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हाइड्रोजन उत्पादन के लिए Cu-Cl ताप रासायनिक चक्र के क्रिस्टलीकरण चरण का अनुकरण करने हेतु ग्राफिकल यूज़र इंटरफेस के साथ एक कोड का विकास

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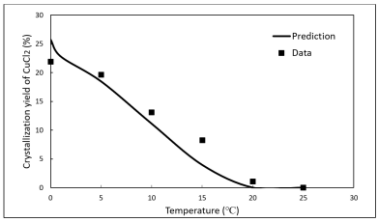

2 M CuCl, 8 M HCl के विद्युत विश्लेषक फ़ीड हेतु अलग-अलग इलेक्ट्रोलाइटिक रूपांतरण के लिए $CuCl_2$ का क्रिस्टलीकरण उत्पाद। क्रिस्टलीकरण तापमान 10° C; ▬ संभावित, ■ प्रयोगात्मक डाटा।

सारांश

परमाणु ऊर्जा स्रोत के साथ ताप-रासायनिक CuCl चक्र ग्रीनहाउस गैसों के उत्सर्जन के बिना H_2 उत्पादन हेतु एक आश्वस्थ प्रक्रम है। क्रिस्टलीकरण भुक्तशेष विद्युत विश्लेषक विलयन से $CuCl_2$ क्रिस्टल को अलग करने के लिए इस चक्र के संचालन में से एक है। उन स्थितियों की सीमित सीमा के कारण जिनके तहत यह क्रिस्टलीकरण होता है, हर भुक्तशेष विलियन से ठंडा होने पर वांछित क्रिस्टल नहीं मिल सकते हैं। $CuCl_2$ क्रिस्टल संवृत्त तरीके से एक निरंतर चक्रीय प्रक्रिया हेतु आवश्यक हैं, इसलिए क्रिस्टलीकरण की सीमा पर भावी प्रचालन के लिए लाभदायक हैं। यहाँ, एक ग्राफिकल यूज़र इंटरफेस (जीयूआई) के साथ एक कोड (पायथन 3 में) विकसित किया गया है विभिन्न पैरामीट्रिक स्थितियों के अंतर्गत क्रिस्टलीकरण प्रक्रिया के विलयन द्रव्यमान संतुलन का उपयोग करते हुए $CuCl_2$ के उत्पादन की संभावना तापमान, HCl सांद्रता, इलेक्ट्रोलाइटिक रूपांतरण, और विद्युत विश्लेषक भरण CuCl सांद्रण जैसी उत्पादन की संभावना व्यक्त की गई है। इस उद्देश्य के लिए कोड में घुलनशीलता सहसंबंध अंतर्निहित हैं। जीयूआई प्रदत्त विद्युत विश्लेषक भुक्तशेष विलयन के लिए वांछित क्रिस्टलीकरण की सीमा की संभावना व्यक्त करने में उपयोगी है। इस अध्ययन में किया गया कार्य, जिससे क्रिस्टलीकरण उत्पादन की संभावना व्यक्त होती है, बंद-लूप ताप-रसायनिकी Cu-Cl चक्र के प्रचालन में बहुत लाभदायक है।

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Development of a Code with a Graphical User Interface to Simulate the Crystallization Step of the Cu-Cl Thermochemical Cycle for Hydrogen Production

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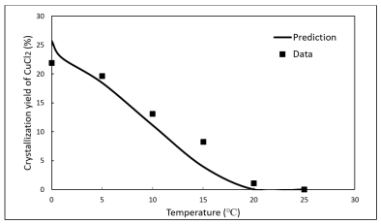

Crystallization yield of $CuCl_2$ for varying temperatures for 70% converted electrolyser feed of 2 M CuCl in 8 M HCl; ▬ Prediction, ■ Experimental data.

ABSTRACT

The thermochemical Cu-Cl cycle coupled with a nuclear energy source is a promising process for H_2 generation without emission of greenhouse gases. Crystallization is one of the operations of this cycle for the separation of $CuCl_2$ crystals from the spent electrolyser solution. Due to the limited range of conditions under which this crystallization occurs, not every spent solution may yield the desired crystals upon cooling. As $CuCl_2$ crystals are necessary for a sustained cyclic process in a closed manner, predictions on the extent of crystallization are beneficial for the operation. Here, a code with a graphical user interface (GUI) has been developed (in Python 3.0) to predict the yield of $CuCl_2$ crystallization under different parametric conditions, viz., temperature, HCl concentration, electrolytic conversion, and electrolyser feed CuCl concentration, using the solute mass balance of the crystallization process. Solubility correlations are embedded in the code for this purpose. The GUI is useful for predicting the extent of desired crystallization for a given electrolyser spent solution. The work carried out in this study, leading to the prediction of crystallization yield, is very much beneficial in the operation of the closed-loop thermochemical Cu-Cl cycle.

