

# SHADOW IMAGING OF PARTICLE DYNAMICS AND DISSOLUTION RATES IN AQUEOUS SOLUTIONS FOR HYDROGEN PRODUCTION

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## ABSTRACT

This paper presents experimental studies of particle dynamics, dissolution and transport processes for hydrogen production and thermochemical water decomposition. The processes involve multiple steps, some consisting of multiphase reaction systems. It examines the importance of design optimization of gas-solid-liquid phase systems and process integration of a thermochemical copper-chlorine cycle for hydrogen production. The dissolution of copper (I) chloride particle in hydrochloric acid is examined. This dissolution step is investigated in order to provide a predictive modeling method for more complex multiphase reacting systems.

## 1. INTRODUCTION

Unsustainable human activities and practices are emitting greenhouse gases into the atmosphere, releasing compounds that diminish the Earth's stratospheric ozone layer, and polluting water supplies. Many unsustainable characteristics are exhibited by energy processes, which are one of the largest contributors to climate change. Due to the increasing impact on the health of humans and ecosystems and the economic costs associated with global warming and other environmental impacts, engineers, scientists and others are increasingly pursuing clean energy technologies. One approach is based on a hydrogen economy, in which the two main energy carriers are hydrogen and electricity. Hydrogen production is a key aspect of a hydrogen economy, and one promising renewable option for large-scale hydrogen production is thermochemical water decomposition. Thermochemical cycles are promising alternatives for large scale hydrogen production. These cycles for hydrogen production use a series of reactions to achieve the overall splitting of water into hydrogen and oxygen:



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Thermochemical water decomposition generally involves at least three distinct steps: hydrogen production, oxygen production, and re-cycling of other byproducts and compounds internally. The chemical reactions form a closed internal loop and re-cycle all chemicals on a continuous basis, without emitting any greenhouse gases to the atmosphere. One of the advantages of thermochemical cycles over direct one-step thermal water decomposition is their ability to split water into hydrogen and oxygen at much lower temperatures (usually below 1,000°C) [1].

One of the promising thermochemical cycles that operates at even lower temperatures (under 600 °C) is the thermochemical copper-chlorine (Cu-Cl) cycle. The Cu-Cl cycle splits water into hydrogen and oxygen through intermediate copper and chlorine compounds. The copper-chlorine thermochemical cycle uses mainly thermal energy to split water into hydrogen and oxygen through intermediate copper and chlorine compounds, which are recycled continuously without releasing pollutants into the environment. The thermochemical hydrogen production cycle involves multiple auxiliary steps and multiphase reaction systems. To improve the system efficiency, it is important to optimize the multiphase system design and the process integration. This paper introduces a new model for the past reported experimental data [2], which aids in the integration of the Cu-Cl cycle for hydrogen production.

There are several variations of the Cu-Cl cycle reported in past literature. Such variations include 5-step, 4-step and 3-step cycles [3,4]. An example of a proposed Cu-Cl cycle is shown in Figure 1. The first step of the cycle is electrolysis, in which hydrogen is generated as a result of copper (I) chloride (CuCl) oxidation in the presence of hydrochloric acid (HCl) during an electrochemical reaction. The overall cell reaction is given by [3]:



Several relatively inexpensive electrode materials have been tested and hydrogen production has been achieved at potentials as low as 0.5 V [3]. Also, three different membranes were investigated to identify membranes with lower copper diffusion rates but similar proton conductivities [4]. The second step of the cycle consists of reducing the water from aqueous copper (II) chloride [2]. Once the water is reduced, the solid or slurry CuCl<sub>2</sub> is supplied to the hydrolysis reactor to produce copper oxychloride (Cu<sub>2</sub>OCl<sub>2</sub>) and HCl gas [4], via an endothermic non-catalytic gas-liquid or gas-solid reaction. The last step of the cycle involves the multiphase reaction, in which oxygen gas and molten CuCl are obtained from decomposition of solid copper oxychloride. Several gaseous products exit the reactor such as oxygen, CuCl vapour and side-reaction products such as HCl gas, Cl<sub>2</sub> gas and water vapour [3,4]. It can be found that the CuCl produced in the last step of the cycle is in a molten state, by comparison, the existing state of the CuCl used in the first step is the dissolved state of the CuCl in hydrochloric acid. This means, the following physical process is needed in order to link the first and last steps of the cycle:



One key aspect in solid-liquid flows (i.e. solid CuCl dissolving in aqueous HCl) is to understand the particle's behavior in the mixture; that is, whether the particles distribute evenly within the mixture and remain suspended or segregate and deposit. Particle behavior within the liquid continuum depends of the grain size, shape and density, properties of the liquid such as viscosity and density of the liquid, on the velocity of the flow, flow direction, pipe diameter and solid concentration [5]. In this paper, the critical settling velocity of coarse particles is investigated in order to determine a relative fluid velocity that would keep the particles suspended. This is a necessary condition to ensure CuCl particles dissolve evenly in liquid HCl and the dissolution rate is accelerated.

Past studies [6-8] have presented techniques to monitor dissolution reactions over small timescales in the range of femtoseconds to large timescales over hours or days. It is relatively straightforward to monitor the kinetics of a slow process (e.g., a chemical reaction) but more challenging to monitor fast processes, which in general require highly specialized techniques for accurate monitoring. In general, kinetics experiments often consist of initiating a reaction by mixing reactants. The timescale of the initiation is negligible relative to that of the reaction. Once the reaction is initiated, the concentrations of the reactants and products are monitored. The techniques are either batch or continuous. In batch techniques, concentrations are monitored as a function of time after the reaction is initiated. In a continuous technique, the reaction initiation occurs on a continuous basis and the different concentration regions in the reaction vessel infer the reaction mixture composition and time [6-8].

Since the dissolution of solid CuCl in aqueous HCl is a dynamic process, a different method of monitoring the dissolution rate was utilized in this paper. In this paper, the dissolution was initiated and the dynamic size change of particles was monitored via a camera system. The advantage of this technique is that it monitors the changes in area of the particle to ensure an even dissolution. The dissolution of CuCl in HCl is an important aspect of the thermochemical Cu-Cl cycle for hydrogen production as the system integration design depends on the dissolution kinetics. Hence, this paper examines the optimal dissolution rate of solid CuCl particles in HCl for improved efficiency of the cycle. The solution obtained is then supplied to the first step of the cycle (i.e. electrolysis reactor) for the system integration. Note that the solidification of molten CuCl is not discussed in this paper.

## **2. EXPERIMENTAL SETUP**

In order to better understand the transport processes of liquid-solid systems and the dissolution rate of CuCl in HCl, an experimental apparatus has been designed and built at the University of Ontario Institute of Technology (UOIT) in the Clean Energy Research Laboratory (CERL). The

experimental apparatus consists of an 8-in high, 4-in diameter clear pyrex vessel filled with liquid and a camera system (see Figures 2 and 3).

A FlowSense 2ME camera with an effective sensor size of 1600 by 300 pixels was used to capture images. Images were captured in single frame mode with a trigger frequency of 91 Hz when observing the particle dynamics and 1 Hz when observing the dissolution rate. The particle motion imaging was captured with the aid of a short light flash and a synchronizer. A glass diffuser was used to obtain an even light sheet so that the camera can acquire a shadow image of the particles. DynamicStudio software, an advanced edge detection algorithm to extract the particle shape information, is used to acquire and process the images.

