Mathematical analysis of reduction of copper oxide pellets by hydrogen using the shrinking core model

Rupsha Bhattacharyya*, Kalyan Bhanja, Sadhana Mohan

Heavy Water Division, BARC, Mumbai 400 085, India

H I G H L I G H T S

- Reaction of single spherical copper oxide pellet in hydrogen-helium stream studied.
- No controlling regime assumed beforehand.
- Non-linear reaction kinetics considered.
- Low concentration of hydrogen taken for isothermal behaviour.
- Ash layer diffusion and chemical reaction determined to be rate controlling.

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A B S T R A C T

Reduction of copper oxide by hydrogen at high temperatures to metallic copper is one of the ways of removing hydrogen gas or its isotopes from its mixture with an inert gas like helium which is the coolant for plasma facing first wall of tritium breeding blanket modules in fusion reactor systems. The kinetics of the reaction of hydrogen with copper oxide was obtained from literature and it was used to model the reduction of a single particle of copper oxide using the well-known shrinking core model along with the pseudo-steady state hypothesis. No controlling regime was assumed a priori and the various interfacial gas concentrations were calculated by an iterative procedure based on the pseudo steady state hypothesis as function of the core radius at any time and for given operating conditions. The time required for complete reaction of the pellet was then calculated by numerical integration. A spherical geometry was considered in this work for the purpose of illustrating the technique, but the method is applicable to any kinetic model and any geometry of the pellets after simple modifications to the governing equations.

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1. Introduction

The use of hydrogen and its isotopes as fuel for fusion reactors is well documented. Hydrogen isotopes have been proposed as the fuels for fusion reactors [1]. As part of the process to purify the coolant helium that will be used for the plasma facing first wall of test blanket modules and free it of any hydrogen isotope before recycling it, heated metallic oxides have been proposed to be used. Copper oxide has been given particular importance in this context [2]. The conversion of copper oxide to metallic copper by the residual hydrogen isotopes in the coolant helium stream accomplishes the removal of these impurities. The process is generally envisaged to be carried out in fixed bed reactors with periodic replacement of the reduced CuO. While there are several ways to remove

hydrogen from helium including cryogenic adsorption, recombination with oxygen over supported noble metal catalysts and membrane permeation; the use of a heated metal oxide is a relatively simple and inexpensive process as compared to the other techniques. While there is the cost of heating the fixed bed and its contents to a temperature around 450 °C and the costs of gas recirculation involved, the infrastructure required is simpler and more direct than most other techniques. Moreover owing to the rather small driving forces likely to be available for the mass transfer based separation-purification techniques in this case, a reactive separation appears more feasible.

The work presents an analysis of the high temperature reduction of cupric oxide by hydrogen using the well-known shrinking core model under the pseudo-steady state hypothesis for gas transport through various resistances in series. Unlike most analyses of this nature, no controlling regime has been identified prior to the analysis in this work and all the intermediate gas concentrations have been calculated by iterative calculations based on the

* Corresponding author.
E-mail address: rupshabhattacharyya1986@gmail.com (R. Bhattacharyya).

Nomenclature

b	stoichiometric coefficient for CuO in the reduction reaction, dimensionless
C_a	concentration of hydrogen gas, mol m^{-3}
C_b	inlet concentration of hydrogen gas, mol m^{-3}
C_c	initial concentration of hydrogen gas in the mixer, mol m^{-3}
D_{AB}	fusivity of hydrogen through helium, m^2 s^{-1}
D_e	effective diffusivity of hydrogen through the porous ash or metal layer, m^2 s^{-1}
D_p	CuO pellet diameter, m
k_g	mass transfer coefficient in the fixed bed reactor, m s^{-1}
k_r	intrinsic surface reaction rate constant, mol0.4 m−0.2 s^{-1}
M_1	rate of film diffusion, mol s^{-1}
M_2	rate of ash diffusion, mol s^{-1}
M_3	rate of surface reaction on unreacted core, mol s^{-1}
M_{H2}	molecular weight of hydrogen, kg mol^{-1}
M_{He}	molecular weight of helium, kg mol^{-1}
n	order of reaction, dimensionless
rc	core radius, m
$(-r_{H2})$	rate of reduction reaction, mol m^{-3} s^{-1}
R	pellet radius, m
Rg	universal gas constant, 8.314 J mol^{-1} K^{-1}
Rep	Particle Reynolds number, dimensionless
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
Sg	specific surface area of the pellets, m^2 kg^{-1}
t	time, sec
T	absolute temperature, K
ρB	pellet molar density, mol m^{-3}
τ_actual	actual time for complete reaction of CuO pellet considering all processes, s
τ_calculated	calculated time for complete reaction of CuO pellet based on one assumed controlling regime, s

pseudo-steady state assumption. The kinetics of cupric oxide reduction by hydrogen follows fractional order kinetics (i.e. non-linear kinetics) which makes it necessary to use numerical techniques for the solution of the equations. For a given value of the bulk gas concentration of hydrogen and a given initial pellet radius, the gas concentrations have been calculated as function of the unreacted core radius of the pellet. It is then possible to use the results of these calculations to determine the time for complete reaction of the pellet. Based on the calculated gas concentration gradient along each resistance, the controlling regime (i.e. external mass transfer, ash diffusion or chemical reaction) can be identified.

