the scrubber was never run without first establishing helium flow.

4.3.4. Flow Test 2

The second scale-up test was again performed with Sn/ I_2O_5 pellets. This time the first pellet had an I_2O_5 ratio of 1 and the subsequent 5 pellets had an I_2O_5 ratio of 2. The AspenPlus run depicted in Fig. 5 had not been generated at this time and it was thought that the stoichiometric ignition pellet would burn hotter to preheat the tube minimizing iodine plate-out and the subsequent pellets would generate conditions similar to the first run. As indicated in Fig. 33, plate-out remained a problem and in subsequent runs, the tube was trace heated to reduce iodine plate-out.

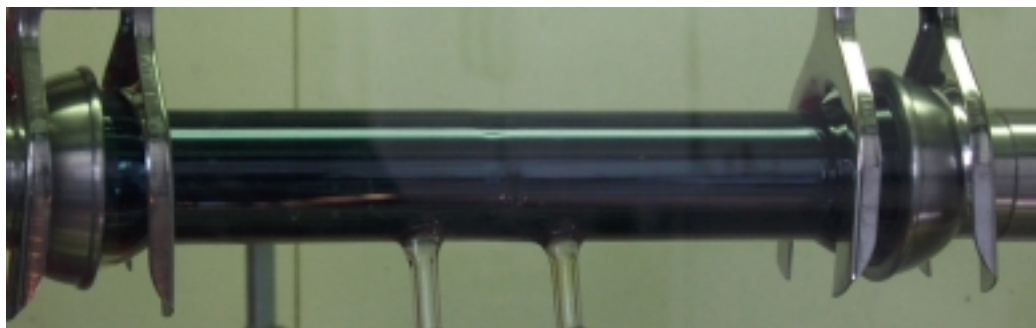


Fig. 33. Second burn test of iodine plated-out on view tube.

This time, after the iodine deposit was purged away, a fine white granular powder was apparent on the walls of the viewing tube. A sample of this powder was measured by EDEX and it was found to contain tin and oxygen in an approximately 1:2 ratio (SnO_2). At this point it was believed that the SnO_2 had been carried out of the reaction chamber into the flow tube and this could be prevented by incorporating additives, such as SiO_2 , or by incorporating filtration into the cartridge.

4.3.5. Flow Test 3

A third burn test was performed using three 3/8 in. diameter $\text{C}_2\text{I}_4/\text{I}_2\text{O}_5$ pellets. The first pellet has a stoichiometric mixture and the subsequent two were twice stoichiometric in I_2O_5 . The higher heat generation of the first pellet was again intended to preheat the tube and the adiabatic temperature rise of the second two pellets was calculated to be 140°C , taking into account the effect of the helium diluent. This test had a noticeably less “energetic” iodine gas release than the first two tests and a significant amount of iodine was left in the reaction chamber. The heat from the reaction, already lowered by the lean composition of the pellets, was not sufficient to prevent iodine plate-out in the reaction chamber.

4.3.6. Flow Test 4

All three pellets of the fourth burn test were a stoichiometric mixture of C_2I_4 and I_2O_5 to provide additional heat to the reaction chamber, but again, a large amount of iodine plated out inside the reaction chamber. One problem noted at the small scale of the experiments is that the relatively large volume of the vessel containing the pellets provides a sink for I_2 . Thereafter, a small inert gas purge flow was introduced through the reaction chamber to minimize plate-out and the diameter of the pellets in subsequent runs was increased to 1/2 in., to decrease the rate of radial heat loss to heat generated.

4.3.7. Flow Tests 5 and 6

The fifth and sixth scale-up tests each consisted of three 1/2 in. stoichiometric $\text{C}_2\text{I}_4/\text{I}_2\text{O}_5$ pellets. Very little, if any, iodine plate-out was evident in the reaction chamber. Figure 34 shows a series of video stills, illustrating the I_2 gas front traversing the viewtube.

