

# Calcium Oxide / Steam Chemical Heat Pump for Upgrading Waste Heat in Thermochemical Hydrogen Production

A. Odukoya <sup>1\*</sup> and G. F. Naterer <sup>2</sup>

<sup>1,2</sup> Memorial University of Newfoundland, St. John's, Newfoundland, Canada

## Abstract

This paper presents a numerical study of a chemical heat pump (CHP) for upgrading waste heat from a cement plant for thermochemical hydrogen production. A calcium oxide/steam CHP is investigated as a potential system to upgrade waste heat from industrial processes for thermochemical hydrogen production. The heat produced by the CHP drives the decomposition of copper oxychloride ( $\text{CuO}\cdot\text{CuCl}_2$ ) in a copper-chlorine (Cu-Cl) thermochemical cycle. A transient analysis of the temperature distribution in each sub process in the combined CHP/Cu-Cl cycle is presented in this study. The numerical results of hydration temperature distribution are compared with experimental results to validate the predictive model. A maximum hydrogen production of  $12.28\text{mol/kg Ca(OH)}_2$  can be achieved from the combined system analyzed in this study. The effect of heating load and oxygen decomposition supply temperature is reported for the hydration, dehydration, condenser and evaporator heat transfer processes.

## Nomenclature

- A cross sectional area ( $\text{m}^2$ )
- C concentration (mol)

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<sup>1\*</sup>Corresponding Author: Research Project Engineer, Faculty of Engineering and Applied Science, Memorial University, St. John's, Newfoundland, 240 Prince Phillip Drive, St. John's, NL Canada A1B 3X5, Email: [aodukoya@mun.ca](mailto:aodukoya@mun.ca), Phone: 1-709-864-2395, Fax: (709) 864-8975

<sup>2</sup> Dean and Professor, Faculty of Engineering and Applied Science, Memorial University, St. John's, Newfoundland, 240 Prince Phillip Drive, St. John's, NL Canada A1B 3X5

$\dot{C}$	molar flow rate (mol/s)
$C_p$	specific heat capacity (J/mol K)
$C_{p,r}$	specific heat capacity reactor (J/mol K)
$H$	enthalpy (kJ)
$I$	current (Amps)
$K$	rate of reaction
$m_r$	mass of reactor (kg)
$\dot{N}_{H_2}$	molar flow rate hydrogen (kJ/mol)
$Q_{cell}$	heat transfer from electrolytic cell (kJ)
$Q_{cond}$	heat transfer from condenser (kJ)
$Q_f$	energy available from flue gas (kJ/mol)
$Q_{H_2O}$	heat transfer to steam (kJ)
$R_u$	universal gas constant (kJ/mol.K)
$R$	electrical resistance ( $\Omega$ )
$T$	temperature (K)
$t$	time (s)
$U$	overall heat transfer coefficient (W/m <sup>2</sup> K)

## Subscripts

*a* reactor 1

*b* reactor 2

*c* condenser

*d* decomposition

*e* evaporator

*f* flue gas

*fgH<sub>2</sub>O* latent heat of vaporisation water (kJ/mol)

*h* hydration

*H* reactor 1

*l* reactor 2

*p* particle

*r* reactor

## 1. Introduction

Chemical heat pumps (CHP) represent a viable method for upgrading waste heat from industrial processes. The typical operating temperature for thermochemical splitting of hydrogen ranges between 500 and 800°C. Using a CHP to upgrade the waste heat from energy intensive industrial processes such as cement and steel plants can be effectively utilized for thermochemical hydrogen production. Combining the hydrogen production system with industrial processes could

potentially reduce the carbon footprint of the industrial process. This study specifically investigates the upgrading waste heat from a cement plant using a Calcium oxide/ steam (CaO/H<sub>2</sub>O) CHP for thermochemical production of hydrogen.

Several studies have investigated the commercial viability of the copper-chlorine (Cu-Cl) cycle [1]. An efficiency of about 45% has been reported when combined with Generation IV nuclear power plants [1]. Steam methane reforming is the most common commercial method of producing hydrogen, while high temperature steam electrolysis is another alternative. Hydrogen is required as a feedstock in many applications such as the oil sands industry, pharmaceutical, biochemical and food industries. The use of hydrogen as a fuel can significantly reduce the greenhouse gas emissions of industrial processes. This paper investigates the viability of using hydrogen as a fuel in a cement plant to reduce the overall greenhouse gas emissions from the plant and increase the overall efficiency of its operation.

Electrolysis is a commercial technology to produce hydrogen. When the overall efficiency of a system including the generation of electricity is considered, this efficiency typically becomes 18 to 24% [2]. Thermochemical splitting of water is an emerging technology and promising alternative to electrolysis of water. Two of the thermochemical cycles are the sulphur-iodine (S-I) and copper-chlorine (Cu-Cl) cycles. The Cu-Cl cycle (up to 550°C) requires lower temperature heat input to produce hydrogen than the S-I cycle (up to 825-900°C) [3,4]. Naterer et al. [1] have demonstrated a large-scale Cu-Cl cycle at the University of Ontario Institute of Technology (UOIT). Brown et al. [4] have studied the S-I cycle.

This paper combines the thermochemical cycle presented by Naterer et al. [1] to a CaO/H<sub>2</sub>O CHP by using the flue gas of the cement plant as heat input to the CHP. The precalciner

(340°C) and the kiln (1067°C) of a cement plant produce high temperature flue gas. This paper investigates a CaO/H<sub>2</sub>O CHP to upgrade the flue gas from the cement plant to provide the heat required by a Cu-Cl plant for the decomposition of copper oxychloride (CuO.CuCl<sub>2</sub>) when the flue gas temperature is 340°C. This flue gas is typically not recycled in the plant and it is sent directly through the stack. The heat pump is used to upgrade the flue gas from the cement plant to a temperature required in the oxygen decomposition reactor. The higher temperature (1067°C) available from the kiln is normally recirculated within the cement plant to improve the efficiency of the cement plant. Fig. 1 shows a schematic of the proposed system when combined with the oxygen reactor in the Cu-Cl cycle.

Several working pairs for CHPs were investigated by Wongsuwan et al. [5], who outlined the preferred combination for the appropriate working conditions. Oguru and Mujumdar [6] proposed a CHP which produces hot dry air for an industrial drying process based on CaO hydration and dehydration of CaCO<sub>3</sub>. The system had a COP of about 1.52 with an output temperature of about 550°C. Fujimoto [7] extended the work of Oguru et al. [8,9] experimentally and numerically for a smaller system with an output temperature of about 400°C.

