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Thermochemical cycle of a mixed metal oxide for augmentation of thermal energy storage in solid particles

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Abstract

Solid particle heat transfer and storage media have been shown to be able to operate at temperatures >1000°C in concentrated solar power (CSP) applications, much higher than the operational limit of 600°C for current state-of-the-art molten nitrate salt heat transfer fluid. Solid particles can be endothermically reduced by direct exposure to concentrated solar energy, thus absorbing and storing thermal energy beyond that possible with sensible heating alone. The particles can then be oxidized exothermically at a later time, releasing the stored chemical heat and effectively augmenting the thermal energy storage capacity of the solid particles. A mixed metal oxide spinel material that reduces in the temperature range of interest (1000-1200°C) has been examined for applicability to this thermochemical energy storage concept. A description of this application, prospective materials, and details of the thermochemical cycle are presented. The heats of reduction and oxidation for the thermochemical cycle have been determined for various operating conditions to evaluate the amount of thermal energy that may be stored. Various possible implementations of this augmented storage concept are considered, and alternate means of controlling the thermochemical cycle are explored.

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1. Introduction

There is a fundamental limit on the amount of energy that can be obtained from finite fossil fuels, and carbon emissions from energy generation and consumption are rising [1]. Solar and wind energy can provide renewable and carbon-free electricity, but there is a concern with the transient nature of these energy sources [2]. Therefore, a way to store energy in order to match demand will be required for a reasonable long-term energy solution. Concentrated solar power (CSP) uses mirrors to concentrate the sun's rays onto a receiving material, heating it to a higher temperature. This thermal energy is then used to drive a power cycle for the production of electric power. There are various configurations of CSP technologies, including central receiver systems (also called "power towers"). In these systems, a field of mirrors (called heliostats) tracks the sun in two axes and reflects the image onto a receiver on top of a tower. Dish systems use mirrors arranged in a 3-dimensional parabolic shape to reflect the sun to a central point at the focus. These systems track the sun in two axes and can achieve very high solar concentration ratios, leading to higher temperatures and higher efficiencies than other CSP technologies.

1.1. Thermal Energy Storage

Thermal energy storage (TES) is a key benefit of CSP, as it mitigates the issue of solar transience by decoupling power production and solar irradiance. This means that power production can continue when the sun is not shining, such as passing clouds or at night. The simplest type of TES is sensible energy storage, where thermal energy is stored in a material by raising its temperature. Another method of storing energy is thermochemical energy storage, which uses a reversible chemical reaction to store thermal energy: energy is absorbed via an endothermic reaction, and then released via an associated exothermic reaction. This method offers some of the highest energy density values of any of the thermal energy storage methods, since the energy is stored in chemical bonds [3].

There is currently no commercial technology that takes advantage of thermochemical cycles to store thermal energy at high temperature. Thermochemical energy storage using an ammonia synthesis reaction ($NH_3 + \Delta H \leftrightarrow 1/2\ N_2 + 3/2\ H_2$) has been studied extensively [4]. This technology has some drawbacks: the N_2 and H_2 gases must be stored at high pressure, making storage of these gases difficult and costly [4]. Additionally, the ammonia synthesis reaction is constrained by very slow ramp rates, limiting this technology's ability to provide power to match varying loads [4]. Another concern is the exergetic efficiency loss of the system. The high-temperature ammonia-splitting reaction occurs at ~700°C [4], whereas the low-temperature synthesis reaction occurs at ~500°C. This means that the high-grade process heat loses 11.5% of its exergy (useful heat) even if no actual energy is lost. Furthermore, since the reactants are stored at near-ambient temperatures, they must be re-heated before undergoing the exothermic reaction to release the stored thermochemical energy, leading to efficiency losses. Another process has also been studied which uses a chemical cycle based upon the decomposition of sulfuric acid [5], where the decomposed H_2SO_4 produces SO_2, which is sent to a disproportionation reaction to produce pure sulfur. The sulfur is then combusted to produce heat to produce electricity [5]. However, this cycle features indirect heating of the reactants and a corrosive environment that can make the cycle difficult to operate efficiently.