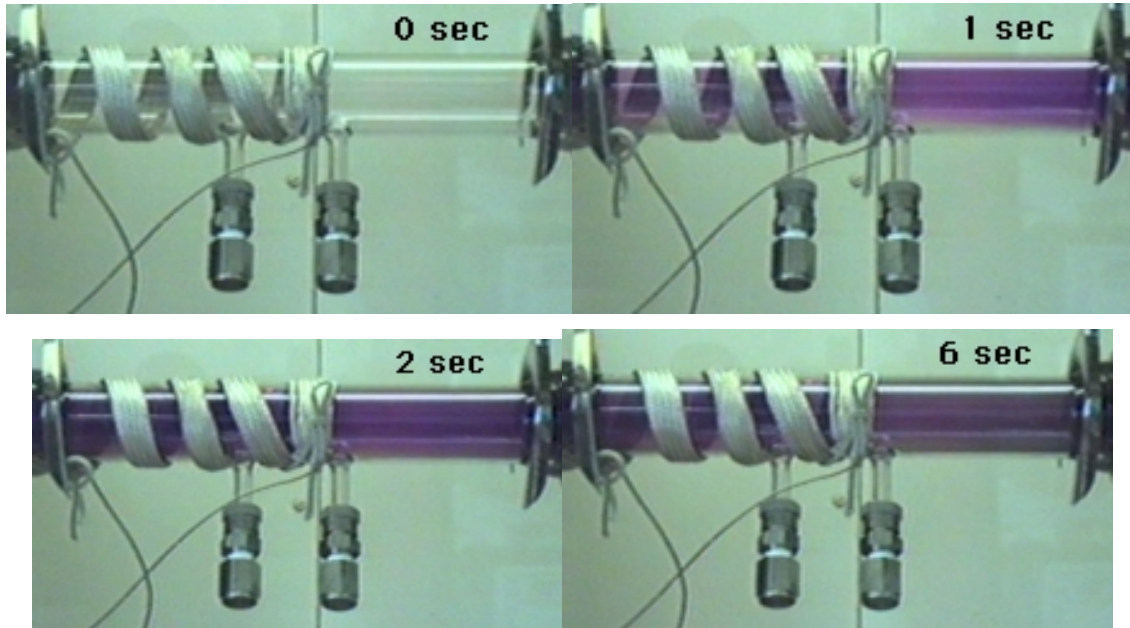


Fig. 34. Series of video stills showing the iodine front traversing down the view tube.

4.3.8. Flow Test 7

After two successful C_2I_4/I_2O_5 tests it was time to return to the solid plate-out problem of the Sn/I_2O_5 system. For Test 7 the pellets diameter was increased to 1/2 in. but the four pellets were fabricated at an I_2O_5 ratio of 1.25 instead of the intended 2.5. This test resulted thick coating of fine white powder inside view tube and in the reaction chamber. Again, the powder was shown to be SnO_2 by EDEX.

From the results shown in Fi. 5 it is obvious that and I_2O_5 ratio of 2 was marginal and that a higher I_2O_5 ratio would be desirable. If the reaction temperature is too high, the reaction will not go to completion (Le Chatelier's Principle) but apparently the resultant temperature is high enough that the Sn was vaporized and transported downstream where the carrier gas cools it and it reacts with the excess oxygen. Future tests scheduled to explore operation at high I_2O_5 ratios where the temperature will be such that the tin is completely oxidized.

4.3.9. Untoward Event

While preparing the materials for the next burn test, a detonation/deflagration event occurred while ejecting a completed pellet from the press. This led to a significant effort to determine the cause of the reaction and to verify that the program can continue without hazard to personnel or equipment.

Analysis of the detonation/ deflagration event indicated that the probable immediate cause of the accident was that corrosion of the die led to high ejection forces. The die was polished immediately before use, as steel corrodes rapidly in the presence of iodine compounds. Although the die had been polished, the removal of die material from the location of the pellet caused the diameter of the pellet to be larger than the hole through

which it was ejected. Material pressed into the pits could be sheared while ejecting the pellet from the die. The shearing leads to high temperature particularly if the die and plunger were stuck due to misalignment and hydraulic pressure accumulated. Then, when the plunger started to move, the movement would be rapid, triggering the event.

One third of the pellet was left unreacted in the die and about a sixth of it was found as unreacted shards under the press. After the incident, the die was pitted in the region where the pellet is located during pressing. It should be noted that the reaction stopped as soon as the pressure was reduced. We do not believe that detonation or rapid deflagration can occur under operating conditions of IOD. Such reactions are known to be very pressure dependent and the fact that the reaction did not propagate throughout the pellet indicates that the high reaction rates observed during the incident will not occur during iodine generation operation.

Never the less, the pellet pressing system was modified so that fragments would be contained if there were a detonation at any point during the pressing operation and that personnel do not handle the die between pellet pressing and pellet ejection from the die. The main modification to the process is to replace the die and plunger used to pelletize the mixed fuel/oxidizer powder at the first signs of corrosion, in order to prevent shearing effects inside the die due to pitting. The apparatus was altered to protect personnel from unsafe conditions by encasing the working parts of the pelletizing press with metal shields and pipe, as depicted in Figs. 35 through 38. Additionally, the die is automatically aligned with the plunger while pressing and ejecting the pellet and the die can be moved from the pressing position to the ejection position without manual intervention.

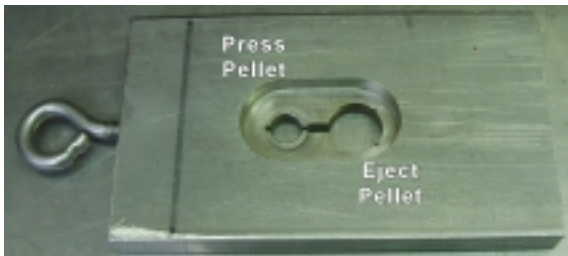


Fig. 35. Anvil slide for die.



Fig. 36. Apparatus oriented onto press.

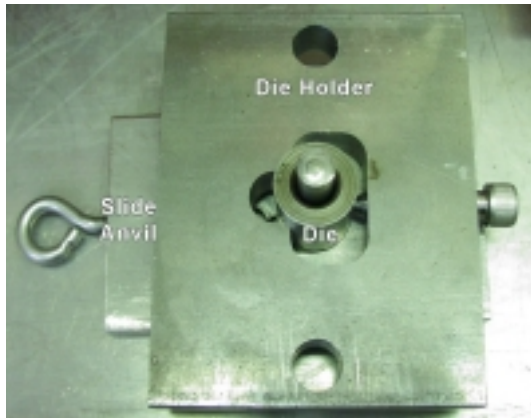


Fig. 37. Modified pelletizing apparatus.

