Exergy analysis of the Cu-Cl cycle

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Abstract

The CuCl cycle is a hybrid thermochemical cycle to produce hydrogen using both electricity and heat to split water into hydrogen and oxygen. Already described in the early 70s, it has recently been revisited because of its low maximal temperature and its high potential efficiency. Furthermore, raw materials are cheap, which allows a drastic diminution of constraints for industrial deployment.

All steps have been demonstrated in laboratory. However they have been demonstrated in conditions where they cannot be easily coupled together, which may induce unexpected issues in an effective cycle. This paper will focus on issues for cycle integration, as well as giving potential improvement ideas from the exergetic point of view.

Introduction

Among the various low temperature thermochemical cycles described in the open literature, the hybrid copper-chloride (Cu-Cl) thermochemical cycle is an interesting candidate. It has been studied extensively at Argonne National Laboratory (United States) and in AECL (Canada), where it is anticipated to be coupled with a supercritical water reactor.

The Cu-Cl hybrid cycle was first described by Dokiya (1976), then Carty (1981). Its initial formulation was based on the electrolysis of cuprous chloride CuCl to cupric chloride $CuCl_2$ and H_2, and on $CuCl_2$ decomposition at high temperature combined with the reverse Deacon reaction. Recent studies involve an intermediate copper oxychloride Cu_2Cl_2O formed during the decomposition of $CuCl_2$, as well as reaction of solid copper Cu with hydrogen chloride HCl to produce hydrogen (Lewis, 2005). We will focus our analysis on this version of the cycle, before studying some potential improvements from the exergetic point of view.

Description of the hybrid copper-chloride thermochemical cycle

Following Argonne National Laboratory (Lewis, 2005) and the University of Las Vegas (Khan, 2005), the cycle can be split into five steps.

Table 1 summarises the main thermodynamic data and steps for this cycle.

Table 1: Thermodynamic data for Cu-Cl cycle

Step	Equation	T (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)
1	$2Cu(s) + 2HCl(g) \Rightarrow 2CuCl(l) + H_2(g)$	450	0	-54
2	$4CuCl(s) \Rightarrow 2Cu(s) + 2CuCl_2(aq)$	60	See below	62-72
3	$2CuCl_2(aq) \Rightarrow 2CuCl_2(s)$	60-200	See below	70-80
4	$2CuCl_2(s) + H_2O(g) \Rightarrow Cu_2Cl_2O(s) + 2HCl(g)$	400	30 (e)	110 (e)
5	$Cu_2Cl_2O(s) \Rightarrow 2CuCl(s) + \frac{1}{2}O_2(g)$	550	-11(e)	140

Data presented here have been extracted from JANAF tables except the following:

Values for Eqs. (2) and (3) are dependant on the molar concentrations of CuCl and $CuCl_2$ in HCl-H_2O solution.

The sum of Eqs. (2) and (3) gives the following equation:

$$4CuCl(s) \Rightarrow 2CuCl_2(s) + 2Cu(s)$$
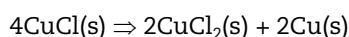
As these are pure component, enthalpy and free enthalpy changes can be found in thermodynamical tables:

$$\Delta G_2 + \Delta G_3 = \Delta G_{4CuCl \Rightarrow 2CuCl2 + 2Cu} = 2 \times (-161) - 4 \times (-120) = +158 \text{ kJ/mol}$$

$$\Delta H_2 + \Delta H_3 = 2 \times (-205) - 4 \times (-138) = +142 \text{ kJ/mol}$$

Estimations for ΔH_3 can be found based on Kahn (2005) and Kosa (1994), and therefore ΔH_2 can be deduced.

ΔG_2 is linked to the effective reversible voltage in Eq. (2) by Faraday's law. Then ΔG_3 can be deduced from this reversible voltage.

Data for Cu_2Cl_2O are not well known. Estimation (e) for the free enthalpy of reaction is based on preliminary CEA experiments (Doizi, 2009) and calculations (Boerio-Goates, 2008). CEA demonstrated that the reaction could be processed close to completion using an over-stoichiometry of $15H_2O$ for $1CuCl_2$ at a pressure of 0.02 bar H_2O for a temperature around 390°C. Using these results and the mass action law, ΔG could be estimated around $-RT \ln((P_{HCl})^2/P_{H2O}) \bullet 40$ kJ/mol, probably a little less due to kinetic issues. Extrapolation of JBG calculations gives a close value around 30 kJ/mol.

