Reduction behaviour of iron ores by H_2 at multi-stage reduction

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Chapter I. Introduction

1. Research purpose and scope

2. Research background

2.1. Traditional ironmaking process and CO_2 emissions

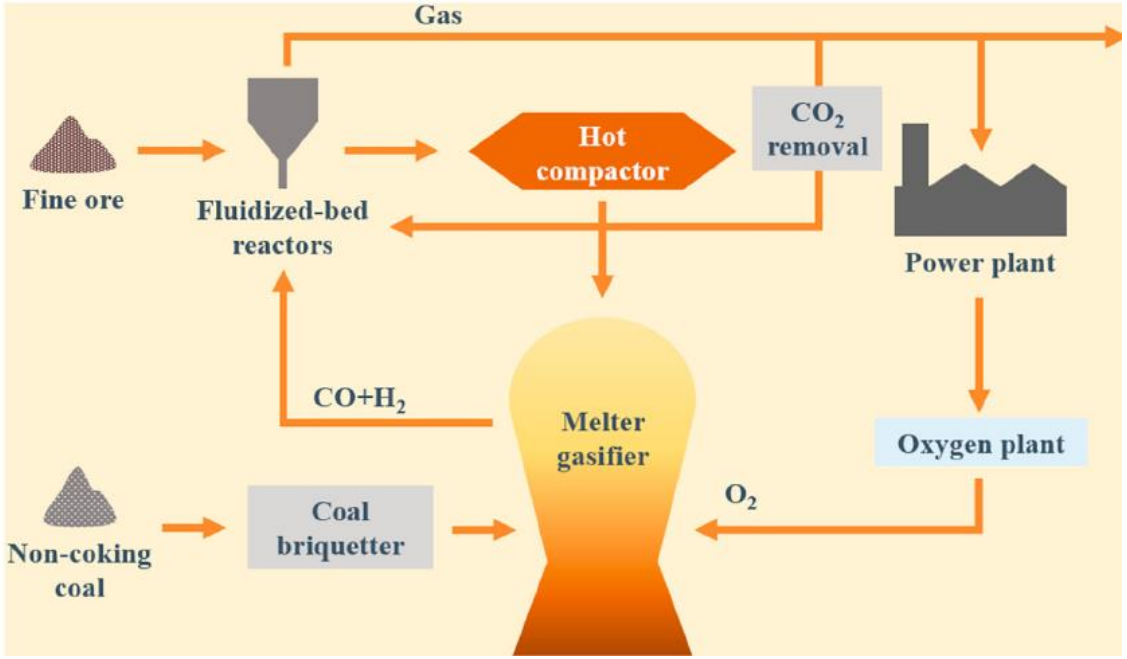
2.2. Alternative processes for achieving carbon neutral

2.3. Reduction behavior or iron oxides with hydrogen as reducing agent

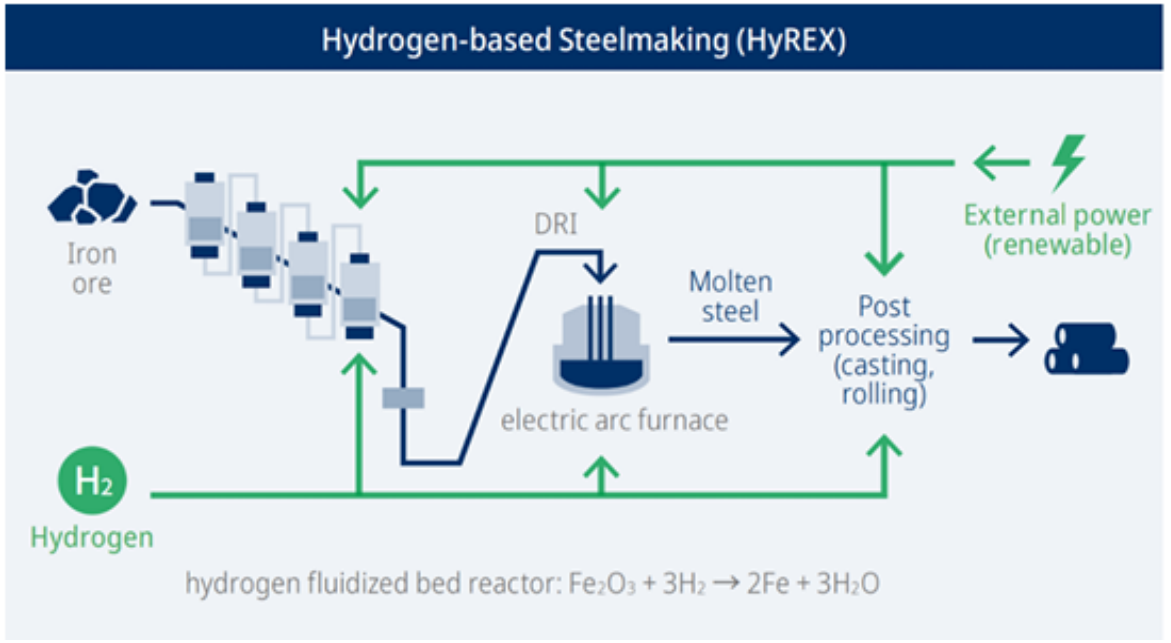
1. Research background

[Zhao 2020][POSCO report]

❑ Fluidized bed reduction process



FINEX process



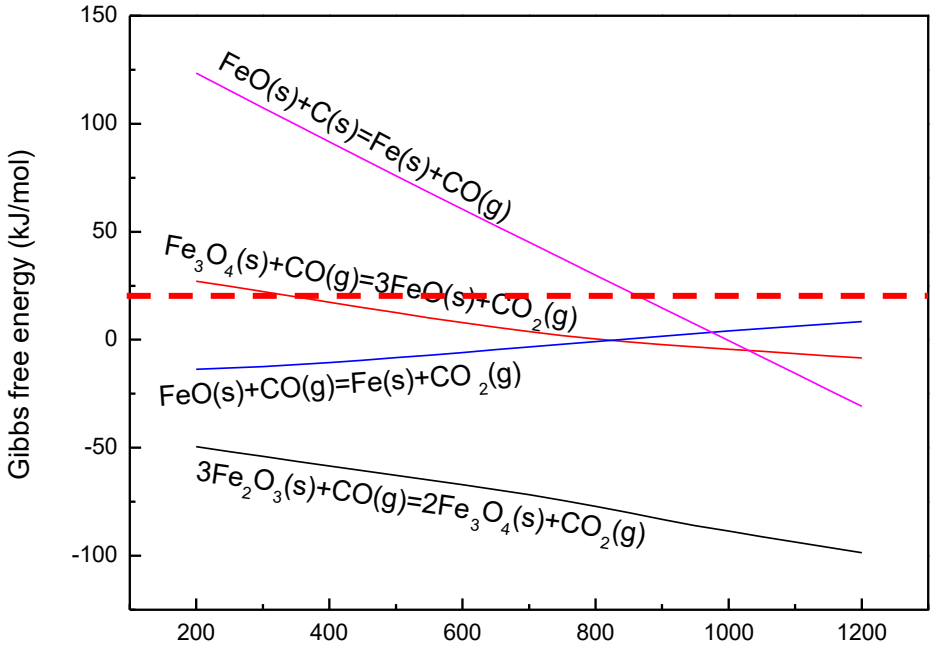
HyREX process

- ✓ **Fluidized bed reduction** processes include **FINEX** and **HyREX**. These processes offer the **advantage of using fine iron ores without the pre-treatment** such as **pelletizing or sintering**.
- ✓ However, these processes require a **large amount of hydrogen gas relative to the amount of iron ore** charged **to fluidize** the ore and show **low utilization degree of hydrogen for reduction**.

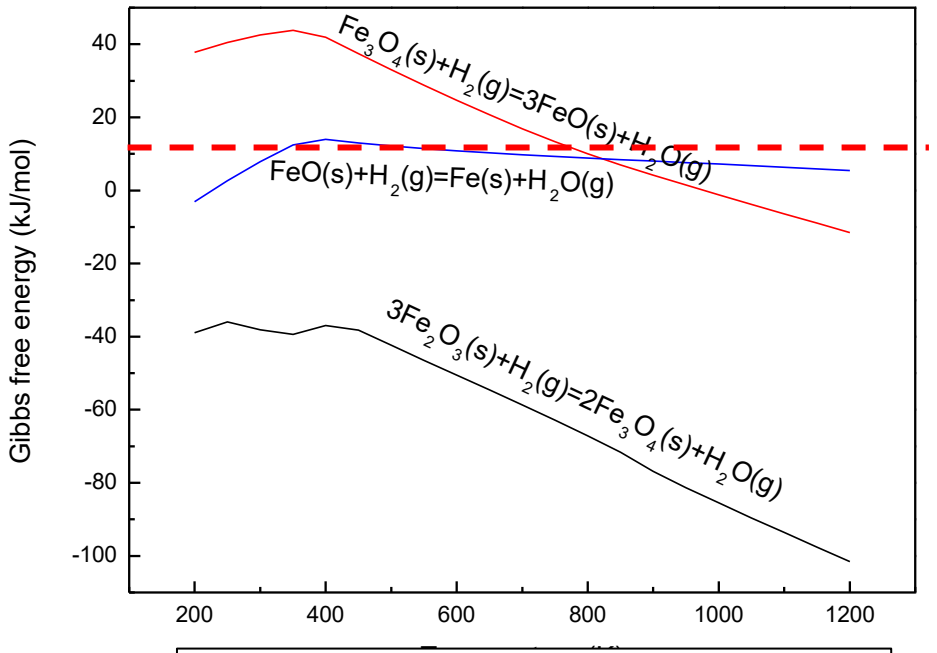
2. Theoretical background

1.2. Comparison of reduction behavior between CO and H_2

❑ **Iron ore reduction by CO and H_2**



ΔG^0 **of iron oxides reduction with CO**



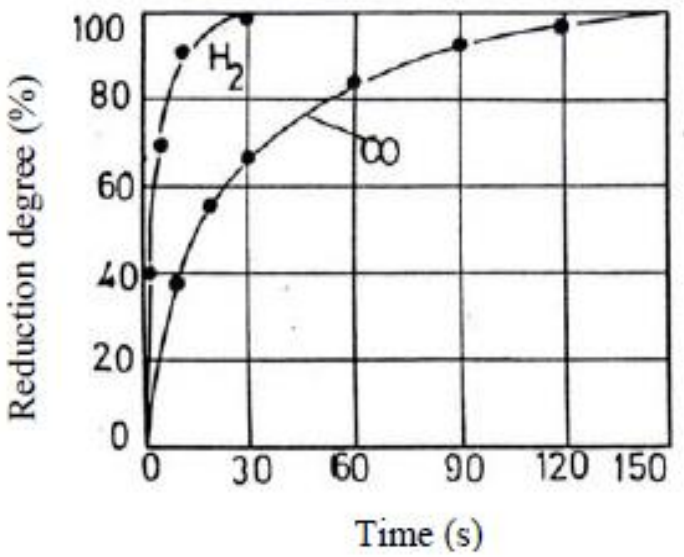
ΔG^0 **of iron oxides reduction with H_2**

- ✓ In the **high temperature** range, **reduction of Fe_2O_3 and Fe_3O_4** with **CO gas** shows **negative values** of Gibbs free energy of reaction.
- ✓ In the case of reduction of **iron oxides using hydrogen**, the reduction of wustite shows a **positive Gibbs free energy of reaction**, indicating that the **utilization degree of hydrogen might be very low**.

