Morphology and Agglomeration of Copper Chloride Particles in the Thermochemical Cu-Cl Cycle of Hydrogen Production

H. Radwan¹, K. Pope¹, K. Hawboldt¹, G.F. Naterer²

¹Faculty of Engineering and Applied Science, Memorial University of Newfoundland, 240 Prince Phillip Drive St. John’s, Newfoundland and Labrador A1B 3X5, Canada
²Faculty of Sustainable Design Engineering, University of Prince Edward Island, Charlottetown, PEI, Canada

Abstract. Hydrogen generation from the thermochemical copper-chloride (Cu-Cl) cycle is a promising clean energy process due to lower operating temperature relative to comparable cycles and can be integrated with solar and nuclear systems. This study focuses on the impact of CuCl₂ particle size and morphology in the hydrolysis reaction step. The particle size was studied using crushing and crystallization, and the morphology was analyzed using a scanning electron microscope (SEM). This data was used as input into the shrinking core model (SCM) and compared with previous experimental data. Prior to crushing and crystallization, the material had a monodisperse size distribution with a diameter between 70 - 200 µm and a length of 200 - 650 µm. After crushing, the material was non-uniform in shape and sizes with a cylindrical or cuboid shape with a diameter of 20 - 70 µm and length range of 30 - 150 µm. Particles less than 10 µm were spherical in shape. Agglomerated particles forming irregular flakes were observed after crystallization. Furthermore, the SCM indicated that the reaction control step with spherical particle assumption is the most accurate model.

Keywords: CuCl₂ cycle, hydrolysis reaction, shrinking core model, hydrogen production, crystallization.

I. INTRODUCTION

Alternative and cleaner energy sources have become increasingly important for net-zero including hydrogen. Hydrogen is considered an effective and safe energy carrier. However, hydrogen produced using fossil fuels typically produce carbon and therefore, emission-free processes such as water splitting are considered more environmentally friendly depending on the process used to split the hydrogen from the water [1]. Water splitting via the thermochemical copper chloride (Cu-Cl) cycle can be integrated with other energy sources like solar and nuclear systems, thereby minimizing carbon and other emissions [1]. This is a four-part process: electrochemical reaction, drying, hydrolysis reaction, and thermolysis reaction. This work focuses on the hydrolysis reaction, where the copper chloride is reacted with steam to form Cu₂OCl₂ and HCl as per equation (1). The reaction occurs between 375 °C and 400 °C and is usually operated with excess steam. The steam-to-copper ratio is defined as the mole of steam to the mole of solid CuCl₂ [1].

\[ 2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{Cu}_2\text{OCl}_2(\text{s}) + 2\text{HCl}(\text{g}) \]  

Hydrolysis is a gas-solid reaction that can be modeled using uniform conversion (VM) or shrinking core models (SCM). The SCM limits the reaction zone to a thin layer that advances from the particle’s outer surface, where gaseous reactant diffuses through a film surrounding the particle, then penetrates and diffuses through an ash layer to the unreacted core [2]. In the SCM, particle morphology and size are significant parameters [2]. They can affect overall reaction rate, by shifting the rate controlling step [2]. This study investigated the morphology and particle size for commercial CuCl₂·2H₂O using a scanning electron microscope (SEM). The study compares the effect of crushing and crystallization on morphology and particle size. Also, a numerical analysis of the SCM was conducted and compared with the literature.

Hydrolysis has been studied for a variety of reactors such as fluidized beds, packed beds, spray, and falling particle reactors, operating as batch or semi-batch. Studies on semi-batch fixed beds are the earliest models studied. The conceptual process design and sensitivity studies provided a method to identify the most critical operating parameters. The CuCl₂·2H₂O was dried and crushed using a ball mill and then sieved into three sizes a) 250 - 300 µm b) 150 - 250 µm c) Ball milled (undetermined smaller size) [3]. The concluded results were made based on the formation of the side product (CuCl). In general, smaller particle sizes and higher steam-to-copper ratio achieve better conversion and reduce the by-product (CuCl) due to the enhancement of mass transfer [3]. Thermogravimetric analyzer (TGA) was used to study the reaction, the TGA operates as a very small scale semi-batch fixed bed reactor. The temperature, particle size, and reaction time impact on the conversion and side reaction was studied [4]. The particle size was reduced using a ball mill from 46 - 47 nm to study three size ranges a) 25 - 27 nm b) 20 - 22 nm c) 15 - 17 nm. The particles were reported to have a flat surface with sharp corners forming cuboids particles for the 46-47 nm commercial CuCl₂·2H₂O. In contrast, the ball-milled particle...
morphology was described as regular-shaped cubes. Particles of size 20 - 22 nm achieved the best results with a yield of approximately 95% compared to a 55% yield for 46 - 47 nm particles [4].