As some intermediate thermodynamic data are missing or not well known (enthalpy of mixing of CuCl and $CuCl_2$ in HCl/H_2O mixtures for example) and some heat exchanges or separation are not linear (for instance, HCl/H_2O mixture has an azeotrope which cannot be crossed), we decided to proceed to a global exergy analysis instead of a flow sheet analysis.

Bases of exergy analysis applied to water-splitting thermochemical cycles

Exergetic efficiency η_{ex} for hydrogen production by thermo water-splitting at a temperature T_a can be defined as the quotient of the recoverable work (here equal to the free enthalpy of water formation) divided by this quantity plus the sum of the exergy losses $D_i = T_a \Delta S_i$ in the process [Eq. (6)]. Thermal efficiency η_T from a heat source at temperature T is linked to this efficiency by transformation of heat into work [Eq. (7)].

$$\eta_{ex} = \frac{\Delta G_{H_2O}^{\circ}(T_a)}{\Delta G_{H_2O}^{\circ}(T_a) + \sum_i T_a \Delta S_i} \qquad (6)$$

$$\eta_T = \eta_{ex} * \frac{\Delta H_{H_2O}^{\circ}(T_a) * \left(1 - \frac{T_a}{T}\right)}{\Delta G_{H_2O}^{\circ}(T_a)} \qquad (7)$$

ΔS_i is the internal entropy generation of the process, and $D_i = T_a \Delta S_i$ is the exergetic loss associated with the temperature T_a.

As not all thermodynamic data are known, it is not possible to give a good estimate of exergy efficiency of the cycle. But in many cases, a minimal exergy loss can be found, which will eventually give an upper bound efficiency for the exergy efficiency of the cycle (as all exergy losses are cumulative) and therefore for the thermal efficiency of the cycle.

Bases of the minimal exergy loss estimation

In a thermochemical process we will always find irreversibilities listed below.

Heat exchange

There are many heat exchanges in thermochemical cycles, because of the large flows of materials which need to be handled, and always one heat demand or heat release for each chemical reaction.

Assuming constant pinch $\Delta T = T_2 - T_1$ between one heat source at T_1 and a heat demand at T_2, exergy loss for a heat flow Q at temperature T_a can be evaluated to:

$$D_{H min} = -Q \ T_a \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (8)$$

Separations

Separation of remaining reactants and products are one of the main issues in many thermochemical cycles or high temperature electrolysis. Usually "reversible" chemical reactions are used. Here the term "reversible" is used in terms in chemical reversibility, but in terms of exergy the chemical reaction usually has to be handled in a very irreversible manner to ensure that reactants and products do not mix together.

Two strategies can be used to drive a chemical reaction:

- *Try to complete the reaction.*

  This is done using a clear negative free enthalpy change of the reaction $\Delta G_r(T)$. In this case we will always have the following entropy generation for N moles of product: $\Delta S = -N \, \Delta G_r(T)/T$ implying an exergy loss:

$$D_{R\,min} = -N \, \frac{T_a}{T} \Delta G_R \tag{9}$$

- *Try to handle an incomplete reaction.* This is usually done using a ΔG close to 0. In this case, an extra exergy loss has to be added to separate the products and the remaining reactants. This depends on the phases of the products and can sometimes be handled later in the process; in any case an additional step for handling this separation has to be added (distillation, membrane separation, etc.).

  For instance, separating a two-gas mixture requires a minimum amount of energy equal to their free enthalpy of mixing; therefore for separating N moles of two gases with an x molar fraction for the first gas we have, assuming a mixture of two ideal gases:

$$D_{S\,min} = NRT\big(x\ln(x) + (1-x)\ln(1-x)\big) \tag{10}$$

  In practice this value is usually 5 to 10 higher, even more if no simple separation can be found.

  Liquid-gas or solid-gas separation exergy loss can usually be neglected as long as the saturation vapour pressure of the liquid (solid) phase is low (and kinetics fast enough).

Use of electricity

As soon as electricity is used, it has to be transformed from heat. This induces an exergy loss, first in the heat to electricity conversion then in the isentropic behaviour of the machine using the heat:

$$D_{W\,min} = W * \left(\frac{1 - \dfrac{T_a}{T}}{\eta_{el}\eta_i} - 1 \right) \tag{11}$$

where η_i is the isentropic efficiency of the machine.