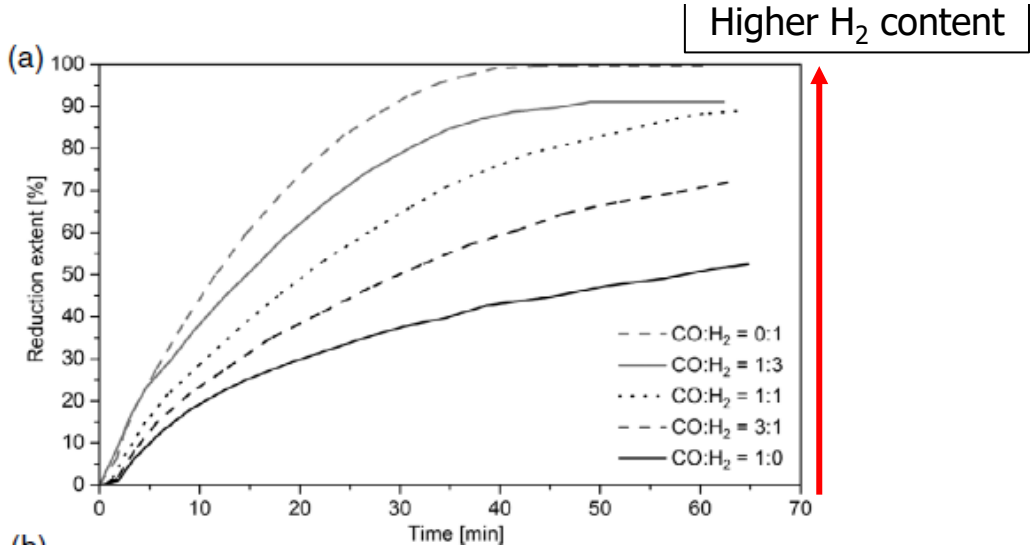
2. Theoretical background

❑ **Comparison of reduction rate between CO and H_2**

[Komatina 2017][Spreitzer 2019]



Comparison of reduction rate between CO and H_2



Change in reduction rate with different H_2 content

✓ Reduction by **H_2 showed a faster reduction** rate compared to CO, suggesting that **H_2 has a stronger reducing power** than CO.

- When the **two gases were mixed**, the **reduction rate also increased** as the hydrogen content increased.

2. Theoretical background

[Patisson 2020]

❑ Enthalpy change during reduction

- Reduction of iron oxides using CO (1200 K)

$3Fe_2O_3(s) + CO(g) = 2Fe_3O_4(s) + CO_2(g)$ $\Delta H^0 = -45.34 kJ/mol$

$Fe_3O_4(s) + CO(g) = 3FeO(s) + CO_2(g)$ $\Delta H^0 = 13.83 kJ/mol$

$FeO(s) + CO(g) = Fe(s) + CO_2(g)$ $\Delta H^0 = -13.10 kJ/mol$ $\boldsymbol{Fe_2O_3(s) + 3CO(g) = 2Fe(s) + 3CO_2(g)}$ $\Delta H^0 = -32.11 kJ/mol$

- Reduction of iron oxides using H_2 (1200 K)

$3Fe_2O_3(s) + H_2(g) = 2Fe_3O_4(s) + H_2O(g)$ $\Delta H^0 = -12.85 kJ/mol$

$Fe_3O_4(s) + H_2(g) = 3FeO(s) + H_2O(g)$ $\Delta H^0 = 46.31 kJ/mol$

$FeO(s) + H_2(g) = Fe(s) + H_2O(g)$ $\Delta H^0 = 19.38 kJ/mol$

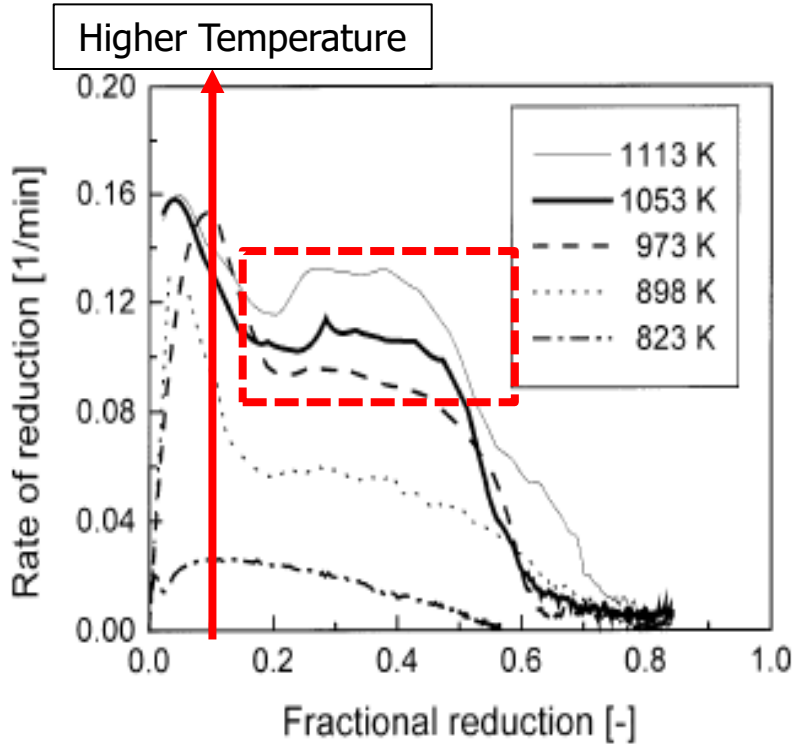
- $\boldsymbol{Fe_2O_3(s) + 3H_2(g) = 2Fe(s) + 3H_2O(g)}$ $\Delta H^0 = 65.36 kJ/mol$

- The **reduction** using **H_2 is endothermic**, whereas the reduction using **CO is exothermic**.
  - This difference led to **variation** in the **temperature** and **reduction degree** distribution within shaft furnace.

2. Theoretical background

[Habermann 2000]

❑ **Effect of temperature on hydrogen reduction**



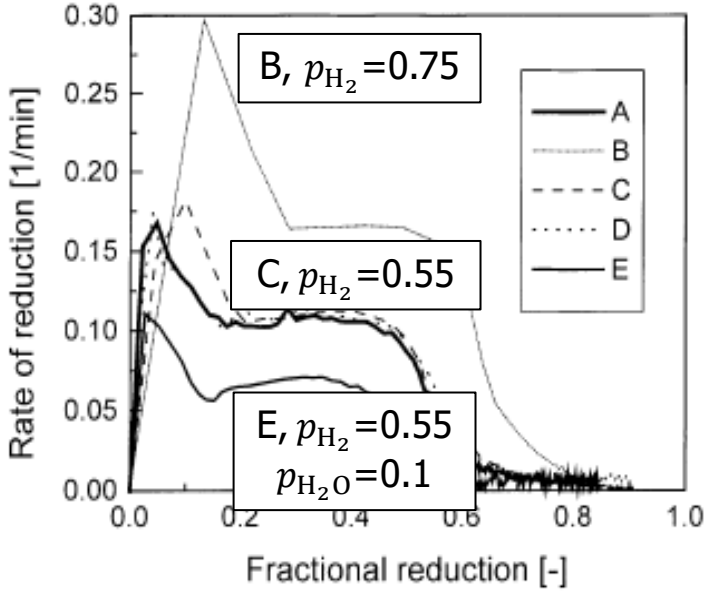
Effect of temperature on the reduction rate (55 vol% H_2, 9 vol% CO, 5 vol% CO_2, 31 vol% N_2)

- ✓ As the **temperature increased**, the **reduction rate consistently improved**. However, this effect gradually diminished at temperature above 700 °C.
- ✓ The **reduction rate continuously varied** with the reduction degree, and the **reduction from wustite** with a reduction degree above 0.6 to metallic iron **proceeded very slowly.**

2. Theoretical background

❑ **Effect of gas composition on hydrogen reduction**

[Habermann 2000]



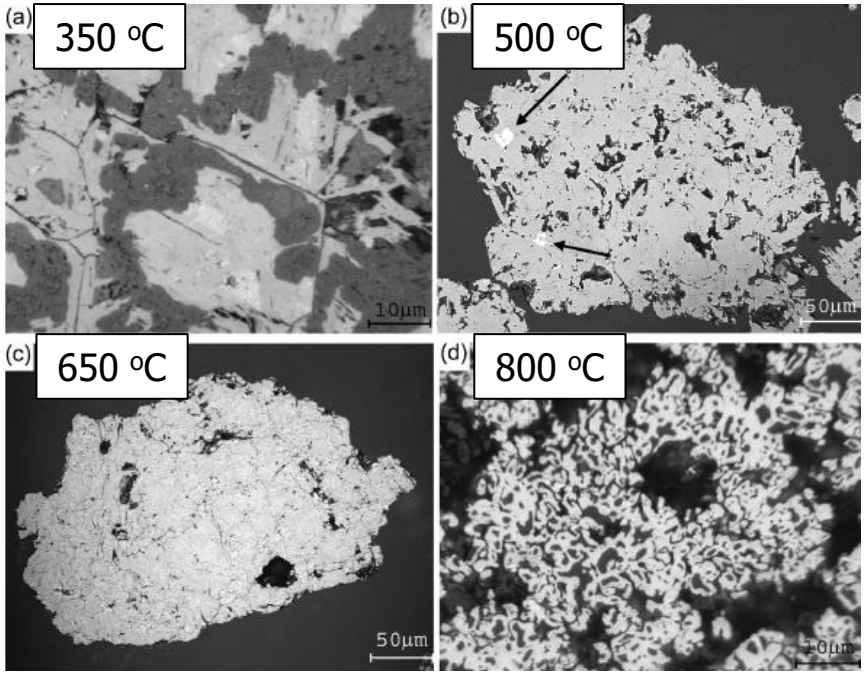
Effect of reducing gas composition on the reduction rate of hematite at 1 bar and 830 °C
A: p_{H_2}=0.55 bar, p_{CO}=0.09 bar, p_{CO_2}=0.05 bar,
B: p_{H_2}=0.75 bar,
C: p_{H_2}=0.55 bar,
D: p_{H_2}=0.55 bar, p_{CO}=0.09 bar, p_{CO_2}=0.05 bar, p_{CH_4}=0.06 bar
E: p_{H_2}=0.55 bar, p_{CO}=0.09 bar, p_{CO_2}=0.05 bar, p_{H_2O}=0.1 bar
Balanced by N_2

- ✓ The comparison between **A and C** allows for the analysis of effect of **small amount of CO addition** on the reduction behavior. The **reduction rate showed little to change**, suggesting that a small amount of CO does not significantly impact H_2 reduction.
- ✓ In the case of **D**, both **CO and CH_4 were added, but no significant change** in the reduction rate was observed.
- ✓ Experimental condition **E** is expected to one of the most significant results. In this case, **small amount of H_2O**, which is a product of H_2 reduction, **significantly impacts** the reduction reaction. Therefore, in operation setting, **adjusting the ratio of H_2 and H_2O is to be crucial** in determining the reduction rate

2. Theoretical background

❑ **Effect of pre-reduction on hydrogen reduction**

[Thurnhofer 2005]



Microstructures of reduced iron ore during pre-reduction stage at different temperature. (a) 350 °C, (b) 500 °C, (c) 650 °C, and (d) 800 °C

- ✓ In **Figure (b)**, where the **temperature was increased to 500 °C**, the **entire iron ore was reduced to magnetite**. However, the **dense microstructure** appears to have resulted in a **lower final reduction degree**.
- ✓ When the temperature was **further increased**, leading to the **formation of wustite**, the microstructure became as shown in Figure (c). This formation of **porous wustite** was explained as contributing to the **improvement in final reduction degree**.