Naterer [10] also investigated the second law viability of upgrading waste heat for thermochemical hydrogen production using a magnesium oxide/vapor CHP. The results showed that the COP increased with a higher evaporator temperature. The Carnot cycle for both cooling and heating were also reported and compared analytically. Sharonov and Aristov [11] compared the thermodynamic performance of CHPs and adsorption heat pumps for non-regenerative cycles. The results indicated that nearly the Carnot efficiency can be obtained for mono-variant equilibrium gas-solid reactions but cannot be applied to di-variant equilibrium systems. Kato et al. [12-14] also investigated a high temperature heat pump using a combination of CaO/CO<sub>2</sub> and

PbO/CO<sub>2</sub>. A temperature of about 860°C was achieved experimentally and optimal kinetics of the reactions was presented. The possibility of lead poisoning makes the system less attractive for commercialization.

The CaO/H<sub>2</sub>O CHP is well suited for thermochemical production of hydrogen since Ca(OH)<sub>2</sub> can be produced from limestone used to produce cement. This will reduce the possibility of contamination within the cement plant and also enhance possible integration. This paper numerically investigates a combined system using a transient energy balance of the heat flow streams and chemical mass transfer reactions. A pinch analysis is used to determine the molar flow rate of hydrogen produced from the combined system. The effect of heating load from the cement plant and temperature required by the oxygen decomposition reactor are analyzed for the hydration, dehydration, condensation, and evaporation processes.

## 2. System Description

Various cycle configurations have been proposed for thermochemical hydrogen production using the Cu- Cl cycle. These ranges from three to five major chemical reactions [1,15]. The four-step cycle has been chosen as the preferred cycle because it avoids the problem associated with transporting solid copper particles. The chemical reactions for the four-step cycle are outlined in Table 1. The cycle configuration for the four-step process is shown in Fig. 2.

The CHP is used to provide the heat required by the oxygen decomposition reactor as shown in Fig. 3. The heat upgrading of the flue gas from the cement plant is achieved by the hydration of CaO. The exothermic reaction of CaO and water vapor results in a high temperature Ca(OH)<sub>2</sub>. The extent of the reaction depends on the reaction coefficient, which is determined by the temperature and pressure of the reaction. The hydration reaction is given as follows:



The upgraded heat is passed through a heat exchanger to the oxygen decomposition reactor in the hydrogen production cycle. The cooled  $Ca(OH)_2$  is then fed into the dehydration/decomposition reactor, where  $CaO$  and  $H_2O$  are formed in the reverse reaction (from right to left) at a different temperature but at the same pressure. This reaction is endothermic and achieved by supplying the hot flue gas from the cement plant to form the desired products ( $CaO$  and vapor). The experimental setup by Fujimoto [7] used tubular reactors to achieve the reaction and heating load supplied by electric heaters. This paper equates the flue gas from the cement plant to an equivalent electrical load. The vapor is throttled to the condenser pressure, where it is cooled to the saturation temperature by the pressurized liquid flowing into the hydration reactor. The liquid water is collected and pumped to the pressure of the hydration reactor. The circulation of steam in the reactors can be achieved in batches or operated continuously. This analysis assumes that two reactors are used for continuous operation of the plant. The steam/liquid flows are cycled between both reactors. The high pressure liquid is then passed into a heat exchanger where steam from the decomposition reactor is used to produce steam at the required temperature for the hydration reaction.

The following section establishes the transient energy balance of the combined  $CaO$ /steam CHP and oxygen decomposition reactor of the Cu-Cl cycle. The temperature distribution and rate of hydrogen production is determined for each of the condenser, hydration, dehydration, and evaporator for the CHP.

### 3. Analysis of Chemical Heat Pump

A parametric analysis of the combined system is performed to determine the applicability of the CHP for the thermochemical production of hydrogen using the Cu-Cl cycle. The study is simulated based on the type III reactor developed by Matsuda et al.[16]. The CHP consist of two reactor chambers with 345mm x 490mm (Reactor a, 30kg) and 345mm x 300mm (Reactor b, 15kg) made of stainless steel. One reactor is used for the hydration /dehydration reaction and the other for the condensation/evaporating the steam/water. The heat used in the dehydration chamber is analogous to the heat required from the cement plant for hydrogen production is supplied by cylindrical electric heaters. An energy analysis of each component and the interaction between different modules are considered in modeling the temperature distribution. The system is designed to produce  $\text{Ca}(\text{OH})_2$  between 550°C and 600°C. The molar flow rates and inlet temperature of the reactants in the hydrolysis reactor ( $\text{CaO}$  and vapor) were determined analytically. The Gibbs relation is used to determine the chemical exergy of the reaction in Eq. (1).

The change in enthalpy of the reaction in Eq. (1) is used to determine the inlet temperature of  $\text{CaO}$  and  $\text{H}_2\text{O}_{(\text{g})}$ . Earlier studies by Ogura [9] reported an optimal pressure for the reaction in Eq. (1) based on the required exit temperature. The rate of the reactions was determined experimentally by Fujimoto et al. [7]. The rate of the reactions for the hydration and decomposition can be expressed as:

$$K_a = 5 \cdot \exp\left(\frac{18.305 - 3816.443}{T - 46.13}\right) \quad (2)$$

$$K_b = \frac{875 \times \exp(-4.81 \times 10^4 / RT)}{1 + 51.1 \times \exp(-1.1096 \times 10^4 / RT)} \quad (3)$$

An energy balance around the dehydration reactor is expressed as:

$$\left( C_{Ca(OH)_2} C_{p(Ca(OH)_2)} + m_r C_{p,r} \right) \frac{dT_d}{dt} = Q_{Ca(OH)_2}^{out} + Q_f^{in} + Q_r - Q_f^{out} - Q_{H_2O} \quad (4)$$

where  $C$  in the molar concentration,  $C_p$  is the specific heat capacity,  $m_r$  is the mass of the reactor, and  $Q$  is the energy content of each flow stream in and out the reactor. The energy content of each stream in the dehydration reaction is defined as:

$$\left\{ \begin{array}{l} Q_{Ca(OH)_2}^{out} = U_a A_a (T_h - T_p); Q_f^{in} = I^2 R t \\ Q_r = k_a C_{Ca(OH)_2} H_r; Q_f^{out} = U_b A_b (T_p - T_a) \\ Q_{H_2O} = \dot{C}_{H_2O} H_{H_2O} \end{array} \right\} \quad (5)$$

