

Review of the Thermal Hydraulics of Multi-Phase Oxygen Production Reactor in the Cu-Cl Cycle of Hydrogen Production

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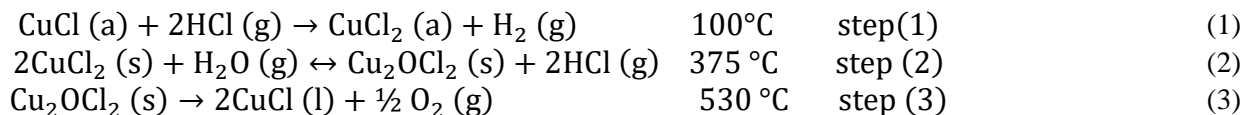
Abstract - The thermochemical water splitting process via the Cu-Cl cycle generates oxygen gas through a thermolysis reaction involving molten salt, a solid reactant, and gaseous oxygen. This paper aims to contribute to the advancement of the thermochemical Cu-Cl cycle for the production of hydrogen. A review of the multiphase oxygen generation reactor is conducted for this aim. The review discusses the kind and description of oxygen reactor, its material features, and the variables affecting the reactor's size. Additionally, the scale-up evaluations of the oxygen reactor from the material and thermal balance viewpoints are extensively discussed.

Keywords: Hydrogen Production; Cu-Cl Cycle; Thermolysis; Oxygen Production; Scale up.

1. Introduction

Hydrogen is commonly cited as a key answer to the environmental issue of greenhouse gases caused by the world's reliance on fossil fuels. Hydrogen is generally thought to be a substantial contributor to future sustainable energy supply [1], since its usage would decrease atmospheric pollution, which contributes to climate change, by lowering greenhouse gas emissions. Numerous businesses need large amounts of hydrogen. Thus, global hydrogen consumption is likely to rise during the next decade. The great majority of hydrogen produced on a global scale is produced by methods such as steam-methane reforming or partial oxidation of heavy hydrocarbons, both of which generate significant quantities of carbon dioxide. These, however, face substantial obstacles due to growing greenhouse gas emissions, depleting gas sources, and escalating carbon capture and storage costs. Despite the exponential growth in demand for hydrogen, the hydrogen economy's primary issue is sustainable hydrogen generation (without reliance on fossil fuels) in large scale at lower costs than present technologies. Nuclear energy has the potential to be a source of large-scale, sustainable hydrogen generation.

Thermochemical cycles are intriguing alternatives that might be used in conjunction with nuclear reactors to thermally breakdown water into oxygen and hydrogen through a sequence of intermediate processes. Through heat exchangers that provide or recover heat from particular processes, these cycles transmit heat between different endothermic and exothermic reactors. Argonne National Laboratories (ANL) has identified the copper-chlorine (Cu-Cl) cycle as one of the most promising low temperature cycles [2, 3]. This cycle consists of three reactions, two of which are thermal in nature and one of which is electrochemical in nature. One of the most significant benefits of the cycle is that it requires less temperature than many other cycles. Additionally, the cycle may be performed in such a way that it requires little high-quality energy and solids exchanges. The Cu-Cl cycle consists of three chemical steps:



where a , s , l and g denote to aqueous, solid, liquid and gas respectively.

The Cu-Cl cycle's oxygen generation stage (step 3) involves the decomposition of an intermediate chemical, solid copper oxychloride (Cu_2OCl_2), into oxygen gas and molten cuprous chloride (CuCl). The oxygen generation reactor receives the solid input of anhydrous solid Cu_2OCl_2 from the CuCl_2 hydrolysis process (step 2), which works at a temperature range of 350–450°C. The oxygen reactor's gaseous output includes oxygen gas (which is generated at temperatures ranging from 450 to 530°C) and perhaps contaminants from side reactions such as CuCl vapor, chlorine gas, HCl gas (in trace amounts), and H_2O vapour (trace amount). The substances exiting the reactor are molten CuCl , perhaps solid CuCl_2 from the upstream

hydrolysis process, owing to the incomplete breakdown of CuCl_2 below 750°C [4], and reactant particles entrained in the flow of molten CuCl .

