Evaluation of Promising Alternative Thermochemical Cycles

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Introduction

The focus of the Nuclear Hydrogen Initiative (NHI) of the U.S. Department of Energy's Office of Nuclear Energy (DOE-NE) is to identify and ultimately commercialize hydrogen production technologies that are compatible with nuclear energy systems and that do not produce greenhouse gases. The NHI objective is to operate a nuclear hydrogen production plant at a cost competitive with other alternative transportation fuels by 2019. The NHI is supporting development of several hydrogen production options, including high-temperature steam electrolysis and two sulfur-based thermochemical cycles. The purely thermochemical sulfur-iodine cycle is considered the baseline process within the program. The viability of the S-I cycle, however, has yet to be demonstrated and its high temperatures (> 900°C) and aggressive chemical environments pose serious challenges. To ensure that the NHI is considering the most promising hydrogen production options, DOE-NE is supporting an effort to reevaluate other thermochemical cycles identified in the literature . Two good summary reports are those by McQuillan and Carty [1, 2], which described over 200 cycles. Some cycles have been extensively investigated, but none have ever been commercialized. The R&D effort begun in the 1970's as a response to the energy crisis was abruptly terminated when oil became inexpensive again in the 1980's. The NHI program today is reexamining this past work and has funded Argonne National Laboratory and a group of universities to lead this effort. The goal is to determine which alternative cycles have sufficient merit to justify additional R&D and whose development can meet the timeline established by the NHI.

There are two objectives for reexamining the 200+ cycles in the literature for the NHI:

- (1) to consider if current technologies might overcome the barriers identified in the 1970's for cycles for which extensive R&D effort was completed; and
- (2) to take a second look at cycles that were not fully investigated.

The reexamination identified eight alternative cycles as promising: the cerium-chlorine (Ce-CI), the copper-chlorine (Cu-CI), the iron-chlorine (Fe-CI), the vanadium-chlorine (V-CI), the copper sulfate (Cu-SO₄), the magnesium-iodine (Mg-I), the hybrid chlorine, and a proprietary one. Proof-of-principle experiments were completed in the 1970's for all but the Cu-Cl cycle and the proprietary one. In most cases, barriers for further development were identified. The Cu-Cl cycle was proposed during this early research period, but the proof-of-concept work was only recently completed [3, 4]. The proprietary cycle was proposed two years ago and no proof-of-concept work has been completed yet. The Cu-Cl, the Mg-I, and the proprietary cycles require lower temperatures (< 600° C) than the baseline sulfur-iodine cycle currently being developed by the NHI and, therefore, balance the NHI's thermochemical cycle portfolio over a wide temperature region.

The tasks for the universities and Argonne were (1) to re-evaluate the efficiencies of the eight promising cycles using a consistent methodology and (2) to determine if the barriers identified in the literature could be overcome with new technologies or approaches. Some barriers, such as separations, excess water handling, and corrosion, are common to nearly all cycles but vary in their impact on energy costs.

In this report we discuss the status of the evaluation program for four cycles, the Mg-I, the hybrid chlorine, the Fe-CI, and the Cu-SO₄ cycles. Sufficient details of the evaluations are described to illustrate the method of the ongoing work and to demonstrate how new technologies and new ideas might eliminate barriers identified in the past. Results for the other cycles will be published at a later time. By mid 2007 the most promising of the eight alternatives will be selected for more intensive laboratory testing.

Approach

The criteria that were used in the general screening process for the NHI effort were element abundance, simplicity, chemical viability, thermodynamic feasibility, and safety. Cycles were eliminated from further consideration if they had one or more of the following characteristics:

- 1. Required process heat greater than 850°C.
- 2. Contained elements with low natural abundances. (See Figure 1.)
- 3. Specified more than four elements (including hydrogen and oxygen) and more than five reactions.
- 4. Contained Hg, Se, or Cd (because of the low releases allowed under Resource Conservation and Recovery Act (RCRA) standards or reactions that were explosive.
- 5. Consisted of one or more reactions characterized with significant competing reactions, slow kinetics, or low yields; i.e., had non-chemically viable reactions.
- 6. Contained reactions for which the free energy change exceeded ± 63 kJ (all other factors being equal); i.e., had thermodynamically unfeasible cycles.

