BLACKLIGHT POWER

Rowan University

Anomalous Heat Gains from Regenerative Chemical Mixtures:
Characterization of BLP Chemistries Used for Energy Generation and Regeneration Reactions

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Executive Summary

BlackLight Power (BLP) of Cranbury, NJ is pursuing the development and characterization of chemical reactions that generate significant quantities of heat beyond the amounts anticipated from conventional chemical reactions. These reactions could have significant commercial power applications should the results be shown to be valid and are commercially scalable. The source of this excess heat is claimed to derive from relaxation of the hydrogen atom to stable energy states below the ground state. The BLP chemistries are designed to create favorable conditions that allow transitions to these new hydrogen states.

This report describes the results of work recently conducted at Rowan University (RU) to independently test and validate these claims.

Reactants and Products

The reaction mixtures consist of a metal halide salt ($SrBr_2$, $BaCl_2$ or LiCl), a hydrogen source, (NaH or KH), a reducing agent (Mg), and a support matrix material (TiC or WC). All reactants are in crystalline form. The quantities of reactants used in each mixture are fully described to encourage other laboratories to reproduce the results disclosed. Reactants and products were analyzed using a combination of XRD, ICP-MS, TPD, and XRF in order to evaluate purity and composition.

Calorimetry

The heat produced in the chemical reactions was measured using continuous water flow calorimetry. This method uses a cylindrical chamber with a tube heat exchanger wrapped externally along the major axis. Water is flowed at a measured rate through the heat exchanger; inlet and outlet temperatures are measured. The entire chamber is placed in a thermally insulated enclosure. A small cylindrical reaction test cell is placed within an electrical resistance heater; the heater-test cell assembly is placed coaxially within the heat exchanger. A Type-K TC is placed inside a thermowell in the reaction test cell to measure test cell temperature. Additional measurements of ambient temperature and chamber pressure complete the calorimeter measurement suite. Four 5X scale (0.05 moles of the metal halide reactant) and nine 8X scale (0.08 moles of metal halide reactant) heat runs were performed using the chemical reactants detailed in Table 6.

Results

The results obtained for the tests of the chemical mixtures are detailed in Table 6. The heat gains obtained for the various chemistries assayed range from 1.28-6.55 when the nominal thermal loss of the calorimeter (2%) is accounted for. Analysis of the reaction products supports the claims that the reactants

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are not capable of generating the quantities of heat observed in the absence of some additional heat source. Additional chemical assay using liquid ^{1}H NMR indicated the presence of a signature which could be due to the novel form of hydrogen claimed by BLP.

Introduction

The primary objectives for this work included: (i) analysis of chemicals used by BLP for their energy generation process to characterize reactants and products; (ii) thermal characterization of the reaction heats; and (iii) preliminary investigation into regeneration reactions for these chemicals.

General Relationships

The reaction mixtures used for this study consist of crystalline forms of a halide salt ($SrBr_2$, $BaCl_2$ or LiCl), a hydrogen source, (NaH or KH), a reducing agent (Mg), and a support matrix material (TiC or WC). The energy producing reactions are initiated by heating the mixtures in a closed reaction cell; the total energy for the process is measured using a water-flow calorimeter. Enthalpy of reaction, $\Delta_r H^0$, is computed as the difference between the sum of the enthalpies of formation at standard conditions, $\Delta_f H^0$, for the N products, P_i, and the enthalpies of formation for the M reactants, R_j, as shown in Eqn. 1.

$$\Delta_r H^0 = \sum_{i=1}^{N} v_i \Delta_f H^0_{P_i} - \sum_{j=1}^{M} v_j \Delta_f H^0_{R_j} \tag{1-a}$$

where v is the stoichiometric coefficient of chemicals in the reaction. Table 1 summarizes enthalpies of formation at standard conditions, $\Delta_f H^0$ for many of the reactants and products for the chemistries investigated.

The theoretical predicted energy output, ΔE_T, in kilojoules, are expressed in kJ/mol, which requires that the number of moles of the limiting reactant be used to scale the predicted energy.

$$\Delta E_T = -\Delta_r H^0 \tag{1-b}$$

The reaction mixtures used for this study consist of crystalline forms of a halide salt ($SrBr_2$, $BaCl_2$ or LiCl), a hydrogen source, (NaH or KH), a reducing agent (Mg), and a support matrix material (TiC or WC). The energy producing reactions are initiated by heating the mixtures in a closed reaction cell; the total energy for the process is measured using a water-flow calorimeter.

The sign of ΔE_T indicates whether the process is net exothermic (ΔE_T is positive) or net endothermic (ΔE_T is negative).

The net energy balance for a reaction cell with the chemistry that is being evaluated is defined by Eqn. 2,

$$\Delta E_{Total} = E_{Out} - E_{In}, \tag{2}$$

where E_{In} is the energy input to the reaction cell in the form of electrical resistance heating of the cell to initiate the reaction, and E_{Out} is the total output heat energy resulting from the reaction plus the original input energy.

Table 1. Enthalpies of formation for specific reactants.

Note: All $\Delta_f H$ obtained from [2] unless otherwise noted

Component	$\Delta_f H$, 25C, 1 atm (kJ/mol)
KI	-372.9
MgH_2	-75.3
$MgCl_2$	-641.3
$MgBr_2$	524.3
Mg_2Sr	-21.0[12]
Mg_2Ba	-6.3[4]
KBr	-393.8
SrH_2	-179.91[3]
$SrBr_2$	-717.6
$BaCl_2$	-855.0
LiCl	-408.6
K_2MgH_4	-236[6]
$KMgH_3$	-167[7]
NaCl	-411.20
KH	-57.7
KCl	-436.5
NaH	-56.3
BaH_2	-178.66[3]
LiH	-90.5[1]
$NaMgH_3$	-144[5]

The expected output heat energy should be nominally equal to the input energy, E_{In}, plus the amount of energy produced by the net reaction, ΔE_T. However, if this energy balance is not met, any additional source or sink of energy can be represented as E_X, as shown in Eqn. (3)

$$E_{Out} = E_{In} + \Delta E_T + E_X \tag{3}$$

It is the term, E_X, that is the primary focus of BLP's work and the motivation for this study.

A water-flow calorimeter is used to measure the heat produced by the system. The difference in temperature for water entering the water jacket, T_{In}, and the temperature of the water leaving the heat exchanger, T_{Out}, are the primary inputs used to determine an estimate, $\hat{E}_{Out}$, of the total energy of the system as shown in Eqn. (4).

$$\hat{E}_{Out} = \int_{Ti}^{Tf} \dot{m} c_p (T_{Out} - T_{In}) dt \tag{4}$$

The total energy estimate, $\hat{E}_{Out}$, is found by integrating the product of mass flow rate, $\dot{m}$, of the cooling water by its specific heat, c_p, and the temperature difference between outlet and inlet of the heat exchanger. The integration period begins at T_i, defined by departure from the quiescent starting point temperature, and ends at T_f, when the outlet temperature returns to the original quiescent temperature. In operation, the mass flow rate is set to a fixed value for the duration of the experiment, and since c_p is also a constant, (4) can be rewritten as

$$\hat{E}_{Out} = k \int_{Ti}^{Tf} (T_{Out} - T_{In}) dt \tag{5}$$

For a typical setting of 0.500 l/min flow rate and with c_p= 4.183 J/g·°C, k evaluates to

$$k = \left(4.183 \frac{J}{g \cdot °C} \right) \left(500 \frac{ml}{min} \right) \left(1 \frac{g}{ml} \right) = 2.0915 \frac{kJ}{°C \cdot min} \tag{6}$$

For an ideal calorimeter,

$$\hat{E}_{Out} = E_{Out} \tag{7}$$

However, a practical calorimeter will have some loss, E_L. If the calorimeter is operated above ambient, then the loss term, E_L, would be expected to result in an estimate, $\hat{E}_{Out}$, that is less than the true value, E_{Out}, due to heat loss to the environment. If the calorimeter is operated below ambient, then the loss term, E_L, will result in an estimate, $\hat{E}_{Out}$, that is greater than the true value, E_{Out}, due to heat gain from the environment. Eqn. (8) shows the addition of the loss term to (7).

$$\hat{E}_{Out} = E_{Out} - E_L \tag{8}$$

Calorimeter calibration is performed to determine the magnitude of E_L. Ideally, a calibration run should yield a zero net energy difference—i.e., E_{Out} should be equal to E_{In}, which means that E_L=0.

For an exothermic reaction triggered by the heat input to the reaction cell, then (3) can be rewritten to now incorporate the loss term, E_L, and recognizing that the calorimeter measurement is an estimate per (8):

$$\Delta E_{Total} = (E_{In} + \Delta E_T + E_X + E_L) - E_{In} \tag{9}$$

Experiments that more closely meet the following constraints should provide the best performance:

$$E_L \to 0 \tag{10-a}$$

$$\Delta E_T + E_X \gg E_L \tag{10-b}$$

$$\Delta E_T + E_X > qE_{Input} \tag{10-c}$$

$$E_X > r\Delta E_T \tag{10-d}$$

Eqn. (10-a) states that the smaller the loss term, then the closer to ideal the calorimeter's behavior is; (10-b) states that if the magnitude of the energy production terms are much greater than the loss term then there is higher sensitivity to the reaction energies vs. the loss energy—i.e., it gives a better signal to noise ratio (SNR); (10-c) indicates that the sum of the energy production terms should be a significant amount more than the base input heat; and (10-d) states that the most convincing measurements of any possible added energy sources occur when they are significantly more than the expected theoretical energy production. Finally, a relative energy gain, E_{Gain}, for a reaction can be expressed as

$$E_{Gain} = \frac{\Delta E_T + E_X}{\Delta E_T} \tag{11-a}$$

Eqn (11-a) yields a unity gain thermal system if $E_x = 0$. Eqn. (11-a) is a conservative gain because it does not account for losses in the calorimeter. To account for the losses, (11-b) includes the maximum theoretical expected loss from the uncertainty model (-3%); (11-c) includes the average losses from the calorimeter operating in the energy regime for the heat runs: 300 kJ, which yielded an average loss of -2%.

$$E_{Max} = \frac{\Delta E_T + E_X + E_{LMax}}{\Delta E_T} \tag{11-b}$$

$$E_{Ave} = \frac{\Delta E_T + E_X + E_{LAve}}{\Delta E_T} \tag{11-c}$$

Earlier Work

In previous work, the Department of Chemistry and Biochemistry synthesized compounds using procedures provided by BLP in a search for potential sources of the anomalous heat being generated by those reactions. The RU Chemistry Department was able to confirm the presence of unusual hydrogen in the reaction products using both liquid ^{1}H NMR and MAS ^{1}H NMR studies. Alkaline halides were heated in the presence of hydrogen and a catalyst. According to BLP, the alkali metal halide is capable of trapping the 'lower energy' or 'hydrino' hydrogen as a high binding energy hydride ion called the 'hydrino hydride' ion and as the corresponding molecular hydrino. In the generation-2 chemistry previously reported, KH, Mg

and a support material (TiC or activated carbon), and a halide salt were mixed, loaded in a cell and heated to initiate a chemical reaction. The energy generated was in excess of what was predicted based on the known chemical reactions. The post reaction products in the reaction mixture were analyzed using XRD, liquid ^{1}H NMR, and MAS ^{1}H NMR. Liquid ^{1}H NMR indicated the presence of an unusual state of hydrogen to which the excess energy generated is attributed.

Project Objectives

The objectives for this work included:

1. Analytical study of reactants. The BLP chemicals used for energy generation were analyzed using XRD, TPD, ICP-MS and XRF to determine their purity level.

2. Regeneration. Regeneration reactions were briefly examined. We used BLP protocols to carry out a typical regeneration reaction to demonstrate that reaction products can be processed to obtain starting reactants.

3. Thermal characterization of reactions. Chemical mixtures consisted of (i) a hydrogen source (NaH or KH), (ii) a high surface area support material (TiC or WC), (iii) magnesium, a reducing agent, and (iv) a metal halide salt ($BaCl_2$, $SrBr_2$, or LiCl). Following BLP protocols, the chemical mixtures were placed in a reaction cell and the reaction triggered by application of local heating to the vessel. Continuous water flow calorimetry was used to measure the amount of energy generated during a given run. The calorimeter measured the heat balance to determine the difference between heat output and heat input. The difference quantifies the amount of energy produced by the reaction.

Chemicals and Procedures

Analytical Study of Reagents

Titanium carbide, TiC, tungsten carbide (WC), magnesium metal (Mg), potassium hydride (KH), sodium hydride (NaH), strontium bromide ($SrBr_2$), barium chloride ($BaCl_2$), lithium chloride (LiCl), strontium metal (Sr), potassium bromide (KBr), barium metal (Ba) and potassium chloride (KCl) were obtained from BLP and analyzed using multiple techniques to confirm purity. Note that these chemicals were procured by BLP from standard chemical supply houses and provided to RU as factory-sealed containers whether drop-shipped from the supplier or shipped from BLP.

Analysis of Reagents

A combination of XRD, ICP-MS, TPD, and XRF were used to evaluate the purity of the reagents. The strength of XRD is that it can detect crystalline phase materials so long as they constitute at least 0.2-0.5%

by weight of the sample. ICP-MS can detect most of the metallic elements as low as 0.005 ppb providing they can be dissolved in water. XRF can be used to analyze other non-metallic elements such as halides and other elements with atomic numbers greater than 7. TPD can be used to confirm the presence of water or other volatile materials. In general, a combination of these techniques can provide accurate information about the nature and purity of the chemical species. Details of each of these analytic approaches and their results are summarized below.

The halide salts ($SrBr_2$, LiCl, and $BaCl_2$) were analyzed using i) temperature programmed desorption (TPD), ii) X-ray diffraction (XRD), iii) X-ray fluorescence (XRF), and iv) inductively coupled plasma mass spectrometry (ICP-MS). The XRD analyses indicated no impurity phases in the halide salts chemicals. The TPD studies indicated negligible amounts of water. In addition, the titanium carbide (TiC) used as support, showed insignificant amounts of water using TPD and had no impurity phases as observed from a detailed XRD investigation. ICP-MS and XRF techniques indicated greater than 98% purity of the starting chemicals. Mixtures of starting chemicals Mg, a hydride (sodium or potassium), a support material (TiC or WC), and a salt ($SrBr_2$, LiCl, or $BaCl_2$) were loaded in the cell in a dry box, then transferred to a calorimeter and heated to initiate the reaction. The reaction yielded more energy than expected from known chemical reactions. The heat generated during these reaction experiments was determined by carrying out detailed calorimetric studies in the Department of Engineering calorimetry laboratory at the SJTP. For different reaction mixtures approximately 1.28-6.55 times energy more than expected for conventional chemistry was observed. Liquid ^{1}H NMR study after extraction with DMF-d7 showed a weak peak at approximately 1.26 ppm confirming presence of an unusual state of hydrogen. In what follows, we present the results of some of the experimental studies that were carried out.

Temperature Programmed Desorption

Temperature programmed desorption (TPD) studies were used to rule out the presence of water in the starting materials. TPD was used to quantify the presence of water in TiC, WC, $BaCl_2$, LiCl, and $SrBr_2$. The analysis was done using a Chembet 3000 chemisorption system (Quantchrome Corp.) fitted with a thermal conductivity detector (TCD). Argon was used as a carrier gas and dry ice was used for the separation of water by condensation during the chemisorption experiments. Approximately 0.1 gram of sample was loaded into a TPD cell under argon. The cell was then placed in a furnace and connected to a gas line (including stainless steel tubing and reservoir).

The condensable water vapor or other gas(es), if any, from the thermal desorption was trapped and immobilized in the cold trap. After evacuating the non-condensable gas(es), the cold trap was allowed to thaw by removing the dry-ice jacket. The condensed gas evaporated as the temperature increased. Fig. 1

shows the TPD of a blank run (empty cell) and cell containing strontium bromide. The blank run (Fig. 1a) peak was not different from the $SrBr_2$ run (Fig. 1b). The small peak is found in both runs and therefore cannot be due to a hydrated $SrBr_2$ sample. TPD runs for TiC, $BaCl_2$, and LiCl are shown in App. A.1. Analytic results showed negligible amounts of water in these chemicals, too.
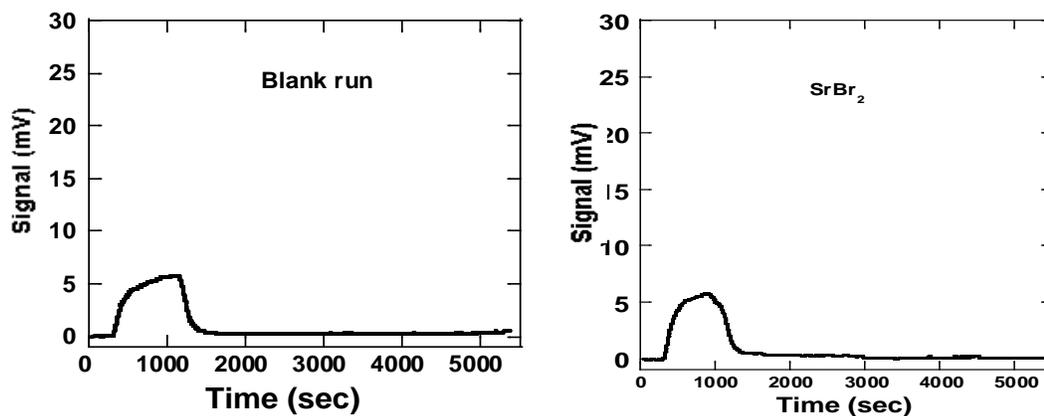

Figure 1. TPD of (a) blank cell (b) cell containing $SrBr_2$.

Elemental Analysis

Precise elemental analysis of salts was done using inductively coupled plasma mass spectrometry (ICP-MS) employing standard analytical procedures. 1000 ppm stock ICP-standards solutions were diluted to pre-determined levels using de-ionized water of ICP standard quality. The analysis was done using Chemstation Software in conjunction with an ICP-MS (Agilent 7500). The instrument was tuned using a special tuning solution containing 10 ppb of ^{7}Li, ^{89}Y, and ^{205}Ce. The ICP-MS detection limit for most of the ions was about 0.005 ppb. Elemental analysis results are summarized in Table 2.

