

Combustion of Rechargeable Metal Fuels in Fluidized Bed Boilers

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Reaction kinetics for metal oxidation and oxide metal reduction

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Executive summary

This Deliverable provides experimentally validated kinetic models for the oxidation and reduction of FERELET MT iron powder, the material selected for medium- and large-scale CORAL pilot plants. The corresponding reaction models and kinetic parameters are provided to be implemented in subsequent reactor and process modelling tasks in WP3.

The reaction kinetics for both oxidation with oxygen and reduction with hydrogen was determined from mass variation curves obtained under well-defined conditions using a thermogravimetric analyser (TGA), and they were converted to conversion values for the fitting procedure to determine the kinetic parameters.

The influence of temperature (oxidation 923–1073 K; reduction 723–873 K), particle size (from $<40\text{ }\mu\text{m}$ to $300\text{--}500\text{ }\mu\text{m}$) and reactive gas concentration (oxygen: 5–21 vol.%; hydrogen: 5–60 vol.%), in addition to the steam concentration (0–15 vol.%) for the reduction reaction, was assessed.

Oxidation of FERELET MT from Fe to Fe_2O_3 proceeds in two distinct kinetic steps: an initial fast stage controlled by chemical reaction, followed by a slower stage controlled by diffusion. A shrinking-core model is used for the first step and a 3D diffusion (Zhuravlev–Lesokhin–Tempelman) model for the second one, with kinetic constants expressed as functions of temperature, oxygen concentration, and particle size. A detailed formulation for the transition from the chemically controlled step to the diffusion-control step is also presented.

Reduction of fully oxidized Fe_2O_3 with hydrogen follows thermodynamically consistent multi-step pathways involving different intermediate iron oxides. Reduction of Fe_2O_3 to Fe_3O_4 was always observed regardless the operating conditions, which was mainly affected by temperature and H_2 concentration. Only subsequent steps were additionally affected by steam concentration and particle size. Below 860 K, Fe_3O_4 reduces directly to Fe, while above 860 K, FeO appears as an additional intermediate. In all cases, characteristic S-shaped conversion curves are captured using 2D nuclei or 3D diffusion models, which were used to calculate a complete sets of kinetic parameters for the reduction reaction.

These models enable accurate prediction of the evolution of the conversion with time and the reaction rate as a function of operating conditions. The models were formulated for its direct implementation in the reactor models.

1. Introduction

This report is focused on the determination of the reaction kinetics of iron powder both for oxidation and reduction reactions. The material used for the kinetic determination is the one selected for use in medium and large-scale pilot plants, namely FERET MT. In the project framework, oxidation is performed with air, while renewable hydrogen is used for the reduction stage.

The kinetic models have been selected evaluating the characteristics of the oxidation and reduction reactions, and also considering that these models must be implemented in reactor models in subsequent tasks, mainly:

- Oxidation:
 - T3.3. Development and validation of a 1.5-D fluidized bed oxidation model.
 - T3.4. Development and validation of a dynamic process oxidation model.
 - T3.6. Development and validation of a CFD oxidation model.
- Reduction:
 - T3.2. Development and validation of a fluidized bed reduction model.
 - T3.5. Development and validation of a dynamic process reduction model.
 - T3.7. Development and validation of a CFD reduction model.

Kinetic parameters have been determined by fitting the predicted conversion vs. time curves with those experimental curves obtained from TGA tests. The main operating conditions affecting the reaction rate have been evaluated, mainly the concentration of reacting gases, the reaction temperature and the particle size of the metal powder.

2. Materials and methods

2.1. Iron powder

FERET MT powder has been selected to be used at the medium- and large-scale pilot units. This material presents a broad particle size distribution (PSD); see Figure 2.1. FERET MT powder was mainly composed by metallic iron. The oxidation kinetics was determined with the powder as received.

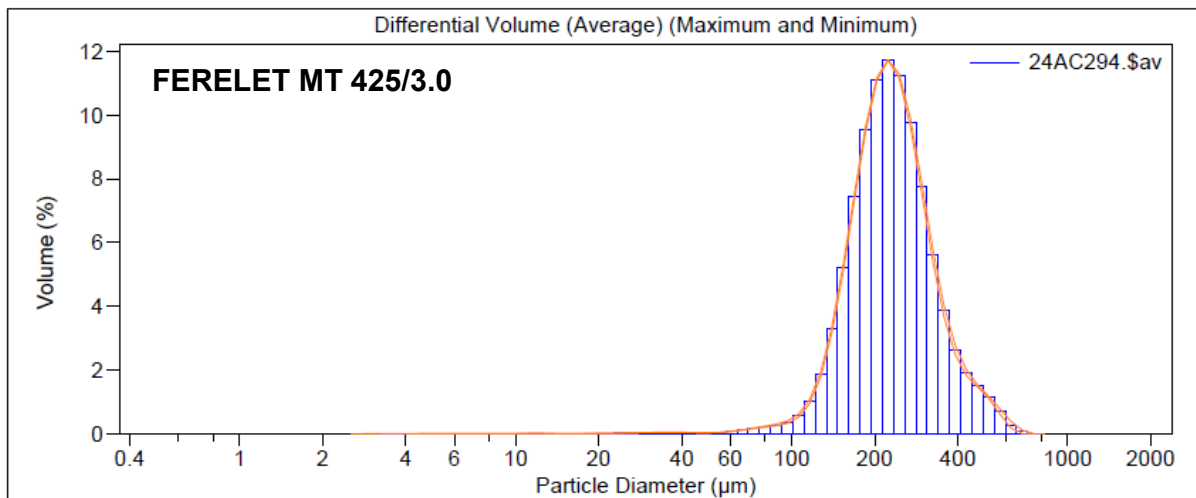


Figure 2.1. Particle size distribution (PSD) of FERET MT powder.

For the determination of the reduction kinetics, the FERELET MT powder was previously oxidized in a fluidized bed reactor (55 mm I.D.). For that, a batch of 400 g of the material was loaded in the reactor and heated to 1023 K in N₂. Once the desired temperature was reached, the fluidizing gas was switched to diluted air (5% O₂) in order to minimize agglomeration issues that could appear during the oxidation of the fully reduced powder. The oxygen concentration at the reactor outlet was continuously monitored in order to assess the oxidation process. After 3 hours of oxidation under diluted air, the oxygen concentration was gradually increased up to 21 % and maintained until the oxidation was completed, i.e. the concentration at the reactor outlet was equal to that at the inlet, indicating that no further oxygen was consumed by the oxidized powder.

Prior to the kinetic determination, both reduced and oxidized materials were sieved into different particle sizes, which were used to evaluate the effect of particle size on the reaction rate. Thus, the following material samples were used: <40 µm, 40-80 µm, 80-150 µm, 150-200 µm, 200-250 µm, 250-300 µm and 300-500 µm.

2.2. Thermogravimetric analyzer (TGA)

To determine the reaction kinetics of this material, tests in a TGA -see Figure 2.2- were carried out at well-known conditions, depending on the studied reaction:

- Oxidation: different oxygen concentration (5, 10, 15 and 21 vol.%) and reacting temperatures (923, 973, 1023 and 1073 K) values were selected for the kinetics determination. The evolution of the sample mass with the reacting time was recorded and used to calculate the conversion of the sample by using Eq. (2.1).

$$X(t) = \frac{\Delta m(t)}{R_{ox} m_{red}} \quad (2.1)$$

Here, m_{red} is the initial mass of the fully reduced iron sample and R_{ox} is the maximum gain in the mass of the iron material after its complete oxidation calculated by Eq. (2.2).

$$R_{ox} = \frac{\Delta m_{max}}{m_{red}} = 0.43 \quad (2.2)$$

- Reduction: different hydrogen concentration (5, 15, 30 and 60 vol.% H₂; N₂ to balance) and reacting temperatures (723, 773, 823 and 873 K) values were selected for the kinetics determination. These relatively low temperature values were selected considering several aspects: reactivity and maximum conversion, H₂ conversion, and likely an improved thermal efficiency during the reduction process. In addition, the possible effect of the steam concentration on the reduction rate was evaluated by using different steam concentration values (5, 10 and 15 % H₂O), while H₂ concentration was maintained at 60 vol.% H₂. The steam was added by bubbling the gas stream through water heated to a controlled temperature, which was selected as a function of the saturation partial pressure of steam.

The evolution of the sample mass with the reacting time was recorded and used to calculate the conversion of the sample by using Eq. (2.3).

$$X(t) = \frac{-\Delta m(t)}{R_{red} m_{ox}} \quad (2.3)$$

Here, m_{ox} is the initial mass of the oxidized iron sample and R_{red} is the maximum gain in the mass of the iron material after its complete reduction calculated by Eq. (2.4).

$$R_{red} = \frac{\Delta m_{max}}{m_{ox}} = 0.30 \quad (2.4)$$

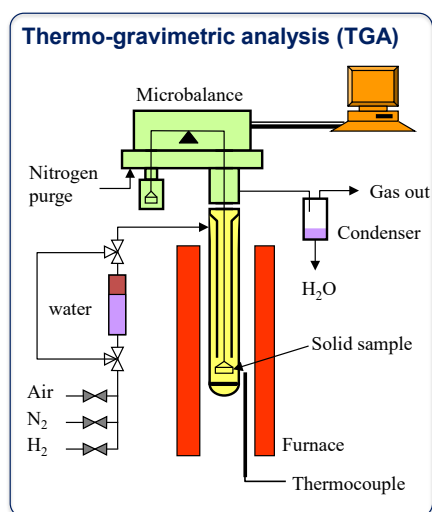


Figure 2.2. Scheme of the thermogravimetric analyzer used to determine reaction rates under controlled operating conditions.

3. Determination of oxidation kinetics

The effect of the reacting conditions -namely oxygen concentration, reacting temperature and particle size- on the reacting rate was determined by TGA analysis. Prior to conducting the tests for this purpose, thermogravimetric tests were performed for different particle size intervals. It was observed that the particle size highly affected to the oxidation rate of the particles; see Figure 3.1. However, it was observed that the particle size barely affected the oxidation rate below 80 μm . Therefore, it was decided to evaluate the effect of oxygen concentration and reacting temperature on the reaction rate with particles in the 40-80 μm interval, and then, to evaluate the effect of the particle size on the reaction rate under selected conditions, namely under 10 and 21 vol.% O_2 at 973 and 1073 K.

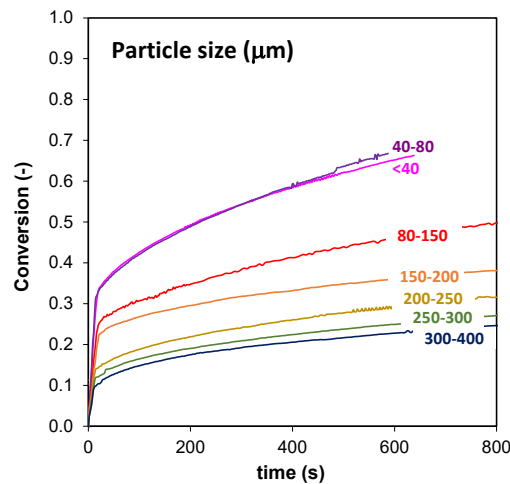


Figure 3.1. Conversion vs. time curves for different particle size intervals of FERET MT powder. Temperature: 1073 K; oxygen concentration: 21 vol.%.

3.1. Effect of operating conditions on the oxidation rate

The main operating conditions affecting the oxidation rate are the reacting temperature, the oxygen concentration and the particles size. Figure 3.2 shows the conversion vs. time curves obtained during the TGA tests at different temperatures (923, 973, 1023 and 1073 K) and oxygen concentration values (5, 10, 15 and 21 vol.%).

