

Analysis of the Copper Sulfate Cycle for the Thermochemical Splitting of Water for Hydrogen Production

Presented at

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Summary

The Copper Sulfate cycle has a long history – original work and experiments were performed in the late 1970's. This cycle involves two major steps: (1) hydrogen production from the reaction of water, $\text{SO}_2(\text{g})$ and $\text{CuO}(\text{s})$ at room temperature and (2) the thermal decomposition of the products of the first phase to form oxygen and to regenerate reagents for the first step. The first step has been performed electrolytically and the second step appears to be possible at a temperature of about 850 °C. More complex versions of the Copper Sulfate cycle, called H-5 and H-7, involve 4 and 6 reactions, respectively.

An earlier report gave estimates of the process efficiency based on heats of reactions and sensible heats as well as on equilibrium yield considerations (all of these estimates were in the neighborhood of 47%).

The current report gives “Level 3” results that are based on an Aspen Plus simulation of a proposed flowsheet for cycle H-5. This cycle can be simulated using standard Aspen Plus features and the Peng-Robinson equation of state for all separations involving oxygen and sulfur oxides (this represents a significant departure from ideality).

The flowsheet contains a significant section devoted to the separation of oxygen from sulfur oxides. A sizeable portion of the plant costs are associated with these separation processes.

Pinch technology was used to optimize heat integration. A sensitivity analysis revealed that it is economically attractive to use a 10 °C approach temperature (rather than a 20 °C one) since significantly more energy can be recovered in the heat exchange processes while maintaining process realizability.

A cost analysis of the designed plant (to deliver 100 million kmol/y of hydrogen) indicates a total major equipment cost of about \$35 million. This translates (using a rule of thumb factor of 8) to a turnkey plant price of approximately \$280 million. Based on a selling price for hydrogen of \$5 per kg the yearly plant profit could be on the order of \$1 billion. Using a more conservative estimate based on the current price of natural gas, yearly plant productivity would be about \$200 million. In either case, the plant has a very short pay back period.

The results of this investigation do not rule out the Cu-SO_4 cycle as a viable one. With some improvements in the hydrogen producing step (and other possible enhancements) it is estimated that the cycle efficiency can be as high as 70%. In order to achieve these potential cycle upgrades, it is recommended that experiments be performed (1) using excess liquid SO_2 at elevated pressure in the hydrogen producing step and (2) fluidized bed experiments on the decomposition reactions of CuSO_4 and its hydrates.

Introduction

Researchers at Tulane University are one of a group of 8 teams that are investigating the viability and practicality of thermochemical cycles for the production of hydrogen and oxygen from water. The work is supported by Argonne National Laboratory and DOE. The objectives are to analyze the theoretical (and if possible the practical) efficiency of proposed cycles at three levels:

Level 1: Reactions go to completion with stoichiometric amounts of reactants. Realistic temperatures are assumed and atmospheric pressure is used. 50% efficiency of work terms are used when calculating the cycle efficiency. An energy balance based on heats of reaction as well as sensible and latent heats provides the basis of the efficiency calculation.

Level 2: Equilibrium concentrations for each reaction are assumed. Temperatures are dictated by the equilibrium considerations. Calculation of cycle efficiency at this level also assumes 50% work efficiency. The use of elevated pressure and/or excess reagents may be considered. Competing product formation may also be considered. Further, the effect of shaft work from a simplified flowsheet might be included.

Level 3: A proposed flowsheet is constructed for the cycle. Optimization of operating conditions and excess reagents are included and practical separations are simulated to provide sufficiently pure hydrogen and oxygen. Hydrogen in the amount of 1 million kmol per year is to be delivered at 99.999% purity at 300 psig and 25°C. On-site uses for oxygen are to be considered.

An initial report (Law, et al. 2006) documented progress on the project through Levels 1 & 2. A very preliminary Aspen Plus flowsheet for the simplified chemistry version of the cycle was included. Level 1 analysis gave an efficiency of 48.1% for the simple chemistry case (two reactions only) and about 47% for cycle H-5 (Carty, et al. 1977). The Level 2 efficiency for the simple chemistry case was 47.4%. Further work on cycle H-5 was deferred to this report.

Screening Criteria

The following guidelines were to be followed throughout the analysis of the Copper Sulfate cycle. If any of these “ground rules” are not met then it should be recommended that the proposed cycle be discarded from the list of potentially viable ones.

- Maximum temperature requirement of ≤ 850 °C
- Abundance of chemical components
- Toxicity (all cycles containing Hg, Se, and Cd eliminated per the very low releases allowed by RICA regulations)
- Chemical viability (are the proposed reactions those that actually occur?)
- Thermodynamic feasibility (can the reactions take place?)

The following criteria apply to inputs and outputs of the cycle:

- Water at 20-25 °C and atmospheric pressure
- Hydrogen at 20-25 °C and 300 psig (and of 99.999% purity)
- Oxygen at 20-25 °C and atmospheric pressure (initially of no value)
- Any by-product streams are safe to discharge

The Copper-Sulfate Cycle

The Copper-Sulfate cycle for the thermochemical production of hydrogen by water splitting utilizes the following reagents:

Water (H₂O)
Sulfur Dioxide [SO₂(g)]
Copper Oxide (CuO)

Products of the cycle are:

Hydrogen [H₂(g)]
Oxygen [O₂(g)]

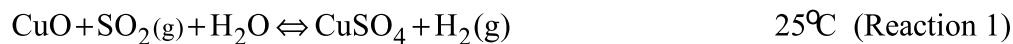
Intermediate components that are believed to appear in the cycle are as follows:

Copper Sulfate (CuSO₄)
Copper Sulfate Monohydrate (CuSO₄ • H₂O)
Copper Sulfate Trihydrate (CuSO₄ • 3H₂O)
Copper Sulfate Pentahydrate (CuSO₄ • 5H₂O)

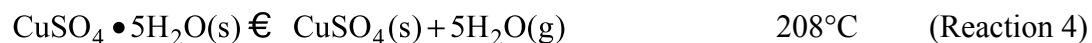
The following compounds are ones that possibly form and the consequences of their existence must be considered:

Cupric Oxide (Cu₂O)
Cupric Sulfate (Cu₂SO₄)
Copper(II) sulfate - copper(II) hydroxide (1:3) [CuSO₄ • 3Cu(OH)₂]

Simplified chemistry (two reactions only) for the Copper-Sulfate cycle is shown as Reactions 1 and 2.



Foh, et al. (1978) presented a sulfur-based cycle using CuO and CuSO₄, and designated it Cycle H-5. This cycle consists of four basic steps as follows:





Foh, et al., 1978 calculated a cycle efficiency of about 36%.

Schreiber, et al. (1980) introduced an additional cycle using Copper Sulfate and Copper Oxides (designated as H-7). This cycle was discarded since one of the reactions requires temperatures in excess of 1000°C.

Literature Survey

The Copper-Sulfate cycle has its origins in the Westinghouse cycle (Brecher, et al. 1977). The Westinghouse cycle consists of an electrochemical step in which water and SO₂ form hydrogen and sulfuric acid. This is followed by the thermal decomposition of sulfuric acid into oxygen and SO₂. Excess water and SO₂ are the only components in the recycle.

Carty, et al. (1977), examined the sensitivity of a proposed flowsheet for the Westinghouse cycle. Acid concentration, process pressures and reaction temperatures were varied in over 125 combinations. The conclusion was that at a maximum process temperature of 1144K (871 °C) the optimum acid concentration is between 65 and 85 wt.% and the optimum pressure in the decomposition loop is 75 – 150 psia (5.15 – 10.3 bar).

Soliman, et al. (1976) appear to be the first to propose the use of metal oxides as catalysts in the basic Westinghouse cycle. They concluded that the use of metal oxides can lead to enhanced efficiencies.

Foh, et al. (1978) presented a sulfur-based cycle using CuO and CuSO₄, and designated it Cycle H-5. This cycle consists of four basic steps as show in Reactions 3 – 6 given in an earlier section of this report.

Schreiber, et al. (1980) introduced an additional cycle using Copper Sulfate and Copper Oxides (designated as H-7), which as stated earlier in this report, has been discarded since one of the reactions requires a temperature of about 1000 °C.

The most definitive and detailed work associated with both cycles H-5 and H-7 was performed by Carty, et al. (1981). The “workability” of both of these cycles was demonstrated in small laboratory experiments. Appendix B of Volume 3 of the “Carty Report” has an extensive section on these cycles including kinetic correlations gleaned from the experiments. Paradoxically, all experiments were performed at or near atmospheric pressure but a process flow diagram (PFD) is presented where the operating pressure is approximately 30 bar. This work was performed before the advent of modern process simulators, so the actual simulation of the PFD was not possible. Therefore, the efficiencies reported for the cycle H-5 PFD, which ranged from about 22% up to nearly 50%, must be scrutinized further. Similarly computed efficiencies for cycle H-7 were reported to range from about 25% to nearly 60%. We plan to utilize the data from the

“Carty Report” to every extent possible since this is the only current source of quality experimental information. Perhaps this exercise will suggest additional experiments that might be useful, especially if the final recommended PFD operates at elevated pressure.

A good starting point for a literature survey on any hydrogen cycle is the UNLV Database (2006). This interactive online system has links to seminal papers on a multitude of cycles.

The baseline reference for the proposed work on the Copper Sulfate cycle, as well as that of the cycles being studied by the other 7 institutions involved in the current effort, is a report (still in draft form) by Lewis & Masin (2006). Level 1 and level 2 results are shown using the simplified chemistry given by Reaction 1 and Reaction 2. These data have been very useful, especially in becoming familiar with the HSC Software (2002). HSC is an interactive database that provides, along with several other capabilities, thermal and free energy data for reactions as well as equilibrium compositions for given chemical constituents.

Other works that are not specific to the Copper Sulfate cycle, but which may contain useful information are enumerated below:

Carty & Conger (1980). An in-depth heat penalty and economic analysis of the Westinghouse cycle is presented. The methodology is applicable to any cycle.