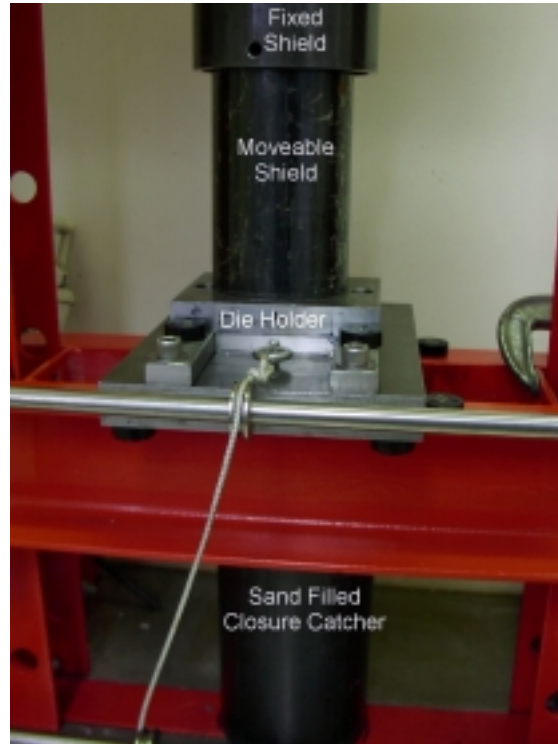


Fig. 38. Enclosed pelletizing apparatus on press.

Four additional pelletizing tests were performed to validate the new pellet pressing system. Each test utilized the Sn/I₂O₅ fuel/oxidizer system and each pellet was well formed.

A safety analysis was performed to assess the consequences of detonation during burn testing as well. The analysis assumed detonation of a stack of five Sn/I₂O₅ pellets inside the 1.5 in. diameter stainless steel pipe body of the test apparatus. The pellets were modeled in the analysis by substituting 5 grams of TNT for each of the Sn/I₂O₅ pellets. It is not expected that the burn test will initiate detonation, as the pellets are not confined. The burn rate of an explosive or propellant is proportional to the reaction pressure and when unconfined, propellants do not detonate. However, if it is assumed that 25 grams of TNT detonates within the apparatus, the shock impulse will cause the 1.5 in. SS pipe to fail. A protective shield, consisting of a system of telescoping 6 and 8 in. pipes, was designed to enclose the burn test apparatus. These shields, previously shown in Fig. 17, were analyzed to assess their integrity when exposed to the assumed detonation and found capable of containing the shock impulse.

4.3.10. Flow Tests 8 and 9

The final two burn tests were completed after installation of the new safety shielding. The tests were designed to examine the effects of increasing the ratio of oxidizer to fuel in a Sn/I₂O₅ system. Test 8 used three pellets with an I₂O₅ ratio of 3 and test 9 used four pellets with an I₂O₅ ratio of 4. In each test, iodine was viewed flowing through the viewtube at ignition. After the tests were complete, the reaction chamber was examined

to assure complete reaction of the pellets. The 3 times stoichiometric burn test showed complete reaction of the pellets, with a white, sandy residue (SiO_2). The 4 times stoichiometric test had similar residue, however the lower reaction temperature resulted in some iodine plate-out in the reaction chamber. In neither test was SnO_2 observed anywhere outside the mullite tube that held the pellets.

5. CONCLUSIONS

All systems chosen for study passed the safety tests, with the exception of systems containing aluminum powder. The use of aluminum powder was questioned as a “bang” was heard when driving a stuck pin out of the die. Subsequently, it seems that totally ruling out the use of aluminum may be excessive. The safety tests, particularly the pressure test, the thermal ignition tests and the long term pellet aging test were very useful in predicting which fuel/oxidizer systems would be appropriate for use in an iodine pyrotechnic.

The scale-up testing confirmed that metal powder fuels, combined with I_2O_5 , can produce the desired molecular iodine flow without visible solids contamination, as long as the I_2O_5 ratio is sufficiently above 2. The minimum I_2O_5 ratio which prevents downstream transport of tin and the maximum I_2O_5 ratio to prevent condensation of iodine in the combustion chamber are yet to be determined but they will ultimately depend on the pellet diameter and other geometric considerations. The need or benefit of additives to consolidate the SnO_2 product was not demonstrated. Recycle of the SnO_2 will be easier if additives are not required but the necessity of producing a solid-free off-gas will supersede any desire for easy recycle. The testing program was terminated before scale-up tests were made using zinc as the fuel and it remains a candidate. We are confident that a combination of additives and filtration can produce a fieldable iodine pyrotechnic based on tin and I_2O_5 .

C_2I_4/I_2O_5 also resulted in the acceptable production of iodine vapor. The range of acceptable I_2O_5 ratios is somewhat limited due to the potential for formation of carbon monoxide if the I_2O_5 ratio is less than 1 and the plate-out of iodine if the ratio is much greater than 1. The operational window will be larger for larger cartridge diameters where the relative heat loss is less and there is less propensity for iodine plate-out. Also, the complete IOD concept includes preheating the flow path and purging any iodine remaining in the cartridge. Addition of carbon powder to the system remains an option if higher reaction temperatures are required.