Electrolysis step

For an electrolyser, instead of an isentropic coefficient, we take into account the overvoltage necessary for driving the electrolysis (ohmic resistance, anodic-cathodic overvoltage); here the exergy loss is simply connected to this overvoltage by Faraday's law:

$\Delta G_r = n \, F(E-E_{rev})$ where F is Faraday's constant (96 500 C.mol^{-1}) and n the number of electrons involved.

Typical values are between 0.2 (optimistic goals for industrial high temperature electrolysis) to 0.6-0.8 V (effective overvoltage of alkaline electrolysis) or even more for some acid electrolysis.

Eq. (11) becomes for the electrolyser, to take into account the exergy loss for the conversion of heat to work:

$$D_E = nFE * \left(\frac{1 - \dfrac{T_a}{T}}{\eta_{el}} - 1 \right) + nF(E - E_{rev})T_a / T \tag{12}$$

Evaluation of exergy losses in the Cu-Cl cycle

In this study we take the following assumptions and simplifications into account in our calculations:

- an average temperature for nuclear heat T around 773 K for heat to electricity conversion in Eqs. (11,12) and an electrical efficiency $\eta_{el} = 0.42$;

- a temperature pinch of 50 K for any heat transfer between a nuclear heat and heat demand in thermochemical process, assuming heat is provided at least at 673 K;

- a reference temperature T_a for exergy of 298 K.

Step 1: $2Cu(s) + 2HCl(g) \Rightarrow 2CuCl(s) + H_2(g)$

In this step, the chemical reaction and the solidification of the generated copper chloride release an important amount of heat at high temperature (54 + 36 =90 kJ/mol). But this heat can be used in Step 4.

Using Eq. (8) assuming T = 623 K (and 563 K for Step 4), we find:

$$D_H = 90*(1/563 – 1/623)*298 = 5 \text{ kJ}$$

In this range of temperature, the free enthalpy of reaction at 1 bar is always close to 0. Therefore it is not possible to complete the reaction and extra energy must be brought to separate H_2 from HCl. According to Eq. (9) $D_{Smin} = 13$ kJ. The usual value will be at minimum 5 to 10 times this value so over 100 kJ/mol (for example it is possible to operate at very high pressure to shift the reaction to the right which requires compressing 2 moles of HCl, recovering only work for decompressing 1 mole of hydrogen).

Exergy loss type	Estimation
Heat exchange	5 kJ
Chemical reaction	Negligible ($\Delta G \approx 0$)
Separation issues	Min = 13 kJ probable > 100 kJ

Step 2: $4CuCl(aq) \Rightarrow 2CuCl_2(aq) + 2Cu$

In this step CuCl needs first to be dissolved in the HCl/H_2O matrix. If it is close to the solubility limit, this can be minimised and exergy loss can probably be limited to low values, around 5-10 kJ/mol (if not, extra exergy loss should be taken into account).

As electricity is needed, an exergy loss for converting heat to electricity is required. The reversible voltage could be in the range 0.3 V to 0.6 V, depending on the concentrations of the species. It has to be noted that the low voltage found by ANL for this reaction may be unrepresentative of an effective voltage, because the $CuCl_2$ concentration obtained was very low (Lewis, 2005), which will increase the exergy loss to separate $CuCl_2$ from water in Step 3 (see below).

An overvoltage is necessary to drive the electrolytic reaction, and also to allow that most of CuCl and not only a few per cent will be transformed. We will assume a minimal overvoltage around 0.2 V but this could be probably in the range 0.6 V.

This gives an effective voltage between 0.5 and 1.2 V. According to Eq. (12), exergy loss for heat to electricity conversion can be estimated between 76 and 230 kJ/mol.

The electrolyser also releases some heat Q = (2FE – ΔH) at a temperature T_e around 360 K, generating an exergy loss equal to (2FE – ΔH) (1 – T_a/T_e). This implies an exergy loss around 20-30 kJ. This could probably however be recovered for cogeneration of hot water.

In any case, there will also be some CuCl remaining with $CuCl_2$ in the mixture, but it can remain with $CuCl_2$ for the rest of the process.

Exergy loss type	Estimation of exergy loss
Heat release from electrolyser	20-30 kJ (may be used for cogeneration)
Electrolyser voltage	76-230 kJ
CuCl absorption	5-10 kJ
Remaining CuCl	Can be done in next step

Step 3: $CuCl_2(aq) \Rightarrow CuCl_2(s)$

$CuCl_2$ has to be separated from its HCl/H_2O aqueous matrix. In practice there is 1 to 2 moles of HCl and 10 moles or more of water for one mole of $CuCl_2$ [or even more than 20 in some experiments (Lewis, 2005)].