Lin & Flaherty (1983). These authors study the design of a reactor for the thermal decomposition of sulfuric acid, first into SO_3 and water and the further decomposition of SO_3 into SO_2 and oxygen. Cycle H-5 involves the decomposition of SO_3 into SO_2 and oxygen, so this source might provide insight regarding this reaction.

Neumann, et al. (1984). Phase diagrams and phase data for the Cu – O system are presented. These diagrams indicate the conditions under which CuO and Cu_2O exist. Cycle H-7 includes reactions involving both oxides of copper while H-5 includes only CuO. Therefore, this phase information is potentially valuable toward future work on these cycles.

Teo, et al. (2004). An energy efficiency analysis is undertaken of cycle UT-3 (Calcium Bromide cycle) using contemporary databases, pinch analysis, and other modern tools. The methodology used can provide a template for analyzing other cycles.

Kent, et al. (1977). This paper provides information on the adsorption and reactions of SO_2 on CuO particles. These data might be useful when designing a reactor for hydrogen production.

Rosen (1996). Analyzes hydrogen production (including direct hydrolysis, steam-methane reforming, coal gasification and thermochemical cycles) using energy and exergy analysis. This is the only reference found that deals with exergy analysis. Aspen Plus was used for simulation work.

Brown, et al. (2000). An initial screening process for hydrogen from water cycles was established based on criteria such as the number of reactions, number of elements, cost of process chemicals, etc. This produced a “short list” of 25 cycles. The Westinghouse cycle was rated highest, with Sulfur-Bromide, Br-Ca-Fe, and Sulfur-Iodine (S-I) receiving very high marks.

Brown, et al. (2002). Based on the initial screening work published in 2000, a further refinement of the cycle ratings was performed and the S-I cycle was chosen for further development. The final result of this study is a detailed flowsheet, modeled using Aspen Plus, and an economic analysis showing the ultimate cost of hydrogen to be between \$1.50 and \$2.00/kg. This report will provide valuable guidance for Level 3 work on the current project.

Summers, et al. (2005). These authors also claim that the S-I and Westinghouse cycles have emerged as leading candidates for ultimate development.

Perkins & Weimer (2004). A recent paper that also praises the S-I cycle. It also includes discussions on materials of construction.

McQuillan, et al. (2004). This is a comprehensive report that evaluates cycles based on a high temperature source from solar energy. The S-I cycle, among several others, was highly rated by these researchers.

Yerimin, et al. (2006). This Russian project provides independent data on the free energy of formation of several constituents in the Copper Sulfate cycle.

Savitsky, et al. (1982). Information is provided on the corrosion resistance of some metal alloys to high temperature sulfuric acid and its decomposition products.

Lu (1983). The technological aspects of sulfur dioxide electrolysis for hydrogen production are discussed.

Yannopoulos and Pierre (1984) report on catalyst developments for converting SO_3 to SO_2 . This work is important since our Phase 3 flowsheet has a step to perform this conversion. It is necessary in order to obtain an acceptable separation of SO_2 and O_2 .

Level 3 Analyses

Introduction

From the Statement of Work for this project, Level 3 analysis includes “the process flowsheet, evaluation of any non-idealities that were considered, assessment of the need for additional thermodynamic data, definition of unit operations, stream data, determination of operating conditions, the results of sensitivity studies, and subsequent process optimization. Possible solutions to the challenge(s) identified from earlier work should be included as well. The evaluation should also include recommendations for needed critical research.”

It was decided that Level 3 work would proceed using cycle H-5 as a basis. The Carty, et al. (1981) report contains a significant amount of data on this cycle. The quality of some of these data is questionable, but this was the best starting point for process design and analysis work. The designed plant is scaled for a production rate of 202,000,000 kg/y (100,000,000 kmol/y) of hydrogen, delivered at 300 psig.

Aspen Flowsheet for Cycle H-5

If the published reactions for cycle H-5 are considered (Reactions 3 – 6), the equilibrium yield for Reaction 5 is such that temperatures higher than 850 °C are required for significant product formation. However, Foh, et al. (1978) claim (based on experimental evidence) that Reactions 5 and 6 are not discrete. That is, some SO₂(g) and O₂(g) are formed in Reaction 5. When these components are added to the equilibrium “mix”, the compositions at 850 °C are potentially acceptable.

The preliminary process design Cycle H-5 consists of five distinct regions – as shown in the flowsheet of Figure 1. Each of the first four regions represents the subsequent steps of Cycle H-5 as described by Foh, et al. (1978). The fifth and final region of the flowsheet represents an added element of the process design—the synthesis of SO₃(g) to further purify the O₂(g) product stream. Each region is characterized by a distinct reactor and associated streams as shown in Table 1. For example, region 1 is distinguished by a reactor labeled RXN-1 in the flowsheet and all streams associated with this reactor are labeled A1, A2, etc. Heat exchangers appear throughout the flowsheet and, for those streams where energy is transferred, the associated energy streams are labeled Q1, Q2, etc. (indicated by dashed lines).

Table 1. A breakdown of the flowsheet, by region.

Region	Reactor	Stream Class
1	RXN-1	A
2	RXN-2	B
3	RXN-3	C
4	RXN-4	D
5	SO ₃ -SYN	E
ALL	Heat-Exch	Q

The overall system contains five input/output streams. $\text{H}_2\text{O}(\text{l})$ is fed to the system at a rate of 12,500 kmol/hr. $\text{H}_2(\text{g})$ is produced at roughly the same rate. $\text{O}_2(\text{g})$ is produced at a rate of about 6,120 kmol/hr. Additional amounts of $\text{SO}_2(\text{l})$ and $\text{O}_2(\text{g})$ must be fed to the system at rates of 304.1 kmol/hr and 192.4 kmol/hr, respectively, in order to make up for losses. The primary loss of SO_2 is via the O_2 product stream (O2-PROD) in the form of SO_3 and SO_2 – fractions of roughly 4.1 mole-% and 0.6 mole-%, respectively. Annual SO_2 requirements will be approximately 2.43 million kmol/yr. A relatively small amount of O_2 from the product stream is diverted to the RXN-3 section of the flowsheet to compensate for oxygen leaving this section with the liquefied SO_3 .

The $\text{O}_2(\text{g})$ product stream (O2-PROD) can be purified further by scrubbing the sulfur species with either water or a mild NaOH solution. Water would be the preferred scrubbing liquid resulting in the production of a mild sulfuric acid, which could be sold. Alternatively, this oxygen stream could be utilized in a coal gasification unit. Typical oxygen requirement for integrated gasification combined cycle (IGCC) units is 2000-5000 short tons/day (76000-190000 kg/hr) (Shelley, 2006). The oxygen stream for the thermochemical cycle would supplement the cryogenic air separation units currently used.

There are seven points of heat interchange (streams Q1 through Q7) in the flowsheet. Additional points of heat recovery exist and could be integrated into onsite processes external to the thermochemical cycle. Five heat exchanges involve energy interchange between two streams. In the other two cases, energy from a stream is used to supply heat to the reboiler of a column. Additionally, there are eleven heaters/coolers in the flowsheet.

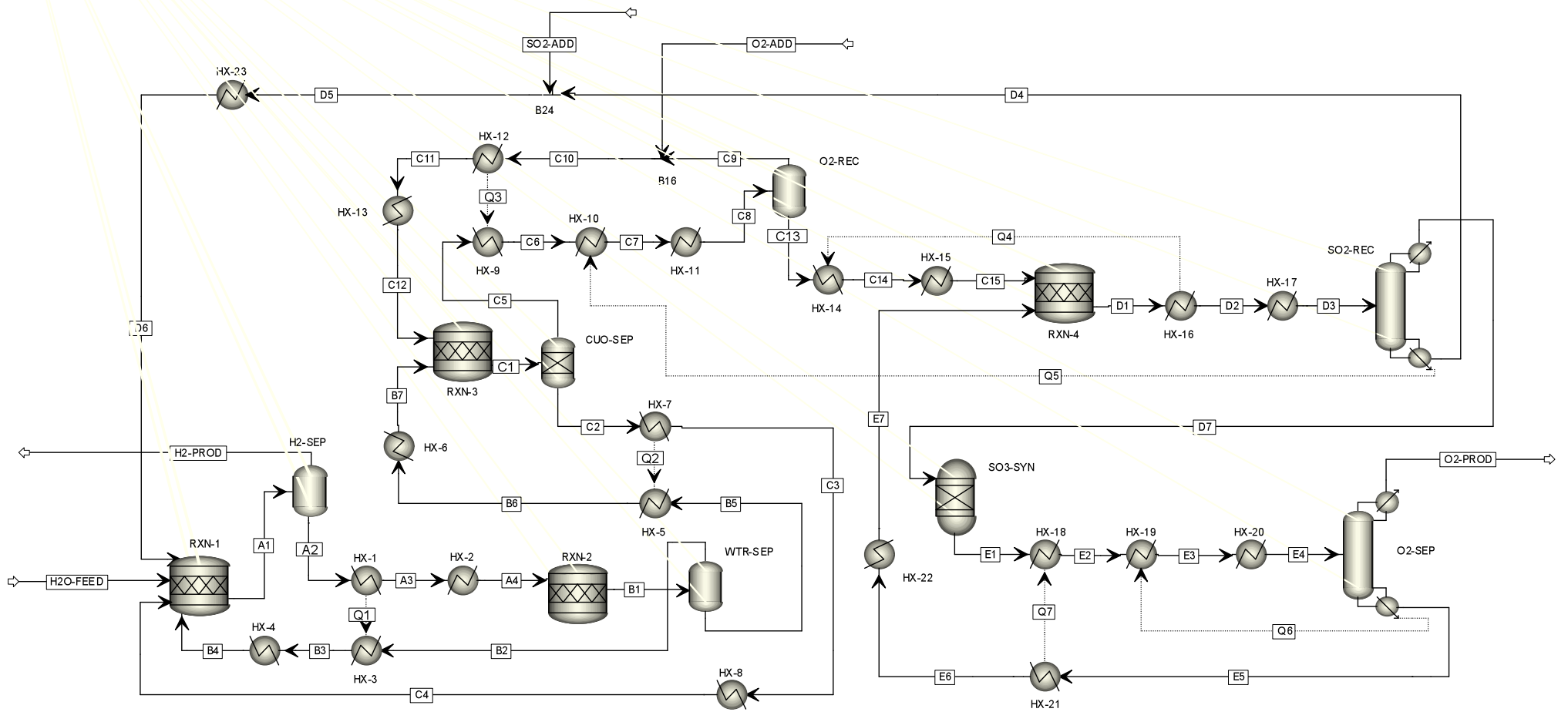


Figure 1. Flowsheet of process simulation for proposed layout of process design for Cycle H-5.

