

Thermodynamics and kinetics of the thermal decomposition of cupric chloride in its hydrolysis reaction

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Abstract The hydrolysis of copper (II) chloride is the water splitting process in the copper-chlorine thermochemical hydrogen production cycle. In this paper, a simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC / TGA) technique is used to determine the transitional temperature and kinetics of the thermal decomposition of CuCl_2 . Thermodynamic analysis is performed on the decomposition reaction for a comparison with the thermogravimetric analysis results. The CuCl_2 decomposition temperature obtained from thermogravimetric experiments is found to be higher than that predicted from the thermodynamic analysis. This broadens the available operating temperature range of the CuCl_2 hydrolysis step for the Cu-Cl cycle. It is also found that the decomposition product CuCl may completely evaporate if the temperature is higher than its melting point, so the CuCl_2 hydrolysis reaction should be operated below the melting point of CuCl (430°C) to avoid the undesirable CuCl and Cl_2 by-products. A preliminary correlation was proposed in this paper for the decomposition kinetics in terms of the extent of converting CuCl_2 to CuCl and Cl_2 .

Keywords thermal decomposition • copper chloride • hydrolysis • SDC / TGA analysis

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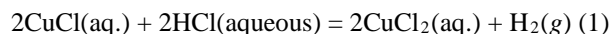
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Introduction

The utilization of fossil fuels has been generating pollutants and green house gases that affect our environment and climate negatively. Hydrogen is a potential clean fuel that does not have the emissions if it is produced from clean energy. However, most of the world's hydrogen is currently produced from fossil fuels through several types of reforming processes such as steam methane reforming and coal gasification [1-3]. These processes also emit pollutants and greenhouse gases. Thus, a key to the future clean hydrogen production is utilizing non-fossil fuels for a sustainable large-scale production of hydrogen.

Thermochemical water splitting cycles using various clean heat sources such as nuclear and solar thermal energy are alternative clean processes for hydrogen production [4]. A number of thermochemical cycles for hydrogen production have been developed over the past four decades [5-9]. Among them, copper-chlorine (Cu-Cl) cycle is one of the most promising options because its temperature requirement is much lower than most of other cycles [10]. This may reduce the challenge of equipment materials and broaden the available heat sources. A hybrid thermochemical copper-chlorine (Cu-Cl) cycle [11, 12] involves the following three reactions:

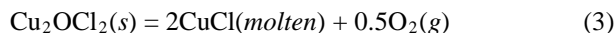
Reaction 1: Electrolytic hydrogen production, at $30\text{-}90^\circ\text{C}$



Reaction 2: Hydrolysis (endothermic), at $300\text{-}500^\circ\text{C}$



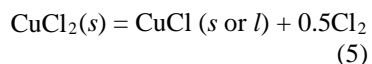
Reaction 3: Oxygen production, at $500\text{-}550^\circ\text{C}$



Summation of the three reactions:



In order to decompose water into hydrogen and oxygen without bringing in other undesirable byproducts, side reactions should be minimized. Particularly, reaction (2) is an endothermic reaction and hence it favours high temperature for the increase of reaction kinetics. However, the following undesirable side reaction may exist competing with the desirable one if the temperature is too high:



where the CuCl (cuprous chloride) product may exist in either solid or liquid form, depending on temperature, and the melting point of CuCl is 430°C. Other investigators recommended higher steam-to-copper (H₂O-to-CuCl₂) ratios (i.e., 7-17) than the stoichiometric ratio (i.e., 0.5) of reaction (2) in order to increase the yield of desirable products, and accordingly 375°C was suggested as the optimum temperature [13, 14]. However, if the steam-to-copper ratio is too high, the thermal energy requirement by the steam generation will be increased. Therefore, it is important to know if the side reaction takes place when the steam quantity is small.

Also, if reaction (2) does not go to a full completion, then CuCl₂ will be entrained to its downstream step, i.e., reaction (3). As the temperature of reaction (3) is much higher than that of reaction (2), the entrained CuCl₂ may experience the undesirable decomposition of reaction (5) again to release toxic chlorine (Cl₂) gas and introduce the mass imbalance of the whole Cu-Cl cycle, causing a deviation from the water splitting balance indicated by equation (4). Thus, reaction (5) should be examined at different temperatures.

A combination of experimental work and thermodynamic analysis is necessary to examine the side reaction. Several types of thermal experimental techniques currently exist for the decomposition analysis [15]. The basic techniques include Thermo-gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermo Magnetometry (TM), and Dielectric Thermal Analysis (DTA). A review of techniques suggested that TGA is an appropriate technique to monitor thermal decomposition of materials, among others. The results of DSC / TGA are usually reported in the form of curves relating mass losses from the sample against temperature or time. Furthermore, past literature reported some data of the dehydration of CuCl₂ and other similar substances using TGA [16, 20-22]. The data was found useful when comparing possible paths of decomposition. It is concluded that DSC / TGA is a very appropriate technology that allows for a comparison with other experimental setups where the majority of larger scale experiments were conducted. In the analysis with DSC /

TGA, the sample is contained in a closed chamber and the environment is continuously purged with a predetermined flow of inert gas. The instrument has a capability of decomposing a very small amount of samples while supplying a predetermined constant heat rate and monitoring weight losses. The temperature of the sample is closely monitored through a thermocouple in direct contact. Unless integrated with a chromatographic analyzer, DSC / TGA does not provide the monitoring of the composition of gas or vapor species. Rather, it provides valuable data for the rate analysis of weight losses that can then be correlated to decomposition kinetics.

This paper will utilize DSC / TGA instrument to examine the occurring of the side reaction and analyze the thermodynamics. An optimum operating range for the hydrolysis step will be proposed accordingly, and the related process integration challenges of the Cu-Cl cycle will be discussed as well.