There has also been some prior work done concerning reduction and oxidation cycles for thermochemical energy storage with metal oxides. Multiple metal oxide cycles at various temperatures have been explored both theoretically and experimentally, with cobalt oxide showing strong re-oxidation reactivity [6]. Mixed metal oxides have also been explored, with a ~10% addition of Fe_2O_3 to Mn_3O_4 showing improved re-oxidation [6]. Packed bed configurations were simulated using a cobalt oxide cycle; the pressure drop over packed beds were found to be significant, and tradeoffs were identified in operation at different temperatures [7].

1.2. High Temperature Operation

The collection and concentration of the solar resource (e.g., heliostats) generally compose over half of the capital cost of the entire solar plant [8]. Because of this, any reduction in the number of heliostats needed for a given level of power production will have a significant impact on the overall capital cost of the plant. If the thermal-to-electric

conversion efficiency is higher, then less thermal energy is required to produce the same amount of electric energy, meaning fewer heliostats are needed.

There are some issues with high temperature operation, however, which can limit the boost to performance. While it seems trivial to indicate that higher temperature operation will lead to higher thermal losses, it is especially worth noting for the temperatures being considered (≥650°C). Conduction and convective heat losses scale linearly with temperature while thermal radiation scales with T^4. Another thermal loss issue with operation at higher temperature is when the system has stopped and must restart. The transient nature of solar power means that the solar collection must restart at least once a day, and sometimes even more often. When the receiver begins starting up in order to begin operating at design temperatures, the equipment itself must first be warmed up from the ambient temperature [9]. This is not necessarily accounted for when analyzing the system at the design point, this can constitute quite a significant loss for plant operation, since it must be incurred at least once a day.

2. Thermochemical Augmentation Concept

An energy storage concept that is of interest would be a material that stores heat both sensibly and thermochemically. In this way, the reactants would be stored at the high temperature of sensible thermal energy storage, but augmented with a thermochemical cycle. This concept avoids the issue of cooling and re-heating reactants down to near-ambient temperature for storage, but can still take advantage of the significant energy storage density benefits of thermochemical energy storage systems. Gas-solid reactions are of interest due the ease of product separation (relative to gas-gas separations).

2.1. Hercynite Reaction

It has been shown at the University of Colorado (CU) that cobalt or nickel ferrite can react with an alumina (Al_2O_3) substrate to undergo a redox cycle through a hercynite ($FeAl_2O_4$) pathway: $(Co,Ni)Fe_2O_4 + 3\ Al_2O_3 + \Delta H \leftrightarrow (Co,Ni)Al_2O_4 + 2\ FeAl_2O_4 + 1/2\ O_2$. This redox cycle has been studied as a solar thermochemical water splitting cycle, where the oxidation is done with H_2O or CO_2 in order to produce H_2 or CO [10]. However, this cycle is also of interest for thermochemical energy storage for solar thermal power generation if the endothermic reduction forward reaction can be used to absorb extra heat in the solar beam, which can be released later. This allows energy dense thermal energy storage at temperatures of interest to solar thermal power production. Additionally, the hercynite cycle solid materials are dark in color, meaning that they could be effective in a direct absorption receiver.

2.2. Potential System Concepts

There are various concepts that could be potentially useful for this type of thermochemical augmentation. One way would be an augmentation of a solid particle receiver (SPR), where the solid particles serve as the heat transfer and thermal storage media. These particles could be formulated to be thermochemically cycled in order to absorb additional heat via an endothermic reduction reaction in the receiver, and then release that additional heat through the exothermic oxidation reaction to produce steam. The main benefit to this type of system is that the reactive solid particles are both the heat transfer fluid and storage media, eliminating the need for additional transfers of energy, each of which will necessarily impart an energetic or exergetic penalty, lowering the system efficiency. However, the solid particles are difficult to move and control, which can introduce potentially significant parasitic loads and particle breakage. Furthermore, an SPR configuration is best suited for use with highly-dense sintered particles [11]. This high density could lead to reaction conversion limitations of the material, since potentially only the surface of each particle will be able to react.