*Generated using ASPEN Plus® (v. 2004.1)

Region 1

In the first region of the flowsheet, the hydrogen-producing reaction of Cycle H-5 is conducted at a temperature of 25°C and 300 psig pressure (therefore, SO₂ is in the liquid state).



The reactor (RXN-1) is an electrolyzer. There are four feed streams and one product stream. Water is fed via two streams—one is fresh water fed into the reactor at 12,500 kmol/hr (H₂O-FEED) and the other is a recycle stream (B4) from the copper sulfate-hydrate decomposition reaction (RXN-2) with a flow rate of about 62,500 kmol/hr. Another feed stream (C4) contains solid copper oxide at a rate of 12,500 kmol/hr, which is recycled from the copper sulfate decomposition (RXN-3). The fourth and final input stream (D6) is liquid sulfur dioxide fed to the reactor at a rate of 12,500 kmol/hr. Sulfur dioxide is obtained from the decomposition of sulfur trioxide (RXN-4) and subsequent separation from oxygen (SO₂-REC) in a distillation column.

The product stream (A1) contains gaseous hydrogen and solid copper sulfate-pentahydrate at about 12,500 kmol/hr. Hydrogen is collected (H₂-SEP) at a rate of 12,500 kmol/hr and the pentahydrate is depressurized to 14.7 psia, heated to 300°C, and sent to Region 2 at 12,500 kmol/hr.

In commercial practice, the electrolyzer would be operated batchwise with a large excess of either water or liquid sulfur dioxide as the slurry transfer medium. In either case, the liquid in the slurry would remain at 25°C during the transfer to RXN-2 and filtration steps. Since no energy transfer is expected to occur, neither excess water nor excess liquid SO₂ was not included in the ASPEN simulation.

Copper Oxide solids transfer to the electrolyzer could be conducted using a venturi eductor similar to those commercially available from Fox Valve, Inc., www.foxvalve.com, (see Figure 2).

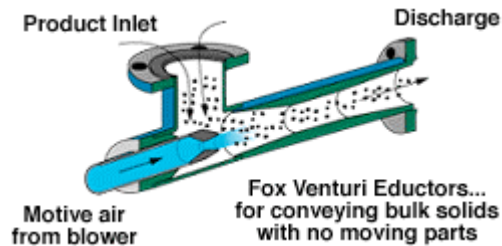
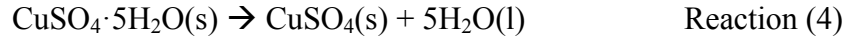


Figure 2: Solids Conveying via a Fox Venturi Eductor.

Region 2

The second region of the flowsheet contains the copper sulfate-pentahydrate decomposition reaction of Cycle H-5 [Reaction (4), repeated here for convenience]



This reaction takes place in a fluidized bed reactor (RXN-2) at 300°C and 14.7 psia. The fluidization gas will be the steam produced during the reaction. There is one feed stream (A4), which contains the pentahydrate, and one product stream (B1) containing anhydrous copper sulfate. The steam generated would be used to heat and decompose additional pentahydrate entering this portion of the flowsheet.

One energy recovery scheme would be to employ three reactors configured as illustrated in Figure 3. Steam, which is produced in reactor 3 from monohydrate decomposition, would heat reactor 2 where a batch of primarily trihydrate would be decomposing to monohydrate. Steam from reactor 2 would, in turn, heat reactor 1 where a new batch of pentahydrate was charged. As shown in Figure 3, because of the high temperature requirements for decomposition of the monohydrate, high-pressure steam would be used to heat reactor 3. Once all the monohydrate has been completely converted to anhydrous CuSO_4 within reactor 3, the solids would be transferred to the reactor in Region 3 (i.e. RXN-3) using a venturi eductor and the make-up O_2 from stream O2-ADD as the conveying gas. Fresh pentahydrate would be charged to reactor 3, the connections between reactors would be changed (via automated valves) to reflect a rotation in configuration (i.e. from 3->2->1 to 2->1->3), and dehydration of the monohydrate in reactor 2 would commence. Reactor rotation is common in several commercial processes (e.g. gas cleaning, ion exchange, etc.) and is easily conducted with computer sequencing and automated valves.

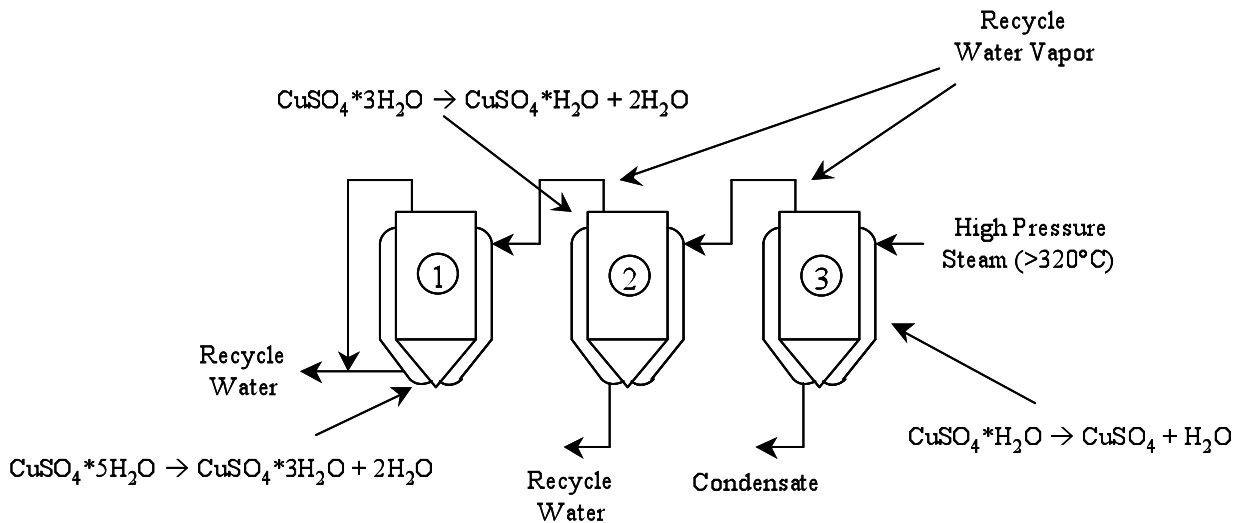
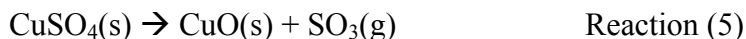


Figure 3: Dehydration reactor train for Region 2

The pentahydrate is fed at the rate of about 12,500 kmol/hr while the product stream is exits at 62,500 kmol/hr. Water is separated (WTR-SEP) and sent back to the hydrogen-producing reaction (RXN-1) in Region 1 after being cooled to 25°C and pressurized to 300 psig. The anhydrous copper sulfate is heated to 850°C, pressurized to 300 psig, and sent to Region 3 at 12,500 kmol/hr.

Region 3

Decomposition of anhydrous copper sulfate is conducted in the third region [Reaction (5), repeated here for convenience].



This reaction is carried out in a fluidized bed reactor (RXN-3) at 850°C and 300 psig. There are two feed streams and one product stream. The first feed stream (B7) is anhydrous copper sulfate and is enters at the rate of 12,500 kmol/hr. The second feed stream (C12) is oxygen gas used to fluidize the bed. It enters the system at 250,000 kmol/hr. This flowrate was chosen arbitrarily and is subject to further optimization. Stream (C12) also contains about 7900 kmol SO₃(g)/hr and 7 kmol SO₂(g)/hr. While, in practice, both units labeled RXN-3 and CUO-SEP will be part of the fluidized bed unit, the limitations of ASPEN Plus require modeling it as two units. The lone product stream (C1) leaving RXN-3, therefore, contains solid copper oxide and sulfur trioxide along with oxygen and some sulfur dioxide in the gas phase. Copper oxide is collected (CUO-SEP) and recycled at about 12,500 kmol/hr to the hydrogen-producing reaction (RXN-1) in Region 1. The residual heat from this stream is used to warm the anhydrous copper sulfate entering RXN-3. The gaseous products are cooled to 25°C, sent to a flash drum at roughly 270,400 kmol/hr where oxygen is separated from the sulfur oxides (O2-REC). Oxygen is then heated, using the residual heat to cool the gaseous mixture, and returned to the fluidized bed (RXN-3).

This region of the flowsheet is operated at elevated pressures to ensure an efficient means of separating the sulfur oxides from oxygen. Carty, et al. (1981) indicated that oxygen's solubility in sulfur oxides (SO₃ or SO₂) is higher than what would be expected from ideal vapor/liquid behavior. Figure 4 compares the x-y diagram from Peng-Robinson with one where ideal behavior is assumed. Note that with the Peng-Robinson equation of state, oxygen is predicted to be more soluble in SO₂, as suggested. Hence, all regions of the flowsheet where oxygen is separated from SO₃ or SO₂ were described using the Peng-Robinson equation of state.