The reaction proceeds when the temperature reaches the equilibrium temperature, which allows the reaction to proceed to the right of Eq. (1). After complete dehydration of  $Ca(OH)_2$ , the equilibrium constant approaches zero ( $k_a \approx 0$ ). The control valves are opened and the steam flows into the reactor b, where condensation occurs. The energy balance for the condensation process is expressed as:

$$\left( C_{H_2O} C_{p(H_2O)} + m_r C_{p,r} \right) \frac{dT_c}{dt} = k_a C_{H_2O} H_{H_2O} + k_a C_{H_2O} H_{fg,H_2O} - Q_{loss} \quad (6)$$

The steam is throttled to the evaporator pressure, where it is used to generate steam for the hydration reaction. The energy balance around the evaporator is expressed as:

$$\left( C_{H_2O} C_{p(H_2O)} + m_r C_{p,r} \right) \frac{dT_e}{dt} = Q_{cond} + \dot{C}_{H_2O} H_{fg,H_2O} - \dot{C}_{H_2O} H_{H_2O} \quad (7)$$

where  $Q_{cond}$  is the heat from the dehydration reaction transferred to the condenser. The heat for the evaporation reaction is supplied by the decomposition reaction, for continuous operation of the

CHP. The high temperature steam is used for the hydration reaction. The energy balance around the hydration reactor is expressed as:

$$\left( C_{CaO} C_{p(CaO)} + m_r C_{p,r} \right) \frac{dT_h}{dt} = Q_{CaO} + Q_{H_2O} + Q_r - Q_{Ca(OH)_2}^{in} \quad (8)$$

where the heat flows of the hydration reaction are expressed as:

$$\left\{ \begin{array}{l} Q_{Ca(OH)_2}^{in} = U_a A_a (T_h - T_p) \\ Q_r = k_b C_{CaO} H_r; Q_{CaO} = \dot{C}_{CaO} H_{CaO} \\ Q_{H_2O} = \dot{C}_{H_2O} H_{H_2O} \end{array} \right\} \quad (9)$$

A pinch point analysis is used to determine the exit temperature of Ca(OH)<sub>2</sub> from the oxygen decomposition reactor. The chemical decomposition from the CuO.CuCl<sub>2</sub> reactor is expressed as:



The heat required for the reaction to proceed was determined by Lewis [2] as 285kJ/molH<sub>2</sub>. The energy balance for the oxygen decomposition reactor is expressed as:

$$\dot{N}_{H_2} \cdot \Delta H_{CuO.CuCl_2} = \dot{N}_{Ca(OH)_2} \cdot (H_{Ca(OH)_2}^{in} - H_{Ca(OH)_2}^{out}) \quad (11)$$

where  $\dot{N}_{H_2}$  is the molar flow rate of hydrogen. The CuCl<sub>2</sub> and oxygen (O<sub>2</sub>) exit the oxygen decomposition reactor at about 450°C. Assuming a pinch point of 10°C, the molar flow rate of Ca(OH)<sub>2</sub> can be determined for the required temperature for the reactor operation. The oxygen from the reactor is used to preheat the steam in the Cu-Cl cycle. The cooled Ca(OH)<sub>2</sub> is sent into

the dehydration reactor. The transient temperature distribution in each process and its effect on hydrogen production is discussed in the following section.

#### 4. Results and Discussion

A Newton-Rapson algorithm is used to solve the differential equations for temperature distribution in the hydration, dehydration, condenser and evaporator respectively. The result from each process is fed into the execution of the next iteration. The molar flow rate of water, the resistance of the electric heater and the exit temperature from the hydration reaction were determined as key factor, which could affect the rate of hydrogen production. In order to validate the model, similar mass of reacting species were used by Fujimoto et al.[7] for CaO (6kg) and H<sub>2</sub>O(3kg) are used in simulating the CHP.

Increasing the heat supplied to the CHP results in an increased rate of reaction in the hydrolysis reactor as observed in Fig. 4. The increase in heat transfer to the hydration reactor also increases the heat loss to the surroundings. The result from Fig. 4 suggests that a resistance of about 0.2Ω is sufficient to allow the reaction to proceed in the desired direction. Although a resistance of 0.5Ω increases the rate of the reaction, the feed rate required to achieve complete decomposition in the oxygen decomposition reactor will determine the optimum heat load requirement supplied to the CHP. In a continuous reactor, the valve will be opened after about 500s and the flow stream supplied to the oxygen decomposition reaction which operates at about 530°C. The maximum temperature difference observed is about 47% between resistance load of 0.2 and 0.5Ω for the range of temperature considered.

The effect of changing the heating load supplied has a similar effect on the rate of hydrogen production as shown in Fig. 5. The maximum amount of hydrogen production from the combined

CHP/Cu-Cl system is about 12.28mol/kg Ca(OH)<sub>2</sub>. As expected, an increased rate of reaction also increases the rate of hydrogen production. These results are dependent on the actual flow rate from the Cu-Cl cycle. The change in resistance from 0.2Ω to 0.5Ω increases the rate of hydrogen production by about 62%.

The dehydration of Ca(OH)<sub>2</sub> is simulated for a fixed heating resistive load of 0.5Ω. The range of temperatures to the oxygen decomposition reactor is based on maximum and minimum temperatures achievable from the hydration reactor. The increased temperature results in an increased exit temperature from the oxygen decomposition reactor. This accounts for the increased rate of reaction for the higher supply temperature as shown in Fig. 6. As the equilibrium temperature of the reaction is reached (670K) a further increase in the rate of the reaction is observed at all supply temperatures considered in this study (Fig. 6). The maximum difference in the rate of reaction between 600°C and 550°C is only about 3.3%, which occurs at about 500s after the start of the heating cycle.

The effect of temperature supplied to the oxygen decomposition reactor on the rate of hydrogen production is illustrated in Fig. 7. The maximum amount of H<sub>2</sub> produced after 500s of the closing the reactor valve is about 4.6mol/kg Ca(OH)<sub>2</sub>. This occurs at the highest temperature considered in this study. The trends observed in Fig.6 and Fig. 7 indicates the range of temperatures will have a similar effect in variation (3.3%) of H<sub>2</sub> production. The initial start which indicates hydrogen is produced at the start of the process is due to the preceding process in the oxygen decomposition reactor where hydrogen has already been produced.

The condensation process takes the longest time of all four processes in the CHP. The increased heating load results slower rate of condensation as shown in Fig. 8. The mass flow rate

of cooling fluid is kept constant during the simulation. These results in the increased temperature required at lower heating load to maintain same quality of steam required to heat the steam in the evaporator. The size of the CHP will determine the optimal heating load required to produce a specific quantity of hydrogen based on the scale of the Cu-Cl cycle. The minimum condensation temperature for continuous hydrogen production is about 574K for the range of heating load considered in this study.