KEYWORDS: *Cu-Cl thermochemical cycle, Crystallization, Graphical user interface*

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Introduction

Hydrogen, having a high energy density of 40 kWh/kg, is the fuel of the future because it does not emit greenhouse gases while burning. Conventional methods of hydrogen generation via fossil fuels lead to massive greenhouse gas (GHG) emissions (~11 kg CO_2/kg H_2) [1]. GHG emissions have become a vital issue, in view of the current scenario of global warming and its associated disadvantages to life. Alternatively, H_2 can also be produced through water splitting using electrical/ thermal energy [2].

Thermolysis and Electrolysis of water, based on the single-step decomposition of water, can produce hydrogen. Thermolysis of water, using heat for the decomposition of water, requires a very high temperature (>2000 °C) and is thus found impractical. Electrolysis of water is a promising process, but it uses energy in terms of electricity, which is comparatively expensive.

On the other hand, thermochemical cycles for hydrogen production use heat for the decomposition of water in multiple steps arranged in a closed loop. Thermochemical cycles use a sequence of chemical reactions for splitting water and thus adequately reducing the temperature requirement. Here, low-grade industrial waste heat can be utilised for heating requirements. These cycles can be coupled with a nuclear reactor to obtain heat and electricity [3]. Among these cycles, the Copper-Chlorine (Cu-Cl) cycle has a comparatively lower heat grade requirement (≈ 550 °C) [4-5]. The 4-step thermochemical Cu-Cl cycle is selected here because of its reduced equipment, lower heat requirement, and good energy efficiency [6-7].

In a 4-step Cu-Cl cycle, electrolysis, crystallization, hydrolysis, and thermolysis steps are used to attain closed-loop breaking of water into hydrogen and oxygen (Fig.1). It uses energy both in the form of heat and electricity, and thus makes it a hybrid thermochemical cycle. The electrolysis step takes considerable less energy in the form of electricity, while the rest of the steps take energy in the form of heat only.

In the electrolysis step, the electrolyser produces H_2 gas at the cathode and converts Cu(I) into Cu(II) at the anode (Eq.1). As a result of the oxidation reaction at the anode, CuCl is partially converted to $CuCl_2$, having around 50% to 75% of CuCl oxidation. Because of partial oxidation, the spent electrolyser solution consists of an aqueous solution of $CuCl_2$ (cupric chloride), CuCl (cuprous chloride), and HCl. This spent solution becomes feed to the crystallizer for the separation of $CuCl_2$ from the aqueous solution (Eq.2).

The $CuCl_2$ crystals, obtained from the crystallizer, are sent to hydrolysis reactor and its reaction with the steam produces copper oxychloride (Cu_2OCl_2) along with the HCl (Eq.3). Now in thermolysis reactor, Cu_2OCl_2 is decomposed resulting in molten CuCl along with generation of the oxygen (Eq.4). This molten CuCl is cooled and then dissolved in HCl for preparation of the anolyte solution of the electrolyzer. The HCl for dissolution is obtained from a hydrolysis reaction. Thus, all chemicals are recycled in a closed manner [8] (Fig.1) with net generation of hydrogen and oxygen from the splitting of water using multiple steps.

Electrolysis:	$2CuCl\ (aq) + 2HCl\ (aq) \leftrightarrow 2CuCl_2\ (aq) + H_2\ (g)$	~ 80 °C	(1)
Crystallization:	$2CuCl_2\ (aq) \leftrightarrow 2CuCl_2\ (s)$	~ 10 °C	(2)
Hydrolysis:	$2CuCl_2\ (s) + H_2O\ (g) \leftrightarrow Cu_2OCl_2\ (s) + 2HCl\ (g)$	~ 350 °C	(3)
Thermolysis:	$Cu_2OCl_2\ (s) \leftrightarrow 2CuCl\ (l) + ½\ O_2\ (g)$	~ 500 °C	(4)

