

## Chemomagnetic Measurements of Electric Signals in Combustion Reactions of “Metal-Oxide”

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### Abstract

The affect of an external magnetic field of 0.2 T on the Self-propagating High-temperature Syntheses (SHS) of a mixture of first row transition metals (Fe, Co, Ni, Mn and Ti) and their oxides (Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, MnO and TiO<sub>2</sub>) with solid oxidizer (NaClO<sub>4</sub>) was studied for the first time with respect to the chemomagnetic signals generated of each system during the transformations in the combustion wave under different external conditions. Reactions were carried out in zero and an applied magnetic field of 0.2 T and effect of magnetic fields on the combustion wave propagation were also studied.

### Introduction

In physical inorganic chemistry there are numerous techniques for synthesis. The most common and traditional root for materials synthesis is termed as “Heat and Beat synthesis”. This process involves a solvent-free technique. The major deficiency with this technique is that it is difficult to overcome the solid state diffusion barrier [1]. This barrier is resolved by processing the starting material through repeated grinding, heating, and cooling stages. There is a current search for faster and more economical methods for solid state synthesis [2, 3]. In 1967 Russian scientists (*Merzhanov and his co-workers*) performed the first characterization and identification of *solid flame* phenomenon [4]. This characterization was completed in a gasless solid-state reaction in which both the reactant and product remain in the solid state even at elevated reaction temperatures and has come to be known as Self-propagating High-temperature Synthesis (SHS) [5, 6].

It has been shown that magnetic fields can have significant influence on the chemical reactions in gas, liquid, and solid states. In gaseous reactions the first reports of the influence of an external magnetic field gradient on a candle flame were made in 1840s by Michael Faraday [7]. The results of this experimentation showed that the candle flame is deflected towards a weaker magnetic field. Faraday also noted that gases, such as nitrogen and hydrogen, in air made detours around the magnetic poles, while other gases such as oxygen were attracted towards the stronger field. Flames can be categorized as “diffusion”, “partially mixed” or “premixed” flames, depending on the origin of the oxygen source [8]. The application of an external magnetic field to a diffusion flame can greatly alter the combustion. *Wakayama* [8] has studied that effects by applying an external magnetic field to a methane/oxygen flame and found that the flame became rapidly shorter in length, sharper, and more intense. The flame temperature increased while the magnetic field was in place, yet decreased once the magnetic field was removed and thus returned to its original burning pattern. The flame temperature was observed to vary almost linearly with magnetic

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field gradient, from 790°C at zero field to 900°C at a magnetic field gradient up to 40 T<sup>2</sup>m<sup>-1</sup>. The magnetic field increased combustion when the fuel gas flowed in the direction of decreasing field strength. The magnetic field was only seen to promote combustion for diffusion or partially mixed flames and not premixed flames (air/methane). Magnetic induced air flow can help promote combustion in diffusion flames [9].

The best examples of the effects of magnetic fields on liquid phase reactions can be seen in electro-deposition. A uniform magnetic field altered the formation of copper deposits grown in a flat electrochemical cell. It was shown that the direction of the magnetic field in respect to the cell affected the pattern of the deposition. When no magnetic field was applied to a flat cell of solution CuSO<sub>4</sub>, the electro-deposition and radial growth showed a dense growth pattern. This observation is in contrast to the application of magnetic field perpendicular to the plane of the cell, where a branching spiral pattern was observed and, if the field direction was inverted, the chirality was reversed for the deposition. When the magnetic field was applied parallel to the plane of the cell, a string-like deposition was noted. Coey observed that fields in the range of 1 T could influence the rate of metal deposition in a simple redox reaction. The mechanism behind the noted differences with magnetic field is that the field alters ion concentration near the electrode surface and that the convection currents were enhanced by the Lorentz forces acting on charged species in solution [10, 11].

The research area of solid reactions in an external magnetic field is at an early stage, as most of the work carried out with solid phase chemical reactions in magnetic fields has been done in the last 10 years. SHS reactions have been the one of the main areas of focus in this field. The reaction involves highly exothermic solid state combustions [12]. Common SHS reactions studied in an external field use the element or elemental oxides as a starting material with M+E transforming to ME, where M is the metal or metal oxide and E the non-metal. In 1986 a Russian team reported an increase in the reaction rate and speed in SHS reactions carried out under conditions of applied magnetic field for the formation of titanium carbide. Reaction in an external magnetic field yielded a higher degree of final product formation. Their studies focused on the reaction of ferromagnetic metals: Fe, Co, or Ni with S or Al, and non-ferromagnetic

metals such as Ti, Mo, Cr, Mn, and Cu. This was the first report of the effects of an applied field on SHS reaction [13]. Further work was carried out on SrFe<sub>12</sub>O<sub>19</sub> and showed similar trends [14].

Our team at University College of London (UCL) has also studied the effects an applied magnetic field on the preparation of materials by SHS. Experiments were carried out in high magnetic fields between the range of 0-20 T to investigate the effects of preparation of hard and soft ferrite magnets, for example BaFe<sub>12</sub>O<sub>19</sub> *via* SHS [15].