We recommended that work on both systems be continued in Phase 2 with the goal of demonstrating laser operation using iodine from a pyrotechnic source.

APPENDIX A

TABLE A-1
SUMMARY OF FUEL/OXIDIZER SYSTEM EXAMINED WITH HSC

Reaction	Notes ^(a)	ΔH (kJ/mole I ₂)	ΔG (kJ/mole I ₂)	T _a (°C)
10/3 Al + I ₂ O ₅ = I ₂ (g) + 5/3 Al ₂ O ₃		-2572	-2610	8770
10/3 Al + I ₂ O ₅ + 5/3 SiO ₂ = I ₂ (g) + 5/3 Al ₂ SiO ₅	(b)	-2740	-2787	5920
10/3 AlI ₃ + I ₂ O ₅ = 5/3 Al ₂ O ₃ + I ₂ (g)		-208	-253	2340
5/2 C + I ₂ O ₅ = I ₂ (g) + 5/2 CO ₂ (g)		-763	-962	4080
5/2 Cl ₄ + I ₂ O ₅ = 6 I ₂ (g) + 5/2 CO ₂ (g)	(c)	-92.6	-162	1500
5/2 C ₂ I ₄ + 2 I ₂ O ₅ = 7 I ₂ (g) + 5 CO ₂ (g)	(d)	-199	-272	2380
5Ca + I ₂ O ₅ = 5 CaO + I ₂ (g)		-2955	-2933	7560
5 CaI ₂ + I ₂ O ₅ = 5 CaO + 6 I ₂ (g)		+6.90	-38.5	-75
5 CaI ₂ + 5 MgI ₂ + 2 I ₂ O ₅ + 5 SiO ₂ = 5 CaMgSiO ₄ + 12 I ₂ (g)	(b)	-92.7	-139	920
5 CaI ₂ + 5 MgI ₂ + 2 I ₂ O ₅ + 10 SiO ₂ = 5 CaMgSi ₂ O ₆ + 12 I ₂ (g)	(b)	-112	-157	840
Ca(IO ₃) ₂ + 5 CaI ₂ + 6 SiO ₂ = 6 CaSiO ₃ + 6 I ₂ (g)	(b)	-42.9	-125	334
Ca(IO ₃) ₂ + 5 CaI ₂ = 6 CaO + 6 I ₂ (g)		+46.1	-35.5	-273
Ca(IO ₃) ₂ + 5 MgI ₂ = CaO + 5 MgO + 6 I ₂ (g)		-67.3	150	804
5 Cu + I ₂ O ₅ = I ₂ (g) + 5 CuO		-560	-617	1780
10 Cu + I ₂ O ₅ = I ₂ (g) + 5 Cu ₂ O		-633	-715	1240
5 CuI + I ₂ O ₅ = 7/2 I ₂ (g) + CuO		-18.5	-63.5	210
5 CuI ₂ + I ₂ O ₅ = 6 I ₂ (g) + 5 CuO		-35.4	-77.4	480
10 CuI ₂ + I ₂ O ₅ = 11 I ₂ (g) + 5 Cu ₂ O		+5.70	-37.2	-66
5 Fe + I ₂ O ₅ + 5 SiO ₂ = I ₂ (g) + 5 FeSiO ₃	(b)	-1297	-1281	1740
15/4 Fe + I ₂ O ₅ = I ₂ (g) + 5/4 Fe ₃ O ₄		-1177	-1245	3340
5 FeI ₂ + I ₂ O ₅ = 5 FeO + 6 I ₂ (g)		-46.8	-91.5	590
15/4 FeI ₂ + I ₂ O ₅ = 5/4 Fe ₃ O ₄ + 19/4 I ₂ (g)		-116	-159	1280
I ₂ O ₅ + 5 CaI ₂ + 5 SiO ₂ = 5 CaSiO ₃ + 6 I ₂ (g)	(b)	-67.3	113	550
I ₂ O ₅ + 5 MgI ₂ + 5 SiO ₂ = 5 MgSiO ₃ + 6 I ₂ (g)	(b)	-137	183	1030
11 I ₂ O ₅ + 5 C ₄ H ₆ = 20 CO ₂ (g) + 15 H ₂ O(g) + 11 I ₂ (g)	(e)	-864	-1073	4020
4 I ₂ O ₅ + C ₈ H ₈ = 8 CO ₂ (g) + 4 H ₂ O(g) + 4 I ₂ (g)	(f)	-834	-1044	4020
5 Mg + I ₂ O ₅ = 5 MgO + I ₂ (g)		-2785	-2820	6970
5 MgI ₂ + I ₂ O ₅ = 5 MgO + 6 I ₂ (g)		-106	-153	1360
5 MgI ₂ + 2 NaIO ₃ + 6 SiO ₂ = 6 I ₂ (g) + Na ₂ SiO ₃ + 5 MgSiO ₃	(d)	-111	-153	730
5 MgI ₂ + 2 NaIO ₃ = 6 I ₂ (g) + Na ₂ O + 5 MgO		-41.9	-84.4	500
Mg(IO ₃) ₂ + 5 CaI ₂ + 6 SiO ₂ = CaMgSi ₂ O ₆ + 4 CaSiO ₃ + 6 I ₂ (g)	(b,g)	-53.1	-133	400
Mg(IO ₃) ₂ + 5 CaI ₂ = MgO + 5 CaO + 6 I ₂ (g)	(g)	+30.9	-48.5	-270
Mg(IO ₃) ₂ + 5 MgI ₂ + 6 SiO ₂ = 6 MgSiO ₃ + 6 I ₂ (g)	(b)	-119	-199	810
Mg(IO ₃) ₂ + 5 MgI ₂ = 6 MgO + 6 I ₂ (g)	(g)	-82.4	-166	980
5/2 Sn + Ca(IO ₃) ₂ = I ₂ (g) + 5/2 SnO ₂ + CaO		-988	-1247	2930
5 Sn + I ₂ O ₅ = I ₂ (g) + 5 SnO †		-1183	-1235	3070
5/2 Sn + I ₂ O ₅ = I ₂ (g) + 5/2 SnO ₂ †		-1224	-1265	4500
5/2 Sn + Mg(IO ₃) ₂ = I ₂ (g) + 5/2 SnO ₂ + MgO		-1079	-1325	3060
5/2 Sn + 2 NaIO ₃ = I ₂ (g) + 5/2 SnO ₂ + Na ₂ O		-836	-853	2110
5 Zn + I ₂ O ₅ = I ₂ (g) + 5 ZnO		-1532	-1578	3880