As expected, the increase of temperature and oxygen concentration improved the oxidation rate. It should be highlighted that a temperature as high as 1073 K is required to achieve almost full oxidation after 1 h of oxidation. Also for that, the oxygen concentration should be relatively high. Thus, it would be recommended to operate with high air excess to promote the oxidation of FERET MT material during the experimental campaigns at medium and large scale units.

It should be noted the presence of two steps during the oxidation rate at all the experimental conditions tested. Thus, a fast oxidation rate is found at the beginning of the reaction, which suddenly changes to a slower rate at a determined conversion. The conversion value at which this change is observed is lower as the temperature decreases. In addition, the oxidation rate during the second stage -characterized by a slow oxidation rate- decreases noticeably as the temperature decreases. This fact prevents from obtaining high oxidation conversion at low temperature values.

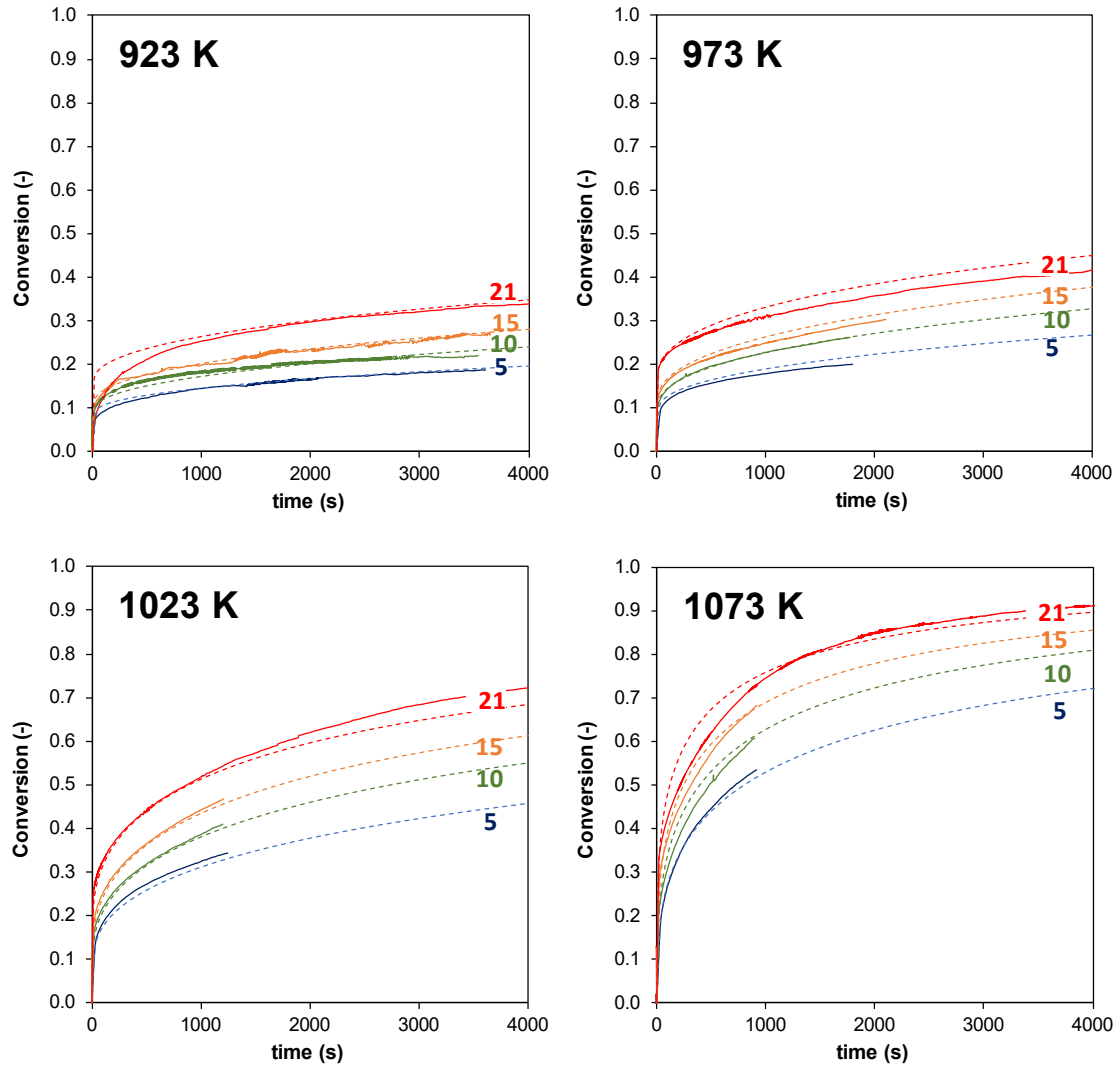


Figure 3.2. Conversion vs. time curves for the oxidation of FERET MT at different temperatures and oxygen concentration values. Continuous lines: experimental curves from TGA tests; broken lines: model predictions with the determined kinetics parameters. $d_p = 60 \mu\text{m}$.

The effect of the particle size on the oxidation rate was evaluated at selected temperatures (973 and 1073 K) and oxygen concentration values (10 and 21 vol.%); see Figure 3.3. In all cases, the particle size has a relevant effect on the oxidation rate, which significantly decreases as the particle size increased. This fact highlights the great importance of having high temperatures and oxygen concentration to obtain relatively high oxidation conversions, although the complete oxidation of the FERET MT would require long oxidation times. Also the presence of two distinct step during the oxidation was found for any particle size, which should be considered in the model formulation to determine the kinetic parameters and to accurately predict the experimental conversion curves

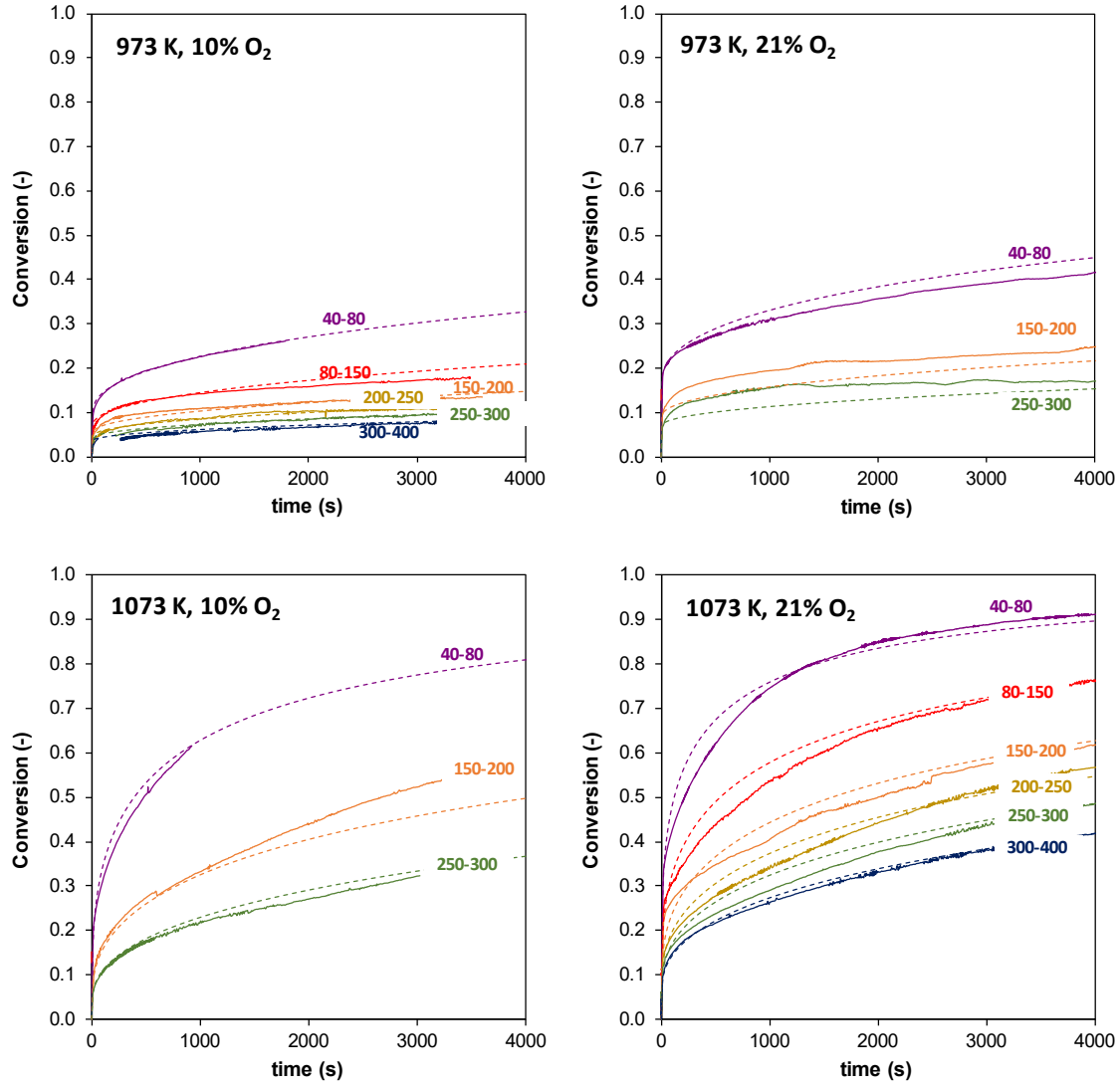
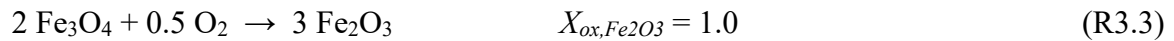
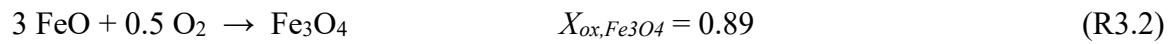
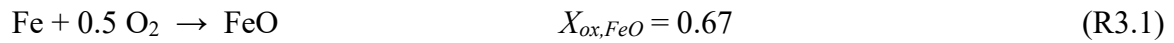


Figure 3.3. Effect of the particle size on the conversion vs. time curves for the oxidation of FERET MT at selected temperatures and oxygen concentration values. Continuous lines: experimental curves from TGA tests; broken lines: model predictions with the determined kinetics parameters.

3.2. The oxidation kinetic model

From the conversion vs. time curves, it was observed that the oxidation proceeds in two clearly distinguishable steps; see Figure 3.4. Step I is characterized by a fast reaction, followed by a sharp decrease in the oxidation rate (Step II). It should be noted that the oxidation reaction may proceed through different intermediate oxides; see reactions (R3.1)-(R3.3). The conversion at which each reaction is completed, i.e. $X_{ox,FeO}$, X_{ox,Fe_3O_4} and X_{ox,Fe_2O_3} defined by Eq. (2.1), is shown below.



No obvious changes in reaction rate have been observed around these high conversion values ($X_{ox,FeO}$, X_{ox,Fe_3O_4}). Then, the change in the reaction rate was not related to the oxidation of different iron oxides, and a lump reaction kinetics for the whole oxidation from Fe to Fe_2O_3 was considered following reaction (R3.4).