2. Oxygen Reactor Type

Three phases comprise the oxygen reactor: the solid phase (copper oxychloride particles), the liquid phase (molten salt), and the leaving gaseous phase (oxygen). In chemical, petroleum, and biological processes, multiphase reactions such as gas/liquid/solid are often employed. The industry offers various different kinds of multiphase reactors, which may be grouped into two broad categories: fixed bed reactors and slurry phase reactors. Fixed bed or packed bed reactors have a stationary solid phase. Because the oxygen reactor's solid phase is continuous, it cannot be termed a fixed bed reactor [5]. Stirred tank reactors (STR) and slurry bubble column reactors are the most common continuous slurry phase reactors (SBCRs). The continuous stirred tank reactor (CSTR), which is often used for liquid-phase or multiphase processes with moderate reaction rates, is a mechanically agitated reactor in which small particles are suspended in the liquid phase by agitation. Continuous reaction streams are supplied into the vessel, while product streams are removed. In general, a continuous flow stirred tank reactor (CFSTR) implies that the fluid is properly mixed, ensuring that the reaction mixture's parameters (e.g., concentration, density, and temperature) remain uniform throughout the system. As a result, the conditions throughout the reactor are same, and the temperature at the reactor output is identical. The solid phase in the SBCR is composed of small particles suspended in the liquid phase as a result of gaseous bubbles supplied from the bottom, often through a sparger [5-6].

Oxygen reactors may be classified as CFSTRs or SBCRs. The decision between these two kinds of reactors is determined by the heat transfer rate efficiency, the agitation efficiency, the ability to scale up, and other design requirements. The oxygen reactor's thermal design demands adequate agitation inside the reactor and a sufficiently high rate of heat transfer to the solid particles. Agitation may be accomplished mechanically, as in the CFSTR, or by gaseous bubbles, as in the SBCR. Although the rate of agitation is faster with a mechanical agitator than with bubbles, an agitator is undesirable in a highly corrosive medium such as an oxygen reactor due to the numerous internals required, such as the propeller, shaft, baffles, and other accessories that support the mixing system [5,7].

Heating may be accomplished in two ways: indirectly or directly. The two most often used indirect procedures are to surround the vessel with a jacket or to use an inside coil. Direct heating may be accomplished by the use of gaseous bubbles and is more efficient than indirect heating, but is more complicated to scale up. The oxygen gas that exits the oxygen reactor at around 530°C may be heated to a higher temperature (such as 600°C) and then re-injected into the oxygen reactor from the bottom through a sparger. Direct contact heat transfer between the hot oxygen gas and the slurry within the oxygen reactor is possible in this instance [5].

According to the comparison above, SBCR is more efficient in heat transmission than CFSTR but more difficult to scale up. However, with SBCR, thermal energy may be delivered to the reactor directly through gas bubbles, which can also be utilized to agitate the reactor's contents.

3. Oxygen Reactor System Description

As with many chemical reactors, the oxygen reactor needs careful regulation of heat transfer to operate at peak efficiency. Cu_2OCl_2 decomposition into oxygen and molten CuCl is an endothermic process in the oxygen reactor, requiring a reaction heat of 129.2 kJ/mol and a temperature of 530°C , the highest temperature in the Cu-Cl cycle. As a result, heat must be provided to increase and maintain the temperature of the reactor's bulk [8]. The total amount of heat needed is the sum of reaction heat and the heat necessary to elevate the reactant temperature from 375°C (the temperature of solid particles formed during the hydrolysis process) to 530°C . The heat transfer coefficient, the difference between the bulk and surrounding temperatures of the heat transfer fluid (i.e. the driving force), and the size of the contact region where the heat transfer occurs all affect the heat transfer. Additionally, the heat transfer coefficient is dependent on the oxygen generation process's operating conditions, the physical qualities of the inventory materials, and the geometry of the equipment. Typically, this coefficient is established by the use of empirical correlations.