CHAPTER II – Effect of reduction behavior from Fe_2O_3 to FeO on the formation of metallic Fe in multi-stage hydrogen reduction

1. Introduction

➢ Backgrounds

- ✓ Compared to the FINEX process, the **HyREX process** uses **hydrogen** gas as reducing agent, resulting in a **higher reduction degree** of produced DRI.
  - It is necessary to measure the **reduction degree** achieved at **each stage** of the four-stage reduction process.
- ✓ Achieving a **high reduction degree of DRI** is one of the operation target.
  - Previous study[**Thurnhofer 2005**] have indicated that reduction conditions in **initial stage influence the final reduction degree**.

➢ Research Contents

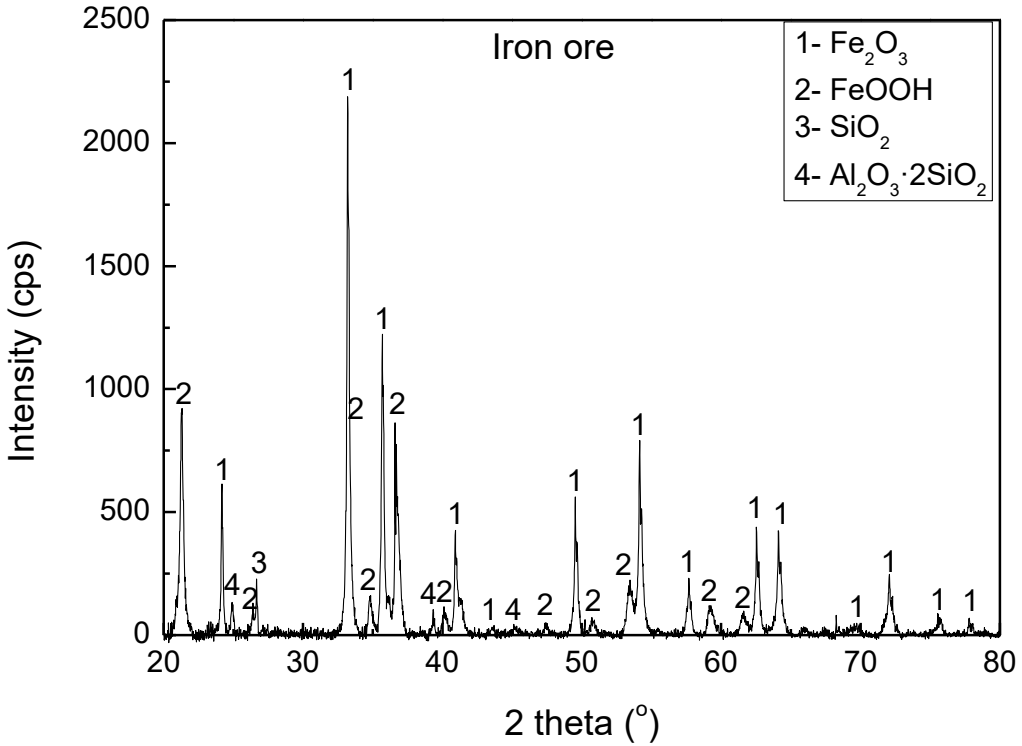
- ✓ To measure the **reduction degree** of iron ore for **each reduction stage**
- ✓ Analysis of the **residual iron oxides** after reduction
- ✓ **Improvement** of the **final reduction** degree by **varying conditions** during the **initial stage reduction**
- ✓ **Development** of strategies to enhance the final reduction degree through investigation of **reduction mechanism**

➢ Research objectives

- ✓ **Evaluation of iron ore reduction behavior under HyREX condition**

2. Experimental

❑ Phase analysis of MAC ore



Phase composition (wt%)			
Fe_2O_3	FeOOH	SiO_2	$Al_2O_3 \cdot 2SiO_2$
61.7	32.3	3.9	2.1

✓ Fe_2O_3 and FeOOH are main phases of MAC ore.

❑ Chemical composition of samples

Sample size: 1.4 ~ 1.7 mm

Iron ore chemical composition (wt%)											
Ore	**T. Fe**	**FeO**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**S**	**P_2O_5**	**MnO**	**TiO_2**	**Main Phase**
MAC	62.1	0.31	3.49	1.33	0.05	0.05	0.02	0.15	0.19	0.06	**Fe_2O_3 + FeOOH**

2. Experimental

MAC ore (wt%)	
Fe_2O_3	FeOOH
62	32

- ✓ **400 mg** of MAC ore
  - **248 mg Fe_2O_3, 128 mg FeO(OH)**
  - During **dehydration**

$$\mathbf{2FeO(OH)}(s) = \mathbf{Fe_2O_3}(s) + \mathbf{H_2O}(g)$$

128 mg of FeO(OH) become **115 mg of Fe_2O_3**

- ✓ After dehydration, **totally 363 mg of Fe_2O_3**
  - Maximum **oxygen removal: 109 mg**

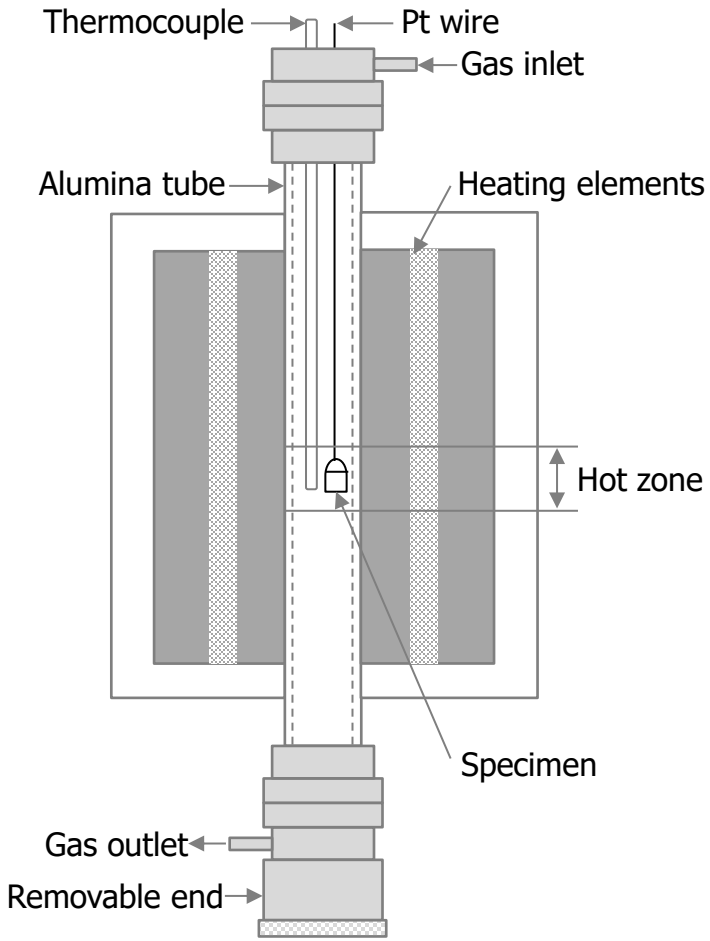
Weight loss from 400 mg MAC				
	Dehydration (~250 °C)	Fe_2O_3->Fe_3O_4 (R4)	Fe_3O_4 -> FeO (R3)	FeO -> Fe (R2, R1)
Expected weight loss	13 mg	12 mg	24 mg	73 mg
Expected reduction degree	-	11%	33%	100%

- ✓ Based on the maximum weight loss during reduction, reduction degree was evaluated.

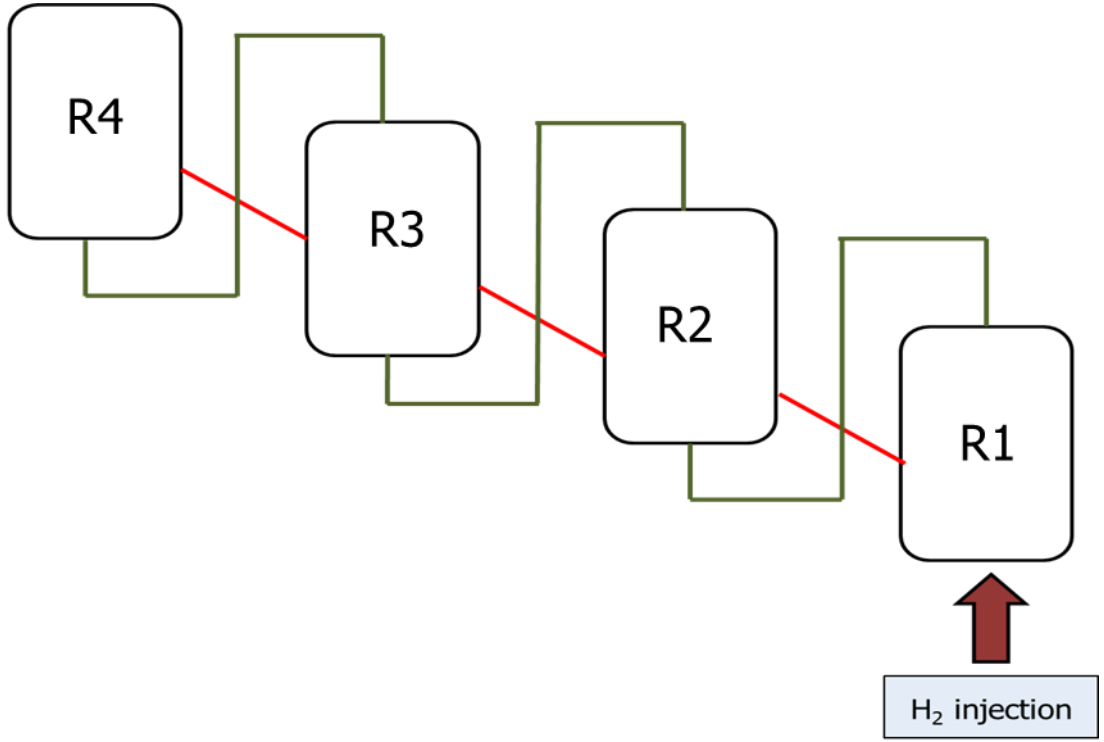
$$Reduction\ degree\ (\%) = \frac{Weigh\ loss\ during\ 4{-}stage\ reduction\ (mg)}{Maximum\ weight\ loss\ with\ stoichiometic\ calculation\ (mg)} \times 100$$