Using an applied magnetic field has produced results that are easily observable, such as an increased reaction temperature together with a general increase in wave velocity. It was also possible to see that there was a difference in the final phase composition but a marked difference in the microstructure of the final products. Results have shown that the post-annealed products show differences, such as change in magnetization and coercivity. Strong evidence showing that magnetic field has a notable influence on this reaction process was seen with the observation that it is impossible to obtain Nb<sub>5</sub>Si<sub>3</sub> by SHS in absence of magnetic field. It is apparent that ferromagnetic compounds will align with the magnetic field, thus some groups have carried out experiments with the source materials pressed into pellets. This compressed reactant is thought to restrict the alignment seen with the reactions in powders. In 1999 Kirdyashkin and his co-workers worked on pellet reactions of intermetallic compounds such as Ni-Al, Co-S, and Ti-C. A comparison was made with the powdered version of experiments. X-ray microanalysis scans were made and showed a smaller proportion of the initial materials in the final sample. For the reactions which were carried out in applied field, a larger region of each phase was noted in the product [16]. Much of the early work on SHS with applied magnetic fields was completed using powders. The first reported SHS reaction in applied magnetic fields were conducted with ferromagnetic material and were found to be altered by the application of a field. Much of the early explanations to these changes were concentrated on the iron-based reagents aligning to the magnetic field lines; this results in an increase in the thermal conductivity. This explanation can't easily be applied to work done using pressed pellets, as the iron particles are restricted from aligning with the field lines. Kirdyashkin performed reactions in applied and zero magnetic fields and

found a greater degree of product formation in an applied field compared to zero field reactions. Thus their explanation to this observation is that the magnetic field improves the mass transport in the reaction product behind the wave front. It was proposed that the charged particles move as a fluid under the influence of the magnetic field [17, 18].

SHS occur in a high temperature range (1000 – 3500 K), with a narrow wave front that propagates at high velocity and with transforming combustion wave that converts reactant into product. In this process, the high rate of chemical reaction follows rapid change of oxidation states of the reactants and may create movement of charged ions (which is different from zero field reactions) and transient magnetic and electric fields [19-27]. Observations of the electric fields generated by high temperature chemical reaction have been made in the gas phase surrounding burning magnesium particles and in binary systems such as Ti-C and Mo-Si [27]. In SHS process the synthesis wave front may generate a temporal electric field during the combustion of the reactants. It has been reported previously [20, 21] that a voltage difference of up to 1.5 V was observed during several SHS reactions. It is known that in order for an electric field to be generated during SHS reactions, there must be an associated magnetic field. Later, it has been reported at very low detected intensity of the order of nT magnetic fields (chemomagnetic) using a Superconducting Quantum Interference Devices (SQUIDS) magnetometer [28-30]. The formation of electric and magnetic fields by the movement of the combustion front is not currently fully understood. It is, however, clear that these fields are generated as a result of a chemical reaction occurring at the wave front. The shape and intensity of the signals varied according to the systems investigated. Furthermore, the duration of the electric and magnetic field lasted even when the wave-front had passed both the metal probes, indicating that the ionization process that created the magnetic and electric field also occurred in the post-combustion zone possibly due to transient intermediate phases [31-33]. The other factors such as mode of propagation, the Pt (and other materials) electrode separation, initial electric resistance of the sample, the influence of oxidizing agent, and temperature of reaction can have an impact on the shape and intensity of the signal.

During SHS, the combustion reaction causes the formation and motion of charged ions and electrons by convection, diffusion, and thermal emission. The

net ionic currents and displacement during the combustion of metals generated a transient electric potential on the order of 1 V and a weak magnetic field up to 20 nT [34]. The movement of the wave front gave the directional flow of charged species within and behind the combustion front. The transient electric current (field) most likely involved formation of charged species on individual particle surfaces and depended on the sample condition such as temperature, chemical and phase composition, as well as conductivity.

The role of electric and magnetic fields on the combustion of various metals in oxygen to form complex oxides has been studied previously. For the formation of  $\text{LiMn}_2\text{O}_4$  a transient electrical signal of 0.42 V was noticed on passage of the SHS wave through a compacted powder sample whereas the signal for  $\text{SrFe}_{12}\text{O}_{19}$  was 0.40 V,  $\text{PbFe}_{12}\text{O}_{19}$  was 0.45 V, and  $\text{BaTiO}_3$  was 0.5 V [19, 35-36]. In this paper we describe the oxidation of some first row transition metals in the presence of their corresponding oxides and sodium perchlorate. The electrical potential generated by the passage of the SHS wave was determined in zero field and an external magnetic field of 0.2 T. It was noted that the application of the external field had a key role in the magnitude of the observed electrical pulse—this was attributed to interaction between the charged ions generated during the SHS process and the direction of the propagation wave.

## Experimental

All the reagents were obtained from the Aldrich Chemical Company (UK) and used as supplied. The affinity for the metal powders to oxidize in air was sufficiently low in comparison to the time it took to mix, compress, and initiate the reactions. In accordance with that, all the experiments were carried out in air. The pellets were prepared for the simple elemental conversion of metal to its metal oxide. In all the systems (except the Ti-system) used sodium perchlorate ( $\text{NaClO}_4$ ) as an internal oxidizing agent. The addition of sodium perchlorate is necessary, because the SHS reaction proceeds rapidly and simple diffusion of air is not a practical way of supplying oxygen inside of the sample. The oxidation of metals is extremely exothermic and as such, this is the driving force of the reactions. The ratios of the metal, metal oxide, and sodium perchlorate were ascertained after many pre-tests. In general, all the pellets were made to a weight of 0.75 g. Metals and metal oxides were crushed in a

mortar and pestle separately from the sodium perchlorate to prevent pre-ignition. The crushed metal and metal oxide mixture was added to the crushed sodium perchlorate in a gentle manner, to produce homogeneous mixture. The pellets were pressed under one-ton pressure and used within 20 min of preparation, as there is evidence from previous work that the mixture once prepared, it could degrade over time [37].