Table 2. ICP-MS analysis results.

Analyte	Purity
Mg	98%
KH	97%
NaH	97%
LiCl	93%
	Trace amounts of K (0.1%) and other transition elements (0.3%)
KCl	97%
$BaCl_2$	99%
$SrBr_2$	95%
	Less than 0.1% transition elements
	Note: Negligible amounts detected of Be, Cr, Mn, Ni, Co, Zn, As, Ag, Cd, Sb, Ba, and Pb

More detailed studies indicated that other elements were also in negligible amounts. Some of the chemicals were analyzed using XRF (Bruker S4 Explorer, Rh radiation) in a commercial laboratory (H&M Analytical, Inc.). All elements between Na and U were investigated. Elements such as Li, B, C, O & F cannot be determined accurately using this technique because of their smaller atomic numbers. Table 3 summarizes the results of the commercial analyses.

Table 3. XRF analysis results.

Analyte	Purity
$SrBr_2$	99%
TiC	99.5%
LiCl	99.77%
$BaCl_2$	99.15%

X-ray Diffraction (XRD) of Starting Chemicals

Starting chemicals were characterized using XRD. Slow scans of starting chemicals, TiC, Mg, KH, NaH, $BaCl_2$ and $SrBr_2$ were analyzed. Diffraction patterns were recorded (Scintag X2 Advanced Diffraction System) at an operating voltage of 40 kV and current of 30 mA. Patterns were recorded in a step mode [0.02 Deg/min] in the 2θ range of 5-70 degrees using a residence time of 8 seconds. The diffraction patterns from the JCPDS-library were matched to the diffraction pattern obtained. Fig. 2 shows XRD patterns from Mg superimposed on the library pattern. No secondary phases were visible from this pattern. Fig. 3 shows the pattern from KH. Similarly, no evidence of any other crystalline impurity phases are seen with this technique. XRD patterns obtained for TiC, NaH and $BaCl_2$ are available in App. A.2. We also note here that the diffraction technique is sensitive only for phases with reasonable crystallinity, but limits to within 0.5 % can be obtained in the absence of amorphous phases observed by a continuum background increase. There was no observable background in these starting materials.
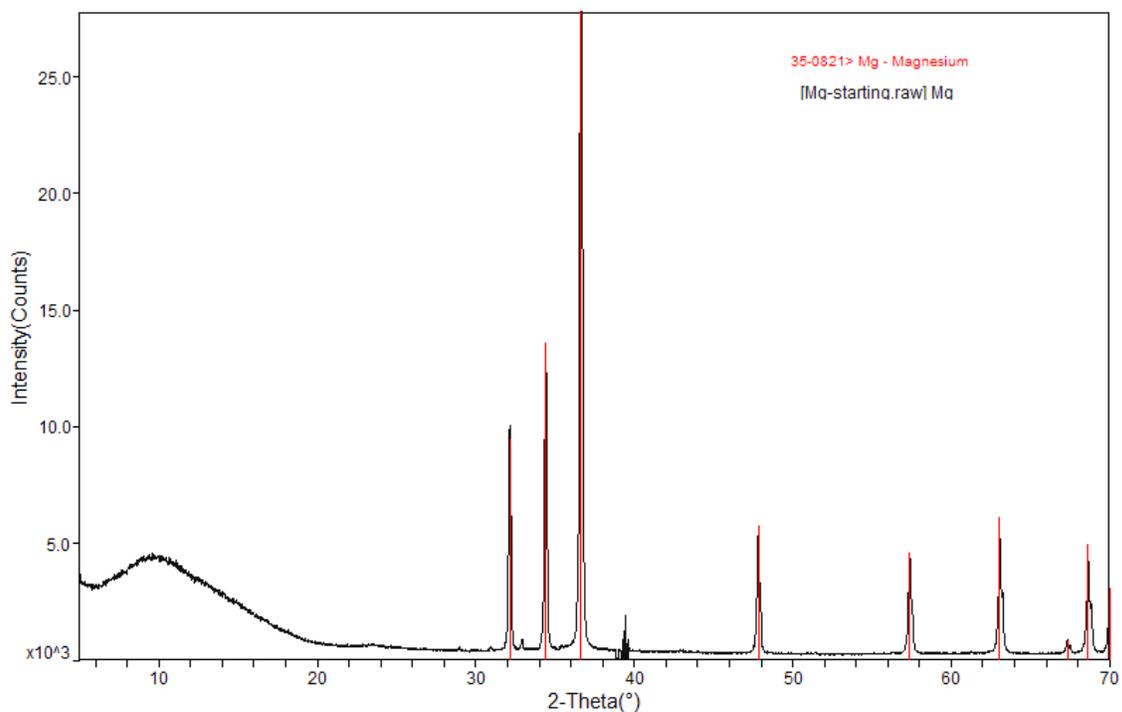
Figure 2. XRD patterns of Mg starting material.
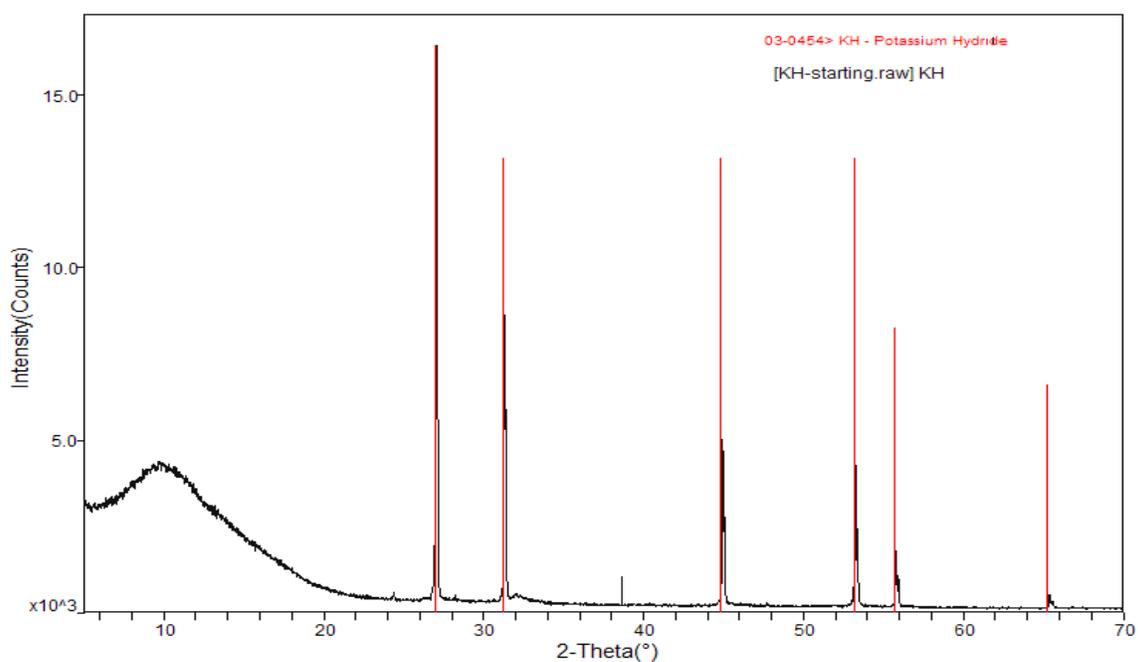

Figure 3. XRD patterns of KH from BLP.

Summary of Analytical Results

The combination of XRD, ICP-MS, TPD and XRF indicates that the chemicals are of sufficient purity to make the determinations required for the current analysis. XRD of the chemicals does not indicate presence of crystalline impurities. TPD of the halide salts and support materials (TiC) does not indicate

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presence of water. The elemental analysis of the chemicals using ICP-MS and XRF techniques indicates negligible amounts of other elements that would be impurities in the starting chemicals.

Energy from Reactions

The reaction mixtures used for energy generation involve a halide salt ($SrBr_2$, $BaCl_2$ or $LiCl$), a hydrogen source, (NaH or KH), a reducing agent (Mg), and a support matrix material (TiC or WC). The primary products according to XRD include potassium or sodium halide and lithium hydride in those cases involving $LiCl$ as a starting reactant. The starting chemicals, previously analyzed to confirm composition and purity, were loaded in a cell inside a glove box. Each cell contained a mixture of four chemicals in a crystalline state: (i) the halide salt ($BaCl_2$, $SrBr_2$, or $LiCl$), (ii) the hydrogen source (NaH or KH), (iii) Mg, and (iv) the support material (TiC or WC). The cells were sealed tightly and transported to SJTP for calorimetric measurements. The cells were returned to the RU Chemistry Department for analysis of the post reaction products. Table 4 summarizes the reactants tested and the theoretical energy expected from each combination for the dominant energy-producing reaction. Appendix F details the methodologies used to determine the maximum theoretical energy formation for the $SrBr_2$ chemistry.

Table 4. Summary of reactant test mixture compositions and expected reaction energies

Test Mixture Name	Chemical Composition, g, mol								Predicted energy, $\Delta_r H^0$ based on Halide Salt, kJ/mol	Predicted energy, ΔE_T for mole fraction tested, kJ
	Halide Salt			H Source		Reducing Agent	Support Matrix			
	$BaCl_2$ 208.2354 g/mol	LiCl 42.3937 g/mol	$SrBr_2$ 247.428 g/mol	KH 40.10627 g/mol	NaH 23.998 g/mol	Mg 24.305 g/mol	TiC 59.891 g/mol	WC 195.861 g/mol		
BKMT-1	10.4 g, 0.0499 mol			8.3 g, 0.2070 mol		5.0 g, 0.2057 mol	20.0 g, 0.3339 mol		-81.26	4.05
BKMT-2	16.6 g, 0.0797 mol			13.2 g, 0.3292 mol		8.0 g, 0.3292 mol	32.1 g, 0.5360 mol		-81.26	6.48
BKMW	16.6 g, 0.0797 mol			13.2 g, 0.3292 mol		8.0 g, 0.3292 mol		32.2 g, 0.1644 mol	-81.26	6.48
LKMT		3.4 g, 0.0802 mol		13.2 g, 0.3292 mol		8.0 g, 0.3292 mol	32.0 g, 0.5343 mol		-60.7	4.87
LKMW		3.4 g, 0.0802 mol		13.2 g, 0.3292 mol		8.0 g, 0.3292 mol		32.0 g, 0.1634 mol	-60.7	4.87
LNMT		3.4 g, 0.0802 mol			8.0 g 0.3334 mol	8.0 g, 0.3292 mol	32.0 g, 0.5343 mol		-36.8	2.95
LNMW		3.4 g, 0.0802 mol			8.0 g 0.3334 mol	8.0 g, 0.3292 mol		32.0 g, 0.1634 mol	-36.8	2.95
SKMT-1			12.4 g, 0.050 mol	8.3 g, 0.2070 mol		5.0 g, 0.2057 mol	20.0 g, 0.3339 mol		-134.5	6.73
SKMT-2			19.8 g, 0.0800 mol	13.2 g, 0.3292 mol		8.0 g, 0.3292 mol	32.0 g, 0.5343 mol		-134.5	10.76
SKMW			19.8 g, 0.0800 mol	13.2 g, 0.3292 mol		8.0 g, 0.3292 mol		32.0 g, 0.1634 mol	-134.5	10.76

Reactions involving BaCl$_2$ (16.6 g), KH (13.2 g), Mg (8.0 g), and TiC (32.1 g) or WC (32.0 g). BKMT-1, BKMT-2, and BKMW.

The most probable reaction for these combinations of reactants is:

$$BaCl_2(c) + 2KH(c) \xrightarrow{\text{Mg+(TiC or WC)+Heat}} 2KCl(c) + BaH_2(c) + \Delta H$$
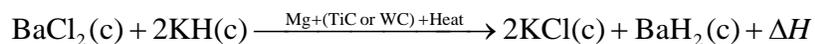
$$\Delta H = -81.26 \text{ kJ/mole BaCl}_2$$

XRD of the post reaction product from the reaction mixture above is shown in Fig. 4. Again the major peaks are those of TiC, Mg, and KCl. Quantitative XRD from H&M also indicates TiC and Mg as major products, KCl and KMgH$_3$ as minor products, and trace amounts of Ba, K$_2$MgCl$_4$, K$_2$MgH$_4$, and BaCl$_2$. BaCl$_2$ is not observed in the products using XRD.

The calorimetric data for RU052010A using 16.6 g (0.079 moles) of BaCl$_2$ generated 8.44 kJ of energy, which is a factor of 1.30 energy gain over the 6.48 kJ expected. Other calorimetric data for similar reactions, RU020910, and RU021510 using 10.37g (0.05 moles) of BaCl$_2$ gave 4.08 and 4.51 energy gains respectively.

The above reaction was repeated substituting 32 grams of WC with 32 grams of TiC (RU052010B). Using the new support material, 10.47 kJ (1.62 energy gain) was obtained with 0.08 moles of BaCl$_2$. The theoretical maximum expected according to the reaction above is 6.48 kJ.

Figure 4. XRD of post reaction products with reactants BaCl₂, KH, Mg, and TiC.

Reactions involving LiCl (3.4 g), KH (13.2 g), Mg (8.0 g), and TiC (32.0 g) or WC (32.0 g). LKMT and LKMW.

The reaction expected to be most exothermic is as follows:

$$\text{LiCl(c)} + \text{KH(c)} \xrightarrow{\text{Mg}+(\text{TiC or WC})+\text{Heat}} \text{KCl(c)} + \text{LiH(c)} + \Delta H$$
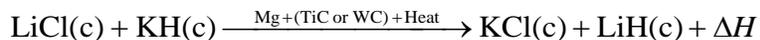
ΔH = -60.7 KJ mole LiCl

The calorimetric data for RU051710 using 3.4 g (0.08 moles) of LiCl generated 13.16 kJ of energy which is a 2.70 energy gain. Theoretically, this mixture would have been expected to generate 4.87 kJ of energy.

The above reaction was repeated substituting 32 grams of WC (RU051910). Using the new support material, 8.48 kJ (1.74 energy gain) was obtained with 0.08 moles of LiCl.

Reactions involving LiCl (3.4 g), NaH (8.0 g), Mg (8.0 g), and TiC (32.0 g) or WC (32.0 g). LNMT and LNMW.

The most exothermic reaction can be estimated as follows:

$$LiCl(c) + NaH(c) \xrightarrow{\text{Mg+(TiC or WC)+Heat}} NaCl(c) + LiH(c) + \Delta H$$

ΔH = -36.8 kJ mole LiCl
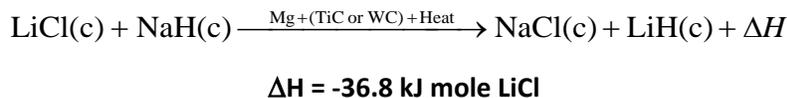
XRD of post reaction product of the reaction mixture above is given in Fig. 5. The major peaks are those of TiC and Mg. The XRD indicates presence of NaCl. Again LiCl is absent in the post reaction product. The calorimetric data for RU031010 and RU051310, using 3.4 g (0.08 moles) of LiCl generated 19.31 kJ, and 9.35 kJ of energy respectively. This translates into an energy gain of 6.55 for RU031010 and a gain of 3.17 for RU051310. Theoretically, this mixture would have been expected to generate 2.95 kJ of energy.