The “shadow sizer processing” method is used to extract information such as size, position, shape and velocity of particles. In this method, the outline of the particle is obtained based on the grey level profile; that is, a value corresponding to the outline is assigned when the pixel’s intensity changes from high intensity to low intensity. Once determined, the outline is plotted and the size, position and shape are given in terms of pixels. For accurate processing, a set of calibration images was acquired prior to image processing. For the calibration images, an electronic digital display caliper with an accuracy of 0.02 mm was set to 1 cm. Images of the caliper were acquired and then a “Measure Scale Factor” function was employed in DynamicStudio. This step enables the measurement of the scale factor to determine the conversion of pixel units into metric units. The distance between the tips of the caliper in the acquired image was measured and the scale factor was obtained. To ensure that the scale factor is consistent across the diameter of the vessel, multiple images were acquired and the scale factors were determined. Also, images of the caliper were acquired outside and inside the vessel to determine the distortion introduced by imperfections in the wall of the vessel as well as the circular shape of the vessel. The velocity information is then extracted by combining a correlation algorithm and measuring displacement between two successive images via a dedicated particle-tracking algorithm. The setup was designed based on Refs. [9-11] so that the uncertainty associated with the experiment can be minimized. The experimental error introduced due to the equipment and analysis as well as the deviation is shown in Table 1. It is observed that the highest error is due to calibration of the camera. In order to minimize this error, a calibration technique suggested in [12-14] was employed and compared with the calibration technique presented in DynamicStudio software.

In the first setup of the experimental loop (Figure 2) CuCl particles dynamics travelling through liquid are examined so that the descending velocity of the particles can be determined. Since water’s density is comparable to that of HCl acid, the dynamics of the CuCl particles was observed when traveling through quiescent water at room temperature. The dynamics of irregular shaped particles of mass ranging from 4 mg to 45 mg was observed with the aid of the camera system

described. Captured images were analyzed and information such as size and velocity of the particle was obtained. This information is useful for calculating the force balance on the particle so that a counter flow may be introduced in order to keep the particles suspended. Introducing a counter flow will also enhance dissolution by refreshing the interface of bulk liquid without introducing additional mechanical components. The effect of mixing through gas cross flow and counter flow for different injection angles has been reported [15-17]. However, the scope of this part of experiment was to investigate the motion of the particles without examining reaction kinetics that would occur when the particle is dropped in HCl and dissolution would occur.

To investigate the dissolution rate of solid CuCl in HCl acid, a second setup was constructed. Similar to the previous experiment, this setup consists of the pyrex vessel and the camera system, as shown in Figure 3. In this experiment, irregular shaped particles with a mass of ~7 mg are dropped in HCl solution. Although the CuCl particles start dissolving in HCl solution immediately, the camera starts recording when the particle settles at the bottom of the vessel. Also, it is assumed that dissolution occurs evenly across the surface of the particle. As the particle settles at the bottom of the vessel, molecular diffusion takes place until equilibrium is achieved. However, it has been observed that local saturation around the particle significantly slows down the dissolution rate. This could be detrimental for the cycle since the byproducts are recycled continuously and a slow dissolution rate could result in an accumulation of byproducts. Hence, methods for enhancing the dissolution rate are necessary. Although a stirrer would be the simplest solution, introducing mechanical components as well as coatings to prevent corrosion due to high concentrations of HCl would increase the cost of the cycle. Therefore, the research group is investigating different methods of mixing for enhancing the dissolution rate such as introducing gas to create disturbance in the liquid. In this set of experiments, nitrogen gas is supplied from the bottom of the pyrex vessel. The flow of nitrogen generates a steady mixing quality of the liquid without disturbing the particle. Although disturbing the particle due to turbulence in the fluid would further enhance dissolution rate, it is necessary to keep the particle stationary so that the camera could capture pictures of the same surface so that the change of the surface area can be determined. Nitrogen was supplied at a flow rate of 4L/min. This flow generated some turbulence in the liquid to reduce the local saturation of dissolved CuCl, however it was assumed small relative to the magnitude to significantly disturb the motion of particles.