The next phase of the evaluation was a calculation of the efficiency for various levels of development. Thermal efficiency, η , was defined by Beghi [5] as

$$\eta = \frac{-\Delta H_{25^{\circ}C}^{\circ}(H_2O)}{Q_{hot} + \frac{W}{0.5}}.$$

The numerator is the standard enthalpy of the formation of water at 25°C, 285.83 kJ/mol for high heating value (HHV) or of steam at 25°C, 241.83 kJ/mol for low heating value (LHV). The denominator includes the thermal heat, Q, supplied externally, and different types of work (chemical, electrochemical, mechanical, electrical, separation, etc.) converted to the thermal equivalent (assuming a 50% efficiency factor). For this Level 1 assessment water is presumed to enter the system at 25°C and both hydrogen and oxygen are released at 25°C and atmospheric pressure. Electrochemical work is defined by the Nernst equation, or $\Delta G = nFE$, where E is the cell potential in volts, F is Faraday's constant, 96,493 coulombs, and ΔG is in Joules. The concentration term is not considered at this stage, because of the unavailability of sufficient information. Work of separation is defined by the equation $\Delta G_{sep} = -RT \Sigma_i n_i ln y_i$,

where R is the gas constant, T is the absolute temperature, n_i is the flow rate of each component, and y_i is the mole fraction. Chemical work is given by the free energy for the reaction if it is positive and no credit is given when the free energy of the reaction is negative. Pinch analysis is used for optimizing energy usage that is, exothermic heat is recovered and used for endothermic processes only when temperatures can be matched. In some early work, we used a 10°C driving force but are now using a 20°C driving force as a more achievable engineering value. Shaft or mechanical work is not included in the Level 1 assessment. The calculations are normalized to one mole of water. For a Level 1 efficiency calculation, all reactions are assumed to go to 100% completion and it is assumed that there are no competing reactions.

For cycles that appear promising after the Level 1 analysis, a more detailed Level 2 efficiency is calculated. Level 2 considers equilibrium data and, if available, kinetic data. Experimental parameters, i.e., pressure, temperature, excess reagents, are set to minimize competing product formation and to obtain the highest yields. Product recycle is allowed in Level 2. Methods for accomplishing the separations or chemical work are undefined for Levels 1 and 2. In our early Levels 1 and 2 analyses, pressure was not a variable. However, in the more recent work with the universities, pressure was used as a variable. If experimental conditions cannot be adjusted to minimize competing product formation or to produce reasonable yields of desired products, the cycle is eliminated from further consideration because the chemistry is not viable for a cyclic process. All the cycles described in this report, however, have been proven.

More advanced calculations for Level 3 are based on real chemistry, including consideration of azeotropes, hydrated species, solvation effects, etc. The level of complexity is much higher and a process design simulator is used. A heat exchanger network may be used for heat management rather than pinch analysis. The following guidelines were established for Level 3 calculations using a process simulator:

- 1. Hydrogen is produced at 15 bar instead of at atmospheric pressure.
- 2. Water enters the process at 25°C.
- 3. The annual capacity of the plant is 200 million kg hydrogen per year.
- 4. The heat exchanger driving force is 20°C.
- 5. Pressure, temperature, and concentration can be varied for optimization.
- 6. SI units are used.

Engineering expertise from the universities provided for process optimization.