The above reaction was repeated substituting 32 grams of TiC with 32 grams of WC (RU051810). Using the new support material, 6.24 kJ (2.12 energy gain) was obtained with 0.08 moles of LiCl. The theoretical maximum expected according to the reaction above is 2.95 kJ.
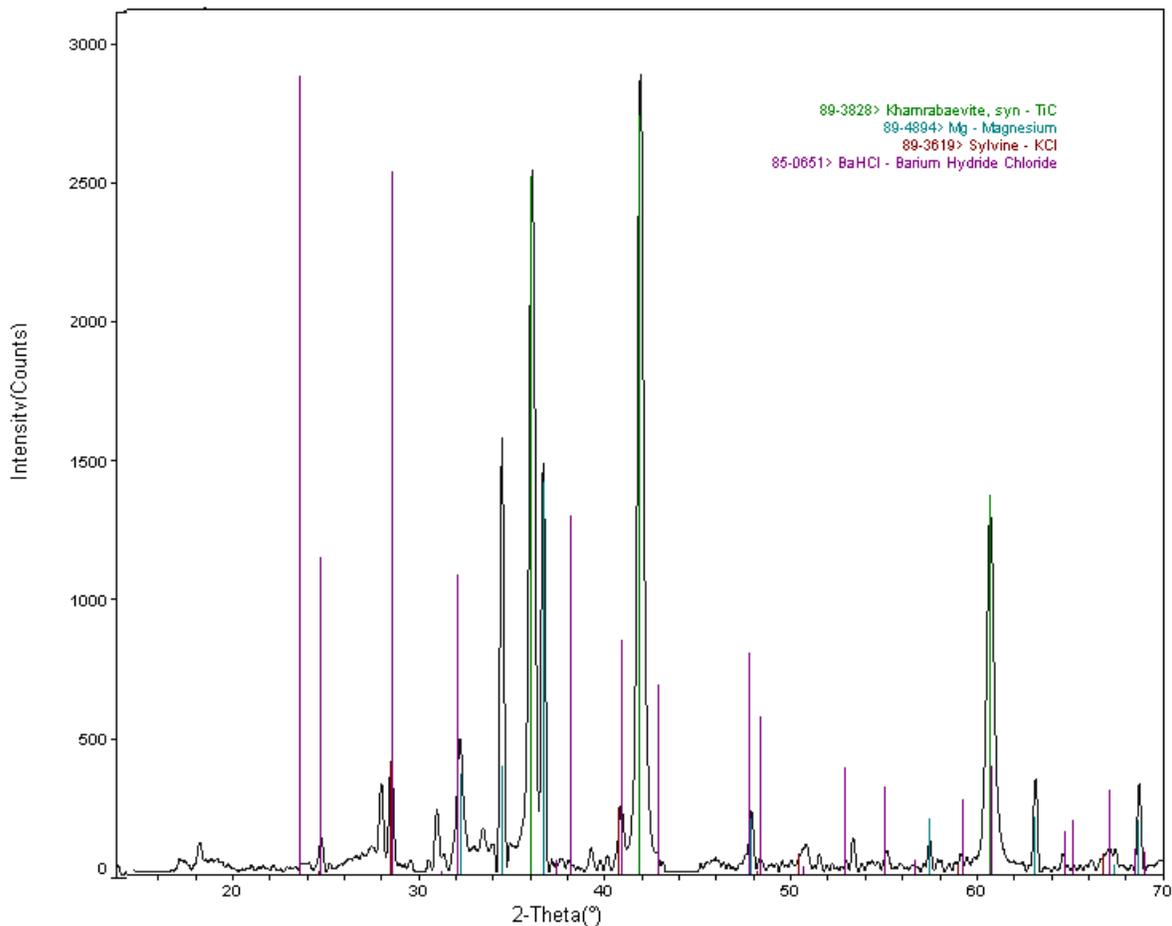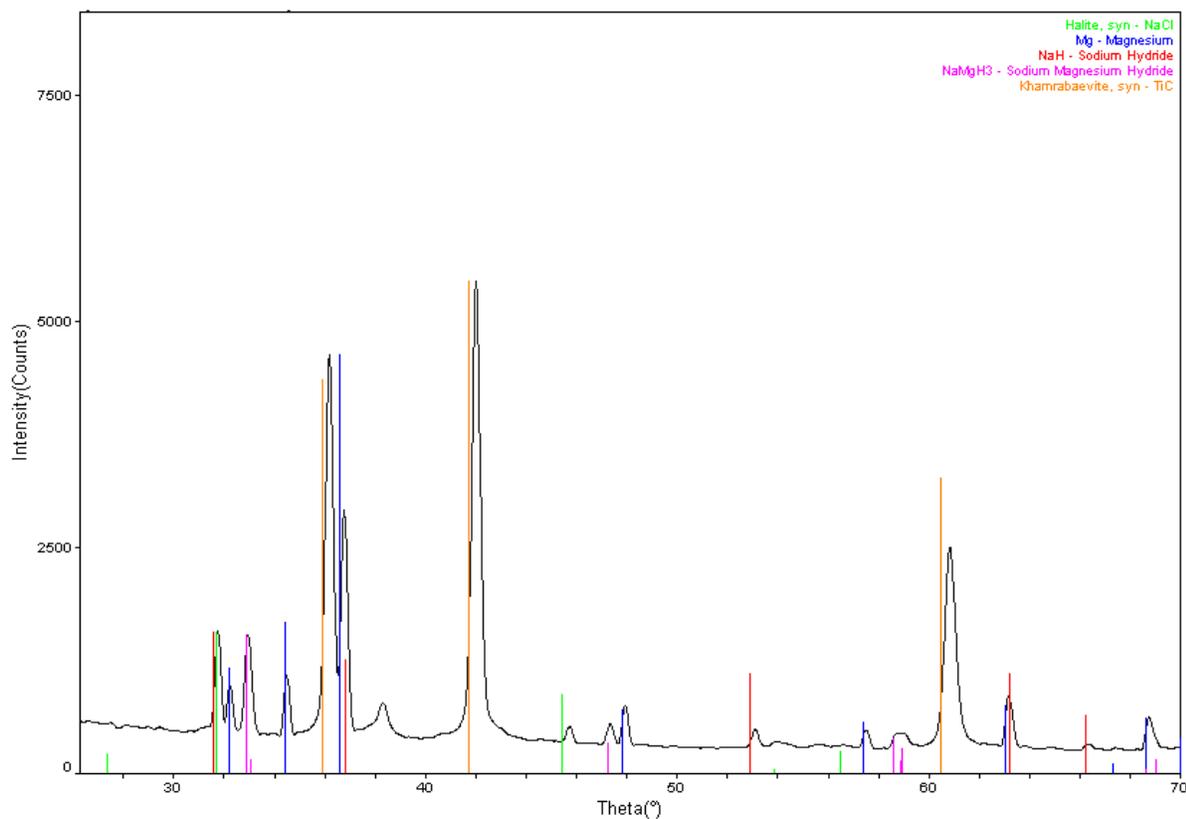

Figure 5. XRD of post reaction products with reactants LiCl, NaH, Mg, and TiC.

Reactions involving SrBr₂ (19.8 g), KH (13.2 g), Mg (8.0 g), and TiC (32.0 g) or WC (32.0 g). SKMT-1 and SKMT-2.

The expected reaction is:

$$SrBr_2(c) + 2KH(c) \xrightarrow{\text{Mg+TiC +Heat}} 2KBr(c) + SrH_2(c) + \Delta H$$
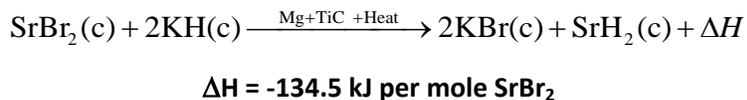
ΔH = -134.5 kJ per mole SrBr₂

Fig. 6 shows the XRD Diffraction patterns of one of several post-reaction samples. From the pattern, we can conclude that no $SrBr_2$ was present in the post reaction mixture. The most significant peaks are those of TiC, KBr and Mg. Quantitative XRD from H&M Analytical, Inc. indicated Mg (21.2 ± 0.4%), TiC (57.4 ± 0.8%), KBr (9.2 ± 0.2%), SrH_2 (3.5 ± 0.2%), K_2MgH_4 (2.4 ± 0.3%) and $KMgH_3$ (6.3 ± 0.3%). Based on these products we can assess the possible reactions occurring and their exothermic production as compared to the enthalpies of the anticipated reactions with the actual heat production observed. $SrBr_2$ is the only reactant not found in the products.

The calorimetric data RU020410: 22.18 kJ, RU020510: 27.62 kJ for 12.4g (0.05 mole) of $SrBr_2$ and RU052010C: 13.80 kJ; RU052110: 17.47 using 19.8 g (0.08 moles) of $SrBr_2$ exhibit energy gains of 3.30, 4.10, 1.28 and 1.62.

The same reaction was carried out using 32 grams of WC instead of 32 grams of TiC. The XRD pattern of the post reaction products is found in App. A.2. Using this support, 17.47 kJ of energy was obtained using 19.8 g (0.08 moles) $SrBr_2$. This translated to -218.4 kJ per mole of $SrBr_2$, which is 1.62 times more than would have been expected from the maximum theoretical reaction above. To rule out any oxide formation, TPD was carried out on $SrBr_2$, TiC, and WC. From the TPD results the amount of water present is negligible.
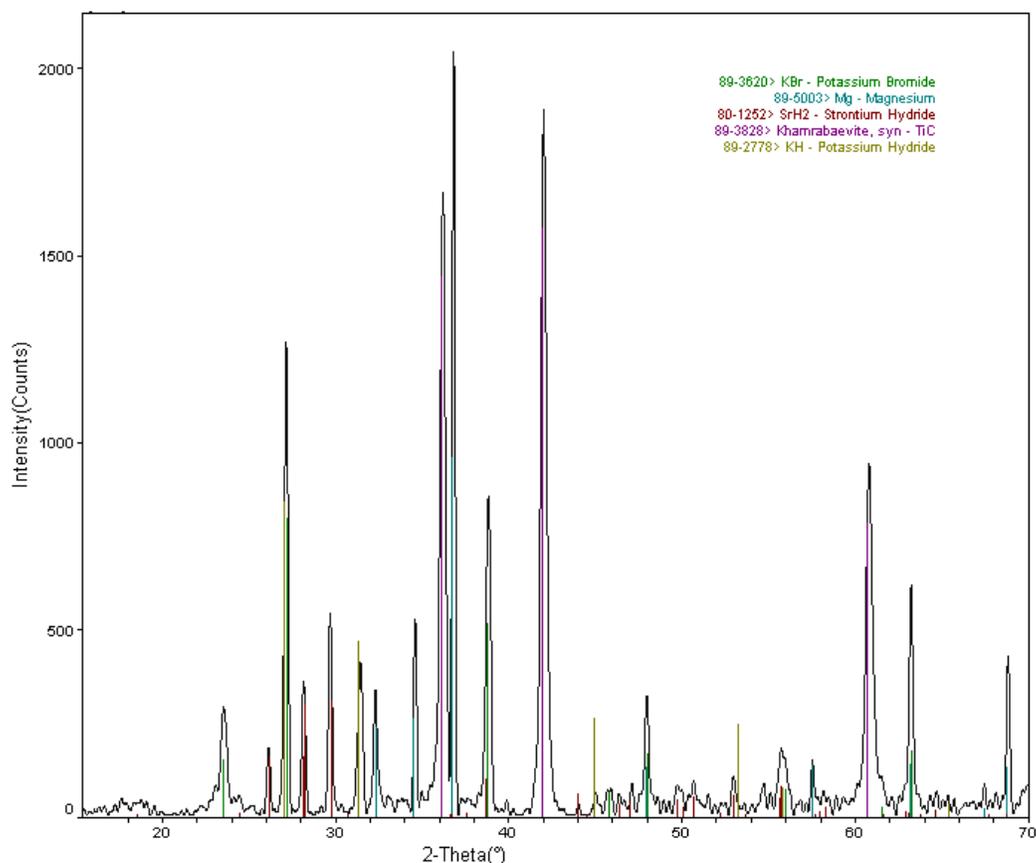
20

Figure 6. XRD of post reaction products with reactants SrBr$_2$, KH, Mg, and TiC.

Investigation into Possible Sources of Excess Energy Using Solution ^{1}H NMR Characterization of Post Reaction Products

In general, the reaction mixtures discussed above generate more energy than the theory predicts. According to BLP, the excess energy arises due to the formation of "hydrinos"—fractional states of hydrogen—during the reaction. Using one of the post-reaction mixtures, we carried out ^{1}H NMR to determine presence or absence of unusual hydrogen peaks using a post-reaction sample from KH + Mg + TiC + SrBr$_2$. The sample was extracted using DMF-d$_7$ solvent in a glove box. The clear liquid, just above the solid material was transferred to a NMR tube and tightly capped. Solution ^{1}H NMR spectra of the salts were obtained in the DMF-d$_7$ solvent. Proton NMR was obtained using a 400 MHz Varian Oxford AS400 NMR system. All NMR spectra were relative to a proton at 8.03 ppm from the DMF molecule.[1]

Fig. 7 shows the ^{1}H NMR spectra of the solution obtained. A singlet at 8.03 ppm and two quintets centered at 2.92 ppm, and 2.74 ppm are from the DMF solvent. There is another very weak upfield shifted

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[1] The Cambridge Isotope Labs NMR solvent reference chart
(http://www.isotope.com/cil/products/images/nmrchart.pdf) downloaded Sept 30, 2010.

peak at 1.27 ppm not due to the solvent. BLP has previously attributed the upfield shifted peaks at 1.2 ppm to $H_2(1/4)$. This NMR peak had previously been observed in our earlier report in reactions involving hydrogen gas in the presence of a catalyst and an alkaline salt at high temperature. Repetition of this reaction yielded similar upfield shifted peaks (App. A.3).

^{1}H NMR of other post-reaction mixtures has not been performed at this time, but would be suggested as possible future work.
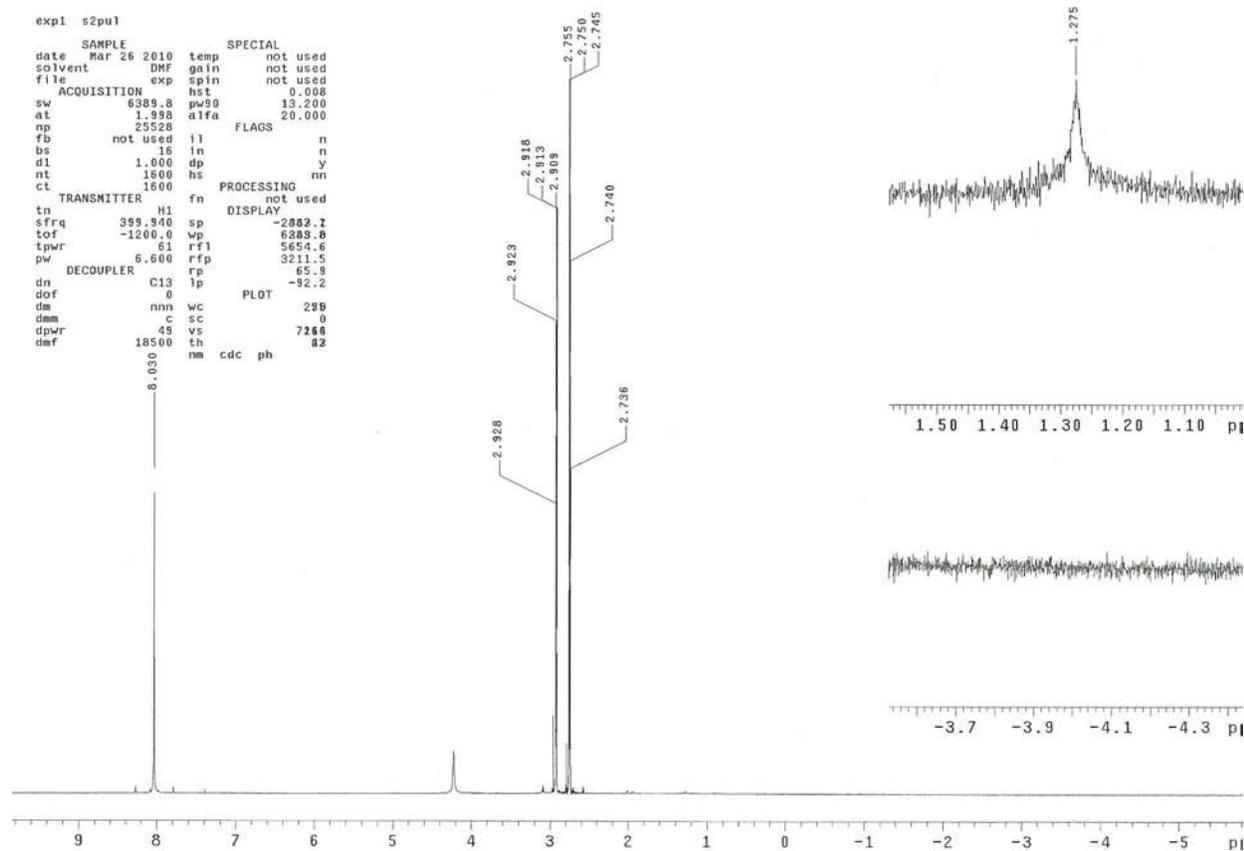
Figure 7. Liquid ^{1}H NMR spectrum of an extract of a post reaction sample containing 8.3061 g KH + 5.0083 g Mg + 20.0019 g TiC + 12.4007 g SrBr$_2$ + DMF-d$_7$ solvent.

Regeneration

Duplicating the BLP procedure, we have successively carried out three regeneration reactions involving i) KBr with Sr to form SrBr$_2$, ii) Ba with KCl to form BaCl$_2$, and iii) LiH with NaCl to form LiCl. To demonstrate regeneration reactions, reactants were pre-mixed inside an Ar-filled glove box and the mixture was placed in a small stainless steel (SS) crucible. This small tube containing the mixture of chemicals was placed in a larger SS tube closed at one end. The two nested SS tubes were then put into a larger quartz tube, which was capped with an Ultra-Torr (Swagelok) fitting. The entire assembly was made

air-tight using a valve. The quartz tube was connected to vacuum/gas line before placing it in the furnace. The quartz tube was evacuated and then filled with helium at 1 atmosphere. The system was kept supplied with helium during the experiment. The furnace temperature was gradually raised to 780 °C and held at this temperature for 30 min, then allowed to cool to 500-600 °C before the helium was turned off. The temperature was again raised to 780 $^{\circ}$C for 30 minutes; the apparatus was placed under a vacuum during this time. The furnace was allowed to cool down before taking the quartz tube to the glove box to retrieve the sample for analysis. The regeneration assembly is pictorially depicted in Fig. 8.
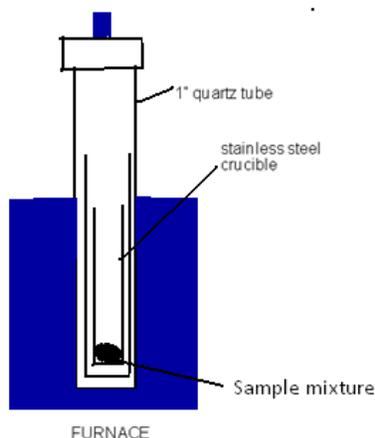
Figure 8. The experimental apparatus used for regeneration.

The first regeneration involved reacting KBr with strontium metal according to the reaction outlined below.

$$2KBr(c) + Sr(c) \xrightarrow{+\text{Heat}} SrBr_2(c) + 2K$$
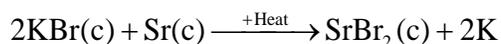
XRD of the samples obtained are given in Fig. 9. From these studies, the regeneration products involving KBr and Sr reactants indicated the presence of $SrBr_2$ as one of the reaction products.

The reaction was repeated using potassium chloride and barium metal as shown:

$$2KCl(c) + Ba(c) \xrightarrow{+\text{Heat}} BaCl_2(c) + 2K$$
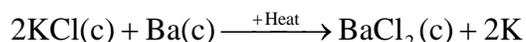
XRD of the reaction products indicated the presence of $BaCl_2$ as one of the products (Fig. 10).