### **3. RESULTS AND DISCUSSION**

For successful operation of the Cu-Cl cycle for hydrogen production, it is important to carefully design intermediate processes that aid in the integration of the main steps. As depicted in Figure 1, molten CuCl salt leaves the oxygen reactor, enters an intermediate step which recovers the heat thus changing its state to solid and it finally reaches the electrolysis reactor where it aids in the

production of hydrogen. Similarly, HCl gas leaves the hydrolysis reactor and enters the electrolysis reactor as hydrochloric acid. For improved performance of the cycle, it is necessary to dissolve the solid CuCl particles in aqueous HCl before reaching the electrolysis cell. Hence, a second intermediate step is required between the oxygen reactor and electrolysis reactor. Before introducing this step, a series of experiments have been performed to understand the dynamics of solid CuCl particles in aqueous HCl. A clear understanding of the dynamics of the particles and the dissolution rates will aid in the design of the mixing step and effective integration of the cycle. Two different sets of experiments have been performed as presented in the previous section. A source of error is introduced as the CuCl(s) particles begin dissolving immediately when dropped in HCl(aq) as opposed to when dropped in water and no dissolution takes place. Therefore, the dissolution of the particle would affect its dynamics as well as the density of the solution. In this paper it is assumed that the CuCl(s) particle does not begin dissolving until it settles on the bottom of the vessel.

To better understand the dynamics of the particles in water, Figure 4 depicts the processed images with velocity vectors taken in the same reference time frame at 0.956 s and 1.011 s, respectively. It is observed that the particle's velocity changes as it changes orientation (see Table 2). Due to the irregular shape, the particle changes orientation until it settles on the bottom of the vessel with a settling velocity [18,19].

The instantaneous velocities for different mass particles are tabulated in Table 3. It is important to note that the particles are irregular in shape and the area is the cross sectional area of the particle parallel to the direction of motion. Thus the mass and area values in Table 3 are not necessarily correlated, explaining why the particle in Table 2 with a mass of 33 mg has a smaller cross sectional area than the one with a mass of 31 mg.

The second set of experiments consisted of dropping CuCl(s) particles in HCl(aq) and recording the time required to dissolve. The cross sectional area of the particle was recorded with the aid of the camera system from the time the particle was dropped in the acid until it fully dissolved. Initially, the particle was dropped in stagnant HCl(aq) and local saturation could be observed. To speed up the dissolution rate and to avoid local saturation occurring near the particle surface, nitrogen was injected from the bottom of the container. The flow of nitrogen provided mixing and refreshed the particle surface without disturbing the particle so that the camera can capture the same view of the particle as when dropped in the acid. As expected, mixing increased the dissolution rate and prevented local saturation.

The results pertaining to the CuCl(s) particle dropped in quiescent 6M HCl(aq) is presented in Figure 5. It is observed that the particle's area decreases exponentially and the equation of the line is:

$$A = 9.874e^{-0.00031t} \quad (4)$$

where A represents the surface area, and t is the time. This representation returned an R-squared value of 0.974, which indicates a good correlation between the variables. Also, it can be estimated that a change in area of approximately 3.5 mm<sup>2</sup> would take about 1,500 seconds. Similarly, the data pertaining to the dissolution rate of CuCl(s) in 6M HCl(aq) in the presence of nitrogen as the mixing agent is observed in Figure 6. An exponential dissolution rate is again observed and the equation is given by:

$$A = 11.87e^{-0.00074t} \quad (5)$$

This returned an R-squared value of 0.9938, which indicates a good correlation between the points. From Figure 6, it is estimated that a change in the area of the particle of approximately 4 mm<sup>2</sup> would take about 700 seconds. Therefore, when nitrogen bubbles are introduced as a mixing agent, the time to dissolve a particle with the same area is halved.

These findings coupled with the dynamic data can provide valuable information regarding the kinetics of the dissolution, the type of mixing required and the size of the dissolution vessel to satisfy the kinetics (i.e., determine the height given the velocity and time required for the particle to dissolve). An investigation on the dissolution rate as a result of varying the molarity of the solution will be performed in future studies to ultimately improve the efficiency of the hydrogen production cycle.