Experimental details

Isothermal experiments were conducted in a thermo-gravimetric analyzer. The DSC / TGA experiments utilized an SDT Q600 InterTech equipment with a sample capacity up to 200 mg on a microbalance, possessing a sensitivity of 0.1 µg and precision of ±2%. The instrument provides measurements of heat flow and weight change. The temperature of the sample was monitored and controlled via multiple type R thermocouples. A type R thermocouple is made of a platinum-rhodium alloy consisting of 13% rhodium for one conductor and 100% platinum for the other conductor in a two wire system. The maximum working temperature of type R thermocouple is 1600 °C. It is operating tolerance is ±1.0°C in the range of 0 - 1100 °C, which covers both the thermolysis and hydrolysis of CuCl₂. The type R thermocouples were built inside the instrument chamber and control units. Special care was taken in the preparation of samples for the DSC / TGA experiments due to the small amount of the samples. The procedures are described as follows:

(1) A total of 10 g CuCl₂ samples were placed and thin-spread in a drying oven at 150 °C to remove any hydrated water and moisture, because CuCl₂ is very hygroscopic and the hydrated water could be 1 to 4 times the molecular number of CuCl₂, i.e., in a molecule of CuCl₂·nH₂O, depending on temperature, n could be any number in the range of 1-4 [17, 23-27].

(2) The drying in the oven was operated at least 24 hours to ensure the complete removal of hydrated and free water from the CuCl₂ sample.

(3) The samples were carefully packed in a sealed glass container.

(4) Then the samples were divided and placed in the DSC / TGA chamber.

(5) Carry out a continuous purge with argon gas at a flow rate of 50 ml/min in 5 minutes until initial isothermal equilibrium at 30 °C was reached.

(6) Subsequently ramp the temperature up at a rate of 20 °C/min to 110 °C until isothermal equilibrium was reached and retained for 10 minutes.

(7) Continue the temperature ramp up at a rate of 20 °C/min to other different testing temperatures, i.e., 450, 470, 490, and 500°C, to examine the decomposition. And the isothermal equilibrium was retained up to 120 minutes.

(8) When the measurements were stopped, cooling air was introduced to gradually reduce the temperature.

The samples consisted of 15 to 25 mg of CuCl₂. The results were analyzed using the DSC / TGA accompanying data analysis software, namely, Universal Analysis 2000. Experiments were repeated under similar conditions of initial weight, pressure, and purge gas flow.

The usage of argon in the DSC / TGA experiments was expected to well simulate the Cl₂ removing by steam and the zero initial Cl₂ in the start-up. If further looking into reaction (2), the reactant gas is steam removing the produced Cl₂ of reaction (5) in a continuous operation. As a result, the Cl₂ pressure may not be built up to strengthen the reverse direction of reaction (5), although the steam may at the same time favour reaction (2). Also, there is no initial pressure of Cl₂ in the start-up of reaction (2). In addition, since the sample amount in the experiments was very small, the mass transfer resistance of Cl₂ in the bulk phase of argon gas would be reduced significantly. Consequently, the Cl₂ release rate would be closer to intrinsic kinetics that is mainly contributed by the surface decomposition rate and molecular diffusion in the pores of particles. Thus, the kinetics could be used for reactor scale-up.

Thermodynamic analysis

In order to have an in-depth understanding of reaction (5) and SDC / TGA experimental results, thermodynamic analysis on the reaction spontaneity for various temperatures and pressures was performed in advance. The spontaneity of reaction (5) can be predicted from the change of the Gibbs free energy of the reaction, $\Delta_T G$, which is calculated by:

$$\Delta_T G = \Delta_T G^\theta + RT \ln(J_r) \quad (6)$$

where $\Delta_T G$ represents the change of Gibbs free energy of the reaction at standard pressure and temperature, and J_r is the reaction quotient. Since CuCl and CuCl₂ in Eq. (6) exist in the form of a condensed state and low pressure is

preferred for reaction (2), the quotient of reaction (5) can be calculated with the partial pressure of Cl₂:

$$J_r = (P_{Cl_2} / P^\theta)^{1/2} \quad (7)$$

where P^θ is the standard pressure (100 kPa) and P_{Cl_2} is the actual partial pressure of Cl₂. At reaction equilibrium, the quotient is reduced to the reaction equilibrium constant K as defined by:

$$K = J_r \quad (8)$$

As Gibbs energy is only a function of state, the Gibbs energy change can be calculated from the standard molar Gibbs free energy of formation of the products and reactant:

$$\Delta_T G^\theta = [\Delta_f G^\theta(CuCl) + 0.5\Delta_f G^\theta(Cl_2)] - \Delta_f G^\theta(CuCl_2) \quad (9)$$

where $\Delta_T G^\theta(CuCl)$, $\Delta_T G^\theta(CuCl_2)$, and $\Delta_T G^\theta(Cl_2)$ are the standard molar Gibbs free energy of formation for CuCl, CuCl₂ and Cl₂ respectively, which can be calculated from their enthalpy and entropy of formation:

$$\Delta_f G^\theta = \Delta_f H^\theta - T \cdot \Delta_f S^\theta \quad (10)$$

where $\Delta_f H^\theta$ and $\Delta_f S^\theta$ are the standard enthalpy and entropy of formation at temperature T. However, few data have been reported for CuCl for the temperatures higher than 400°C. In this paper, they are calculated from the specific heat of CuCl, Cu, and Cl₂ with the following imagined thermodynamic paths that can utilize known data of enthalpy and entropy at ambient temperature, and specific heat at different temperatures:

$$\begin{aligned} \Delta_f H^\theta(T) = & [\Delta_f H^\theta(25^\circ C) + \Delta H^\theta(CuCl)_{25}^T] \\ & - [\Delta H^\theta(Cu)_{25}^T + 0.5\Delta H^\theta(Cl_2)_{25}^T] \end{aligned} \quad (11)$$

$$\begin{aligned} \Delta_f S^\theta(T) = & [\Delta_f S^\theta(25^\circ C) + \Delta S^\theta(CuCl)_{25}^T] \\ & - [\Delta S^\theta(Cu)_{25}^T + 0.5\Delta S^\theta(Cl_2)_{25}^T] \end{aligned} \quad (12)$$

where the enthalpy and entropy changes for Cu and Cl₂ are calculated from the following equations:

$$\Delta_{25}^T H^\theta = \int_{25}^T C_p dT \quad (13)$$

$$\Delta_{25}^T S^\theta = \int_{25}^T \frac{C_p dT}{T} \quad (14)$$

The correlations of C_p and the values of $\Delta_f H^\theta$ (25°C) for Cu, Cl₂ and CuCl reported by NIST [18] are adopted in this paper. As discussed previously, the undesirable product CuCl may experiences a melting process at the melting point T_m (430°C or 803.15 K). The entropy change at the melting point is calculated with the following equation:

$$\Delta_m S^\theta = \frac{\Delta H_{melting}^\theta}{T_m} \quad \text{and } T_m = 803.15\text{K} \quad (15)$$

Similar calculation procedure for the thermodynamic properties of Cu₂OCl₂ and CuCl under similar and other conditions was reported in a past study [28], so the details won't be repeated here. The highlight in this paper is the Gibbs energy change of the CuCl₂ thermolysis reaction at different pressures using the calculated properties and equation (6).