For a fixed mass of  $\text{Ca(OH)}_2$  with no continuous replenishment of the reaction species in the hydration reactor, higher heating loads increase the rate of reaction. This is evident from Fig. 9. Since the condensation reaction takes the longest time of all processes, the combined Cu-Cl-CHP system must be designed based on the cooling rate of the condensation process. A resistance load of  $0.2 \Omega$  takes about double the time to completely consume all the reacting species when compared with a load of  $0.5\Omega$  as shown in Fig. 9. The heat removed from the condenser is used in the evaporator hence a similar trend will be observed when examining the evaporator.

The numerical prediction is validated by comparing the temperature distribution of the hydration process of the CHP with experimental results reported by Fujimoto et al. [7]. The trend of the numerical simulation over predicts the start of the hydration process. This is may be due to the inability to adequately account for heat losses from the reactor chamber and the experimental errors in estimating the rate of the reaction before the equilibrium temperature is attained. The average difference between the predicted and experimental results is about 5.4%. It can be concluded that the results fall within a 90% confidence interval for the range of temperatures considered.

## **6. Conclusions**

The results from this study show the possibility of using the CaO/steam CHP as a heat source for the Cu-Cl thermochemical cycle for hydrogen production. The transient study of temperature distribution in all processes will be used to scale the experiments of a combined Cu-Cl/CHP system. The maximum temperature achievable from the CaO/steam CHP cycle is determined to be about 600°C for a reacting ratio of 2:1 for CaO and steam respectively. The condensation process was determined as the key processes in determining the production flow rate of hydrogen for the combined system. The heating load requirement of the CHP clearly indicates the kiln of the cement is sufficient to generate similar heating requirement for the dehydration reactor.

## **Acknowledgements**

Financial support from the Canada Research Chairs program and the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

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Step	Reaction	Temp. Range (°C)	Feed Output*	
1	$2\text{CuCl}(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow \text{H}_2(\text{g}) + 2\text{CuCl}_2(\text{aq})$	<100 (electrolysis)	Feed: Output:	Aqueous CuCl and HCl + V + Q H <sub>2</sub> + CuCl <sub>2</sub> (aq)
2	$\text{CuCl}_2(\text{aq}) \rightarrow \text{CuCl}_2(\text{s})$	<100	Feed: Output:	Slurry containing HCl and CuCl <sub>2</sub> + Q Granular CuCl <sub>2</sub> + H <sub>2</sub> O/HCl vapours
3	$2\text{CuCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{Cu}_2\text{OCl}_2(\text{s}) + 2\text{HCl}(\text{g})$	400	Feed: Output:	Powder/granular CuCl <sub>2</sub> + H <sub>2</sub> O(g) + Q Powder/granular Cu <sub>2</sub> OCl <sub>2</sub> + 2HCl (g)
4	$\text{Cu}_2\text{OCl}_2(\text{s}) \rightarrow 2\text{CuCl}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$	500	Feed: Output:	Powder/granular Cu <sub>2</sub> OCl <sub>2</sub> (s) + Q Molten CuCl salt + oxygen
* Q = thermal energy, V = electrical energy				