Oxygen was chosen as the fluidization gas to minimize the formation of cupric oxide (Cu₂O). While the work of Neumann, et al. (1984) (Figure 5) suggests that a partial oxygen pressure in excess of 1 bar would ensure the formation of only CuO, further experimental work is required to understand how the presence of SO₃, SO₂, and CuSO₄ will affect this phase diagram.

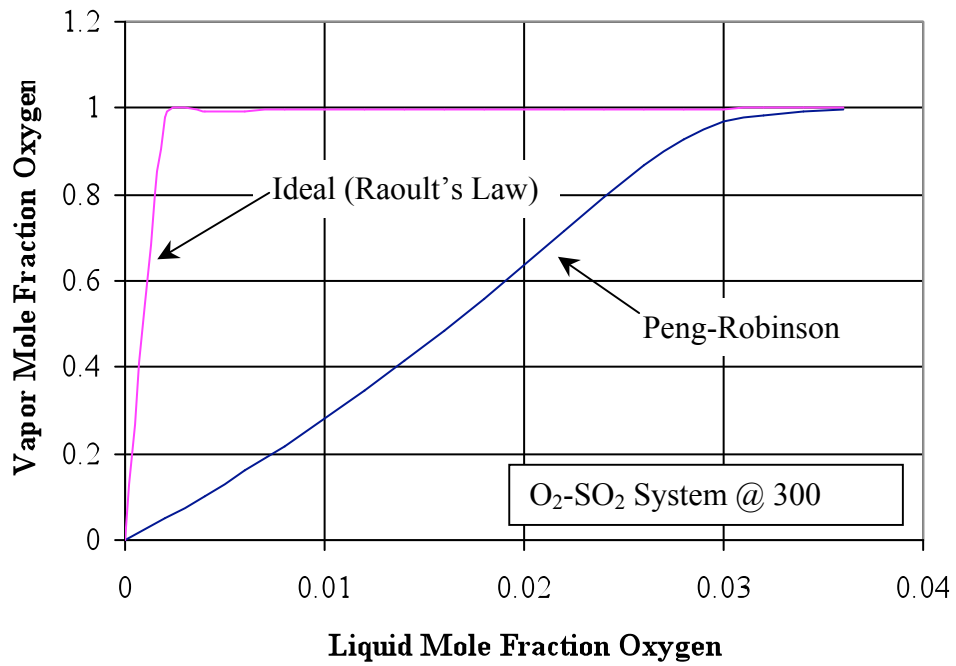


Figure 4: Non-idealities in O₂-SO₂ system

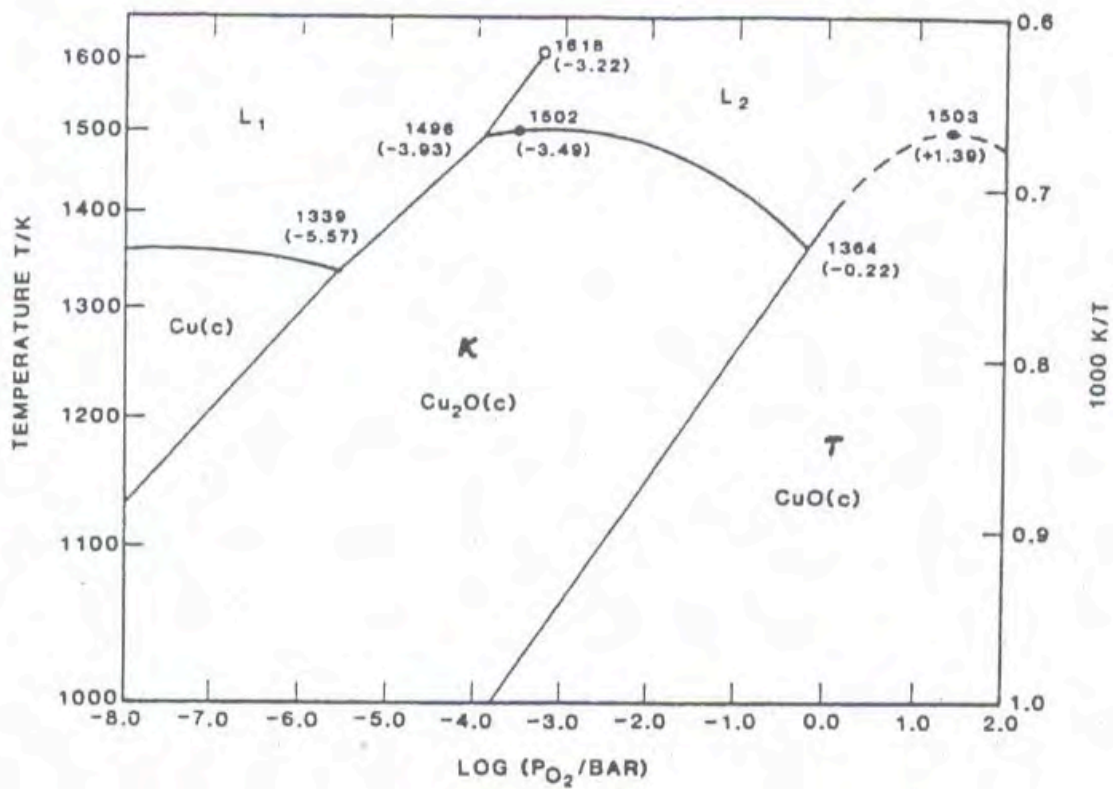


Figure 5: Phase stability diagram for the CuO-Cu₂O system.

After being separated from oxygen, sulfur trioxide is heated to 850°C and sent to a packed bed reactor (RXN-4) in Region 4 at roughly 12,700 kmol/hr. This stream has a composition of approximately 98.5 mole% SO₃(g), 1.5 mole% O₂(g), and traces of SO₂(g).

Region 4

As depicted in Reaction (8), sulfur trioxide is converted to sulfur dioxide and oxygen in the fourth region of the flowsheet.



This reaction takes place in a packed bed reactor (RXN-4) at 850°C and 300 psig. A ferrite-based catalyst supported on alumina (Yannopoulos, et al., 1984) has been demonstrated to achieve conversions of 98-100%. There are two feed streams and one product stream. The first feed stream (C15) delivers the sulfur trioxide mixture at a rate of 12,700 kmol/hr. The second feed stream (E7) is a recycle of sulfur trioxide from Region 5; it enters at 1700 kmol/hr and contains about 1 mole% SO₂(g). The product stream (D1), flowing at a rate of 21,522 kmol/hr, contains a mixture of 33.9 mole% oxygen and 66.1 mole% sulfur dioxide. This stream is sent to a distillation column (SO₂-REC) where a majority of the sulfur dioxide exits from the bottoms, is cooled to 25°C, and recycled to the hydrogen-producing step in the electrolyzer (RXN-1) of Region 1. Because of sulfur oxides lost with the oxygen stream (O₂-PROD), a make-up SO₂ flowrate of 304.1 kmol/hr is required to maintain the recycle rate at the desired 12,500 kmol/hr.

Since no cryogenic refrigeration was assumed to be available, the column overhead temperature was limited to 25°C, which allowed a significant portion of the sulfur dioxide to leave with the oxygen (21.8 mole% SO₂ in overhead stream). The equipment in region 5 was conceived to recover this sulfur dioxide and further purify the oxygen stream.

Region 5

To increase the purity of the oxygen stream leaving region 4, it is sent through a loop (Region 5) in which sulfur dioxide is converted to sulfur trioxide as given in Reaction (9).



Conversion of SO₂ back to SO₃ is performed because sulfur trioxide is more easily separated from oxygen by distillation. In addition, SO₃ is more water-soluble than SO₂, allowing any non-recoverable sulfur species to be readily absorbed from the oxygen product (O₂-PROD). If adequate refrigeration were available (i.e. approximately 50MM kJ/hr at -200°C), this region of the flowsheet could be eliminated. However, the availability of such cryogenic refrigeration is unlikely.

Reaction (9) is conducted in a packed-bed reactor containing commercially available vanadium-pentoxide (V_2O_5) catalyst (SO₃-SYN) at 200 psig. This reaction is highly exothermic with the equilibrium shifted far to the right. Because of the almost instantaneous reaction rate, commercial reactors are typically operated adiabatically with an excess of one of the reactants. The feed stream (D7) is a gaseous mixture of oxygen and sulfur dioxide entering at approximately 9,325 kmol/hr and is made up of 78.2 mol-% oxygen and 21.8 mol-% sulfur dioxide. Operating the reaction adiabatically raises the temperature from 25 to approximately 600°C, which is within the range of commercial operation. The single product stream (E1) is a mixture of oxygen, sulfur trioxide, and trace amounts of sulfur dioxide. The reactor product exits at a flowrate of 8,340 kmol/hr and has a composition of 75.7 mole% oxygen, 23.6 mole% sulfur trioxide, and 0.7 mole% sulfur dioxide. Energy liberated by cooling the reactor effluent stream (E1) to 25°C is used to operate the SO₃/O₂ column (O2-SEP) reboiler and to heat the recovered sulfur trioxide (E5).

Sulfur trioxide is then separated from oxygen (O2-SEP) in a distillation column and recycled (at an approximate rate of 1,700 kmol/hr) to the packed bed reactor (RXN-4) of Region 4 for decomposition. This column's overhead temperature is also limited to 25°C. The oxygen product stream exits the overall process at a rate of 6,625 kmol/hr and contains 4.1 mole% sulfur trioxide and 0.6 mole% sulfur dioxide. This level of sulfur trioxide should be easily removed by water scrubbing, producing a dilute sulfuric acid co-product.

Heat Integration

The seven heat exchangers, labeled (HX-1/HX-3), (HX-5/HX-7), (HX-9/HX-12), (HX-10/SO₂-REC Reboiler), (HX-14/HX-16), (HX-18/HX-21), and (HX-19/O₂ SEP Reboiler) were analyzed using Pinch Technology (Lindhoff & Hindmarsh, 1983) as described in Douglas (1988). In each case a 20 °C approach temperature was used. Note that on the process flow diagram each exchanger pair appears as a separate item but they would be implemented as a single exchanger (shell and tube). Simple heaters and coolers were not considered in the pinch analysis.