The oxygen reaction is a high temperature reaction that requires a source of high temperature heat. This heat may be generated by generation IV nuclear reactor designs such as the sodium-cooled reactor, the Canada Deuterium Uranium (CANDU) supercritical water reactor (CANDU-SCWR), Canada's Generation IV reactor, and the high temperature gas reactor (HTGR). While the first two reactors operate at lower temperatures (510°C – 625°C), they are ideally suited for matching a low temperature Cu-Cl thermochemical cycle. However, coupling low temperature cycles to the HTGR (1000°C) may enable more cogeneration, resulting in much better hydrogen production efficiency. Solar energy is another non-polluting source of high-temperature heat.

In an indirect cycle system, an intermediate heat exchanger (IHX) is utilized to transmit heat from the main fluid in the nuclear reactor core to the secondary fluid, which then delivers the heat to the hydrogen plant's oxygen reactor. Helium, a nitrogen/helium combination, or a molten salt may be used as the secondary fluid. IHX is designed to collect heat from the main fluid at the maximum temperature achievable (the reactor output temperature) for use in the hydrogen generation process. Harvego studied several setups for an intermediate heat exchanger between a hydrogen generation cycle and an NGNP [9]. The flow rates, temperature distribution across the loops, and other IHX needs were also suggested based on the design, and the reactor output temperature was set at 900°C in an earlier research by [10].

4. Material Properties of Oxygen Reactor

Ikeda and Kaye [11], as well as Trevani et al. [12], have investigated the thermochemical characteristics of copper oxychloride. Because copper oxychloride is not commercially accessible, these two investigations discovered strategies for its manufacture. Ikeda and Kaye [11] used stoichiometric quantities of CuO and CuCl₂ in their approach. To prevent the presence of moisture, the procedure was carried out in a glove box filled with argon. Trevani et al. [12] used a more straightforward method. Cu₂OCl₂ was created in their approach using a typical horizontal tube furnace equipped with a quartz tube and stainless-steel gas injection connectors. CuCl or CuCl₂ was placed into an alumina crucible and subjected for 48 hours to a flow of high-quality dry air at 370°C. The X-Ray Diffraction (XRD) analysis indicated that this approach produced very pure Cu₂OCl₂ samples. The approach is more scalable, and it is capable of producing the quantities necessary for large-scale oxygen generation tests. Cu₂OCl₂ is a solid that decomposes in the presence of water, hence it is essential to preserve it under nitrogen or dry air.

Parry reported calorimetric measurements of copper oxychloride's heat capacity in the range of 20-410°C [13]. The Debbiee-Einstein technique was used to extrapolate thermodynamic data to 550°C. Uncertainty developed in the low-temperature range due to the quick change in heat capacity in this area. The slope of the calorimetric specific heat curve drops to less than 5 J/mol.K every 100°C above 400°C. Differences in observed data were attributed to undetected heat leakage. The standard deviation of results acquired using this approach was calculated to be 1.1%.

Abdulrahman [5, 14-15] has derived a linear function of CuCl surface tension with temperature as follows:

$$\sigma_{\text{CuCl}} = 0.115 - 5.312 \times 10^{-5} T \quad (4)$$

The derivation was based on the approximate linear reduction of the surface tension with temperature and the equality of the surface tension to zero at the critical temperature of the liquid. The critical temperature that is used in deriving Eq. (4) is equal to 2435 K [16]. The surface tension of molten CuCl in contact with air is equal to 0.092 N/m at the melting temperature of CuCl (430°C) [17].