Cycle Selection

Information on elemental abundance can be found on various websites, e.g., http://en.wikipedia.org/wiki/Image:Relative abundance of elements.png#file and http://www.seafriends.org.nz/oceano/abund.htm. Figure shows 1 elemental crustal abundance. Abundance of a chemical species is an important consideration for evaluating the potential of a cycle. For example, one cycle that was tentatively identified as promising contained Bi. The stoichiometry (which was somewhat uncertain) of the reactions indicated that 0.5 to 1.5 mol of bismuth was required for every mol of hydrogen produced. For a thermochemical plant that produces 100 million kg mol of hydrogen per year, approximately 500 to 1500 metric tons of bismuth would be required for a residence time of 15 minutes. Longer residence times would require more bismuth. Figure 1 shows that the crustal abundance of Bi is relatively small. Data from the U.S. Geological Survey from January 2005 indicated that there is no domestic refinery production of bismuth in the U.S. and that 95% of the bismuth consumed in the U.S. was imported [6]. This source also indicated that the world production of bismuth in 2004 was 3800 metric tons and that world reserves were 330,000 metric tons. Since the amount of bismuth required for one thermochemical plant represents about 13 to 25% of the world's annual production and since the world's reserves are relatively low, cycles containing bismuth are not likely to be economic.



Figure 1. Crustal Abundance of the Elements (http://en.wikipedia.org/wiki/Image:Relative_abundance_of_elements.png#file)

After considering abundance and the other criteria listed above, the following eight alternative cycles were identified as promising:

- Cerium-chlorine (Ce-Cl) [2],
- Iron-chlorine (Fe-Cl) [2],
- Magnesium -iodine (Mg-I) [7-11],
- Vanadium-chlorine (V-Cl) [12, 13],
- Hybrid copper-chlorine (Cu-Cl) [3, 4],
- Hybrid copper-sulfate (Cu-SO4) [2],
- Hybrid chlorine [1-2, 14], and
- A proprietary cycle.

Proof-of-concept work has been completed for the first seven cycles and chemical viability has been proven [2-4, 7-14, and references therein]. Most of these cycles require 850°C process heat, similar to that needed for the baseline sulfur-iodine cycle being explored by the NHI. Three of the cycles, the hybrid Cu-Cl, the Mg-I, and the proprietary cycles, require process temperatures of 600°C or less. Hybrid cycles are those that require an electrochemical step. Electrochemical reactions are energy intensive and are likely to have poorer economic scaling factors than thermal reactions. With all other factors equal, then, thermal cycles are preferred over hybrid cycles. Other challenges identified in the literature were examined and new ideas for improving cycle performance emerged, some of which will be briefly described below.

Hybrid Chlorine

The hybrid chlorine cycle is relatively simple, consisting of two reactions: (1) the reverse Deacon reaction and (2) electrolytic HCl decomposition, as shown below. The analysis of this cycle at Levels 1 and 2 provides information on the challenges that must be met if this cycle can be used to produce hydrogen efficiently.

$CI_{2}(g) + H_{2}O(g) \iff 2HCI(g) + \frac{1}{2}O_{2}(g)$	850°C	(CI-1)
2HCI (g) \Leftrightarrow H ₂ (g) + Cl ₂ (g) (electrolytic)	75°C	(Cl-2)

This cycle's efficiency was calculated as 25.5% when the electrolysis was based on the Udhe process [1]. However, Argonne National Laboratory and Clemson University reexamined this cycle, with an electrolyzer design based on polymer electrolyzer membrane fuel cell (PEMFC) technology. The PEMFC technology appears to offer advantages over the Udhe process for this application in that it uses gaseous HCI and has lower electrical power consumption. Currently, the PEM cell prototypes require 1.65 V for a current density of 6 kA/m². Further optimization may lead to a reduction to 1.5 V or possibly less [14]. A cell emf of 1.5 V has a heat equivalent of 577.4 kJ when the source efficiency is 50%. If there are no other heat requirements, the efficiency corresponding to the cycle with this amount of electrochemical work alone is 42% (LHV). With other heat and work demands, the efficiency is considerably less, 34.3% (LHV) for Level 1 calculations where reactions are assumed to go to 100% completion. The energy inputs for the Level 2 calculation are higher because the reverse Deacon reaction does not go to completion. At 850°C, the equilibrium conversion is Conversion can be increased by increasing the molar ratio of water to Cl₂. onlv 60%. However, the penalty for this approach is higher energy costs for separations and for heat management, and the resulting efficiency is 30-32%.

