X-RAY DIFFRACTION OF CRYSTALLIZATION OF COPPER (II) CHLORIDE FOR IMPROVED ENERGY UTILIZATION IN HYDROGEN PRODUCTION

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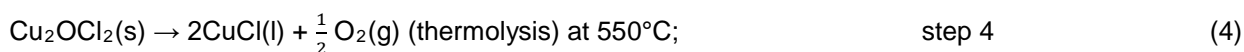240 Prince Phillip Drive, St. John's, Newfoundland, Canada, A1B 3X5

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ABSTRACT

Crystallization is an effective method to recover solids from solution, due to its relatively low energy utilization, low material requirements and lower cost compared to other alternatives. Hence, crystallization is of particular interest in the thermochemical copper-chlorine cycle for hydrogen production as an energy-saving means to extract solid $CuCl_2$ from its aqueous solution. It has been determined from experiments that there is a range of concentrations that will demonstrate crystallization. If the initial concentration exceeds the upper bound of this range, the solution will be saturated and instantly become paste-like without forming crystals. Conversely, if the initial concentrations fall below the lower bound of a specified range, the solution will remain liquid upon cooling. As a result, it has been observed that crystallization does not occur for HCl concentrations below 3M and above 9M. Also, it has been found that anhydrous $CuCl_2$ does not crystallize under any of the conditions tested. To analyze the composition of the recovered solids, X-ray diffraction (XRD) was employed. It has been determined that an impurity was present before and after the experiment. The samples were also analyzed using thermogravimateric analysis (TGA) in order to determine their thermochemical properties such as melting and decomposition temperatures. The stationary point on the TGA curve was found to be 442 °C which is below the normal melting temperature of $CuCl_2$. Also, the vaporization of the samples was found to be approximately 600 °C.

1. INTRODUCTION

One version of the copper-chlorine cycle for hydrogen production consists of a series of four chemical reactions. One of the steps is crystallization which is employed in step 2 (the drying step), and is given by equation (2) of the following Cu-Cl cycle [1]

$$2CuCl(s) + 2HCl(aq) \rightarrow 2CuCl_2(aq) + H_2(g) \text{ (electrochemical) at 25-90°C;} \quad \text{step 1} \tag{1}$$

$$2CuCl_2(aq) \rightarrow 2CuCl_2(s) \text{ (physical) at 60-200°C;} \quad \text{step 2} \tag{2}$$

$$2CuCl_2(s) + H_2O(g) \leftrightarrow Cu_2OCl_2(s) + 2HCl(g) \text{ (hydrolysis) at 350-450°C;} \quad \text{step 3} \tag{3}$$

$$Cu_2OCl_2(s) \rightarrow 2CuCl(l) + \frac{1}{2}O_2(g) \text{ (thermolysis) at 550°C;} \quad \text{step 4} \tag{4}$$

Initially, spray drying was used to extract solid $CuCl_2$ from solution; however this has proven to be energy-intensive, and alternatives, primarily crystallization, are currently being investigated at UOIT. Spray drying involves a third material flow such as hydrogen chloride (HCl) that might mix with evaporated water, which is harder to separate in a further process. Also if the spray drying and condensation are associated with vaporization of other components than water that might affect the environment, crystallization may prove preferable [2]–[6] Since the crystallization of $CuCl_2$ requires cooling a solution from a higher temperature to ambient temperature, it is inexpensive because ambient air and cooling water are normally readily available.

The process of forming salts from their solution, from a molten state salt or from vapour is called crystallization. Crystallization is an attractive method to recover solids from solution, because of its low energy and material requirements as well as its lower financial cost. Hence, it is of particular interest in the copper-chlorine cycle for hydrogen production as a means to partially extract solid $CuCl_2$ from its aqueous solution. The theory behind crystallization is that the solubility of solid solute in a liquid solvent increases as the temperature of the solvent increases. Conversely, the solubility decreases as the solvent cools. Thus, the solvent is heated to a higher temperature and the solute is added such that the concentration at that temperature is greater than the saturation concentration at a lower temperature. Upon cooling to the lower temperature, the excess solute