Table 1: Steps and chemical reactions in the Cu-Cl cycle

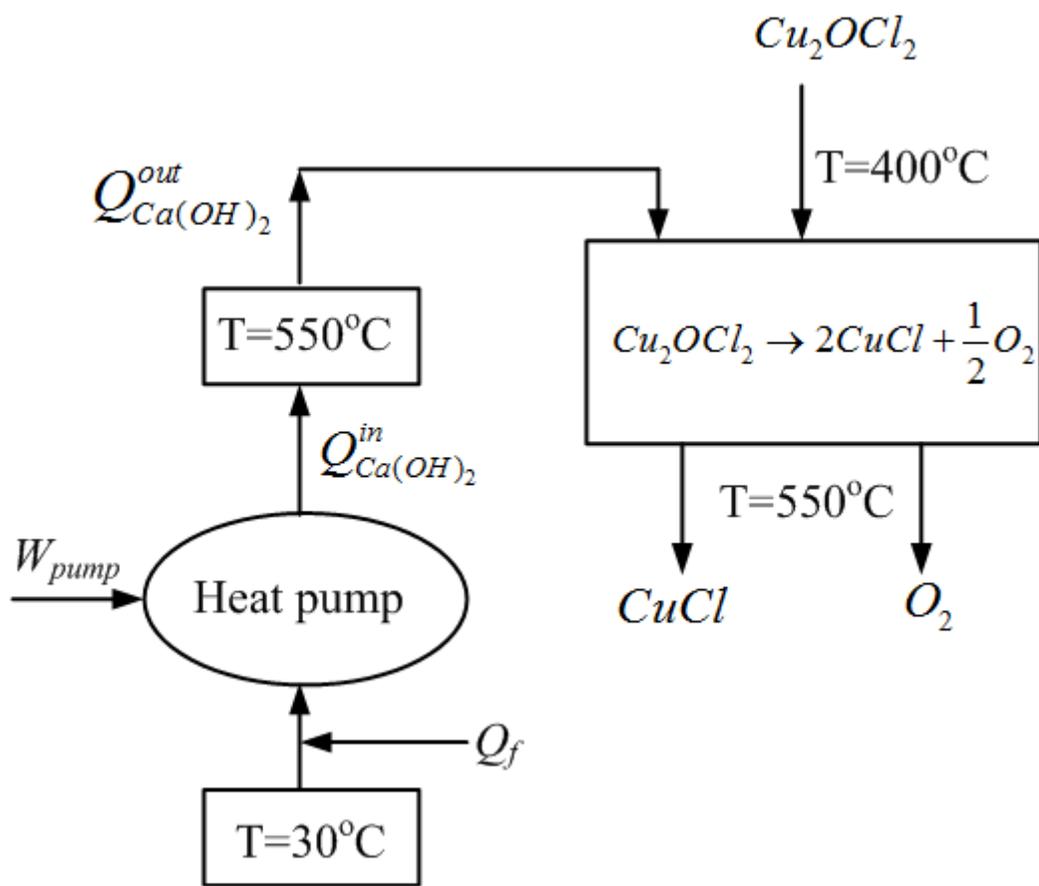


Fig. 1: Schematic of combined CHP and Cu-Cl cycle

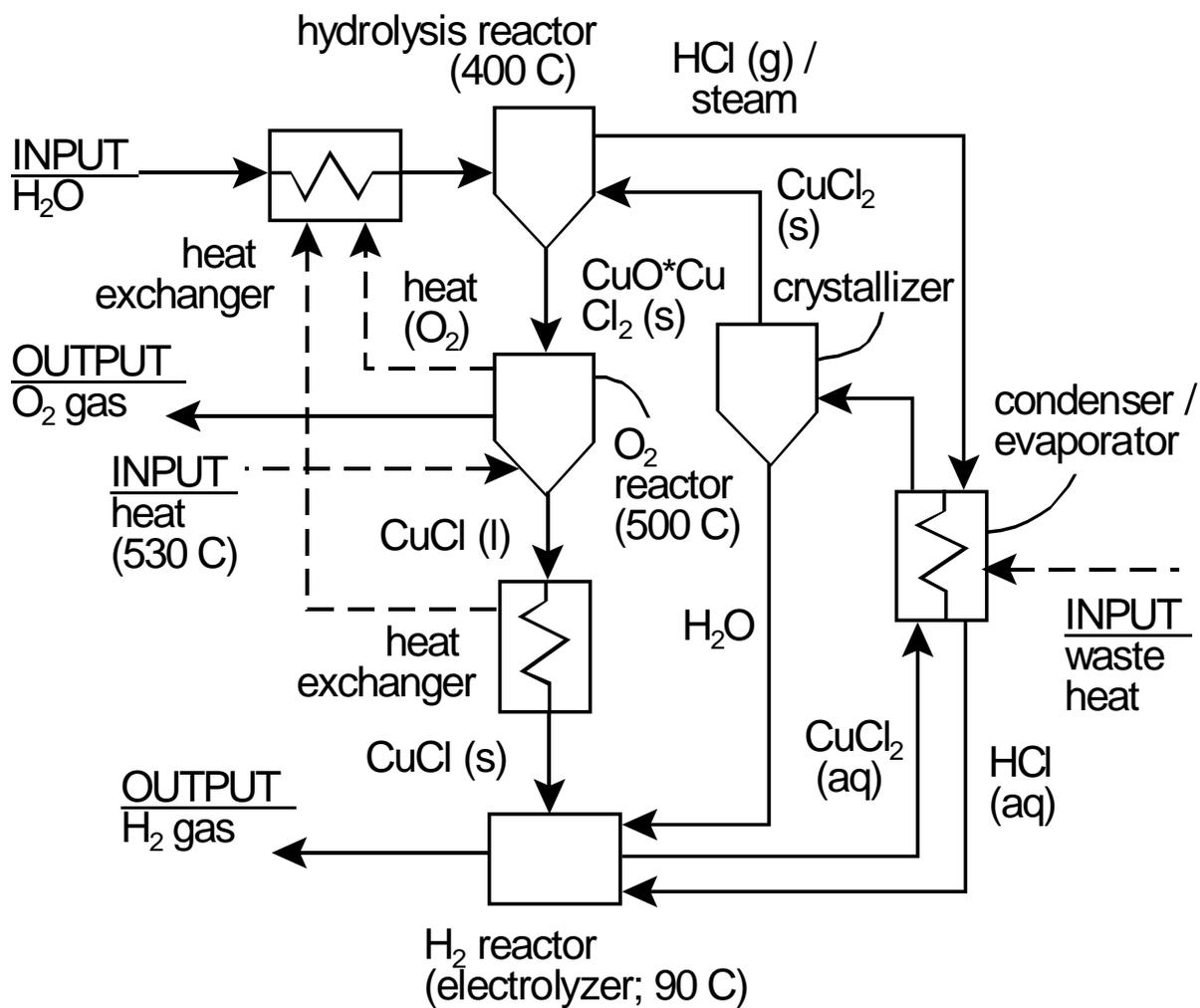


Fig. 2: Schematic of the copper-chlorine (Cu-Cl) cycle.

