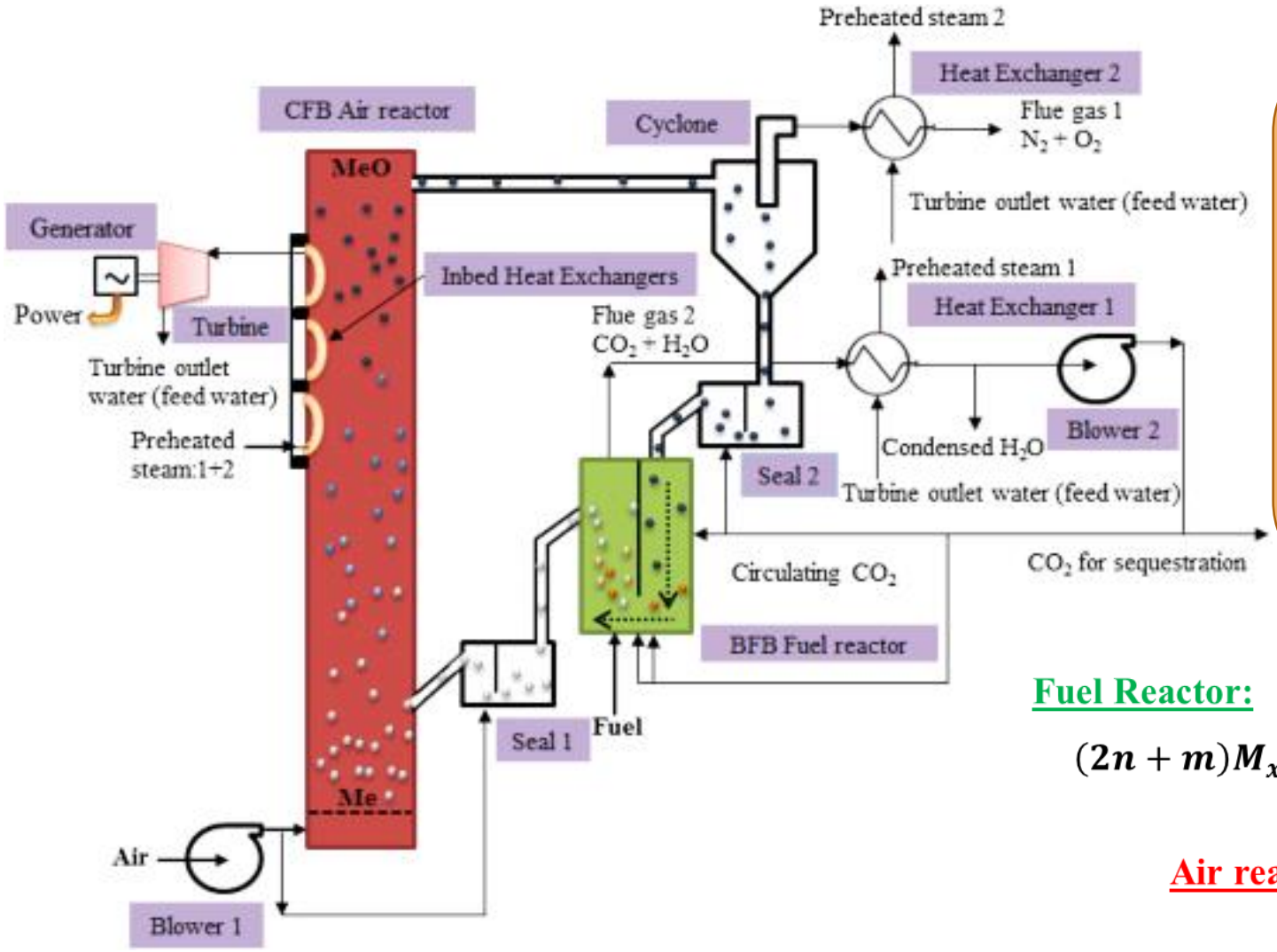
REDUCTION KINETIC STUDIES OF INDIAN ILMENITE AS OXYGEN CARRIER FOR CHEMICAL LOOPING COMBUSTION

Prabakaran V, Jayanti S
Department of Chemical Engineering &
National Centre for Combustion Research and Development
Indian Institute of Technology Madras, India.