solidifies in the form of crystals. The rate of cooling has an effect on the number and size of the crystals [7]–[9]. To determine the number of crystals, researchers have identified a metastable zone where crystallization occurring instantaneously [10]. This zone is determined when the solution with a constant concentration at the corresponding temperature given by the solubility line is cooled at a constant cooling rate such that the initial concentration changes due to the change in temperature. There are many ways to characterize the metastable zone to determine the amount of crystals formed during this process. Barret and Glennon [11] used the Lasentec Focused Beam Reflectance to estimate the nucleation kinetics of potash alum solutions. Additionally, they used a Lasentec Particle and Measurement system to validate the obtained metastable zone and solubility curve [11]. Mielniczek-Brzoska used a potassium nitrate aqueous solution to determine the effect of the sample's volume on crystallization [12]. The nucleation has been observed using a UV-vis spectrometer and visual observation of the nuclei. It has been found that the metastable zone width depends on the volume of the solution in unstirred solutions and it is attributed to the diffusion processes in the solution.

A comparison between different experimental methods to determine the metastable zone width is given in [13]. To compare the techniques, the authors used a solution of ammonium oxalate monohydrate under polythermal conditions. They concluded that the relevance and physical meaning of the results are uncertain under the specified conditions. The metastable zone is widely predicted using the Nyvlt's equation [14]. Mersmann and Bratosch presented a simplified model to predict the metastable zone, determined based on 28 inorganic compounds [15]. The authors developed a theoretical model to represent the crystals in the solution and their growth. However, the model accuracy decreases for solutions following flat curve solubility. In recent years the model obtained by Sangwal is prevalent [16]. A nucleation order was introduced in this model and it was determined that a low solubility of the system corresponds to a high nucleation order and low activation energy. Kubota [17] presented a different interpretation of the metastable zone width in which the nucleation order is given by the log of the metastable zone versus the log of the cooling rate. This model addresses the problem of determining the amount of crystals generated during different nucleations by considering the induction time.

Crystallization can have disadvantages as its residual solutions still contain the solutes after crystals are formed, and the crystallized amount depends on the initial concentrations and crystal forms. Although extensive research has been carried out to determine the metastable zone width, there is limited information on the nature of the crystals formed. Lv et al. conducted research on characterizing the crystals extracted from a solution of CuX dissolved in HX where X = Cl, Br [18]. Similar to their study, in this paper the crystallization of the $CuCl_2$ salt from binary and ternary solutions is examined, in order to improve understanding of the process and its behavior. Since crystallization is the opposite of dissolution, a colder solution generally yields more crystals formed. Hence, this paper also examines the crystallization for temperatures below ambient level. Additionally, the study investigates the nature of the crystals formed by analyzing then using XRD and TGA.

2. EXPERIMENTAL SETUP AND PROCEDURE

Distilled water is used to dissolve solids in order to form an aqueous solution with minimum impurities introduced. The distilled water is measured in a graduated cylinder and added to a reactor jar. If the temperature range is 30 °C-60 °C, then the flask is sealed with a stopper, and an alcohol thermometer is inserted through one of the two holes in the stopper (the other hole being plugged with a nylon thermal well) to prevent mass loss via evaporation. The water is heated to 60°C on a hot-plate/stirrer. The approximate amount of $CuCl_2$ (determined by reading the solubility table) is weighed using an analytical balance with readability of 0.1 mg. The high purity $CuCl_2$ (i.e. 98%) is gradually poured into the reactor jar while the water in the jar is being stirred with a magnetic stir rod on the hot plate. The reactor jar remains on the hot plate until the $CuCl_2$ poured is fully dissolved. After that, the stir is stopped and the necessary amount of HCl (depending on the required molarity) is poured in the reactor jar. HCl with assay of 36.5% - 38.0% was used for this study.

A sample of 10 mL of the final solution is extracted via pipet, weighed and left in the oven at 120 °C immediately after adding the HCl. The mass of the sample is recorded every half hour for three hours and it is then plotted as a function of time. The rest of the solution in the jar is either left to cool down to room temperature (if it was heated to 60 °C before) or taken to an ice bath (or chiller) to cool down to about 0 °C. For the case when the reactor is cooled down to about 0 °C, the temperature is recorded and monitored using three Omega T-Type thermocouples and LabView 8.5, a National Instruments software. See Fig. 1 for a diagram showing the configuration of the experimental apparatus that can operate at a temperature of about 0 °C.