## 2. Kinetics of the reaction of hydrogen and cupric oxide

There are a few experimental studies on the kinetics of the reduction of CuO with hydrogen that have been reported in literature [3–6]. Their major findings are summarised in Table 1. CuO is a well-known catalyst for various organic reactions involving hydrogen but in this study the actual reduction of CuO by hydrogen gas at elevated temperatures has been considered.

The present work aims to illustrate a technique that allows the shrinking core model be used to study non-catalytic gas solid reactions with non-linear kinetics and with no a priori assumption of the rate controlling regime. Thus the non-linear kinetic data reported by [5] have been used for the subsequent calculations.

3. Model equations and solution procedure

The shrinking core model [7] used for the analysis is shown schematically in Fig. 1. The core radius at any time is rc and the overall pellet radius remains unchanged with time at R. As the reaction proceeds, the core radius decreases from R to rc and finally to zero when the pellet is completely consumed. The layer of solid product (copper in this case) accumulates around the core region and its thickness increases as reaction proceeds to keep the overall particle radius at the same value R. The implicit assumption in this is that the molar density of reactant and product solid is the same. It is assumed that the ash or solid product layer is porous through which reactant and product gases can diffuse while the core is impermeable to gas and the reduction reaction takes place at the interface between the metal (i.e. ash) and the oxide core. Additionally isothermal conditions have been assumed to be maintained and the gas and pellet have been assumed to be at the same temperature throughout the entire time of reduction, for the purpose of establishing the technique. The bulk or feed concentration C_b remains unchanged with time while C_a and C_c change as rc changes on account of the reaction.

The chemical reaction is represented as [3]

$$CuO + H_2 = Cu + H_2O, \Delta H_{rx} = -130.5 \text{ kJ mol}^{-1} H_2 \tag{1}$$
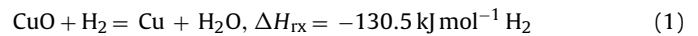
The reaction rate equation obtained from literature is [5]

$$(-r_{H2}) = (k_r C_c^n)/R \tag{2}$$

Based on the pseudo-steady state hypothesis, the following equations can be written for the external convective flux of hydrogen, diffusive flux of hydrogen through the copper layer and the reaction rate on the unreacted core surface respectively [3,8]:

$$M_1 = 4\pi R^2 k_g (C_b - C_a) \tag{3}$$

$$M_2 = \frac{4\pi r_c D_e (C_a - C_c)}{(1 - r_c/R)} \tag{4}$$

$$M_3 = 4\pi r_c^2 k_r C_c^n \tag{5}$$

The value of k_r is obtained from literature [5] and it is given by

$$k_r = 1.0 \times 10^{-4} \exp\left(\frac{-33000}{8.314 * T}\right) \text{ mol}^{0.4} \text{ m}^{-0.2} \text{ S}^{-1} \tag{5a}$$

and the reaction follows an order $n = 0.6$ [5].

Under the pseudo steady state assumption, the rates M_1, M_2 and M_3 are all equal, the unit for the rate being mol s^{-1} for each process. This allows Eq. (6) to be written by eliminating C_a to get an implicit equation relating C_c with rc in terms of C_b and other known quantities.

$$C_b - \frac{r_c^2 k_r C_c^n}{R^2 k_g} = C_c + \frac{r_c k_r C_c^n (1 - {}^{r_c}/R)}{D_e} \tag{6}$$

The coefficient kg is calculated from the following correlation for convective mass transfer to a single sphere [9]:

$$Sh = \frac{k_g(2 * R)}{D_{AB}} = 2 + 0.6 \ Sc^{0.33} Re_p^{0.5} \tag{7}$$

The various physical and transport properties of the reactant and product gases and solids used for the analysis are presented in Table 2.

C_b is known from the conditions maintained during experiments or operational runs, as also the various kinetic and transport coefficients from empirical equations. Thus Eq. (6) can be solved iteratively to obtain C_c as a function of rc for the given set of conditions. The time of complete disappearance of a CuO pellet can be obtained by numerically integrating equation while accounting for the dependence of C_c on the instantaneous value of rc. The effect of