To separate $CuCl_2$ it is first necessary to evaporate water and HCl, which implies over 40 * 20 kJ of heat of vaporisation plus the heat of mixing of HCl and H_2O, so over 500 kJ of heat per mole of $CuCl_2$. This has to be handled in a multi-stage process at different temperature and pressure to minimise the final heat demand, by condensing H_2O and HCl. We will assume a minimal pinch of 20 K because we are handling solid-gas mixture and an average temperature of this process around 473 K. The internal minimal heat exchange loss is then: $D_{H1} = 2 * 500 (1/473 – 1/493) *298 = 25$ kJ.

The global free enthalpy change (around 100 kJ) to separate $CuCl_2$ and HCl from water ΔG_{mix} has also to be provided.

Assuming that this free enthalpy change is provided by heat, the best case scenario is heat provided by nuclear heat at 673 K with a heat release at 350 K (the evaporation process will not work below this temperature), and applying Carnot's law, a minimum heat demand would be around $(100)/(1-350/673) = 210$ kJ with a minimal heat release of 110 kJ at 350 K.

The exergy loss due to the pinch of 50 K with nuclear heat can be estimated to $D_{H2} = 210 * 298 * (1/673 – 1/723) = 6$ kJ.

The heat release generates a minimal exergy loss of $D_{H3} = 110 * (1/350 – 1/673) * 298 = 16$ kJ according to Eq. (8).

Exergy loss type	Estimation of exergy loss
Heat exchange with nuclear heat	Min = 6 kJ
Internal heat exchanges	Min = 25 kJ
Heat release at low temperature	Min = 16 kJ

Step 4: $2CuCl_2(s) + H_2O(g) \Rightarrow Cu_2Cl_2O(s) + 2HCl(g)$

Here the free enthalpy change is clearly positive. This implies handling of a large amount of water (15 or more) to produce the 2 moles of HCl required, and also working at low pressure.

This large amount of water has to be separated from the HCl product. According to Eq. (10), the minimum exergy loss in this separation is around 34 kJ. This separation is in practice not easy, as there is an azeotrope between HCl and H_2O around 1 mole of HCl for 10 moles of water.

The heat demand has to be provided by nuclear heat, which generates a small exergy loss according to Eq. (8): $D_H = 3$ kJ.

Exergy loss type	Estimation of exergy loss
Heat exchange with nuclear heat	3 kJ
Separation of products and reactants	Min = 34 kJ probably over 150 kJ

Step 5: $Cu_2Cl_2O(s) \Rightarrow 2CuCl(s) + 0.5O_2(g)$

The reaction is operated with a negative enthalpy change, generating some entropy loss (5 kJ) according to Eq. (9).There is no separation issue. As this reaction is endothermic, heat has to be provided by nuclear heat. Assuming an average pinch of 50 K we find a small exergy loss $D_H = 3$ kJ.

Exergy loss type	Estimation
Heat exchange	3 kJ
Chemical reaction	5 kJ
Separation issues	0 kJ

Global evaluation

A global evaluation of the main exergy losses in all these steps can be deduced:

Step	Minimal exergy loss	"Realist" exergy loss
Step 1	18 kJ	100-150 kJ
Step 2	101 kJ (20 can be recovered)	120-260 kJ
Step 3	47 kJ	100-200 kJ
Step 4	37 kJ	100-200 kJ
Step 5	8 kJ	8 kJ
Global evaluation	211 (191) kJ	328-700 kJ*

* Global evaluation for realist exergy losses is lower than the sum of the different steps, as some separation issues can be dealt with at the interfaces between two steps.

These exergy losses can be compared with industrial alkaline electrolysis.

For an effective voltage of 1.8 V (against reversible voltage of 1.12 V) and a temperature of 90°C, exergy losses of alkaline electrolysis are "limited", according to Eq. (12), to $D_E = 267$ kJ and $D_H = 18$ kJ for the heat release at 90°C

Possible improvements

The global exergy analysis described above shows that this version of the cycle needs important modifications to become competitive, mainly because of separation issues of products and reactants.

A generic idea is to try to handle different steps together, to avoid separation issues between two steps. Different strategies are quickly checked here.