A chiller was used to cool and circulate an 80-20 (molar ratio) solution of ethylene glycol and water, respectively, through a jacket flask. It comprises a digital setpoint, which is set slightly lower than the desired

solution temperature. After the reactor jar is cooled down, the contents of the reactor are filtered using filter paper to separate the crystallized solid from the residual aqueous solution. A final sample of 10 mL of the liquid part remaining is pipetted onto a watchglass, weighed and then placed in the oven at 120 °C. Another sample of the crystals obtained is simply taken and placed immediately in a sample flask. Ultimately, each watch-glass sample must be transferred to a corresponding flask for analysis (e.g., XRD, TGA) and for storage. The transfer is made in a pure nitrogen environment of a glove box, so as to avoid contact with the oxygen in air and hence greatly minimize oxidation of samples. The pure nitrogen environment is achieved by constantly circulating compressed nitrogen (Ultra High Purity 5.0) through the glove box.

3. RESULTS AND DISCUSSION

It is observed that most crystallization occurs within minutes from the formation of the first crystal around which the growth propagates. It was also noticed that crystallization will take time if no crystallizing agent was added to the mixture. For most of the samples tested at molarities lower than 5, the crystallization only starts after the temperature of the system falls below 30 °C.

It was also determined that a colder solution yields larger particles. Fig. 2 shows the crystallized $CuCl_2$ before filtering out the clear solution. Compared to crystal size of other salts, $CuCl_2$ crystals are relatively small yet still observable with naked eye, however, investigating the size of the crystals formed is beyond the scope of this paper.

The HCl concentration was observed to affect the amount of crystallization. This was determined when measuring the amount of clear solution and a significant drop was observed, reflecting an increase in the crystallized amount. Additionally, it was determined that crystallization does not occur at concentrations above 9M or below 3M. As mentioned previously, the chemicals are added in the following order: Water, $CuCl_2$, HCl. When adding chemicals in the aforementioned order, it is observed that the HCl acts as a "crystallizing agent" in the sense that crystallization begins to occur immediately after adding HCl, despite there being negligible change in ambient temperature. Experiments have also been performed at various temperatures and concentrations using anhydrous $CuCl_2$. After careful investigation, it has been determined that anhydrous $CuCl_2$ does not crystallize regardless of the temperature or HCl concentration. These findings are very useful for the integration of the reactors of the Cu-Cl cycle since it provides information on whether this technique can be utilized. The research team is currently investigating the type of $CuCl_2$ produced during electrolysis to determine the feasibility of this crystallization method within the cycle.

After removing the clear solution as described in the previous section, the crystals were placed in the oven at 120 °C to dry completely. Measurements have been recorded at 30 minutes intervals to determine the time it takes to remove water from sample. Figure 3 shows the sample's drop in mass and its mass stabilizing at about 40 grams within 100 minutes. This step was necessary in order to prepare the samples for X-ray diffraction (XRD) and thermogravimetric (TGA) analysis.

X-ray diffraction is a phenomenon in which atomic planes of a crystal causes the incident beam of x-rays to interfere with each other as they leave the crystal. The spacing between layers of atoms is measured through this technique so that the orientation of a single crystal is determined. Once the orientation is determined, the crystal structure size, shape and internal stress of crystalline regions of the material can be found. Since the crystal structure describes the atomic arrangement of the material, a different arrangement of atoms would create a different diffraction pattern. The XRD pattern for the $CuCl_2$ obtained through crystallization is shown in Figs. 4 - 6. The plots indicate that the crystals formed through the method described are $CuCl_2$ and hydrate $CuCl_2$ for all concentrations of HCl independent of the temperature to which the solution is cooled down. Table 2 indicates the amount of $CuCl_2$ and $CuCl_2$ hydrite determined by XRD analysis in the original sample dissolved in the aqueous solution and in the crystals extracted through the method described in the experimental setup section. To further validate the nature of the crystals, another analytical technique (i.e. thermogravimateric analysis) was employed. In this technique, the composition of the recovered solids is determined by observing its melting temperature. As can be seen in Fig. 5, the melting temperature of the crystalized solid is 441.6 °C. Also, the decrease in the plot at approximately 600°C corresponds to the vaporization of the sample. The stock $CuCl_2$ was also investigated and the melting temperature was 461.65 °C, which is comparable to the melting temperature of the crystalized sample.