Another potential system configuration for this type of thermochemical energy storage is for dish systems. The basic storage concept is shown in Figure 1. In this type of system, a gaseous heat transfer fluid is used to transport the heat from the receiver to the storage and power generation systems. Solid particles that are used for thermal energy storege can be reduced to absorb additional heat. The main advantage here is that the proposed system here

would allow for more energy to be stored in a smaller volume and mass than would otherwise be possible, making it much more realistic to place the storage on the dish structure itself [12]. However, when the solid material is stationary, the heat transfer to the particles will not be nearly as good. Furthermore, the temperature difference necessary for heat exchange means that each time energy goes through a heat exchanger, it will lose exergy due to the fact that it will be at a lower temperature. This is a general issue for any sort of indirect storage system (where the heat transfer fluid is not the storage media). This issue will need to be considered in any possible system design and consideration.

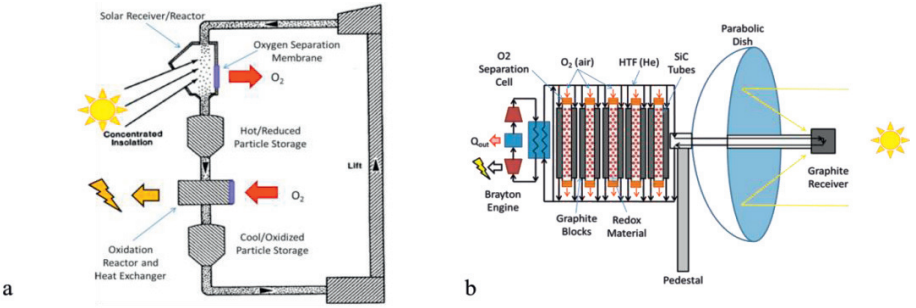


Figure 1: Schematic Diagrams of (a) Augmented Solid Particle Receiver (base schematic diagram from [11]) and (b) Dish Concept (both schematics not to scale)

2.3. Oxygen Control and Separation

Aside from operating temperatures, the equilibrium of the thermochemical cycle depends on the partial pressure of oxygen. The oxygen content of the solar reactor can be controlled via an ion transport membrane solid electrolyte oxygen separator (ITM SEOS), which uses an electrochemical cell to transport oxygen ions [13]. ITM SEOS stacks are generally operated at 800-900°C (600°C minimum), which is necessary to ensure oxygen ion conductivity in the electrolyte [13]. The cell can de-oxygenate a gaseous feed stream even when the oxygen in the feed is very dilute (~2 ppm) [14]. This is especially helpful for the reduction reaction, when temperatures are highest and oxygen concentrations must be kept low.

3. Theoretical Exploration of Hercynite Cycle

In order to examine the effect of a thermochemical boost on a sensible thermal energy storage system, it is useful to examine various reaction chemistries at various conditions and make predictions about the amount of energy that can be stored. Here, the FACTSage^{TM} 6.2 Gibbs free energy minimization software is used to predict reaction chemistries and heats of reaction [15].

Equilibrium predictions were made for isothermal reduction-oxidation cycles at various temperatures, and these are shown in Figure 2. These calculations estimate the extent to which thermochemical energy can be stored with no temperature change, using only the presence or absence of oxygen to control the reaction (see Figure 2). The thermochemical heat storage is being evaluated as an augmentation to the sensible energy that can be stored in the solid material. The sensible energy at the indicated temperatures and O_2 concentration study was compared to the thermochemical heat of reaction. The thermochemical fraction of energy storage increases at higher temperatures from the heat of reaction, despite the fact that the amount of sensible energy at higher temperatures will be higher as well. This reaches a maximum at 18.53%, which occurs at 1400°C at 0% O_2.