#### **4. CONCLUSIONS**

This paper has presented new experimental data on the particle dynamics and dissolution associated with cuprous chloride dissolution in hydrochloric acid. These transport processes have importance to the thermochemical copper-chlorine cycle of hydrogen production. Correlations were developed to provide new insight into the velocity of the particles and concentration of the solution with respect to a change in mass due to dissolution as the particle. Using these results, an optimum mixing technique for improved efficiency can be achieved. The thermochemical Cu-Cl cycle has the ability to produce large amounts of hydrogen without releasing greenhouse gases to the atmosphere. Shortcomings regarding the integration of the first and last steps of the cycle were discussed and a method to overcome the shortcomings for efficiency improvement has been presented in this paper.

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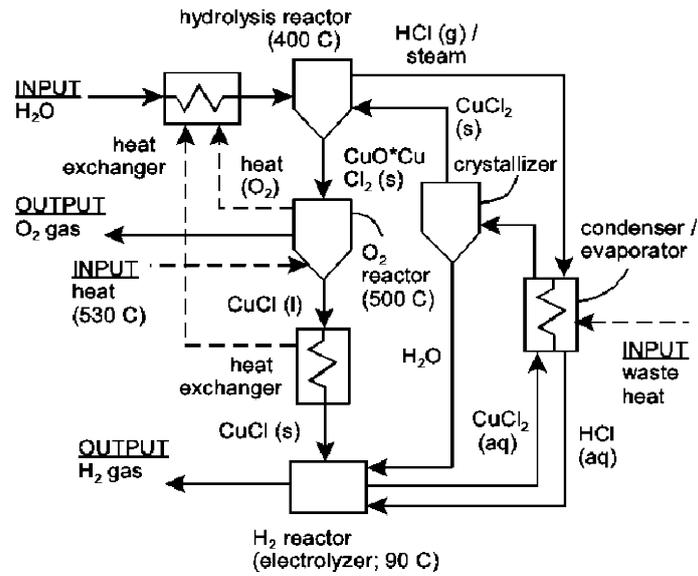


Figure 1. Schematic of a thermochemical copper-chlorine cycle [3]