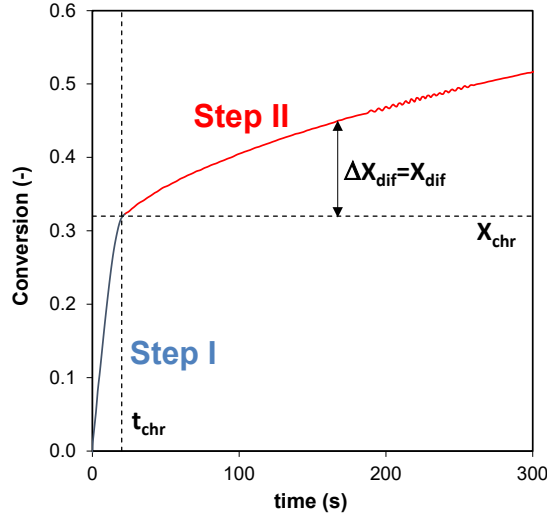


Figure 3.4. Evolution of the iron conversion and its relationship with different oxidation steps. Temperature: 1073 K; oxygen concentration: 21 vol.%; $d_p=60 \mu\text{m}$.

The particle reaction model considers this sharp decrease in the oxidation rate by defining two distinct reaction mechanism:

- Step I has been defined as a reaction mainly controlled by chemical reaction. To describe the conversion progress, the Shrinking Core Model controlled by chemical reaction in the solid interphase has been selected; see Eqs. (3.1-3.3).

$$\frac{t}{\tau_{chr}} = 1 - (1 - X)^{1/3} \quad (3.1)$$

$$\frac{dX}{dt} = \frac{3}{\tau_{chr}} (1 - X)^{2/3} \quad (3.2)$$

$$\tau_{chr} = \frac{1}{k_{chr} C_{O_2}^{n_{chr}}} \quad (3.3)$$

- Step I proceeds until Step II becomes the limiting step. The point at which the mechanism changes is defined by the conversion rate X_{chr} and time t_{chr} . The subsequent Step II should be described by a reaction model that takes into account conversion values ranging from 0 to 1. Therefore, a variable transformation must be applied to the conversion parameter, so that it can be used during the diffusion-controlled stage. Therefore, the conversion during Step II is defined by X_{dif} , which is calculated by Eq. (3.4). The time elapsed in Step II is calculated with the Eq. (3.5).

$$X_{dif} = \frac{X - X_{chr}}{1 - X_{chr}} \quad (3.4)$$

$$t_{dif} = t - t_{chr} \quad (3.5)$$

- The suitability of several reaction models to predict the conversion evolution for the Step II has been evaluated; see Figure 3.5. Among them, the 3D-diffusion model introduced by Zhuravlev–Lesokhin–Tempelman (ZLT function) has been identified as the most likely mechanism for Step II. Thus, for $X > X_{chr}$, the evolution of the oxidation conversion is defined by Eqs. (3.6-3.8).

$$\frac{t_{dif}}{\tau_{dif}} = \left[(1 - X_{dif})^{-1/3} - 1 \right]^2 \quad (3.6)$$

$$\frac{dX_{dif}}{dt_{dif}} = \frac{3}{2\tau_{dif}} \frac{(1 - X_{dif})^{4/3}}{\left[(1 - X_{dif})^{-1/3} - 1 \right]} \quad (3.7)$$

$$\tau_{dif} = \frac{1}{D_{ef} C_{O_2} n_{dif}} \quad (3.8)$$

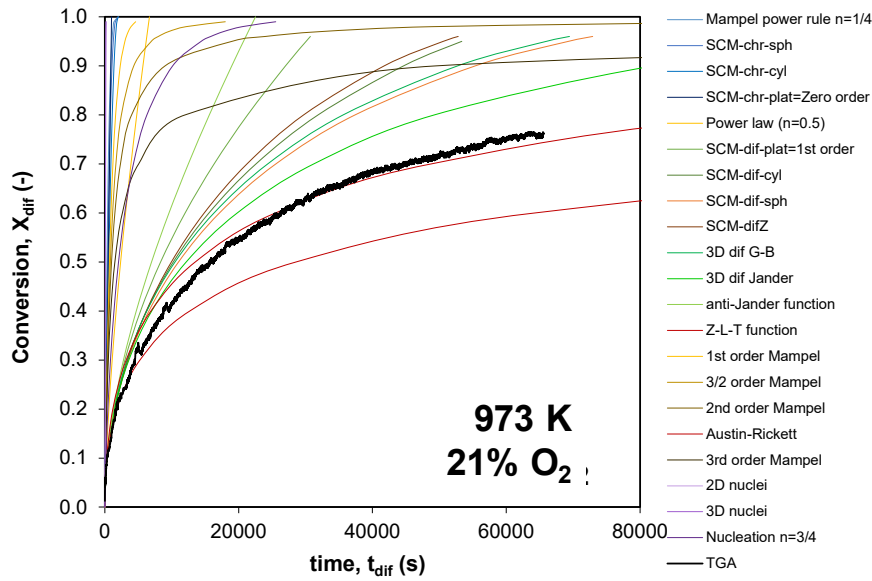


Figure 3.5. Comparison of experimental X vs t curve with predictions from a variety of proposed models for gas-solid reactions.

3.3. Parametric evaluation and determination of oxidation kinetic

The progress of the oxidation reaction is described by the model presented above. The model is described by three main parameters, namely the reaction kinetic constant (k_{chr}), the effective diffusivity in the particle (D_{ef}) and the conversion value at which the limiting mechanism change from chemical reaction to diffusion (X_{chr}). The determination of the kinetics parameters has been performed by fitting the experimental conversion vs. time curves obtained at different oxygen concentration values, reacting temperatures and particle size intervals. Thus, the corresponding τ_{chr} and τ_{dif} values has been determined for the different conditions tested. The following results have been achieved:

- Step I, being $X < X_{chr}$: the reaction order is determined considering the effect of the oxygen concentration on τ_{chr} for particles with an average size of 60 μm . Linearization of Eqs. (3.3) is shown in Figure 3.6(a). The reaction order is determined by the slope of the linear fitting with the oxygen concentration, being $n_{chr}=1$ for all tested temperatures. The kinetic constant at each temperature is calculated from the intercept, and its variation with the

temperature is shown in Figure 3.6(b). Then, the effect of the particle size on the chemical reaction constant was determined by fitting results shown in Figure 3.3. Assuming the dependence with the radius of the particle, r_p , shown in Eq. (3.9), Figure 3.7 shows the plot to determine the parameter $n_{k,rp}$. Table 3.1 compiles the calculated values for the different kinetic parameters.

$$k_{chr} = k_{chr,o} \left(\frac{30}{r_p} \right)^{n_{k,rp}} e^{-E_{chr}/R_g T} \quad (3.9)$$

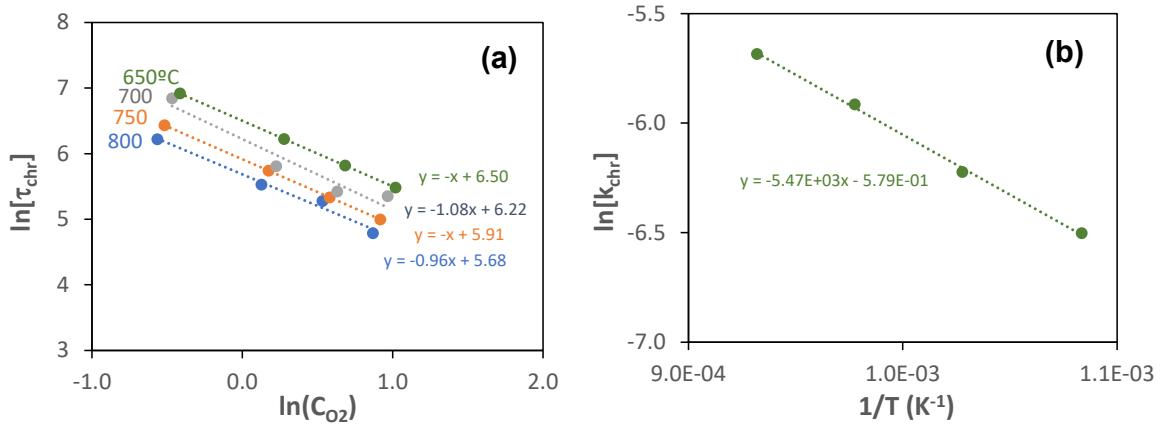


Figure 3.6. (a) Determination of the reaction order and (b) Arrhenius plot to determine pre-exponential factor and activation energy of the chemical reaction constant for the Step I controlled by chemical reaction ($X < X_{chr}$). $d_p = 60 \mu m$.

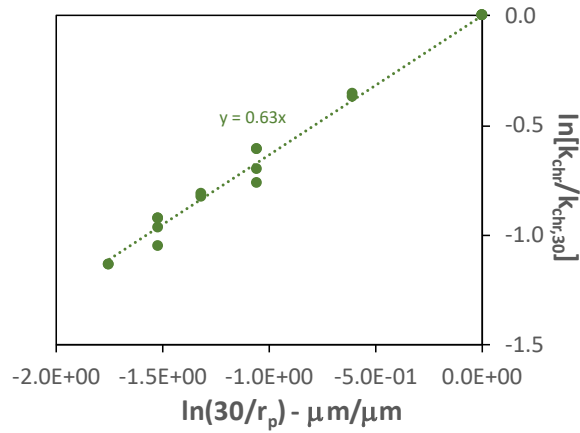


Figure 3.7. Determination of the parameter $n_{k,rp}$ considering the Eq. (3.9).

Table 3.1. Kinetic parameters calculated for Step I controlled by chemical reaction ($X < X_{chr}$)

n_{chr}	1
$n_{k,rp}$	0.63
$k_{chr,o}$ (m ³ mol ⁻¹ s ⁻¹)	$5.61 \cdot 10^{-1}$
E_{chr} (J/mol)	45500

- Step II, being $X > X_{chr}$: the reaction order for the diffusion mechanism has been calculated from Eq. (3.8) by fitting the determined τ_{dif} value as a function of the oxygen concentration for each temperature; see Figure 3.8(a). A value of $n_{dif}=1$ is calculated for all temperatures. The diffusion coefficient is calculated from the intercept and plotted in Figure 3.8(b) as a function of the temperature. Analyzing this figure, it has been identified two different diffusion mechanism in parallel which accounted for the effective diffusion: (a) gas diffusion at low temperature; and (b) diffusion in the solid at high temperature. Thus, the activation energy for the gas diffusion (D_g) is lower than that for the diffusion in the solid (D_s). The effective diffusion coefficient is calculated as the addition of the corresponding coefficients for gas and solid diffusion. The dependence of the diffusion coefficients with the temperature and particle size are given by Eqs. (3.10-3.12). Eventually, the effect of the particle size is determined by parameter $n_{D,rp}$ in Eq. (3.10), and calculated from Figure 3.9. Table 3.2 compiles the calculated values for the different parameters related to the diffusion coefficients.

$$D_{ef} = [D_g + D_s] \left(\frac{30}{r_p} \right)^{n_{D,rp}} \quad (3.10)$$

$$D_g = D_{g,o} e^{-E_g/R_g T} \quad (3.11)$$

$$D_s = D_{s,o} e^{-E_s/R_g T} \quad (3.12)$$

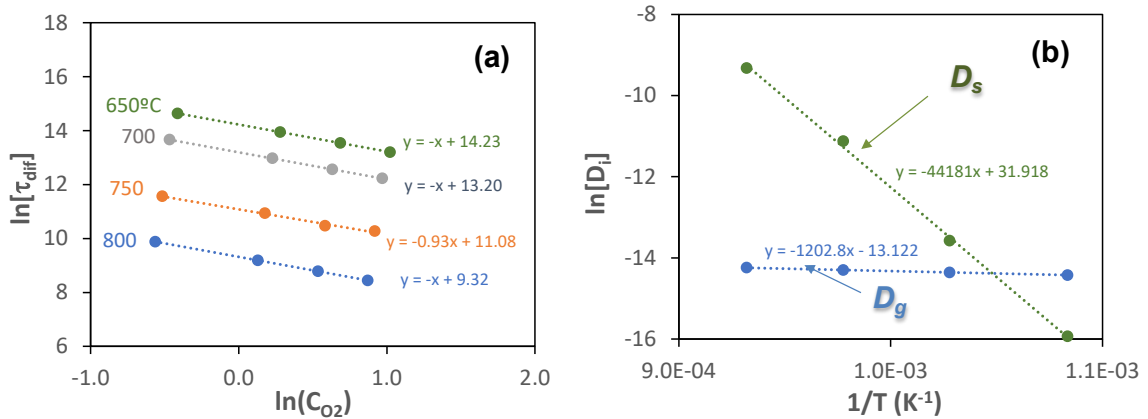


Figure 3.8. (a) Determination of the reaction order and (b) Arrhenius plot to determine pre-exponential factor and activation energy of diffusion coefficient for the Step II ($X > X_{chr}$).