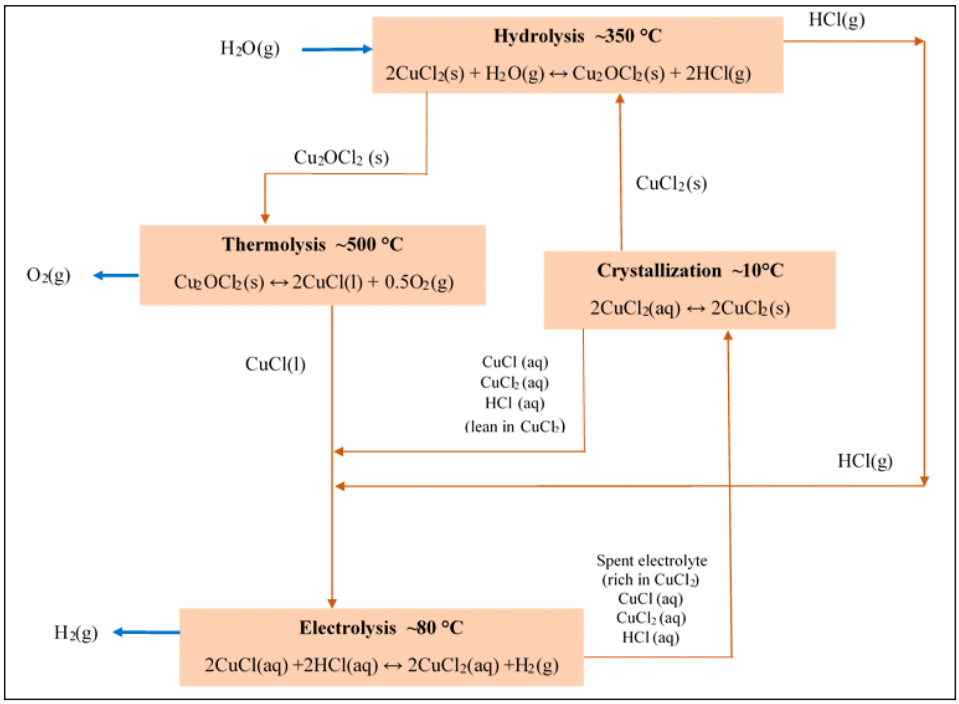

Fig.1: Cu-Cl thermochemical cycle for hydrogen production.

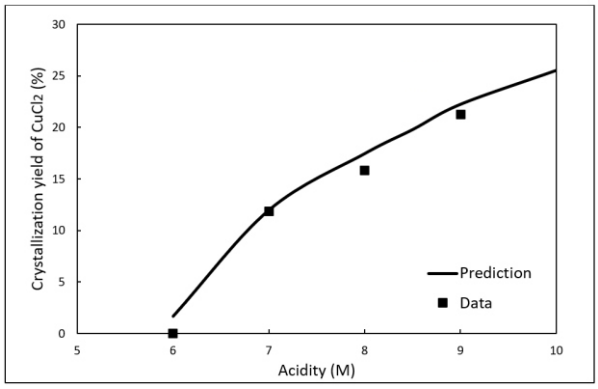

Fig.2: Crystallization yield of $CuCl_2$ for varying HCl concentration in the electrolyser feed for 75% conversion. CuCl concentration in the feed is 2 M and crystallization temperature is 10 °C;
▬ Prediction, ■ Experimental data.

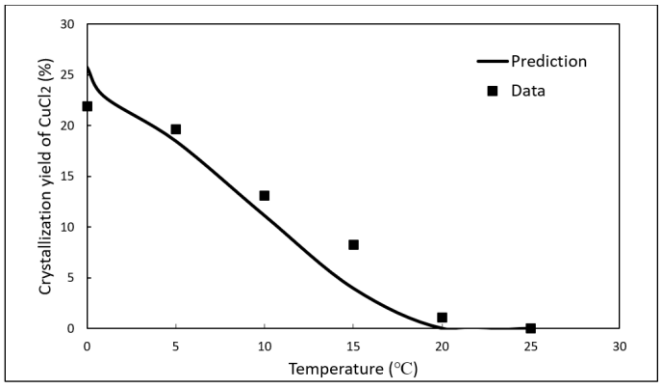

Fig.3: Crystallization yield of $CuCl_2$ for varying temperatures for 70% converted electrolyser feed of 2 M CuCl in 8 M HCl;
▬ Prediction, ■ Experimental data.