Results and discussion

Figure 1 shows the thermodynamic analysis results in terms of the dependence of Gibbs energy change of the CuCl₂ decomposition reaction on temperature at different partial pressures of Cl₂. The partial pressure

range varies from 10⁻⁶ bar to 1 bar to predict the CuCl₂ decomposition spontaneity at different chlorine vacuum conditions. If the Gibbs energy change is a negative value, it indicates a spontaneous process. It can be observed that the spontaneous decomposition temperature (the transition temperature at which the Gibbs energy changes its symbol undergoing a value of zero) increases with increasing the partial pressure of Cl₂, from 180°C to 470°C corresponding to 10⁻⁶ bar to 1 bar. Table 1 lists the transition temperatures for different partial pressures of Cl₂. Since 1 bar is often termed as standard pressure, the decomposition temperature at this pressure is called standard decomposition temperature in order to differentiate it from other lower pressure conditions

The thermodynamic analysis indicates a spontaneous decomposition of the CuCl₂ at a relatively low temperature if the initial partial pressure of Cl₂ is very low. If this really happens, the hydrolysis reaction indicated by equation (2) will always be accompanied by the decomposition of CuCl₂ and hence the evolution of toxic Cl₂. However, whether the decomposition will occur does not only depend on the thermodynamic spontaneity, it also depends on reaction kinetics, which can be examined by the DSC / TGA technique.

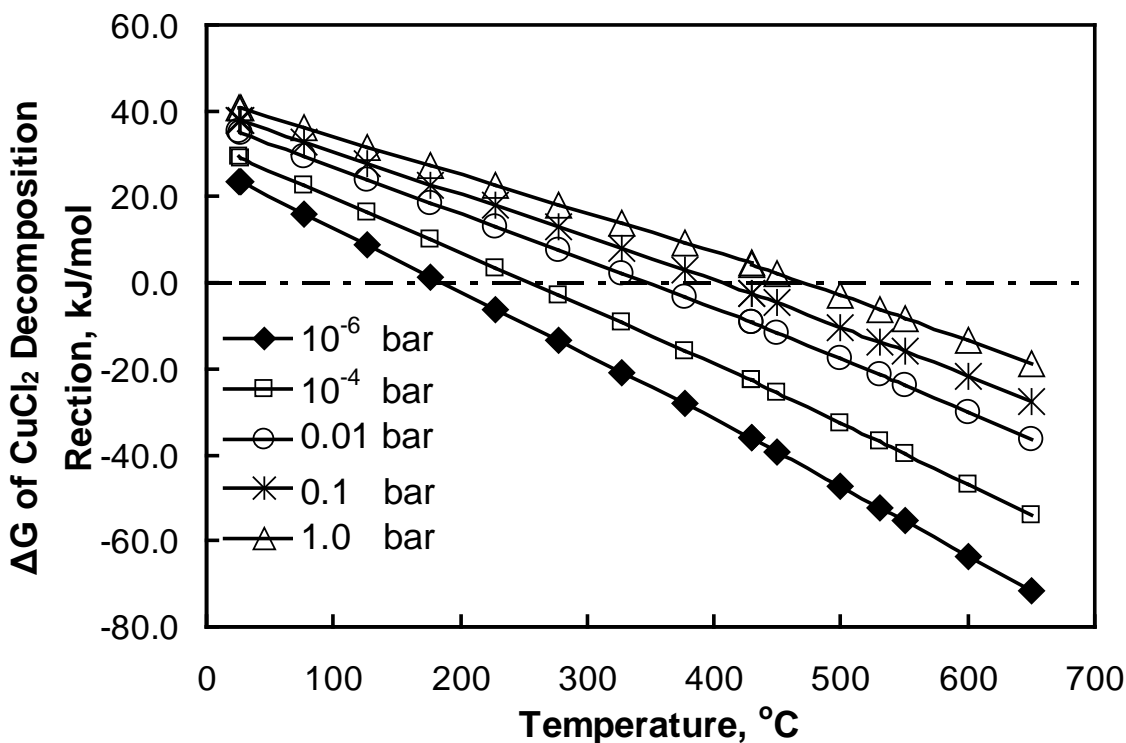


Fig. 1 Gibbs energy change of CuCl₂ decomposition versus temperature at different pressures of Cl₂.

Table 1. Transition temperatures of the CuCl_2 decomposition spontaneity in thermodynamics.

P, bar	10^{-6}	10^{-4}	0.01	0.1	1
Transition T, °C	180	260	360	425	470

Figures 2(a) and 2(b) show the dependence of sample weight on time, temperature and heat flow obtained from DSC / TGA experiments for the CuCl_2 decomposition. The vertical coordinate indicates the percentage of the residual liquid and solid weight relative to the original CuCl_2 sample amount. From equation (5), it can be observed that the solids are CuCl_2 and CuCl , and the liquid is molten CuCl when the temperature is higher than its melting point. Chlorine gas is not counted in because it was carried out by argon.

It can be observed that the weight of CuCl_2 sample starts to decrease by 2% after about 25 minutes of process heating. This indicates the start of CuCl_2 decomposition, and the corresponding transition temperature is at about 420°C. This temperature is significantly higher than the spontaneous values (180-360°C for 10^{-6} - 10^{-2} bar) of Table 1 obtained from the thermodynamic analysis for vacuum partial pressures, but not much lower than 470°C for a partial pressure of 1 bar. In order to assure the repeatability of the data, we performed 3 more decomposition experiments with DSC / TGA under similar conditions, and the thermogravimetric curves are shown in figures 3-5. For sake of comparison and study of the kinetics, the dependence of the residual percentages on time in Figures 2-5 are combined together, as shown in figure 6. Table 2 lists the transition temperatures at different partial pressures. For sake of comparison, Table 2 also gives the decomposition temperatures observed by other investigators [19], which were found to be in the range of 390-450°C by TGA experiments also utilizing argon as the carrier gas, and 450°C by a fixed bed experiment.