$d_p=60 \mu m$.

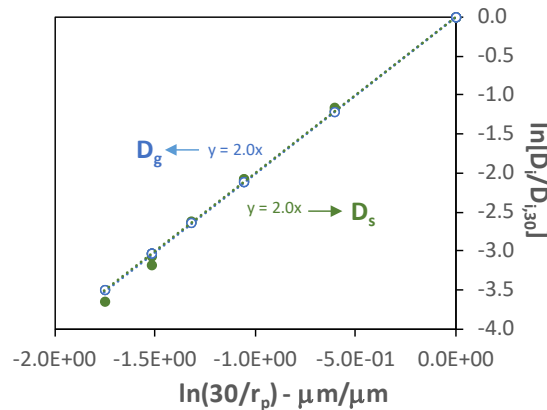


Figure 3.9. Determination of the parameter $n_{D,rp}$ considering the Eq. (3.10).

Table 3.2. Kinetic parameters calculated for Step II controlled by diffusion in the particle ($X > X_{chr}$)

n_{dif}	1
n_{D,r_p}	2
$D_{g,o}$ ($\text{m}^3\text{mol}^{-1}\text{s}^{-1}$)	$2.0 \cdot 10^{-6}$
E_g (J/mol)	10000
$D_{s,o}$ ($\text{m}^3\text{mol}^{-1}\text{s}^{-1}$)	$7.28 \cdot 10^{13}$
E_s (J/mol)	367300

- X_{chr} value: the conversion value at which there is a change in the limiting mechanism is a function of all the operating conditions. In general, it has been found an exponential dependence with the oxygen concentration and temperature (type $y = y_0 + ae^{bx}$), as well as a potential dependence with the particle size (type $y = mx^n$); see Eqs. (3.13-3.16). Figure 3.10(a) shows the dependency of X_{chr} with the oxygen concentration to determine the parameters X_{chr,O_2} , a_{O_2} and b_{O_2} in Eq. (3.13). The dependency of these parameters with the temperature following Eqs. (3.14)-(3.16) is shown in Figure 3.10(b). The additional effect of the particle size on X_{chr} is plotted in Figure 3.11 according to the corresponding expression in Eq.(3.13). The calculated values for the parameters used to calculate the X_{chr} value are compiled in Table 3.3.

$$X_{chr} = [X_{chr,O_2} + a_{O_2} e^{b_{O_2} C_{O_2}}] \left(\frac{30}{r_p} \right)^{n_{X_{chr},r_p}} \quad (3.13)$$

$$X_{chr,O_2} = X_{chr,O_2,a} e^{X_{chr,O_2,b}/T} \quad (3.14)$$

$$a_{O_2} = a_{O_2,o} + a_{O_2,a} e^{a_{O_2,b}/T} \quad (3.15)$$

$$b_{O_2} = b_{O_2,a} e^{b_{O_2,b}/T} \quad (3.16)$$

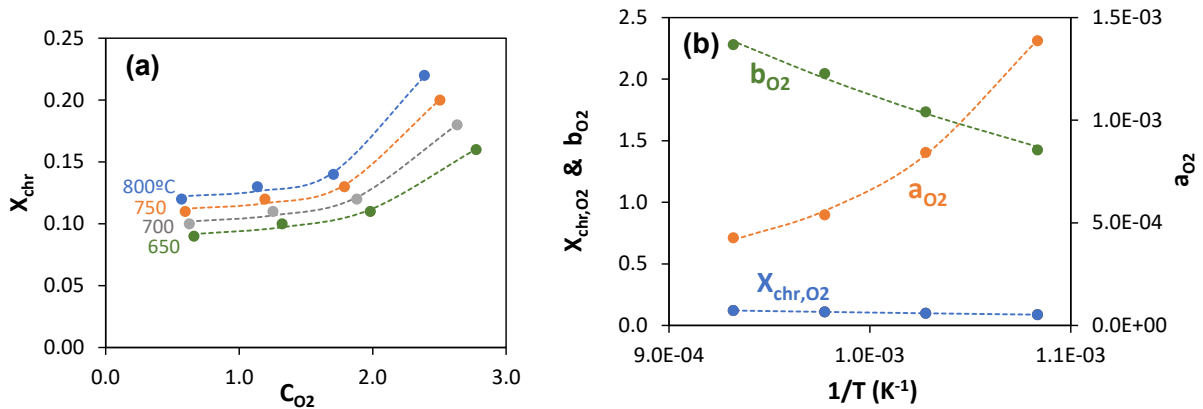


Figure 3.10. (a) Plot to determine the parameters in Eq. (3.13) to calculate X_{chr} as a function of the oxygen concentration, namely X_{chr,O_2} , a_{O_2} and b_{O_2} ; and (b) plot to determine the T-related parameters according Eqs. (3.14)-(3.16). $d_p = 60 \mu\text{m}$.

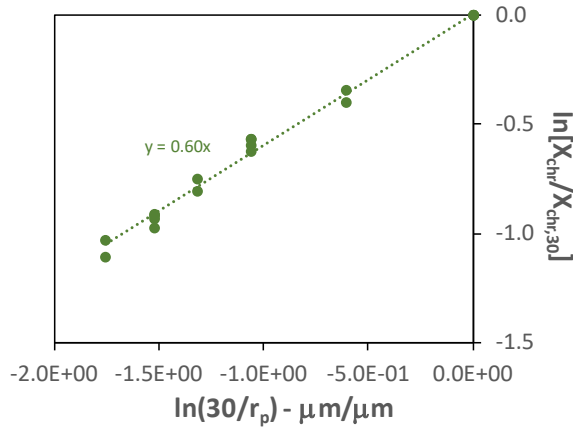


Figure 3.11. Determination of the parameter $n_{X_{chr},rp}$ considering the Eq. (3.13).

Table 3.3. Values of the parameters required to calculate X_{chr} .

$n_{X_{chr},rp}$	0.6	$a_{O_2,o}$	$2.127 \cdot 10^{-4}$		
$X_{chr,O_2,a}$	$8.351 \cdot 10^{-1}$	$a_{O_2,a}$	$4.28 \cdot 10^{-9}$	$b_{O_2,a}$ (m ³ mol ⁻¹)	$4.00 \cdot 10^1$
$X_{chr,O_2,b}$ (K)	-2073	$a_{O_2,b}$ (K)	11560	$b_{O_2,b}$ (K)	-3060

Finally, the goodness of the kinetic model with the determined kinetic parameters for the oxidation of FERELET MT material is checked. Thus, the kinetic model is described by Eqs. (3.1)-(3.8) considering two steps: first, controlled by chemical reaction, followed by a diffusion controlled second step. The model requires the determination of two kinetic constant, k_{chr} and D_{ef} , with the corresponding reaction orders n_{chr} and n_{dif} . In addition, the conversion at which the controlling step changes from chemical reaction to diffusion, X_{chr} , should also be determined. For that, the following procedure should be followed:

- Kinetic constant k_{chr} is calculated from Eq. (3.9) and parameters in Table 3.1.
- Diffusion coefficient, D_{ef} , is calculated from Eqs. (3.10)-(3.12) and parameters in Table 3.2.
- The value of X_{chr} is calculated from Eq. (3.13), which requires the application of the kinetic parameters in Table 3.3 in Eqs. (3.14)-(3.16).

This procedure allows the calculation of the kinetic parameters as a function of the reacting temperature, the oxygen concentration and the particle size. Then, the evolution of the conversion with the reacting time was predicted for the conditions used in the TGA tests, and compared to the experimental ones in Figures 3.2 and 3.3. In general, the developed model with the determined kinetic parameters accurately predicts the evolution of the conversion over time for different operating conditions and the two stages of the oxidation reaction.

3.4. Nomenclature for the oxidation kinetic

a_{O_2}	pre-exponential factor of the oxygen concentration dependence of X_{chr} (-)
$a_{O_2,o}$	correction factor to calculate the temperature dependence of the pre-exponential factor a_{O_2} (-)
$a_{O_2,a}$	pre-exponential factor to calculate the temperature dependence of the pre-exponential factor a_{O_2} (-)
$a_{O_2,b}$	exponential factor to calculate the temperature dependence of the pre-exponential factor a_{O_2} (K)
b_{O_2}	exponential factor of the oxygen concentration dependence of X_{chr} ($m^3 mol^{-1}$)
$b_{O_2,a}$	pre-exponential factor to calculate the temperature dependence of the exponential factor b_{O_2} ($m^3 mol^{-1}$)
$b_{O_2,b}$	exponential factor to calculate the temperature dependence of the exponential factor b_{O_2} (K)
C_{O_2}	oxygen concentration ($mol m^{-3}$)
D_{ef}	effective diffusion coefficient ($m^3 mol^{-1} s^{-1}$)
D_g	gas diffusion coefficient ($m^3 mol^{-1} s^{-1}$)
$D_{g,o}$	pre-exponential factor of the gas diffusion coefficient ($m^3 mol^{-1} s^{-1}$)
D_s	solid diffusion coefficient ($m^3 mol^{-1} s^{-1}$)
$D_{s,o}$	pre-exponential factor of the solid diffusion coefficient ($m^3 mol^{-1} s^{-1}$)
E_{chr}	activation energy of the chemical reaction constant (J/mol)
E_g	activation energy of the gas diffusion coefficient (J/mol)
E_s	activation energy of the solid diffusion coefficient (J/mol)
k_{chr}	chemical reaction constant ($m^3 mol^{-1} s^{-1}$)
$k_{chr,o}$	pre-exponential factor of the chemical reaction constant ($m^3 mol^{-1} s^{-1}$)
m	mass (kg)
n_{chr}	reaction order of the chemical reaction mechanism (-)
n_{dif}	reaction order of the diffusion mechanism (-)
$n_{D,rp}$	exponent for the particle size dependence of the diffusion coefficient (-)
$n_{k,rp}$	exponent for the particle size dependence of the chemical reaction constant (-)
$n_{X_{chr},rp}$	exponent for the particle size dependence of X_{chr} (-)
r_p	radius of the particle (μm)
R_g	ideal gas constant ($=8.314 J mol^{-1} K^{-1}$)

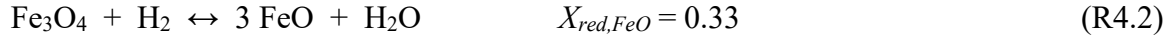
R_o	maximum oxygen gain (-)
t	time (s)
t_{chr}	time at which the reaction mechanism changes from Step I to Step II (s)
t_{dif}	time defined for the Step II controlled by diffusion in the particle (s)
T	temperature (K)
X	conversion (-)
X_{chr}	conversion at which the reaction mechanism changes from Step I to Step II (-)
X_{chr,O_2}	correction factor to calculate X_{chr} as a function of the oxygen concentration (-)
$X_{chr,O_2,a}$	pre-exponential factor for the temperature dependence of the correction factor X_{chr,O_2} (-)
$X_{chr,O_2,b}$	exponential factor for the temperature dependence of the correction factor X_{chr,O_2} (K)
X_{dif}	conversion defined for the Step II controlled by diffusion in the particle (-)