Regeneration of LiCl was carried out with the mixture of LiH and NaCl following the same procedure.

$$LiH(c) + NaCl(c) \xrightarrow{+\text{Heat}} LiCl(c) + NaH$$
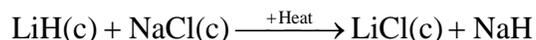
XRD results indicated LiCl as a predominant product (Fig 11). The data also revealed that a small portion of unreacted NaCl was included in the LiCl product lattice as a solid solution ($Li_{0.85}Na_{0.15}Cl$), which is a well-known fact that two alkali halides at certain ratios tend to form a eutectic salt.
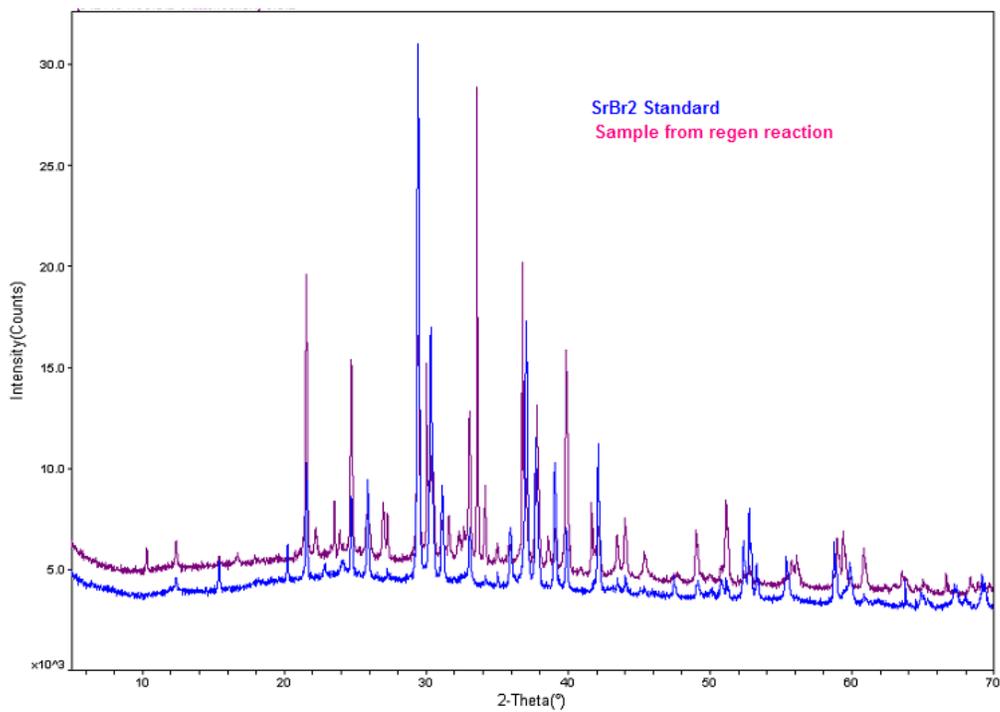
Figure 9. XRD patterns of SrBr$_2$ analytical grade with SrBr$_2$ formed from reactions of Sr metal with KBr.
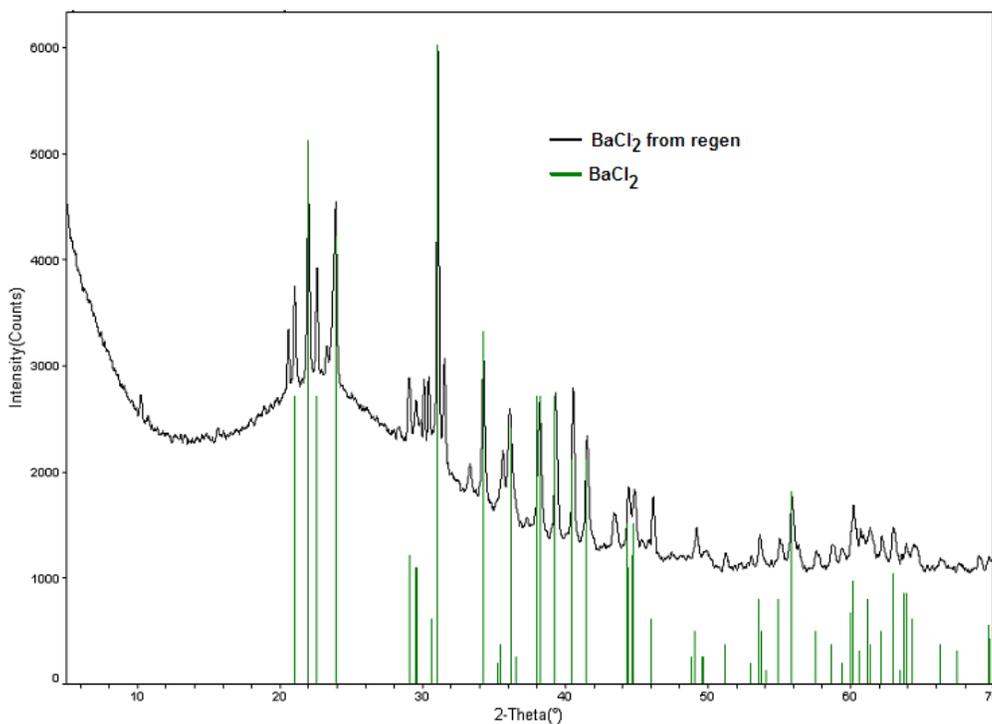
Figure 10. XRD patterns of BaCl$_2$ analytical grade and BaCl$_2$ from regeneration reaction.
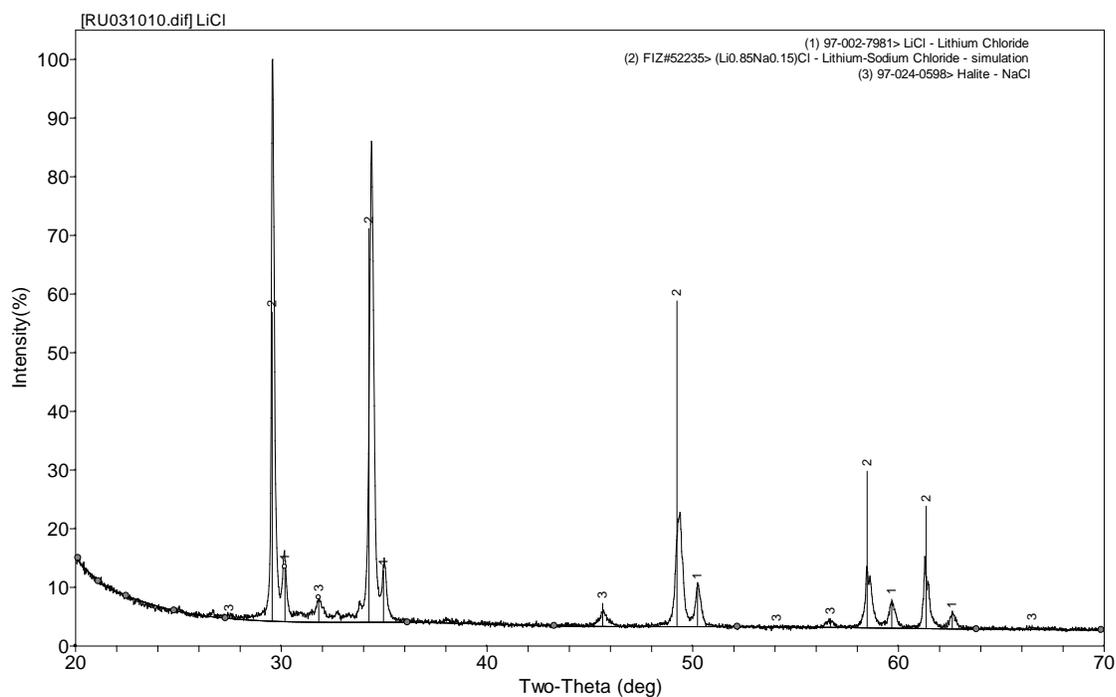
Figure 11. XRD patterns of LiCl regeneration reaction formed from reactions of LiH and NaCl.

Calorimetry

The heat produced in the chemical reactions was measured using continuous water flow calorimetry. This method uses a cylindrical chamber with a tube heat exchanger wrapped externally along the major axis. Water is flowed through the heat exchanger; inlet and outlet temperatures are measured. The entire chamber is placed in a thermally insulated enclosure. The smaller cylindrical reaction test cell is placed within an electrical resistance heater; the heater-test cell assembly is placed coaxially within the chamber. A Type-K TC is placed inside a thermowell in the reaction test cell to measure test cell temperature. Additional measurements of ambient temperature, chamber pressure, and water flow rate complete the calorimeter measurement suite.
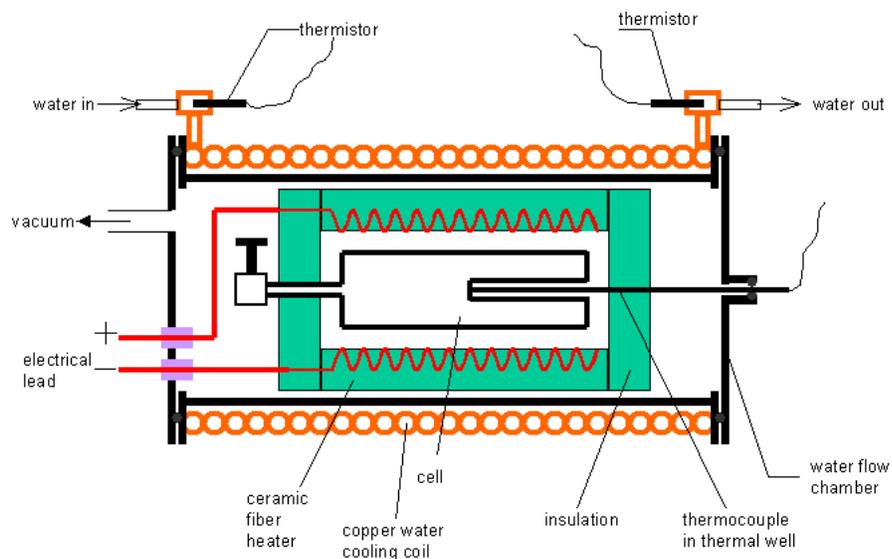
Figure 12. Calorimeter Design.

Calibration

The calorimeter was characterized by conducting a series of calibration runs on empty reaction cells to measure the standard loss of energy to ambient. In prior reported studies available on the BLP website [8, 9, 10, 11], this calorimeter was calibrated using known chemical reactions to confirm measured enthalpy correlated with known heats of reaction. This confirmed the ability of the calorimeter to detect and measure heat production from a reaction cell. Calibration runs were also performed in conjunction with heat runs to validate equipment operation and reduce measurement error. Details of calorimeter calibration procedures can be found in App. B. Table 5 summarizes data collected during calibration runs completed since January 2010. Figs. 13, 14, and 15 depict the final energy computation, recorded cell temperature, and change in water temperature respectively for a calibration run with an input energy of 300 kJ. The MatLAB program used to generate the plots can be found in App. C. Calibration performance for the 44 runs yielded an average loss of 1.92%--that is, for a nominal 300 kJ input, the average measured energy was 0.9808 * 300 kJ = 294.24 kJ.
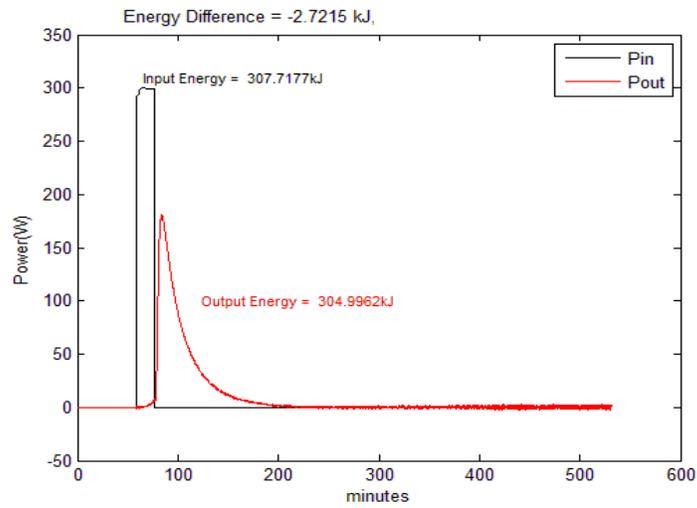
Figure 13. Calorimeter calibration: Input vs. output energy.
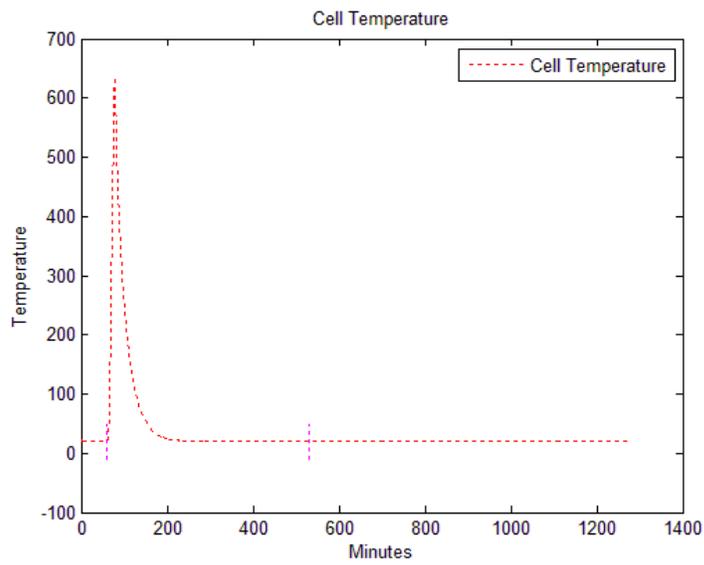
Figure 14. Reaction cell temperature.

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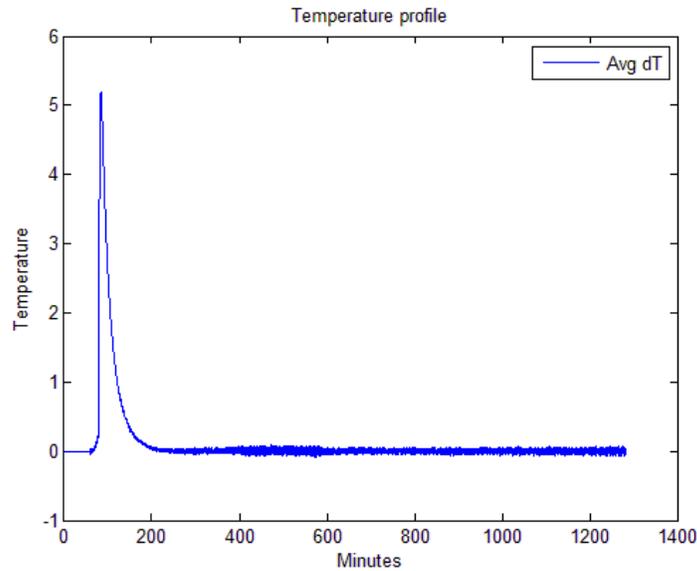
Figure 15. Delta Temperature (Heat exchanger outlet – inlet temperatures).

Table 5. Summary of 5X Cell Calibrations

Date	E_{Input}	E_{Output}	ΔE_{Total}	% Difference	Coupling
2/3/2010	347.75	346.54	-1.21	-0.35%	99.65%
2/11/2010	427.57	417.36	-10.21	-2.39%	97.61%
2/12/2010	369.39	362.70	-6.69	-1.81%	98.19%
2/17/2010	300.55	298.32	-2.23	-0.74%	99.26%
2/20/2010	299.81	291.93	-7.88	-2.63%	97.37%
2/21/2010	408.84	405.27	-3.57	-0.87%	99.13%
2/25/2010	265.29	262.43	-2.86	-1.08%	98.92%
2/26/2010	307.62	305.62	-2.00	-0.65%	99.35%
3/1/2010	297.36	294.31	-3.05	-1.03%	98.97%
3/3/2010	496.58	490.14	-6.43	-1.29%	98.71%
3/9/2010	294.73	288.99	-5.73	-1.94%	98.06%
3/23/2010	133.19	130.20	-2.99	-2.24%	97.76%
3/25/2010	300.03	291.99	-8.04	-2.68%	97.32%
3/26/2010	300.04	290.99	-9.05	-3.02%	96.98%
3/27/2010	301.28	290.57	-10.71	-3.55%	96.45%
3/28/2010	300.46	291.23	-9.23	-3.07%	96.93%
5/10/2010	299.79	294.89	-4.90	-1.63%	98.37%
5/11/2010	301.00	293.91	-7.09	-2.36%	97.64%
5/12/2010	300.05	295.76	-4.29	-1.43%	98.57%
5/17/2010	299.91	291.77	-8.14	-2.71%	97.29%
5/18/2010	299.84	293.70	-6.14	-2.05%	97.95%
5/24/2010	300.03	293.21	-6.82	-2.27%	97.73%
5/25/2010	300.01	293.05	-6.96	-2.32%	97.68%
Average	315.27	309.34	-5.92	-1.92%	98.08%
STDV	66.61	66.12	2.75	0.87%	0.87%