Chemical Looping Combustion



Key parameters for the design, optimization and scale up…

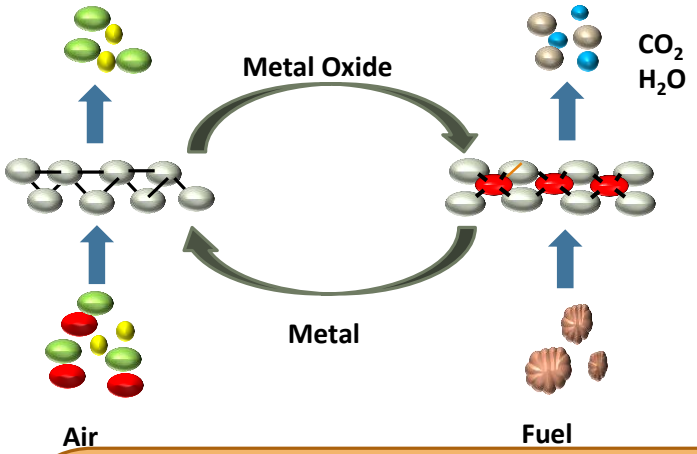
- ✓Selection of oxygen carriers
- ✓Kinetics of redox reactions
- ✓Reactor design
- ✓Energy integration
- ✓Gas cleaning etc.,

Fuel Reactor:

$$(2n+m)M_xO_y + C_nH_{2m} \rightarrow (2n+m)M_xO_{y-1} + mH_2O + nCO_2$$

Air reactor: $M_xO_{y-1} + 1/2O_2 \rightarrow M_xO_y$

Oxygen Carriers



Selection of OC's based on…

- ✓**Composition and density**
- ✓**Oxygen carrying capacity (high reactivity)**
- ✓**Fluidization properties**
- ✓**Economic viability**
- ✓**Chemical and thermal degradation etc.,**

Properties	Oxygen Carriers	
	Synthetic OCs	Natural Ores
Cost of preparation		+ +
Availability	-	+ +
Reactivity	+ +	-
Health effects	-	+ +
Stability	-	++
Fluidization properties	++	++

- ✓ **Synthetic OCs:** NiO, CuO, Fe_2O_3, Mn_3O_4 etc., with Al_2O_3, SiO_2, TiO_2 or ZrO_2 supports.
- ✓ **Natural ores:** Ilmenite, hematite, magnetite etc.,

Kinetics of Redox Reactions

- **The key parameters for the design, optimization and scale-up of a CLC system is the kinetics of redox reaction.**
- **It depends on the reactivity of the oxygen carrier material and its morphology and the concentration of fuel gases.**
- **The important aspect of the redox reactions in the CLC system is that the OC must be fully converted in the fuel reactor and be regenerated in the air reactor.**
- **On the fuel side, the fuel gas must be fully oxidized so as not to waste fuel.**
- **Reflecting these requirements, the kinetics of the reduction has been studied with different temperatures and concentration of gases.**

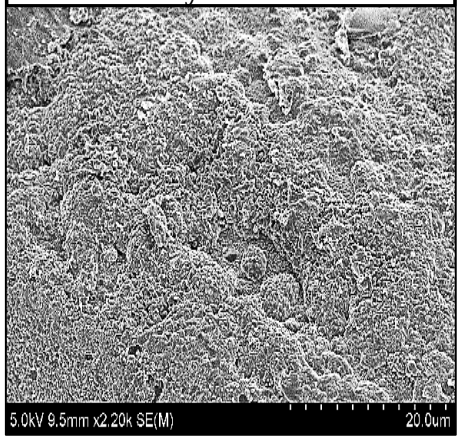
Objectives

- **To select natural ore (Indian Ilmenite) as an oxygen carrier for CLC system**
- **Characterization of OCs (SEM, EDX and XRD)**
- **To analyze the reactivity of Indian ilmenite ore in TGA analyzer**
- **To find a kinetic model for both low and high concentration of CO**