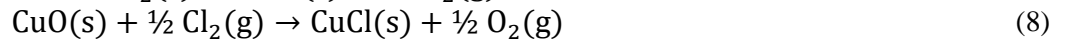
There are various obstacles and challenges in utilizing the real materials from the thermolysis reactor products in the experimental research for the scale up analysis (i.e. molten salt CuCl and oxygen gas). Abdulrahman [5, 14-15] developed alternative materials by simulating the hydrodynamic and heat transport characteristics of actual materials utilizing dimensional analyses of the Buckingham pi theorem. These alternate materials have been identified as liquid water at a temperature of 22°C and helium gas at a temperature of 90°C. Alternative materials offer a safe environment for experimental runs and operate at a lower temperature. Additionally, these materials are readily available and inexpensive. Abdulrahman's material simulation is a unique tool for assessing hydrodynamic and heat transport behaviors in a simulated environment prior to adaptation to the Cu-Cl cycle thermolysis reactor.

5. Oxygen Production Chemical Reaction

Walter-Levy et al. [18] described a mechanistic method to copper oxychloride decomposition. Experiments were carried out to determine the volatility of CuCl and the products of Cu₂OCl₂ decomposition. Copper oxychloride retained its chemical characteristics at temperatures up to 370°C. Cl₂ was released between 375°C and 470°C during the production of CuCl. Cl₂ then reacted with CuO to form oxygen and CuCl, as well as trace quantities of unreacted CuCl₂. Between 475°C and 550°C, XRD analysis demonstrated an increase in the quantity of CuCl₂ in the products, whereas the amount of CuO decreased. The decomposition reaction (called path I) has the following form:



Parallel to the competitive reaction, experimental data suggested that the secondary reaction was responsible for the partial drop in CuO caused by the Cl₂ generated in the former reaction. This collection was named "reaction "path I." Another way to generate oxygen is by the decomposition of a combination of CuO and CuCl₂, as Serban et al. investigated [3]. The studies were conducted in a vertical reactor at 500°C using an equimolar combination of CuO and CuCl₂. The XRD measurement of the solid products revealed a pure CuCl solid phase. The investigation used a mechanistic approach and determined that oxygen evolution is constrained by CuCl₂ decomposition. As specified in the following equations "path II," the reaction proceeded in two steps.



The competing reaction in Eq. (7) is cupric chloride's heterogeneous and endothermic thermolysis. Even while only 60% decomposition of CuCl₂ occurs at 530°C, the addition of CuO seems to enhance decomposition. Additionally, it was found that the Cl₂ produced is completely consumed in the reaction with CuO, as indicated by Eq. (8), since no free Cl₂ was found in the gaseous products. The Gibbs free energy of the reaction suggests that it enters equilibrium around 500°C and then proceeds spontaneously, with increasing amounts of chlorine available to react with CuO as the temperature rises. However, experimental data suggested that CuCl₂ does not completely decompose until it reaches 600°C.

Lewis et al. [19] utilized 40 mg of laboratory-produced Cu₂OCl₂ heated to 530°C for the oxygen generation process in their experiment. Based on the quantity of copper oxychloride used in the experiment, it was found that the observed mass of oxygen was more than the theoretical limit. The presence of chlorine peaks was found to be below background values. Lewis et al. [2, 19] utilized a stoichiometric combination of CuO and CuCl₂ heated to 500°C to achieve an oxygen output of 85%. The X-ray diffraction (XRD) analysis of products revealed the presence of CuCl and negligible levels of CuCl₂. At 500°C, 0.02 mol of an equimolar combination of CuO and dehydrated CuCl₂ was decomposed in a separate experiment. The oxygen production was more than what thermodynamic equilibrium studies expected. The amount of chlorine released was not determined. Continuous oxygen removal was used in the experiments. The XRD investigation of the solid products revealed the presence of CuCl and CuCl₂. The findings indicate that the oxygen released during copper oxychloride decomposition is more than the predicted yield from a combination of CuCl₂ and CuO. The reason chlorine was not found is unclear, however it might have been due to the presence of chlorine gas or a low yield of chlorine below the chlorine analyzer's detection threshold.