Symbols

τ_{chr}	characteristic time for the chemical reaction control (s)
τ_{dif}	characteristic time for the diffusion mechanism (s)

4. Determination of the reduction kinetics

The oxidized FERELET MT powder is used to evaluate the capability to be reduced with hydrogen. The fully oxidized iron oxide is in the form of Fe_2O_3 , which is able to be reduced to Fe by reaction with H_2 following a cascade reaction mechanism:



While the hydrogen consumption for the reduction to Fe_3O_4 is highly favoured, there is thermochemical constrictions in the subsequent reductions to FeO and Fe. The equilibrium constant for reactions (R4.2) and (R4.3) are calculated by Eqs. (4.1) and (4.2).

$$\ln(K_{\text{eq,Fe}_3\text{O}_4/\text{FeO}}) = \ln\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right) = 6.6567 - 6476.4\left(\frac{1}{T}\right) - 181141\left(\frac{1}{T}\right)^2 \quad (4.1)$$

$$\ln(K_{\text{eq,FeO/Fe}}) = \ln\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right) = 0.8513 - 1395.5\left(\frac{1}{T}\right) - 253791\left(\frac{1}{T}\right)^2 \quad (4.2)$$

Figure 4.1 shows the binary Baur-Glaessner diagram for the reduction of iron oxide with hydrogen. Above 860 K, a non-stoichiometric phase (Fe_{1-x}O , but FeO is here considered for stiochiometric simplicity) is stable, which allows the reduction of Fe_2O_3 following the scheme shown by reactions (R4.1)-(R4.3), namely $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Below this, Fe_{1-x}O is not stable and decomposes into iron and magnetite. Thus, the reduction proceeds avoiding the formation of Fe_{1-x}O ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$) and forming a new equilibrium between Fe_3O_4 and Fe; see reaction (R4.4) and Eq. (4.3).



$$\ln(K_{\text{eq,Fe}_3\text{O}_4/\text{Fe}}) = \ln\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right) = 1.5131 - 1394.9\left(\frac{1}{T}\right) - 745520\left(\frac{1}{T}\right)^2 \quad (4.3)$$

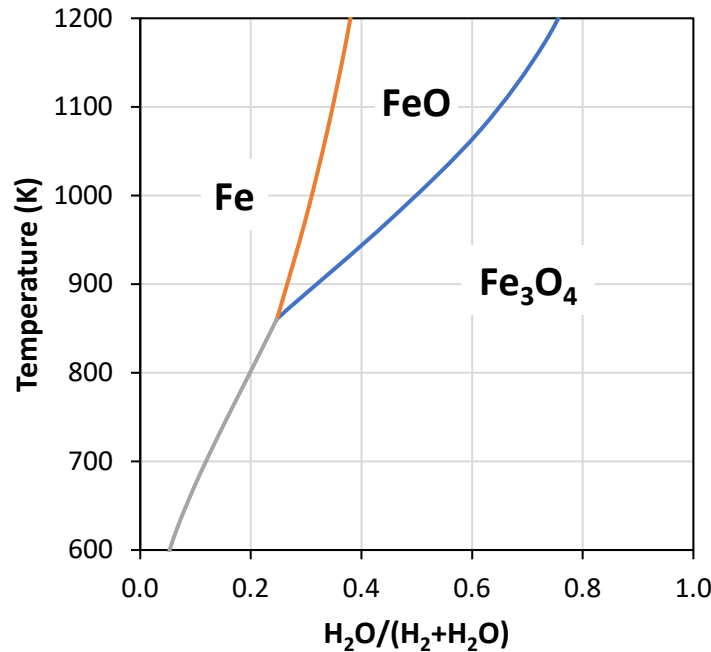


Figure 4.1. Baur-Glaessner diagram for the reduction of iron oxide with hydrogen.

Reduction to Fe is desired in order to maximize the energy storage capacity of the iron powder. From Figure 4.1, it can be deduced that the maximum conversion of H_2 to H_2O -which is limited by the thermochemical equilibrium- increases with temperature. However, supporting the endothermic iron reduction at high temperature requires energy expenditure. But for the purposes of this study, the appropriate temperature range will be evaluated through a study of its reactivity and reaction capacity.

Figure 4.2(a) shows an example of the effect of temperature on the reduction process. The reduction rate increased with the temperature from 723 to 823 K, achieving complete conversion assuming the maximum theoretical capability of the FERELET MT powder; as calculated from Eq. (2.3). This fact confirms that the iron powder in the 40-80 μm size interval was completely converted during the preliminary oxidation process in the batch fluidized bed reactor. However, the conversion was limited to 70 % at 873 K, likely due to some sintering effect. The higher temperature or the presence of FeO as an intermediate in the reduction process may have caused this behaviour. Thus, the active iron content was limited to 70% at 873 K, and such high temperatures may not be advisable for the reduction process. Nevertheless, relevant information may be obtained by comparing the reduction progress in this temperature interval. Therefore, the conversion vs. time curves obtained at 873 K were also used for the kinetic determination, but they were modified in order to use curves with the conversion ranging from 0 to 1; see Figure 4.2(b).

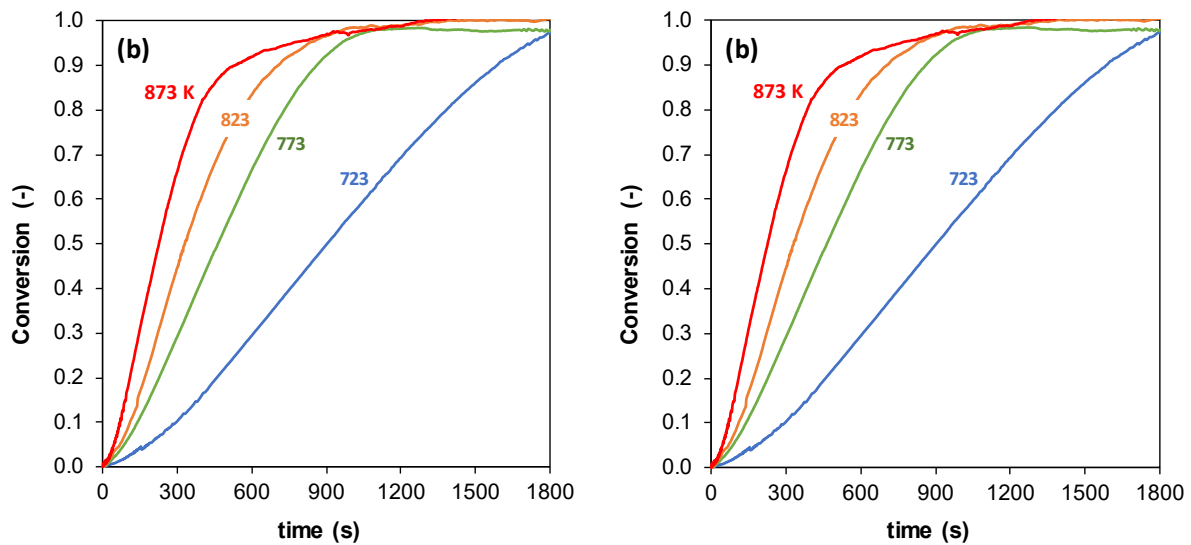


Figure 4.2. Conversion vs. time curves for the reduction of oxidized FERELET MT at different temperatures: (a) curves assuming 100% iron active; (b) modified curve for 873 K, assuming 70% iron active at this temperature. Conditions: $d_p = 40-80 \mu m$; 15 % H_2 ; 0 % H_2O .

Another feature of the reduction process observed in Figure 4.2 is a characteristic S-shaped conversion curve, with an increase in the reaction rate at the beginning of the reduction, reaching a maximum in intermediate conversions, and finally decreasing again at the end of the reduction. This behaviour may be caused by several phenomena, namely:

- Relevance of a nucleation process on the iron oxide sites at the beginning of the reaction.
- An increase in the particle porosity due to a molar volume reduction in the solid.

- c) Several consecutive reactions, e.g. following the reacting scheme (R4.1), (R4.2) and (R4.3).

This shape of the conversion vs. time curves should be predicted by the kinetic model. Table 4.1 shows different models predicting the S-shaped curve.

Table 4.1. Reaction models following a S-shaped conversion curve and the corresponding algebraic differential and integral expressions.

Reaction model	Differential form (rate)	Integrated Eq.
2D nuclei (Avrami-Erofe'ev n=2)	$2(1 - X)[-ln(1 - X)]^{1/2}$	$kt = [-ln(1 - X)]^{1/2}$
3D nuclei (Avrami-Erofe'ev n=3)	$3(1 - X)[-ln(1 - X)]^{2/3}$	$kt = [-ln(1 - X)]^{1/3}$
3D diffusion (Jander)	$6kt[1 - (kt)^2]^2$	$kt = [1 - (1 - X)^{1/3}]^{1/2}$
Austin-Rickett	$2X^{1/2}(1 - X)^{3/2}$	$kt = \left(\frac{X}{1 - X}\right)^{1/2}$

Among these equations, the 2D nuclei and 3D diffusion are the models that best fit the curvature of the evolution of conversion over time for the reduction of FERELET MT with hydrogen. The most suitable model to be used in modeling tasks may be related to avoiding some numeric issues during its implementation. For example, 3D diffusion is a simple expression, but it can offer conversion values over 1, which should be avoided during the computing calculation. This issue is avoided using the 2D nuclei expression, but it must manage very high numbers if the conversion is calculated from time. Thus, this expression includes an exponential equation ($X = 1 - e^{-(kt)^2}$), which could not be computed for high values of the exponent.

However, despite all of the above, this analysis does not allow us to determine the possibility of a combined reaction mechanism involving reactions (R4.1), (R4.2), (R4.3) and/or (R4.4). For that, the effect of the hydrogen and steam concentration on the reduction reaction should be evaluated. Figure 4.3 shows the conversion curves for different H₂ concentration values. As expected, the reduction rate increases with the H₂ concentration. Again, the characteristic S-shaped curve can be observed for any hydrogen concentration used, although it is less noticeable as it increases. Therefore, the previously selected models remain valid for capturing the evolution of the reduction conversion over time. But no conclusions can be drawn about the mechanism during the reduction either.

Additional information may be obtained from Figures 4.4, which show the effect of the steam concentration on the reduction process at 873 and 823 K. Steam is the combustion product when iron oxide is reduced by H₂, and it is expected to decrease the reduction rate in reactions where the equilibrium between H₂ and H₂O is relevant, namely reactions (4.2), (4.3) and (4.4).

At 873 K three stages can be clearly observed, which approximately corresponds to the conversion values for each reduction step according Figure 4.1; see (R4.1), (4.2) and (4.3). The first part of the reaction is mainly related to the reduction of Fe₂O₃ to Fe₃O₄, which is not

affected by the steam concentration. Then, the reduction of Fe_3O_4 to FeO appears with a decreased reduction rate as the steam concentration increases due to the addition of the product compound in reaction (R4.2) and whose progress is limited by the value of the equilibrium constant $K_{eq, \text{Fe}_3\text{O}_4/\text{FeO}}$. After that, the reduction to Fe proceeds until reaction is completed. This last step is highly affected by the steam concentration due to the lower value of equilibrium constant $K_{eq, \text{FeO}/\text{Fe}}$.

