METAL SULFATE WATER-SPLITTING THERMOCHEMICAL HYDROGEN PRODUCTION CYCLES

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ABSTRACT

A compilation of 350 thermochemical cycles to split water and the subsequent assessment of these cycles has pointed to several metal sulfate cycle as viable candidate cycles with high thermal efficiency. However, studies of the hydrogen generation step in two of the cycles showed alternate side reactions that make this class of metal sulfate cycles a poor candidate for further study.

KEYWORDS: solar hydrogen, thermochemical cycles

1. Introduction

Thermochemical cycles (TC’s) are efficient means to split water and produce hydrogen (H2). Solar thermal devices are especially suitable to drive some of the TC’s as they can provide a heat source in excess of 1500°C, which is the reaction temperature required by many TC’s. Many water splitting solar TC’s typically consist of a high temperature endothermic dissociation step to reduce an oxidized metal into its reduced form plus oxygen. The high temperature step couples with one or more low temperature exothermic reactions that react the reduced metal with H2O to spontaneously generate H2. An example of such a TC is

Dissociation: \[ \text{ZnO(s)} \rightarrow \text{Zn(g)} + \frac{1}{2} \text{O}_2(g) \quad 2000^\circ \]

H2 generation: \[ \text{H}_2\text{O(g)} + \text{Zn(s)} = \text{ZnO(s)} + \text{H}_2(g) \quad 500^\circ \]

Net reaction: \[ \text{H}_2\text{O} = \text{H}_2 + \frac{1}{2} \text{O}_2 \]

A number of solar TC’s have been calculated to have thermal efficiency of 50% or higher, which makes them among the most efficient H2 generating processes known. The Solar Hydrogen Generation Research (SHGR) project was established by the US Department of Energy to conduct research and development into the feasibility of using concentrated solar powered TC’s to produce H2. The team members are from UNLV, General Atomics, Sandia National Lab, University of Colorado, and Argonne National Lab. The program’s goal is to identify TC’s that can be demonstrated in a solar- H2 pilot plant. As a first step of this process, group members have performed an extensive search to find all the TC’s that have been proposed in the literature. So far, more than 350 TC’s have been identified and assessed. The results are listed in a publicly accessible, interactive database (http://shgr.unlv.edu).

2. Thermochemical Cycle Evaluation

An evaluation was undertaken to screen all published TC’s that will work best with high temperature solar devices. The goal is to select 10 TC’s for laboratory verification which will then yield one to three cycles for pilot scale studies. The screening process took place in two phases. In phase I, more than 350 TC’s
that were found in the literature were evaluated based on i) economic and practicality considerations, ii) applicability to solar devices, iii) level of previous effort and iv) environmental and safety issues. The highest scoring 67 cycles were then selected for phase II evaluation. In this phase, a detailed flow sheet was constructed for each TC to determine the cycle thermal efficiency [1, 2]. HSC software was employed to perform the thermodynamic calculations [3]. One of the key issues encountered during this evaluation process was the existence of side reactions that had not been accounted for in many of the previous works. Their existence can result in a bypass of the proposed H\textsubscript{2} generation step, which can render the TC invalid. Further details will be discussed in the next section.

Table 1 list the TC’s with the highest calculated thermal efficiency from the phase II studies. They can be classified into five groups: sulfuric acid, metal sulfate, volatile metal oxide, non-volatile metal oxide and hybrid chloride. These TC’s have been selected for experimental verification in the laboratory. Among them, the metal sulfate cycles are of great interest because the high temperature reaction step has been calculated to be favorable at around 1000°C, significantly lower than most other non-hybrid TC’s:

\[
\text{Dissociation: } \text{MSO}_4(s) = \text{MO}(s) + \frac{1}{2}\text{O}_2(g) + \text{SO}_2(g) \quad 1000 - 1100^\circ C
\]

\[
\text{H}_2 \text{ generation: } \text{MO}(s) + \text{SO}_2(g) + \text{H}_2\text{O}(g) = \text{MSO}_4(s) + \text{H}_2(g) \quad 25-250^\circ C
\]

\[M = \text{Mn, Cd, Ba}\]

The applicable metals include manganese, cadmium and barium. For the metal sulfate cycles to qualify as legitimate H\textsubscript{2} solar TC’s, both the high temperature and the low temperature reactions will have to have favorable kinetics and thermodynamics. Since the low temperature H\textsubscript{2} formation step is not well documented in the literature, the goal of this work is to explore the reaction conditions that can produce H\textsubscript{2} at a practical rate for the metal sulfate cycle.

Table 1. Calculated efficiency of the qualified TC with which experimental work will proceed [1].