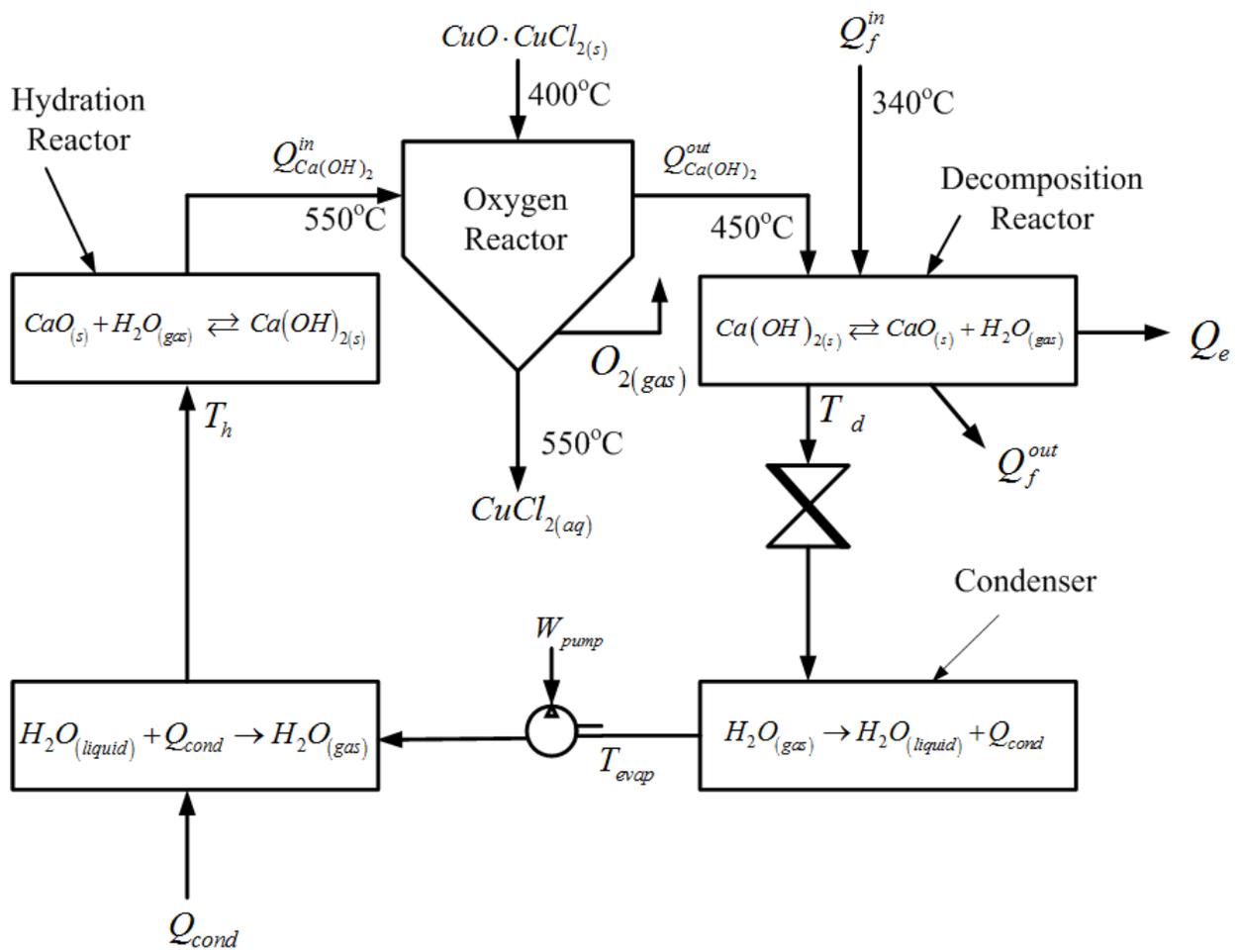


Fig. 3: Schematic of chemical heat pump for heat upgrading to the oxygen decomposition reactor.

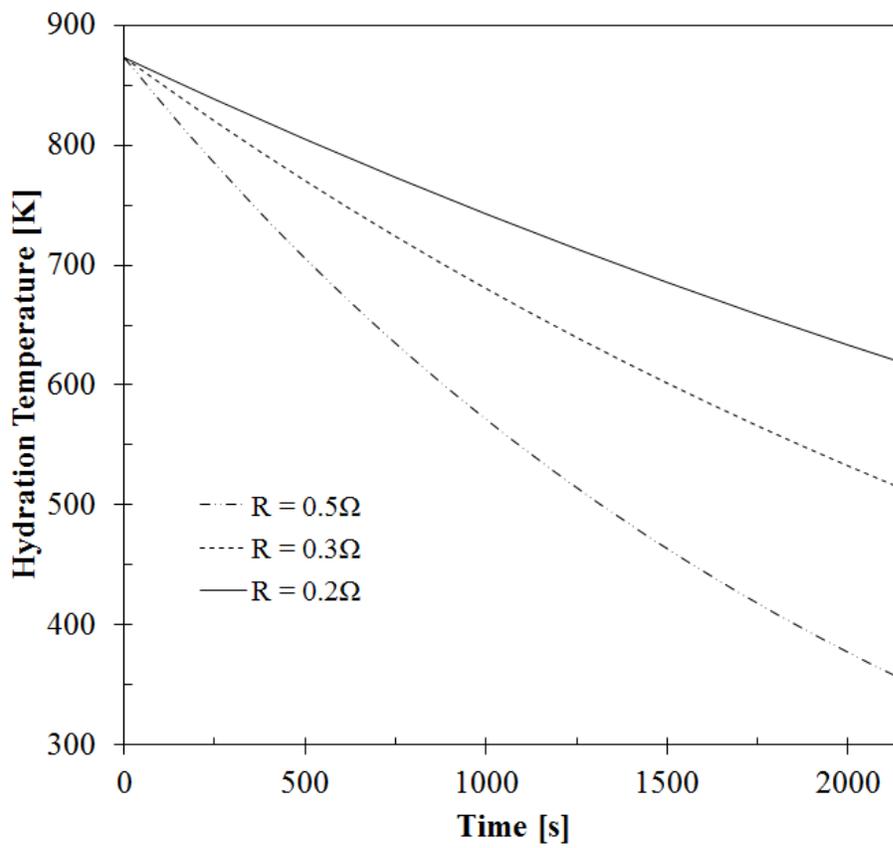


Fig. 4: Effect of electrical load on hydration reaction time.

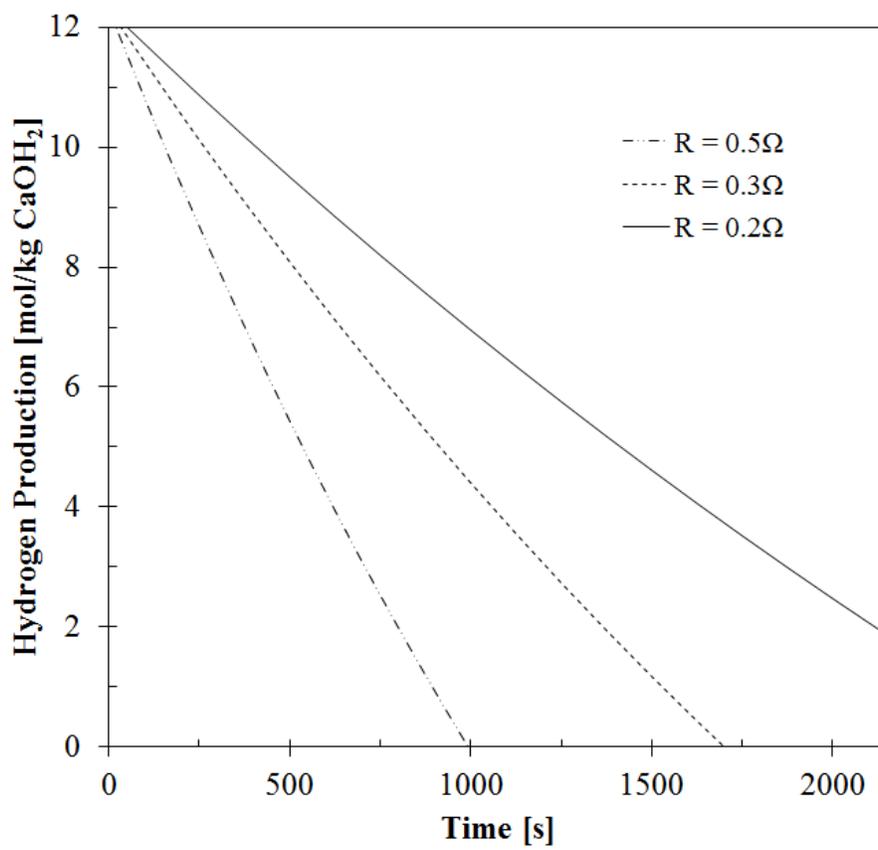


Fig. 5: Effect of heating load supplied by cement plant on rate of hydrogen production.