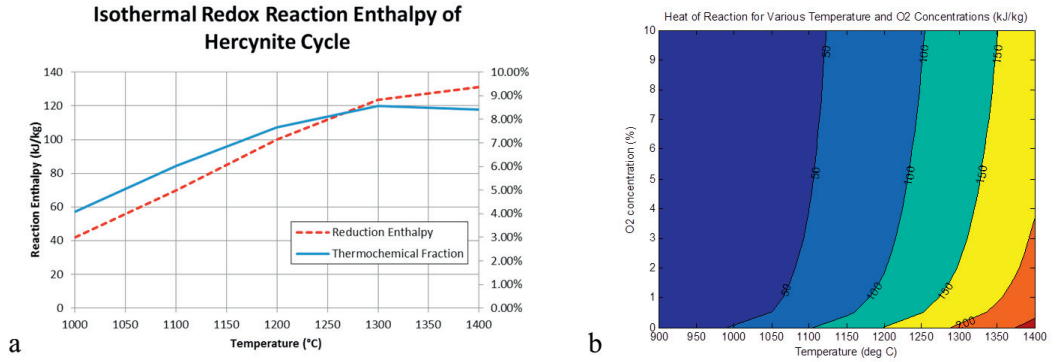


Figure 2: (a) Isothermal Thermochemical Energy Storage for Hercynite Cycle Using Changes in Equilibrium Compositions and Enthalpy with Comparison of Reduction Enthalpy to Total Energy (Sensible and Thermochemical) in Solid Material and (b) Thermochemical Reaction Enthalpy Change for Stoichiometric Hercynite Cycle Material Based on Thermodynamic Equilibrium Calculations at Temperatures between 900°C and 1400°C and Oxygen Concentrations between 0% and 10% with Balance Inert Argon

The temperature difference from 23°C to >1000°C is very large, and so the sensible energy of this temperature difference is subsequently very large. Operational limits for materials in use in the system may restrict operation from such an extreme (>1000°C) temperature change. It may be that the system would be operable (if not optimal) if the temperature swing was more limited. As such, it is illustrative to compare the predicted thermochemical heat of reaction to a more limited enthalpy. As a limiting case on the other end of the spectrum would be a minimum enthalpy case, in which the minimum temperature is 900°C. In this case, the sensible energy is only the enthalpy of the solid material from 900°C to the indicated temperature of interest. Comparing the thermochemical heat of reaction to this limited energy reveals some implications which are somewhat counterintuitive. The maximum fraction of the thermochemical energy to sensible energy is 66.08% and occurs at 950°C and 0% O_2. This is due to the fact that 950°C has the smallest non-zero sensible energy above 900°C. This is somewhat surprising due to the fact that the extent of reduction is very low. As such, there will not be a very large enthalpy change to compare to the sensible energy.

This illustrates an important point that the temperature change over which a thermochemical cycle operates should match the overall operational temperature change of the system itself as closely as possible. This is not necessarily saying that a system using the hercynite cycle would only operate at temperatures down to 900°C; operating at such a high rejection temperature means that there is a very large amount of potential exergy not being utilized. Thermochemical energy storage is more useful relative to the sensible energy at temperatures of interest if the temperature range of the thermochemical cycle is relatively close to the sensible operational temperature range, especially for reactions that do not react fully.

There is one issue that is somewhat unique to the hercynite cycle. The predictions above are a single enthalpy change value based on the amount of material, which is then corrected for the mass of that amount of material to find a specific heat in terms of energy per unit mass. The stoichiometry of the hercynite cycle has 4 moles of solid material ($CoFe_2O_4$ + 3 Al_2O_3) for a full reaction; this fairly large amount of material makes the specific heat of the reaction much smaller. Other solid oxide reactions that react to evolve the same amount of oxygen with only a single mole of material may then have a larger reaction enthalpy, even when normalized per unit mass.

4. Experimental Exploration of Hercynite Cycle

The previously discussed theoretical predictions provide useful information about the possibility of thermochemical energy storage, but experimentation is needed to actually demonstrate this. An experimental

exploration was done to validate theoretical predictions and demonstrate the possibility of thermochemical augmentation to the sensible energy storage in a solid material.