Details of the preparation procedure were follows. The each sample was used to prepare, under one-ton pressure, a standard pellet of 16 mm in diameter:

*Co/Co<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> pellets.* (6Co+Co<sub>3</sub>O<sub>4</sub>+NaClO<sub>4</sub>)  
Composition. 2.1

*Mn/MnO/NaClO<sub>4</sub> pellets.* (5Mn+MnO+NaClO<sub>4</sub>)  
Composition. 2.2

*Ti/TiO<sub>2</sub>/NaClO<sub>4</sub> pellets.* (Ti+TiO<sub>2</sub>+ NaClO<sub>4</sub>)  
Composition. 2.3

*Ni/NiO/NaClO<sub>4</sub> pellets.* (5Ni+NiO+NaClO<sub>4</sub>)  
Composition. 2.4

*Fe/Fe<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> pellets.* (4Fe+Fe<sub>3</sub>O<sub>4</sub>+NaClO<sub>4</sub>)  
Composition. 2.5

#### Setup for the electric potential measurements

Electric potential measurements were acquired by placing the pellet on a mount, either with the permanent 0.2 T magnets in place or not, depending if the reaction was carried out in zero or applied magnetic field. The pellet was in the vertical position; two platinum electrodes are placed so that they are in contact with the pellet surface and about 6 mm from each other. The electrodes were attached to two wires that are connected to oscilloscope (which acts as a data collection system and direct current (DC) voltmeter). The voltmeter was attached to a computer and the data collection process can be manipulated. A butane burner ignited the reactions and all experiments were conducted in a fumehood. The overall setup is presented in Fig. 1. The collected data are plotted on a software package (Microsoft Excel) with voltage on the y-axis and time on the x-axis. Thus the plot produced describes the change in voltage generated by passage of SHS wave past two platinum electrodes over time. Such plots are collected for all the studied systems in zero and applied magnetic field for comparison.

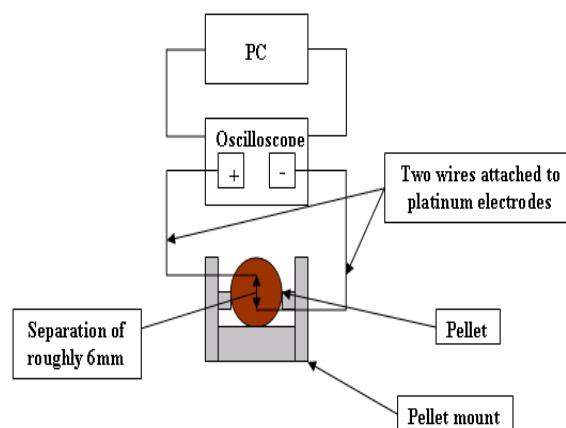


Fig. 1 General setup for acquisition of electric potential measurements.

#### Electric potential System 1

Experiments were conducted under system 1 wherein we investigated the electric field generated during the combustion of various systems of first row transition metals (Fe, Co, Mn, Ni and Ti), and their associated oxides, which act as a moderator, using a purpose-built apparatus. All the systems also contained sodium perchlorate as an internal source of oxygen and their electric potentials were measured. Experimental setup consisted of the previously described normal pellet mount and two NdFeB magnets which were inserted into the mount, to allow experiments to be conducted in and out of a 0.2 T magnetic field. The pellet mount had a steel container with three pairs of accurately spaced holes on either side of the mount. One pair of holes on opposite sides of the container was used to allow for the attachment of the nickel frame to the mount. Two vacant holes on one side of the steel mount were used to allow two insulated copper wires to pass through. The ends of the copper wires were attached to two platinum probes, which physically came into contact with the pellet. The probes were separated by about 5-6 mm. The copper wires were attached to an oscilloscope, which acted as a data collection system and a DC voltmeter. Finally, the oscilloscope was connected to a computer where the data was analyzed.

This setup was later modified slightly in order to give easier access to the electrodes, to facilitate their cleaning. Constant manipulation of the platinum electrodes resulted in the erosion of the insulation around the copper wire, which occasionally resulted in a short circuit. The

experimental setup is shown below in Figure 2 and Figure 3.



Fig. 2. Front view of experimental setup for electric potential measurements



Fig.3. View of experimental setup from above for electric potential measurements. This image was taken before the combustion of the pellets was initiated by a butane torch.

## Electric Potential system 2

Electric potential measurements were performed in an identical fashion except that rather than system 1 where the Pt original electrodes were foil-like and shaped in a dome fashion. The electrodes were shaped and flattened to allow greater contact with the pellet. It was noted in system 1 that an oxide layer formed on the electrodes. In repeated experiments, this problem was ameliorated by regular cleaning. In system 2 a less regular cleaning cycle was required.