4. ERROR ANALYSIS

The main source of error is evaporation of HCl due to its high volatility. Although the flasks used were sealed as fast as possible, so that the solution would not be exposed for a long period of time, this source of error must be considered. Also, the instrument limitations should be considered. When weighing every piece of apparatus used in the experiment, there is the analytical balance error to be considered, with a precision limit of half of the readability. Thus, the precision limit used is ±0.005 g. The bias limit for masses is calculated as the deviation of the three measurements made for each part weighed. The other precision limits were estimated as the tolerance, half of the readability of the equipment.

5. CONCLUSIONS

There is a narrow range of concentrations that demonstrates crystallization. If the initial concentration exceeds the upper bound of this range, the solution is saturated and precipitation occurs instantly. Conversely, when the initial concentrations fall below the lower bound of this range, the solution remains liquid upon cooling. Significant findings from this series of experiments are: anhydrous copper (II) chloride does not crystallize, crystallization does not occur at concentrations >9M, and HCl can act as "crystallizing agent", causing near-instantaneous crystallization when it is added to aqueous $CuCl_2$ solution. Overall, the experimental results largely agree with the theory. Crystallization is achieved frequently and consistently when the solution temperature drops below the saturation temperature. Further studies based on these experiments will determine the amount of crystals formed during the crystallization process. The findings will establish whether the method of extracting $CuCl_2$ from the aqueous solution presented in this study is suitable for the Cu-Cl cycle for hydrogen production.