Marin [20] established a novel experimental and theoretical basis for scaling up a CuO*CuCl₂ decomposition reactor while considering the effect on the yield of the thermochemical copper-chlorine cycle for hydrogen production. He utilized a Stefan boundary condition in conjunction with a new particle model to monitor the location of the moving solid-liquid interface as the solid particle decomposes due to surface heat transfer. Thermo gravimetric Analysis (TGA) microbalance and laboratory scale batch reactor studies were used to investigate the conversion of CuO*CuCl₂ and

estimate the rate of endothermic reaction. At high temperatures and low Reynolds numbers, a second particle model finds characteristics that affect the transient chemical decomposition of solid particles embedded in a bulk fluid composed of molten and gaseous phases. For a particle suddenly submerged in a viscous continuum, the mass, energy, momentum, and chemical reaction equations were solved. Numerical solutions were generated and evaluated using experimental data on the chemical decomposition of copper oxychloride ($\text{CuO} \cdot \text{CuCl}_2$).

6. Factors Affecting Oxygen Reactor Size

There are many factors that affect oxygen reactor size. These factors include the residence time of the thermal decomposition for solid particles, terminal settling velocity of solid particles, production rate of hydrogen (mass balance), and reactor heating rate (heat balance) [5, 21].

6.1 Terminal Settling Velocity of Particles

The amount of time it takes for solid particles to settle in a reactor with a limited volume is an essential metric to consider while designing the reactor [22]. The rate at which particles descend has a considerable impact on the height of the reactor. It is advised that the particle fall speed be kept as low as possible in order to provide adequate time for the decomposition process to be completed before reaching the bottom of the reactor. It is not necessary to have a high reactor in this situation.

Due to the fact that the density of the solid Cu_2OCl_2 particle is larger than that of molten CuCl , the falling velocity of a single particle under gravity will be greater than that of molten CuCl . The particle will continue to accelerate for a brief period and then descend at a constant velocity, where the effective weight of the particle and the drag force are identical. Thus, the most essential period is the period of constant-velocity descent (terminal settling velocity). The terminal velocity of solid particles is determined by a number of characteristics, including their size, shape (roundness), solid concentration and density, as well as the liquid's viscosity and density [23].

Particle size: In industry, solid particles are often not uniform in size, but rather contain a variation of sizes. It is commonly established that bigger particles settle at a faster rate than smaller ones. Baldi et al. [25] indicated that when dealing with a distribution of particle sizes, it is appropriate to describe the particle diameter as the mass-mean diameter when computing the settling velocity.

Particle shape: In most theoretical computations, the form of solid particles is assumed to be spherical. The size of non-spherical particles may be described in terms of an equivalent volume of a sphere. A spherical particle's falling velocity is greater than that of a non-spherical particle with the same volume and density [23].

Particles concentration: When a cloud of solid particles falls through a quiescent liquid, extra impeding actions have an impact on its falling velocity. These include the increased drag created by the close proximity of the particles inside the cloud and the liquid up flow induced by the falling particles. The impeding effects are highly dependent on the volumetric solid concentration in the cloud. The velocity of a hindered falling object is typically a fraction of the velocity of a free-falling object. For instance, with a solid concentration of 30% and a solid particle diameter range of 0.074-2 mm, the sand's impeded velocity is around 20%-40% of the single particle terminal velocity [25].

It is important to define in the design of the oxygen reactor's size if the settling velocity of the solid particles allows for sufficient residence time for complete decomposition of these particles before they settle to the reactor's bottom. It is widely established that the maximum settling velocity occurs when a single spherical particle falls infinitely deep into a fluid. Other factors such as particle shape, reactor wall, and impeding effects all contribute to the particles' settling velocity being reduced. The up-flow motion of the oxygen bubbles also reduces the fall of particles in the oxygen reactor.