## Results and Discussion

The results obtained from the electric potential measurements using foil type electrodes was tabulated for each of the systems investigated. The table below gives average results of repeated experiments on all the systems studied together with an experimental error (standard deviation). The average peak of voltage and the average duration for the electric potential signal for all the systems in an external applied magnetic field experiments was an average of four repeat measurements, while three results were averaged to give the peak voltage in zero field. Table 1 also summarizes the results obtained for six applied field and 5 zero field experiments from system 2 using flat electrodes, with the indicated standard deviation, for average peak electric potential seen and the duration of the peak. These experiments were completed to confirm the differences seen in the applied field reactions for nickel, as was determined from system 1. These experiments were also designed to improve on the previous techniques used and to verify results with a higher success rate for the reactions and lower experimental error.

**Table 1**

Average peak voltage together with the duration of signal for all the systems containing Metal/Metal oxide/ $\text{NaClO}_4$  for repeat experiments performed in System 1 and in System 2 in zero field and applied magnetic field of 0.2 T.

| Chemical composition                           | Zero field        |                              | Applied 0.2 T magnetic field |                              |
|--|-------------------|------------------------------|------------------------------|------------------------------|
|  | Peak Voltage (mV) | Duration of Peak Voltage (s) | Peak Voltage (mV)            | Duration of Peak Voltage (s) |
| Ni/NiO/ $\text{NaClO}_4$                       | 44(1)             | 4.1(0.5)                     | 141(15)                      | 7.0(1)                       |
| Mn/MnO/ $\text{NaClO}_4$                       | 82(4)             | 3.8(0.3)                     | 155(8)                       | 8.6(1.6)                     |
| Co/ $\text{Co}_3\text{O}_4$ / $\text{NaClO}_4$ | 73(7)             | 9.8(2.6)                     | 170(1)                       | 16.4(1)                      |
| Ti/ $\text{TiO}_2$ / $\text{NaClO}_4$          | 98(28)            | 0.4(0.2)                     | 215(74)                      | 1.6(0.4)                     |
| Fe/ $\text{Fe}_3\text{O}_4$ / $\text{NaClO}_4$ | 160(56)           | 1.8(0.9)                     | 252(38)                      | 4.1(1)                       |
| Ni/NiO/ $\text{NaClO}_4$ (L)                   | 56(15)            | 4.7(2.3)                     | 94(17)                       | 7.8(1.6)                     |



### Results obtained for the Fe/Fe<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system

From the Table 1 and Figure 4, the average peak potential for the iron-containing system when external magnetic field of 0.2T was applied during the SHS process was 252 mV whereas without an applied field the peak potential was about 160 mV. This data indicate that applying an external magnetic field of 0.2 T affected the electric potential generated by SHS wave. In this particular system, when a field was applied, the peak potential increased by 57%. It has been reported previously that the duration of electrical signal is related to the local reaction rate and fluxes in the charge carriers [38]. For example, if the duration of electric potential signal in an applied field is 4.1 seconds and in zero field – 1.8 seconds, the local reaction rate is faster in zero field reaction, possibly indicating that the applied field reaction results in a more complete reaction. The significantly higher value of 4.1 seconds for the electrical potential reported for an applied field is notably different and suggests that application of a 0.2 T field has an effect on the duration of the electric potential signal and on the maximum peak potential seen. If the local reaction rate proceeds for longer in the applied field, the prolonged reaction over a localized area resulted in a more complete oxidation reaction and generation of a larger electric potential signal.

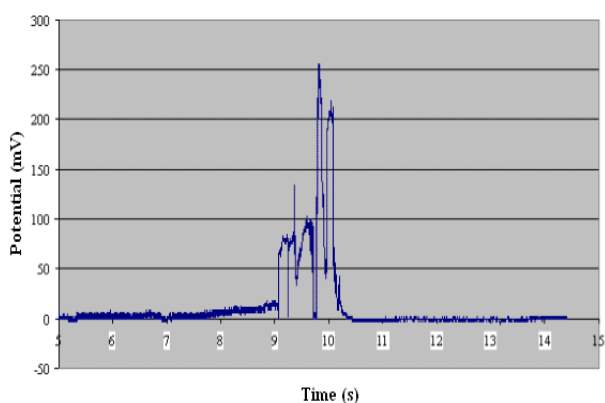


Fig. 4. Typical electric potential signal seen for the Fe/Fe<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system (Applied field 0.2 T).

It is known that the mode and stability of the propagation wave front affects the electric potential signal. The mode of propagation for the Fe/Fe<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system in an applied field was observed to be oscillating (reaction pulses forward) and in zero field was noted as a steady mode (uniform propagation mode). The signal may also

be affected by the melting of the reactant, as the oxygen penetration (oxygen ions) through the sample would be lowered by the melting of the metal or metal oxide. Both iron and magnetite have melting points between 1540 and 1600°C and the highest average maximum temperature seen for the applied reaction as judged by thermal imaging was at 1464 +/- 19°C which is below the melting point of the starting material. Additionally, sodium perchlorate started melting and decomposing at ~400°C providing the oxygen required for the oxidation process.