Calorimetry of Heat Generation Reactions

Thirteen heat runs were completed using strontium bromide, barium chloride, and lithium chloride as the reactants within the cell as described previously. The purpose of these heat runs was to measure the energy resulting from the exothermic chemical reactions initiated by heating of the reaction cell loaded with reactants according to an experimental protocol (see App. D). For each heat run completed a set amount of reactants were used. A temperature window for the reaction was also provided, in order to determine when to shut down the power supply once the reaction has occurred. As shown in Table 6, all of the heat runs completed at the Technology Park, when corrected for the calibrated heat loss, resulted in an output energy greater than the input energy. Figure 16 represents an energy profile that was recorded during a $BaCl_2$ heat run. Figure 17 depicts the cell temperature profile during this run, and Figure 18 shows the outlet-inlet heat exchanger temperature difference.
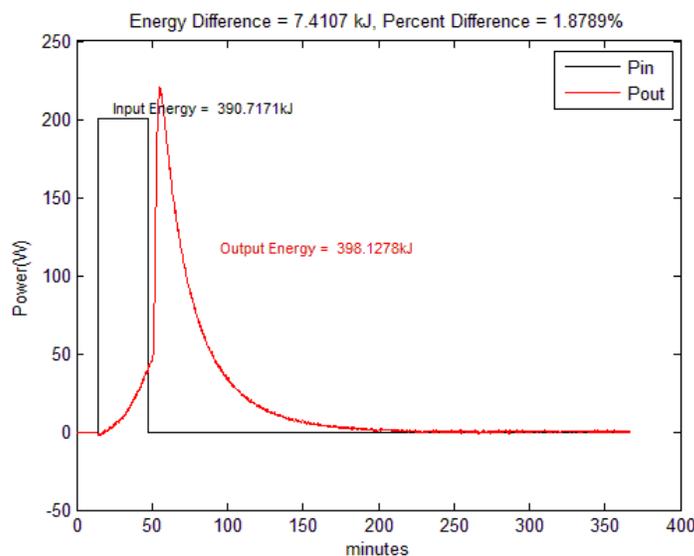
Figure 16. Heat run energy profile of Barium Chloride on 2/15/2010.
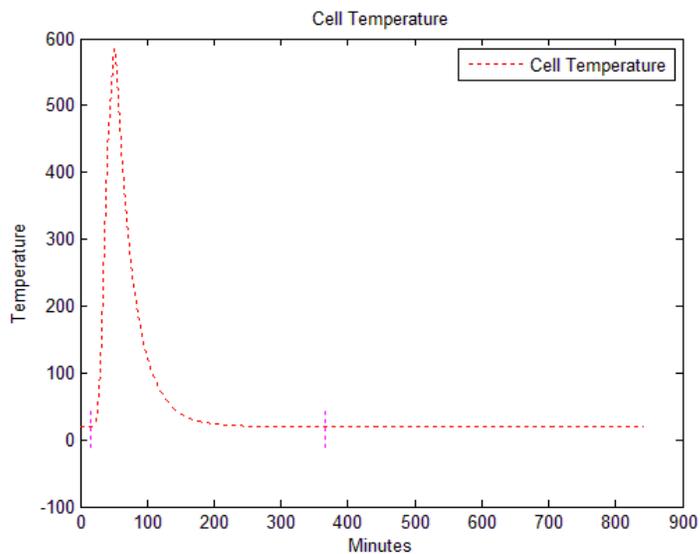
Figure 17. Reaction cell temperature profile for BaCl$_2$ heat run on 2/15/2010.
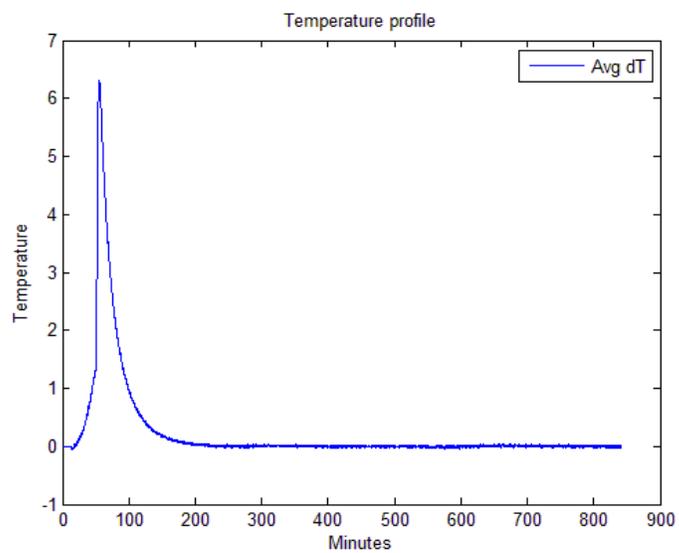
Figure 18. Outlet-inlet temperature difference for BaCl$_2$ heat run on 2/15/2010.

Table 6. Heat Run Summary

Note: Gains have been calculated using (11-c)

Date	Cell Name	Chemical Composition	Actual Measured Data		Calculated Data With 2% E_L average				
			E_{Input}	E_{Output}	E_{Output}	ΔE_{Total}	ΔE_T	E_X	Gain
2/4/2010	RU020410	8.3 g KH + 5.0 g Mg + 20.0 g TiC + 12.4 g SrBr$_2$	379.38	393.69	401.56	22.18	6.73	15.45	3.30
2/9/2010	RU020510	8.3 g KH + 5.0 g Mg + 20.0 g TiC + 12.4 g SrBr$_2$	424.02	442.78	451.64	27.62	6.73	20.89	4.10
2/10/2010	RU020910	8.3 g KH + 5.0 g Mg + 20.0 g TiC + 10.4 g BaCl$_2$	392.10	400.62	408.63	16.53	4.05	12.48	4.08
2/15/2010	RU021510	8.3 g KH + 5.0 g Mg + 20.0 g TiC + 10.4 g BaCl$_2$	390.72	400.97	408.99	18.27	4.05	14.22	4.51
3/10/2010	RU031010	8.0 g NaH + 8.0 g Mg + 32.0 g TiC + 3.4 g LiCl	330.05	342.51	349.36	19.31	2.95	16.36	6.55
5/13/2010	RU051310	8.0 g NaH + 8.0 g Mg + 32.0 g TiC + 3.4 g LiCl	302.84	306.07	312.19	9.35	2.95	6.40	3.17
5/18/2010	RU051810	8.0 g NaH + 8.0 g Mg + 32.0 g WC + 3.4 g LiCl	308.47	308.54	314.71	6.24	2.95	3.29	2.12
5/17/2010	RU051710	13.2 g KH + 8.0 g Mg + 32.0 g TiC + 3.4 g LiCl	311.63	318.42	324.79	13.16	4.87	8.29	2.70
5/19/2010	RU051910	13.2 g KH + 8.0 g Mg + 32.0 g WC + 3.4 g LiCl	281.81	284.60	290.29	8.48	4.87	3.61	1.74
5/24/2010	RU052010A	13.2 g KH + 8.0 g Mg + 32.2 g WC + 16.6 g BaCl$_2$	293.92	296.43	302.36	8.44	6.48	1.96	1.30
5/25/2010	RU052010B	13.2 g KH + 8.0 g Mg + 32.1 g TiC + 16.6 g BaCl$_2$	292.80	297.32	303.27	10.47	6.48	3.99	1.62
5/26/2010	RU052010C	13.2 g KH + 8.0 g Mg + 32.0 g TiC + 19.8 g SrBr$_2$	310.75	318.19	324.55	13.8	10.76	3.04	1.28
5/26/2010	RU052110	13.2 g KH + 8.0 g Mg + 32.0 g WC + 19.8 g SrBr$_2$	321.95	332.76	339.42	17.47	10.76	6.71	1.62

Calorimetry Performance

The strength of conclusions regarding heat generation is dependent on high quality calorimetry measurements. One source of calorimetry error is inaccurate measurement of the inlet/outlet temperatures for the heat exchanger, because they are used to compute the total energy according to:

$$E = \int_{Ti}^{Tf} \overset{\bullet}{m}\, c_p (T_{out} - T_{in}) dt$$

where the total energy, E in joules is found by integrating the product of mass flow rate, $\overset{\bullet}{m}$, specific heat, c_p, and the temperature difference between outlet and inlet. The integration period spans the beginning and end of the experiment as defined by departure time, T_i, from the quiescent starting point temperature and the return to that same quiescent temperature at the end of the experiment, T_f.

If $\overset{\bullet}{m}$ and c_p are assumed constant, as confirmed experimentally, then the principal source of error is the temperature measurement. The basic technique for measuring inlet and outlet temperature uses thermistors. Their accuracy and repeatability were determined by comparing them to a high-accuracy, four-wire resistance temperature detector (RTD). The test involved placing the transducers into a temperature-controlled water bath and recording the indicated temperatures over a range of 10^0C to 30^oC in increments of 5^oC. LabVIEW was used to record the inlet and outlet temperature data. Using this data, a quadratic fit was created for both inlet and outlet thermistors as shown in Fig. 19. These equations were based on the RTD readings as the reference. These improved thermistor equations were applied to several calibration runs. The results showed a better calorimeter performance. All calorimeter data analysis was performed using the improved thermistor calibrations.
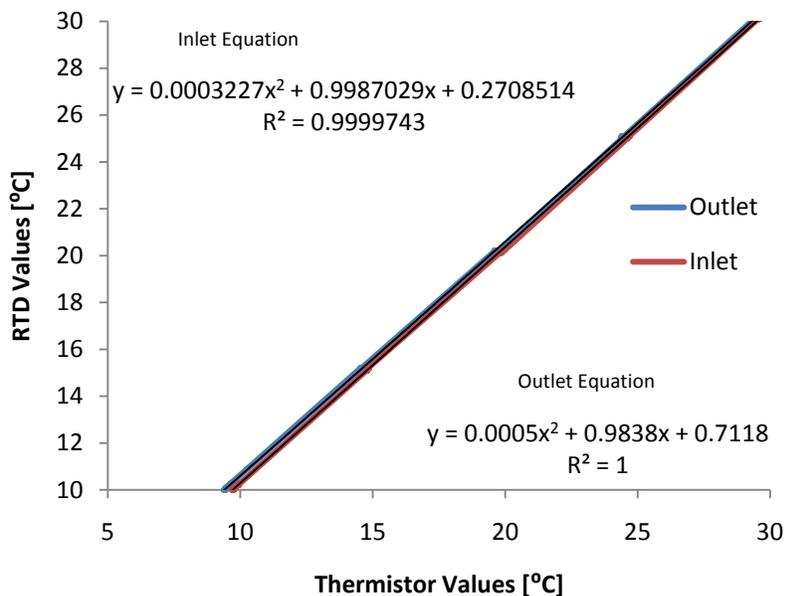
Figure 19. Calibration equations for Inlet and Outlet Thermistors.

The chart displays:

Inlet Equation
$$y = 0.0003227x^2 + 0.9987029x + 0.2708514$$
$$R^2 = 0.9999743$$

Outlet Equation
$$y = 0.0005x^2 + 0.9838x + 0.7118$$
$$R^2 = 1$$

Legend: Outlet, Inlet

Y-axis: RTD Values [$^{\circ}$C]
X-axis: Thermistor Values [$^{\circ}$C]

Calorimetry Assessment

An independent assessment of the overall measurement scheme was performed by Silver Wolf Technologies, Inc., hired by Rowan University. A preliminary uncertainty model was recently completed as part of this work and is included in Appendix G for completeness. The interim finding of this evaluation is that the calorimeter is expected to yield a 0% to -3% measurement uncertainty.

Discussion and Conclusions

This work has characterized heat production from a suite of BLP chemistries designed for energy generation. The reaction mixtures consisted of a metal halide salt ($SrBr_2$, $BaCl_2$ or LiCl), a hydrogen source, (NaH or KH), a reducing agent (Mg), and a support matrix material (TiC or WC). All reactants were in crystalline form. Chemical composition of reactants and reaction products were analyzed using a combination of XRD, ICP-MS, TPD, and XRF. XRD of the starting materials indicated that there were no crystalline impurity phases present. $BaCl_2$, $SrBr_2$, LiCl and TiC analyzed with TPD indicated that no water is present in these starting materials and therefore no oxides were expected or found during the product analysis. Elemental analysis using ICP-MS and XRF did not show any significant amounts of other elements such as Be, Cr, Mn, Ni, Co, Zn, As, Ag, Cd, Sb, Ba and Pb that could influence the reactions.

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Calorimetric measurements on reaction cells with thirteen combinations of starting chemicals were conducted and resulted in measured heats that demonstrate energy gains higher than predicted by conventional energy balance calculations for the associated reactants and products. The calorimeter demonstrated highly repeatable performance based on overall error analysis as confirmed with calibration results. The heat gains were computed using Equation (11-c). Equation (11-c) expresses the gain with an average loss obtained from calorimeter calibration runs and is approximately 2%. Resulting gains for the nominal case with 2% loss yields heat gains in the range of 1.28 – 6.55.

The possibility of regeneration reactions was demonstrated using a mixture of KBr and Sr metal at high enough temperatures to produce $SrBr_2$ among other products. This is the reverse reaction of the energy producing reaction that used Sr. XRD pattern of the regeneration product superimposed with analytical grade $SrBr_2$ shows an excellent match. In another demonstration of regeneration reactions Ba metal reaction with KCl indicated that $BaCl_2$ was one of the products of the reaction. XRD of the regeneration product with analytical grade $BaCl_2$ also showed an excellent match. Another reaction involving LiH with NaCl indicated the presence of LiCl as one of the reaction products.

Future Work

The work presented in this report suggest a number of fruitful follow-on studies including:

- Calorimeter characterization. Preliminary analysis of the calorimeter to determine measurement uncertainty will be strengthened by complete modeling of the calorimeter elements and the measurement instrumentation.

- Calorimeter improvement. Several modifications to the calorimeter can improve its performance—for example, by lowering the loss. One approach is to enclose the existing calorimeter in another enclosure to provide additional isolation from ambient. Improvements to the mounting methods for the catalyst reaction chamber will provide more repeatability. Finally, the water jacket can be improved to include better coverage of the entire vacuum chamber.

- Developing statistical significance. It would be advantageous to conduct multiple heat runs on the identical chemistry in order to develop meaningful statistics for the process.

- Characterization of the reverse reaction. The net efficiency of the reversibility process should be studied by measuring the amount of heat required to reverse the process and developing efficiency measures for assessing the quality of the reversal products.

- Pilot scale implementation. The commercial feasibility of power extraction from the novel chemistries requires that one or more of the chemistries be scaled up.

Glossary

Glossary of Terms	
ΔE_T	Theoretical Predicted Energy Output
$\Delta_f H^0$	Enthalpy of Formation
ΔE_{Total}	Net Energy Balance
E_{Input}	Input Energy
E_{Output}	Output Energy
E_x	Additional Source or Sink of Energy
$\hat{E}_{Output}$	Total Energy Estimate
T_f	Ending of Integration Period
T_i	Beginning of Integration Period
c_p	Specific Heat Constant
$\dot{m}$	Mass Flow Rate
T_{Outlet}	Outlet Water Temperature
T_{Inlet}	Inlet Water Temperature
E_L	Loss Term for Calorimeter
qE_{Input}	Sum of Energy Production Terms
$r\Delta E_T$	Most Convincing Measurement for Any Possible Added Energy Sources
E_{Gain}	Energy Gain
SNR	Sensitivity
TPD	Temperature Programmable Desorption
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
NMR	Nuclear Magnetic Resonance
DMF	Dimethylformamide

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Appendix A – Chemistry Information