In a fluidized bed reactor the particle had a mean average of 265 μm, operating parameters were optimized, and particle conversions were achieved using excess steam [5]. The physical reaction resistances during the initial 30 min reduced the reaction rate by 40% and was attributed to an increase of film diffusion resistance [5]. In a study by Thomas et al. (2020) [6], the impaction of temperature, reaction time, and steam mole fraction on reaction rate was studied [6]. The reactant CuCl2, with an average particle size of 350 μm, was mixed with glass beads in a fluidized bed reactor. Operating conditions that achieved the best conversion was 300 – 325 °C with 0.5 steam mole fraction and a residence time of 20 – 40 min [6]. Spray reactors have been studied where the CuCl2 is in the form of slurry and is atomized and sprayed into steam [7]. Maintaining uniform temperature, optimum operating pressure, and controlling the droplet resident time are critical parameters for efficient contact and reaction [7]. The CuCl2 water droplets (25 mm) were introduced to the reactor by an ultrasonic nozzle or pneumatic nebulizer. The ultrasonic nozzle achieved a higher product yield in counter-current flow compared to the nebulizer. A 95% yield was achieved using a 24 steam-to-copper molar ratio [7].

Daggupati et al. (2010) [8], used VM and SCM to study CuCl2 hydrosylysis in reactive spray drying (a combination of drying and hydroslysis). The analysis showed that reducing particle size reduces diffusion resistance. By varying the excess steam, pressure, and adding an inert gas at 375 °C, a complete conversion of CuCl2 can be achieved [8]. Similar modeling was conducted for a free-falling reactor. Where an average particle size of 200 μm falls freely from the reactor top to interact with the reflux steam, natural convection draws steam from the cold side of the reactor, allowing sufficient residence time for the reactant [9]. In another study, a model was developed to predict the hydrodynamic behavior and conversion of CuCl2 particles and steam using the VM and SCM [10]. The effect of superficial velocity and bed inventory (mass of CuCl2) on conversion was presented. The solid particle conversion increased with superficial velocity and a higher bed inventory [10]. CuCl2 particles are produced in the electrolysis step of the cycle as an aqueous solution. Crystallization has been studied to dry the reactant (CuCl2) before introduction into the hydroslysis reactor [1]. Crystallization is a process that retrieves the soluble solid from its solution based on the solubility change of the saturated solution [11]. It was reported that crystallization of aqueous CuCl2 can be achieved using HCl as an anti-solvent in a concentration between 3-9 M [12].

This study investigates the morphology and particle size of CuCl2 after drying, crushing, and crystallization using SEM. The characteristic X-ray information for the elements in the sample generated from the energy-dispersive X-ray spectroscopy microanalysis (EDXMA) was used to confirm that no change occurred during the sample processing. Based on the results, the reflected morphology was compared with past literature data.

II. METHODOLOGY

Particle size and morphology of the material are significant factors in SCM as the particle size might affect the conversion and rate of reaction and change of the controlling resistance. The particle size of CuCl2 can be modified using: manual crushing using pestle and mortar, ball milling, crystallization, or a spray drier. This study used manual crushing and crystallization. Pestle and mortar were used to crush CuCl2·2H2O. Another sample was dried at 90 - 110 °C and then crushed.

For crystallization CuCl2·2H2O particles were dissolved in distilled water to form a saturated solution. HCl with an assay of 36.5% - 38.0% was added to create a solution molarity of 6 M. The solution flask was heated on a hotplate until it reached 60 °C. A sample of 10 mL was taken immediately after adding the HCl and dried in the oven at 110 °C for further analysis. The solution was cooled at room temperature. The final step was the solution filtration to separate the crystals. A sample of 10 mL of the final solution was also stored for analysis. A sieve analysis was performed by meshing the sample through three stainless steel meshes of 1000, 400, and 74 μm. The average particle size allowed through mesh 1000 and 400 was 914 and 381 μm, respectively. For mesh 74, the wave style is plain Dutch, where the average particle size allowed through the mesh is 40 μm and the largest particle size allowed is in the range of 58 - 63 μm.