### Results obtained for the Ti/TiO<sub>2</sub>/NaClO<sub>4</sub> system

The data in Table 1 and Figure 5 indicate that for the Ti/TiO<sub>2</sub>/NaClO<sub>4</sub> system, the average peak potential in an applied magnetic field was 215 mV and in zero field - 98 mV. The oxidation of titanium powder in an applied field reaction generated more than two times greater signal than zero field reaction. The electric potential signal generated for the applied magnetic field reaction lasted 1.6 seconds and in the zero field reaction the signal lasted 0.4 seconds. It has been previously reported that for a mixture of 8 % of Ti powder to 92 % TiO<sub>2</sub>, the peak electric potential seen for a zero field reaction was about 120 mV. This value compares relatively well to the average maximum peak potential reported here of 98 mV. Applied field reactions showed the same trend where the localized reaction was slower, possibly indicating a more controlled and complete reaction. In both cases SHS waves were shown to propagate in a steady fashion, without an effect on the signal duration. As stated earlier, there was however a large difference in the electric potential measurements, which can be attributed to the external field applied to the reactions. From Figure 5, it can be seen that the signal was quite smooth, with respect to the shape of the signal, which is another indication of steady wave propagation. Due to the high exothermicity, there was significantly more oxide deposited on the electrode. The reaction was fast and vigorous, emitting sparks from the reactant pellet as the reaction proceeded. Many holes were seen in the post-SHS pellet, possibly as a result of sodium perchlorate addition. The reason for the observed sparking during the reaction could be due to ejection of NaCl from the pellet as the SHS wave propagated through. In previous experiments without sodium perchlorate, holes did not develop. These observations imply that the

reaction sparking may be due to the sodium perchlorate converting to NaCl, which is then ejected from the pellet during the reaction. The holes were also observed in the iron system, which also contained sodium perchlorate. The melting point of titanium is 1668°C and titanium dioxide is 1870°C. Thermal imaging experiments were carried out on the titanium system for the maximum temperature of reaction and were averaged to 1633 +/-4°C, for the green mixture that did not contain sodium perchlorate. The average maximum temperature in the experiments with absence of sodium perchlorate was comparatively lower due to lack of oxygen. It was observed that melting and deformation of the pellet did occur, as in some cases the pellet moulded to the nickel mount during the reaction. From the electric potential signal, it was seen that for applied field reactions, in some cases, the initial negative peak expanded with time as a result of melting and slower diffusion of the oxygen ions to the site of combustion and slower propagation of the reaction.

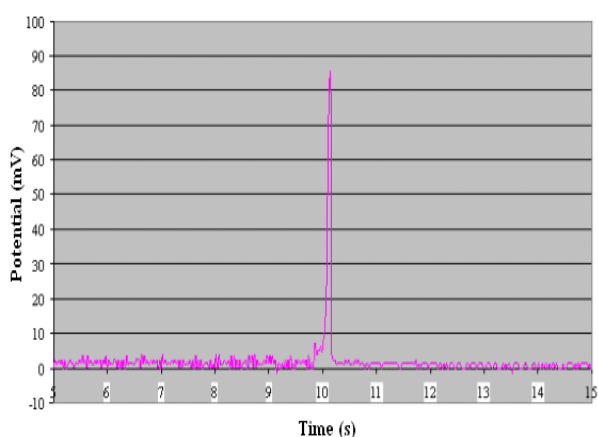


Fig. 5. Representative electric potential signal seen for the Ti/TiO<sub>2</sub>/NaClO<sub>4</sub> system (Zero field).

#### **Results obtained for the Co/Co<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system**

The maximum peak potential for an applied magnetic field seen for the Co/Co<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system was 170 mV and for a zero field was 73 mV, so an applied reaction generated a signal with a 58 % greater electric potential than the zero field reactions. The error for this system is very low. The electric potential signal generated for applied field reaction lasted 16.4 seconds, whereas the zero field reaction the signal lasted 9.6 s before the signal fell to a resting potential. The difference seen was more than two standard deviations, suggesting that the

duration of applied field signal was significantly longer, as was noted in the previous experimental systems reported above. It has been previously reported that electric signal of 80 to 100 mV for a mixture of 25 % of Co powder to 75 % Co<sub>3</sub>O<sub>4</sub>, which is comparable to the value of 73 mV reported in our experiments for the similar system where sodium perchlorate was added to the reaction mixture. Like the other systems reported, the applied electric potential was higher than the zero field potential. The post-SHS pellet was often fragmented for the Co/Co<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system, which sometimes caused the electrodes to lose contact in both zero and applied field. Cobalt is ferromagnetic and so in an applied field the pellet was also fragmented during some of the experimental trials. The fragmentation of the pellets generally occurred in post-SHS samples, but in some instances it was noted to have occurred during combustion. These factors resulted in many unsuccessful combustion attempts. In this system an unsteady mode of propagation was displayed. The spinning mode was observed for both applied and zero field reactions. As the spinning mode has two vectors V<sub>x</sub> and V<sub>y</sub>, we can say that wave is propagating at a constant velocity in the y direction and unsteady manner in the x direction. The spinning mode is a steady mode of propagation in the y direction. From Figure 6 it can be seen that generated signal for this system was quite steady and did not have large oscillations. The melting point of cobalt is 1495°C and for cobalt dioxide - 1933°C and the average maximum temperature seen in the thermal section for this system was 1271 +/- 17°C. Melting was not a factor for these experiments.