Appendix A.1 - TPD Runs

BaCl$_2$

TiC

LiCl
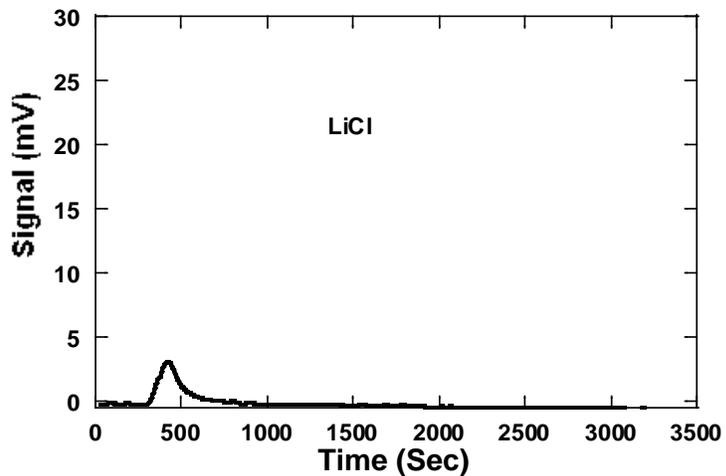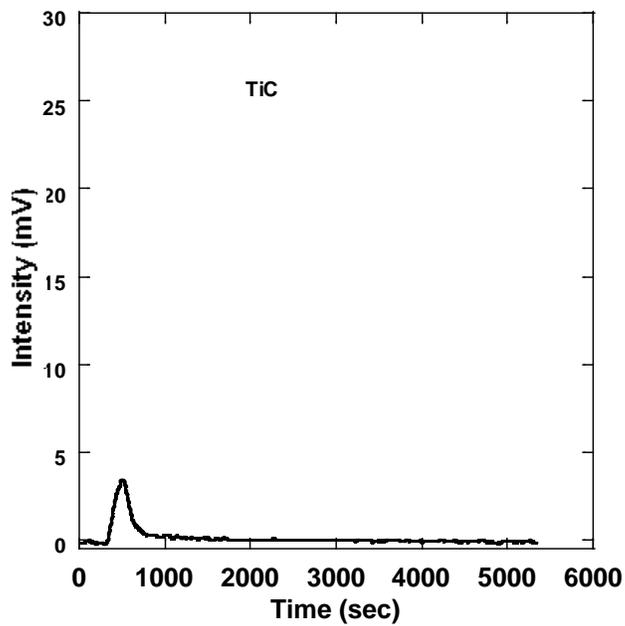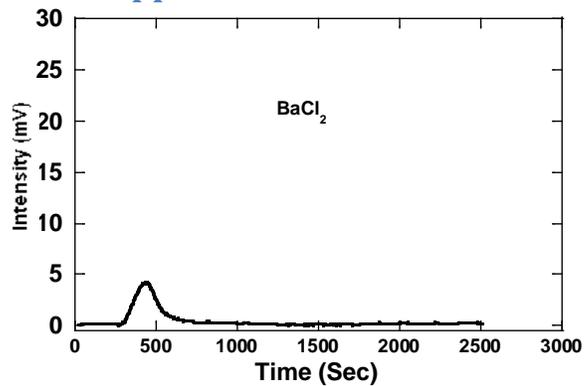
Appendix A.2 - XRD of BLP Chemicals
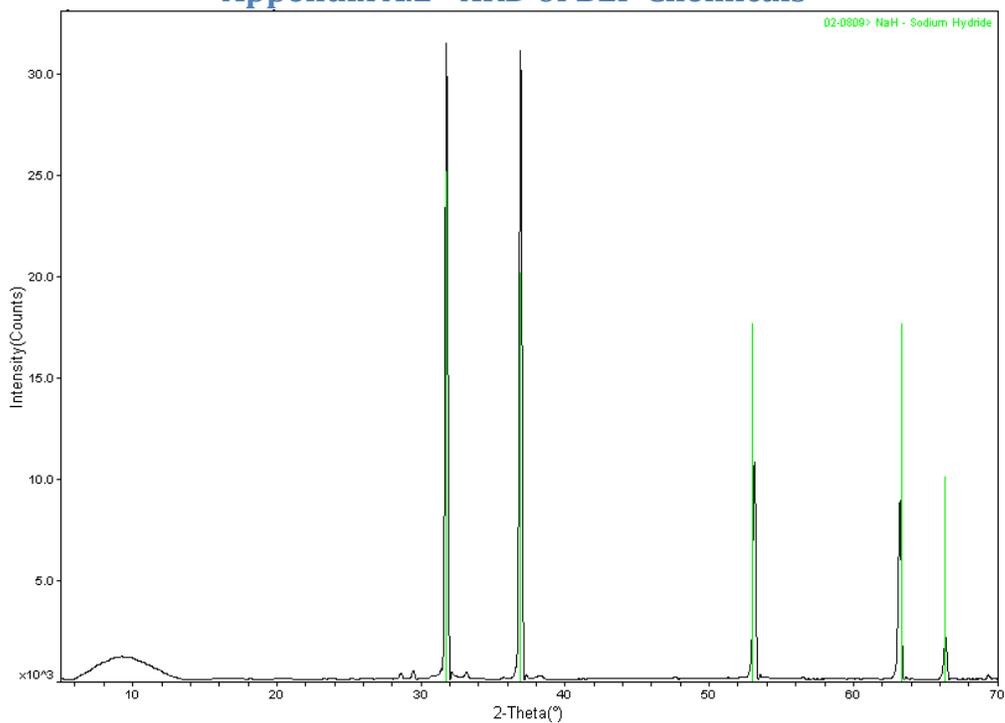
XRD patterns of NaH from BLP
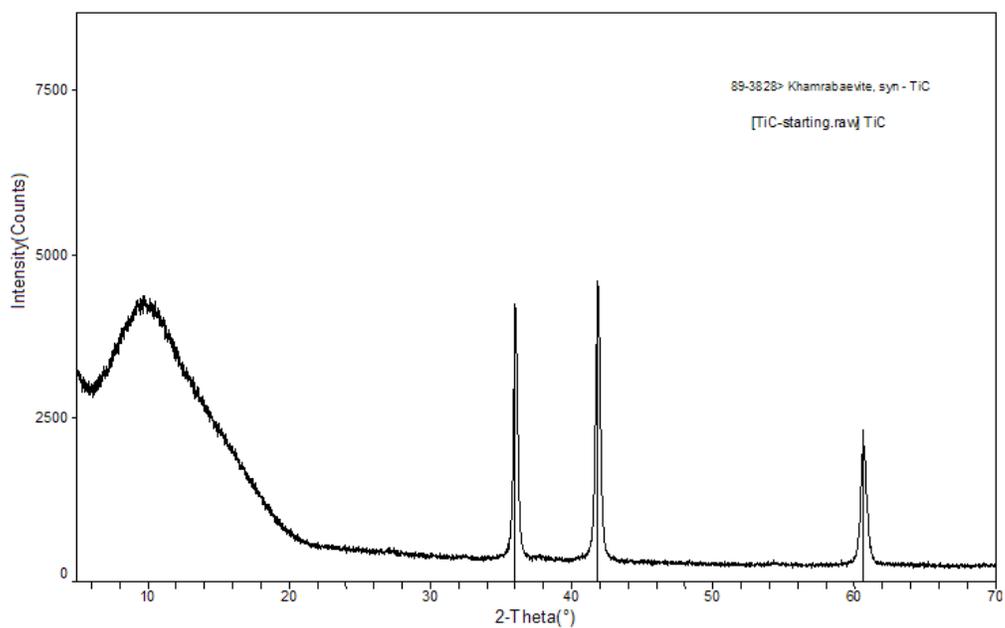
XRD patterns of TiC
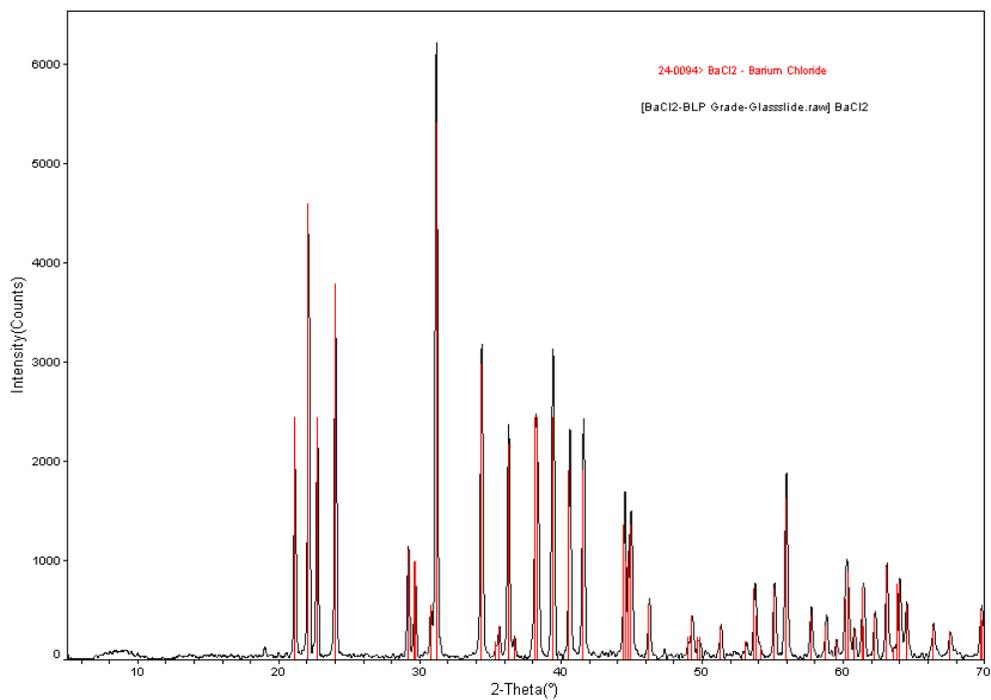
XRD patterns of analytical grade BaCl$_2$ and from BLP
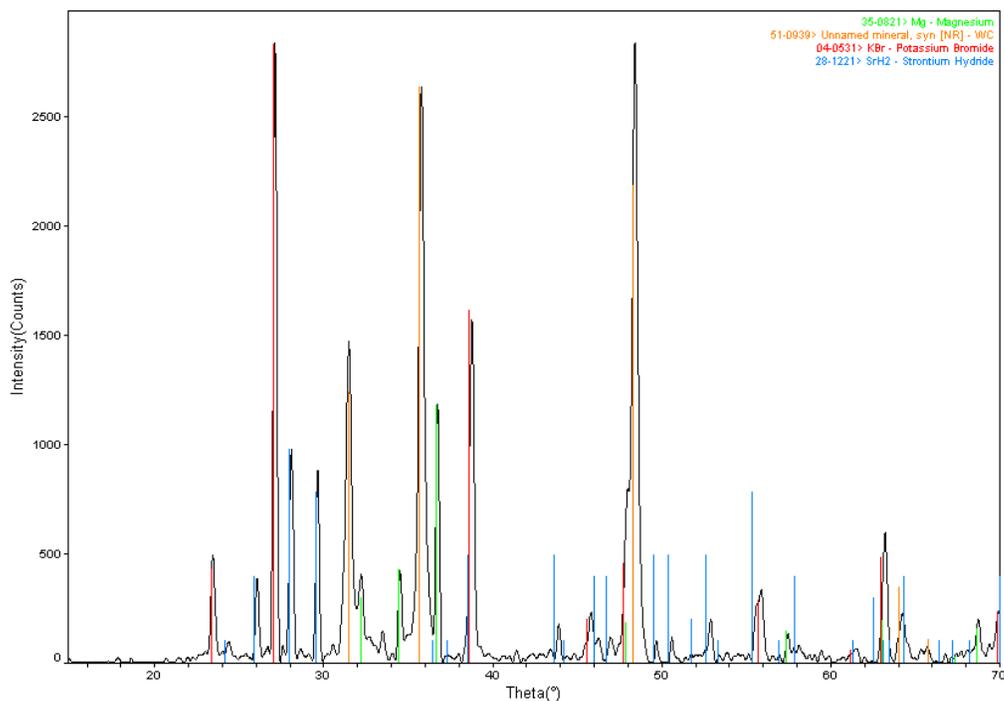
XRD of pattern of post reaction products: Starting Material: 13.2311g KH, 8.0345g Mg, 19.8397g SrBr$_2$, 32.0361g WC

Appendix A.3 - Proton NMR
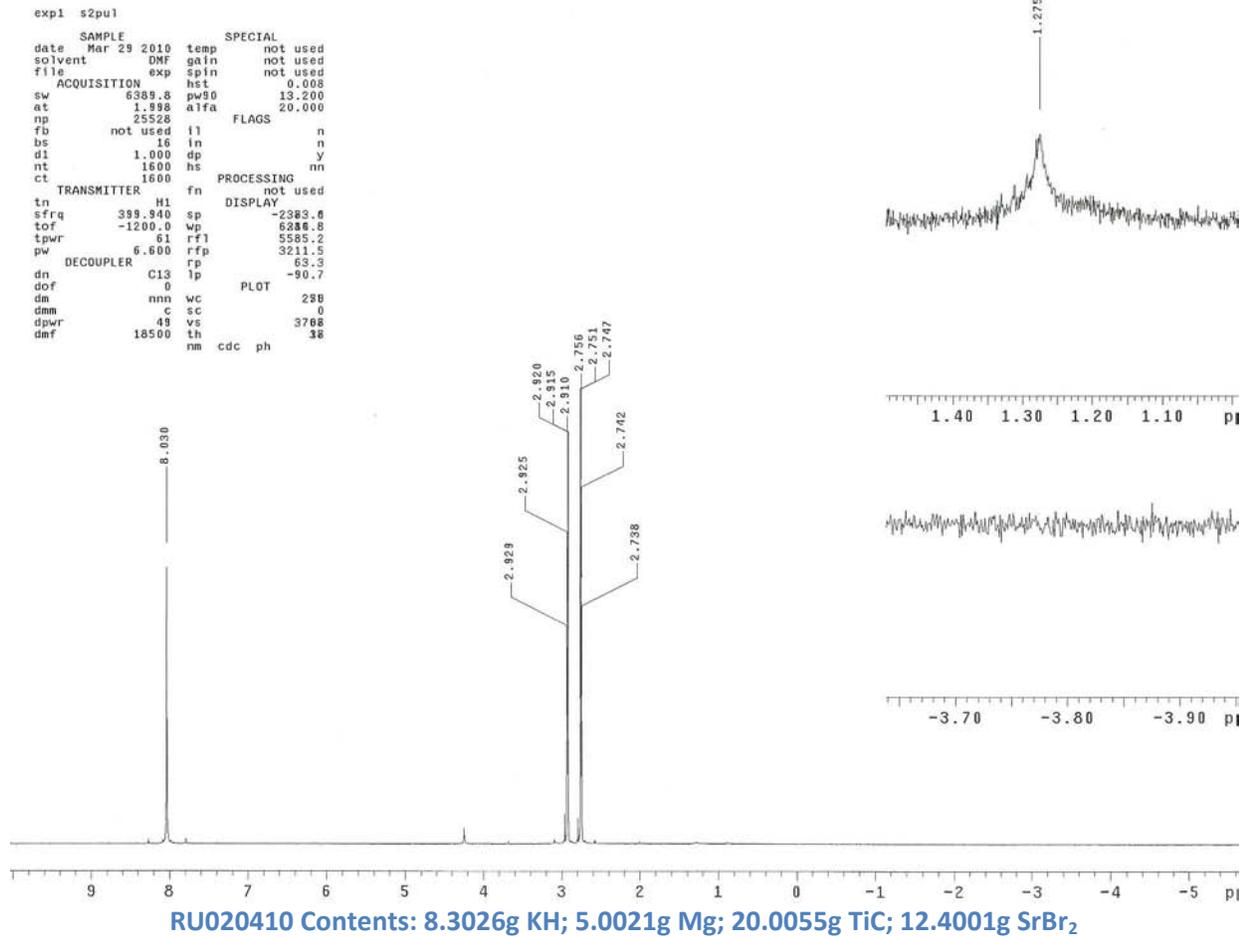
exp1 s2pul

	SAMPLE		SPECIAL	
date	Mar 29 2010	temp	not used	
solvent	DMF	gain	not used	
file	exp	spin	not used	
ACQUISITION		hst	0.008	
sw	6389.8	pw90	13.200	
at	1.998	alfa	20.000	
np	25528	FLAGS		
fb	not used	il	n	
bs	16	in	n	
d1	1.000	dp	y	
nt	1600	hs	nn	
ct	1600	PROCESSING		
TRANSMITTER		fn	not used	
tn	H1	DISPLAY		
sfrq	399.940	sp	-2383.6	
tof	-1200.0	wp	6386.8	
tpwr	61	rfl	5585.2	
pw	6.600	rfp	3211.5	
DECOUPLER		rp	63.3	
dn	C13	lp	-90.7	
dof	0	PLOT		
dm	nnn	wc	298	
dmm	c	sc	0	
dpwr	49	vs	3768	
dmf	18500	th	38	
		nm cdc ph		

RU020410 Contents: 8.3026g KH; 5.0021g Mg; 20.0055g TiC; 12.4001g SrBr$_2$
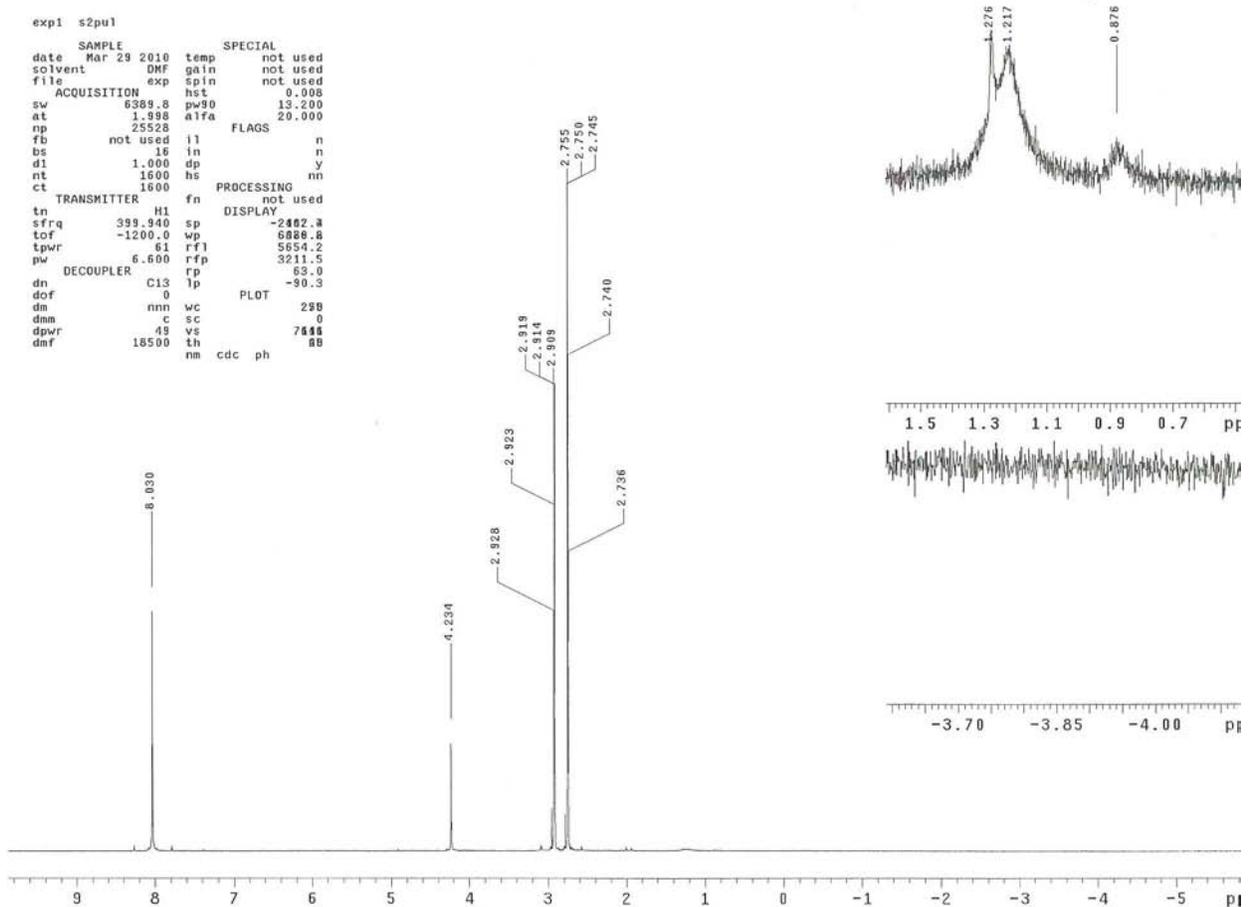
RU020510 Contents: 8.3016g KH; 5.0018g Mg; 20.0011g TiC; 12.4036g SrBr$_2$

Appendix B - Experimental Procedures

B.1 - Calibration/Heat Run Procedure

1. If calibration cell is not in chamber, load calibration cell (Criterion for loading Heat Run as well)
   1.1. Make sure vacuum is off (i.e. system is not at ~0 torr)
      1.1.1. If vacuum is on, close valve V1
      1.1.2. Introduce helium to bring to 1 atm (i.e. ~ 760 torr) - see 3.1 to 3.3
      1.1.3. Wait for a brief period while chamber de-pressurizes
   1.2. Remove container lid and foam cover and vacuum out foam pellets
   1.3. Remove chamber and place in stand on top of container
   1.4. Unplug red and black power connectors as well as thermocouple from front plate of chamber
   1.5. Loosen clamps on front plate and remove entire front plate and calibration (or heat run) cell from chamber
   1.6. At work station, while keeping thermocouple in front plate, remove thermocouple from center of current cell and disconnect power connectors from back of the front plate, leaving the wiring connected to the ceramic heater core containing the cell
   1.7. Remove current cell from ceramic heater core and be certain to store it with proper label (i.e. date of heat run and chemical composition for heat runs, "calibration" for calibration cells if not already specified)
   1.8. Snugly wrap small strip of fiberglass insulation around front of calibration cell while inlaying another small strip of fiberglass in the rear of the ceramic heater core, tying tight with wire
   1.9. Load cell into ceramic heater core, making sure that it is not touching the inside (i.e. fiberglass insulation in tightly suspending cell in the center of the ceramic heater core)
      1.9.1. Place metal T-bar braces on front and back of ceramic heater core, being certain that hole on front T-bar is centered with the hole in the calibration cell, tie down tightly
      1.9.2. Place insulation on front and back of ceramic heater core and tie down with wire.
   1.10. Reinsert thermocouple into calibration cell **(BE SURE IT IS IN ALL THE WAY!!!!!!)** and reconnect power from ceramic heater core to front plate of chamber
   1.11. Place ceramic heater core with cell back into main chamber **(DO NOT PUSH INTO CHAMBER AND THEN PULL OUT, THIS WILL CAUSE THERMOCOUPLE TO PULL OUT OF THE CALIBRATION/HEAT CELL!!!!!!)**
   1.12. Push cell all the way into main chamber until front plate is flush with the heat exchanger, then turn on vacuum (V1) to ensure proper seal
   1.13. Tighten clamps back onto the front plate in a clockwise fashion to ensure proper seal
   1.14. Reconnect thermocouple wire as well as power to the front panel
   1.15. Place chamber back into foam insulation, fill open areas with foam pellets, place foam cover back on top and close container
      1.15.1. **Be certain that no wires or hoses are being pulled on or compressed when placing foam cover and container lid back on!!!!!!**
   1.16. Test power supplied to calorimeter
      1.16.1. Flip power supply switch on and set voltage to 10 volts, current to 1 amp, and power to 1 watt
         1.16.1.1. To set voltage: hit VOLTAGE button, enter desired input, hit ENTER button
         1.16.1.2. To set current: hit CURRENT button, enter desired input, hit ENTER button
         1.16.1.3. To set power: hit MENU button nine times, hit ENTER, enter desired input, hit ENTER again
      1.16.2. Hit OUT ON/OFF button, if CP appears on LCD readout, then power is connected properly
         1.16.2.1. Hit OUT ON/OFF button again to turn off power, then flip power supply off