Combining Step 1 and Step 4

Using this strategy, HCl generated in Step 4 can be directly used in Step 1 and therefore does not need to be separated from H_2O. Also the heat from Eq. (1) can be directly used in Eq. (4).

But obviously, Step 1 has to be handled at high pressure and Step 4 at low pressure, so no practical solution can be found.

Combining Step 1 and Step 2

This idea refers to the Dokiya cycle (1976) where H_2 was directly generated by $CuCl_2$ electrolysis. AECL recently performed some experiments on this electrolysis (Solber, 2008). One of the main issues here is to avoid the deposit of copper according to Eq. (2) of the ANL cycle:

$$4CuCl \Rightarrow 2CuCl_2 + 2Cu$$
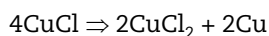
A good way to avoid this is to do it in conditions where Eq. (1) can process to the right side in aqueous solution:

$$Cu + 2HCl(aq) \Rightarrow 2CuCl(aq) + H(g) \text{ (1 bis)}$$

This can be done using high concentrated HCl because this lowers HCl free enthalpy of mixing with H_2O close to zero and also increases the solubility of CuCl and therefore the variation of the free enthalpy of mixing of CuCl with the HCl/H_2O solution (Fritz, 1982). However under such conditions the purity of the hydrogen needs to be checked.

Combining Step 4 and Step 5

As we have seen before, use of intermediate oxychloride is very problematic, because it can only be produced with a large over-stoichiometry of H_2O and only at low pressure. An alternative is to try to directly decompose $CuCl_2$ at high pressure and use the reverse Deacon reaction:

$$2CuCl_2(s) \Rightarrow 2CuCl(l) + Cl_2(g)$$

$$Cl_2(g) + H_2O(g) \Rightarrow 2HCl(g) + 0.5O_2(g)$$
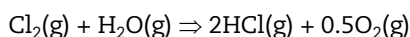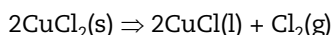
The reverse Deacon reaction is usually conducted at high temperature over 600°C, but can be handled at 500°C or even lower using an H_2O over-stoichiometry. Also $CuCl_2$ decomposition should usually be performed at a temperature over 600°C, but if Cl_2 is removed by the reverse Deacon reaction, the temperature can be lowered to 500°C or less.

This seems interesting, but the separation of O_2 from the remaining Cl_2 and the separation of HCl from the large over-stoichiometry of H_2O will remain important issues.

Pushing this idea to some extreme, it could be interesting to see if the global reaction:

$$2CuCl_2 + H_2O \Rightarrow 2CuCl + 2HCl + 0.5O_2$$
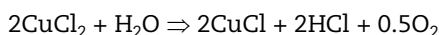
could be directly done in aqueous solution at high pressure and temperature (around 350°C).

If so, a new version of the CuCl cycle (without any solid phase!) could be:

- first oxygen generation in large amounts of H_2O with low HCl concentration:

$$2CuCl_2(aq) + H_2O \Rightarrow 2CuCl(aq) + 2HCl(aq) + 0.5O_2(g) \text{ (P = 150 bar, T = 350°C)}$$
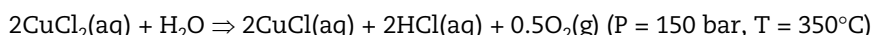
- hydrogen will be generated in high concentrated HCl solutions at low temperature:

$$2CuCl(aq) + 2HCl(aq) \Rightarrow 2CuCl_2(aq) + H_2(g) \text{ (T = 60-90°C, electrolysis)}$$
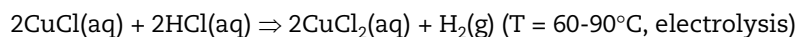
These two chemical steps have to be combined to an intermediate distillation step where H_2O and HCl solvent concentrations are adjusted.
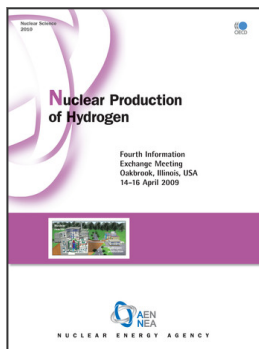
Conclusion

The global exergy analysis shows that the CuCl cycle requires important modifications to become competitive due to problematic separation issues. However multiple variations and simplifications are possible and could help to solve these issues. We have proposed a variation of the cycle, which requires only low temperature heat (below 400°C) and avoids the use of solid phases.

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