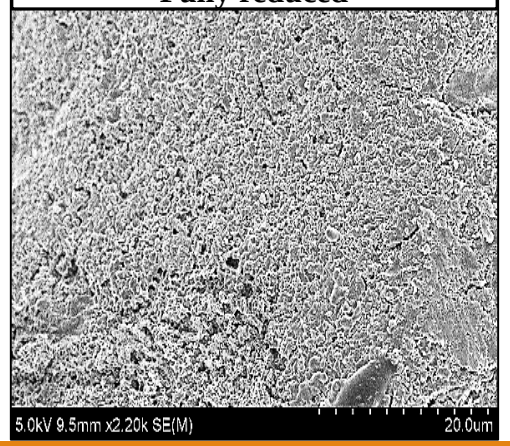
Indian Ilmenite

Calcined ilmenite

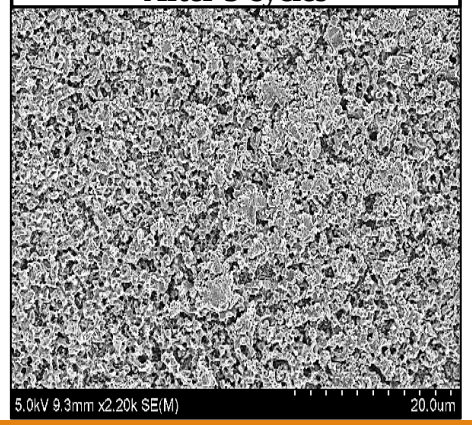
Fully Oxidized



Fully reduced



After 5 cycles



✓**It was calcined at 950 ºC in the presence of air for about 12 hours**

✓**XRD results show that the calcined ilmenite is mainly composed of Fe_2TiO_5 and TiO_2**

✓**The chemical composition was analyzed by EDX results**.

Chemical Composition (weight %)	SR Minerals South India
Fe_2O_3	51.70
SiO_2	5.09
Al_2O_3	7.16
TiO_2	30.72
CaO	1.2
MgO	1.76
Others	2.37

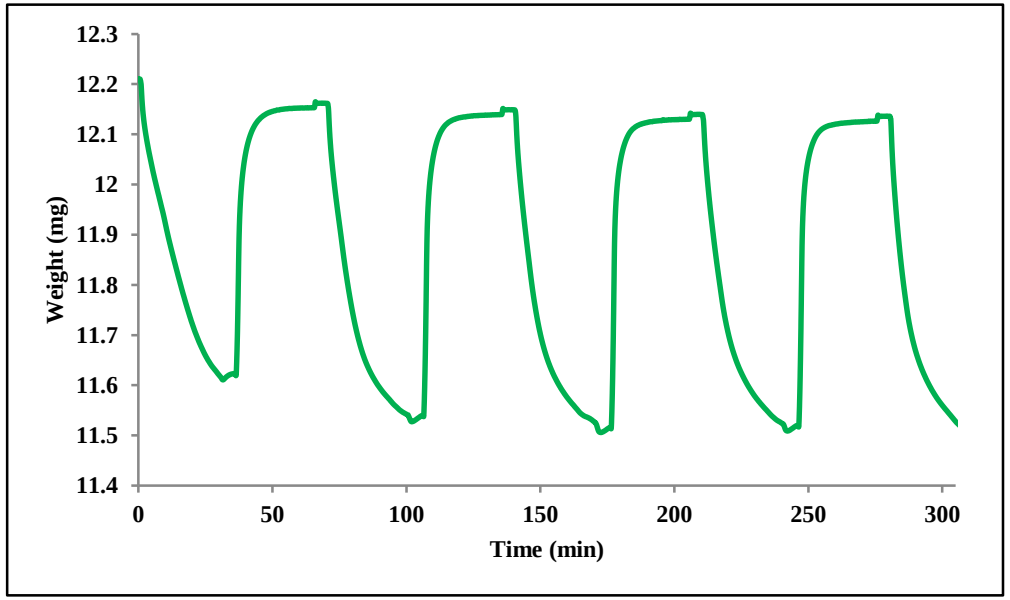
TGA Experiments

- ✓The redox cycles testing of ilmenite particles were performed in TGA analyzer (SDT Q600)
- ✓Weight of sample: 10-15 mg
- ✓Heating rate : 25 °C/min
- ✓Particle size : 100 microns
- ✓Number of cycles : 5
- ✓Purging gas : N_2

% Molar concentration of CO (diluted with N_2)	Temperature (°C)			
	850	900	950	1000
10			*	
15			*	
20			*	
30	*	*	*	*