4.1. Sample Preparation and Methods

The sample powder analyzed in this study was prepared via a solid state synthesis method. The component materials were weighed out and milled for 8 hours with zirconia milling media of nominal diameter of 1.5 mm in ethanol. After drying, the resulting powder was then placed into a furnace to calcine at 850°C for 2 hours. The "Base" material was formulated using Sigma-Aldrich® Cobalt(II) oxide, -325 mesh,; Sigma-Aldrich® Iron(II,III) oxide, powder, <5µm, 95%; and Sigma-Aldrich® Aluminum oxide, powder, <10 micron, 99.7%, in the stoichiometric ratio of 1:1:3 for $CoO:Fe_3O_4:Al_2O_3$. Though not strictly in the nominal stoichiometric ratio, the Fe_3O_4 powder was used due to material availability. A compositional study in FACTSage™ was done to ensure that the oxidation states of the iron oxide at elevated temperatures will be similar for Fe_2O_3 and Fe_3O_4, and this correction was made for theoretical comparisons. Additional samples, hereafter referred to as Alumina-6 and Alumina- 9, were made using molar ratios for $CoO:Fe_2O_3:Al_2O_3$ of 1:1:6 and 1:1:9, respectively. These samples used Alfa Aesar® Iron(III) oxide, 325 mesh, 99.5% (metals basis), instead of the Fe_3O_4 powder used above, but otherwise were similar to the base powder in composition and synthesis method.

The samples were then imaged using a JEOL JSM-6480LV SEM. Additionally, a Scintag PAD X diffractometer from Thermo Electron, Inc., (Waltham, MA) was used to analyze samples in-situ at high temperatures. Sample powders were analyzed in alumina crucibles for TGA/DSC analysis in a NETZSCH® STA 409 C/CD, with a TG-DSC sample carrier with radiation shield and type S thermocouples. For reduction, 60 sccm of argon gas was used, and 40 sccm of air with 20 sccm argon was used for oxidation steps. Ramp rates between temperatures vary, but are between 5 and 15 K/min. The hold times at each temperature also vary, but always include a 15 minute period at the oxidation temperature to allow the DSC signal to steady before air is introduced. The TGA and DSC data were analyzed using NETZSCH® Proteus® – Thermal Analysis – Version 5.2.0 software.

4.2. Experimental Results

The results of the TGA/DSC data analysis are shown in Figure 3. Each horizontal line in Figure 3 shows a single heat of oxidation value obtained at the reduction and oxidation temperatures indicated at the endpoints of the horizontal line. Lines that appear as single points are for isothermal redox.

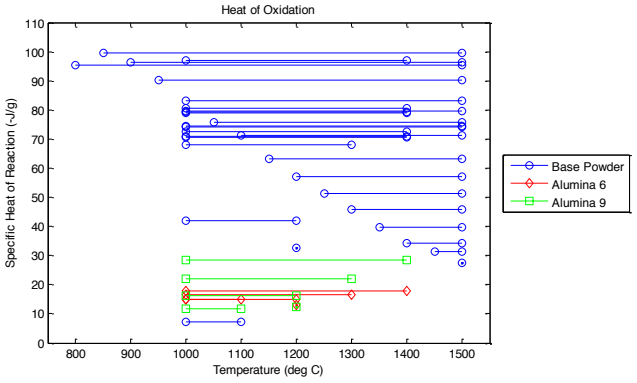


Figure 3: Heat of Oxidation for Base, Alumina-6, and Alumina-9 Material Formulations at Indicated Reduction and Oxidation Temperatures

It can be easily seen that the longer lines (indicating larger temperature changes between reduction and oxidation) have higher heats of reaction per unit mass. This is due to the fact that with larger temperature changes, the conversion of each reaction is higher, meaning that the observed enthalpy change will be larger. Additionally, there

are clear differences between the Base and Alumina formulations, due to the fact that the Alumina samples have additional aluminum oxide. As can be seen from Figure 3, the Alumina-6 and Alumina-9 formulations have lower observed oxidation enthalpy changes than in the Base powder formulation. Another important thing to note is that the data displayed in Figure 3 spans a wide range of reaction enthalpies, depending on reduction and oxidation temperatures.