2. Experimental

2.2. Experimental apparatus and conditions



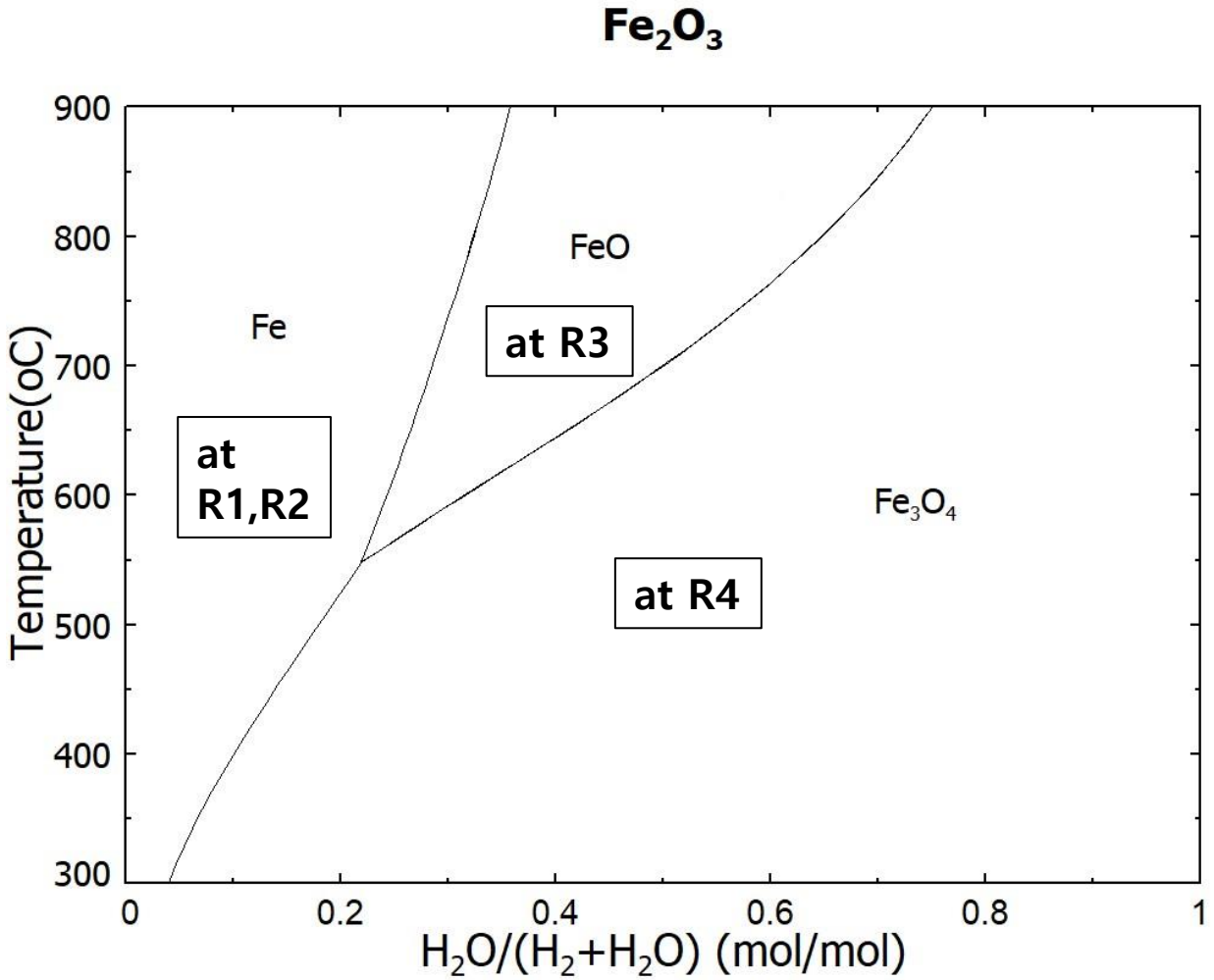
Thermogravimetric analysis



- **Sample:** MAC, 0.4g
- **Experimental condition:** Specific conditions under R4, R3, R2 and R1
- **Total flow rate:** 1L/min

2. Experimental

2.2. Experimental apparatus and conditions



Baur-Glassner diagram and experimental conditions at four stages (FactSage)

Experimental conditions at each reduction stage				
Conditions	R4	R3	R2	R1
Temperature	450 °C	630 °C	700 °C	750 °C
H_2 (ml/min)	600	620	670	720
H_2O (ml/min)	230	210	160	110
N_2 (ml/min)	170			
Time (min)	30	30	40	40

Change of residence time at R4

at R4 (0-10 min)

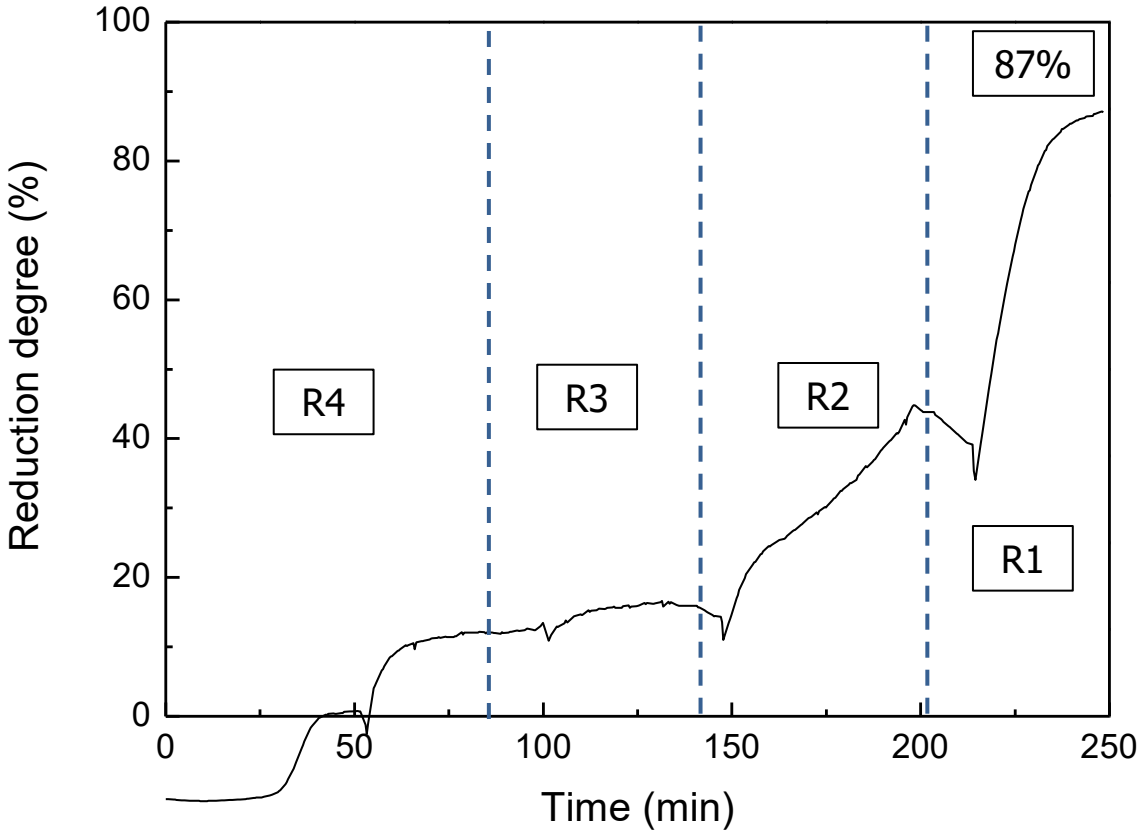
at R3 (30 min)

at R2 (40 min)

at R1 (40 min)

3. Results and discussion

❑ Reduction of MAC ore



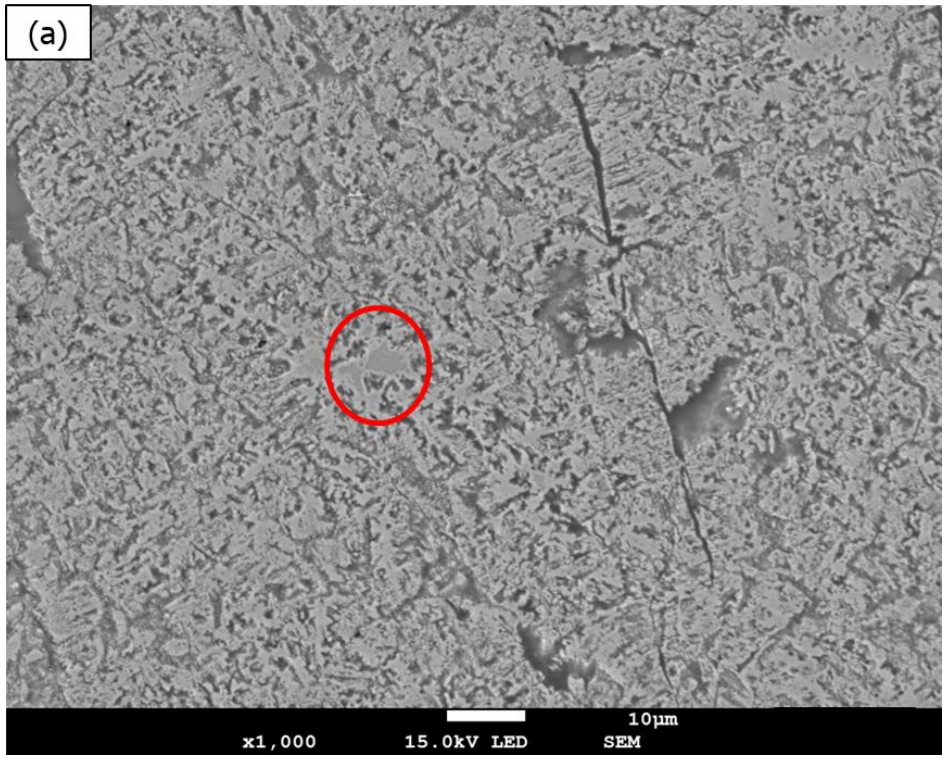
Change in the reduction degree at four reduction stages