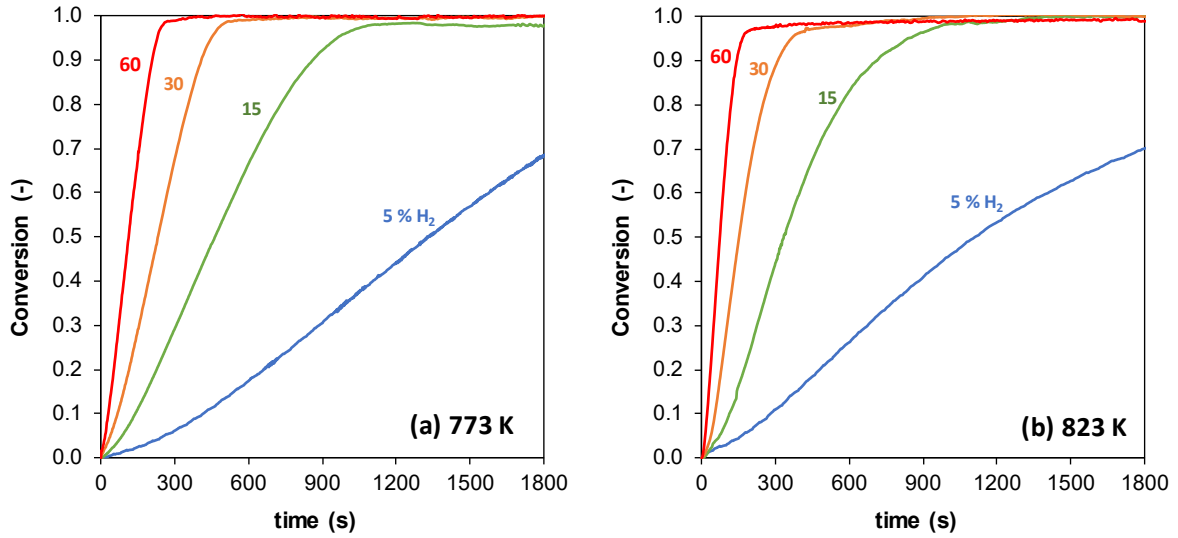


Figure 4.3. Conversion vs. time curves for the reduction of oxidized FERELET MT with different H_2 concentration. Conditions: $d_p = 40\text{--}80 \mu\text{m}$; 0 % H_2O .

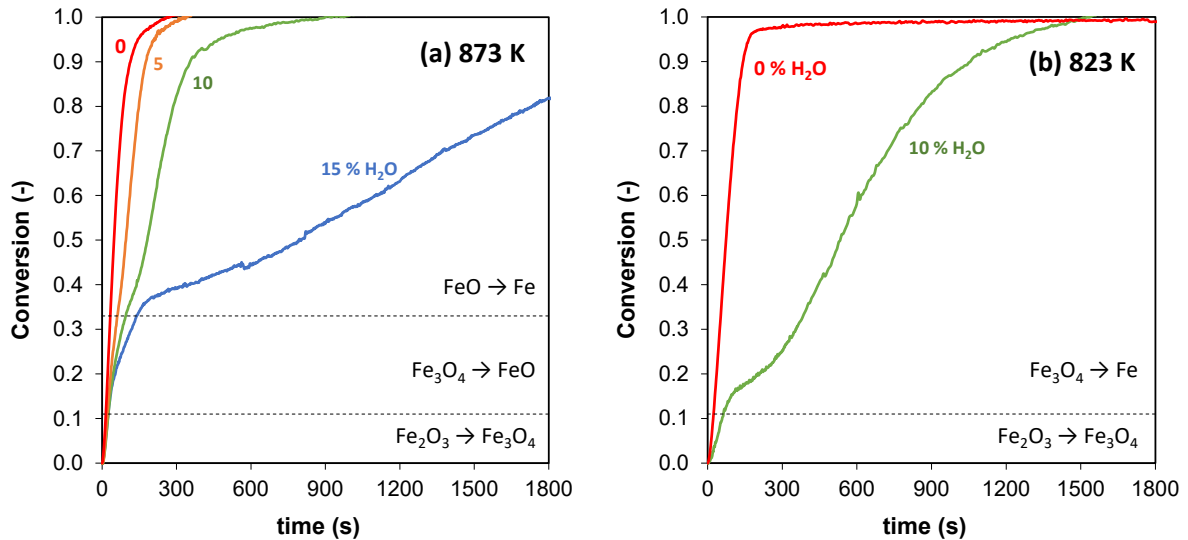


Figure 4.4. Conversion vs. time curves for the reduction of oxidized FERELET MT with different steam concentration. Conditions: $d_p = 40\text{--}80 \mu\text{m}$; 60 % H_2 ; (a) $T = 873 \text{ K}$ and (b) $T = 823 \text{ K}$.

The reduction at 823 K is also affected by the steam concentration, but some relevant differences are found compared to the reduction at 873 K. Thus, only two steps can be clearly identified, which is in agreement with the reduction mechanism described by reactions (R4.1)

and (4.4) according to Figure 4.1, namely $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$. In addition, the effect of the steam concentration is evidenced from the beginning of the reaction. This fact suggest that reduction of Fe_3O_4 -(R4.4) affected by steam concentration- happens simultaneously to reduction of Fe_2O_3 to Fe_3O_4 by (R4.1) as Fe_3O_4 is being generated.

FERELET MT is supplied with a PSD ranging from ca. 60-500 μm with the main particle size being about 200 μm . The analysis shown above was carried out using small particle size (40-80 μm) in order to minimize diffusional effects that could affect the determination of the intrinsic kinetics. Now, the reduction rate as a function of the particle size is determined, which will be required for the modeling tasks. Figure 4.5 shows the conversion curves at 773 K for samples with different particle size. Final conversion values close to the unity are achieved in all the cases, meaning that oxidized FERELET MT particles can be easily reduced to iron regardless the particle size, as well as the preparation method to obtain oxidized particles allowed the complete oxidation in the batch fluidized bed reactor.

In addition, the characteristic S-shape is maintained regardless the particle size, indicating that the same reaction model may be applied for the entire PSD of the iron powder. However, a sligh decrease in the reaction rate is observed as the particle size increased, mainly in the second part of the reaction.

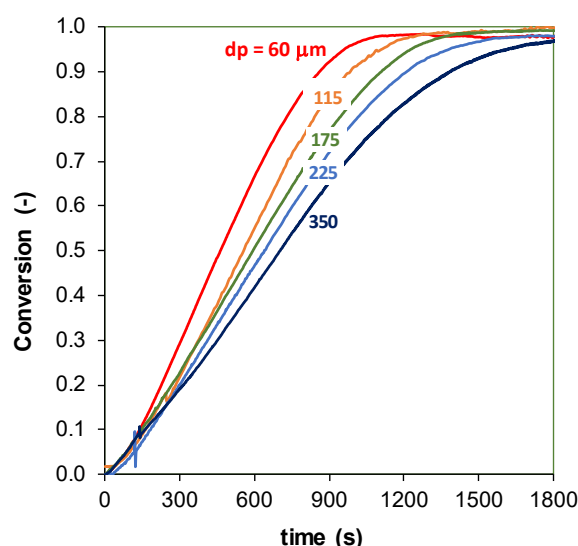


Figure 4.5. Conversion vs. time curves for the reduction of oxidized FERELET MT with different particle size. Conditions: $T=773$ K; 60 % H_2 ; 0 % H_2O .

4.1. The reduction kinetic model

Before proposing a suitable model for determining the kinetics, it is necessary to elucidate the reaction mechanism. Taking into account the sequence of reactions described by (R4.1), (R4.2), (R4.3) and/or (R4.4), two cases can be considered depending on the behavior of the intermediate compounds:

- a) Sequential reaction: only one reaction occurs at a time, and the next step does not begin until the previous one has finished. Thus, intermediate products such as Fe_3O_4 or FeO does not react until the reaction by which it is being formed has finished.

- b) Simultaneous reaction: all the reactions may happen simultaneously as the intermediate reactants are produced by previous steps.

Previous observation regarding the effect of steam at 823 K from the beginning of the reduction support the hypothesis of simultaneous reaction. This difference was not observed at 873 K, but it may be due to a lesser effect of steam during the second stage of reduction; see Figures 4.4. However, the changes in the reaction rates in these figures are observed at some higher conversion values than that expected from the consecutive mechanism. This fact suggests that some simultaneous reductions must happen, supporting the hypothesis of simultaneous reaction.

According to the simultaneous reaction mechanism, the global reaction rate (or conversion) are calculated as the addition of the individual reaction rates (or conversion) for each step. In general, the following equations are used:

$$\frac{dX}{dt} = \Delta X_I \frac{dX_1}{dt} + \Delta X_{II} \frac{dX_2}{dt} + \Delta X_{III} \frac{dX_3}{dt} \quad (4.4)$$

$$X = \Delta X_I X_1 + \Delta X_{II} X_2 + \Delta X_{III} X_3 \quad (4.5)$$

ΔX_I , ΔX_{II} and ΔX_{III} are the variation in the global conversion corresponding the the stages I, II and III, calculated by:

$$\Delta X_I = X_{red, Fe_3O_4} = 0.11 \quad (4.6)$$

$$\Delta X_{II} = X_{red, FeO} - X_{red, Fe_3O_4} = 0.22 \quad (4.7)$$

$$\Delta X_{III} = X_{red, Fe} - X_{red, FeO} = 0.67 \quad (4.8)$$

In the case that only two steps are considered, steps II and III may be lumped into only one step.

X_I , X_2 and X_3 are the individual conversion values for steps I, II and III, respectively. These conversion values may be calculated with Eq. (2.3) but using the corresponding R_{red} value for each step, namely $R_{red,1}=0.033$, $R_{red,2}=0.066$ and $R_{red,3}=0.201$. Anyway, only the experimental global conversion (X) was calculated, but X_I , X_2 and X_3 were used in the theoretical model to calculate X from Eq. (4.5). The conversion for each step is calculated by selecting a suitable reaction model from Table 4.1. In this case, two reaction models have been selected, namely:

- 2D nuclei: $k_{c,i}t = [-\ln(1 - X_i)]^{1/2} \quad (4.9)$

- 3D diffusion: $k_{c,i}t = [1 - (1 - X_i)^{1/3}]^{1/2} \quad (4.10)$

In this project, different models will be developed, which may present differences in the implementation of reaction kinetics. As explained above, each kinetic model has some numeric issues that must be addressed during its implementation. For this reason, the reduction kinetics are determined for both models (2D nuclei and 3D diffusion) so that the most suitable one can be chosen for its implementation in the reactor model developed for each partner.

$k_{c,i}$ is a global apparent kinetic constant for the step i , and it contains the effect of the reaction temperature, as well as the hydrogen and steam concentration. This kinetic constant is defined by the following equation:

$$k_{c,i} = k_i C_{H_2}^n \left(1 - \frac{C_{H_2O}}{C_{H_2} K_{eq,i}} \right)^s \quad (4.11)$$

For the step I, namely Fe_2O_3 reduction to Fe_3O_4 is assumed that $1 \gg \frac{C_{H_2O}}{C_{H_2} K_{eq,i}}$.

At $T > 860$ K, two additional steps are considered. Thus, $K_{eq,i}$ is the equilibrium constant for steps II or III, -i.e. reactions (R4.2) or (R4.3)- and calculated by Eqs. (4.1) or (4.2), respectively. At $T < 860$ K, only one additional step is assumed, and $K_{eq,i}$ is the equilibrium constant for the direct reduction of Fe_3O_4 to Fe, namely reaction (R4.4), and calculated by Eq. (4.3).