The composition of the spent solution from the electrolyser may change due to variation in the electrolyser feed composition and its operating conditions, viz., flow rate and temperature. This spent solution becomes feed for the crystallizer, where a super-saturation state is attained by cooling the feed solution. $CuCl_2$ solubility continuously decreases with increasing HCl concentration [9-10]. On the other hand, CuCl solubility continuously increases with increasing HCl concentration [9]. Thus, there is an intermediate acidity range in which selective crystallization of $CuCl_2$ is viable. The rate and the yield of crystallization of $CuCl_2$ are also affected by HCl concentration [10].

Due to a particular range of conditions under which crystallization of $CuCl_2$ takes place, every feed solution may not give crystals, irrespective of the crystallization temperature. For sustained operation of the cycle, it is required to have a prior idea of the extent of crystallization for a given feed solution before the physical run. Accordingly, in the present work, a code with a graphical user interface (GUI) is developed for the prediction of crystallization yield for different parametric conditions, viz., temperature, HCl concentration, electrolytic conversion, and electrolyser feed CuCl concentration for the operational range of interest. Values of crystal yield obtained through GUI code, at different parametric conditions, are beneficial for the smooth operation of the CuCl cycle.

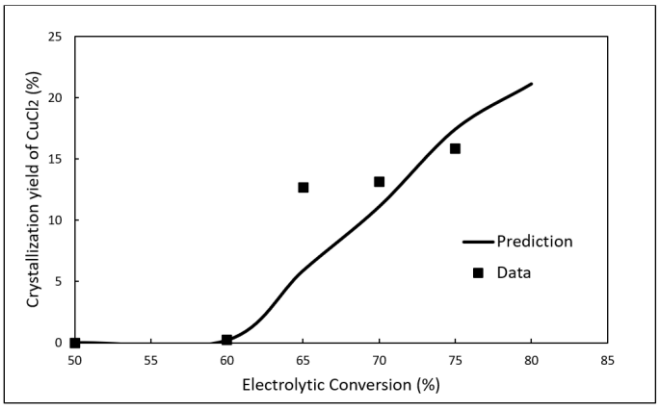

Fig.4: Crystallization yield of $CuCl_2$ for varying electrolytic conversion for electrolyser feed of 2 M CuCl, 8 M HCl. Crystallization temperature 10 °C;
▬ Prediction, ■ Experimental data.

Methods

The developed GUI code (written in Python 3.0 interpreter) predicts the yield of CuCl and $CuCl_2$ crystallization, for varying operational parameters using solute mass balance equations of the crystallization process and solubility data, assuming equilibrium conditions and no evaporation. The operating time of crystallization is optimised (through batch experiments) to around 2 hours, as the major part of $CuCl_2$ is crystallised during this period. Also, this leads to manageable batch time in scaled-up units. However, nearly complete crystallization to achieve equilibrium may take longer than that. This is consistent with that reported [10,11]. Crystallization experiments are conducted at a temperature <=10 °C; at such low temperatures, HCl vapour pressure is also quite low [12], leading to a low possibility of evaporation of HCl. Input parameters of the code are crystallization temperature, feed acidity, electrolytic conversion, electrolyser feed CuCl concentration, feed volume, HCl molarity and its specific gravity. Solubility data of CuCl and $CuCl_2$ are obtained from the literature [9-10], regressed with the *LAB Fit Curve Fitting Software* [13], and correlations for solubility (of CuCl and $CuCl_2$) are obtained with HCl concentration and temperature as the independent variables. These solubility correlations are incorporated in the code to estimate the solubility of CuCl and $CuCl_2$ for a given temperature and HCl concentration. The GUI displays solubilities along with the yields for given user inputs. Validation of the code is done with the generated experimental data. Details of experiments and generated data are presented in the earlier work [14].