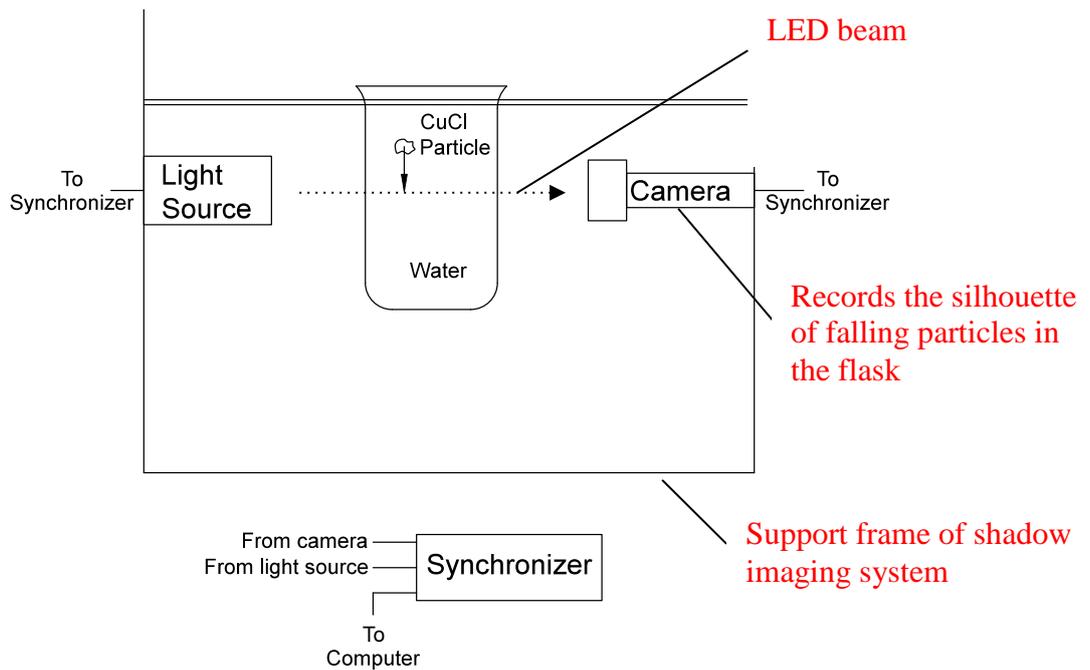


Figure 2. Experimental setup for particle dynamics

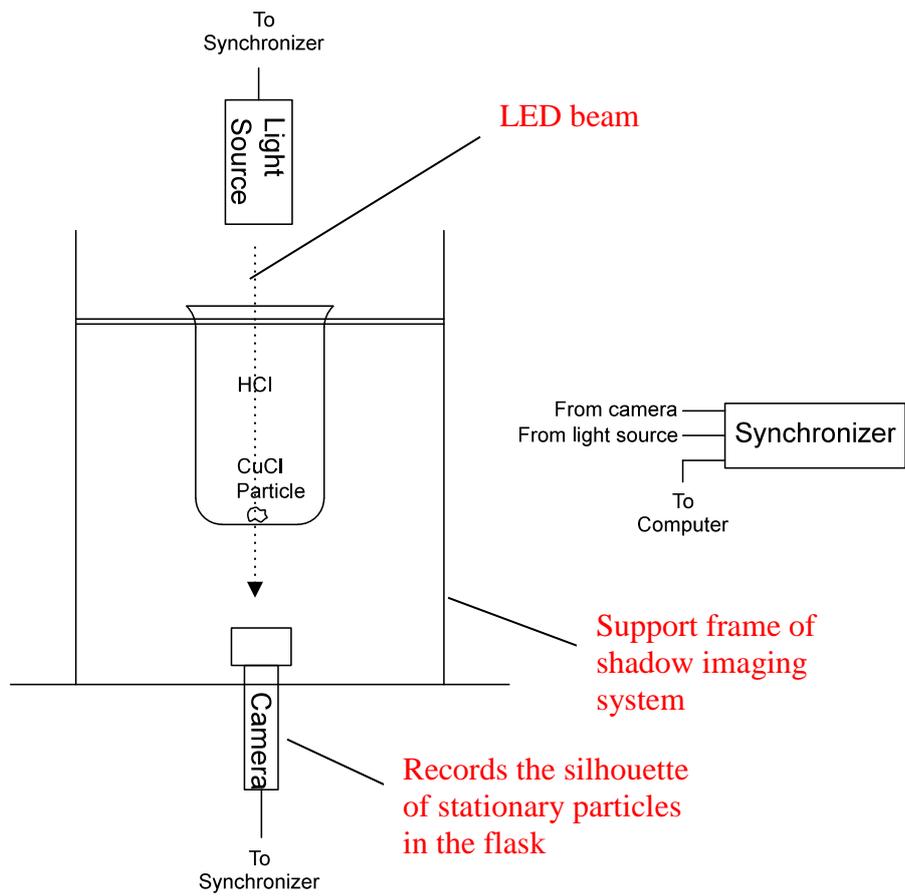


Figure 3. Experimental setup for dissolution rate

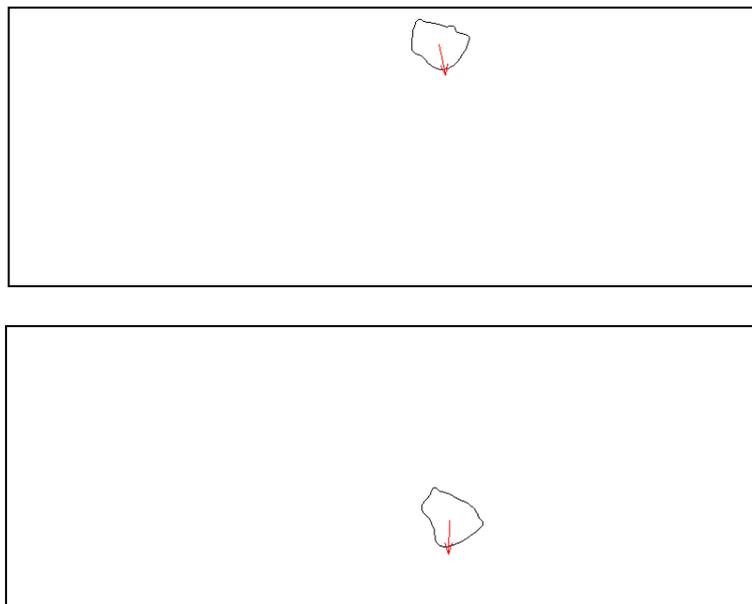


Figure 4. Processed images showing velocity vector for a 45 mg particle at 0.956 s (top) and 1.011 s (bottom)