^(a)All thermodynamic data from HSC Chemistry 4.1 except as noted. All material in solid phase except as noted.

^(b)Adding SiO₂ tends to decrease (make more negative) the ΔH and ΔG of the reaction but the added mass results in a decrease in the adiabatic reaction temperature.

^(c)Thermodynamic properties of Cl₄ estimated: $\Delta H_f = +41.84$ kJ/mole, $\Delta G_f = -28.39$ kJ/mole.

^(d)Thermodynamic properties of C₂I₄ estimated: $\Delta H_f = +41.84$ kJ/mole, $\Delta G_f = -42.86$ kJ/mole.

^(e)Polybutadiene approximated by butadiene(l).

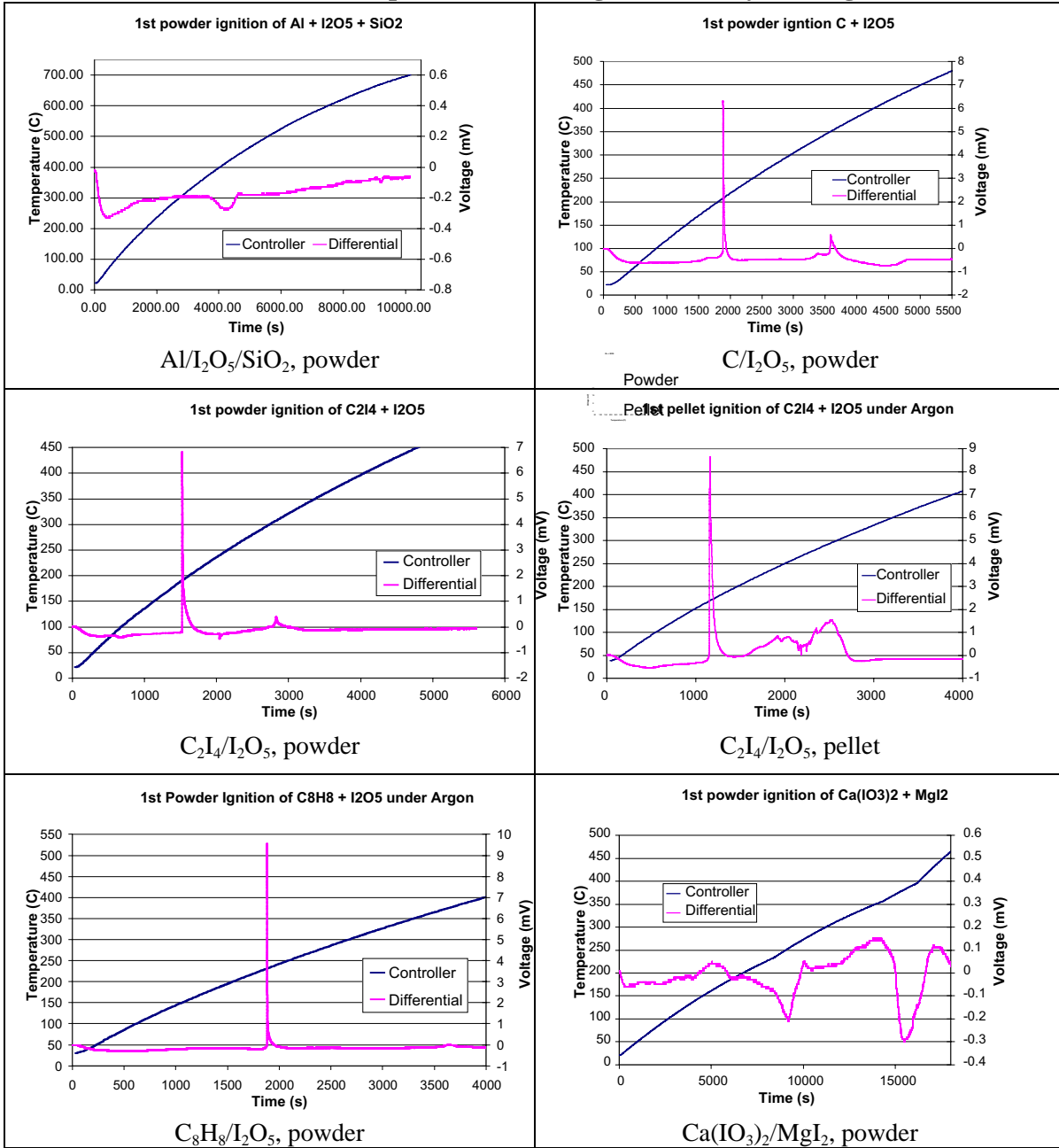
^(f)Polystyrene approximated by styrene(l).