Heat transfer coefficients were estimated using data from both Ludwig (2001) and Peters et al. (2003). The heat duties and subsequently the required heat transfer areas for each exchanger were calculated. A summary of these data for all exchangers in the process flowsheet appears in Appendix A. An estimate of the purchase costs of all exchangers is about \$28 million (using a 20 °C approach temperature).

Cost Analysis

Capital costing has been performed for the major equipment items in the process flowsheet (Figure 1). As previously stated, the estimated purchase costs for all major exchangers is on the order of \$28 million. Estimated purchase costs for all reactors and distillation columns (as shown in Appendix B) is about \$7 million. Costs were not estimated for minor equipment items such as pumps, and blowers. The combined estimated purchase costs for major equipment items is then about \$35 million. A rule of thumb for estimating installed costs (including startup, instrumentation, etc.) is to apply a

factor of 8 to the purchase price. Therefore, an estimate of the total (turnkey) cost of the proposed plant is about \$280 million.

Estimates of the selling price for hydrogen range from about \$3 to \$7 per kg (see, for example, <http://www.primidi.com/2005/06/26.html>). Using a conservative value of \$5 per kg, a plant producing 202,000,000 kg/y (100,000,000 kmol/y) has a theoretical “income” of about \$1 billion per year. A more convoluted calculation using current spot prices for natural gas (\$7/MM Btu) and the heat of formation of water results in an income estimate of about \$200 million per year. Therefore, the pay back period for the proposed plant is under two years, independent of the method used to approximate income.

Sensitivity Analysis

Many different kinds of sensitivity analyses are possible. In the limited time available, it was decided that a sensitivity analysis of high interest would be to check the effect of total exchanger costs when the approach temperature is varied. As shown by the data in Appendix A, the total heat exchanger purchase cost for a 20 °C approach temperature is about \$28 million. If the approach temperature is reduced to 10 °C, the total heat exchanger cost is about \$32 million. The latter allows significantly more energy to be recovered in the process. Since the difference in cost is minimal, it is recommended that the smaller approach temperature be used for further design studies.

Recommendations for Further Research

Proposed Experiments for the Hydrogen Producing Step

Since SO_2 has a vapor pressure at room temperature of about 3.4 bar, experiments are proposed where water is introduced slowly (for safety reasons) into a slurry consisting of liquid SO_2 and CuO(s) . Andrews Glass Co., <http://www.andrews-glass.com/pages/press.tpl?cart=11532293868251>, provides glass reaction vessels that appear to be ideal for the envisioned experiments. Figure 6 shows some of the Andrews Glass products. A schematic of the proposed apparatus is shown in Figure 7.



Figure 6. Andrews Glass Co. Pressure Reaction Vessels

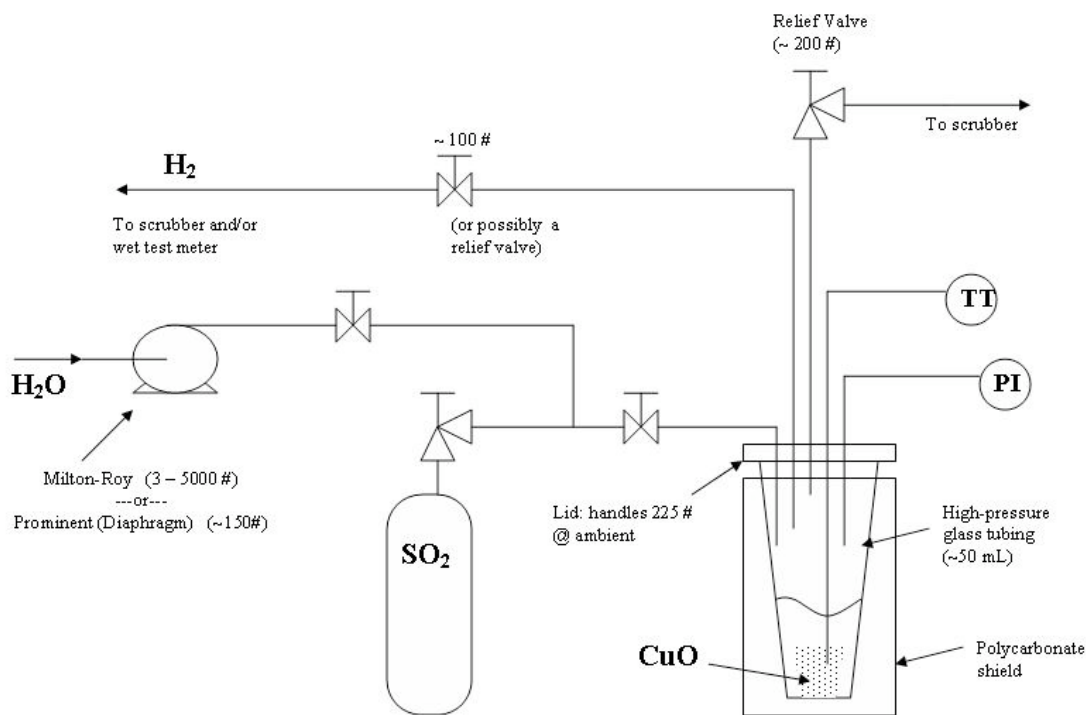
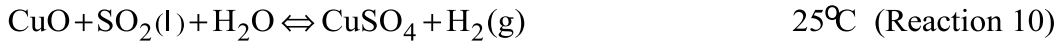
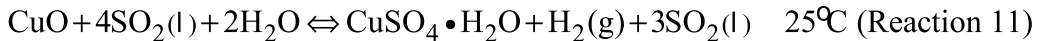


Figure 7. Proposed Experimental Apparatus for Hydrogen Production Step

Water is introduced in small, measured quantities and the formation rate of gaseous products (theoretically hydrogen) are determined (with some samples being collected for identification). The reaction involved is shown as Reaction 10.



A reaction using an excess of $\text{SO}_2(\text{l})$ is shown as Reaction 11, where the monohydrate is the preferred solid product.



The equilibrium yield diagram for this reaction (using HSC software) is shown in Figure 8. Based on these data, Reaction 11 has an equilibrium yield of nearly 100%. The initial quantities of reagents used to generate Figure 8 were 1 mole CuO , 4 moles $\text{SO}_2(\text{l})$ and 2 moles water.

The Gibbs Free energy for Reaction 10 is -15.48 kJ/mol . When the same reaction takes place with $\text{SO}_2(\text{g})$, the G is 4.53 kJ/mol . The significantly more favorable G and the equilibrium yields shown in Figure 8 suggest the efficacy of performing the proposed experiments. If successful, there is no need for an electrochemical cell, which leads to a simpler and economically attractive process design. Note also that there is no need to separate $\text{H}_2(\text{g})$ from $\text{SO}_2(\text{l})$. **Preliminary estimates of the H-5 cycle using liquid SO_2 are on the order of 70%.**

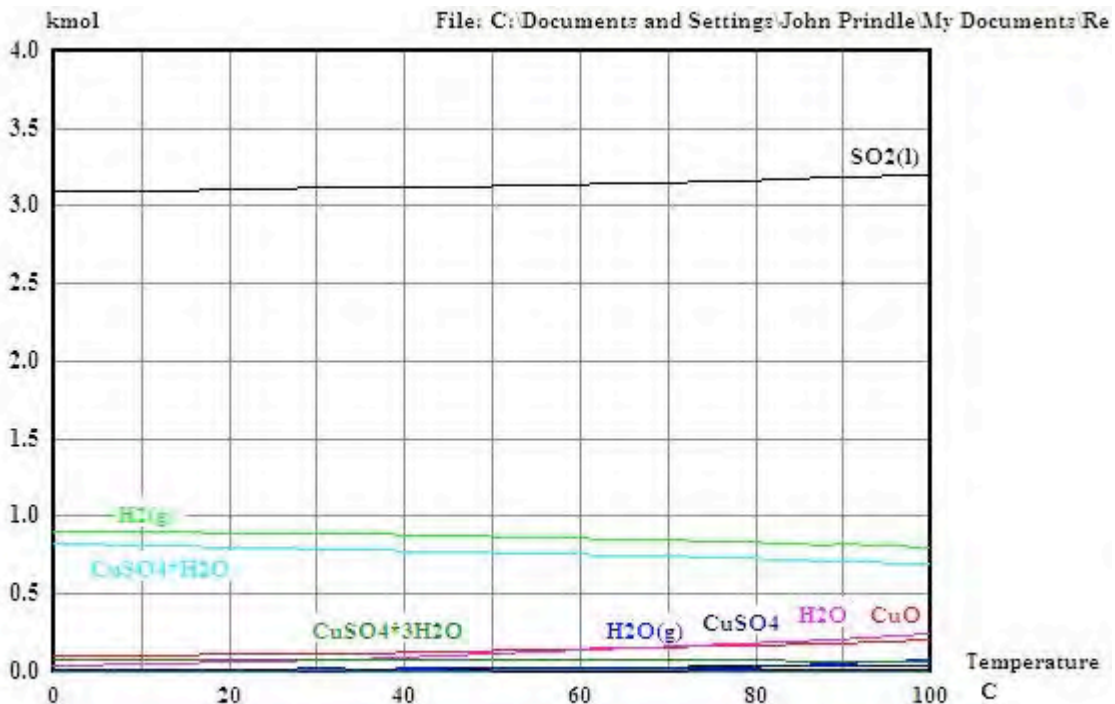


Figure 8: Equilibrium profile for Reaction 2 for a system containing 1 mole of CuO , 4 moles $\text{SO}_2(\text{g})$, and 2 moles H_2O initially.

It is estimated that all equipment required for the proposed experiments is about \$20,000. This includes the cost of all reagents. If these experiments were to be performed under a new research contract, an estimated budget of about \$100,000 would be required.