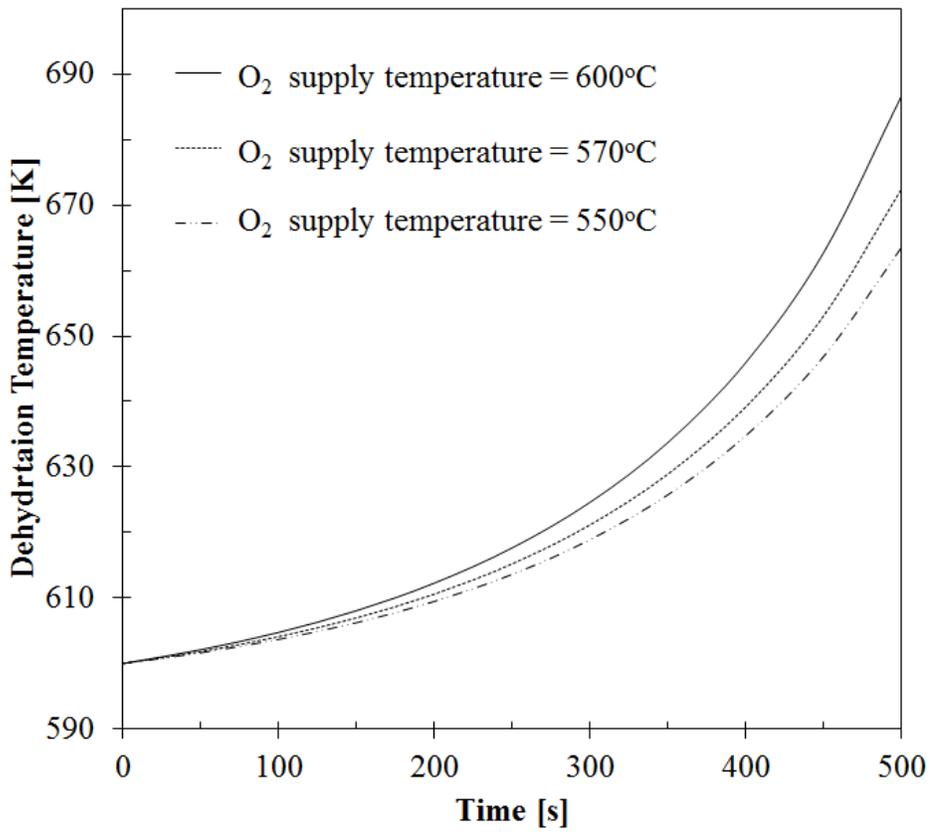


Fig. 6: Effect of supply temperature to oxygen decomposition reactor on temperature distribution in dehydration of  $\text{Ca}(\text{OH})_2$ .

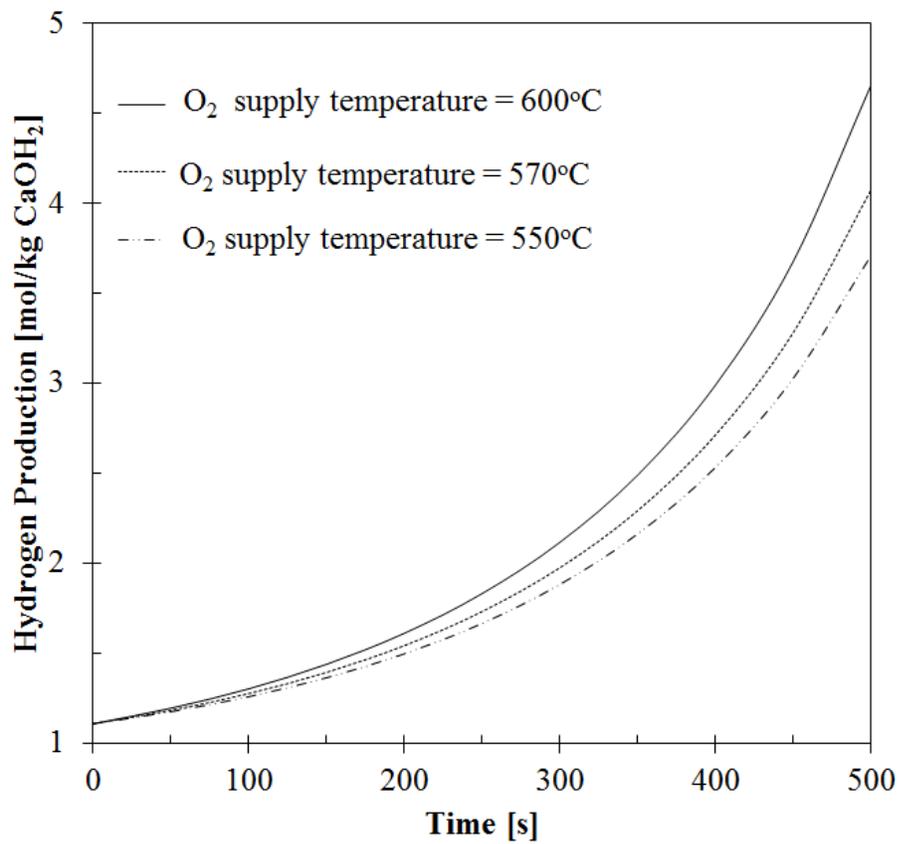


Fig. 7: Effect of supply temperature to oxygen decomposition reactor on H<sub>2</sub> production for a fixed heating load in the dehydration reactor.