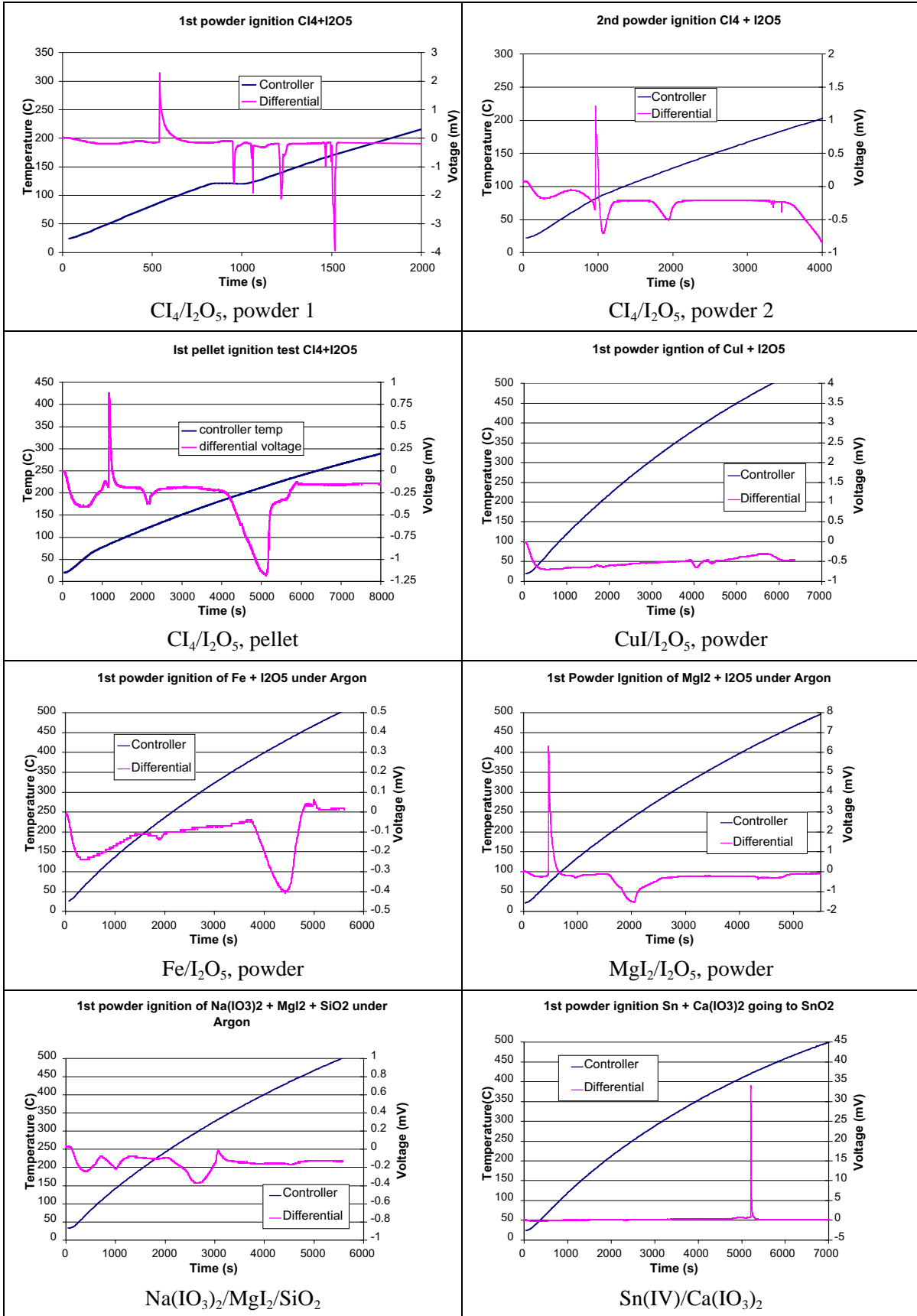
^(g)Thermodynamic properties of Mg(IO₃)₂ estimated: $\Delta H_f = -903.744$ kJ/mole, $\Delta G_f = -741.574$ kJ/mole.