The apparent kinetic constant, k_i , is assumed to have an Arrhenius dependence with temperature.

$$k_i = k_{0,i} e^{-E_{a,i}/R_g T} \quad (4.12)$$

4.2. Determination of the kinetic parameters

The kinetic model described by either Eq.(4.9) or Eq.(4.10) is used to fit each individual conversion curve for different operating condition. In this way, a value for the global apparent kinetic constant for each step i , $k_{c,i}$, is determined according to the operating condition, including different particle size, reacting temperature, and H_2 or H_2O concentration.

The reaction order with the hydrogen concentration $-n$ in Eq. (4.11)- is calculated for tests performed using different H_2 concentration values and without addition of steam to the reaction gas mixture. Interestingly, the same $k_{c,i}$ value was determined for steps II and III at 873 K, suggesting that the Fe_3O_4 reduction may be assumed to happen in only one step to Fe in the absence of steam. Linearizing Eq.(4.11) leads to the representation of the Figure 4.6, with the slopes being the reaction order n and compiled in Table 4.2.

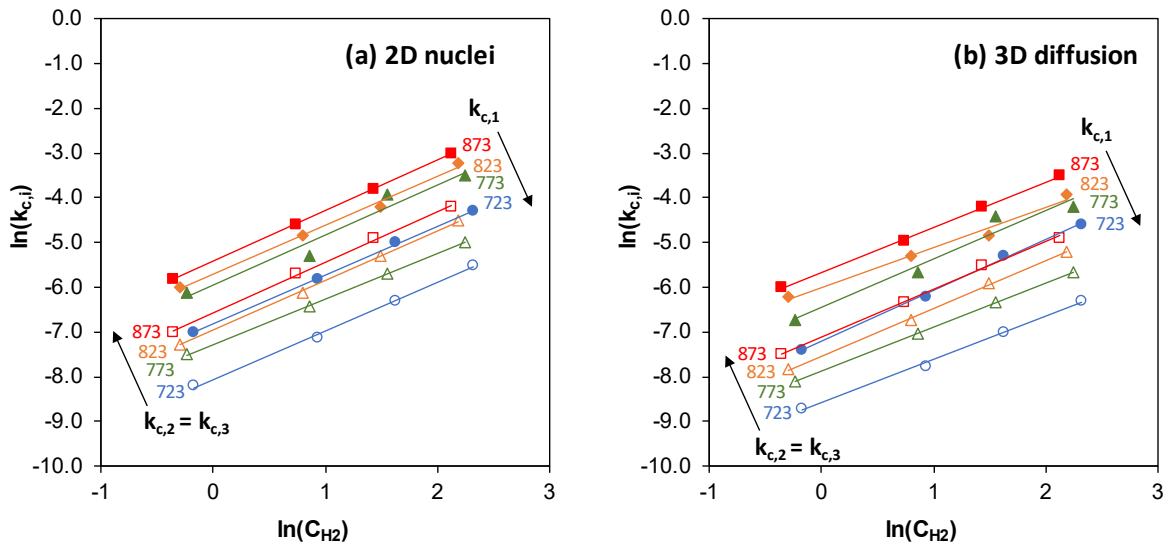


Figure 4.6. Plot of $\ln(k_{c,i})$ vs $\ln(C_{\text{H}_2})$ to determine the reaction order with respect to H_2 of the different steps involving the reduction reaction at different temperatures: (a) 2D nuclei model; (b) 3D diffusion model. Conditions: $d_p = 40\text{-}80 \mu\text{m}$; 0 % H_2O .

The apparent kinetic constant, k_i , is calculated from the intercept of the fitting shown in Figure 4.6, being obtained for the temperatures used in this work, i.e. from 723 to 873 K. Using these values, Figure 4.7 shows the Arrhenius plot to determine the activation energy, $E_{a,i}$, and the pre-exponential factor, $k_{0,i}$, of the apparent kinetic constant k_i ; see Eq. (4.12). The calculated values are shown in Table 4.2. In addition, these values were determined from the calculated $k_{c,i}$ values. As these values were identical for steps II and III, both $E_{a,i}$ and $k_{0,i}$ take also the same values for these steps. Note that steps I, II and III are only relevant at $T > 860$ K, while only the steps I and II are applicable at lower temperatures.

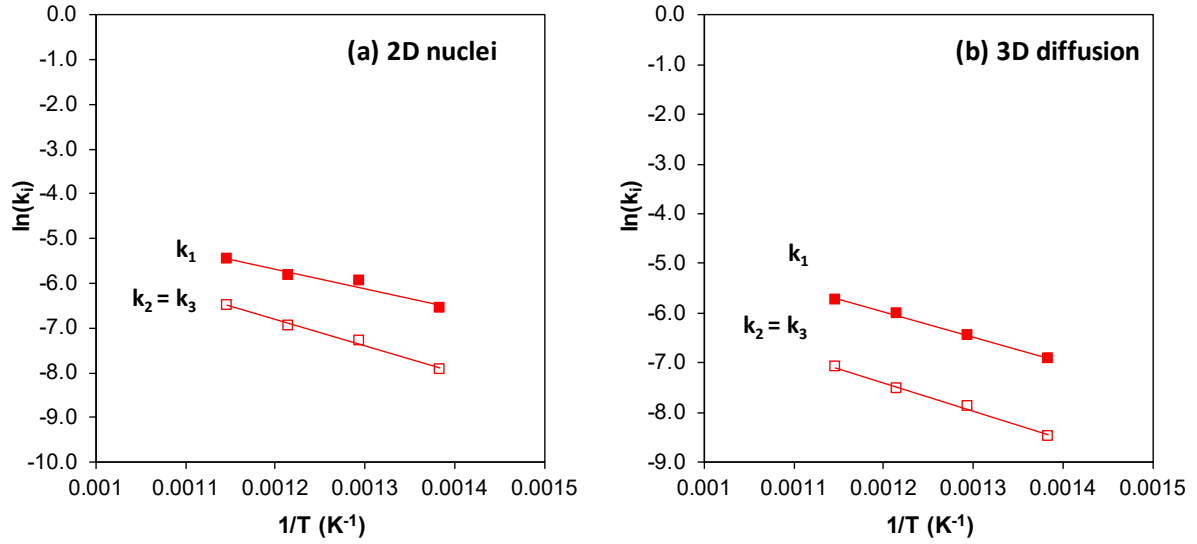


Figure 4.7. Arrhenius plot: $\ln(k_i)$ vs $1/T$ to determine the activation energy and pre-exponential factor following Eq. (4.12): (a) 2D nuclei model; (b) 3D diffusion model. Conditions: $d_p = 40\text{--}80\ \mu\text{m}$; 0 % H_2O .

In fact, the differences found between steps II and III at $T > 860\ \text{K}$ are mainly due to the different equilibrium constant for reactions (R4.2) and (R4.3), which is revealed in the presence of steam. Eq. (4.11) shows the dependence between the determined $k_{c,i}$ values and the steam concentration. Linearizing Eq.(4.11) leads to the representation of the Figure 4.8, with the slopes being the reaction order s for the term that includes the effect of steam concentration, being compiled in Table 4.2.

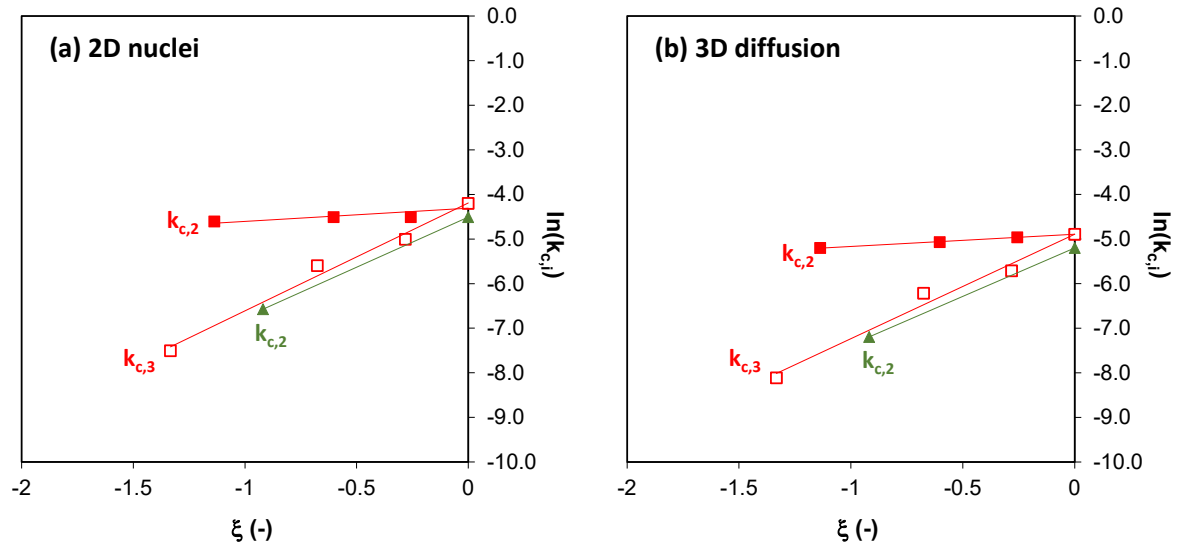


Figure 4.8. Plot of $\ln(k_{c,i})$ vs $\ln(\xi)$ [$\xi = 1 - \frac{C_{\text{H}_2\text{O}}}{C_{\text{H}_2} K_{eq,i}}$ from Eq. (4.11)] to evaluate the effect of the steam concentration on the reduction rate of FERELET MT powder: (a) 2D nuclei model; (b) 3D diffusion model. Conditions: $d_p = 40\text{--}80\ \mu\text{m}$; 60 % H_2 ; red squares: 873 K, green triangles: 823 K.

Finally, the effect of the particle size on the reduction rate was included in the reaction model. For that, it was assumed the dependence of the apparent kinetic constant with the particle size follows the expression shown in Eq. (4.13).

$$k_{c,i}|_{r_p} = k_{c,i}|_{r_p=30} \left(\frac{30}{r_p}\right)^r \quad (4.13)$$

Figure 4.9 shows the fitted data of $k_{c,i}$ for different particle size values following the dependence defined by Eq. (4.13), both for step I and II at 773 K. It was found that the particle size has not a relevant effect on the reduction rate during the step I (i.e. $k_{c,1}$). Thus, this effect was revealed only during the step II ($k_{c,2}$), although the exponent r was quite low (see Table 4.2), in agreement to the relatively low effect of the particle size on the reduction rate shown in Figure 4.5.