Oxygen Transport Capacity

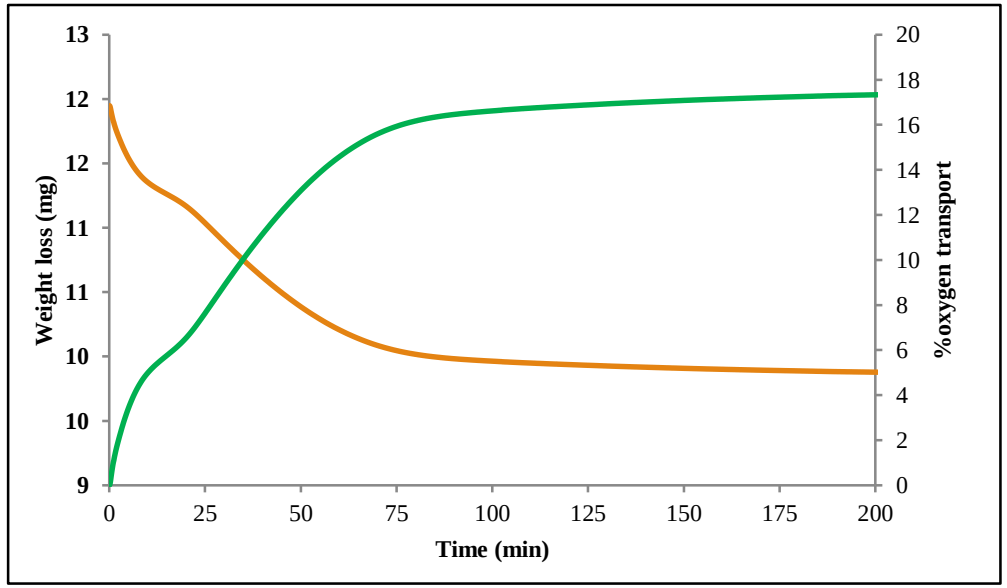
- ✓ The mass loss curves obtained in the TGA at 950 ºC and 30% of CO.
- ✓ The mean value of fourth and fifth cycle data has been taken for kinetic studies.



- ✓ The calcined ilmenite was completely reduced by CO gas (30% CO) at 950 ºC in TGA for about 200 minutes
- ✓ The oxygen transport capacity,

$$Ro = \frac{m_0 - m_r}{m_0}$$

- ✓ The oxygen transport capacity of about 5.74%
- ✓ Possible reaction: Fe_2O_3 to FeO



Models for Gas-Solid Reactions

- The rate of a gas-solid reaction can be generally described by

$$\frac{dX}{dt} = kf(X)$$

$$k = Ae^{-(\frac{E}{RT})}$$

where, ***A*** **- Pre-exponential factor;** ***E*** **- Activation energy;** ***f(X)*** **- Reaction model;** ***X*** **- Conversion of solid reactant**

- The conversion (***X***) of oxygen carrier during the reduction

$$X_r = \frac{m_0 - m_t}{m_0 R_0} = \frac{m_0 - m_t}{m_0 - m_r}$$

where, m_t **- Mass of ilmenite at time** ***t*****;** m_o **- Mass of OC in fully oxidized state;** m_r **- Mass of OC in a reduced state**

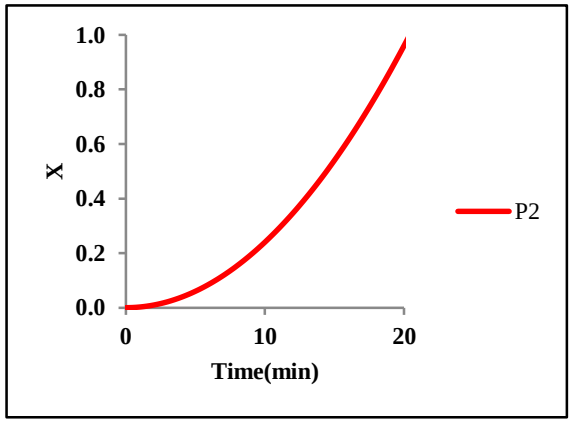
S.No	Shape of the curve	Mechanistic model name	Differential form $f(X) = dX/(kdt)$	Integral form $g(X) = kt$
1	Acceleratory	(a) Power law (P2)	$2X^{1/2}$	$2X^{1/2}$
		(a) Power law (P3)	$3X^{2/3}$	$X^{1/3}$
		(c) Power law (P4)	$4X^{4/3}$	$X^{1/4}$
2	Deceleratory	(a) Contracting area (R2)	$2(1-X)^{1/2}$	$1-(1-X)^{1/2}$
		(a) Contracting volume(R3)	$3(1-X)^{2/3}$	$1-(1-X)^{1/3}$
		(a) 1-D diffusion (D1)	$1/(2X)$	X^2
		(a) 2-D diffusion (D2)	$-[1/\ln(1-X)]$	$[(1-X)\ln(1-X)]-X$
		(a) 3-D diffusion-Jander (D3)	$[3(1-X)^{2/3}]/[2(1-(1-X)^{1/3})]$	$(1-(1-X)^{1/3})^2$
		(a) Ginstling-Brounshtein (D4)	$3/[2((1-X)^{-1/3}-1)]$	$1-(2/3)X-(1-X)^{2/3}$
3	Linear	(a) Zero order (F0/R1)	1	X
4	Sigmoidal	(a) Avrami-Erofeyev (A2)	$2(1-X)[-\ln(1-X)]^{1/2}$	$[-\ln(1-X)]^{1/2}$
		(a) Avrami-Erofeyev (A3)	$3(1-X)[-\ln(1-X)]^{2/3}$	$[-\ln(1-X)]^{1/3}$
		(a) Avrami-Erofeyev (A4)	$4(1-X)[-\ln(1-X)]^{3/4}$	$[-\ln(1-X)]^{1/4}$
		(a) Prout-Tompkins (B1)	$X(1-X)$	$\ln[X/(1-X)]$