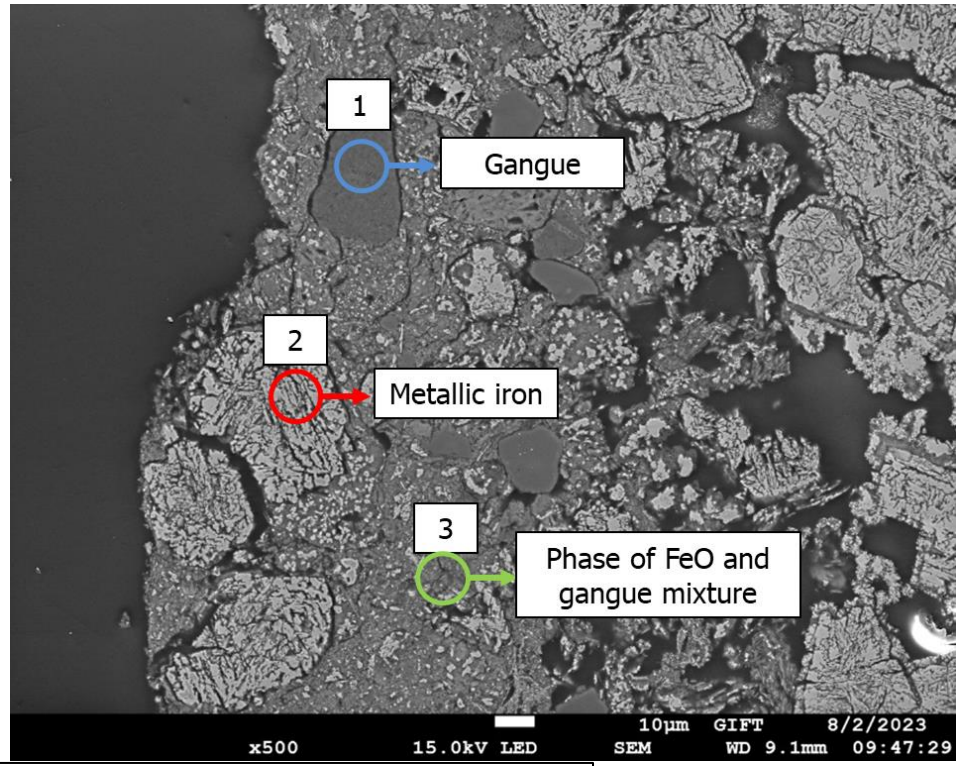
Reduction degree (%)				
	R4	R3	R2	R1
Measured	11	16	44	87
Expected	11	33	100	

- ✓ Under standard condition, **87 %** of **final reduction degree** was obtained after R1 reduction.
- ✓ Within **15 min**, **reduction of hematite to magnetite** was finished under R4 condition.

3. Results and discussion

❑ SEM image of reduced iron ore after four-stage reduction





1 composition (wt%)			
Al	Si	Fe	O
23	26	3	48

2 composition (wt%)
Fe
99

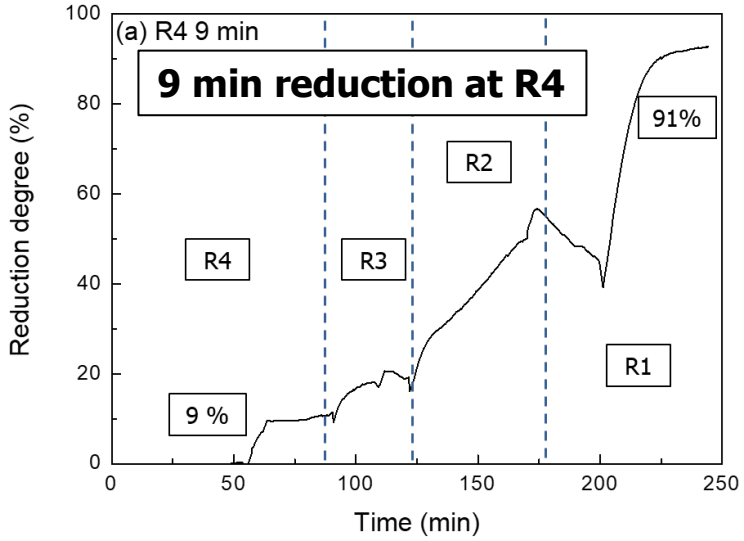
3 composition (wt%)			
Al	Si	Fe	O
4	5	75	15

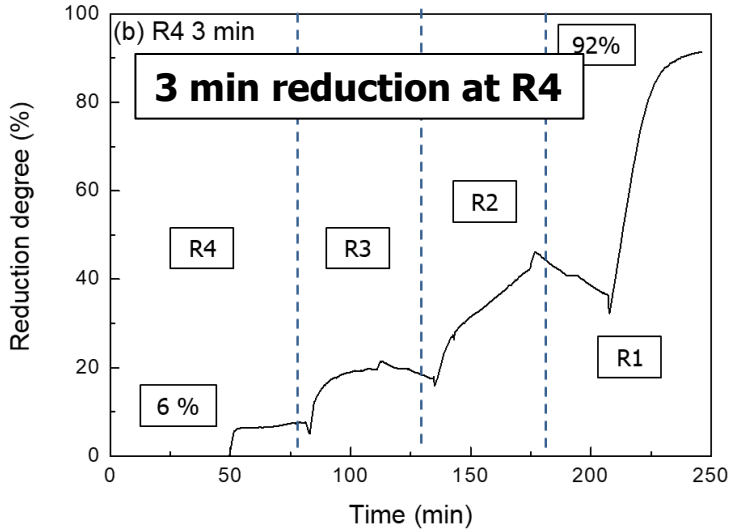
Microstructure of iron ore after reduction (RD: 87%)

✓ There are two kinds of **unreduced iron oxides**.
- **Dual phase** grain (Outer: metallic iron, Internal core: FeO)
- **Mixed phase** of FeO and gangue

3. Results and discussion

❑ Control of residence time at R4 stage (Achieve different reduction degree under R4)



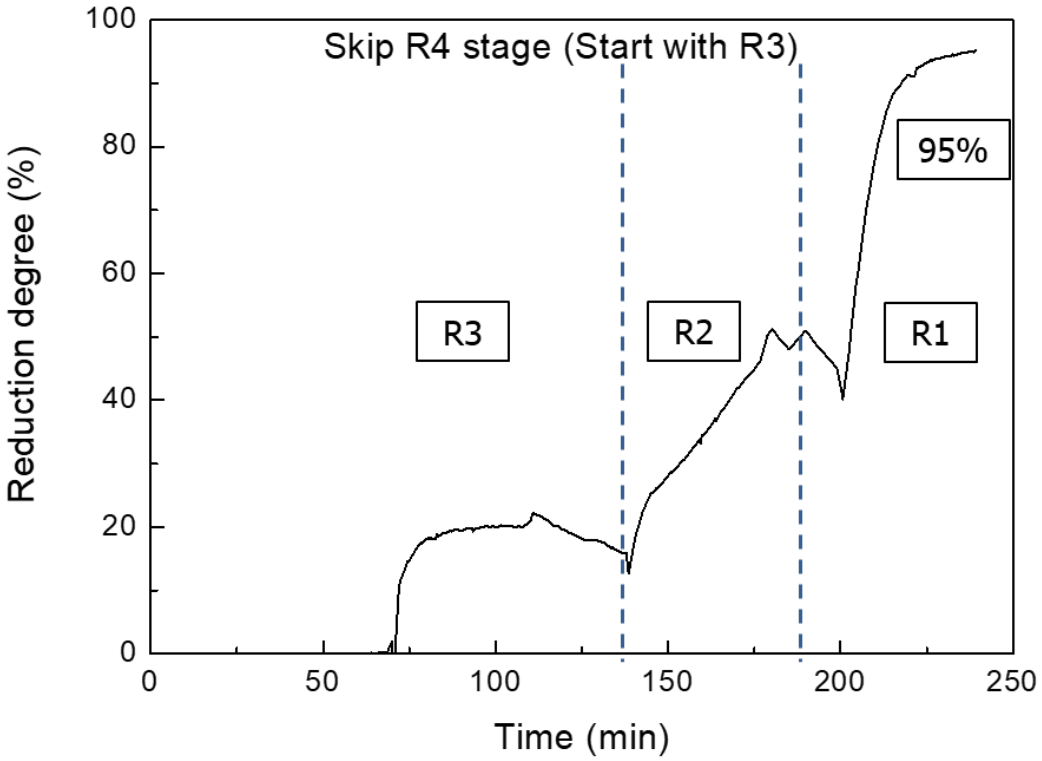


Reduction degree (%)				
Residence time at R4	R4	R3	R2	R1
30 min (Standard)	11	16	44	87
9 min	9	18	50	91
3 min	6	19	42	92

✓ When the **reduction degree become lower at R4, final reduction degree become higher after R1.**

3. Results and discussion

❑ Three-stage reduction (R3 → R2 → R1)

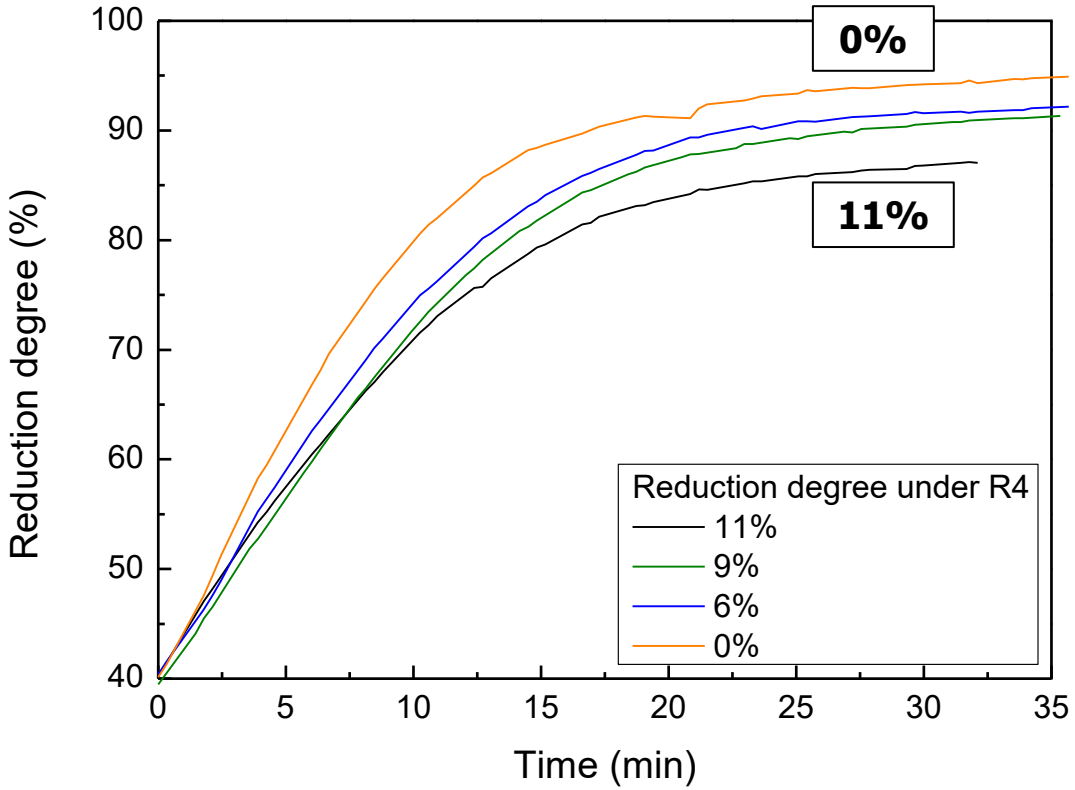


Reduction degree (%)				
Residence time at R4	R4	R3	R2	R1
30 min (Standard)	11	16	44	87
9 min	9	18	50	91
3 min	6	19	42	92
0 min (Skip)	-	21	47	95

✓ **Without R4** condition (**three stage reduction**), **final reduction** degree was evaluated to be **95%**.