Table 2. Transition temperatures of CuCl_2 decomposition in DSC / TGA and fixed bed experiments.

Transition T, °C	Time, min	Sample size, mg	Technique	Source
420	25	22.881	DSC/TGA	present
420	34	22.164	DSC/TGA	present
410	35	17.278	DSC/TGA	present
N/A	24	17.706	DSC/TGA	present
390-450	N/A	50	Fixed bed	[19]
450	30	50	DSC/TGA	[19]

In this paper, the higher decomposition temperatures obtained from the experiments than the values from thermodynamic analysis is accounted for by a boundary layer effect. As shown in figure 7, once the chlorine gas is released, it is close to the surface to form a boundary wherein the chlorine partial pressure is close to the bulk argon pressure, which is much higher than the overall partial pressure that is based on the total amount of argon and chlorine. This may explain why the decomposition temperature of CuCl_2 in argon (the overall Cl_2 partial pressure is low) is close to the standard decomposition value (the overall Cl_2 partial pressure is 1 bar). The finding is encouraging for the hydrolysis reaction indicated by equation (2), because it means the operating temperature range could be enlarged to a broader range to increase the kinetics.

Another reason to explain the higher decomposition temperature is the kinetics. Probably the decomposition does start at the transition value indicated by the thermodynamics, but the reaction rate is too slow to be detected or worth considering in engineering. This needs further investigations.

On the basis of equation (5), if the CuCl_2 fully decomposes to CuCl and Cl_2 , the final residual solid or molten CuCl product should be 73.6% of the original solid reactant CuCl_2 in mass:

$$R_{TGA,f} = (M_{CuCl} - 0.5M_{Cl_2})/M_{CuCl_2} = 0.736 \quad (16)$$

where M_{Cl_2} and M_{CuCl_2} are the molecular mass of Cl_2 (71.0 g/mol) and CuCl_2 (134.5 g/mol), respectively. $R_{TGA,f}$ means the reading of TGA for a full decomposition of CuCl_2 . Equation (16) also means that when the residual mass is 73.6% of the original, a full decomposition has reached, i.e., 100%. Since the decomposition may not go to a full completion, for generalization, the ratio of the CuCl_2 mass change during the decomposition to the initial CuCl_2 amount before the decomposition is defined as the decomposition extent. The decomposition extent can be calculated from the DSC / TGA readings, and the relation is illustrated in Table 3 and can also be written in the following equation:

$$\lambda = 3.789 \times (100 - R_{TGA}) \quad (17)$$

However, figures 2-5 all show much lower values even down to zero. In this paper, this is explained by the evaporation of molten product CuCl when the temperature is higher than melting point 430°C. This explanation can be verified by all figures (b)s where the weight dependence on heat flow is shown. It can be observed that the heat flow experiences an abrupt drop suggesting a phase change, when the residual weight reaches about 75%, which is very close to the theoretical bottom value of 73.6%, as indicated in equation (16). This abrupt drop and the drop location are very well

repeated in all the thermogravimetric graphs we obtained in the experiments.

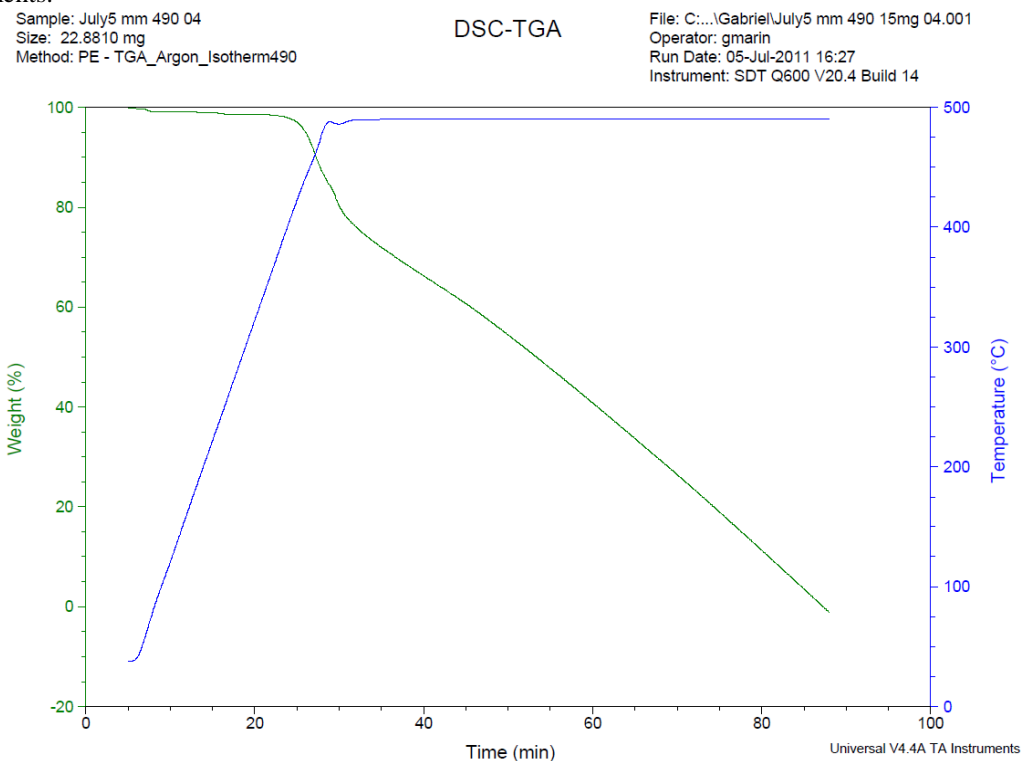


Fig. 2 (a) Dependence of the residual sample weight on time and temperature (22.8810 mg sample)