6.2 Mass Production Rate of Hydrogen

In the design of any chemical reactor, it is necessary to study material balances (mass balances) which are based on the fundamental law of mass conservation. It is difficult to construct or run an oxygen reactor (or any other chemical plant) in a safe and cost-effective manner without proper material balances on hand. The general equation of the material balance is [5, 21]:

$$\frac{dm}{dt} = \dot{m}_i - \dot{m}_o + \dot{G} - \dot{C} \quad (9)$$

where: $\frac{dm}{dt}$ is the rate of change of the material m , \dot{m}_i and \dot{m}_o are the inlet and outlet mass flow rates respectively, and \dot{G} and \dot{C} are the rate of generation and consumption respectively. Abdulrahman et al. [5, 21] investigated the flow material balance for continuous processes running in the steady state. To produce hydrogen, they have investigated the flow rates and chemical compositions of all streams entering and exiting each individual piece of equipment in the Cu-Cl cycle. It has been shown that the flow rate of each component of the Cu-Cl cycle (in the event of full conversion of the components) changes linearly with the rate of hydrogen production throughout the cycle.

Using varying residence times and hydrogen production rates, it was possible to compute the optimal size of an oxygen reactor. It was discovered that the size of the oxygen reactor changes linearly with the rate of hydrogen production and the residence time. According to the findings of Abdulrahman et al. [5, 21], the minimal size of the oxygen reactor can be determined based on the mass balance of the Cu-Cl cycle, and the size is strongly influenced by the residence time and hydrogen production rate of the reactor. Also, the size of the oxygen reactor was anticipated to be large because of the presence of copper (Cu), which has the maximum molecular weight of 63.54 g/mol in the Cu-Cl cycle, and hence the largest molecular weight in the Cu-Cl cycle.

7. Method of Heating Oxygen Reactor

A suitable method of heating the oxygen reactor is needed to provide enough heat that is necessary for solid decomposition. Heating the $\text{Cu}_2\text{OCl}_2(\text{s})$ particles only is undesirable, because of relatively slow rate of heat transfer. A more practical and efficient option is to heat the molten salt inside the oxygen reactor to in turn transfer the heat within the reactor from the liquid (molten CuCl) to the solid Cu_2OCl_2 (reactant) particles. The molten salt bath can be sustained by the reaction product itself. This approach is the most applicable and recommended one.

Due to buoyancy of the gas in the molten salt, the oxygen product will leave the reactant particles immediately. This fast separation aids to minimize heat transfer resistance to the reactant particles, which then helps make the overall reaction rate closer to the intrinsic reaction rate. The design of the reactor requires a high efficiency of heat exchange and separation of reactant (solid particles) from products, as well as one product (oxygen) from another (molten salt).

There are two main heating methods for reactor: electrical heating and fluid heating. The main disadvantage of electrical heating is the limited efficiency of electricity generation from nuclear heat (currently less than 35%). A more suitable method is to heat the molten salt by using a heating fluid (such as helium gas or molten salt) without using electricity.

Two main configurations of molten salt heating by a fluid can be used: direct and indirect heating. Direct heating places the heating fluid in direct contact with the heated medium. The advantage of heating directly is that, heating fluid is nearly 100% efficient with this method. This is because all heat that is generated is absorbed directly by the process. This helps to speed heat-up and eliminate thermal lag. There is no intermediate heat transfer medium that could result in heat losses. Direct heating can be applied by using a Slurry Bubble Column Reactor (SBCR), where the heating gas can be introduced to the reactor from the bottom through a sparger.