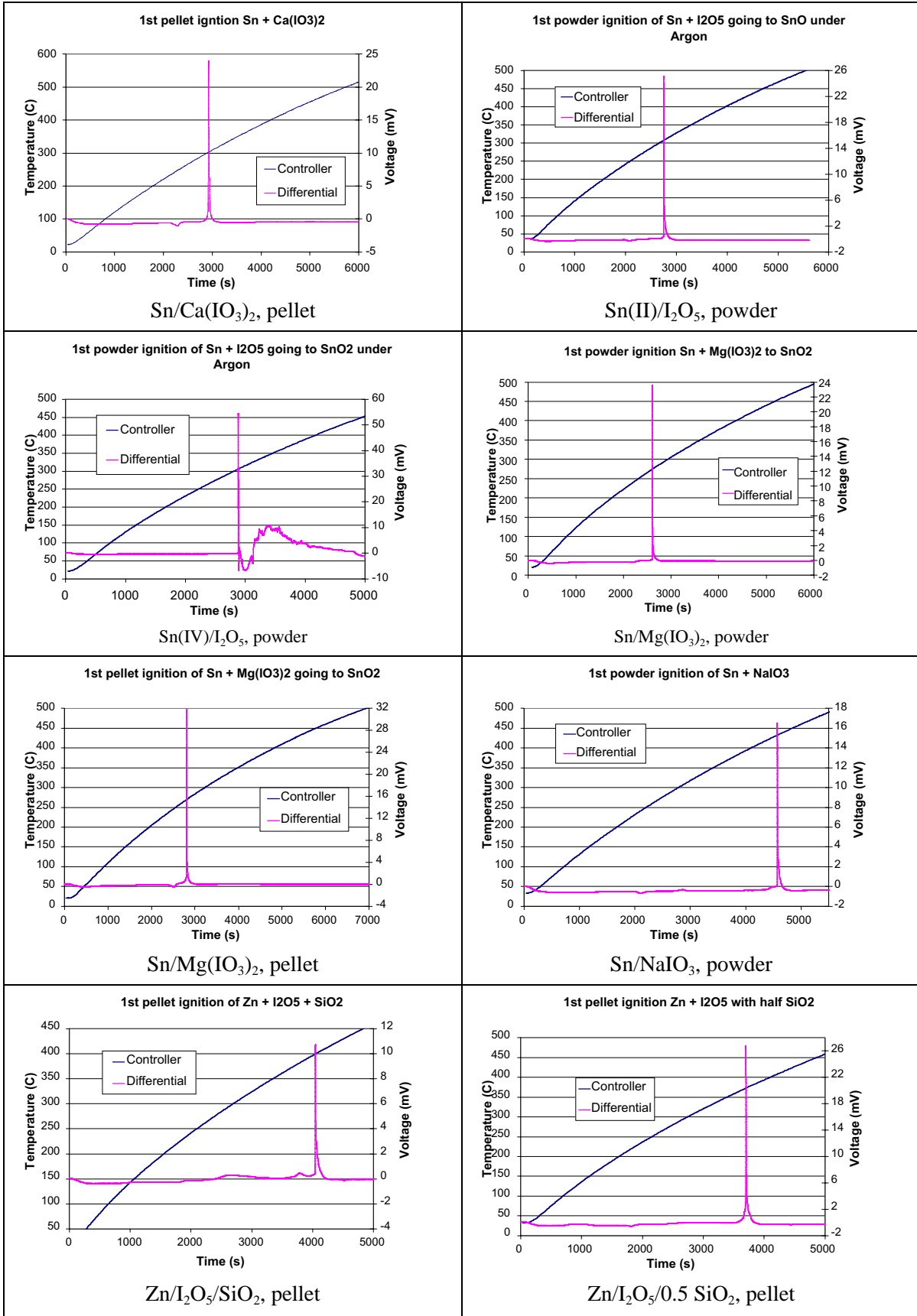
TABLE A-2
LIST OF ALL COMPOUNDS UTILIZED IN PHASE 1 IOD TESTING

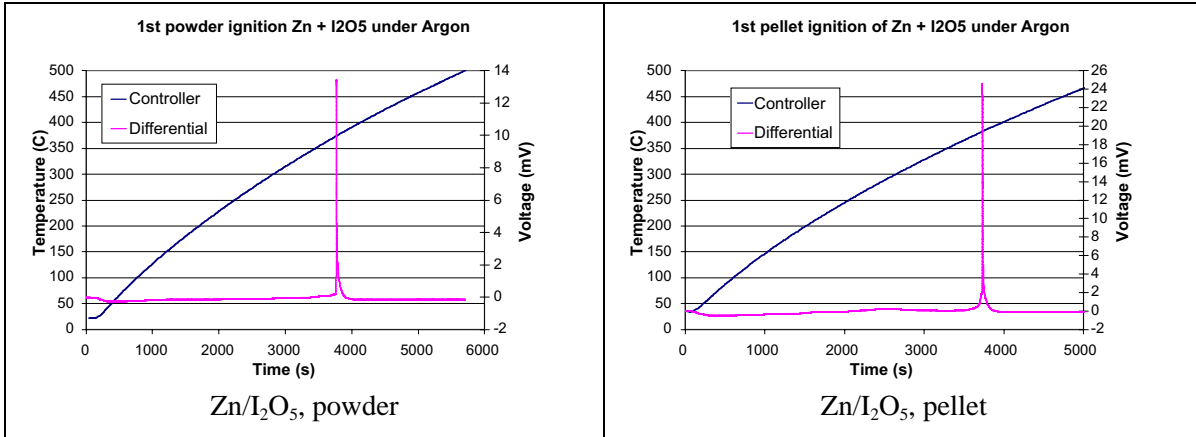
Name	Formula	CAS	Particle Size	Purity	Vendor	Item #
Al powder	Al	7429-90-5	200 mesh	99%	Sigma-Aldrich	214752
Cab-o-sil colloidal silica	SiO ₂	7631-86-9	325 mesh	>99.8%	Cabot	M-5
Calcium iodide	CaI ₂	10102-68-8	-10 mesh	99.95%	Sigma-Aldrich	516244
Calcium iodate	Ca(IO ₃) ₂	7789-80-2	NA	98%	Sigma-Aldrich	341606
Carbon powder	C	82600-58-6	Fine	+99.9%	Alfa Aesar	39724
Tetraiodomethane	CI ₄	507-25-5	NA	97%	Sigma-Aldrich	269220
Tetraiodoethylene	C ₂ I ₄	513-92-8	NA	97%	Sigma-Aldrich	318248
Polystyrene	(C ₈ H ₈) _x	9003-53-6	NA	NA	Sigma-Aldrich	182427
Cuprous iodide	CuI	7681-65-4	NA	>99.5%	Sigma-Aldrich	03140
Iron powder	Fe	7439-89-6	Fine	>99%	Sigma-Aldrich	12310
Fiberfrax ceramic paper		NA	NA	NA	Unifrax	882-JH
Iodine	I ₂	7553-56-2	NA	99.8%	Alfa Aesar	41955
Iodine pentoxide	I ₂ O ₅	12029-98-0	NA	+98%	Sigma-Aldrich	278890
Iodic acid	HIO ₃	7782-68-5	NA	> 99.0%	Sigma-Aldrich	58062
Magnesium iodide	MgI ₂	10377-58-9	NA	98%	Sigma-Aldrich	394599
Magnesium iodate	Mg(IO ₃) ₂ 4H ₂ O	7790-32-1	NA	99.0%	Sigma-Aldrich	MO137
Sodium iodate	NaIO ₃	7681-55-2	NA	99%	Sigma-Aldrich	S4007
Sodium hydroxide, 50% solution	NaOH	1310-73-2	NA	NA	Fisher	SS410-4