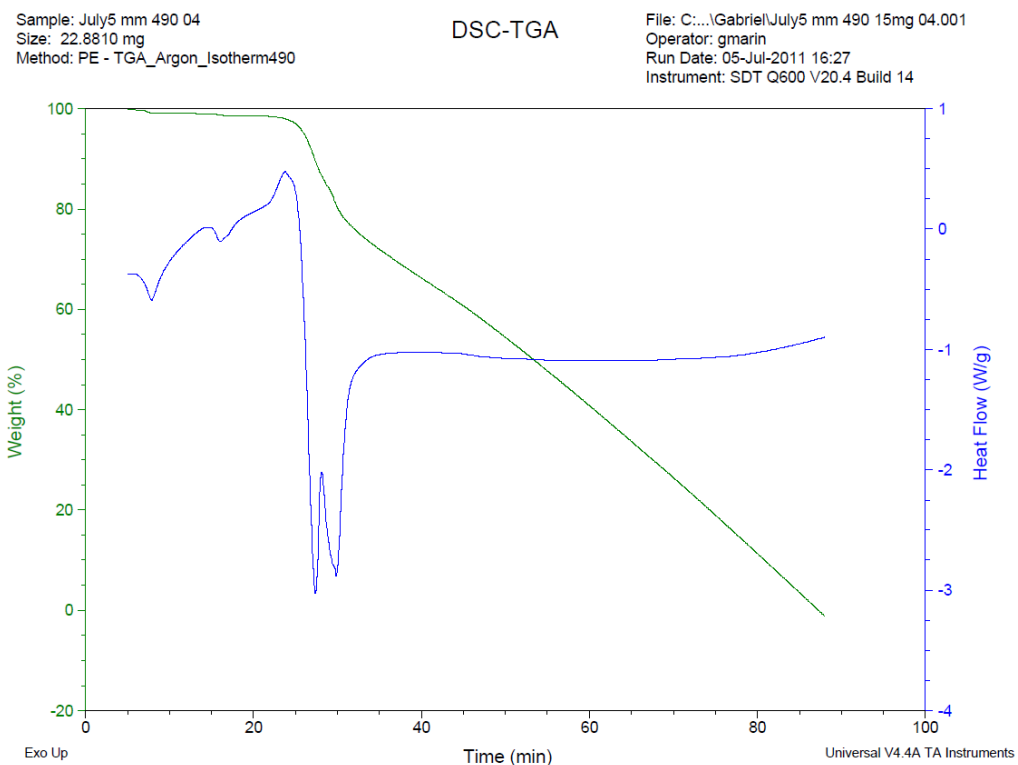


Fig. 2 (b) Dependence of the residual sample weight on time and heat flow (22.8810 mg sample)

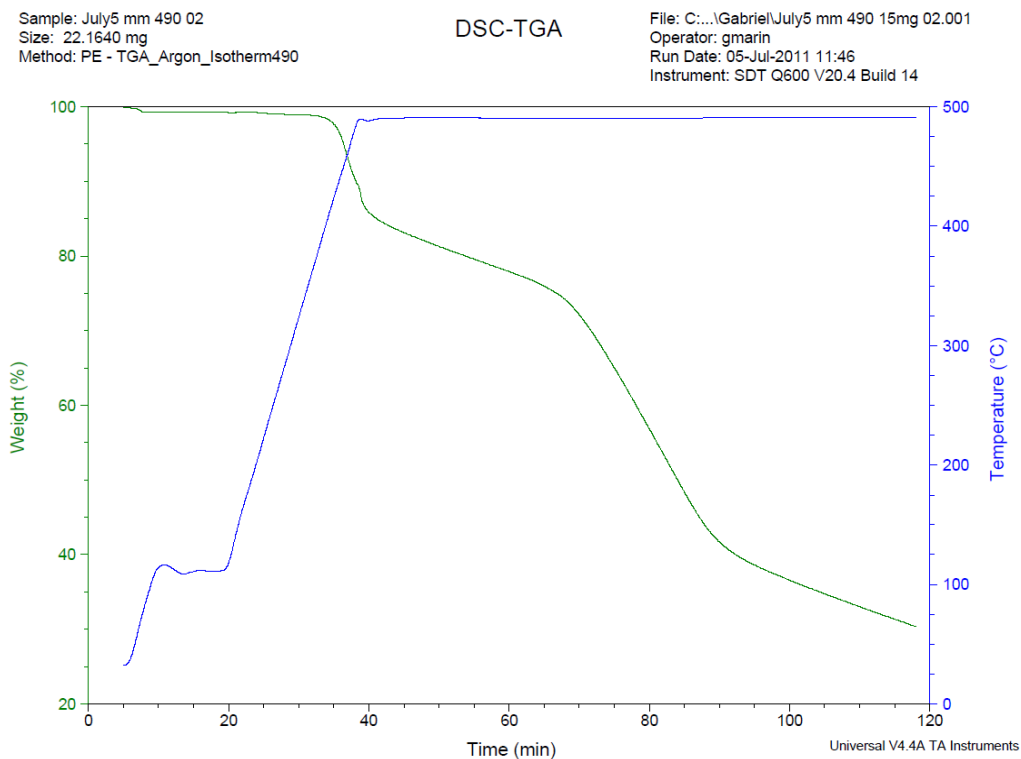


Fig. 3 (a) Dependence of the residual sample weight on time and temperature (22.1640 mg sample)