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FIGURES
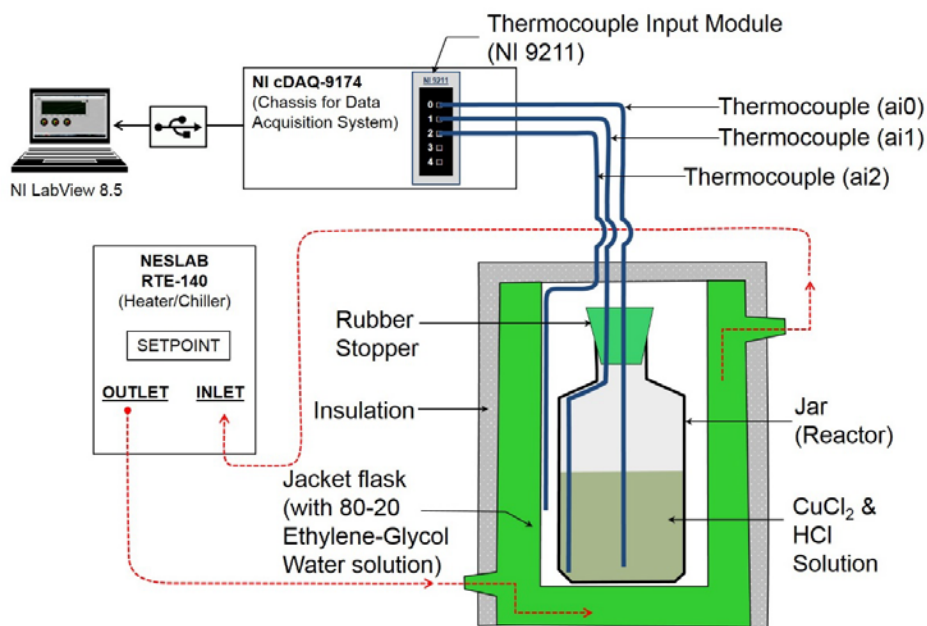
Fig. 1: Configuration of experimental apparatus for crystallization at temperatures below room temperature
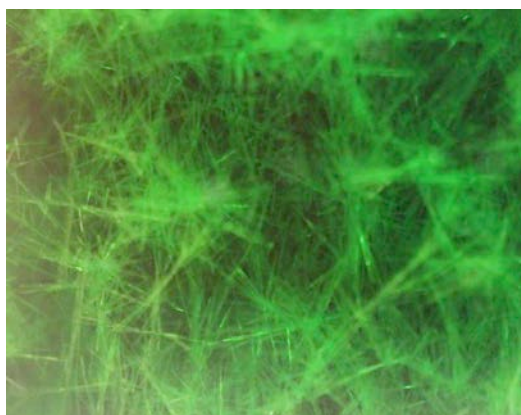