Proposed Experiments for the Oxygen Producing Step

The Tulane Chemical & Biomolecular Engineering Department's Francis M. Taylor (FMT) Laboratory houses two Lindbergh furnaces, each capable of temperatures in excess of 1400°K. Several quartz reactors are available that can accommodate (with an approximately 1 kg charge of solids) batch or fluidized bed experiments. Glassware includes a quencher for cooling reactor outputs and a scrubber for capturing and neutralizing gases. Also in the FMT Lab is a large fluidized bed system made of high quality stainless steel (used mainly for heat transfer experiments). One of the Lindbergh furnaces is shown in Figures 9 and 10. A closer view of one of a quartz fluidized bed reactors appears in Figure 11. A smaller furnace and quartz reactor (capacity about ¼ kg) are also available.



Figure 9. Lindbergh furnace with controller.



Figure 10. Open view of Lindbergh furnace showing quartz fluidized bed reactor.



Figure 11. Close-up view of quartz fluidized bed reactor. Gas distributing fret appears in the lower portion of the reactor.

Within Tulane University there are XRD instruments and gas chromatographs for analyzing samples. The Tulane Coordinated Instrumentation Facility (see <http://www.tulane.edu/~cif/> for details) has a host of instruments and experienced staff to

help leverage our research efforts. The CIF equipment includes the following microscopic instruments:

- Scanning Electron Microscope
- Transmission Electron Microscope
- Fluorescence Microscope
- Multi-photon Laser Scanning Microscope

The Tulane Chemistry Department has a significant NMR facility (see <http://chemistry.las.tulane.edu/facilitiesNMR.html#equipment> for details).

Experiments would include studying the decomposition of the solid product(s) from the hydrogen producing step as well as controlled amounts of the various hydrates of CuSO_4 . An approximate budget required to perform such experiments is about \$150,000.

Conclusions and Recommendations

Based on the work presented in this report, the following conclusions can be drawn:

1. The H-5 Cycle described by Foh, et al. (1978) appears to be one that can be implemented with current technology.
2. Data (especially on kinetics) presented by Carty, et al. (1981) is of limited value since some of the information was found to be questionable.
3. Cycle H-5 can be simulated using standard Aspen Plus features. The Peng-Robinson equation of state was used for all separations involving oxygen and sulfur oxides. This represents a significant departure from ideality.
4. Because of the solubility of oxygen in sulfur oxides [as reported by Carty, et al. (1981)] an entire plant section is devoted to oxygen purification. This part of the plant contributes a high percentage to the overall plant cost.
5. Heat integration was performed using Pinch Technology. A sensitivity analysis using 20 ° C and 10 ° C approach temperatures indicates that the lower driving force is worthwhile since a higher percentage of energy can be recovered in the process.
6. A cost analysis of the designed plant indicates a total major equipment price of about \$35 million. This translates (using a rule of thumb factor of 8) to a turnkey plant price of approximately \$280 million.
7. Based on a selling price for hydrogen of \$5 per kg the yearly plant profit could be on the order of \$1 billion. Using a more conservative estimate based on the current price of natural gas, yearly plant productivity would be about \$200 million. In either case, the plant has a very short pay back period.
8. The results of this investigation do not rule out the Cu-SO₄ cycle as a viable one. With some improvements in the hydrogen producing step it is estimated that the cycle efficiency can be as high as 70%.

It is recommended that the following research projects be undertaken to improve the Cu-SO₄ cycle as implemented in the flowsheet presented in this report:

1. Experiments using excess liquid SO₂ are warranted since equilibrium calculations indicate a significantly more favorable Gibbs Free Energy. This means that the hydrogen producing step can be performed without an electrolyzer and would greatly improve the process efficiency. These experiments can be carried out in inexpensive glass reactors capable of withstanding up to 10 bar pressure.
2. It is recommended that further experiments be performed on the dehydration of CuSO₄ hydrates and the decomposition of CuSO₄ into CuO and SO₃ (or SO₂). These experiments can be carried out in fluidized bed reactors imbedded in electric furnaces (this equipment is currently available at Tulane University).

Literature Cited

- Beghi, G. E., 1986. A decade of research on thermochemical hydrogen at the joint research center, Ispra. *Int. J. Hydrogen Energy*, **11**, p. 761.
- Brecher, L. E., S. Spewock & C. J. Warde, 1977. The Westinghouse sulfur cycle for the thermochemical decomposition of water. *Int. J. Hydrogen Energy*, **2**, pp. 7 - 15.
- Brown, L. C., J. F. Funk & S. K. Showalter, 2000. Initial screening of thermochemical water-splitting cycles for high efficiency generation of hydrogen fuels using nuclear power. General Atomics Report GA-A23373.
- Brown, L. C., G. E. Besenbruch, R. D. Lentsch, K. R. Schultz, J. F. Funk, P. S. Pockard, A. C. Marshall & S. K. Showalter, 2002. High efficiency generation of hydrogen fuels using nuclear power. General Atomics Report GA-A24285.
- Carty, R., K. Cox, J. Funk, M. Soliman & W. Conger and L. Brecher & S. Spewock, 1977. Process sensitivity studies of the Westinghouse sulfur cycle for hydrogen generation. *Int. J. Hydrogen Energy*, **2**, pp. 17 - 22.
- Carty, R. H., M. M. Mazumder, J. D. Schreiber & J. B. Panborn, 1981. Thermochemical Hydrogen Production. Vols. 1 – 4, Gas Research Institute for the Institute of Gas Technology, GRI-80/0023, Chicago, IL 60616 (particularly Appendix B of Vol. 3).
- Carty, R. H. & W. L. Conger, 1980. A heat penalty and economic analysis of the hybrid sulfuric acid process. *Int. J. Hydrogen Energy*, **5**, pp. 7 - 20.
- Douglas, J. M., 1988. Conceptual Design of Chemical Processes. New York: McGraw-Hill, pp. 236 – 261.
- Foh, S. E., J. D. Schreiber & J. R. Dafler, 1978. A copper-oxide, copper-sulfate water splitting cycle. Thirteenth Intersociety Energy Conversion Engineering Conference, San Diego, CA, Aug. 20 – 25, pp. 1158 – 1163.
- HSC Software, 2002. Outokumpu HSC Chemistry for Windows. Version 5.1, Antti Roin, 02103-ORC-T, Pori, Finland.
- Kent, S. A., J. R. Katzer & W. H. Manogue, 1977. Infrared spectroscopic investigation of the adsorption and reactions of SO₂ on CuO. *Ind. Eng. Chem. Fundam.*, **16**, pp. 443 – 452.
- Lewis, M. A. & J. G. Masin, 2006. An assessment of the potential of alternative cycles (draft report). Argonne National Laboratories, Argonne, IL.
- Lin, S. S. & R. Flaherty, 1983. Design studies of the sulfur trioxide decomposition reactor for the sulfur cycle hydrogen production process. *Int. J. Hydrogen Energy*, **8**, pp. 589 - 596.

Linnhoff, B. & E. Hindmarsh, 1983. The pinch design method for heat exchanger networks. *Chem. Eng. Sci.*, **38** 745-763

Lu, P. W. T., 1983. Technological aspects of sulfur dioxide depolarized electrolysis for hydrogen production. *Int. J. Hydrogen Energy*, **8**, pp. 773 - 781.

Ludwig, E. E., 2001. *Applied Process Design for Chemical and Petrochemical Plants, Volume 3, 3rd Edition*, Gulf Publishing Co.

McQuillan, B. W., L. C. Brown, G. Besenbruch, R. Tolman, T. Cramer, B.E. Russ, B.A. Vermillion, B. Earl, H.-T. Hsieh, Y.Chen, K. Kwan, R. Diver, N. Seigal, A. Weimer, C. Perkins & A. Lewandowski, 2005. High efficiency generation of hydrogen fuels using solar thermochemical splitting of water. Annual Report, October 1, 2003 through September 30, 2004, GA-A24972, San Diego, CA.

Neumann, J. P., T. Zhong & Y. A. Chang, 1984. The Cu-O (Copper-Oxygen) System. *Bulletin of Alloy Phase Diagrams*, **5**, pp. 136 – 140.

Perkins, C. & A. W. Weimer, 2004. Likely near-term solar-thermal water splitting technologies. *Int. J. Hydrogen Energy*, **29**, pp. 1587 - 1599.

Perry, R. H. & C. H. Chilton, 1973. *Chemical Engineer's Handbook, 5th Ed.*, p. 312, New York: McGraw-Hill.

Peters, M. S, K. D. Timmerhaus & R. E. West, *Plant Design and Economics for Chemical Engineers*, New York: McGraw-Hill.

Rosen, M. A., 1996. Thermodynamic comparison of hydrogen production processes. *Int. J. Hydrogen Energy*, **21**, pp. 349 - 365.

Savitsky, E. M., E. P. Arskaya, E. M. Lazarev, N. A. Korotkov, Iu. I. Vershagin & Iu. A. Sharov, 1982. Investigation of corrosion resistance of materials in the presence of sulphuric acid and its decomposition products applied in the thermochemical cycle of hydrogen production. *Int. J. Hydrogen Energy*, **7**, pp. 393 - 396.

Schreiber, J. D., R. J. Remick, S. E. Foh, & M. M. Mazumder, 1980. A hybrid water-splitting cycle using copper sulfate and mixed copper oxides. Fifteenth Intersociety Energy Conversion Engineering Conference, Seattle, Wash., August 18-22, pp. 2285 – 2288.

Shelley, S., 2006. Coal Gasification Comes of Age. www.cepmagazine.org, pp.6 – 10.

Soliman, M. A., W. L. Conger, R. H. Carty, J. E. Funk & K. E. Cox, 1976. Hydrogen production via thermochemical cycles based on sulfur chemistry. *Int. J. Hydrogen Energy*, **1**, pp. 265 - 270.