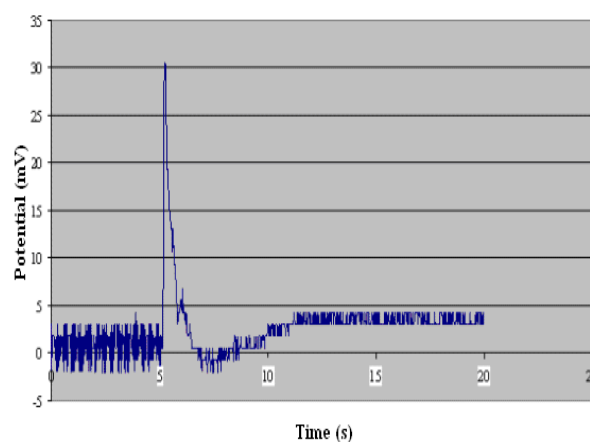


Fig. 6. Representative electric potential signal seen for the Co/Co<sub>3</sub>O<sub>4</sub>/NaClO<sub>4</sub> system (Zero field).

**Results obtained for the Mn/MnO/NaClO<sub>4</sub> system**

The applied magnetic field reaction produced an maximum electric potential of 155 mV, compared to 83 mV produced by the zero field reaction. These results are more than three standard deviations apart and there was more than 50 % higher peak voltage generated by applying a magnetic field of 0.2 T. In these experiments, however, the pellets were very fragile and fell apart very easily when handled during the experiments. It was found that by pressing the pellets twice, made them more rigid. The electric potential signal generated for the applied field reaction lasted 8.6 s and zero field reaction the signal lasted 3.8 s before the signal falls to a resting potential - there is about a three standard deviation between the results and the trend continues of applied field reactions lasting longer than zero field process. It has been previously reported that for a LiMn<sub>2</sub>O<sub>4</sub> system, there was a peak voltage of 420 mV. This value was higher than reported here for the Mn/MnO/NaClO<sub>4</sub> reaction system of 83 mV, but duration of the electric signal in previous work was of 1.4 seconds which compares to 3.8 s seen for zero field reaction in our experiments. These two systems are, however, somewhat dissimilar and thus accurate comparisons may not be consistent between these results.

Applied and zero field reactions for the Mn/MnO/NaClO<sub>4</sub> system both showed a steady mode of wave propagation. Figure 7 shows that the signal generated for this system was quite steady and did not have large oscillations. The melting point of manganese is 1495°C and manganese dioxide decomposes at 1650°C. The average maximum temperature seen for this system was 1325°C +/- 54°C, thus melting is not a factor for these experiments. There was no evidence of a growing negative peak.

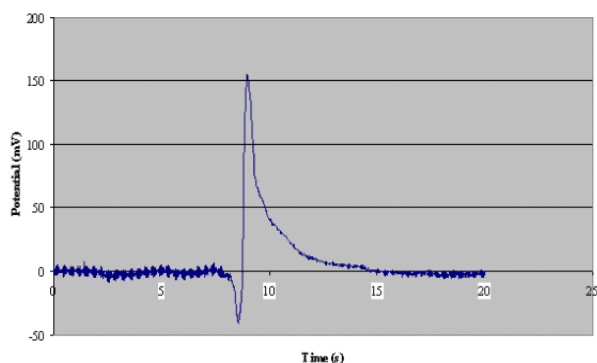


Fig. 7. Representative electric potential signal seen for the Mn/MnO/NaClO<sub>4</sub> system (Applied field 0.2 T).

**Results obtained for the Ni/NiO/NaClO<sub>4</sub> system**

The peak potential for an applied reaction was roughly 141 mV and was nearly three times the value of reactions conducted in zero field. Previously electrical potential measurements have been reported on combustion of single nickel particles [40]. These results were not comparable to our Ni/NiO/NaClO<sub>4</sub> 0.75 g pellet reaction observed in this work, but they reported seeing a maximum voltage of 0.25 V and roughly 0.2 second duration of the signal. Here it was seen that the reaction was partially quenched by the nickel frame of the mount by absorbing the heat produced during the reaction. This quenching caused termination of the SHS wave before it had passed both electrodes. It was found that elevating about 30 % of the pellet above the nickel frame allowed enough thermal energy to be produced to compensate for the heat lost as a result of conduction from the pellet by the nickel frame. The electric potential signal generated for the applied field reaction in Ni/NiO/NaClO<sub>4</sub> system with foiled electrodes lasted 7.1 seconds and for the zero field reaction the signal lasted 4.1 seconds before the signal fell to a resting potential. There was about a three standard deviation difference between the results and the duration of the applied signal was longer. In Ni/NiO/NaClO<sub>4</sub> system with flattened electrodes the applied magnetic field signal lasted for 7.8 seconds and the zero magnetic field signal lasted for 4.7 seconds. Again, the localized reaction time for applied magnetic field reaction was longer and indicated a more complete reaction as greater electric potentials were seen. Both the data acquired in the Ni/NiO/NaClO<sub>4</sub> was relatively similar (Figures 8 and 9). It can be seen that the signal generated for this system was quite steady and did not have large oscillations, which is consistent with a steady mode of propagation.