Fig. 2: Configuration of crystalline solid (green dendrites) at temperatures below room temperature
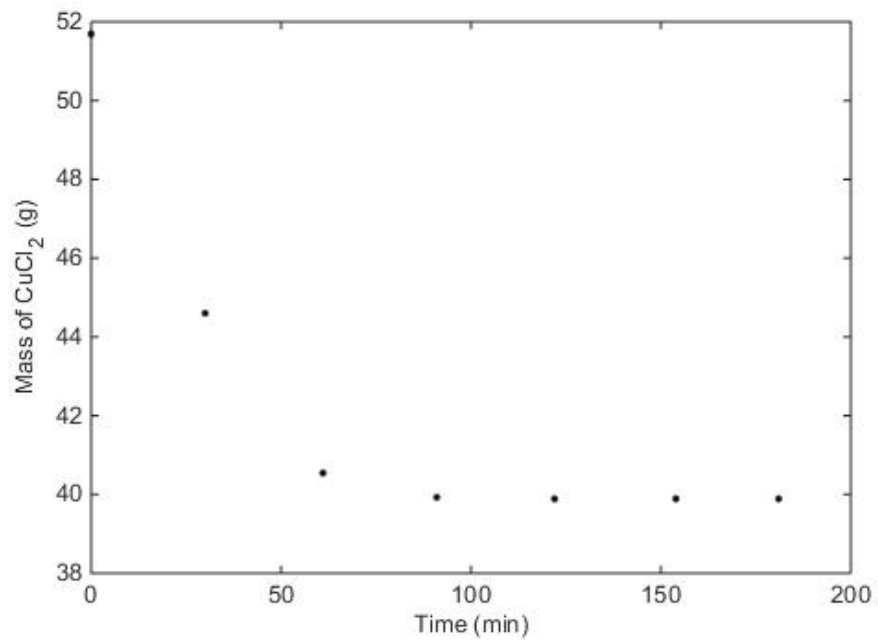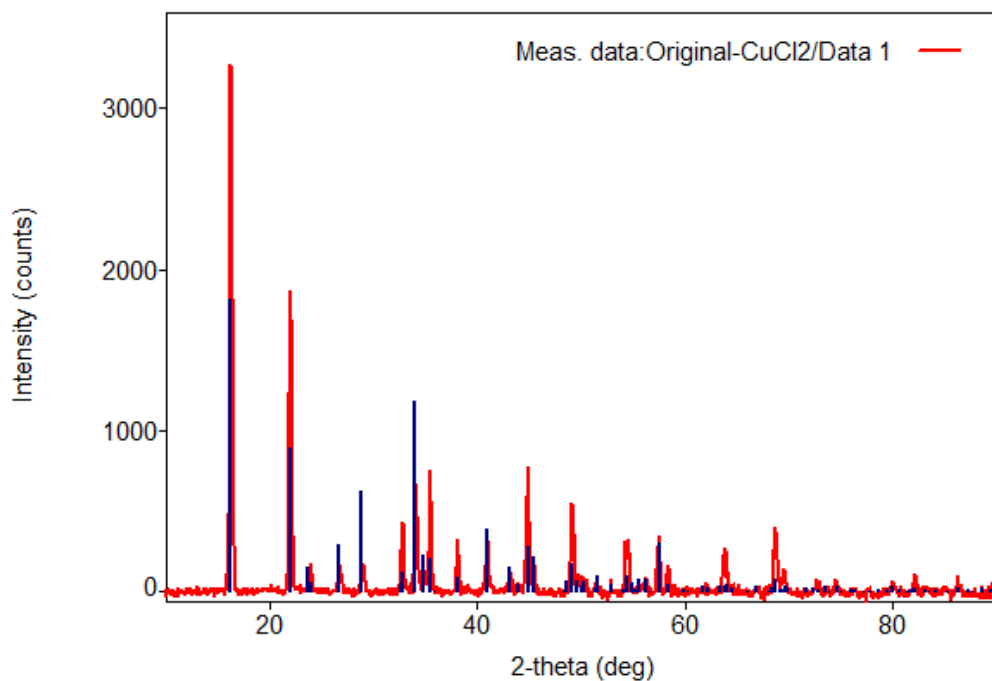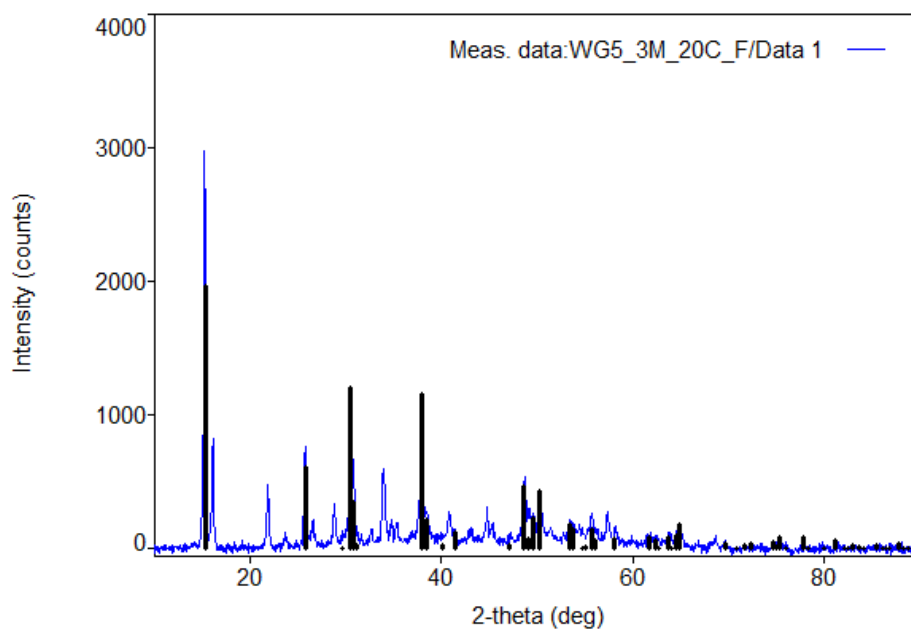
Fig. 3: $CuCl_2$ sample mass change over time
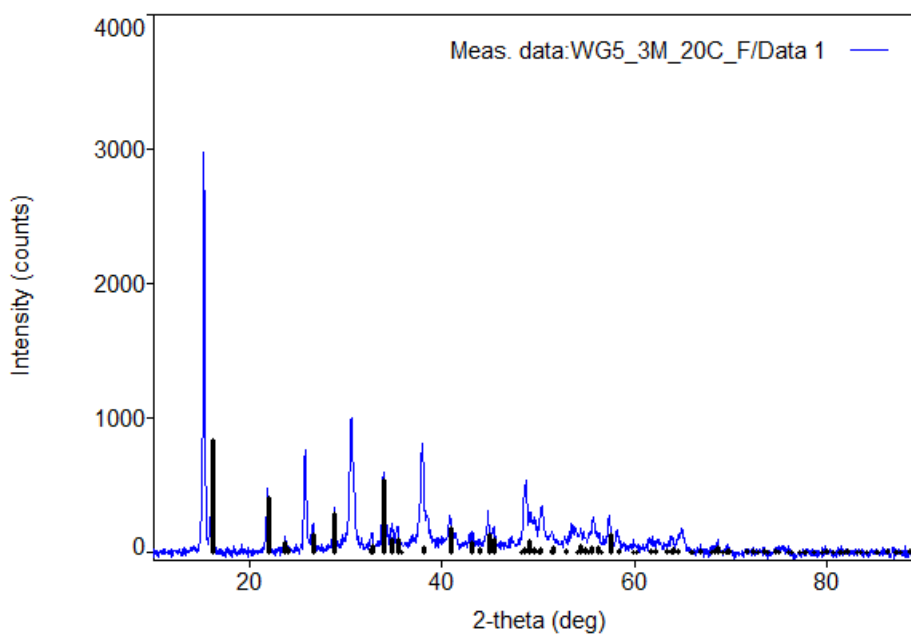