The experimental values were compared to theoretical predictions from FACTSage^{TM}, and this is shown in Figure 4. It can be seen that the relative differences between the theoretical and experimental values are of different magnitudes for the fractional masses and reaction enthalpies. As such, it is not enough to simply scale the partial conversion achieved in the experimental results by the theoretical fractional mass change. It can be seen visually that scaling the reaction enthalpy values in Figure 4 by the extent of reaction from the mass change will not make the experimental values match the theoretical values. This suggests that kinetic limitations alone are not enough to explain the differences.

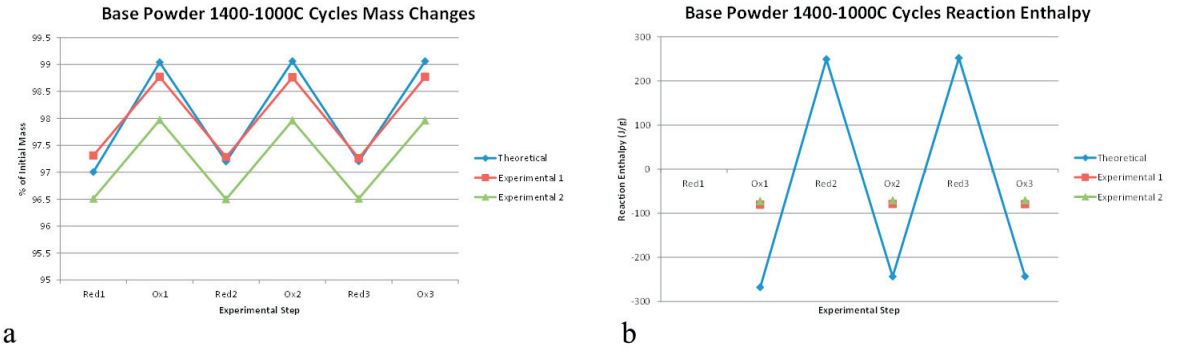


Figure 4: Comparison of (a) Mass Changes and (b) Reaction Enthalpies from Experimental Results for Base Powder 1400-1000 Cycles to Theoretical Predictions. The tie-lines are added as a guide to the eye only, and do not represent any sort of underlying phenomena or interpolation.

If the experimental value difference cannot be explained by purely kinetic limitations, there must be other factors to consider. It is of interest to consider if the expected chemistry is actually occurring. This can be done by analyzing the various XRD patterns shown in Figure 5. As can be seen, the initial scan shows the presence of Al_2O_3 and $CoFe_2O_4$, as would be expected. The scan also shows hematite (Fe_2O_3) and cobalt oxide which did not calcine fully. Above 1200°C, the aluminum oxide peaks reduce in intensity significantly, and peaks signifying hercynite ($FeAl_2O_4$) and cobalt aluminate ($CoAl_2O_4$) appear. There is a noticeable shift of the spinel peaks upon the introduction of air. The aluminum oxide peaks regain some of their intensity but the cobalt ferrite peak does not clearly reappear. Instead, the peaks associated with the spinel phase (hercynite and cobalt aluminate) shift to the right, while other peaks do not. This is potentially due in part to changing temperature; the reduced scan was taken at 1400°C, whereas the oxidation scan was done at 1000°C. The alumina peaks do not shift as much due to the lower coefficient of thermal expansion of the alumina. Furthermore, a change in oxidation state causing structural changes will also affect the spinel peaks from partial re-oxidation. Further testing is necessary to isolate these effects.