The SEM, which produces images of a sample by scanning the surface with a focused beam of electrons, provided information about the morphology of the samples after different processes. It also indicated an estimation of the particle size that can be achieved. Using the same test for the same sample, the energy-dispersive X-ray spectroscopy evolving from the interaction of electrons with the sample produced characteristic X-ray information for the elements in the sample. This information was used as a comparative analysis to ensure that the processes did not change the material elements.

The shrinking core model assumes that the reaction occurs only on the particle's surface, separating the unreacted core by the product layer and moving to the center as the reaction progresses. Yagi and Kunii (1955, 1961) depicted five steps occurring in succession during the reaction, where each step presents a resistance to the solid conversion [2]. Depending on the system, some or all resistances might exist, and the highest resistance or combination of resistances controls the particle conversion. In this study, the diffusion of gaseous reactant through the particle surrounding the film is neglected. The diffusion through the product layer to the surface of the reaction can be expressed by assuming the rate of reaction at any instant is given by the diffusion rate to the reaction surface. Linking to Fick's law for equimolar counter diffusion in Equation (2), and after integration and substitution, the conversion time can be expressed as per Equation (3). Then $t_a$ is presented in Equation (4), where $D_e$ is the effective diffusion coefficient of gaseous reactant in the ash layer. Equations 2-4 are based on the assumption of a spherical particle shape, and Equations (5) and (6) reflect a cylindrical shape.

$$-\frac{4nA}{at} = 4\pi r^2 D_e \frac{dCA}{dr} = \text{constant}$$  

Equation (2)
the flakes are very integratable. Under ion was extracted and dried in an oven. The presence of agglomerated particles forming irregular flakes was observed with non-uniform sizes. The largest size was 1.3 mm, and the smaller flakes were less than 60 μm in size. Figures 5 and 6 present an image for large and small flakes, respectively.

The sample was sieved using three meshes without any further crushing. Figures 7, 8 and 9 present the imaging for particles that passed through mesh 1000, 400, and 74 μm, respectively. Despite the flake irregularity and the cylindrical shape, the sieving range complies with the mesh size, as shown in Table 1. It should be considered that the flakes are very fragile. As a result, some particles were scattered around the flakes during the sample preparation for SEM.

The crystallization process was investigated, and a sample from the solution was extracted and dried in an oven. Under SEM scanning, the particle shape can be approximated as a cylinder or cuboid. The model is applied for CuCl₂ with two different assumptions of particle size between 150 - 250 μm: the effective diffusion coefficient (D_e) and the rate constant (k_e) validated for this size range are generated from the previous experimental data [13]. Matlab was used to generate the results, and the following assumptions were considered: negligible particle porosity; first-order reaction; and negligible side reactions.

III. RESULTS AND DISCUSSION

SEM was used to investigate the morphology of the commercial CuCl₂·2H₂O, at 500 μm imaging scale and under 1.2 x 10⁻⁴ chamber pressure. The crystals have a monodisperse size distribution, stick shape, which can be approximated as cylindrical particles. No flakes or spherical particles were noticed. The approximated cylinder was between 200 - 650 μm in length and 70 - 200 μm in diameter (Fig. 1). The material imaging after drying and crushing indicated non-uniform shapes and sizes. The imaging of these samples in the detector was changed from the Everhart-Thornley Detector (ETD) to a Circular Backscatter Detector (CBS) to get more representative imaging. Figures 2, 3 and 4 present the same spot micro imaging at different scales, where the larger particles in Fig. 2 maintained a cylindrical or cuboid shape with a length range of 30 - 150 μm and diameter of 20 - 70 μm. For particles with a size less than 30 μm, the shape becomes spherical and is more pronounced for particles less than 10 μm (Fig. 4).

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\[
\frac{\tau_{SP}}{\tau_{C}} = \frac{1 - (1 - X_R)^{\frac{1}{2}}}{2(1 - X_R)} \quad (3)
\]

\[
\frac{\tau_{SP}}{\tau_{CY}} = \frac{\rho B R^2}{6bD_e C_{Ag}} \quad (4)
\]

\[
\frac{\tau_{CY}}{\tau_{C}} = \frac{[X_B + (1 - X_B) \ln(1 - X_B)]}{\rho B R^2} \quad (5)
\]

\[
\frac{\rho B R^2}{4bD_e C_{Ag}} \quad (6)
\]

\[
-\frac{1}{4\pi} \frac{dN_A}{dt} = -\frac{b}{4\pi} \frac{dN_A}{dt} = bk'' C_{Ag} \quad (7)
\]

\[
\frac{\tau_{SP}}{\tau_{C}} = 1 - (1 - X_R)^{\frac{1}{2}} \quad (8)
\]

\[
\tau_{C} = \frac{\rho B R}{k'' C_{Ag}} \quad (9)
\]

\[
\frac{\tau_{CY}}{\tau_{C}} = 1 - (1 - X_R)^{\frac{1}{2}} \quad (10)
\]