Polybutadiene	(C ₄ H ₆) _x	9003-17-2	NA	NA	Sigma-Aldrich	434779
Tin powder	Sn	7440-31-5	325 mesh	99.8%	Alfa Aesar	10379
Zinc powder	Zn	7440-66-6	6-9 micron	97.5%	Alfa Aesar	10835
Zinc wire	Zn	7440-66-6	0.25 diam	99.99%	Sigma-Aldrich	267910

Raw Data Graphs of Thermal Ignition Safety Testing









**TABLE A-3
SUMMARY OF SCALE-UP TESTS**

Test Number	Chemical System	Pellet Diameter (in.)	Stack Height	Pellet No.	I ₂ O ₅ Ratio	Max T (°C)	Mass Fuel (g)	Mass I ₂ O ₅ (g)
1	Sn/I ₂ O ₅	3/8	4	1	2	nr	0.48	1.09
				2	2		0.48	1.09
				3	2		0.48	1.09
				4	2		0.48	1.09
2	Sn/ I ₂ O ₅	3/8	6	1	1	nr	nr	nr
				2	2		nr	nr
				3	2		nr	nr
				4	2		nr	nr
				5	2		nr	nr
				6	2		nr	nr
3	C ₂ I ₄ /I ₂ O ₅	3/8"	3	1	1	nr	nr	nr
				2	2		nr	nr
				3	2		nr	nr
4	C ₂ I ₄ /I ₂ O ₅	3/8	3	1	1	110	nr	nr
				2	1		nr	nr
				3	1		nr	nr
5	C ₂ I ₄ /I ₂ O ₅	1/2"	3	1	1	115	2.62	1.35
				2	1		2.62	1.35
				3	1		2.62	1.35
6	C ₂ I ₄ /I ₂ O ₅	1/2	3	1	1	120	2.62	1.35
				2	1		2.62	1.35
				3	1		2.62	1.35
7	Sn/I ₂ O ₅	1/2	4	1	1.25	115	0.86	1.21
				2	1.25		1.72	2.42
				3	1.25		1.72	2.42
				4	1.25		1.72	2.42
8	Sn/I ₂ O ₅	1/2	3	1	3	nr	1.5	5.06
				2	3		1.5	5.06
				3	3		1.5	5.06
9	Sn/I ₂ O ₅	1/2	4	1	4	102	0.75	3.37
				2	4		0.75	3.37
				3	4		0.75	3.37
				4	4		0.75	3.37

nr = not recorded,

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