Results and Discussion

Comparison of predicted yields of crystallization with observed yields for different parameters is presented in Fig.2, 3, and 4. These figures show the variation of predicted and observed yields with HCl concentration, temperature, and electrolytic conversion, respectively. Observed yields are found from batch crystallization experiments using a synthetic electrolyser spent solution of varying composition. The batch time for experiments was 2 hours. The average deviation between the yields predicted by the developed code (y_{Pred}) and

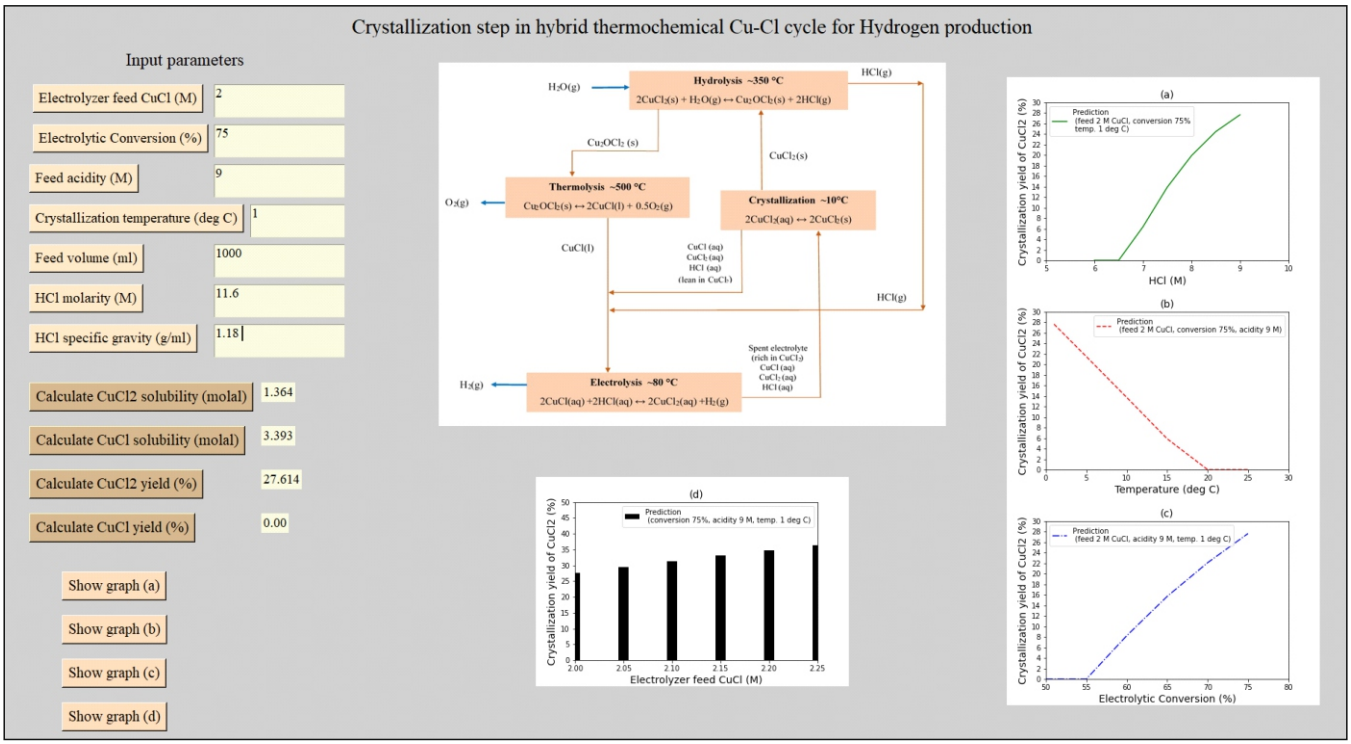

Fig.5: Screenshot of the developed graphical user interface (GUI) of the code for predicting the yield of crystallization of $CuCl_2$ in the thermochemical Cu-Cl cycle.

experimentally measured yields from generated data (y_{Expt}) is around 17%. The deviation between the model prediction and the data is calculated as,

$$\text{Deviation}(\%) = \frac{100}{p}\sum_{m=1}^{p}\left(\frac{\left|y_{Expt,m} - y_{Pred,m}\right|}{y_{Expt,m}}\right) \qquad (5)$$

Where *p* stands for the number of data points, and y represents data values of yield.