Summers, W. A., M.B. Gorenssek & M. R. Buckner, 2005. The hybrid sulfur cycle for nuclear hydrogen production. Proc. of GLOBAL, Tsukuba, Japan, Oct. 9 – 13, paper No. 097.

Teo, E. D., N. P. Brandon, E. Vox & G. J. Kramer, 2005. A critical pathway energy efficiency analysis of the thermochemical UT-3 cycle. *Int. J. Hydrogen Energy*, **30**, pp. 559 - 564.

UNLV Database on Hydrogen Cycles [online]. Available from: <http://shgr.unlv.edu/stchNew/source/login.asp> [cited July 6, 2006].

Yannopoulos, L. N. & J. F. Pierre, 1984. Hydrogen production process; High temperature-stable catalysts for the conversion of SO₃ to SO₂. *Int. J. Hydrogen Energy*, **9**, pp. 383 - 390.

Yerimin, O. V., S. V. Vinnichenko & G. A. Yurgenson, 2006. Evaluation of Gibbs standard potentials for copper sulfates by means of linear programming problems. Institute of natural resources, ecology and criology, the Siberian Branch of the Russian Academy of Science, 672014, Chita, Nedorezova Street 16.

Appendices

Appendix A: Heat Exchanger Cost Data

Appendix B: Reactor/Column Cost Data

Appendix B: Kinetics Analysis of the Carty Report

Appendix A

Heat Exchanger Data

20 °C Approach Temperature

Equipment Identification	Service	Uo		Q		Hot in	Hot out	Cold in	Cold out	ΔT_{LM}	A	Exchanger Type	Internal Pressure (psig rating)	Costs* (Mil \$)
		(Btu/h-ft ² -°F)	(kJ/h-ft ² -°C)	(kJ/sec)	(kJ/h)	(°C)	(°C)	(°C)	(°C)	(°C)	(ft ²)			
HX-2	CuSO ₄ *5H ₂ O/HTF	30	56.97	2.19E+04	7.88E+07	320.0	310.0	280.0	300.0	24.66	56049	Fixed/U	150	0.87
HX-4	Steam/CW	300	569.7	6.62E+05	2.38E+09	100.0	25.0	15.0	25.0	32.26	129582	Fixed/U	300	1.47
HX-5/HX-7	CuSO ₄ /CuO	20	37.98	9.87E+04	3.55E+08	850.0	320.0	300.0	501.7	114.90	81427	Floating Head	300	3.83
HX-6	CuSO ₄ /NHTF	30	56.97	1.84E+05	6.64E+08	870.0	860.0	532.9	850.0	109.89	106055	Floating Head	300	4.75
HX-8	CuO/CW	30	56.97	4.89E+04	1.76E+08	228.0	25.0	15.0	25.0	64.11	48186	Fixed/U	300	0.93
HX-9/HX-12	O ₂ & SO ₃ /O ₂ & SO ₃	30	56.97	1.97E+06	7.08E+09	850.0	122.7	30.8	830.0	47.15	2634078	Fixed/U	300	6.01
HX-10/SO ₂ -REC Reboiler	O ₂ & SO ₃ /Liquid SO ₂	75	142.425	4.60E+04	1.66E+08	122.7	103.6	87.3	88.0	24.31	47871	Fixed/U	300	0.93
HX-11	O ₂ & SO ₃ /CW	75	142.425	4.11E+05	1.48E+09	103.6	25.0	15.0	25.0	33.27	312192	Fixed/U	300	2.22
HX-13	O ₂ & SO ₃ /NHTF	30	56.97	5.25E+04	1.89E+08	870.0	860.0	830.0	850.0	24.66	134469	Fixed/U	300	1.50
HX-14/HX-16	SO ₃ /O ₂ & SO ₂	200	379.8	2.87E+05	1.03E+09	850.0	45.0	25.0	748.3	50.24	54189	Fixed/U	300	0.98
HX-15	SO ₃ /NHTF	30	56.97	2.73E+04	9.84E+07	870.0	860.0	748.3	850.0	53.31	32398	Fixed/U	300	0.77
HX-17	O ₂ & SO ₂ /CW	75	142.425	2.95E+04	1.06E+08	45.0	25.0	15.0	25.0	14.43	51739	Fixed/U	300	0.96
SO ₂ -REC Condenser	O ₂ & SO ₂ /CW	75	142.425	6.36E+03	2.29E+07	34.1	25.0	15.0	25.0	9.57	16791	Fixed/U	300	0.57
HX-18/HX-21	O ₂ & SO ₃ /SO ₃	75	142.425	2.52E+04	9.08E+07	598.6	342.0	126.3	515.0	139.37	4572	Floating Head	300	0.37
HX-19/O ₂ -SEP Reboiler	O ₂ & SO ₃ /Liquid SO ₃	75	142.425	1.41E+04	5.06E+07	342.0	188.2	125.5	126.3	123.82	2868	Floating Head	300	0.26
HX-20	O ₂ & SO ₃ /CW	75	142.425	3.80E+04	1.37E+08	188.2	25.0	15.0	25.0	54.86	17495	Fixed/U	300	0.58
O ₂ -SEP Condenser	O ₂ & SO ₃ /CW	75	142.425	4.33E+02	1.56E+06	27.4	25.0	15.0	25.0	5.32	2060	Fixed/U	300	0.21
HX-22	SO ₃ /NHTF	30	56.97	1.20E+04	4.31E+07	870.0	860.0	515.0	850.0	114.12	6636	Floating Head	300	0.50
HX-23	SO ₂ /CW	125	237.375	1.95E+04	7.01E+07	86.7	25.0	15.0	25.0	28.41	10396	Fixed/U	300	0.45
													TOTAL	28.16

10 °C Approach Temperature

Equipment Identification	Service	Uo		Q		Hot in	Hot out	Cold in	Cold out	ΔT_{LM}	Area	Exchanger Type	Internal	Costs*
		(Btu/h-ft ² -°F)	(kJ/h-ft ² -°C)	(kJ/sec)	(kJ/h)	(°C)	(°C)	(°C)	(°C)				Pressure	
HX-1/HX-3	Steam/CuSO ₄ *5H ₂ O	20	37.98	2.65E+05	9.56E+08	300	100	25	280	41.61	604,778	Fixed/U	300	3.02
HX-2	CuSO ₄ *5H ₂ O/HTF	30	56.97	2.19E+04	7.88E+07	320	310	280	300	24.66	56,049	Fixed/U	150	0.87
HX-4	Steam/CW	300	569.7	6.62E+05	2.38E+09	100	25	15	25	32.26	129,582	Fixed/U	300	1.47
HX-5/HX-7	CuSO ₄ /CuO	20	37.98	9.87E+04	3.55E+08	850	320	300	501.7	114.90	81,427	Floating Head	300	3.83
HX-6	CuSO ₄ /NHTF	30	56.97	1.84E+05	6.64E+08	870	860	532.9	850	109.89	106,055	Floating Head	300	4.75
HX-8	CuO/CW	30	56.97	4.89E+04	1.76E+08	228	25	15	25	64.11	48,186	Fixed/U	300	0.93
HX-9/HX-12	O ₂ & SO ₃ /O ₂ & SO ₃	30	56.97	1.97E+06	7.08E+09	850	122.7	30.8	830	47.15	2,634,078	Fixed/U	300	6.01
HX-10/SO ₂ -REC Reboiler	O ₂ & SO ₃ /Liquid SO ₂	75	142.425	4.60E+04	1.66E+08	122.7	103.6	87.3	88	24.35	47,793	Fixed/U	300	0.93
HX-11	O ₂ & SO ₃ /CW	75	142.425	4.11E+05	1.48E+09	103.6	25	15	25	33.27	312,192	Fixed/U	300	2.22
HX-13	O ₂ & SO ₃ /NHTF	30	56.97	5.25E+04	1.89E+08	870	860	830	850	24.66	134,469	Fixed/U	300	1.50
HX-14/HX-16	SO ₃ /O ₂ & SO ₂	200	379.8	2.87E+05	1.03E+09	850	45	25	748.3	50.24	54,189	Fixed/U	300	0.98
HX-15	SO ₃ /NHTF	30	56.97	2.73E+04	9.84E+07	870	860	748.3	850	53.31	32,398	Fixed/U	300	0.77
HX-17	O ₂ & SO ₂ /CW	75	142.425	2.95E+04	1.06E+08	45	25	15	25	14.43	51,739	Fixed/U	300	0.96
SO ₂ -REC Condenser	O ₂ & SO ₂ /CW	75	142.425	6.36E+03	2.29E+07	34.147	25	15	25	9.57	16,791	Fixed/U	300	0.57
HX-18/HX-21	O ₂ & SO ₃ /SO ₃	75	142.425	2.52E+04	9.08E+07	598.6	342	126.3	515	139.37	4,572	Floating Head	300	0.37
HX-19/O ₂ -SEP Reboiler	O ₂ & SO ₃ /Liquid SO ₃	75	142.425	1.41E+04	5.06E+07	342	188.2	125.5	126.3	123.83	2,868	Floating Head	300	0.26
HX-20	O ₂ & SO ₃ /CW	75	142.425	3.80E+04	1.37E+08	188.2	25	15	25	54.86	17,495	Fixed/U	300	0.58
O ₂ -SEP Condenser	O ₂ & SO ₃ /CW	75	142.425	4.33E+02	1.56E+06	27.39	25	15	25	5.32	2,060	Fixed/U	300	0.21
HX-22	SO ₃ /NHTF	30	56.97	1.20E+04	4.31E+07	870	860	515	850	114.12	6,636	Floating Head	300	0.50
HX-23	SO ₂ /CW	125	237.375	1.95E+04	7.01E+07	86.7	25	15	25	28.41	10,396	Fixed/U	300	0.45
													TOTAL	31.19