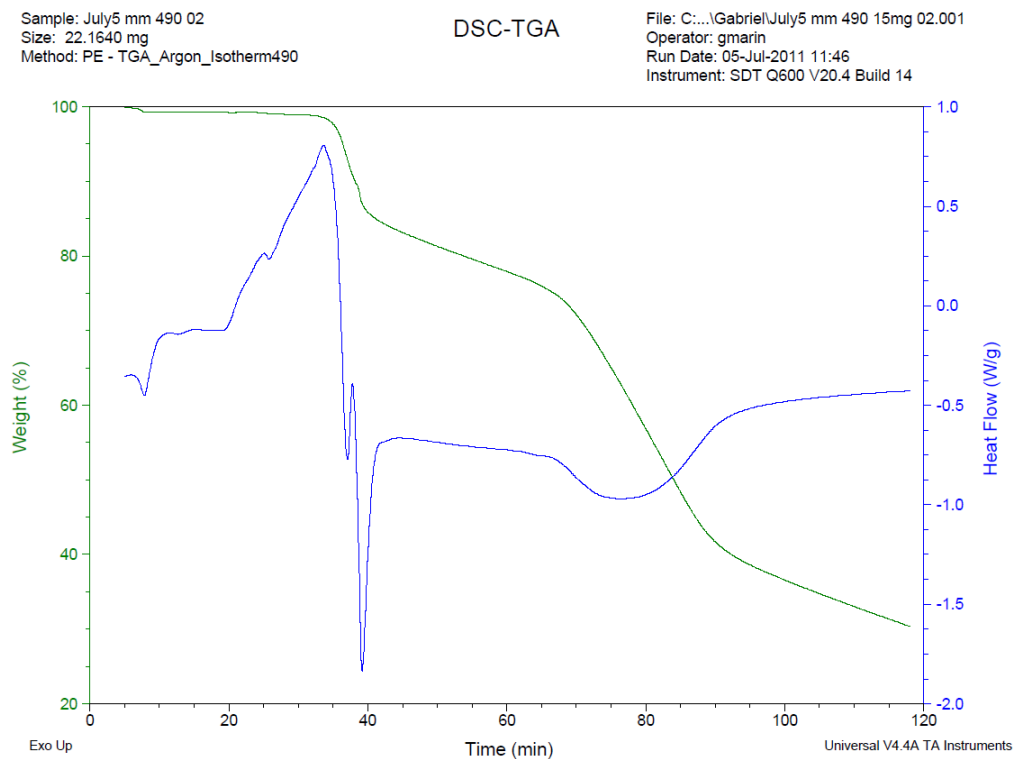


Fig. 3 (b) Dependence of the residual sample weight on time and heat flow (22.1640 mg sample)

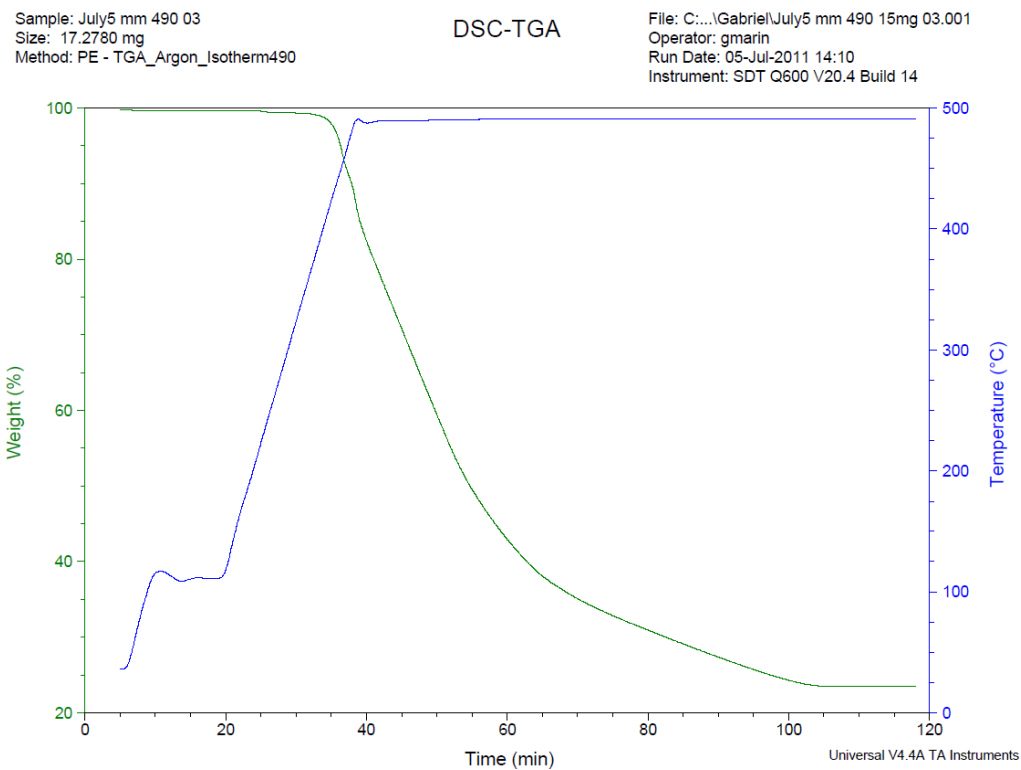


Fig. 4 (a) Dependence of the residual sample weight on time and temperature (17.2780 mg sample)