Level 3 analyses, completed by Clemson University, are based on more realistic chemistry [15]. Clemson considered five process designs, but only one will be discussed here. Clemson proposed the use of a membrane reactor in which oxygen permeates through the reactor walls to shift the reverse Deacon reaction to the right and to eliminate some of the separation costs. In Clemson's process design, the reverse Deacon reaction is run at 850°C and 20 bar. The chlorine-to-steam molar ratio is five and 96% of the water is converted. Clemson proposes the use of a nitrogen sweep gas, but recognizes that a more efficient method might be found. Clemson calculates the Level 3 efficiency as 35% (LHV). The capital costs associated with the hybrid chlorine cycle are expected to be somewhat lower than those for more complicated cycles.

The reverse Deacon reaction, $Cl_2(g) + H_2O(g) \Leftrightarrow 2HCI(g) + \frac{1}{2}O_2(g)$, can be used in the Ce-CI, Fe-CI, V-CI, Cu-CI cycles as well as in the hybrid chlorine cycle. Low yields, separation issues, and the aggressive nature of the chemicals associated with the reverse Deacon reaction were identified independently as barriers in the further development of the Fe-CI and the Ce-CI cycles. Any progress on the reverse Deacon reaction would benefit other cycles containing chlorine and/or HCI.

Magnesium-Iodine (Mg-I)

This purely thermochemical cycle was first studied in Japan [7-11], where proof-ofconcept experiments were completed and process design was started. The simplified reactions that constitute the magnesium-iodine cycle were reported in the literature as the following along with their recommended process temperatures:

$6/5 \text{ MgO}(s) + 6/5 \text{ I}_2(I) \Leftrightarrow 1/5 \text{ Mg}(IO_3)_2(s) + \text{MgI}_2(aq)$	T=120°C	(Mg-1)
$1/5 \text{ Mg}(IO_3)_2 \text{ (s)} \Leftrightarrow 1/5 \text{ MgO (s)} + 1/5 \text{ I}_2 \text{ (g)} + 1/2 \text{ O}_2 \text{ (g)}$	T=600°C	(Mg-2)
$MgI_2 (aq) + 6 H_2O (I) \Leftrightarrow MgI_2 \bullet 6H_2O (s)$	T=120°C	(Mg-3)
$MgI_{2} \cdot 6H_{2}O(s) \Leftrightarrow MgO(s) + 5 H_{2}O(g) + 2 HI(g)$	T=450°C	(Mg-4)
$2 \text{ HI } (g) \Leftrightarrow I_2 (g) + H_2 (g)$	T=500°C	(Mg-5)

The advantages of this cycle are its moderate reaction temperatures, relatively easy separations (most by filtration or solidification of iodine), and availability of thermodynamic data for most of the chemical species. The free energy changes for these reactions (except Mg-3) are either negative or slightly positive, indicating that the reactions do proceed to the right. Reaction rates are reasonable [11].

The representation of the cycle shown above did not allow for the standard Level 1 calculation, in which the pressure is fixed at 1 bar. The Mgl₂ aqueous solution would not be stable at 120°C and one atmosphere pressure. The University of South Carolina (USC) team, therefore, calculated the Level 1 efficiency in two ways. In Level 1a, the Mgl₂ is treated as a solid and in Level 1b, it is treated as a solution at 120°C and about 2 bar [15]. The corresponding efficiencies were calculated as 84% (LHV) and 47% (LHV).

The Level 2 efficiency calculation recognized the results of the earlier experimental work. Kondo et al. suggested a large excess of both water and iodine were necessary to produce insoluble $Mg(IO_3)_2$ and aqueous $MgI_2[9]$. However, a later report indicated molar ratios of $MgO : I_2 : H_2O$ as 1 : 5 : 8 were suitable [11]. The team at the USC chose to do their

simulations with an intermediate concentration; i.e., the molar ratios of MgO : I_2 : H_2O were chosen as 1 : 6.8 : 11.7 for reaction Mg-1. A flowsheet was prepared and process design optimization started. The efficiency was 31% (LHV) [16]. This low value was due to the large amount of heat that Aspen Plus calculates for mixing excess iodine into the aqueous MgI₂ solution. USC could not find an explanation in the literature that would explain why the heat demand increased with increasing I₂ concentrations. When USC corrected for the heat of mixing, the efficiency increased to 45% (LHV).