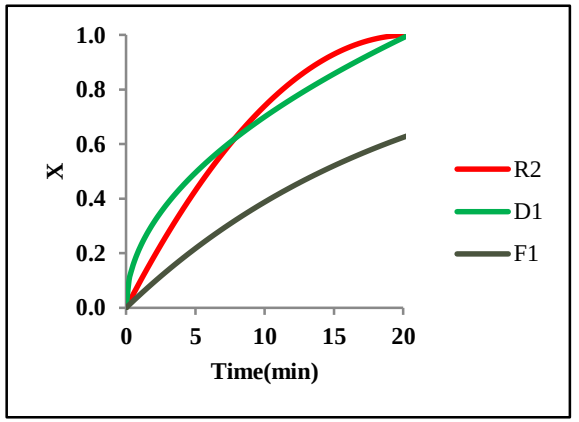
Models for Gas-Solid Reactions

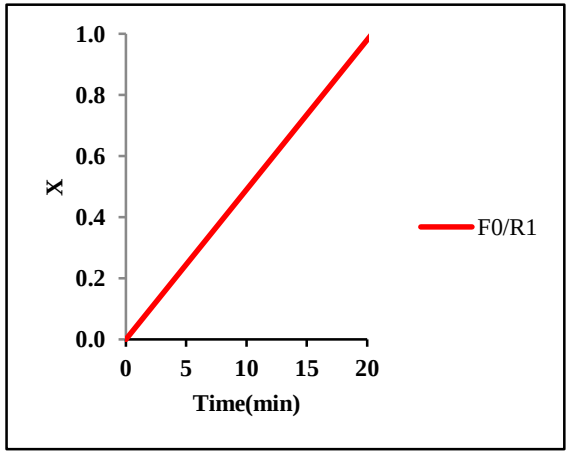
- **The reaction model, *f(X)* is generally classified into**
  - **Acceleratory**
  - **Deceleratory**
  - **Linear and**
  - **Sigmoidal models**

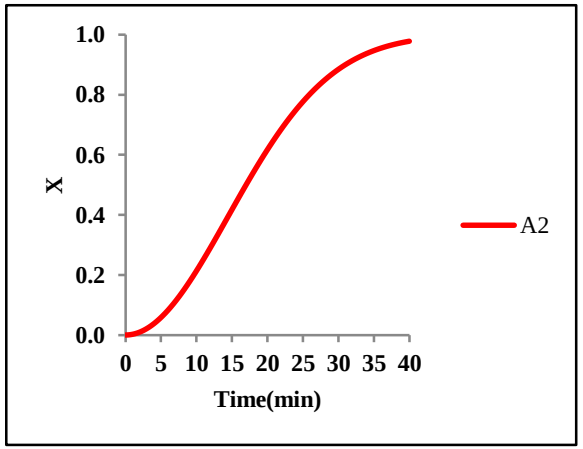
based on the shape of the isothermal curves or on the mechanistic assumptions.

- **The main drawbacks of the mechanistic models are that the data were fitted only for a particular shape, limited time interval and also there was a complete negligence about multiple reactions.**
- **Need a model to consider all the shapes.**









Models for Kinetic Studies

- The reduction rate of OCs is the function of temperature and concentration of fuel gasses
- The generalized model is expressed as