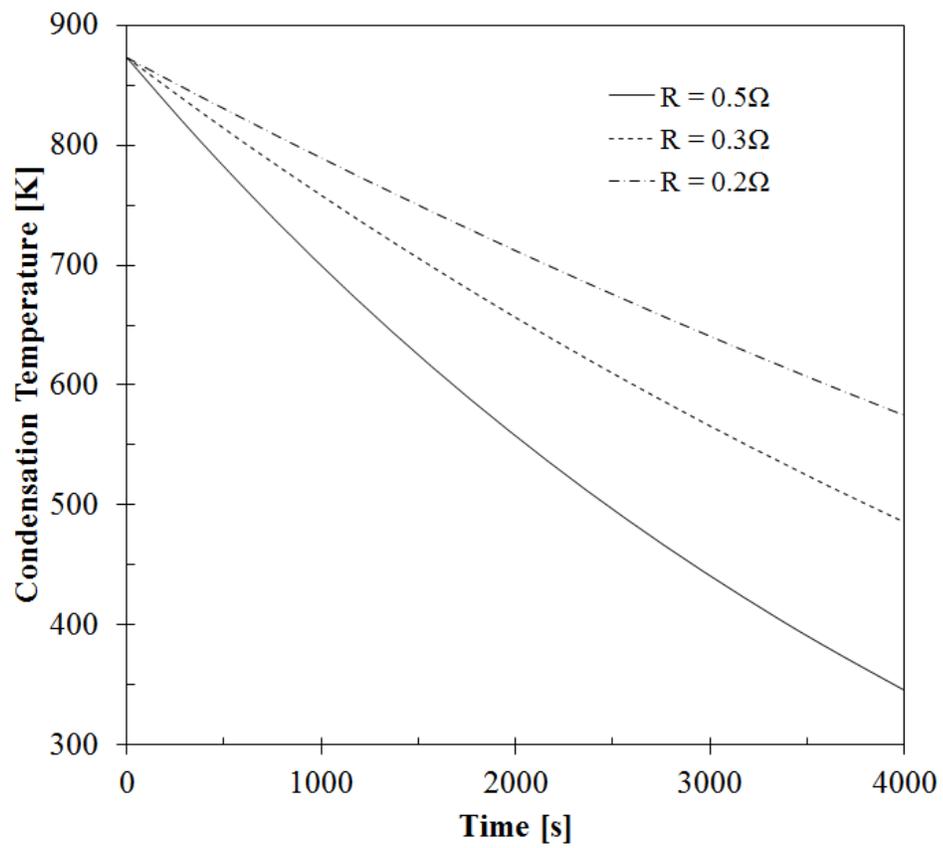


Fig. 8: Effect of heating load on condensation rate of steam in the CHP.

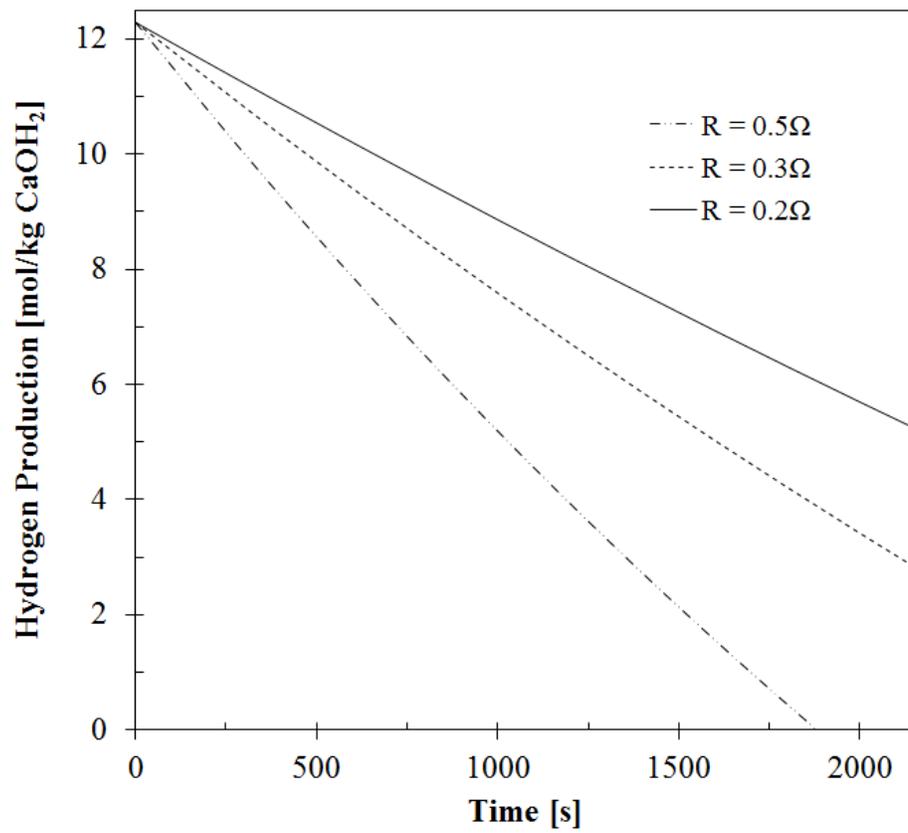


Fig. 9: Effect of condensation rate on hydrogen production for a fixed Cao/steam stream of 9kg.

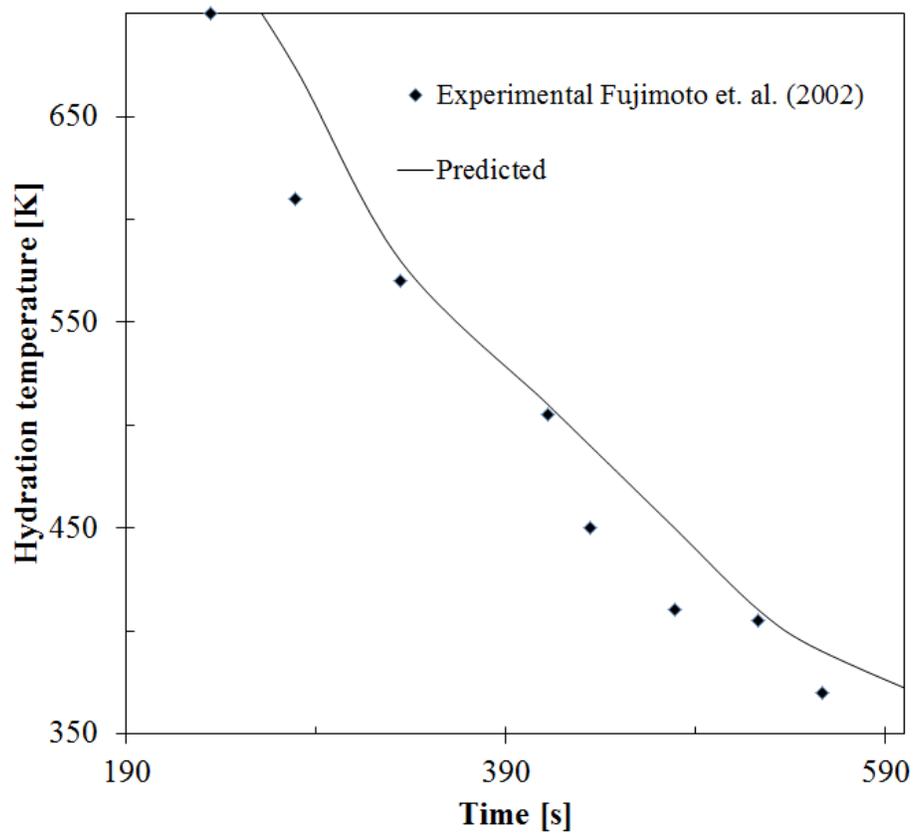


Fig. 10: Comparison of experimental and numerical prediction of hydration temperature distribution