Further simulations will increase the accuracy of the model. For example, reactions Mg-1 and Mg-4 are oversimplified and better insight into the chemistry can be obtained by the following representations of these reactions:

 $\begin{array}{l} 1.2 \ \text{MgO} \ (s) + 8.2 \ \text{I}_2 \ (l) + 14 \ \text{H}_2\text{O} \Leftrightarrow 0.2 \ \text{Mg}(\text{IO}_3)_2 \ (s) + \ \text{MgI}_2 \cdot 6\text{H}_2\text{O}(\text{aq}) + 8 \ \text{H}_2\text{O} + 7 \ \text{I}_2 \ (l) \ (\text{Mg-1a}) \\ \text{MgI}_2 \cdot 6\text{H}_2\text{O} \ (s) + 1 - 3 \ \text{I}_2 \ (l,s) \ \Leftrightarrow \ \text{MgO} \ (s) + 5 \ \text{H}_2\text{O} \ (g) + 2 \ \text{HI} \ (g) + 1 - 3 \ \text{I}_2 \ (g) \ (\text{Mg-4a}) \\ \end{array}$

USC used the stoichiometry shown in Mg-1a in their simulation, but no penalty was assigned for water removal. It was assumed that energy obtained from condensing water within the cycle could be used for evaporation at no additional cost. The excess iodine is problematic. USC did account for the excess iodine in Mg-1a but not in Mg-4a. In the present simulation, all 7 moles of excess iodine are condensed from the aqueous solution formed in reaction Mg-1a. However, Shindo et al. indicates that 1 to 3 mol of iodine remain in the Mgl₂ aqueous solution product and that the products of the decomposition reaction (Mq-4a) are MgO and a gaseous mixture of steam, HI, and I₂ [11]. HI and H₂O form an azeotrope, which was not considered in the present simulation. In addition, the decomposition of HI to I₂ and H₂ is not favored. The equilibrium constant indicates only 18 to 29% of the HI dissociates at 300 to 700°C, respectively and recycle is required [11]. Future simulations will consider as many of these aspects as possible. It is necessary that experimental data and reliable thermodynamic data are available and we are checking the reliability of the data used in the present model. These improvements will improve the accuracy of the model for the cycle.

The USC team has proposed the use of electrodialysis to assist in concentrating the Mgl₂ solution. Electrodialysis consumes relatively small amounts of energy compared to that used for evaporation.

Shindo et al. report that the separation of the mixed gases in Mg-4a (H₂, I₂, HI, and H₂O) is the most challenging aspect of this cycle [11]. They proposed three separation methods, quenching, MgO sorption, and Fe₃O₄ decomposition of HI. None of these methods was completely satisfactory. This issue will be addressed in the future by the USC team.

The iodine chemistry in the Mg-I cycle may be somewhat similar to that in the S-I cycle and its further development may be leveraged by work ongoing for the S-I cycle. For instance, the molar ratio of HI : I_2 : H_2O is 2 :10 : 8 in the more dense phase of the Bunsen reaction in the S-I cycle. (The Bunsen reaction is usually described by the reaction,

$$SO_2 + 2H_2O + I_2 \Leftrightarrow H_2SO_4$$
 (aq) + 2HI (aq),

but a more accurate representation shows the formation of the two phases (each in brackets) as,

$$SO_2 + 17 H_2O + 9 I_2 \iff [H_2SO_4 \bullet 5H_2O] + [2HI + 10 H_2O + 8I_2]).$$

The molar ratio of HI : I_2 : H_2O is 2 : 1 to 3 : 5 in Mg-4 is similar to that in the Bunsen. Thus, the technology being developed to separate I_2 from HI and H_2O mixtures in the S-I cycle may be useful for the same operation in the Mg-I cycle. In addition, the method for decomposing HI and H_2O mixtures and the recycle loop design in the S-I cycle might also be useful for the Mg-I cycle.