3. Results and discussion

❑ Change in reduction degree during R1



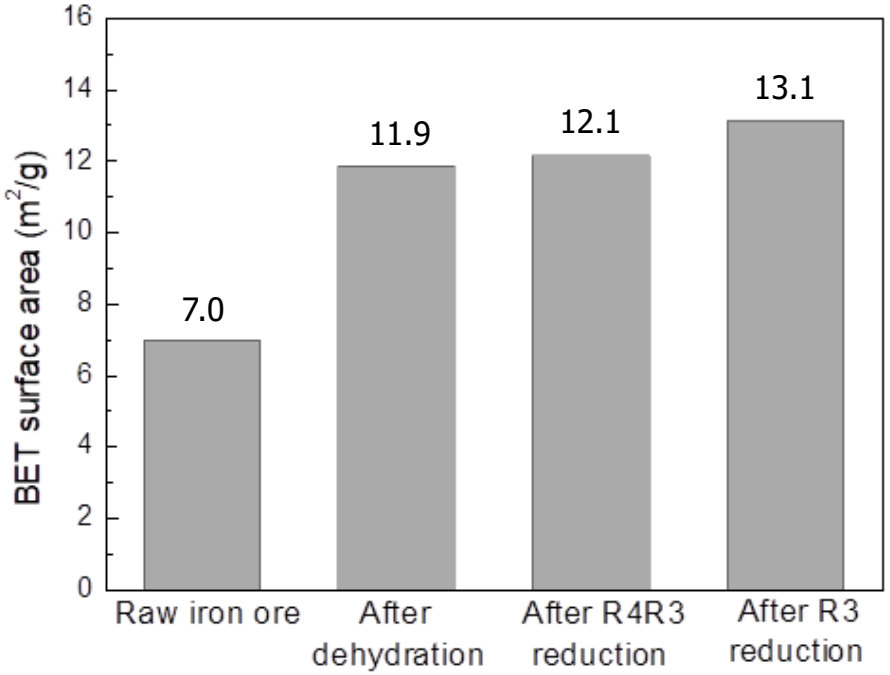
Effect of reduction degree at R4 on the final reduction degree.

✓ When analyzing the most important reaction in the iron oxide reduction which is the reduction of FeO to Fe, it was observed that **as the reduction degree decreased at R4**, the degree and rate of **reduction at R1 increased**.

⇒This suggests that the initial reduction **reaction from Fe_2O_3 to Fe_3O_4 strongly affect the formation of metallic iron**.

3. Results and discussion

❑ Change of surface area during reduction



Surface area of raw iron ore, iron ore after dehydration, reduced iron ore at R4-R3 and R3

- ✓ The surface areas of raw and hydrated iron ores were measured to be 6.97 and 11.85 m^2/g, respectively.
  - D**ehydration increased t**he **surface area** as water **within the goethite crystal was removed**.
- ✓ The ore **reduction degrees at R4-R3 and R3 are similar (18%)**, while the **surface area** after reduction was observed **different (12.1 for R4-R3 and 13.1 for R3).**
  - When ores were **exposed to stronger experimental** conditions (**temperature** or **reduction potential**), it caused **faster reduction** or **dehydration**, which **promoted the formation of more cracks** (higher surface area).

3. Results and discussion

❑ Kinetics analyses

Model		$g(X) = k * t$
Chemical reaction at interface	Mass Transport	X
	Contracting Area	$1-(1-X)^{1/2}$
	Contracting Volume	$1-(1-X)^{1/3}$
Diffusion Control	1-D Diffusion	X^2
	2-D Diffusion	$(1-X)*\ln(1-X)+X$
	3-D Diffusion – Jander	$[1-(1-X)^{1/3}]^2$
	3-D Diffusion – Ginstling	$1-2/3*X-(1-X)^{2/3}$
Reaction Control	1st Order	$-\ln(1-X)$
	3/2 Order	$2*[(1-X)^{-1/2}-1]$
	2nd Order	$(1-X)^{-1}-1$
	3rd Order	$1/2*[(1-X)^{-2}-1]$
Nucleation	Avrami 1.5	$[-\ln(1-X)]^{2/3}$
	Avrami 2	$[-\ln(1-X)]^{1/2}$
	Avrami 3	$[-\ln(1-X)]^{1/3}$
	Avrami 4	$[-\ln(1-X)]^{1/4}$

✓ The **reduction mechanism** at each reduction reaction was analyzed.

- The **fitting model** provides fundamental data for improvement of the reduction degree.

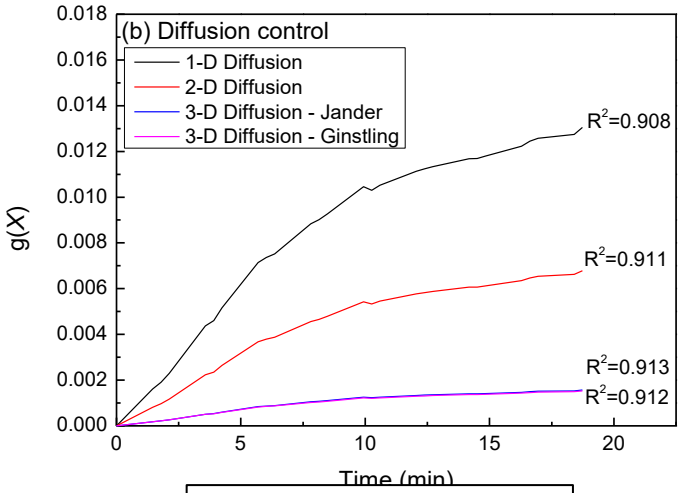
- **Diffusion** control: More surface area, Smaller iron ore size

- **Reaction** control: Higher temperature, Higher hydrogen partial pressure

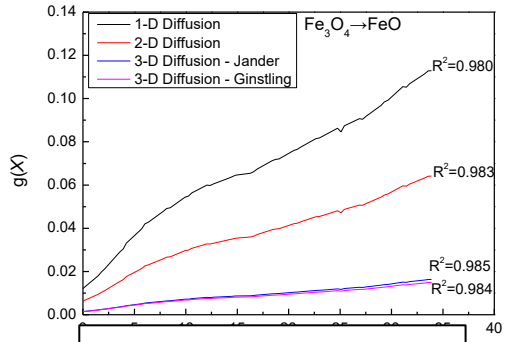
3. Results and discussion

❑ Kinetics analysis for each reduction reaction

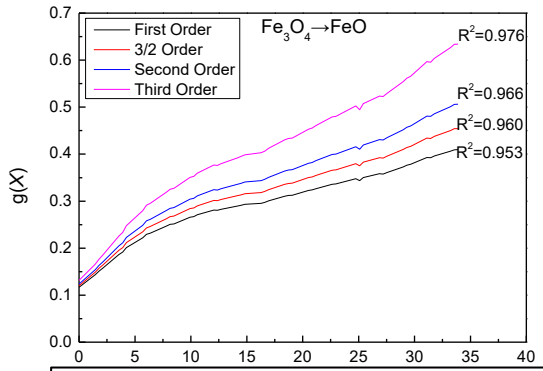
$Fe_2O_3 \rightarrow Fe_3O_4$ → $Fe_3O_4 \rightarrow FeO$ → $FeO \rightarrow Fe$



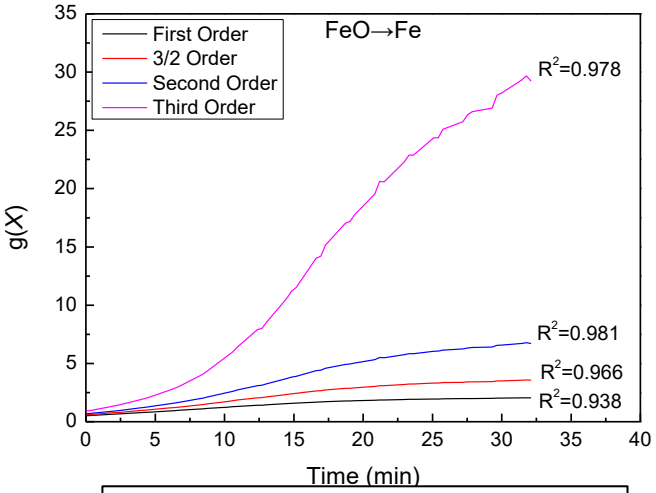
Diffusion control



Diffusion control



Chemical reaction control



Chemical reaction control

✓ Different kinetic mechanisms were identified for each reduction reaction, respectively.

- **Diffusion** ⇒ **Diffusion** and 1st order chemical **reaction (mixed control)** ⇒ Third order **chemical reaction**

3. Results and discussion

Models		R^2 value for each model		
		$Fe_2O_3 \rightarrow Fe3O4$	$Fe_3O_4 \rightarrow FeO$	$FeO \rightarrow Fe$
Phase-Boundary control Geometrical Contraction	Mass Transport	0.777	0.935	0.842
	Contracting Area	0.834	0.944	0.896
	Contracting Volume	0.836	0.947	0.911
Diffusion Control	1-D Diffusion	0.908	0.980	0.886
	2-D Diffusion	0.911	0.983	0.920
	3-D Diffusion – Jander	0.913	0.985	0.953
	3-D Diffusion – Ginstling	0.912	0.984	0.933
Reaction Control	1st Order	0.790	0.953	0.938
	3/2 Order	0.796	0.960	0.966
	2nd Order	0.802	0.966	0.981
	3rd Order	0.814	0.976	0.983
Nucleation	Avrami 1.5	0.677	0.928	0.918
	Avrami 2	0.583	0.913	0.906
	Avrami 3	0.452	0.897	0.892
	Avrami 4	0.371	0.888	0.885

4. Conclusions

- ✓ Change in **reduction degree** was measured during the **four-stage hydrogen reduction** process.
  - **11% → 18% → 40% → 87%**
- ✓ **Residual iron oxides** after the reduction showed in **two types**.
  - **Dual phases grain** (Outer: metallic iron, Inside core: FeO)
  - **Mixed phase of FeO and gangue**
- ✓ As the **duration time of first reduction stage decreased**, the **final reduction degree** was **improved**.
  - Reduction in stronger reducing atmosphere at the early stage led to increase in surface area.
- ✓ **Different reduction mechanism** were identified for **each reduction** reaction.