Fig. 4: Results of XRD analysis for the original sample of $CuCl_2$
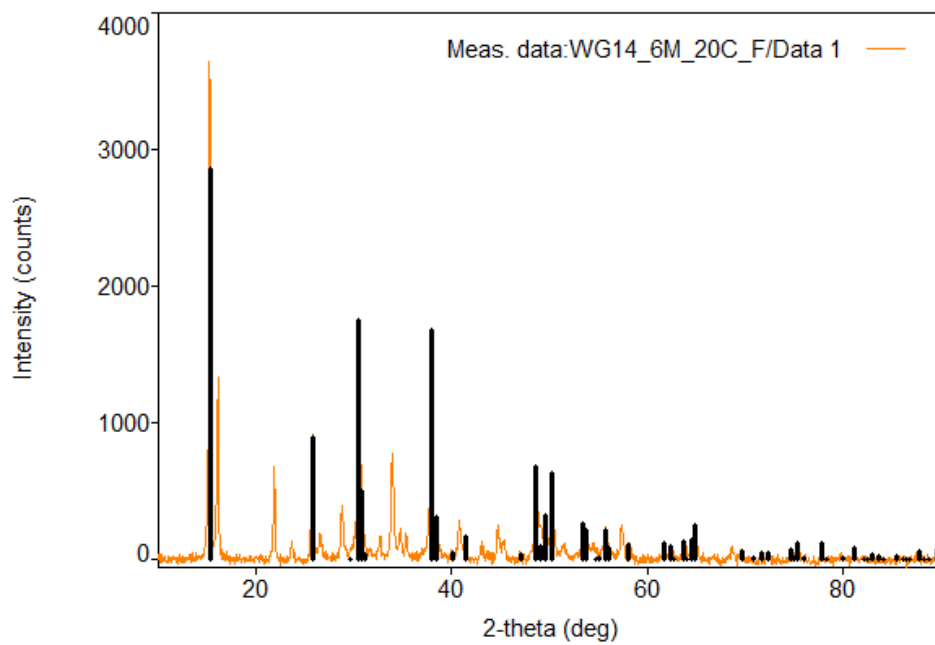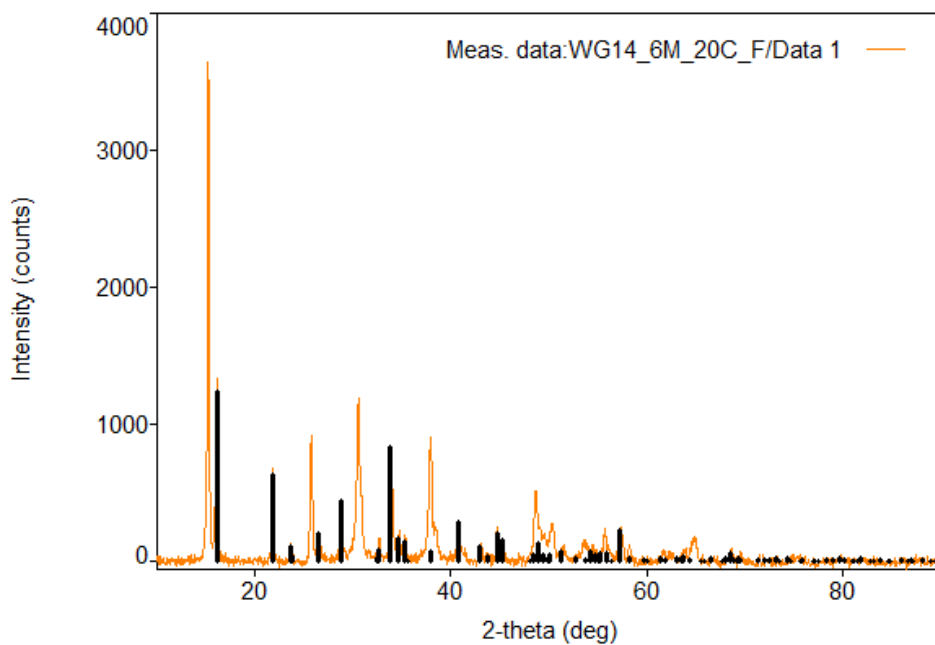
(a)