Indirect reactor heating uses a heat transfer medium to deliver the heat to the reactor vessel. Indirect methods can be external heating of the reactor using the reactor wall (or immersed tubes walls). There are various advantages of indirect heating. The biggest advantage is that the heating fluid can typically be serviced without draining the reactor. Second, indirect heating often allows watt density exposed to the process fluid, which is the number of watts

concentrated per unit surface area of process side, to be lowered by spreading the heat over a larger surface. Finally, overheat conditions can be limited in many instances by simply limiting the temperature of the heat transfer medium, so that the process fluid is never exposed to temperatures higher than the heat transfer fluid temperature.

In spite of the above advantages, the disadvantages of indirect heating may be critical to the oxygen production process. The primary disadvantage is the thermal lag caused by using a heat transfer medium to carry the heat such as the reactor wall. The delay is caused by the fact that the heating fluid must first heat the heat transfer medium before the heat transfer medium can heat the process. If there is a large mass of heat transfer medium, larger heating capacities will be required to raise the temperatures.

Different types of indirect heat transfer surfaces can be used in an industrial oxygen reactor such as jackets, helical tubes immersed directly inside the reactor and vertical tube baffles [26]. A reactor jacket is usually adequate to provide the required heat transfer surface for low and moderate heat duties (in terms of heat duty per unit of vessel volume). As heat duty increases, internal heat transfer surfaces (helical coils, baffle pipes, or plate coils) may be required.

7.1 Indirect Heat Transfer of the Oxygen Reactor

Thermal scaling up of the three-phase oxygen generation reactor in the Cu-Cl cycle was investigated using indirect heat transfer techniques [5, 27-31]. The size of the oxygen reactor necessary to generate sufficient heat input was investigated in these researches for various hydrogen generation rates. The researches employed a continuous stirred tank reactor (CSTR) that was heated by a half pipe jacket [5, 27] or an internal helical tube [5, 28]. The thermal resistance of each part of the reactor system was investigated in order to determine its influence on the reactor's heat balance. The system thermal resistance was found to be dominated by the reactor wall in jacketed reactors [5, 27], and by the helical tube wall and service side in oxygen reactor systems with an internal helical tube [5, 28].

The Cu-Cl cycle was assumed to be powered by a nuclear reactor in the above studies, and two different kinds of nuclear reactors were considered as a heat source for the oxygen reactor. The CANDU Super Critical Water Reactor (CANDU-SCWR) and the High Temperature Gas Reactor (HTGR) were two of these designs. It was established that a larger heat transfer rate is required for CANDU-SCWR by three to four times that of HTGR, due to the HTGR's higher exit temperature, which results in greater temperature differential between the service and process sides than the SCWR.

From a thermal balancing standpoint, the impacts of reactor diameter and aspect ratio on the size of the oxygen reactor were calculated. It was determined that the size of the oxygen reactor reduces nonlinearly when the reactor diameter or aspect ratio increases, with the reactor diameter having a greater influence on the reactor size than the aspect ratio. The pace at which the oxygen reactor's size decreases was discovered to be slowed by increasing the reactor's diameter or aspect ratio.

On the service side, several kinds of working fluids were employed, including helium gas and CuCl molten salt, and their properties were compared. There is no discernible variation in the size of the jacketed oxygen reactor whether helium gas or CuCl molten salt is used [5, 27]. Due to the decrease in the number of oxygen reactors, it was established that utilizing CuCl molten salt in the service side is thermally superior to using helium gas in the oxygen reactor using an internal helical tube for heating [5, 28]. In general, both helium gas and CuCl molten salt have technical concerns, and both should be preserved and investigated until these technical difficulties are answered and an optimum decision can be chosen.

The findings of heat transfer studies conducted on the oxygen reactor with an internal helical tube were compared to the results of material balances and heat transfer analyses conducted on the oxygen reactor with a half pipe jacket. Due to the increased size needed for the heat balance, it was discovered that the size of the oxygen reactor is dictated by the heat balance rather than the material balance. Additionally, it was shown that delivering heat to the oxygen reactor through an internal helical tube is more efficient than utilizing a half pipe jacket.