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<table>
<thead>
<tr>
<th>Mesh (µm)</th>
<th>Nominal Size Range (µm)</th>
<th>Size Range From SEM (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 - 400</td>
<td>914 - 381</td>
<td>850 - 380</td>
</tr>
<tr>
<td>400 - 74*</td>
<td>381 - 40</td>
<td>380 - 65</td>
</tr>
<tr>
<td>Passed 74*</td>
<td>Less than 40*</td>
<td>Less than 60</td>
</tr>
</tbody>
</table>

*For mesh 74, the largest particle size is in the range of 58 - 63 μm.
Figure 3: Micro imaging of CuCl₂ after drying and crushing at 100 μm imaging scale.

Figure 4: Micro imaging of CuCl₂ after drying and crushing at 10 μm imaging scale.

Figure 5: Micro imaging of CuCl₂ large flake after crystallization.

Figure 6: Micro imaging of CuCl₂ small flake after crystallization.

Figure 7: Micro imaging of CuCl₂ after crystallization at mesh 400 μm.

Figure 8: Micro imaging of CuCl₂ after crystallization at mesh 74 μm.

Figure 9: Micro imaging of CuCl₂ after crystallization, passed mesh 74 μm.

The EDXMA analysis was used to compare the X-ray element spectrum of the samples. Figures 11 and 12 present the samples after crushing and crystallization, respectively, and they are compared with Fig. 10, which presents the CuCl₂·2H₂O sample before processing. It was validated that there was no change in the chemistry during drying, crushing, and crystallization except for the water removal from the sample.
CuCl₂ is generated as an aqueous solution from the electrochemical step. The selection of the material processing step between the two steps should be considered based on its feasibility within the cycle. This considers the largest particle or flake size achieved as that might affect the conversion of material or require more reaction time. The SCM rely on the shape and the particle size, and the controlling step might change when the particle size is changed. Figure 13 presents the reaction control and diffusion control for the CuCl₂ hydrolysis reaction for both spherical and cylindrical shape approximation. The results were compared with experimental data [13], according to Fig. 13, assuming spherical particles yields a more representative model than a cylindrical approximation. With the available experimental data, the reaction may be considered the controlling step, although more experimental data is required to validate this conclusion, particularly in the early stage of the reaction (time) where the shape may have a significant effect.

IV. CONCLUSIONS

This study examined the morphology and particle size of CuCl₂ particles in the Cu-Cl cycle. The particle size was changed using crushing and crystallization, and the morphology was analyzed using SEM. The SCM was analyzed for the two-particle shape assumption, and the results were compared with previous experimental data. It was found that commercial CuCl₂·2H₂O particles had a monodisperse size distribution of shapes with a length range of 200 - 650 µm and a diameter between 70 - 200 µm. The material micro imaging after drying and crushing indicated non-uniform shapes and sizes even though it maintained a cylindrical or cuboid shape with a length range of 30 - 150 µm and diameter of 20 - 70 µm. It was noticed that particles tend to become spherical for sizes less than 10 µm. For crystallization results, the particle shape can be approximated to a cylinder or cuboid with irregular shape flakes. The X-ray spectrum indicates that during the material processing, no change occurred. SCM indicated that the reaction control step with spherical particle assumption is the closest representative of the available experimental data in the literature. This study provided more insight into the effect of different processes on the hydrolyses reaction raw material and the reflection of that effect on the reaction modeling and conversion.

APPENDIX – MEASUREMENT ERRORS

The source of bias error of the measurements can be related to the instruments and their precision, as listed in Table 2.

<table>
<thead>
<tr>
<th>Tools</th>
<th>Precision Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graduated Cylinders (100 mL)</td>
<td>± 0.5 mL</td>
</tr>
<tr>
<td>Thermometers</td>
<td>± 0.5 °C</td>
</tr>
<tr>
<td>Pipet (10 mL)</td>
<td>± 0.06 mL</td>
</tr>
<tr>
<td>Balance</td>
<td>± 0.005 g</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

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REFERENCES