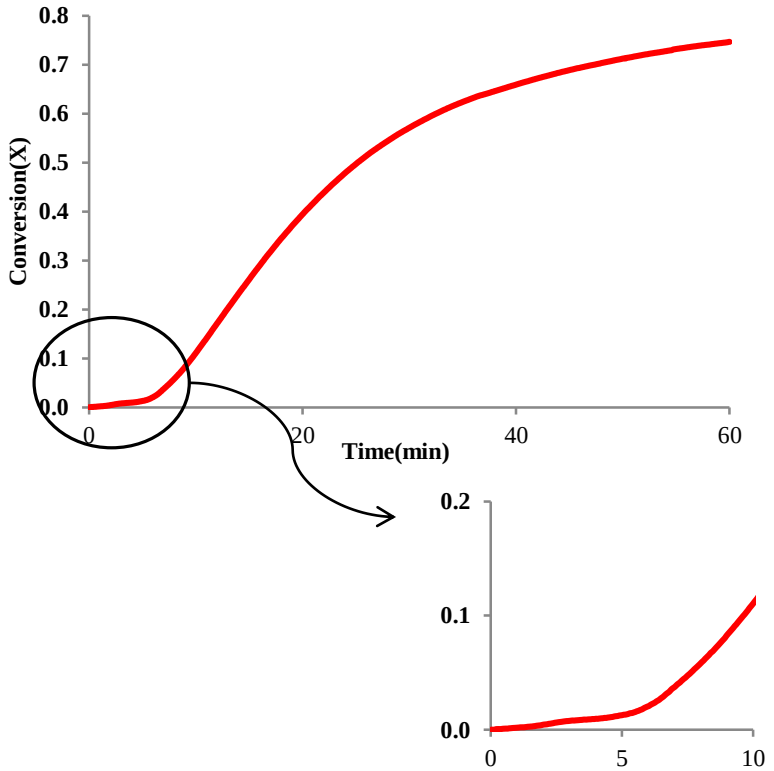
$$\frac{dX}{dt} = k(1-X)^m C_{CO}^n$$

Where, dX/dt - Conversion rate; C_{CO} - CO concentration; *m*and *n* - The order with respect to solid and gas concentration

- At low concentration of CO, the shape of the curve is a combination of two or more shapes
- A composite is proposed as

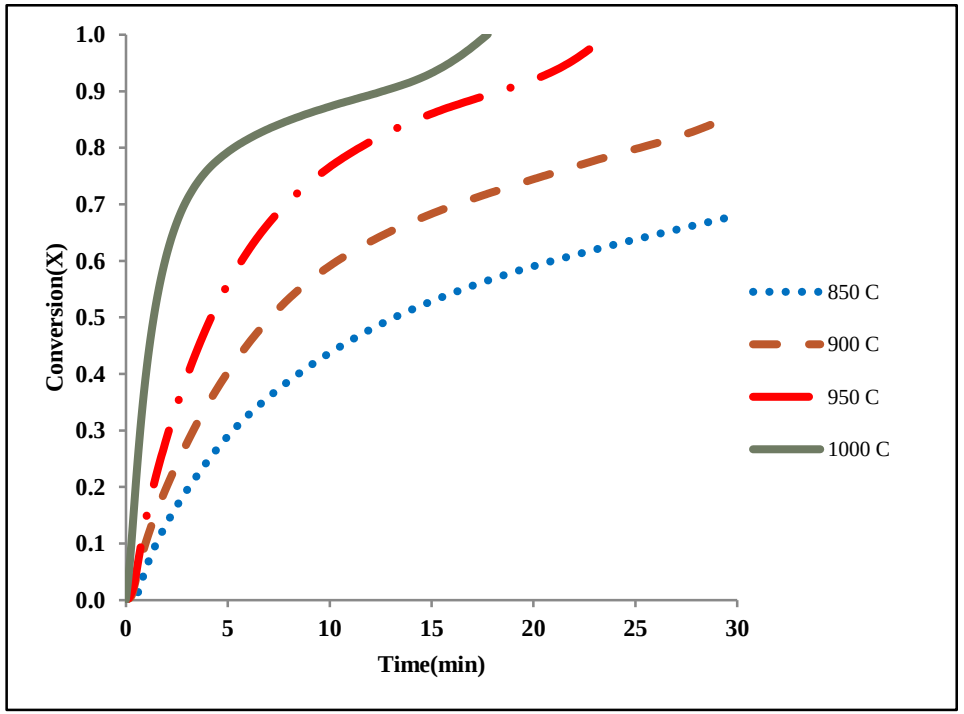
$$\frac{dX}{dt} = C_1 \left[\frac{1}{k(1-X)^{m_1}} + \frac{m_2 X^{m_2-1}}{k_N} \right]^{-1}$$

C_1- The function of concentration of CO gas; $m_1$and m_2- The orders of deceleratory and acceleratory models respectively; *k* and k_N- The rate constants