Reduction mechanism for each reaction		
$Fe_2O_3 \rightarrow Fe_3O_4$	$Fe_3O_4 \rightarrow FeO$	$FeO \rightarrow Fe$
Diffusion control	**Mixed** control (Diffusion + Reaction)	**Chemical** reaction

CHAPTER III – Effect of iron ore type on reduction behavior at multi-stage hydrogen reduction

1. Introduction

➢ Backgrounds

- ✓ Due to the **supply of iron ore**, it is necessary to analyze the reduction behavior of **various iron ores.**
  - Since **HyREX process does not involve pre-treatment** such as **sintering and significant variation** in **reduction behavior** are expected depending on the **iron ore brands**
- ✓ Analysis of effect of **iron oxide phase** (Fe_2O_3, FeO(OH) and $Fe_2O_3 \cdot H_2O$) in raw ores on **reduction behavior**

➢ Research Contents

- ✓ To measure the **reduction degree of each reduction stage** for several iron ore brands
- ✓ Analysis of the **lattice parameter** and **crystallite size** of iron oxides formed during the reduction process for **iron ore** brands and **their effect** on **reduction behavior**
- ✓ To study the effect of **gangue components** on **reduction behavior**

➢ Research objectives

- ✓ **To clarify the effect of iron ore properties on reduction behavior in HyREX conditions**

2. Experimental

❑ Chemical composition of iron ores

Titration/ICP

Sample size: 1.4 ~ 1.8 mm

Iron ore chemical composition (wt%)									
Ore	**T. Fe**	**FeO**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**S**	**P_2O_5**	**Main Phases**
Carajas (Ore A)	65.2	0.46	1.52	1.25	0.07	0.05	0.03	0.15	**Fe_2O_3**
MAC (Ore B)	62.1	0.31	3.49	1.33	0.05	0.05	0.02	0.15	**Fe_2O_3 + FeO(OH)**
Royhill (Ore C)	59.7	0.1	4.69	2.55	0.11	0.11	0.03	0.14	**Fe_2O_3 + $Fe_2O_3 \cdot H_2O$**
Yandi (Ore D)	57.0	0.17	5.39	1.59	0.06	0.08	0.06	0.08	**FeO(OH)**

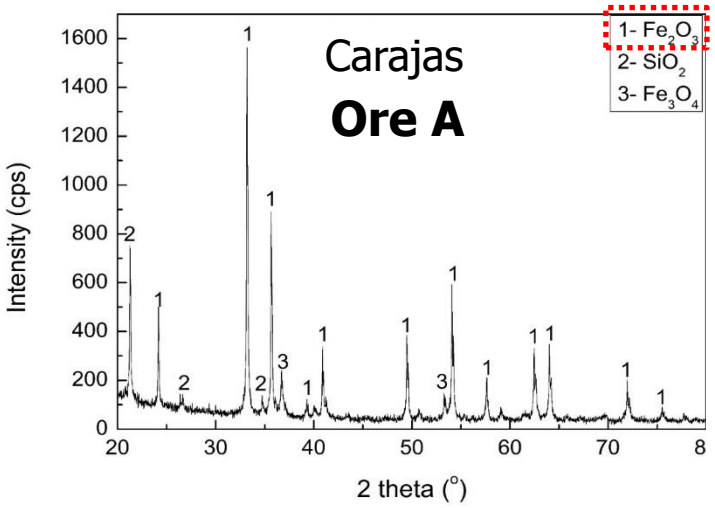
✓ All of them contain **very low FeO content**, which represents **minimal presence of magnetite**.

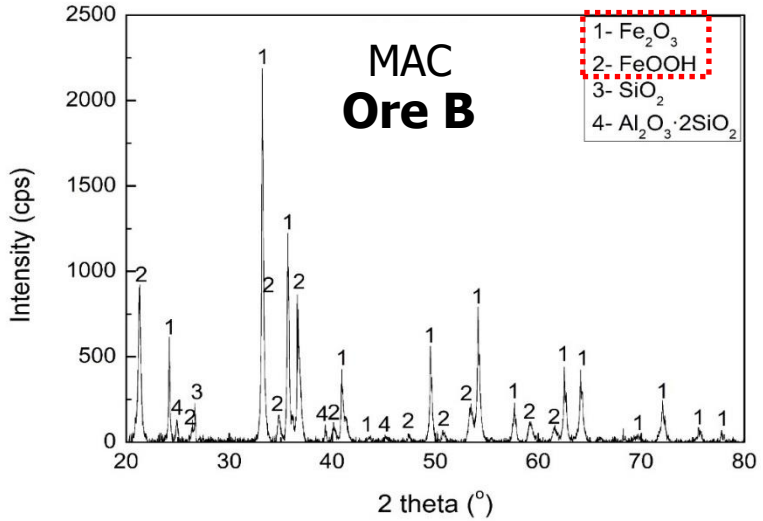
- Ore A is **high-grade Brazilian iron** ore with **low gangue** content and **high amount of total Fe**.

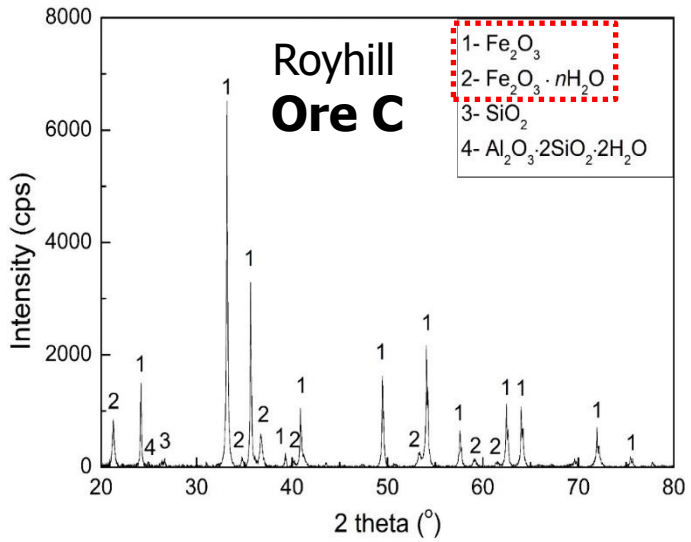
- **Ore B, Ore C and Ore D** are **Australian iron ores** with **higher gangue content** compared with Ore A.