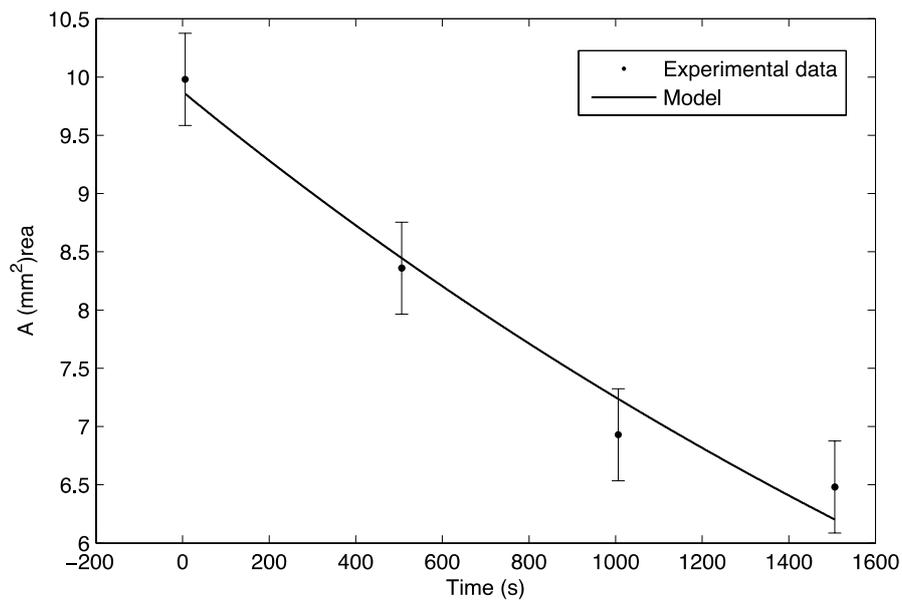


Figure 5. Dissolution rate of solid copper (I) chloride in 6M hydrochloric acid

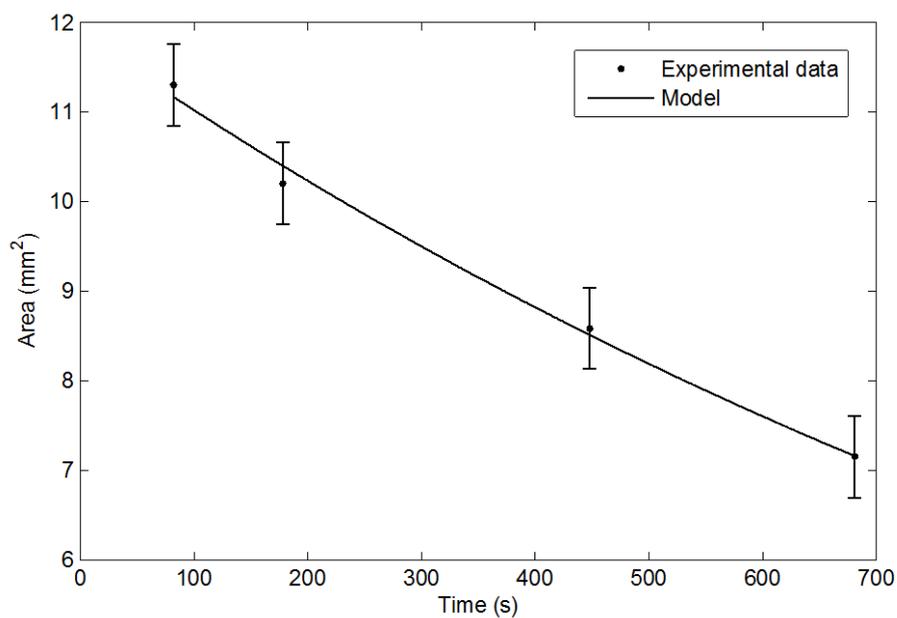


Figure 6. Dissolution rate of solid copper (I) chloride in 6M hydrochloric acid in the presence of nitrogen

Table 1. Shadow imaging system and experimental setup source of error

Source of Error	Deviation (pixels)
Camera calibration	0.019
Residual bulk image due to LED light	0.01
Camera resolution	0.011
Image distortion due to imperfections in the wall of vessel	0.005
Image processing	0.009
<b>Total</b>	<b>0.054</b>

Table 2. Parameters obtained with DynamicStudio

Time (s)	Area <sup>a</sup> (mm <sup>2</sup> )	EqDia <sup>b</sup> (mm)	MajAxis <sup>c</sup> (mm)	MinAxis <sup>d</sup> (mm)	Shape <sup>e</sup>	U <sup>f</sup> (m/s)	V <sup>g</sup> (m/s)
0.956	18.559	0.418	0.249	0.184	0.896	0.005	-0.022
1.011	19.166	0.425	0.24	0.2	0.909	0	-0.023

<sup>a</sup> Cross-sectional area; <sup>b</sup> Diameter of the circle with an area equivalent to the cross-sectional area; <sup>c</sup> Longest axis of particle; <sup>d</sup> Shortest axis of particle; <sup>e</sup> Shape of the particle relative to a sphere enclosing it; <sup>f</sup> Particle's velocity in horizontal plane; <sup>g</sup> Particle's velocity in vertical plane