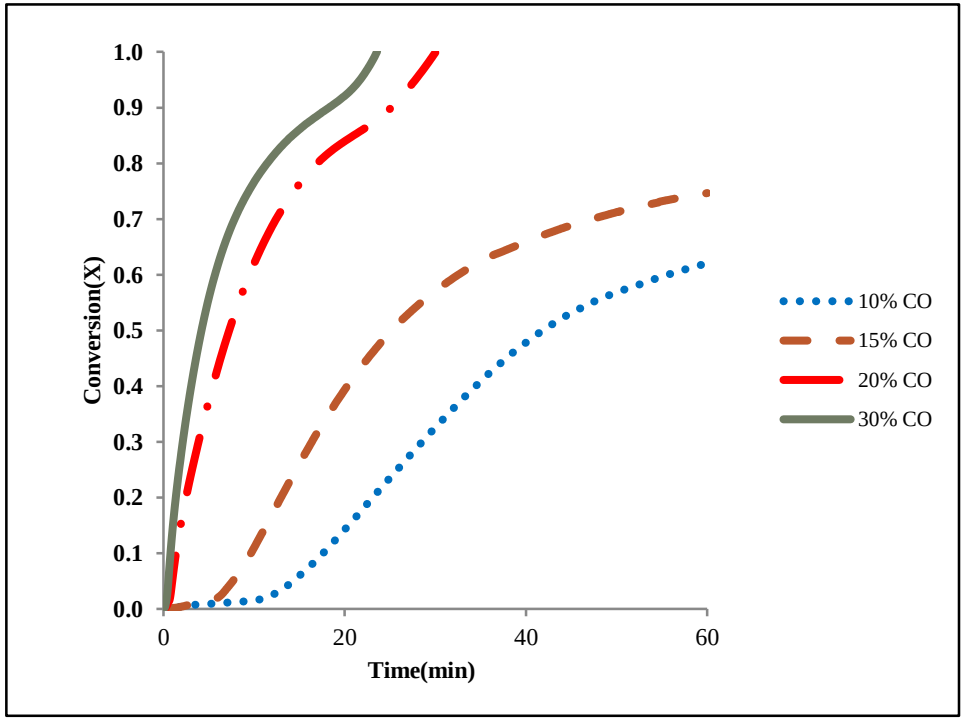


Experiments at Different Reaction Conditions

Effects of temperature



Effects of concentration



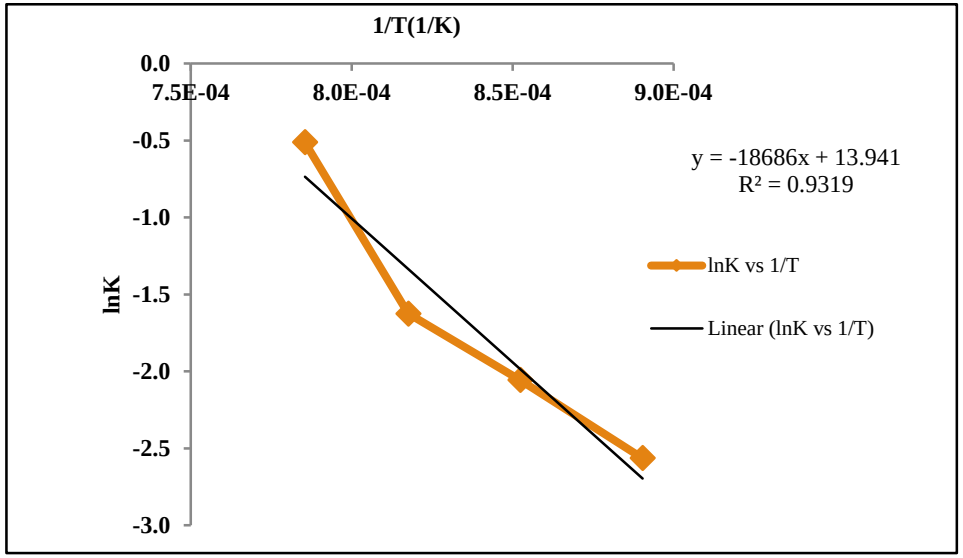
Reduction Kinetic Studies of Indian Ilmenite

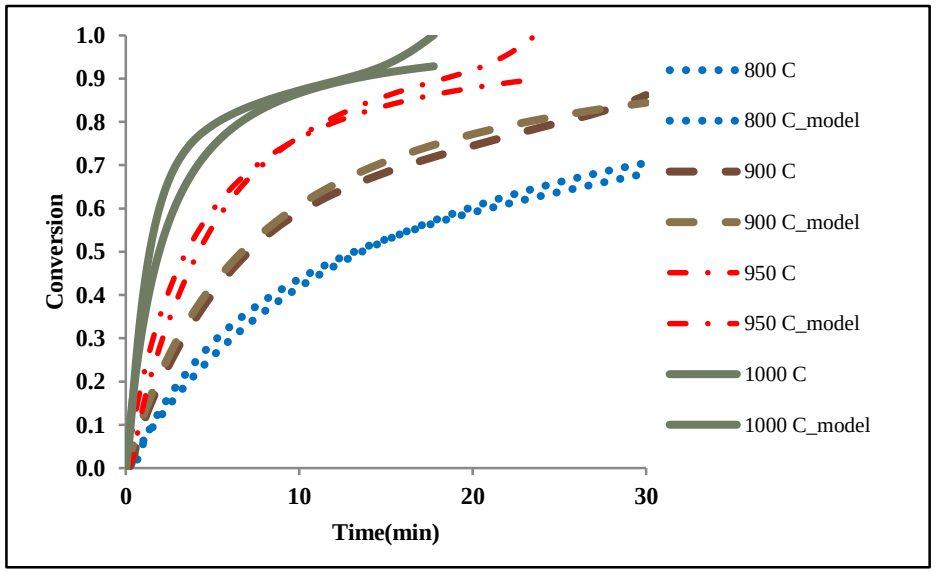
- The generalized model was taken for temperature effects