(b)

Fig. 5: Results of XRD analysis for the crystals extracted from 3M HCl solution cooled down to 20 °C; (a) original signal with intensity peaks representing $CuCl_2$, (b) original signal with intensity peaks representing $CuCl_2$ H_2O

(a)

(b)

Fig. 6: Results of XRD analysis for the crystals extracted from 6M HCl solution cooled down to 20 $^{\circ}$C; (a) original signal with intensity peaks representing $CuCl_2$, (b) original signal with intensity peaks representing $CuCl_2\ H_2O$
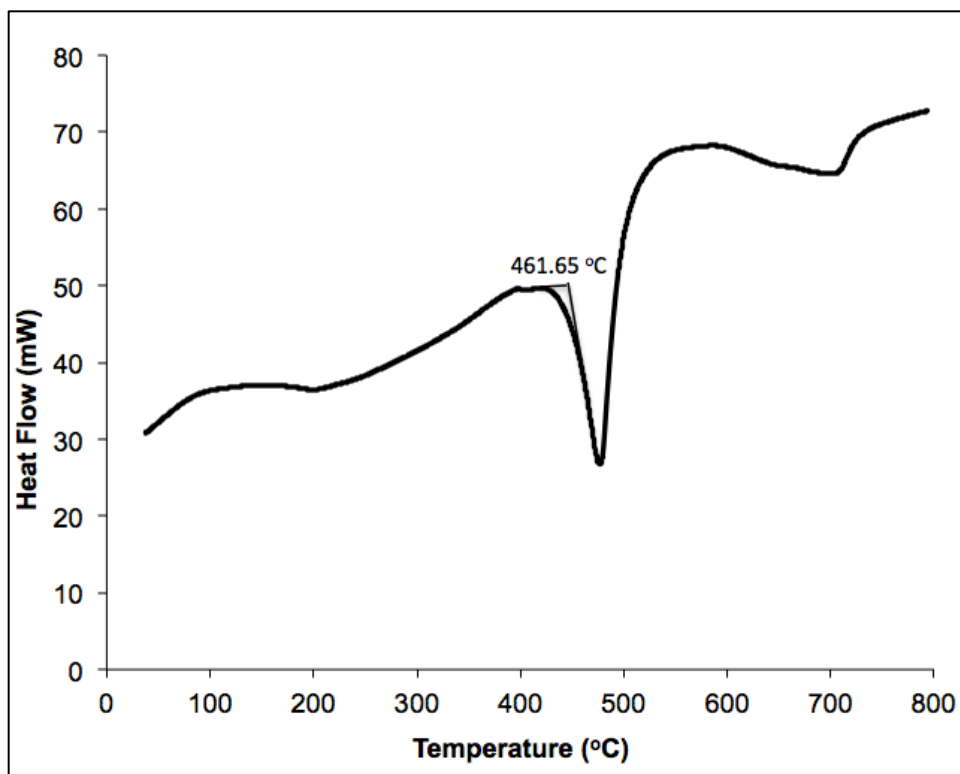
Fig. 5: Results of TGA analysis

TABLES

Table 1: Measurement data for equipment

Equipment	Maximum Capacity	Readability	Operating temperature range (ºC)
Graduated Cylinder	100 mL	1 mL	-
Graduated Cylinder	50 mL	1 mL	-
Thermometers	110 ºC	1 ºC	-20 - 110
Pipet (25 mL)	25 mL	0.1 mL	-
Pipet (10 mL)	10 mL	0.1 mL	-
Analytical Balance	220 g	0.001 g	10 - 30
Digital Scale	410 g	0.01 g	10 - 30
Omega T-type Thermocouple	350 ºC	1.5 °C	-250 - 350

Table 2: Amount of cupric chloride hydride and cupric chloride extracted from different samples

	CuCl$_2$ Original Smaple	CuCl$_2$ in 3M HClCooled down to 20 °C	CuCl$_2$ in 3M HCl Cooled down to 0 °C	CuCl$_2$ in 6M HCl Cooled down to 20 °C
CuCl$_2$ H$_2$O	95.7	54.0	55.2	39.0
CuCl$_2$	4.3	46.0	44.8	61.0

Table 3: Precision and Bias Limits

Equipment	Precision Limit
Graduated Cylinders (100 mL and 50 mL)	± 0.5 mL
Thermometers	± 0.5
Pipet (25 mL)	± 0.1 mL
Pipet (10 mL)	± 0.06 mL
Analytical Balance	± 0.005 g
Digital Scale	± 0.005 g
Clock	± 0.5 s
Omega T-type Thermocouples	Greater of 1.0℃ or 0.75% of FS