2. Starting program for a new run
   2.1. Turn on LABVIEW program if not already running

2.1.1. Double click the Labview Template.vi icon on the desktop
2.2. Turn on Xantrex power supply
2.3. Hit the "Run" button located at the top left of the program window
2.4. Enter save name for run
    2.4.1. Example for Calibration Run: MMDDYYYY_Energy in kJ_calibration
    2.4.2. Example for Heat Run: MMDDYYYY_Cell Name_Chemical 1 Mass_Chemical 1_Chemical 2 Mass_Chemical 2_Chemical 3 Mass_Chemical 3_Chemical 4 Mass_Chemical 4
2.5. Make sure that "0.01" is being read in the current output of the program window
    2.5.1. If program does not read "0.01" for current, stop run and repeat from step 2.2
2.6. Once confirmed, turn off Xantrex power supply
2.7. Log user performing the run, run type ("Cali" and input energy for calibrations; "HR", run name, and ingredients for heat runs), and current time in Lab Notebook

3. Starting a new run
    3.1. Make sure that V1-V4 are closed tightly
    3.2. Open main valve to helium tank, then open V2 and V3
    3.3. **SLOWLY** open V4 until ch2 on the Baratron reads ~760 torr
        3.3.1. Close off valves V2-V4 tightly
    3.4. Allow program to run for at least 15 minutes to acquire a baseline
        3.4.1. Cell temperature should be roughly at chiller temperature and staying constant at that temp (i.e. ΔT ~0 and Cell Temp ~19-20 ^{o}C)
    3.5. If Cell Temp is constant, turn on Xantrex power supply
        3.5.1. If LCL icon on the power supplies LCD screen does not change to RMT within a few seconds, run must be stopped, power supply must be turned off, and the process must be started over from Step 2.2
        3.5.2. Calculate wattage and time step for desire kJ output (ie 250W*20min.=250W*1200sec=300000 W*sec=300kJ)
        3.5.3. Hit LCL/RMT button, press VOLTAGE button and set to 600 V, hit ENTER
        3.5.4. Hit LCL/RMT button, press CURRENT button and set to 10 A, hit ENTER
        3.5.5. Hit LCL/RMT button, press MENU button nine times until you see POWERSETP, set to desired wattage, hit ENTER
    3.6. Perform a manual water flow reading
        3.6.1. Open chiller, remove water line from top of chiller and place in basin
            3.6.1.1. Remove bleeder line from main water line and place in basin
        3.6.2. Tier graduated cylinder on scale
        3.6.3. Fill the graduated cylinder for exactly 1 minute and measure weight (i.e. after tiering the graduated cylinder, the scale should read ~650 g)
        3.6.4. Record measurement in Lab Notebook
        3.6.5. Place bleeder line and main water line back and close the chiller
    3.7. Open V1 all the way until ch1 on the Baratron reads ~0 torr
    3.8. Hit OUT ON/OFF button and simultaneously time the run for the desired time chosen
    3.9. Halfway through the run, repeat step 3.6
    3.10. Hit OUT ON/OFF button as soon as the desired time chosen is reached
    3.11. Allow the Cell Temp to reach a peak and start to drop
        3.11.1. When this drop off occurs, repeat steps 3.1 to 3.3
    3.12. Allow for a cool down until the Cell Temp reaches and appropriate baseline (i.e. ~original Cell Temp for roughly 30 min.) and repeat step 3.6
    3.13. Copy data from computer and run the Matlab_Analysis_V2010.m program on it, input the average of the three water flow readings taken during the run
    3.14. If data seems appropriate, stop run and prepare for another

      3.14.1. **IF YOU ARE UNCERTAIN OF RESULTS OR ANY OF THE PROCEDURAL STEPS, INQUIRE WITH A SENIOR MEMBER OR PROFESSOR!!!!!!**

B.2 - Thermistor Calibration Procedure

1. Preparing Chiller
    1.1. Stop any runs that are currently being performed in the LabView program
    1.2. Unplug pump from back of cart
    1.3. Flip white switch of back of chiller to turn chiller off
    1.4. Undo and plug inlet and hoses from chiller
    1.5. Fasten close-circuit tubing to chiller (such that the chiller inlet and outlet are connected)
    1.6. Turn chiller back on
    1.7. Remove lid and top layer of foam from the container
    1.8. Loosen and remove thermistors from calorimeter
    1.9. Place thermistors into chiller, being sure that they do not touch any coils or the bottom of the chiller
    1.10. Place meter affixed with a thermocouple into chiller bath
    1.11. Place meter affixed with four-wire RTD into chiller bath
    1.12. Adjust chiller temperature to 18 ^{o}C
        1.12.1. Press the SET button on the chiller
        1.12.2. Adjust dial until the chiller reads the desired temperature in ^{o}C
        1.12.3. Press the ENTER button

2. Setting Up the LabView Program
    2.1. Hit the "run" button in the top left of the LabView program
    2.2. Enter a save name (ie 05132010_thermistor_calibration)
    2.3. **POWER DOES NOT NEED TO BE ON !!!!!!** Simply click okay when the box pops up prompting you to have the power supply turned on

3. Running a Thermistor Calibration
    3.1. Perform a three point test from 15-30°C with two "check" points (i.e. 15°, 20°, 22.5^o, 25°, 30°)
        3.1.1. Be certain that all temperature sensors used have stabilized to the desired temperature before testing each time
        3.1.2. Write down starting time for experiment based on the time elapsed shown at the top of the LabView program
        3.1.3. Track changes to Thermocouple and RTD temperatures for one minute, taking readings every 5 seconds
        3.1.4. Repeat steps 1.12.1-1.12.3, this time adjusting for the next test temperature
    3.2. Readjust the chiller temperature to 19.9 ^{o}C
    3.3. Once the chiller reaches 19.9 ^{o}C, turn off chiller
    3.4. Undo and remove close-circuit tubing from chiller
    3.5. Unplug inlet and outlet hoses and fasten them back to the chiller
    3.6. Place thermistors back into calorimeter up to black markings and tighten
    3.7. Place top foam and lid back on the container
    3.8. Turn chiller back on
    3.9. Plug pump back into power strip

Appendix C - MatLAB Code

```matlab
clear all; close all; clc
cd('\\WORKBOXTRES\CSD_Backup\blp_backup\')


%***********Load File, rename it and create a results file and
folder.*****************%
%***************************************************************************
*******%
[FileName,PathName,FilterIndex] = uigetfile('*.*');
name= [PathName,FileName];
Sheet1=importdata(name);
%Sheet1=load(name, 'v1');
mkdir([PathName 'Results\' FileName])

results_file=fopen([PathName 'Results\' FileName '\' FileName
'_MatOutput.txt'],'wt');

%***********Load data from newly created
inputfile*********************************%
%***************************************************************************
*******%
Tin1=Sheet1.data(:,6); %Input Thermistor Temperature
Tout1=Sheet1.data(:,7); %Output Thermistor Temperature

% ****************UNCOMMENT FOR THERMISTOR CALIBRATION******%
% a_in=0.0005303;                                          %
% b_in=1.0049947;                                          %
% c_in=0.5996034;                                          %
%
% a_out=0.0003227;                                         %
% b_out=1.0116126;                                         %
% c_out=0.3740060;                                         %
%
% Tin=a_in*(Tin1).^2+b_in*(Tin1)+c_in;                     %
% Tout=a_out*(Tout1).^2+b_out*(Tout1)+c_out;               %
%
% Tavg=Tout-Tin;                                           %
% ********************************************************%


Tavg=Sheet1.data(:,8);%*IF USING THERMISTOR CALIBRATION, COMMENT THIS LINE OUT*%
Tamb=Sheet1.data(:,15); %Ambient Temperature
Pressure=Sheet1.data(:,10); %Pressure from the 10torr-100torr Baratron
Pin=Sheet1.data(:,3); %Input power from the Xantrex Power Supply
time=Sheet1.data(:,1).*60; %Import Time data and convert to seconds
roomTemp=Sheet1.data(:,2); %Room Temp read by LABView

%Load Cell Temperature & remove gigantic outliers
CellT=Sheet1.data(:,9); %Cell Temperature
for i=1:length(CellT)
    if(CellT(i)> 1000 || CellT(i)<-10)
        %sets a default temp, should be changed according to baseline temp
        CellT(i)= 17;
    end
end
```

```matlab
%***********Plot CellT
vs.Pressure****************************************************%
%****************************************************************************
*******%
y1 = Pressure;
y2 = CellT;
[AX,H1,H2] = plotyy(time,y1,time,y2,'plot');
set(get(AX(1),'Ylabel'),'String','Pressure')
set(get(AX(2),'Ylabel'),'String','Cell T')
set(H1,'color','b')
set(H2,'color','r')
set(AX(2),'xcolor','k','YColor','r')
axis(AX(1),[0 max(time) 0 990]);
axis(AX(2),[0 max(time) (min(CellT)-1) 50 ]);
xlabel('time (s)')
title('Pressure vs. Cell Temperature')



%***********Get the Flowrate, and calculate the
Multiplier***************************%
%****************************************************************************
*******%
%Measurements taken before, during, and after run is performed, then averaged
mflow=inputdlg('Enter the measured flowrate:');
flowrate=mean(Sheet1.data(:,13)); %average of flowrate measured from LABView
multiplier = str2num(mflow{1})/flowrate;
%convert from L/min to g/sec * calibration offset
FlowRate=998.2/60*(Sheet1.data(:,13)* multiplier);



%***********Create Offset Plot, including Markers
etc.*******************************%
%****************************************************************************
*******%
OffsetFigure=figure;
%set(OffsetFigure,'Position',[10 50 1360 768]);%*UNCOMMENT ONLY IF USING IMAGE
IN JOURNAL ARTICLE OR PAPER*%
maxTavg=max(Tavg(2000:length(Tavg)));

[ax, h1, h2] = plotyy(time,Tavg,time,Tamb,'plot');
set(get(ax(1),'Ylabel'),'String','delta T')
set(get(ax(2),'Ylabel'),'String','Ambient T')
set(h1,'color','b')
set(h2,'color','r')
set(ax(2),'xcolor','k','YColor','r')
axis(ax(1),[0 max(time) min(Tavg) maxTavg]);
axis(ax(2),[0 max(time) (min(Tamb)-1) (max(Tamb)+1) ]);



% Setting y-Axis Tics and x-label, title
set(ax(1),'YTick',[min(Tavg):(maxTavg-min(Tavg))/10:maxTavg])
set(ax(2),'YTick',[ceil((min(Tamb)-1)):.5:ceil((max(Tamb)+1))])
xlabel('time (s)')
title('Offset Selection Range')
```

```matlab
% Placing Run Start marker
% Used to both check if enough time was alloted for an appropriate baseline
% to be determined as well as for determining an average initial
% temperature for the run
run_Start_Marker = 1;
while (Pin(run_Start_Marker) < 10)
    run_Start_Marker = run_Start_Marker+1;
end


%************Get Initial/Final Average Cell Temperature and Run
Markers****************%
%***************************************************************************
*******%
if(run_Start_Marker > 10)
    Avg_Initial_CellT = mean(CellT(run_Start_Marker-5:run_Start_Marker+5));
else
%    warndlg(sprintf('The number of points before the beginning of the run is
below threshold.\nPlease check your run_Start_Marker. You may need to set the
initial cell Temperature manually.'),'!! Warning !!', 'modal')
    disp(['Warning!! Only ' num2str(run_Start_Marker) 'points before the
beginning of run.'])
    disp(['You may need to set the initial cell Temperature manually'])
    fprintf(results_file,['Warning!! Only ' num2str(run_Start_Marker) 'points
before the beginning of run.\n']);
    fprintf(results_file,['You may need to set the initial cell Temperature
manually.\n']);
    Avg_Initial_CellT = mean(CellT(1:run_Start_Marker+5));
end

%********************************CHECK HERE********************************%
%********Choose one of the two options below for Avg_Initial_CellT********%
%                        Avg_Initial_CellT=Sheet1.data(1,9);
%                             Avg_Initial_CellT=18.9;

power_Off_Marker = run_Start_Marker;
while (Pin(power_Off_Marker) > 10)
    power_Off_Marker = power_Off_Marker+1;
end

h = waitbar(0,'Calculating CellT Range ...');

%Generates a run end marker, where the temperature has finally reached a
%baseline temperature; used later to calculate average final temperature
run_End_Marker = 0;
CellT_range_modifier=0;
  while(run_End_Marker==0)
      waitbar(CellT_range_modifier/10,h,['Calculating CellT Range ...
Currently:' num2str(CellT_range_modifier)]);
      CellT_range_modifier=CellT_range_modifier+.01;
    for k = power_Off_Marker:length(time)-10
        temp = mean(CellT(k-10:k+10));
        if(temp <= Avg_Initial_CellT + CellT_range_modifier)
            run_End_Marker = k;
            Avg_Final_CellT=temp;
            break;
```

```matlab
        end
    end
  end
  waitbar(1,h,'Calculating CellT Range ...');
  close(h);
  disp(['CellT tolerance range: ' num2str(CellT_range_modifier)])
  fprintf(results_file,['CellT tolerance range: ' num2str(CellT_range_modifier)
'\n']);

%******************************CHECK HERE*******************************%
%**************************Avg_Final_CellT2****************************%

%****************COMMENT THIS SECTION OUT IF ONE OF THE TWO CHOICES FOR
Avg_Initial_CellT ARE CHOSEN
ABOVE*************************************************%
                Avg_Final_CellT2=mean(CellT(run_End_Marker:length(CellT)));
%
                disp(['Avg_Initial vs Avg_Final2: ' num2str(Avg_Initial_CellT)
'|||' num2str(Avg_Final_CellT2)])                                          %
                fprintf(results_file,['Avg_Initial vs Avg_Final2: '
num2str(Avg_Initial_CellT) '|||' num2str(Avg_Final_CellT2) '\n']);
%

%
%    Change for better approximations of Average final Cell Temperature:
%
                disp(['Setting Avg_Initial_CellT (' num2str(Avg_Initial_CellT) ')
to Avg_Final_CellT2 (' num2str(Avg_Final_CellT2) ')'])                    %
                fprintf(results_file,['Setting Avg_Initial_CellT ('
num2str(Avg_Initial_CellT) ') to Avg_Final_CellT2 (' num2str(Avg_Final_CellT2)
')\n']); %
                Avg_Initial_CellT=Avg_Final_CellT2;
%
                h = waitbar(0,'Re-Calculating CellT Range ...');
%
                run_End_Marker = 0;
%
                CellT_range_modifier=0;
%
                  while(run_End_Marker==0)
%
                      waitbar(CellT_range_modifier/10,h,'Re-Calculating CellT
Range ...');                                                              %
                      CellT_range_modifier=CellT_range_modifier+.01;
%
                    for k = power_Off_Marker:length(time)-10
%
                        temp = mean(CellT(k-10:k+10));
%
                        if(temp <= Avg_Initial_CellT + CellT_range_modifier)
%
                            run_End_Marker = k;
%
                            Avg_Final_CellT=temp;
%
```