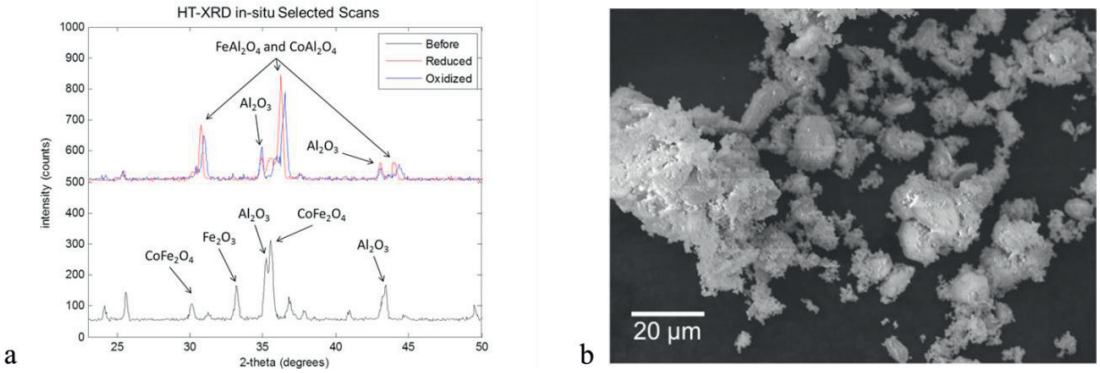


Figure 5: (a) High Temperature in-situ X-Ray Diffraction Patterns for "Base" Sample Powder for Scans on the Initial Calcined Sample, Under Reducing Conditions at 1400°C, and After Re-Oxidation with Air at 1000°C and (b) SEM Image of Base Powder

There are likely two main reasons for this discrepancy between the expected and observed experimental results. The first is the fact that the sample powders were made by solid state synthesis. Small powder sizes were used and the powders were well-mixed, but there was no other mechanism to ensure that the reactants were in good contact, which can greatly limit the reaction extent. The possibility for this effect can be seen in Figure 5; the sample powders are loosely packed at best, and there are obvious voids between particles. However, it was seen previously that the smaller reaction extent is not enough to fully explain this difference. If the reactants are not in good contact in the proper amounts, then other unexpected reactions can occur. These reactions can contribute to or detract from the observed enthalpy changes in the samples. Since it is unknown what materials were in contact and in what proportions, these reactions are difficult to predict and account for by a well-mixed thermodynamic equilibrium calculation. This is not to say that the hercynite cycle does not re-oxidize as predicted; it has been previously shown that the hercynite reaction does occur as expected and can be cycled repeatedly [10, 16]. This was done with reactants made via atomic layer deposition (ALD), and so the reactants would be ensured very good contact [16].

5. Potential New Materials

Based on the low specific energy density of the Hercynite cycle, it is useful to examine other potential solid oxide reactions for thermochemical energy storage, and FACTSage^{TM} predictions of various other solid oxide reactions are given in Table 1. This is by no means a complete list that encompasses all possible reaction temperatures, but rather meant to give an idea of the wide range of reaction cycle possibilities.

Table 1: Predictions of Isothermal Reaction Enthalpies for Other Solid Oxide Thermochemical Reduction Reactions, Including the Currently study of the Hercynite Cycle for Reference

Reaction	$\Delta H_{reduction}$
$Fe_2O_3 \leftrightarrow 2/3\ Fe_3O_4 + 1/6\ O_2$	471 kJ/kg
$Co_3O_4 \leftrightarrow 3\ CoO + 1/2\ O_2$	901 kJ/kg
$Mn_2O_3 \leftrightarrow 2/3\ Mn_3O_4 + 1/6\ O_2$	205 kJ/kg
$Mn_3O_4 \leftrightarrow 3\ MnO + 1/2\ O_2$	853 kJ/kg
$CoFe_2O_4 + 3\ Al_2O_3 \leftrightarrow CoAl_2O_4 + 2\ FeAl_2O_4 + 1/2\ O_2$	131 kJ/kg

Aside from the higher specific heats of reaction than the Hercynite cycle, it is important to note the temperatures at which reduction begins and ends. The hercynite reaction begins at about 800°C, but is not fully complete at 1400°C. By contrast, a composition study (similar to the one described for the hercynite cycle) was done for the manganese oxide reaction cycle. As can be seen in Figure 6, the full reduction reaction occurs over a much smaller temperature range than the hercynite cycle. This can be very promising for thermochemical energy storage, since such a small temperature change is needed to drive the reaction, increasing the potential exergetic efficiency. As was

discussed previously, it is not necessarily a requirement that the entire reaction conversion be used to store thermochemical energy, as energy can still be stored isothermally (see Figure 2 for isothermal energy storage with the hercynite cycle), but it can be very beneficial for high exergetic efficiency values.