Yield is evaluated by Eq.6,

$$\text{Yield} = 100\,\text{x}\,\frac{\text{Crystals of } CuCl_2\,(\text{mole})}{CuCl_2 \text{ in simulated solution}\,(\text{mole})} \qquad (6)$$

Effect of HCl concentration

HCl acts as a crystallising agent for the system. Crystallization of $CuCl_2$ is facilitated by the presence of HCl. Data is generated with an increase in feed HCl concentration at electrolytic conversion of 75% & a crystallization temperature of 10 °C. Fig.2 shows the comparison of the predicted yield of $CuCl_2$ crystals with the experimental yield for varying HCl concentration. Yield is observed to be increasing with an increase in HCl concentration. This goes in accordance with the solubility of $CuCl_2$, which decreases with an increase in HCl concentration [10]. The presence of CuCl in the spent solution may bring further reduction in the solubility of $CuCl_2$ because of the common ion effect. Yield as high as ~ 22% is predicted at the typical maximum acidity expected (9 M), which compares well with the experimentally measured yield of ~ 21%. It may also be noted that at 6 M HCl, no crystal formation is observed for the given conversion and temperature.

Effect of crystallization temperature

Crystallization is favoured by lower temperatures as solubility decreases with the decrease in temperature. Data is generated for a temperature range of 0 °C to 25 °C, and observations are shown in Fig.3 along with the predicted values of crystallization yield. Yield is found to be increasing with the decrease in the crystallization temperature, because of the decrease in solubility with decreasing temperature. It may be noted from Fig.3 that, at 25 °C, yield is predicted to be zero for a given solution composition, which agrees well with the experimental data. Fig.3 also shows that a yield as high as > 25% is predicted at 0 °C for 70% electrolytic conversion. For the feed solution of 50% converted electrolyser feed of 2 M CuCl in 8 M HCl, at 0 °C, the code predicts crystallization yield as zero, which is found close to the experimentally measured yield of around 0.03%.

Effect of electrolytic conversion

Data were obtained using synthetic spent solutions of electrolyser of different electrolytic conversions as feed, to observe the effect of electrolytic conversion on the crystallization of $CuCl_2$. HCl concentration is taken as 8 M, and crystallization temperature is kept fixed at 10 °C. Results are presented in Fig.4 along with the predicted values of yield for the same conditions. It has been observed that both predicted and observed yield values are increasing with the increase in the conversion. This is because increasing conversion leads to increased $CuCl_2$ concentration in the crystallizer feed and, consequently, increased driving force for crystallization. Also, with an increase in the concentration, the metastable zone width (MSZW) of crystallization decreases [15], which leads to

increased nucleation. For lower conversions, such as 50% and 60%, the predicted yield is zero, which matches the zero yield found in experiments at these conversions. For the feed solution of 80% converted electrolyser feed of 2 M CuCl in 8 M HCl, at 1 ^{0}C, the predicted yield is found as 25.21%, which appears in line with the experimental data.

Fig.5 shows the screenshot of the graphical user interface (GUI) developed for the prediction of crystallization yields. The upper left frame of the GUI has tabs for providing user *input parameters*. The middle left frame contains the tabs for calculating *solubilities and yields*. After the input parameters have been specified by the user, the GUI code runs in the background and provides the crystallization yield values of CuCl and $CuCl_2$, on pressing the respective tab. The code also provides the solubilities estimated through inbuilt correlations at a given temperature and acidity. The lower left frame contains the tabs *show graph*, pressing which displays the results in a graphical form, both on the right side and the middle side of the GUI. The $CuCl_2$ yield values, from the crystallization step, obtained from the solution of the model equations for the typical operational range of acidity, temperature, electrolytic conversion, and electrolyser feed CuCl concentration, are shown graphically in the developed GUI.

Conclusion

The thermochemical Cu-Cl cycle is a promising process for hydrogen generation. Crystallization is one of the four steps of this closed-loop cycle. As not every crystalliser feed solution yields desired crystals on cooling, it is required to assess the extent of crystallization of $CuCl_2$ crystals from a given spent electrolyte solution, for efficient looping of the cycle. The composition of the spent electrolyte solution may change due to variation in the electrolyser feed composition and its operating conditions. In this work, a code with a GUI has been developed to predict the yield of crystallization. The GUI provides the tabs for input parameters to be supplied by the user. The model equations are solved in the background, and the yield of crystallization of CuCl and $CuCl_2$ for varying compositions of the spent solution is predicted and displayed. The code is capable of predicting the yield of crystals for a given temperature, HCl concentration, electrolytic conversion, and feed concentration in the operational range of interest. Predicted values of crystal yield are displayed graphically at different parametric conditions for the range of operation. Validation of the code is done with the generated experimental data. The work carried out in this study, leading to the prediction of crystallization yield, is important for the design and scale-up of the crystallization step as well as development of simulator for the thermochemical Cu-Cl cycle for hydrogen production.

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