48

```matlab
                                break;
%                           end
%                       end
%                   end
%                   waitbar(1,h,'Calculating CellT Range ...');
%                   close(h);
%                   disp(['New CellT tolerance range: '
num2str(CellT_range_modifier)])
%                   fprintf(results_file,['New CellT tolerance range: '
num2str(CellT_range_modifier) '\n']);
%
%****************************************************************************
****************************************************************%


% Finding Section of same ambient temperature

Avg_Tamb_sec1 = mean(Tamb(run_Start_Marker:run_End_Marker));

offset_End_Marker = 0;
run_Length=floor((run_End_Marker-run_Start_Marker));
%     run_Length=floor((run_End_Marker-run_Start_Marker)/10);

if(length(time) >= run_End_Marker + run_Length)
    Avg_Tam_sec3=mean(Tamb(run_End_Marker:run_End_Marker+run_Length));
else
    Avg_Tam_sec3=mean(Tamb(run_End_Marker:length(time)));
end


% Find a section of Tamb that coincides on average with the Tamb during the
% run. This section will be a minimum of range_Length points wide. If a section
% cannot be found starting at the end of the run (run_End_Marker) then we
% advance the window by 100 points

k=1.111;
h2 = waitbar(0,['Adjusting run_Length. Currently ' num2str(run_Length) ' ...']);
h3 = waitbar(0,['Calculating Offset Range ...Currently:' num2str(run_Length) '
...']);
while (offset_End_Marker ==0)
    temp_Range=0;
    k=k*.9;
    run_Length=floor((run_End_Marker-run_Start_Marker)*k);
    waitbar((run_Length/((length(time)-run_End_Marker))),h2,['Adjusting run
Length. Currently ' num2str(run_Length) ' ...']);

    while (offset_End_Marker==0 && run_End_Marker+run_Length < length(time))
        temp_Range=temp_Range+.01;
```

```matlab
            waitbar((temp_Range)/(max(roomTemp)-min(roomTemp)),h3,['Calculating
Offset Range ...Currently: ' num2str(temp_Range)]);
    %      disp(['Offset tolerance range: ' num2str(temp_Range)])
            offset_Start_Marker=run_End_Marker-100;

            while (offset_End_Marker==0 && offset_Start_Marker<=length(time-100))
                waitbar(temp_Range/(max(roomTemp)-min(roomTemp)),h3,['Calculating
Offset Range ...Currently:' num2str(temp_Range)]);
                offset_Start_Marker = offset_Start_Marker+100;

                for i = offset_Start_Marker:length(time)-run_Length
                    Avg_Tamb_sec3 =
mean(Tamb(offset_Start_Marker:i+run_Length));
                    if(Avg_Tamb_sec3 >= Avg_Tamb_sec1 - temp_Range &&
Avg_Tamb_sec3 <= Avg_Tamb_sec1 + temp_Range)
                        offset_End_Marker = i+run_Length;
                        break;
                    end
                end
            end

        end


end
   close(h2);
   close(h3);


disp(['Ambient Temp. range for offset section: ' num2str(Avg_Tamb_sec1) 'C'
setstr(176) ' +/- ' num2str(temp_Range) 'C' setstr(176)])
fprintf(results_file,['Ambient Temp. range for offset section: '
num2str(Avg_Tamb_sec1) 'C' setstr(176) ' +/- ' num2str(temp_Range) 'C'
setstr(176) '\n']);


%***********Draw Markers at run start/end, and offset
start/end*********************%
%*************************************************************************************
*******%
x_runStart = [time(run_Start_Marker) time(run_Start_Marker)];
x_runEnd = [time(run_End_Marker) time(run_End_Marker)];
x_offsetStart = [time(offset_Start_Marker) time(offset_Start_Marker)];
x_offsetEnd = [time(offset_End_Marker) time(offset_End_Marker)];

y_line = [-10 50];

line(x_runStart,y_line,'Color', 'm', 'LineStyle', ':')
line(x_runEnd,y_line,'Color', 'm', 'LineStyle', ':')
line(x_offsetStart,y_line,'Color','k', 'LineStyle', '--')
line(x_offsetEnd,y_line,'Color','k', 'LineStyle', '--')
```

```matlab
%***********Calculate Mean of Initial and After run
Offsets***************************%
%************************************************************************
*******%
% Calculate Mean of 10 points pre/post-Pin
if(run_Start_Marker>10)
    before_Run_Offset=mean(Tavg(run_Start_Marker-5:run_Start_Marker+5));
else
    before_Run_Offset=mean(Tavg(1:run_Start_Marker+5));
end

after_Run_Offset=mean(Tavg(offset_Start_Marker:offset_End_Marker));


%*****************************CHECK HERE******************************%
%************************************************************************%
offset=mean([after_Run_Offset,before_Run_Offset]);

% Subtract Offset from All used data (Either using both offsets,
% or just after_Run_Offset
%                           ad_Tavg = Tavg - offset;
ad_Tavg = Tavg - after_Run_Offset;
disp(['dT Offset:        ', num2str(after_Run_Offset)]);
fprintf(results_file,['dT Offset:        ', num2str(after_Run_Offset), '\n']);

%Remove initial cooldown data from Average Temperature
if(run_Start_Marker>5)
    ad_Tavg(1:run_Start_Marker-5)=0;
end


%***********Plot adjusted
Temperature*************************************************%
%************************************************************************
*******%
DeltaTFigure=figure;
%set(DeltaTFigure,'Position',[10 50 1360 768]);%*UNCOMMENT ONLY IF USING IMAGE
IN JOURNAL ARTICLE OR PAPER*%
plot(time/60,ad_Tavg,'b-')
legend('Avg dT')
title('Temperature profile');
xlabel('Minutes');
ylabel('Temperature');
% plot(time,ad_dT2,'r-')
% plot(time,ad_dT1,'k-');


%***********Calculate Ouput Power and Energy
In/Out*********************************%
%************************************************************************
*******%
Pout=(ad_Tavg.*FlowRate*4.183);   % W = (K) * (g/sec) * (J/g*K)

% Calculate Energy in and Energy out
E_in=trapz(time,Pin)/1000;
```

```matlab
%E_in=E_in1(length(Pin))/1e3; % kJ
E_out=trapz(time(1:run_End_Marker),Pout(1:run_End_Marker))/1000;
% E_out=E_out1(length(Pout(1:run_End_Marker)))/1e3; % kJ
% Error in Diff Cal
%energy_percent_diff = (abs(E_out-E_in)/((E_out+E_in)/2))*100;
energy_percent_diff = ((E_out-E_in)/(E_in))*100;
energy_difference = E_out - E_in;



%***********Plot Cell
Temperature******************************************************%
%*************************************************************************
*******%
CellTFigure=figure;
%set(CellTFigure,'Position',[10 50 1360 768]);%*UNCOMMENT ONLY IF USING IMAGE IN
JOURNAL ARTICLE OR PAPER*%
plot(time/60,CellT,'r:');
title('Cell Temperature');
xlabel('Minutes');
ylabel('Temperature');

x_runStart_CellT = [time(run_Start_Marker)/60 time(run_Start_Marker)/60];
x_runEnd_CellT = [time(run_End_Marker)/60 time(run_End_Marker)/60];

line(x_runStart_CellT,y_line,'Color', 'm', 'LineStyle', ':');
line(x_runEnd_CellT,y_line,'Color', 'm', 'LineStyle', ':')
legend('Cell Temperature')


%***********Plot Cell input and output
power*******************************************%
%*************************************************************************
*******%
PowerFigure=figure;
%set(PowerFigure,'Position',[10 50 1360 768]);%*UNCOMMENT ONLY IF USING IMAGE IN
JOURNAL ARTICLE OR PAPER*%
inplot = plot(time(1:run_End_Marker)/60,Pin(1:run_End_Marker),'k-');
hold on;
outplot = plot(time(1:run_End_Marker)/60,Pout(1:run_End_Marker),'r-');

%Add information to plots
legend('Pin', 'Pout')
title(['Energy Difference = ',num2str(energy_difference) ,' kJ, Percent
Difference = ', num2str(energy_percent_diff), '%']);
xlabel('minutes'); ylabel('Power(W)');

% Get the plotted data
x = get(outplot,'XData');
y = get(outplot,'YData');
x2 = get(inplot,'XData');
y2 = get(inplot,'YData');

%Create an uneven length if y (needed to get a usable median value)
if(mod(length(y),2)==0)
    y(:,length(y)+1)=0;
```

```matlab
    end

% Find the index of the median and max of output plot
imed = find(median(y) == y);
imax = find(max(y) == y);
% Find the index of the min and max of input plot
imin2 = find(min(y2) == y2);
imax2 = find(max(y2) == y2);
imed=imed(1);
imax=imax(1);
imin2=imin2(1);
imax2=imax2(1);
%Add calculated energy labels to the graphs
text(x2(imax2),y2(imax2), ['Input Energy =
',num2str(E_in(:,length(E_in))),'kJ'],...
    'VerticalAlignment','bottom','HorizontalAlignment','left','FontSize',8)
text(x(imax)+40,y(imed)+max(y)/2,['Output Energy =
',num2str(E_out(:,length(E_out))),'kJ'],...

'VerticalAlignment','bottom','HorizontalAlignment','left','FontSize',8,'color','
red');

%***********Print plots as well as data pertaining to flowrate and cell
temp***********%
%***************************************************************************
*******%
saveas(OffsetFigure,[PathName 'Results\' FileName '\' FileName '_Offset'],'bmp')
saveas(DeltaTFigure,[PathName 'Results\' FileName '\' FileName '_DeltaT'],'bmp')
saveas(CellTFigure,[PathName 'Results\' FileName '\' FileName '_CellT'],'bmp')
saveas(PowerFigure,[PathName 'Results\' FileName '\' FileName '_PinPout'],'bmp')

disp(['Minimum Offset Length:        ', num2str(offset_End_Marker -
offset_Start_Marker), ' with run Length: ', num2str(run_End_Marker-
run_Start_Marker)])
disp(['Measured Flowrate:            ' mflow{1}])
disp(['Average Flowrate:             ' num2str(flowrate)])
disp(['Flowrate Multiplier used:     ' num2str(multiplier)])
disp(['Avg CellT right before run:  ', num2str(Avg_Initial_CellT)])
disp(['Avg CellT right after run:   ', num2str(Avg_Final_CellT)])

fprintf(results_file,['Minimum Offset Length:        ', num2str(offset_End_Marker
- offset_Start_Marker), ' with run Length: ', num2str(run_End_Marker-
run_Start_Marker) '\n']);
fprintf(results_file,['Measured Flowrate:            ' mflow{1} '\n']);
fprintf(results_file,['Flowrate:                     ' num2str(flowrate) '\n']);
fprintf(results_file,['Flowrate Multiplier used:     ' num2str(multiplier)
'\n']);
fprintf(results_file,['Avg CellT right before run:  ',
num2str(Avg_Initial_CellT) '\n']);
fprintf(results_file,['Avg CellT right after run:   ', num2str(Avg_Final_CellT)
'\n']);
fclose(results_file);
```

Method of Maximal Theoretical Energy Calculation of BLP

(Guibing Zhao, PhD, BlackLight Power, Inc.)

This is an example to show the computational method to determine the maximum theoretical enthalpy of reaction from conventional chemical reactions with respect to the solid fuel calorimetric experiments. Knowing that the starting and ending point of calorimeter experiment used for energy collecting are at the same ambient temperature, the reaction heat can be calculated based on the difference of enthalpy of formation between products and reactants at ambient temperature. Most data for enthalpy of formation can be obtained from "CRC Handbook of Chemistry and Physics," "Lange's Handbook of Chemistry," "Thermochemical Properties of Inorganic Substances," and "Smithells Metals Reference Book." For some specific chemicals, we have to find the thermal data directly from published articles.

Let's consider the reaction system 20g TiC + 5g Mg + 8.3g KH + 12.4g SrBr2, which is 0.333mol TiC + 0.208mol Mg + 0.208mol KH + 0.05mol SrBr2. The products can be identified by XRD analysis, which include

KBr $16.8 \pm 0.1\%$ (437 Å)

$KMgH_3$ $3.9 \pm 0.2\%$ (325Å)

K_2MgH_4 $1.7 \pm 0.2\%$ (638Å)

Mg $11.5 \pm 0.2\%$ (>1,000 Å)

MgSr $3.2 \pm 0.1\%$ (121 Å)

SrH_2 $4.5 \pm 0.1\%$ (>1,000 Å)

TiC $58.5 \pm 0.4\%$ (304 Å)

Heat formations of these products and reactants are shown in Table 1. It is worthy to note that there is no alloy or intermetallic compound of MgSr as the phase diagram of Mg-Sr shows in Figure 1 (Smithells Metals Reference Book). So the closest intermetallic compound, Mg2Sr, was used for the following calculation.

From XRD results, we know that the support TiC does not participate in the reaction. Basically, TiC and WC are very stable supports, which won't participate in the reaction under

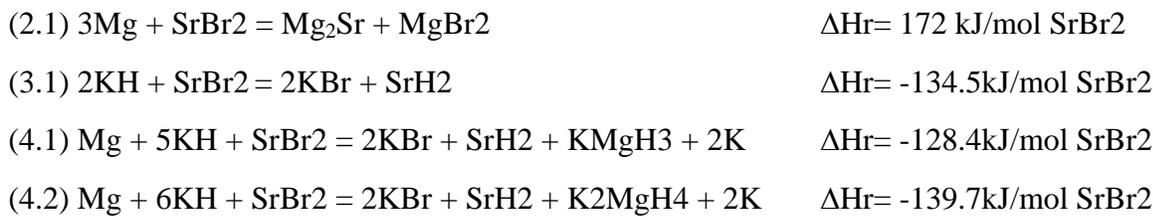running conditions. So, we consider the following reactions based on permutations of the ternary system of $Mg + KH + SrBr_2$:

(1) $Mg + KH$ = products

(2) $Mg + SrBr2$ = products

(3) $KH + SrBr2$ = products

(4) $Mg + KH + SrBr2$ = products

Table. 1 Heat formation of products and reactants of reaction system 20g TiC + 5g Mg + 8.3g KH + 12.4g SrBr2

Chemicals	Heat formation, kJ/mol	Literature
TiC	-184	John A. Dean, Lange's Handbook of Chemistry, 15th Edition, McGraw-Hill (1998).
Mg	0	"
MgH$_2$	75.30	"
MgBr$_2$	524.30	"
KH	-57.7	"
SrBr$_2$	-717.6	"
KBr	-393.8	"
KMgH$_3$	-167.0	A. Klaveness, O. Swang and H. Fjellvåg, "Formation enthalpies of NaMgH$_3$ and KMgH$_3$: A computational study," *Europhys. Lett.*, vol. 76, (2006), pp. 285-290.
K2MgH$_4$	-236.0	A. Klaveness, H. Fjellvåg, A. Kjekshus, P. Ravindran, O. Swang, "A semi-empirical approach to accurate standard enthalpies of formation for solid hydrides," *Journal of Alloys and Compounds,* vol. 469, (2009), pp. 617-622.
SrH$_2$	-179.9	O. Knacke, O Kubaschewski, K. Hesselmann, Eds., *Thermochemical Properties of Inorganic Substances I*, 2nd Edition, Springer-Verlag, 1991.
Mg$_2$Sr	-21.0	M. Aljarrah, U. Aghaulor, M. Medraj, "Thermodynamic Assessment of the Mg-Zn-Sr System, Intermetallics, vol. 15(2), (2007), pp. 93-97.

Then the possible reactions and the corresponding energies, assuming that there is no limiting reagent (i.e. the reagents are a stoichiometric mixture), are:

(1.1) $Mg + 2KH = MgH2 + 2K$ $\qquad\qquad$ ΔHr= 40.1 kJ/mol Mg

(1.2) $Mg + 3KH = KMgH3 + 2K$ $\qquad\qquad$ ΔHr= 6.1 kJ/mol Mg

(1.3) $Mg + 4KH = K2MgH4 + 2K$ $\qquad\qquad$ ΔHr= -5.2 kJ/mol Mg

(2.1) $3Mg + SrBr_2 = Mg_2Sr + MgBr_2$ $\qquad$ $\Delta Hr= 172$ kJ/mol $SrBr_2$

(3.1) $2KH + SrBr_2 = 2KBr + SrH_2$ $\qquad$ $\Delta Hr= -134.5$ kJ/mol $SrBr_2$

(4.1) $Mg + 5KH + SrBr_2 = 2KBr + SrH_2 + KMgH_3 + 2K$ $\qquad$ $\Delta Hr= -128.4$ kJ/mol $SrBr_2$

(4.2) $Mg + 6KH + SrBr_2 = 2KBr + SrH_2 + K_2MgH_4 + 2K$ $\qquad$ $\Delta Hr= -139.7$ kJ/mol $SrBr_2$

From the reaction enthalpies of above reactions, assuming that there is no limiting reagent (i.e. the reagents are a stoichiometric mixture), reaction (4.2) is the most exothermic reaction, which gives–4.84kJ with KH as a limiting reagent of 0.208mol; the second most exothermic reaction is (3.1), which gives –6.73kJ with $SrBr_2$ as a limiting reagent of 0.05mol; the third most exothermic reaction is (4.1), which gives –5.34kJ with KH as a limiting agent of 0.208mol; the fourth most exothermic reaction is (1.3), which gives –0.27kJ with KH as a limiting reagent of 0.208mol. As we can see, reaction (3.1) gives the highest energy by conventional chemistry.

$2KH + SrBr_2 = 2KBr + SrH_2$ $\qquad$ $\Delta Hr= -134.5$ kJ/mol $SrBr_2$, Excess energy: -6.73kJ
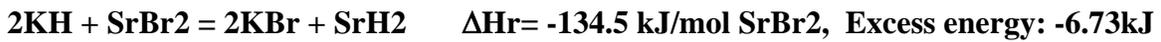
Basically, reaction (4.1) is the addition of reaction (1.2) and (3.1), while reaction (4.2) is basically the addition of reaction (1.3) and (3.1). Because a completion of reaction (3.1) leaves 0.108 mol KH unreacted, the remaining KH may react with Mg as reaction (1.3), which gives another –0.14 kJ. Then, the total maximal theoretical energy is –6.9 kJ. The formation of Mg_2Sr is a very endothermic reaction, and as shown in the product XRD no Mg_2Sr forms during the reaction, therefore, considering reaction (3.1) alone as the most exothermic reaction is conservative.
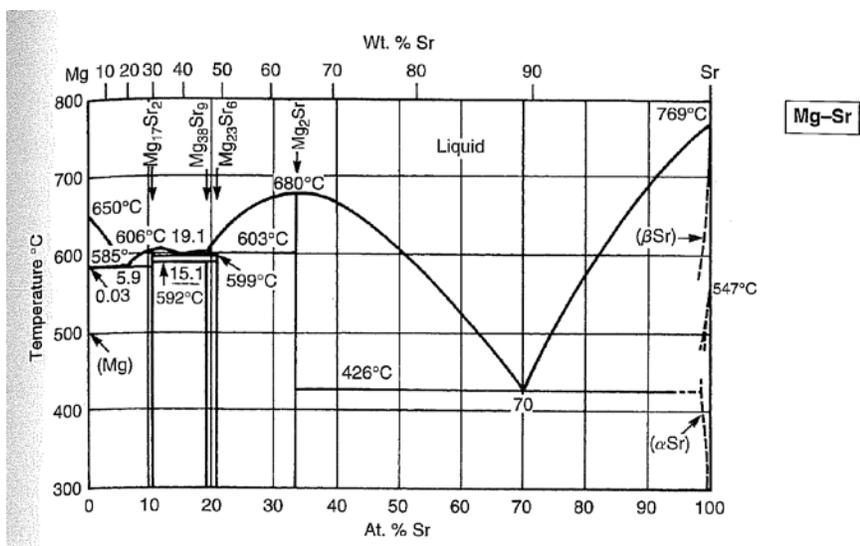

Figure 1. Phase diagram of Mg-Sr