Appendix B

Purchase Cost of Reactors and Columns

	Diam., ft	Length (T-T), ft	Base Cost	Fm	Fp	Purch. Cost (1968)	Purch. Cost (2005)
SO2-REC	18	40	45000	3.67	1.35	222952.5	\$1,001,534.48
O2-SEP	8	17	9000	3.67	1.35	44590.5	\$200,306.90
RXN-1	20	30	40000	3.67	1.35	198180	\$890,252.87
RXN-2A	20	60	60000	3.67	1	220200	\$989,169.86
RXN-2B	20	60	60000	3.67	1	220200	\$989,169.86
RXN-2C	20	60	60000	3.67	1	220200	\$989,169.86
RXN-3	20	40	50000	3.67	1.35	247725	\$1,112,816.09
RXN-4	10	25	15000	3.67	1.35	74317.5	\$333,844.83
RXN-5	10	20	15000	3.67	1.35	74317.5	\$333,844.83
Total:							\$6,840,109.56

Appendix C:

Kinetics Analysis of the Carty Report Data

Reactor Sizing

Initially, we attempted to reproduce reactor volumes calculated in the Carty report for the decomposition of copper sulfate to copper oxide and sulfur trioxide. The following equations were used (Carty, 240):

$$r_p d \left[- (1 - x_S)^{1/3} \right] = 16.28 e^{-12000/T} \left[\frac{p_e - p_b}{p_e} \right] t \quad (1)$$

$$r_p d \left[- (1 - x_S)^{1/3} \right] = 428.4 e^{-16500/T} \left[\frac{p_e - p_b}{p_e} \right] t \quad (2)$$

Where $r_p \equiv$ bed radius, cm

$d \equiv$ bed density, gmol/cm³

$x_S \equiv$ fractional solid conversion

$p_e \equiv$ equilibrium SO₃(g) partial pressure

$p_b \equiv$ bulk SO₃(g) partial pressure

$t \equiv$ time, min

The reason for having two distinct equations for one reaction step is stated in the Carty report (pp. 235, 239). They hypothesize a two-part reaction in which a cupric oxysulfate intermediate is present. The differences between the two equations are in the constants for activation energy and frequency factor.

In order to try to reproduce the results for reactor volume from the Carty report, certain parameters and assumptions were used as they were stated in the report. These include a bed density of 1 g/cm³ (6.27 X 10⁻⁷ gmol/cm³), a fractional solid conversion of 0.99, and the assumption that the bulk partial pressure of SO₃(g) was negligible compared to equilibrium levels, i.e. $\left[\frac{p_e - p_b}{p_e} \right] \approx 1$.

One of the discrepancies realized in our attempts to reproduce the data concerned the bed density (d) listed in Carty, et al. The value of 1 g/cm³ is apocryphal. One of the causes for confusion is the fact that this particular term is listed in a similar equation in two different places, but representing two different quantities. It is first listed in the report as representing particle density (p. 233) and then later as representing bed density (p.240). Furthermore, according to the HSC database, the density of CuSO₄(s) is 3.603 g/cm³. It was unclear how Carty, et al. arrived at a value of 1 g/cm³ for the bed density. After checking a number of chemical manufacturer web sites (e.g., SMICO Manufacturing,

(<http://www.smico.com/pdf/SMICO%20MATERIAL%20BULK%20DENSITY%20REFERENCE%20CHART.pdf>) and noting a reported bulk density of 52 lb_m/ft³, we assumed the value of 1g/cm³ is an approximation (calculations give a value closer to 0.83 g/cm³). In attempts to relate this bed density to the particle density listed in the HSC database, a void fraction of 72.25% (volume) was calculated. This suggests that the bed was approximately 30% copper sulfate by volume. Nowhere in the report was this indicated, however, and so the validity of this assumption is uncertain.

The time unit in Equations 1 and 2 is understood to be residence time. Therefore, using the second of the two empirical relations (Equation 2), a residence time was obtained for a given bed radius and the given parameters mentioned. Based on the requirement to have a copper sulfate decomposition of 6.4 X 10⁵ g-mol/min, the reactor volumes we calculated did not match those listed in Table B-35 in the Carty report (p. 240, 241). See Figure 1 below.

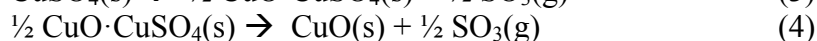
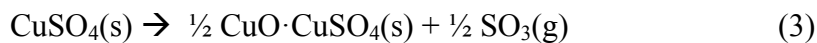
Temp (K)	r _p (ft)	Volume (ft ³)	
		Tulane U.	Carty et al.
1173	4	1.86E+07	4.40E+06
1173	6	3.72E+07	6.60E+06
1173	8	5.57E+07	8.80E+06
1173	10	7.43E+07	1.10E+07
1123	4	3.48E+07	7.80E+06
1123	6	6.95E+07	1.20E+07
1123	8	1.04E+08	1.60E+07
1123	10	1.39E+08	1.90E+07
1073	4	6.89E+07	1.50E+07
1073	6	1.38E+08	2.20E+07
1073	8	2.07E+08	2.90E+07
1073	10	2.76E+08	3.60E+07

Figure 1. A comparison of calculated reactor volumes for a cylindrical reactor.

Regardless of the discrepancies in calculating the reactor volumes, the size of these hypothetical reactors is physically unrealizable. The heights of any one of these reactors is several thousand feet—overshadowing all 1,450 feet of the Sears Tower. This includes the reactor volumes calculated by Carty, et al., although they claim volumes on the order of 10⁶ cubic feet are reasonable (p. 241). Smaller reactor volumes are expected at lower copper sulfate conversions. However, in light of the above reactor volume discrepancy, a detailed review of the kinetic analysis is warranted.

Kinetics Analysis

As indicated by Carty, et al., the decomposition of copper sulfate is taking place in two consecutive sub-steps in which a cupric oxysulfate intermediate is present (Equations 3 and 4).



Lacking almost all of the raw data, however, has contributed to the inherent difficulty in reproducing the results in the Carty report. Nevertheless, some reaction rate data for the copper sulfate decomposition is presented in the report (Table B-32, p. 238). Graphs of $\left[1 - (1 - x_s)^{1/3}\right]$ vs. t were generated in which the slope of the line is equal to the product of the rate constant, bed radius, and bed density ($k \cdot r_p \cdot d$). In a straightforward calculation, the rate constant can be determined for a known bed density and bed radius. Our resulting rate constants, however, were slightly less than half of each value of the average rate constants calculated by Carty, et al (see Figure 2). The experimental trials performed at 1173 K were not verified because Carty, et al. reported a likelihood of error (p. 239).

Temp (K)	Reaction	$k \times 10^4$	
		(gmol/cm ² min)	
		Tulane U.	Carty et al.
1073	3	0.924	2.22
	4	0.3825	0.94
1123	3	1.78	3.68
	4	0.738	1.53

Figure 2. Comparison of calculated rate constants (averages). *Trials at 1173 K were omitted.

One possibility for the discrepancy in average rate constants is that Carty, et al. may have used some unreported technique for discarding outlying data points. Consequently, in our analyses all rate constants (every data point) were included in the calculation of an average for a given reaction and reaction temperature. A different set of reaction rate constants was obtained. New values for activation energy and frequency factor were calculated for each of the two reactions. The comparison can be seen in Figure 3.

Reaction	Activation Energy (E_a)		Frequency factor (k_o)	
	(kcal/mol)		(g-mol/cm ² min)	
	Tulane U.	Carty et al.	Tulane U.	Carty et al.
3	31.39975	23.9	229.683	16.28
4	31.47526	32.8	98.46489	428.4

Figure 3. A comparison of activation energy and frequency factor based on the *different* sets of rxn rate constants.

Furthermore, a similar analysis of the average rate constants published in the Carty report yielded different values for activation energy and frequency factor than were published. This result can be seen in Figure 4 below.

Reaction	Activation Energy (E_a)		Frequency factor (k_o)	
	(kcal/mol)		(g-mol/cm ² min)	
	Tulane U.	Carty et al.	Tulane U.	Carty et al.
3	24.2041	23.9	18.88938	16.28
4	23.32973	32.8	5.306858	428.4

Figure 4. A comparison of activation energy and frequency factor based on the *the same* set of rxn rate constants.

After finding inconsistencies in the reaction rate constants, the graphs were reanalyzed to check the validity of the slopes listed in the reaction rate data. One difficulty in doing this was that the graphs being presented were for a specific bed density and flowrate of argon. Recall that the argon is being used as an inert sweeper to remove sulfur oxides and help drive the reaction. In the experiments, the bed density was 0.98 g/cm³ and the argon flowrate was 75 cm³/min (Carty, et al.). Only two of the reaction rate data points listed, which are already limited in number, were near these conditions. Therefore, the comparison of the slope is an approximation at best. The order of magnitude was in agreement for both temperatures of 1073 K and 1123 K. Still, a significant error was observed for the value of the slope at a temperature of 1073 K. The experimental trials performed at 1173 K were not verified because Carty, et al. reported a likelihood of error (p. 239).

CONCLUSION

In order to design a more feasible simulation, we deemed it necessary to become familiar with the kinetics involved in the reactions of Cycle H-5. Therefore, we initially attempted to reproduce some of the results arrived at in the Carty report. Because the decomposition of anhydrous copper sulfate included the largest, albeit limited, amount of raw data available, we decided to analyze this reaction first. We immediately noticed the extremely large reactor volumes and attempted to reproduce the published results. We were unable to duplicate these values, but still the calculated reactor volumes are physically unrealizable. Through further investigation of the rate data, the attempted reproduction of average rate constants yielded dubious results. The lack of raw data available from the Carty report prevents any further validation of their kinetic analysis.

Lastly, we believe reactions 3 and 4 are occurring simultaneously, whereas Carty et al. assume the reactions take place consecutively (p. 235). Their experimental approach, along with the data they collected, does not allow us to determine rate constants using a simultaneous-reaction approach. Consequently, it would be necessary to perform additional experimentation to further investigate this matter.