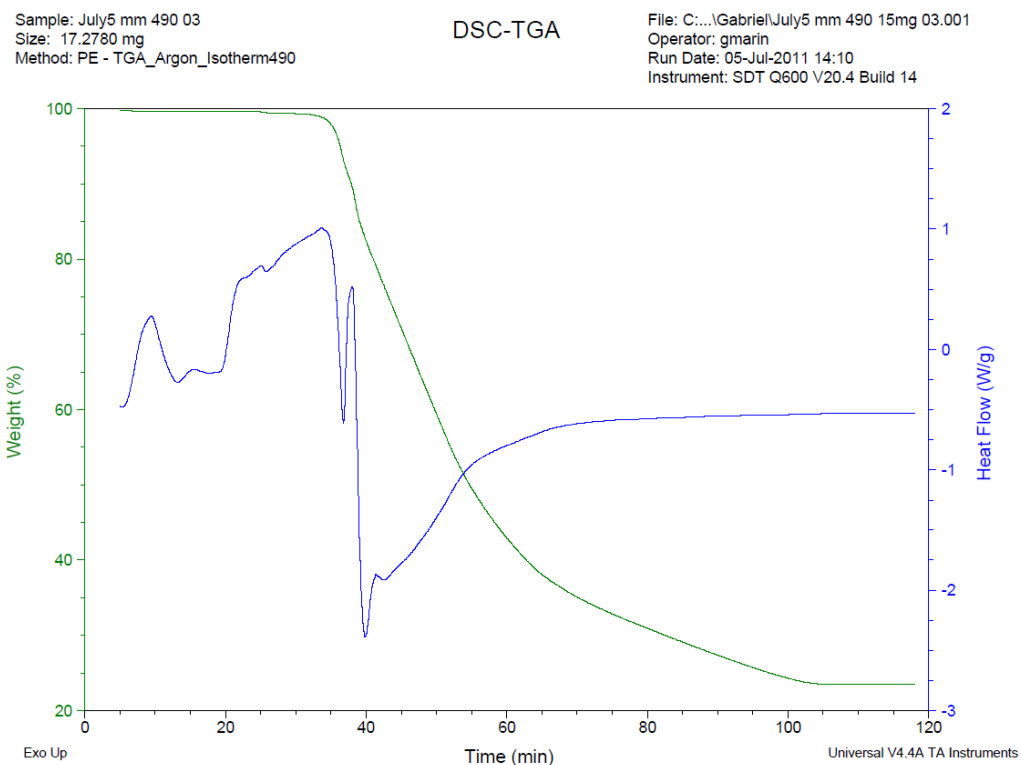


Fig. 4 (b) Dependence of the residual sample weight on time and heat flow (17.2780 mg sample)

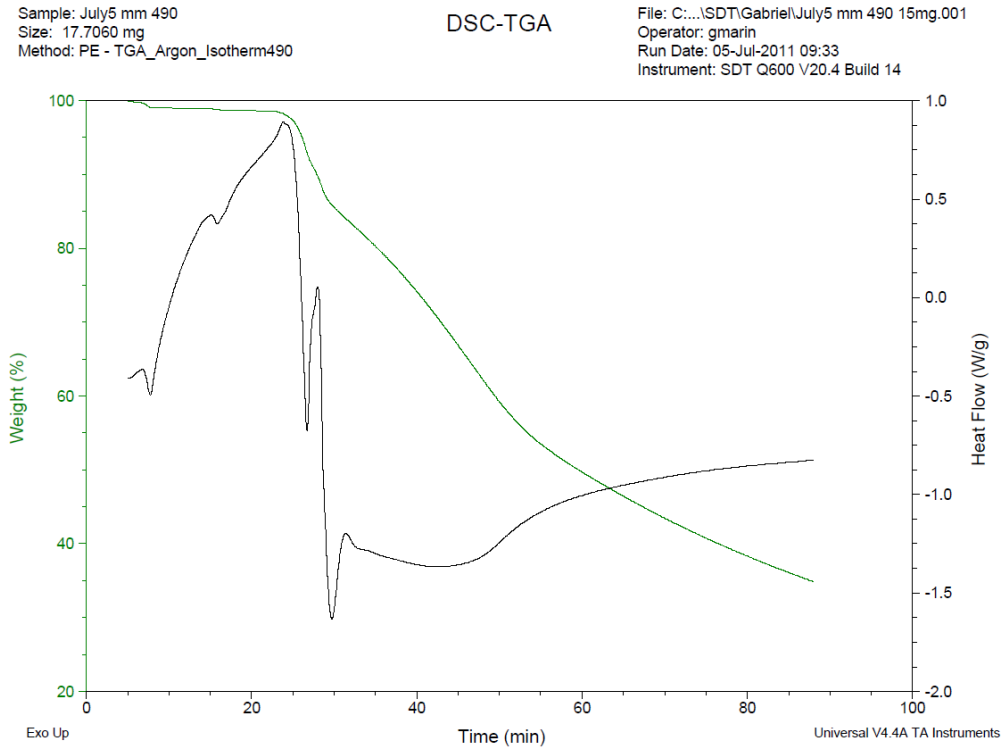


Fig. 5 Dependence of the residual sample weight on time and heat flow (17.7060 mg sample)

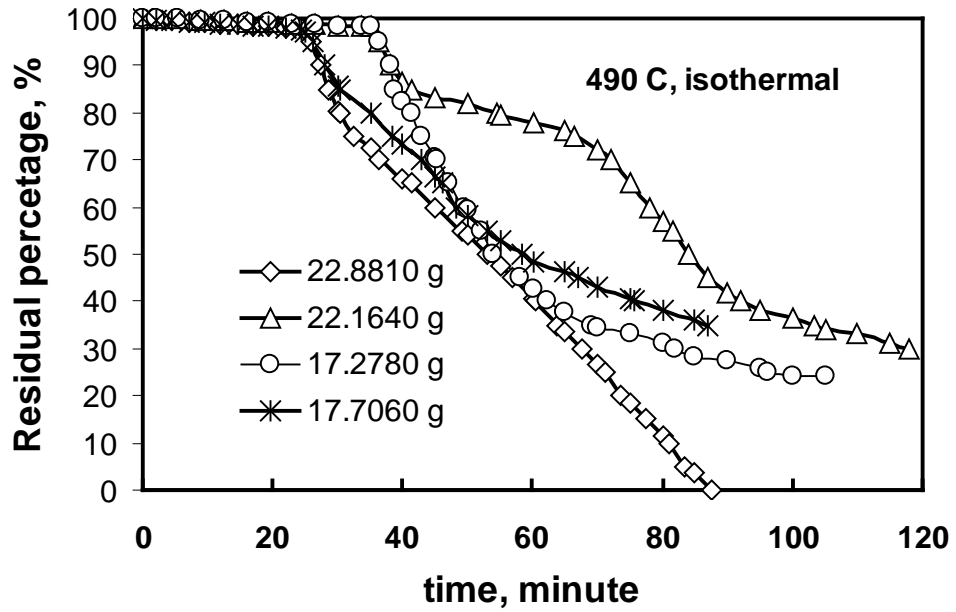


Fig. 6 Dependence of the residual sample weight on time and heat flow (4 samples)

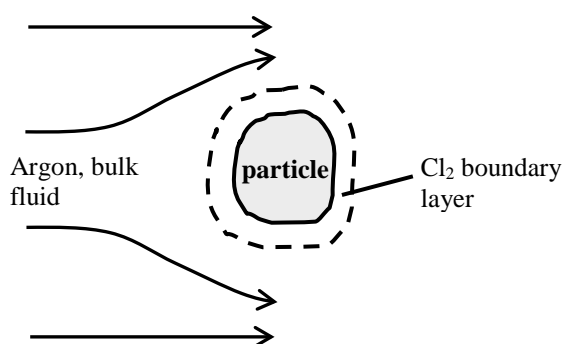


Fig. 7 Chlorine boundary layer near particle surface.