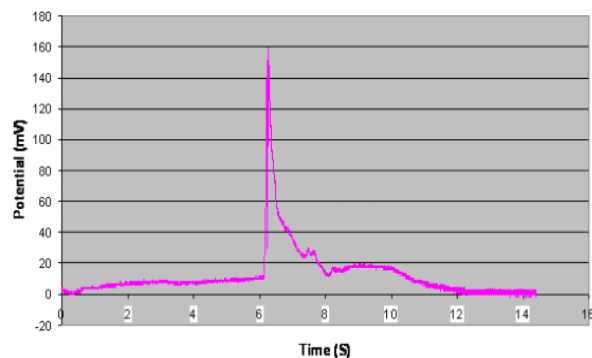


Fig. 8. Representative electric potential signal seen for the Ni/NiO/NaClO<sub>4</sub> system; foiled electrode (Applied field 0.2 T).



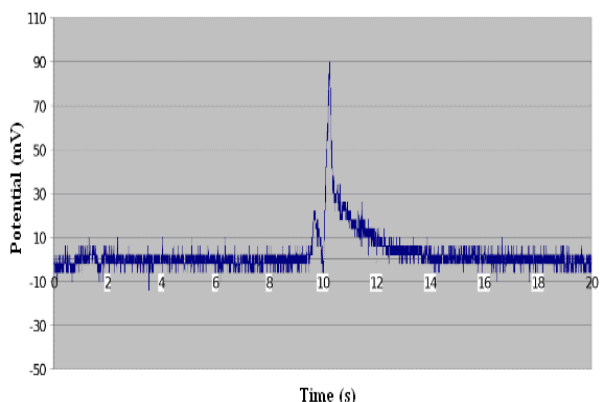


Fig. 9. Representative electric potential signal seen for the for the Ni/NiO/NaClO<sub>4</sub> system; flatened electrode (Applied field 0.2 T).

Figure 10 represents a summary of all the work performed for systems 1 and 2 for the electric potential signal in and out of an applied magnetic field 0.2 T, as the SHS wave propagated through the pellet; error bars for each system are indicated.

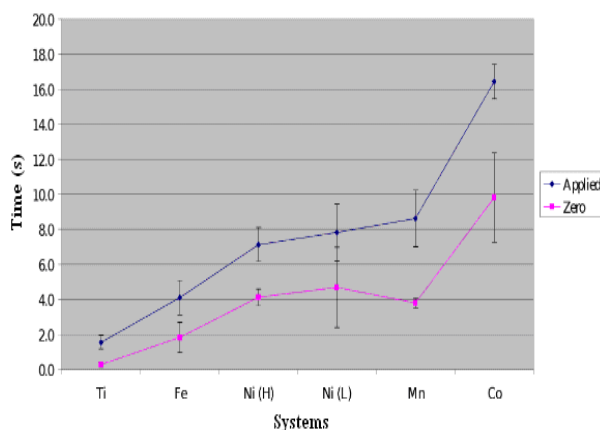


Fig. 10. Graphical representation of the results obtained for the duration of electric potential signal for the oxidation of pressed powders of metal and metal oxides for experiments carried out in system 1 (H) and system 2 (L) with the associated error bars.

In reviewing of all the above presented data, it is possible to conclude that all the systems analyzed showed a significant difference between applied magnetic and zero field experiments, and in all cases a greater potential was seen for an applied field process. A few times difference was seen in some cases. From the produced results it is possible to make a conclusion that for all the systems applied magnetic field reaction had a higher measured potential. The smallest difference was seen in the iron and manganese systems. The

greatest errors were seen in the iron and titanium systems. These were the only two systems that produced holes in the post-SHS pellets. The duration of the electric signal was longer for the applied field reaction in all the systems; a one and half of times greater duration for Ni and Co in an applied field reaction with more than two times greater duration of the potential signal for Fe and Mn and a four times greater reaction duration for the Ti system. These data suggest that the duration of the electric potential signal was affected by the application of an external magnetic field and that the duration of the electric potential and the magnitude of the potential signal seem to be greatly increased by applying a magnetic field of 0.2 T to the SHS reaction. These experiments describe some of the first work to measure an electric potential on a pelletized samples in an applied magnetic field 0.2 T and the results show that significant differences were seen. The field varied according to the systems under investigation. The duration of the electric signal corresponded to the availability of oxygen, suggesting that if an internal oxidizing agent was present then the duration of the signal was smaller. These findings have implications on the localized reaction rate.

It can be seen that applying an external magnetic field increased the signal duration and the time that the electric potential was observed. Applying an external magnetic field could manipulate the transient electric and magnetic fields generated by the combustion reaction itself. The external magnetic field had an additive or a subtractive effect on the internal magnetic and electric fields generated, raising or lowering the reaction rate, exothermicity and had an effect on the completeness of the reaction.