Hybrid Copper sulfate (Cu-SO₄)

The Carty report provided information on the hybrid Cu-SO₄ cycle. This cycle is simply represented by the following two reactions for a Level 1 efficiency calculation:

$CuO + H_2O + SO_2 \Leftrightarrow CuSO_4 + H_2 (g)$	(electrolytic)	25°C	(Cu-1)
$CuSO_4 \Leftrightarrow Cu(g) + SO_2(g) + \frac{1}{2}O_2(g)$		850°C	(Cu-2)

The Carty report specified that reaction Cu-1 cannot be thermally driven even though the free energy of the reaction is only slightly positive. Their experimental work indicated a minimum cell potential of 0.45V that might be achieved with an optimized cell design and electrocatalysts [17]. The heat equivalent for the electrochemical work represents about half of the total heat demand.

A more detailed examination of the chemistry shows that the two reactions given above to describe the cycle are oversimplified and that a more accurate representation is the following:

$CuO + xH_2O + SO_2 \Leftrightarrow CuSO_4 \bullet (x-1)H_2O + H_2 (g)$ (electrolytic)	25°C	(Cu-3)
$CuSO_4 \bullet xH_2O \Leftrightarrow CuSO_4 + xH_2O (g)$	225°C	(Cu-4)
$CuSO_4 \Leftrightarrow CuO + SO_3(g)$	850°C	(Cu-5)
$SO_3(g) \Leftrightarrow \frac{1}{2}O_2(g) + SO_2(g)$	850°C	(Cu-6)

The Cu-SO₄ cycle has the same high-temperature SO₃ decomposition reaction as the baseline sulfur cycles (sulfur-iodine and hybrid sulfur), but it involves less aggressive chemicals because no water is present when $CuSO_4$ decomposes. The Level 1 efficiency with the electrochemical work is about 44% (LHV).

A thermodynamic database, HSC, predicts that the reaction between cupric oxide, water, and sulfur dioxide results in the formation of several hydrated species of CuSO₄ (See Figure 2.) [18]. Hydrogen production is about 99% of theoretical if 10 mol of water are used in reaction Cu-3 for every mole of CuO at 850°C. Removal of this excess water constitutes a thermal burden. Tulane estimated Level 2 efficiencies of 25 to 40% for temperatures in the 850°C range. These estimates varied with the temperature and on the process details used for the CuSO₄ decomposition.

Tulane has a proprietary idea that would convert the electrochemical reaction to a thermal one [19]. Their approach appears very promising based on thermodynamic data. Proof-of-concept experiments have been planned.



Figure 2. HSC Equilibrium Data for Reaction Cu-3 at 25°C and 1 atm

Another challenge associated with the Cu-SO₄ cycle is the relatively high temperature at which CuSO₄ occurs. The HSC database indicates also shows that the decomposition of CuSO₄ occurs at significantly higher temperatures than that of H_2SO_4 as shown in Figures 3 and 4.



Figure 3. HSC Equilibrium Data for the Decomposition of CuSO₄ vs. Temperature



Figure 4. HSC Equilibrium Data for the Decomposition of H₂SO₄ vs. Temperature

Iron-Chlorine (Fe-Cl)

The advantages of the purely thermochemical Fe-Cl cycle are that the chemicals are relatively cheap and the chemistry of various iron oxides and chlorides is well-known. The reactions in the most promising of the Fe-Cl cycles (# B-1) studied by Carty et al. are as follows:

$3\text{FeCl}_2 + 4\text{H}_2\text{O}(g) \iff \text{Fe}_3\text{O}_4 + 6\text{HCl}(g) + \text{H}_2(g)$	925°C	(Fe-1)
$Fe_3O_4 + 8HCI (g) \iff FeCl_2 + 2FeCl_3 + 4H_2O (g)$	125°C	(Fe-2)
$2 \operatorname{FeCl}_3 \Leftrightarrow \operatorname{Fe}_2 \operatorname{Cl}_6 \Leftrightarrow 2 \operatorname{FeCl}_2 + \operatorname{Cl}_2(g)$	425°C	(Fe-3)
$CI_2 + H_2O(g) \iff 2HCI(g) + \frac{1}{2}O_2(g)$	925°C	(Fe-4)