Table 3. Decomposition extent vs. DSC / TGA reading

Recording	Existing chemicals and amount		
	CuCl ₂	= CuCl	+ 1/2Cl ₂
Initial, mole	$N_{S,i}$	0	0
Change, mole	$2N_{Cl_2,f}$	$2N_{Cl_2,f}$	$N_{Cl_2,f}$
Final, mole	$N_{S,i}$	$2N_{Cl_2,f}$	$N_{Cl_2,f}$
DSC / TGA reading, % wt	$R_{TGA} = (M_{CuCl_2}N_{S,i} - M_{Cl_2}N_{Cl_2,f}) / M_{CuCl_2}N_{S,i} \times 100\%$		
Decomposition Extent (λ), %	$\lambda = 2N_{Cl_2,f} / N_{S,i} \times 100\%$ $= 2 \times (M_{CuCl_2} / M_{Cl_2}) (100 - R_{TGA})$		
Ratio constant	$M_{CuCl_2} / M_{Cl_2} = 1.894$		

The information here may be discouraging to the hydrolysis reaction indicated by equation (2): if the hydrolysis is operated at the CuCl₂ decomposition temperature, CuCl vapour may be another undesirable by-product in addition to the toxic Cl₂. Therefore, the hydrolysis reaction temperature must be controlled below the decomposition temperature of CuCl₂. To quantify the decomposition rate of CuCl₂ converting to CuCl and Cl₂, figure 8 shows the dependence of the decomposition extent on time. The decomposition extent is defined as the ratio of the

Since the decomposition started at 410°C and was kept isothermal at 490°C in the SDC / TGA experiments, the decomposition rates are accordingly shown in two parts in figure 7. The isothermal decomposition rate at 490°C can be expressed in the following correlation:

$$\lambda = 19.008 \ln t + 31.713 \quad (18)$$

where λ is the extent of CuCl₂ decomposing to CuCl and Cl₂, t is time in units of minute. The performance of correlation (16) is not satisfactory because the square mean error is only about 0.56. This is partly accounted for by the difference of decomposition conditions. The hollow symbol represents a non-isothermal decomposition, i.e., the decomposition started from 410°C in the DSC / TGA chamber but the temperature was still increasing up to until 490°C. By comparison, the solid symbol corresponds to isothermal decomposition which started at 490°C in the experiments. Another reason is that the decomposition was accompanied by the evaporation of CuCl, which makes the data less predictable. From figure 7 or equation (16), it can be found that the residual solid or molten CuCl product may eventually go to zero in only 30 minutes, if the reaction temperature is higher than the melting point of CuCl. This means the CuCl₂ hydrolysis reaction indicated by equation (2) may not occur significantly if the CuCl₂ decomposition dominates the process. Therefore, the hydrolysis process must be operated below the melting point of CuCl and also the decomposition temperature of CuCl₂. In addition, if the CuCl₂ in the hydrolysis is not fully consumed, it will experience thermolysis releasing chlorine gas in the downstream oxygen production reaction indicated by equation (3), because the downstream process temperature is higher than 500°C. This has been observed in past experiments [29]. Thus, a full consumption of CuCl₂ in the hydrolysis step of the Cu-Cl cycle is strongly recommended for the future industrial operation.

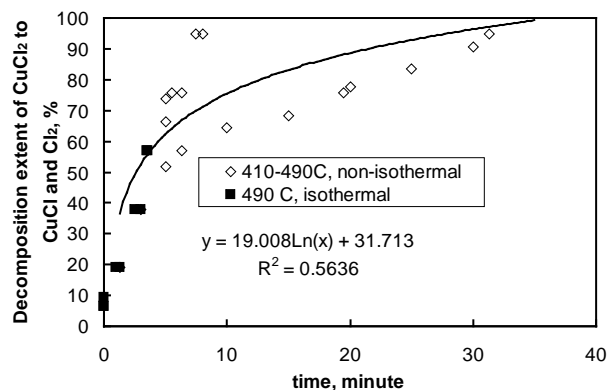


Fig. 8 Dependence of the decomposition extent on the time for reaction (5).

Conclusions

This paper discusses the importance of minimizing the undesirable decomposition of CuCl_2 in the hydrolysis step of the Cu-Cl thermochemical water splitting cycle for sustainable hydrogen production. Thermodynamic analysis is performed on the decomposition transition temperature for various pressures. Then a simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC / TGA) technique was used to experimentally examine the decomposition transition conditions. It is found that the CuCl_2 decomposition temperature obtained from thermogravimetric experiments is higher than that predicted from thermodynamic analysis. This is explained by the boundary layer of Cl_2 formed on the surface of particles. The operating temperature range of the CuCl_2 hydrolysis step in the Cu-Cl cycle can then be broadened to increase the kinetics. The thermogravimetric experiments also show that the decomposition product CuCl may evaporate if the temperature is higher than its melting point. This means the CuCl_2 hydrolysis reaction may be overwhelmed by the CuCl_2 decomposition if the temperature is higher than the melting point of CuCl (430°C) and the decomposition temperature of CuCl_2 (410°C). The optimum operating temperature range of the hydrolysis is recommended in the range of $340\text{--}410^\circ\text{C}$. A preliminary correlation is proposed in this paper for the decomposition extent. A full consumption of CuCl_2 in the hydrolysis step of the Cu-Cl cycle should be assured for the future industrial operation to avoid the release of chlorine gas in the oxygen production step. The research results of this paper provide very important operating constraints for the both the hydrolysis and oxygen production steps of the Cu-Cl cycle.

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Nomenclature

C_p	Specific heat, $\text{J/mol}\cdot\text{K}$
G	Gibbs free energy, kJ/mol
J_r	Reaction quotient
H	Enthalpy, kJ/mol
K	Reaction equilibrium constant
$2N_{\text{Cl}_2, f}$	Final amount of Cl_2 , mol
$N_{s, i}$	Initial sample amount, mol
R_{TGA}	Reading of TGA, % wt
S	Entropy, $\text{kJ/mol}\cdot\text{K}$
T	Temperature, $^\circ\text{C}$ or K
t	Time, sec or min
Greek	
λ	Decomposition extent, %

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