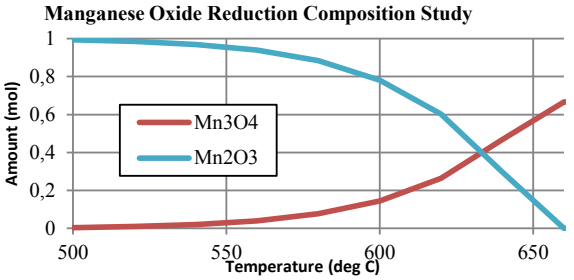


Figure 6: Predicted Composition of Solid Components at Thermodynamic Equilibrium for Manganese Oxide Reaction at Transition Temperatures and with Inert Atmosphere

It must be stressed that these values do not mean that these other reactions will necessarily be more useful in a system, as there can be other problems associated with these reactions. For example, pure iron oxide will sinter readily, which could severely limit the surface area of reactive material. Additionally, while some materials such as cobalt oxide look promising, the cost of the reactive material may be prohibitively high. These and other factors must be considered when designing a potential system for study, but these higher thermochemical energy storage numbers do indicate reactions of interest for future study.

6. Conclusions

The use of a thermochemical cycle to augment sensible energy storage has been suggested for concentrated solar power. A thermochemically active material that is stored at the temperatures of interest would utilize both thermochemical and sensible energy storage, increasing the energy storage density while avoiding the need to cool and re-heat the active material. This could drastically reduce the storage mass and volume necessary to store an amount of thermal energy, thus lessening issues with thermal loss at high temperatures.

This possibility using the so-called “hercynite cycle” has been explored using theoretical thermodynamic equilibrium predictions. Isothermal reaction enthalpy values were compared to the sensible energy at the indicated temperatures, and it was found that the thermochemical to sensible energy ratio ranged from 4.25% at 1000°C to 9.2% at 1400°C. The thermochemical enthalpy change for reactions from 900°C to 1400°C and 0-10% oxygen concentrations were also found to range from 0.32% to 18.5% of the sensible energy at 900°C and 1400°C, respectively.

Various material formulations were made via solid state synthesis and analyzed in a TGA/DSC. The resulting oxidation enthalpy changes spanned an order of magnitude, ranging from 10 – 100 kJ/kg. Material formulations with excess aluminum oxide tended to have lower heats of reaction per unit mass due to the additional inert material. Powders produced via solid state synthesis do not have guaranteed reaction contact, meaning that the thermochemical reactions cannot fully occur, and introducing the potential for side reactions not predicted by thermodynamics; this is corroborated by unexpected XRD patterns.

While an 18.5% thermochemical boost to sensible energy from the Hercynite cycle is not insignificant, it is unlikely that this will prove to be beneficial to process operation due to additional parasitic losses. The exact thermochemical boost that is needed is not known, because it depends on the particular system and associated parasitic losses. Additional metal oxide reduction reactions were explored using similar techniques for comparison purposes, and these reaction enthalpies were found to be higher per unit mass than the hercynite cycle. Additionally,

these other materials were found to have narrower temperature changes necessary for nearly complete reaction conversion, which can be beneficial in terms of exergy.

7. Future Work

In-depth system modeling would allow for a thorough analysis of potential trade-offs in the system, and an exploration of ideal operating conditions. Information gleaned from the explorations done in this study could be used to inform system models. System models could identify beneficial operating conditions and further inform future explorations (both theoretical and experimental) of other materials and reaction cycles for thermochemical storage. Furthermore, an exploration of other materials to identify the best possible material for this application would be useful. Lastly, while some potential system configurations were discussed above, an exploration of actual operation using these types of different solid particle beds would help to quantify potential issues and illustrate a better path forward.

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