348f An Assessment of the Efficiency of the Hybrid Copper-Chloride Thermochemical Cycle

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Argonne National Laboratory (ANL) is developing low temperature thermochemical cycles designed to split water and produce hydrogen with heat at 550°C or less. The rationale for this R&D effort is to produce hydrogen, without greenhouse gas emissions, cost effectively, and at temperatures compatible with lower temperature energy sources. Lower temperature processes should mitigate engineering and materials issues associated with the higher temperatures required for the well known sulfur cycles and, to a lesser degree, the calcium-bromine cycles.

In this paper, we will illustrate the steps for assessing the efficiency of a potential thermochemical cycle's using data obtained during development of the hybrid copper chloride cycle. Two types of efficiency calculations are presented: (1) an idealized efficiency from a scoping flowsheet analysis and (2) an idealized efficiency based on a simple model using a more rigorous flowsheet analysis.

In order to justify a potential cycle's development, the cycle must be assessed from three perspectives: chemical practicality which implies common and relatively inexpensive chemicals, high efficiency, and chemical viability which implies reactions that go to completion with little or no competing product formation. The most important parameter in the assessment of a cycle's potential is its efficiency, which is calculated throughout cycle development with varying degrees of sophistication. The most preliminary of these efficiency calculations, the idealized efficiency, are based on thermodynamic parameters only, using the following equation,

$$\eta = -\frac{\Delta H_o(H_2O(g)(25°C))}{\Sigma Q}$$

where the $\square H_o(H_2O(g)$, is equal to 57.798 kcal/mol or 241.826 kJ/mol, the energy required to decompose steam at 25□C, i.e., the low heating value of hydrogen. In the $\square Q = \square q_i + \square W_i / \square$ term, the $\square q_i$ refers to the sum of the external heat inputs for temperature change (sensible heat), latent heat, and for reaction enthalpies, $\square W_i$ is the sum of the work inputs for electrochemical work and separation work, with each work input is corrected by □, the efficiency of converting heat to work. The expected reaction temperatures were determined in proof-of-principle experiments. In general, a preliminary value of efficiency calculated in this manner should be about 40% (LHV).

The Cu-Cl is one of the most promising low temperature thermochemical cycles based on our preliminary assessments of chemical practicality, idealized efficiency calculations, and proof-of-principle work. Briefly, this cycle consists of three thermal reactions in which hydrogen, oxygen, or HCl are generated and an electrochemical step in which CuCl is disproportionated to copper metal and $CuCl_2$, as shown in Table 1. Details of the various reactions are described elsewhere.[1]

Table I. Reactions in Cu-Cl Cycle

Reaction
1. $2Cu+2HCl(g) \rightarrow (2\ CuCl(l) + H_2(g)$
2. $Cu_2OCl_2 \rightarrow 2CuCl + O_2(g)$
3. $2CuCl_2 + H_2O(g) \rightarrow Cu_2OCl_2 + 2HCl(g)$
4. $4CuCl \rightarrow 2CuCl_2(a) + 2Cu$ (electrochemical)

The temperatures for the various reactions were determined in proof of principle tests as was the voltage for the electrochemical reaction. The oxygen generation reaction is the highest temperature reaction. All of the oxygen in the copper oxychloride is released between 450 and 530°C. In the electrochemical cell, copper metal was deposited at a voltage of 0.4V. While the current density was low at this voltage, no cell optimization work has been done. The measured value seems to be a reasonable compromise for our initial calculations. Using these data, we have calculated the idealized efficiency of the Cu-Cl cycle using the National Hydrogen Initiative (NHI) standardized methodology for evaluating the idealized efficiency using a scoping flowsheet analysis as alternative cycles as 43% (LHV). A similar value, 42%, was obtained in a similar study.

We have also recently completed an Aspen simulation of the hybrid Cu-Cl cycle. The physical configuration of the process equipment is presented in this paper. For this simulation, we have used reaction parameters determined experimentally as much as possible. For the applied potential for reaction 4 we used 0.4 V. The reaction temperatures are those which have been measured experimentally. Other assumptions are process design goals that are used where experimental information is not available. For example, we have not yet determined the amount of water required for complete conversion of $CuCl_2$ to Cu_2OCl_2 (reaction 3) so we have used slightly more than the stoichiometric amount. Another area of uncertainty is the concentration of $CuCl_2$ when discharged from the electrochemical cell. We assumed 5N as a process design goal, which may require some drying, possibly using waste heat. The reactors in this simulation are stoichiometric reactors as we have determined conditions in the laboratory in which the thermal reactions go to completion. We have also assumed for the purposes of the efficiency calculation that the conversion of heat to electricity is 50%, as would be obtained with a HTGR.

Enthalpy changes that accompany the various blocks shown on the flowsheet have been calculated using the temperatures at which the steams enter and leave the blocks. The sum of the enthalpy changes from these blocks shows that $0.95*10^3$ kcal/sec (3.97 MW) must be externally supplied to generate 101.35 kg/h hydrogen. The lower heating value for this much hydrogen is 3.40 MW. The enthalpy equivalent for the electrical power is 2.27 MW using Faraday's law for electrolysis and shaft work for the pumps and turbine in the flowsheet. Using equation 1, the resulting idealized efficiency is 3.42/(4.05 + 2.39 + 0.21) or 51% (LHV).

However, this idealized approach does not consider that a positive temperature differential must be present for heat transfer to occur. We used pinch analysis to optimize the use of energy driving forces. We plotted the sums of the heating and cooling requirements versus temperature level to obtain grand composite curves. The resulting analysis showed a pinch point near 170°C. If an additional $0.42*10^3$ kcal/sec is supplied to the external heating and cooling loads (i.e., there is no waste heat), the pinch point is reduced to 123°C. Since this is a temperature level that could reasonably be provided by other exhaust streams in a nuclear power complex, there should be no further degradation of process thermal efficiency. If this integration is feasible, then the overall thermal efficiency of the Cu-Cl cycle is 39% (LHV).

We are currently using our Aspen model to perform sensitivity studies. We have determined that our method for estimating the free energy of formation for copper oxychloride contains significant uncertainty. Sensitivity studies show this uncertainty has a huge impact on the equilibrium concentration of the HCl product when we switch to equilibrium reactors. Because of the significant uncertainty, we are planning to have the thermodynamic data of the copper oxychloride measured. We are also completing sensitivity studies with regard to the amount of water used in the hydrolysis reaction

(reaction #3). These sensitivity studies allow us to focus our experimental program on the most critical experiments.

Development of the hybrid Cu-Cl cycle is not complete. Our R&D effort is currently concerned with identifying the optimum operating parameters for reactions 3 and 4, which are not as well understood as reactions 1 and 2. While it may not be possible to achieve some of the assumptions made for this current simulation, it is hoped that process optimization studies will be able to overcome any shortfall in the current assumptions. We conclude that the hybrid Cu-Cl cycle has sufficient promise to support continued development based on the results of this idealized efficiency calculation.

Reference:

[1] Kinetic study of the hydrogen and oxygen production reactions in the copper-chloride thermochemical cycle, Serban, Manuela (Argonne National Laboratory, Chemical Engineering Division); Lewis, Michele A.; Basco, John K. Source: 2004 AIChE Spring National Meeting, Conference Proceedings, 2004 AIChE Spring National Meeting, Conference Proceedings, 2004, pp. 2690-2698

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