$$\frac{dX}{dt} = k(1-X)^m C_{CO}^n$$

- The value of k, m and n values were determined from curve fitting method

E (J/mol)	A (L/mol.sec)	m	n
$155x10^3$	$1132.6x10^3$	1.76	1





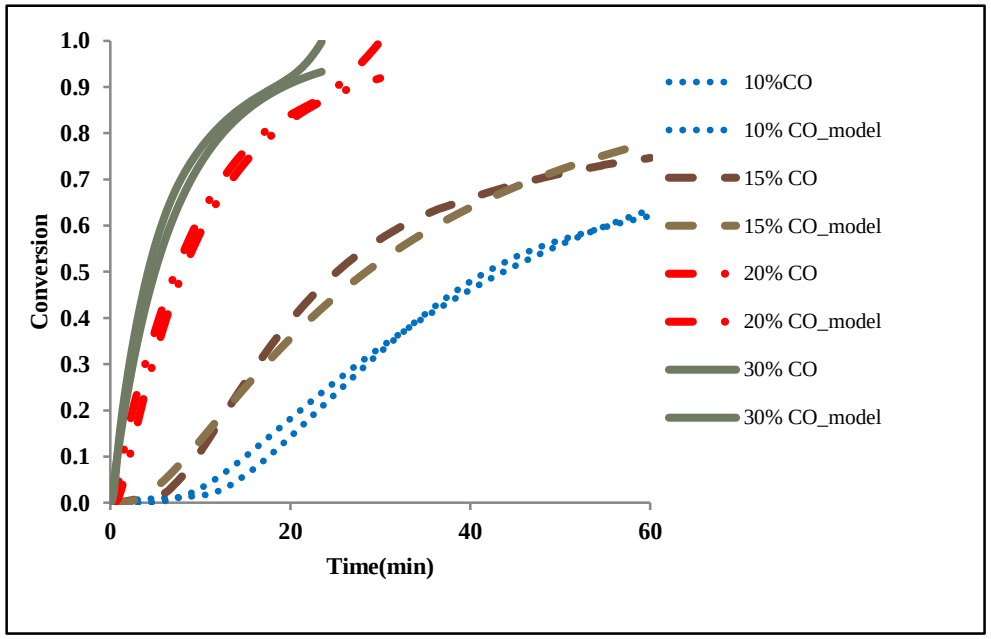
Reduction Kinetic Studies of Indian Ilmenite

- The composite model was taken for concentration effects

$$\frac{dX}{dt} = C_1\left[\frac{1}{k(1-X)^{m_1}} + \frac{m_2 X^{m_2-1}}{k_N}\right]^{-1}$$

- The k value was taken from generalized model.
- The value of C_1, m_1, m_2 and k_N were determined by curve fitting techniques.

CO concentration (mol %)	Temperature (°C)	k_N (mol/m^3.s)	m_1	m_2
10	950	0.60	1.76	0.2
15	950	1.35	1.76	0.2
20	950	15.00	1.76	0.2
30	950	43.00	1.76	0.2



Conclusion

- **Reduction kinetic studies of CO on Indian ilmenite have been studied experimentally in a TGA analyzer over a range of 850-1000 ^{o}C and for four CO concentrations (10, 15, 20 and 30%).**
- **EDX and XRD results show that the calcined ilmenite is in the form of Fe_2O_3 and TiO_2.**
- **Temperature experimental results have been fitted with a generalized kinetic model to obtain the activation energies and pre-exponential factors of 155.4 kJ/mol and 1132.6 x10^3(L/mol.s).**
- **A novel composite model, assuming mixed control by chemical reaction and nucleation, has been able to predict the conversion kinetics for different gas concentrations.**
- **The results suggest that at low concentrations, the reduction rate is jointly controlled by nucleation and chemical kinetics.**

Thank you

Questions???