<table>
<thead>
<tr>
<th>Class</th>
<th>TC</th>
<th>Efficiency (LHV)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid cycles</td>
<td>Hybrid Sulfur</td>
<td>51%</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>Sulfur Iodine</td>
<td>45%</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>Multivalent sulfur</td>
<td>42%</td>
<td>1570</td>
</tr>
<tr>
<td>Metal Sulfate cycles</td>
<td>Cadmium sulfate [4]</td>
<td>55%</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Barium molybdenum sulfate [5,6]</td>
<td>47%</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Manganese sulfate [4]</td>
<td>42%</td>
<td>1100</td>
</tr>
<tr>
<td>Volatile Metal Oxide cycles</td>
<td>Zinc Oxide</td>
<td>53.2%</td>
<td>2200</td>
</tr>
<tr>
<td></td>
<td>Hybrid Cadmium</td>
<td>53%</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>Cadmium Carbonate</td>
<td>52%</td>
<td>1600</td>
</tr>
<tr>
<td>Non-volatile Metal Oxide cycles</td>
<td>Iron Oxide</td>
<td>50%</td>
<td>2200</td>
</tr>
<tr>
<td></td>
<td>Sodium Manganese</td>
<td>59.1%</td>
<td>1560</td>
</tr>
<tr>
<td></td>
<td>Nickel Manganese Ferrite</td>
<td>52%</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>Zinc Manganese Ferrite</td>
<td>52%</td>
<td>1800</td>
</tr>
<tr>
<td>Other</td>
<td>Hybrid Copper Chloride</td>
<td>49%</td>
<td>550</td>
</tr>
</tbody>
</table>
Side Reaction Calculations

To understand the relationship between the \( \text{H}_2 \) formation step and other side reactions, the free energy of all the plausible related reactions products were calculated. For the \( \text{H}_2 \) generation step, the thermodynamics imply a favourable \( \Delta G^* \) for the reaction for all three oxides and the results are shown in Table 2. The reaction appears to be more favourable thermodynamically at low temperatures but the kinetics will be considerably lower at these conditions.

Table 2. \( \Delta G^* \) for the \( \text{H}_2 \) generation step in three metal sulphate cycles.

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \Delta G^* ) at 25°C</th>
<th>( \Delta G^* ) 100°C</th>
<th>( \Delta G^* ) 200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>-13.65</td>
<td>-11.17</td>
<td>-5.26</td>
</tr>
<tr>
<td>Cd</td>
<td>-13.44</td>
<td>-11.24</td>
<td>-5.66</td>
</tr>
<tr>
<td>Ba</td>
<td>-69.40</td>
<td>-67.06</td>
<td>-61.31</td>
</tr>
</tbody>
</table>

The \( \text{H}_2 \) generation step as proposed above is essentially a sulphur oxidation step transforming \( \text{S}^{4+} \) to \( \text{S}^{6+} \), resulting in the formation of \( \text{H}_2 \). Alternatively, there are two sulphur reaction paths that can also lead to MSO₄ formation, yet which do not evolve \( \text{H}_2 \),

\[
3 \text{MO} + 4 \text{SO}_2 + \text{H}_2\text{O} = 3 \text{MSO}_4 + \text{H}_2\text{S} \\
2 \text{MO} + 3 \text{SO}_2 = 2 \text{MSO}_4 + \text{S}
\]

The \( \Delta G^* \) values (per mole of \( \text{SO}_2 \)) for the above reactions at 25°C and 100°C are listed in Table 3. The \( \Delta G^* \) values are more negative than those listed in Table 2 for some of the \( \text{H}_2 \) generation reactions (Mn and Cd). Hence, the disproportionation reactions are thermodynamically favoured compared to the \( \text{H}_2 \) generation reaction.

Table 3. \( \Delta G^* \) for the \( \text{H}_2\text{S} \) and \( \text{S} \) formation in alternate sulphate formation reactions.

<table>
<thead>
<tr>
<th>metal</th>
<th>( \Delta G^* ) at 25°C</th>
<th>( \Delta G^* ) 100°C</th>
<th>( \Delta G^* ) at 25°C</th>
<th>( \Delta G^* ) at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S formation</td>
<td>H₂S formation</td>
<td>S formation</td>
<td>S formation</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-22.64</td>
<td>-19.49</td>
<td>-22.98</td>
<td>-19.36</td>
</tr>
<tr>
<td>Cd</td>
<td>-22.48</td>
<td>-19.54</td>
<td>-22.84</td>
<td>-19.41</td>
</tr>
<tr>
<td>Ba</td>
<td>-64.45</td>
<td>-61.40</td>
<td>-60.14</td>
<td>-56.62</td>
</tr>
</tbody>
</table>