All the reactions were reported to be viable. The maximum efficiency calculated by Carty for this cycle was relatively high, at about 40% (LHV). It was also reported that the two high-temperature reactions could be run at lower temperatures [20]. For example, reaction Fe-1 was proven for the temperature region from 525 to 925°C. Nevertheless, there is significant disagreement regarding the feasibility of this cycle. McQuillan et al. reported efficiencies of 0 to <20% for all Fe-Cl cycles [1]. Van Velzen pointed out that yields are low for two reactions, Fe-1 and Fe-3 [21]. Dimerization of the FeCl₃ is problematic because Fe_2Cl_6 is stable.

Rensselaer Polytechnic Institute (RPI) has evaluated the cycle and reviewed the literature. The RPI team paid particular attention to the claims of a patent that provided a specialized reactor and process for limiting the formation of the ferric chloride dimer and enhancing the decomposition of the FeCl₃ [22, 23]. The conclusion of their studies was that the challenges associated with this cycle cannot be overcome in the near term. Further work was not recommended.

Discussion

The barriers identified for the hybrid chlorine cycle were the energy intensive nature of the HCl electrolysis reaction and the challenges associated with the reverse Deacon reaction, i.e., the difficulty of separating equilibrium mixtures of HCl, O_2 , H_2O , and Cl_2 , and the relatively low product yields, even at 850°C. The new PEMFC technology for electrolyzing gaseous HCl reduces the energy consumption for HCl electrolysis compared to the Udhe process. A membrane reactor and/or proprietary sorbents have the potential to increase yields and minimize separation costs. NHI is providing funds for further research into possible methods for improving yields and separations for the reverse Deacon reaction.

The barriers identified in the Mg-I cycle were the requirements for excess water and iodine, which necessitate the need for energy efficient technologies for separating HI, I_2 , H_2 and H_2O , as well as for water removal. It should be possible to leverage the R&D effort ongoing in the S-I cycle regarding HI, I_2 , H_2O separations to the Mg-I cycle development effort. USC is looking into the feasibility of using electrodialysis for concentrating the MgI₂ solutions and future simulations will consider HI separation and decomposition in more detail.

The barriers identified for the Cu-SO₄ cycle were the electrochemical step for hydrogen production and the high-temperature decomposition of CuSO₄. Tulane has proposed a new thermal step for hydrogen production and has shown how a more detailed analysis of the decomposition of CuSO₄ may increase conversion. NHI is providing funds for proof-of-concept experiments for the thermal production of hydrogen in this cycle. It is expected that the membrane development work that is ongoing for the thermal decomposition of sulfuric acid in the S-I and the hybrid sulfur cycles may help to lower the temperature requirements for the thermal decomposition of CuSO₄.

The barriers identified for the Fe-Cl cycle were competing reactions and low yields. Even though a proprietary method for limiting the dimerization reaction was proposed, it was determined that this barrier could not be readily overcome [22].

The results of the evaluations of the other cycles will be discussed at a later time.

Summary

The results of a current evaluation for several promising cycles have been discussed in this paper. New technologies and new ideas offer pathways around barriers identified in the early literature for the hybrid chlorine, the Cu-SO₄ and the Mg-I cycles. The NHI has provided support for proof-of-concept experiments for the new ideas that resulted from the university evaluations. In addition, both the Cu-SO₄ and the Mg-I cycles may benefit from the R&D effort associated with the development of the baseline S-I cycle. Additional R&D is ongoing for some of the other promising cycles that were mentioned but not discussed in detail here. The sum of the information will be used as the basis for selection of the most promising one or two cycles by mid 2007. The criteria for the down selection will include efficiency, ease of separations, availability of separation methods, and other metrics to be decided upon by the universities and Argonne. The Fe-CI cycle was eliminated from further consideration at this time. It was determined that the Fe-CI cycle has barriers (low yields, competing reactions, and kinetic limitations) for which no near-term solutions were discerned.

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