7.2 Direct Contact Heat Transfer of the Oxygen Reactor:

In the studies of the direct contact heat transfer of the oxygen reactor, both of the experimental and CFD studies were performed [5, 32-40]. In the experimental works [5, 32-35], the actual materials of oxygen reactor such as oxygen gas, molten CuCl, and solid copper oxychloride, were simulated by alternative materials such as helium gas, water, and alumina solid particles. The type of the reactor that was used was a slurry bubble column reactor where helium gas at 90°C injected through a slurry of water at 22°C and alumina solid particles. The parameters that were studied in the experiments were the volumetric

heat transfer coefficient, the slurry temperature, the transition velocity, and the overall gas holdup. The effects of superficial gas velocity, static liquid height, solid particles concentration and solid particle size, on the studied parameters were formulated as empirical equations.

In the Computational Fluid Dynamics (CFD) simulations of direct contact heat transfer in the multiphase oxygen reactor, the effects of superficial gas velocity, static liquid height, and solid particles concentration, on the volumetric heat transfer coefficient, temperature distribution and overall gas holdup were investigated in details [5, 36-40]. The slurry within the slurry bubble column was assumed to be perfectly mixed, and the slurry bubble column was modelled using a 2D planar method. The numerical solutions were obtained using the multiphase Euler-Euler technique, and the turbulence in the bubble column was modelled using the standard $k - \varepsilon$ dispersed turbulence model. The results of both the experimental and CFD works are shown in Table 1.

Table 1: Results of experimental and CFD analyses for direct contact heat transfer.

Volumetric Heat Transfer Coefficient	Average Slurry Temperature	Overall Gas Holdup	Transition Velocity
Increases by increasing the superficial gas velocity with a higher rate of increase at lower superficial gas velocity.		In the industrial SBCRs, the slug flow regime does not exist and there is only one transition velocity, which is between the homogeneous and heterogeneous flow regimes.	
Decreases by increasing the static liquid height.			
Decreases by increasing solid concentration.	The decrease of the slurry temperature with the solid concentration is negligible.	Decreases by increasing solid concentration and at a higher solid concentration, the changing rate of the overall gas holdup with the superficial gas velocity and/or the solid concentration is lower. The effect of the solid particle diameter on overall gas holdup is negligible.	Decreases by increasing solid concentration.
The rate of decrease with the solid concentration are approximately the same for different superficial gas velocities.		The distribution along the cross-section of the column is unequal, where the gas holdup is higher at the centre of the column and lower near the wall region.	
Profiles calculated from CFD models, generally under-predicted the experimental data of Abdulrahman [32-34].			
The CFD models correctly predicted the effects of superficial gas velocity, static liquid height and solid concentration.			
The CFD results were validated for superficial gas velocities up to 0.15 m/s, and aspect ratios up to 4.			

8. Conclusions

Recent improvements in the multiphase oxygen reactor for the copper-chlorine thermochemical cycle were presented and assessed in this review paper. The paper identified previous experimental and theoretical findings acquired from research groups working on the development of scaled-up oxygen reactor facilities. The oxygen reactor's type and description were discussed in details and it is concluded that using SBCR is the best option for the oxygen reactor. Oxygen production chemical reaction was described in details and it was found that the reaction is an endothermic reaction with a reaction heat of 129.2 kJ/mol and a temperature of 530°C which is the highest temperature in the Cu-Cl cycle. The source of heat can be from nuclear reactors or solar energy sources. Also, the material properties of the oxygen reactor contents were extensively explained. Moreover, the factors that affect the size of the oxygen reactor were discussed. The factors include the residence time of the thermal decomposition for solid particles, terminal settling velocity of solid particles, production rate of hydrogen, and reactor heating rate. The techniques of heat transfer required by the oxygen reactor, such as indirect and direct contact heat transfer, were also analysed in this paper. It was concluded that using direct contact heat transfer is preferred to indirect heat transfer methods.

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