### *Factors that affect electric potential signal*

Currently, it is speculated that certain factors affect the shape, size and duration of the associated electric potential seen in ionization reactions. Several groups have also measured the corresponding magnetic and electric potential signals for different systems [34, 39]. The duration of magnetic signal is thought to depend on the local reaction rate and the flux of the charge carriers. The modes and stability of the propagation front affect the signal observed. For the combustion of Nb in oxygen, an oscillatory temporal voltage and magnetic field was observed. The pulsating nature of the combustion front of Mg in oxygen generated

a high frequency oscillation of the signal seen for both the magnetic and electric fields. The shape of signal seen was depending from the mechanism of combustion. It was thought that the large initial negative peak measured for systems containing peroxides could be the result of the peroxide decomposition. Taken together, this finding might indicate that there was an excess of oxygen ions. The electric signal progressively became positive, possibly indicating the consumption of oxygen ions during the reaction [40-42]. Different oxidizing agents were investigated to determine if the signal generated was a result of thermoelectric effect. Using certain oxidizing agents created higher exothermicity for the combustion reaction but did not result in a larger signal being seen, indicating that the signal was a result of the chemical reaction and ion diffusion rather the temperature effect on the electrode probes [34]. The electric signal may also be affected by the melting of the reactant, as the penetration of the oxygen ions through the sample would be lower as the melting of the metal or metal oxide occurred. This effect can be seen as the initial negative signal changed with increased reaction temperature. Where the combustion temperature exceeded the melting point of one of the reactants, the oxygen ions diffusion was slowed down and resulted in a greater negative signal observed. It has been observed that when the Pt probes are separated by a short distance, a consistent measurement of the electric potential signals was seen, both in shape and in amplitude. Separation of the electrodes by 8-15 mm affected the observed electric potential signal by obscuring the shape and amplitude of the wave. A separation of approximately 6 mm was sufficient to allow good signal strength, yet modest enough to eliminate errors associated with the voltage persisted for a longer time span than was seen for narrower separation between the Pt probes [35]. Experiments completed on single metal particles showed that when the initial oxide film was thick or when the ambient oxygen concentration was low, the electric signal persisted until the maximum temperature was achieved. The magnitude and duration of the electric potential generated was highly dependent on the availability of oxygen at the reaction zone. As such, a lower concentration of oxygen at the reaction site transformed the unipolar 2 V signal to a bipolar one. A bipolar signal is a signal with a positive and negative component to it. Increasing the thickness of the initial oxide film lowered the rate of oxygen diffusion to the

shrinking reaction core and led to the bipolar potential [40]. The current consensus in this work is that the electric field is due to formation of an electric double charge layer across the oxide film. The adsorption of oxygen molecules on the surface could lead to generation of electron holes and  $O^{2-}$  ions and the different diffusion velocities of the charge carriers in the oxide shell could create a temporal electric charge on the particle surface. Complete separation of the electrical charges was estimated to occur when the oxide film thickness was large enough and therefore close to the Debye screening length. Particles with an initial oxide film of the Debye thickness of about 10 nm generated high unipolar electric voltages. If the initial oxide layer was a thicker film, it then produced a bipolar electric signal and/or oscillations of smaller amplitude. This effect was due to the slower diffusion of the oxide ions to the reaction surface.

## Conclusion

This work described experimental analysis of the difference between conducting oxidation reactions in applied 0.2 T magnetic field and zero field using the SHS process. The systems examined were first row transition metals and their cognate oxides, including Fe/Fe<sub>3</sub>O<sub>4</sub>, Ni/NiO, Ti/TiO<sub>2</sub>, Mn/MnO, and Co/Co<sub>3</sub>O<sub>4</sub> with addition of sodium perchlorate as an internal solid oxidizer. These systems were chosen as they were simple oxidation reactions and were expected to yield easily understandable mechanisms to give a better understanding of the role that these components may play in more complex reactions. It can be suggested that more complete reactions were seen during the experiments performed in applied magnetic fields. Differences in the mechanisms by which these reactions occurred indicate that the electric potential was generated by the oxidation reaction and these will have a magnetic component that interacts with the externally applied magnetic field associated with them. The external magnetic field could act as a method of tuning the internal chemical reaction by interacting with the electromagnetic fields generated during the reaction. This process can have an additive or subtractive effect, dependent on the orientation of the pellet to the applied field. As the mobile ions progressed in the direction of The SHS wave propagation, magnetic component stays in a perpendicular direction. As the SHS reaction proceeds via ionic intermediates and the

propagation wave has a directional nature an ionic pulse - or in effect a slow movement of charges occurs. The movement of charges is effected by external magnetic field which possibly results in a more complete reaction and preferential phase composition. A possible explanation as to how the magnetic field influences the SHS reaction could be by imagining that the SHS reaction produces charged particles that move in one direction due to the rapidly advancing wave front. The net movement of charges in one direction produces a magnetic field, thus this chemically induced magnetic field, interacts with the applied 0.2 T magnetic field causing more charged particles to move in the direction of the bulk charged species. Therefore with more charged species aligned in the direction of the net movement of charges, the chemically induced magnetic field would be bigger, therefore explaining why a greater electric potential is seen for reactions done under conditions of applied field.

The magnetic field of the applied external field could have a fine tuning effect on the chemically induced magnetic field. Charged species are generated during the SHS process and move in the direction of the SHS wave front and if the charged species interact with the externally applied magnetic field. Then it can be said that the charged species align with external field causing a uniform mixture at the reaction site, that results in a more exothermic reaction and a greater proportion of product due to increased permeability of the oxygen to the reaction site. This would also indicate why in nearly all cases the repeat results of applied magnetic field reaction were similar in value when compared to the same reaction in zero fields where the repeats were not as close together. Thus, the externally applied magnetic field has a profound effect due to its ability to fine tune the reaction as it occurs at the wave front.

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