Finally, the metal oxide may simply react with \( \text{SO}_2 \) to form metal sulfites instead of sulphate, resulting in no \( \text{H}_2 \) formation:

\[
\text{MO} + \text{SO}_2 = \text{MSO}_3
\]

Unfortunately, there is an absence of thermodynamic data for the metal sulfites of interest, so the \( \Delta G^* \) for these reactions cannot be calculated. We also have no literature information on the relative kinetics of these reactions. If the \( \text{H}_2 \) generation reactions are not favored, the possible products will be \( \text{MSO}_3 \), \( \text{MSO}_4/\text{H}_2\text{S} \), or \( \text{MSO}_4/\text{S} \) [7].

3. Experimental Details

Three different approaches were used to study the low temperature \( \text{H}_2 \) generation step in the metal sulfate cycles. The reactions were conducted in both batch and flow systems. There is a low temperature glass flow system, and a high temperature, high pressure flow metal system. For the high temperature batch mode, reactions were done in a one liter Parr autoclave. Oxide powder (MnO or BaO), water and
liquid SO₂ were loaded into the autoclave. An excess of water and SO₂ was used to promote the complete reaction of the oxide. The vessel was then heated to about 250°C, which gave rise to a pressure of approximately 1500 psi inside the vessel. A motor driven blade stirred the powder-water mixture to minimize conglomeration of the oxide particles. The reaction was maintained at 250°C for 4 hours and was then cooled to room temperature. The gas inside the vessel was subsequently released into a residual gas analyzer (RGA) to probe for the presence of H₂ at temperature.

The flow system experiments were conducted both at ambient and evaluated pressure. A schematic of the pressurized flow system is shown in Figure 1. In the ambient set up, SO₂ was bubbled through a flask containing H₂O and oxide powder at the temperatures of 25°C and 100°C while the mixture was stirred. The outlet gas was passed into an RGA for analysis. For the pressurized experiments, the reaction was conducted at 200 psi and up to 300°C. In this case, SO₂ was bubbled through the vessel which contained H₂O at a temperature around 120°C. The SO₂ and H₂O gas mixture was then passed through the MnO powder vessel at temperatures up to 300°C. The H₂O was then condensed in the cold trap and the gas mixture was send to an RGA for analysis.

The reaction of MnSO₃•3H₂O with water vapor was also conducted in a Setaram Setsys Evolution 2400 equipped with either a Setaram Wetsys humidifying system or a Pfeiffer Q422 quaduropole mass spectrometer (MS), which allowed either simultaneous Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA) under humidifying conditions or simultaneous TGA/DTA with mass spectrum analysis of evolved gases. See Figure 2 for a schematic diagram of the instrumentation. About 45 to 60 mg of MnSO₃•3H₂O was place in an alumina crucible for analysis. The reactions were run under a flowing inert atmosphere (argon and/or nitrogen) with a furnace heating rate of 10°C/min from ambient temperature to 600°C. The water vapor was introduced when the furnace temperature reached about 100°C to avoid any initial condensation of the water vapor.

Figure 1. The pressurized flow system.
Figure 2. The Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Mass Spectrum (MS) system.

4. Results and Discussion

Batch Experiments

The RGA profile for the MnO experiment at 250°C is shown in Figure 3. The H₂ signal is 1/200 of the SO₂ signal which amounts to a 10% H₂ yield. This is a negligible amount of H₂ generated. An x-ray diffraction spectrum of the powder that remained after the experiment showed tri-hydrated MnSO₃ as the only product (Figure 4) [8]. Thus, virtually all the MnO formed MnSO₃, with perhaps a few percent MnSO₄ from the H₂ generation reaction which is not seen in the x-ray pattern. Hence, the sulphite formation reaction is more favourable than that of the H₂ generation in this system or the MnSO₃ is a kinetically stable product.
Figure 3. RGA profile of the gas released from the pressure vessel after the MnO + H₂O + SO₂ experiment at 250 C.

Figure 4. Powder X-ray diffraction pattern of the MnSO₄•3H₂O powder after the experiment. The reference spectrum for MnSO₄•3H₂O is superimposed.
In a similar experiment, BaO was used instead of MnO. The resulting RGA profile shows no rise in H₂ pressure and thus only a negligible amount could have been generated. White powder was found to remain in the solution in addition to yellow drops that formed on the cold vessel lid. X-ray diffraction spectrum shows the white powder to be BaSO₄ (Figure 5) and the yellow drops were determined to be sulphur by X-Ray fluorescence. The results show that the sulfur disproportionation side reaction has take precedence over the H₂ reaction:

\[
2\text{BaO} + 3 \text{SO}_2 = 2\text{BaSO}_4 + \text{S}
\]

Hence, the H₂ generation step of this TC is not thermodynamically favoured at high temperature and pressure in a batch mode.