Table 3. Areas and velocities of particles of varying masses

Area <sup>a</sup> (mm <sup>2</sup> )	U <sup>b</sup> (m/s)	V <sup>c</sup> (m/s)	Mass (mg)
3.841	-0.003	-0.012	4.0
3.293	0.000	-0.017	7.0
5.042	-0.007	-0.020	7.0
6.971	-0.002	-0.016	8.0
7.060	-0.001	-0.017	8.0
12.950	-0.001	-0.020	21.0
9.228	0.005	-0.017	22.0
15.562	-0.003	-0.018	26.0
20.816	0.000	-0.026	31.0
13.764	-0.001	-0.023	32.0
8.591	0.004	-0.020	33.0
19.795	0.000	-0.023	45.0

<sup>a</sup> Projected area of the particle parallel to the direction of motion; <sup>b</sup> Particle's velocity in the horizontal plane; <sup>c</sup> Particle's velocity in the vertical plane

Table 4. Dissolution in quiescent 6M hydrochloric acid

<b>Deq<sup>a</sup> (mm)</b>	<b>Uncertainty</b>
1.78	0.030
1.63	0.033
1.49	0.036
1.44	0.038
<b>a - equivalent diameter</b>	

Table 5. Dissolution in 6M hydrochloric acid with mixing

<b>Deq<sup>a</sup> (mm)</b>	<b>Uncertainty</b>
2.04	0.026
1.90	0.028
1.71	0.032
1.56	0.035
<b>a - equivalent diameter</b>	