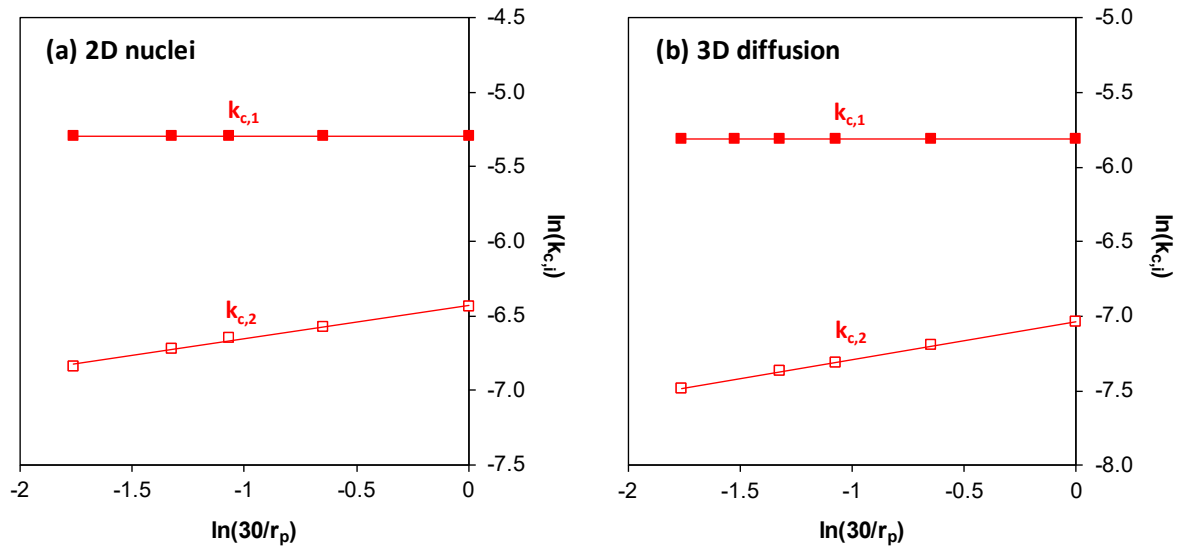


Figure 4.9. Plot of $\ln(k_{c,i})$ vs $\ln(30/r_p)$ –linearization of Eq. (4.13)- to evaluate the effect of the particle size on the reduction rate of FERELET MT powder: (a) 2D nuclei model; (b) 3D diffusion model.

Table 4.2 compiles the kinetic parameters for the reduction models selected in this work, namely 2D nuclei and 3D diffusion. The use of the 2D nuclei model allows for a better fit than the 3D diffusion. However, depending on how the 2D nuclei is implemented in the reactor models, it could generate numerical problems in the computation of reaction rates or conversion values. Thus, both models have been included so a suitable reaction kinetic can be selected in the modeling tasks. The mathematical model summarizing all the parameters affecting the reduction rate is shown in Eqs. (4.14) and (4.15) for the 2D nuclei or 3D diffusion models, together Eq. (4.16) to calculate the global apparent kinetic constant, $k_{c,i}$, for each reduction step.

$$\circ \text{ 2D nuclei:} \quad X = \sum_{i=I,II,III} \left\{ \Delta X_i \left[1 - e^{-(k_{c,i}t)^2} \right] \right\} \quad (4.14)$$

$$\circ \text{ 3D diffusion:} \quad X = \sum_{i=I,II,III} \left\{ \Delta X_i \left[1 - \left(1 - (k_{c,i}t)^2 \right)^3 \right] \right\} \quad (4.15)$$

$$k_{c,i} = k_{i,0} e^{-E_{a,i}/R_g T} C_{H_2}^n \left(1 - \frac{C_{H_2O}}{C_{H_2} K_{eq,i}} \right)^s \left(\frac{30}{r_p} \right)^r \quad (4.16)$$

Table 4.2. Kinetic parameters for the reduction reaction of FERET MT powder according to the 2D nuclei and the 3D diffusion reaction models.

Reaction model	2D nuclei			3D diffusion		
Step	I	II	III	I	II	III
Active Fe T<860 K	100%	100%	100%	100%	100%	100%
Active Fe T>860 K	70%	70%	70%	70%	70%	70%
n (-)	1.1	1.1	1.1	1.0	1.0	1.0
k_0 ($\text{m}^{3n} \text{mol}^{-n} \text{s}^{-1}$)	0.58	1.35	1.35	1.10	0.58	0.58
E_a (kJ/mol)	35.6	49.2	49.2	42.1	47.5	47.5
s (-) T<860 K	-	2.2	-	-	2.2	-
s (-) T>860 K	-	0.3	2.4	-	0.3	2.3
K_{eq} (-) T<860 K	-	Eq. (4.3)	-	-	Eq. (4.3)	-
K_{eq} (-) T>860 K	-	Eq. (4.1)	Eq. (4.2)	-	Eq. (4.1)	Eq. (4.2)
r	0	0.23	0.23	0	0.25	0.25

The theoretical conversion vs. time curves can be calculated for each reaction model (3D diffusion or 2D nuclei) using the kinetic parameters in Table 4.2. Predicted curves for different operating conditions (temperature, H_2 concentration, H_2O concentration and particle size) are compared to experimental curves obtained in TGA tests in Figure 4.10. In general, both reaction models show good predictions, capturing the effect of the operating conditions on the reduction rate, as well as the characteristic S-shape of the curves. In this regard, it should be mentioned that the evolution of the conversion is highly sensitive to the variation of the kinetic constant, especially for the last stage of reduction to Fe.

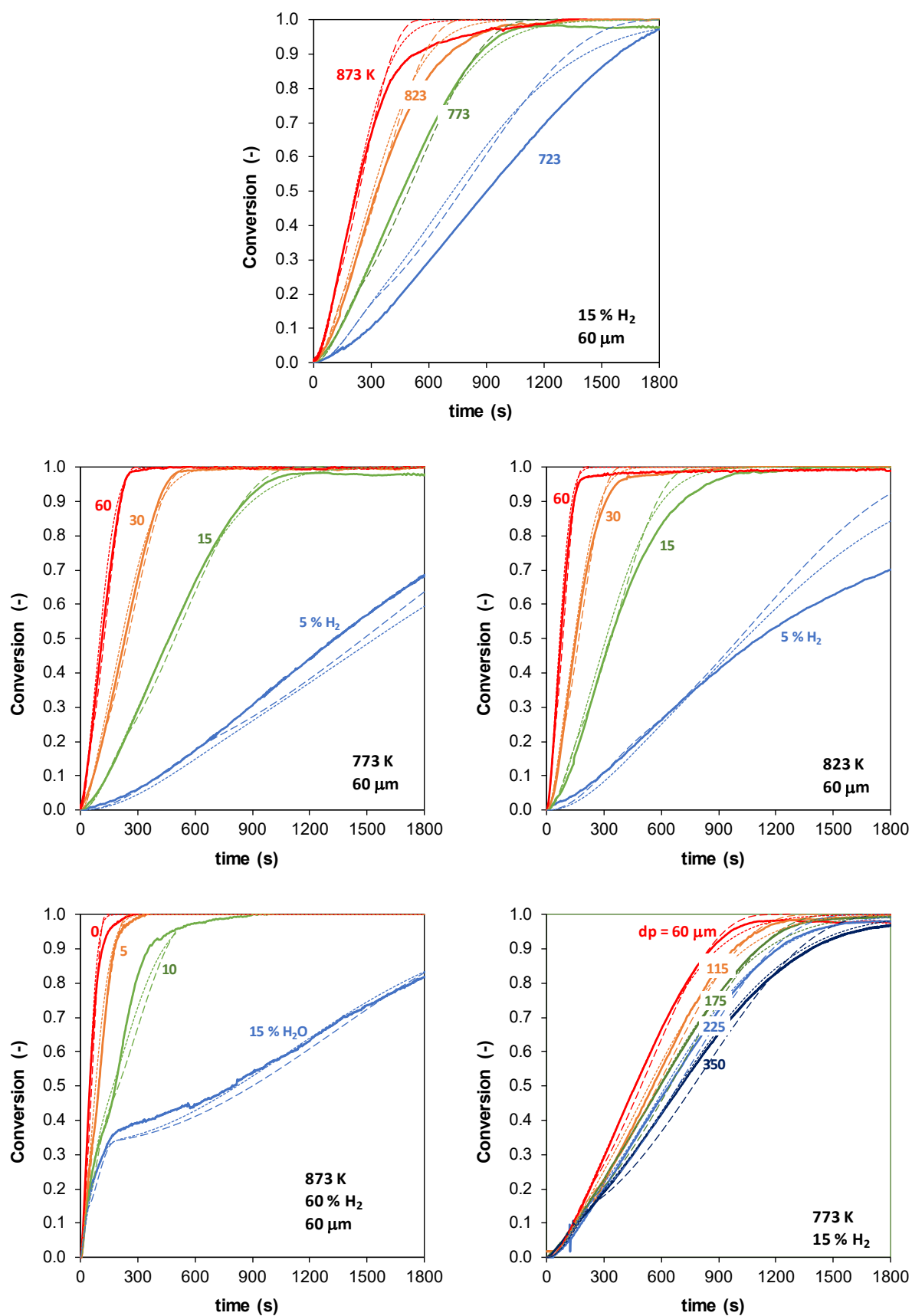


Figure 4.10. Comparison between conversion vs. time curves experimentally obtained in TGA tests (continuous lines) with model predictions with the 3D diffusion model (broken lines) and the 2D nuclei model (dotted lines) using the kinetics parameters in Table 4.2.

4.3. Nomenclature for the oxidation kinetic

C_{H_2}	hydrogen concentration (mol m ⁻³)
C_{H_2O}	steam concentration (mol m ⁻³)
d_p	particle diameter (μm)
$E_{a,i}$	activation energy of the apparent chemical reaction constant of reaction i (J/mol)
$k_{c,i}$	global apparent kinetic constant (s ⁻¹)
k_i	apparent kinetic constant for step i (m ³ mol ⁻¹ s ⁻¹)
$k_{0,i}$	pre-exponential factor of the apparent kinetic constant for step i (m ³ mol ⁻¹ s ⁻¹)
$K_{eq,i}$	equilibrium constant between H ₂ O and H ₂ for the redox pair i (-)
n	reaction order for H ₂ (-)
P_i	partial pressure of gas i (atm)
r	exponent in the term regarding the effect of particle size in Eq. (4.13) (-)
r_p	radius of the particle (μm)
R_g	ideal gas constant (=8.314 J mol ⁻¹ K ⁻¹)
s	reaction order for the term including the effect of H ₂ O on the reduction rate (-)
t	time (s)
T	temperature (K)
X	conversion (-)
X_i	conversion defined for the step i (-)
$X_{red,i}$	conversion at which Fe ₂ O ₃ is fully reduced to the compound i (-)

Symbols

ΔX_i	conversion variation corresponding to the full reaction corresponding to the step i (s)
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5. Conclusions

The kinetic models for the oxidation and reduction reactions of FERET MT powder has been developed. The main operating conditions have been evaluated, including the reacting temperature, gaseous reactant concentration (O_2 for oxidation and H_2 for reduction), and particle size, as well as the effect of steam on the reduction rate.

During the oxidation process, two steps have been identified, but they were not related to the oxidation of different iron oxides as intermediate products. Therefore, the oxidation kinetics was determined for the global oxidation from Fe to Fe_2O_3 . Every step was characterized by a different limiting mechanism during the oxidation process: first, a fast reaction controlled by chemical reaction, followed by a slow reaction controlled by diffusion in the particle. Both processes were highly affected by the reacting temperature and the particle size of the iron powder.

The reduction proceeds accordingly to the thermodynamic properties of the iron oxides. A first step involving the reduction of Fe_2O_3 to Fe_3O_4 was identified regardless the operating conditions. However, subsequent reduction of Fe_3O_4 was affected by the reacting temperature and the steam concentration. At temperatures below to 860 K, Fe_3O_4 is directly reduced to Fe, while an additional step involving FeO as an intermediate product was found at higher temperature. In any case, the reduction of Fe_3O_4 was negatively affected by the presence of steam, in accordance with the thermochemical equilibrium. The particle size of the iron powder showed a limited effect on the reduction rate. The conversion curves showed a characteristic S-shape. The kinetic parameters were calculated for two reaction models, namely 2D nuclei and 3D diffusion.

The models, with the calculated kinetic parameters, are able to predict the evolution of the oxidation and reduction conversion as a function of the operating conditions.