![Figure 5. Powder X-ray diffraction pattern of the reacted powder after the experiment. The reference spectrum for BaSO₄ is superimposed.](image)

**Flow Experiments**

In the ambient pressure experiment, the dark green MnO powders in water turned to a white powder as it reacts with the flowing SO₂(g) over a few hours. Similar to the batch experiment, x-ray diffraction showed the isolated white powder to be MnSO₃•3H₂O. Un-reacted MnO can also be seen in some runs, but no trace of MnSO₄ was found in the diffraction spectrum. In addition to flowing SO₂, H₂SO₃(aq) solutions was used to react with MnO at both 25 and 100°C. Similarly, white MnSO₃•3H₂O was the resulting products after 2 hours of aqueous reaction.

In a similar fashion, H₂SO₃ was added to BaO at 100°C. At the end of 2.75 hours, minimal amount of H₂ was observed. From the solution, a white powder was isolated and the principle product was found to be BaSO₃ via XRD analysis. This result differs from the batch experiment which produced BaSO₄ and sulphur. The combination of the RGA detecting a minimal amount of H₂ and solid product identification implies that there was no significant formation of H₂ under these conditions.

The high pressure flow experiment was conducted with MnO. The experiment was run for two hours with SO₂ and water flowing at pressure. At the end of the experiment, the MnO powder remained green in
colour which indicated that no reaction took place. X-ray diffraction confirmed MnO. This result was in contrast to earlier work [4] which suggested that this system would work.

**High Temperature Studies**

Higher temperatures were employed in an attempt to drive the reaction of MnSO$_3$$\cdot$3H$_2$O and water vapour to produce MnSO$_4$ and H$_2$. A sample of MnSO$_3$$\cdot$3H$_2$O that had been produced in the batch experiment above was heated to 600°C under humidifying conditions. The Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) analysis is shown in Figure 6 below. The time-temperature from ambient to 600°C is shown in red. The TGA mass loss is shown in green, indicating that initially the hydrated water molecules are lost followed by decomposition of the anhydrous MnSO$_3$ to form MnO and SO$_2$. The relative humidity is shown in pink. The DTA is shown in blue and indicates endothermic phenomena for the dehydration and decomposition steps. If H$_2$ were produced in this reaction, we would expect a gain in mass when MnSO$_4$ is formed. The lack of any gain in mass indicates that no H$_2$ was produced in this reaction. The XRD analysis of the end product is shown in Figure 7 and it contains only MnO peaks. A separate experiment with a mass spectrometer to identify the gases coming off, showed the evolved gases were water and SO$_2$ that were produced during the decomposition of MnSO$_3$$\cdot$3H$_2$O.

![Figure 6. TGA/DTA for the MnSO$_3$$\cdot$3H$_2$O + H$_2$O experiment at 600°C.](image-url)
Figure 7. Powder X-ray diffraction pattern of the MnO formed during the TGA/DTA experiment. The reference spectrum for MnO is superimposed.

Conclusions
Under a variety of experimental conditions, no significant hydrogen formation was found in the reactions with MnO or BaO. Side reactions anticipated by thermodynamic analysis were shown to occur. Other metal sulfate cycles, where the proposed reaction is

\[ \text{MO} + \text{SO}_2 + \text{H}_2\text{O} = \text{MSO}_4 + \text{H}_2 \]

are also unlikely to produce a commercially viable quantity of \( \text{H}_2 \).

REFERENCES


3. HSC Chemistry, version 5.11, by Outokumpu Research, Finland.


6. In the barium molybdenum sulfate cycle, the reaction is actually BaMoO₄ + SO₂ + H₂O = BaSO₄ + MoO₃ + H₂. We looked at the BaO reaction, as it would be more favored than from BaMoO₄. Second, the reaction came to us in a database, which did not mention if the cycle was a hybrid. The actual reference shows an electrolysis of sulphurous acid to sulphuric acid. Because other metal sulfate cycles don’t refer to electrolysis, we treated this cycle as a non-hybrid.

7. In M.G. Bowman, “High Temperature Thermochemical Hydrogen Cycles for Solar Heat Sources, Proceedings of Solar Fuels Workshop, Solar Thermal Test Facilities User Association, SERI/9020-3, 1979, Bowman looked at the reaction MSO₃ + H₂O = MSO₄ + H₂ under a variety of unspecified conditions, and never saw significant H₂ yield. For M = Ca, DG is negative for this reaction.