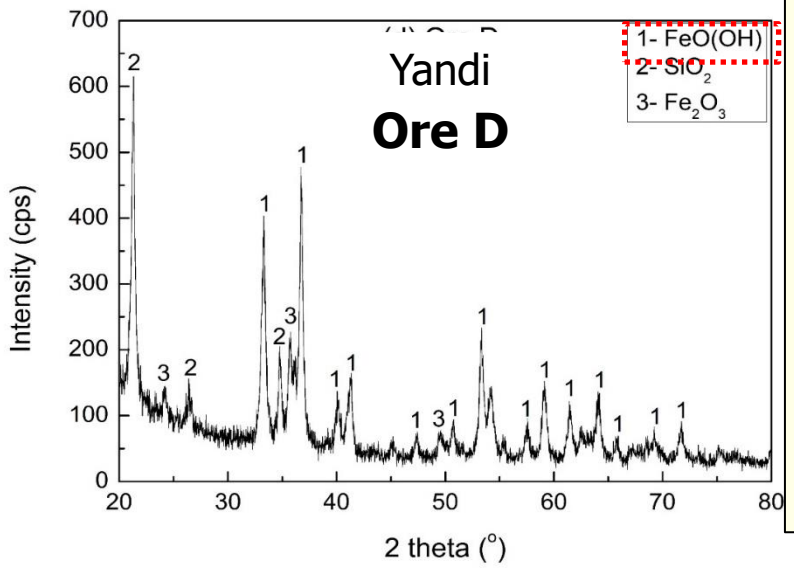
2. Experimental

❑ Phase identification of four iron ores



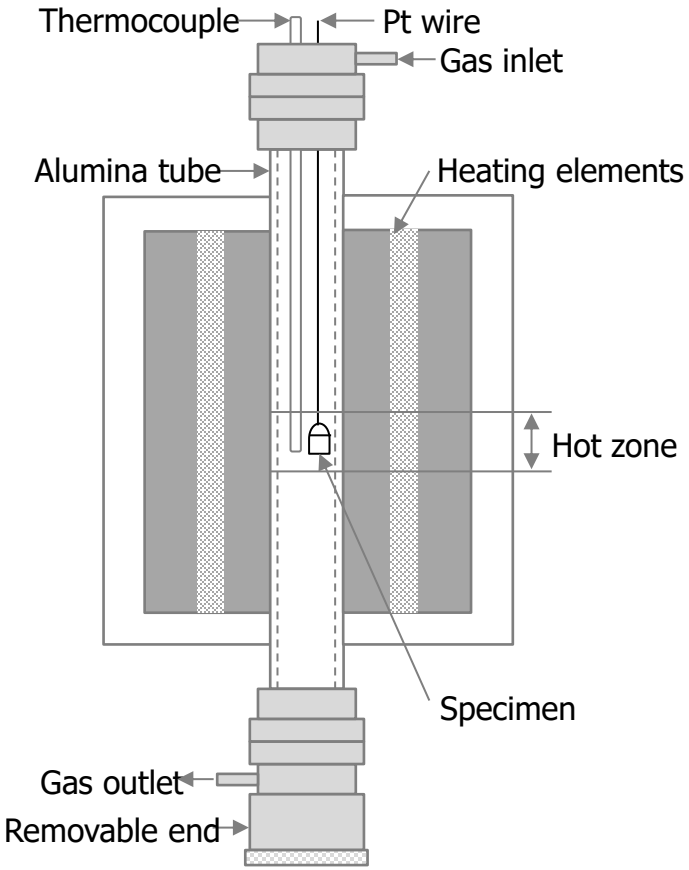




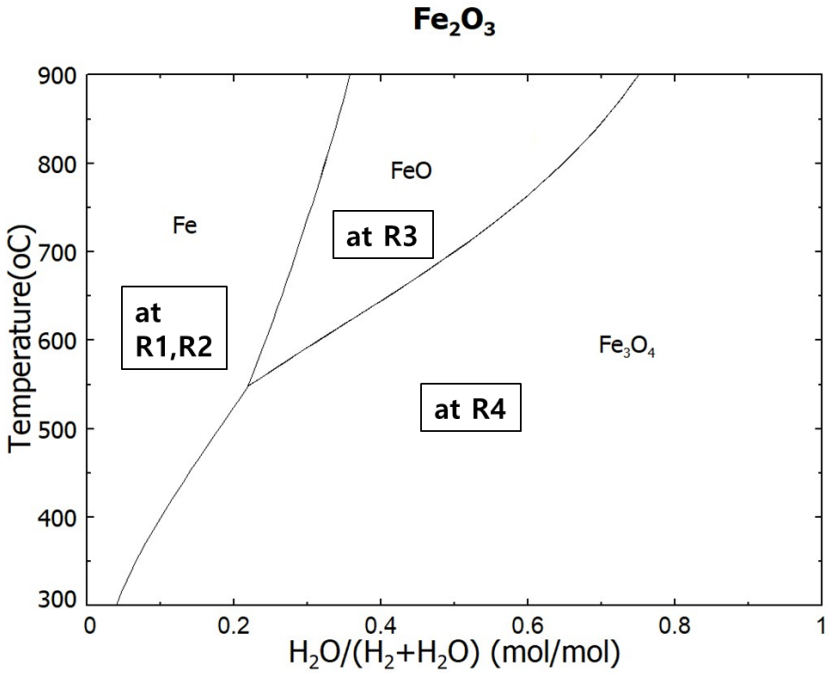


- ✓ **Fe_2O_3** in **Ore A(Carajas)** was identified to be the main phase while **Ore B(MAC)** and **Ore C(Royhill)** consist of **Fe_2O_3, FeO(OH) and $Fe_2O_3 \cdot H_2O$**.
- ✓ Lastly, **Ore D(Yandi)** was primarily composed of **FeO(OH)**.
- ✓ This indicates that **Ore B, Ore C and Ore D** would show the **weight loss due to dehydration** while heating up to target temperature.

2. Experimental



Thermogravimetric analysis



- **Sample:** 0.4g
- **Experimental condition:** Specific conditions

  at R4, R3, R2 and R1
- **Total flow rate:** 1L/min

Experimental conditions at each reduction stage

Conditions	R4	R3	R2	R1
Temperature	450 °C	630 °C	700 °C	750 °C
H_2 (ml/min)	600	620	670	720
H_2O (ml/min)	230	210	160	110
N_2 (ml/min)	170			
Time (min)	30	30	40	40

2. Experimental

Weight loss at each reduction (mg)					
Iron ores	**Dehydration (~250 °C)**	**$Fe_2O_3 \Rightarrow Fe_3O_4$ (R4)**	**$Fe_3O_4 \Rightarrow FeO$ (R3)**	**$FeO \Rightarrow Fe$ (R2/R1)**	**Total weight loss by**
Ore A (Carajas)	-	12	25	76	113
Ore B (MAC)	13	12	24	73	109
Ore C (Royhill)	9	11	22	69	102
Ore D (Yandi)	36	11	21	65	97
Expected reduction degree(%)	-	11%	33%	100%	

✓ Based on the maximum weight loss during reduction, reduction degree was evaluated.

$$Reduction\ degree\ (\%) = \frac{Weigh\ loss\ during\ 4-stage\ reduction\ (mg)}{Maximum\ weight\ loss\ with\ stoichiometic\ calculation\ (mg)} \times 100$$

2. Experimental

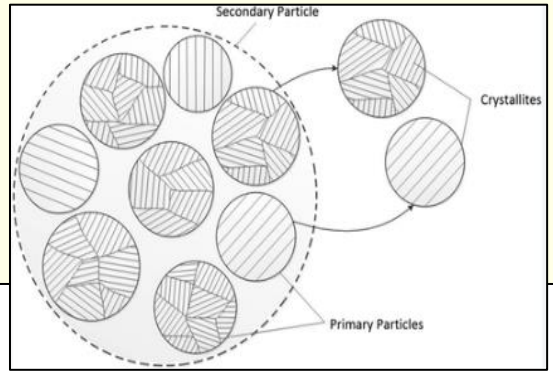
❑ Crystallite size of Fe_2O_3 and Fe_3O_4

- ✓ Since **iron oxide phases** are **different** within iron ores, it is expected that **crystallite size of iron oxide** might be **different** and **affect reduction behavior** in hydrogen reduction.
- ✓ **Crystallite** size analysis

  - The crystallite size was estimated by X-ray diffraction peaks with the **Scherrer formula**.

  $L = \frac{K\lambda}{\beta cos\theta}$ (L: crystallite size, K:a constant related to crystallite shape, normally taken as 0.9, λ is the X-ray wavelength in 0.1506 nm (the wavelength of *K*α Cu X-ray in nanometer), β is full width at half maximum (FWHM) and θ is peak position in degree)

- ✓ $L = \frac{K\lambda}{\beta cos\theta}$ (Constant / Constant) [**Small β (FWHW) → Larger L → Larger crystal size**]

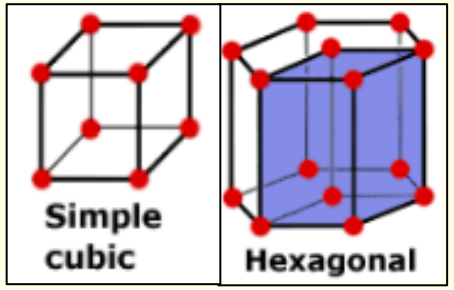


2. Experimental

❑ Lattice constant of Fe_2O_3 and Fe_3O_4

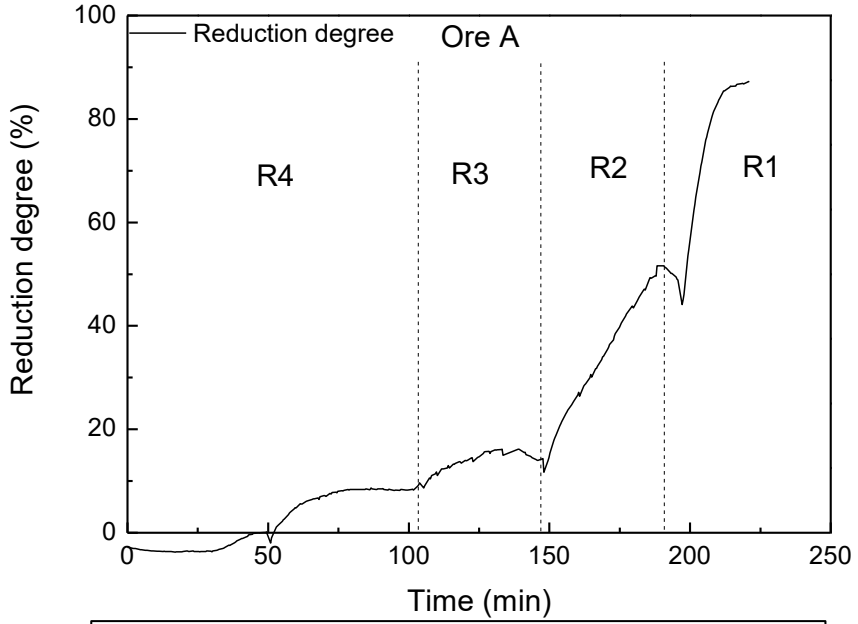
✓ Lattice constant of Fe_2O_3 and Fe_3O_4

- The crystal structures: **Fe_2O_3** (**hexagonal** closed-packed crystal), **Fe_3O_4** (**cubic closed-packed** crystal)
- **(104)** and **(110)** planes in **Fe_2O_3**, **(311)** plane was used in **Fe_3O_4**.
- Bragg's law: $d = \frac{n\lambda}{2Sin\theta}$,
- Hexagonal closed − packed crystal: $\frac{1}{d^2} = \frac{4}{3} \times \frac{h^2+k^2+hk}{a^2} + \frac{l^2}{c^2}$,
- Cubic close − packed crystal: $\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$
- d is the interplanar spacing, a and c are the lattice constants, $\{hkl\}$ is the crystal plane, n is the diffraction order, taken as 1 in this study



3. Results and discussion

❑ Reduction behavior of four iron ores



Change in reduction degree of Ore A at four-stage reduction

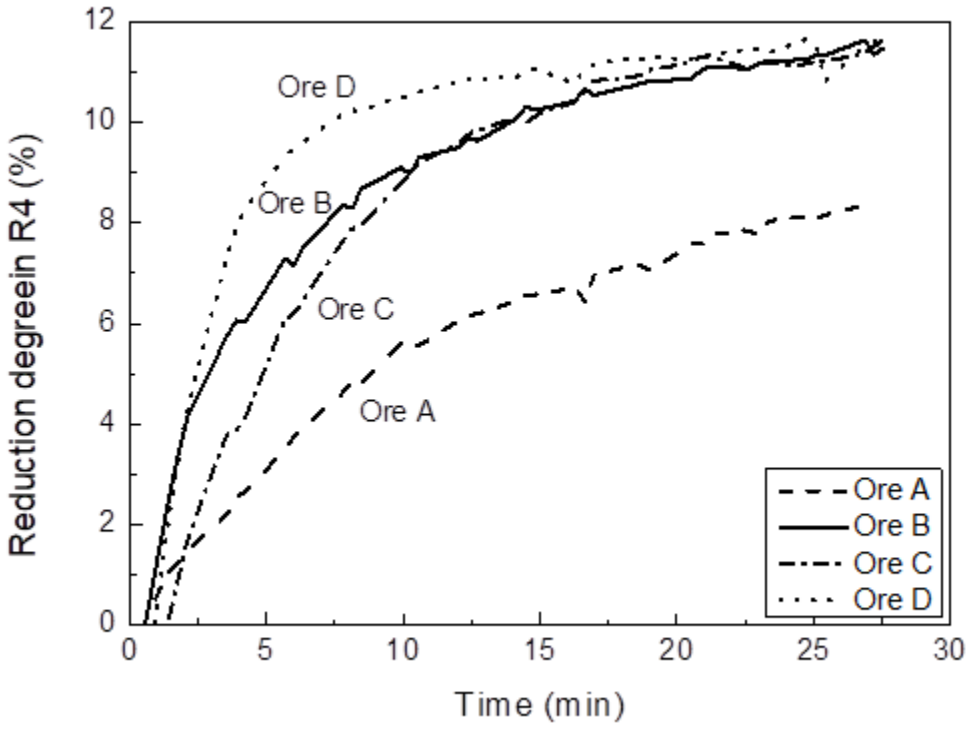
Reduction degree in each stage (%)				
Iron ores	R4	R3	R2	R1
Ore A (Carajas)	9	16.7±0.6	52.3±0.6	89±1
Ore B (MAC)	11	15.6±0.6	37.6±1.1	80±1
Ore C (Royhill)	11	15.6±0.6	37.4±0.7	81±0.6
Ore D (Yandi)	11	17±1	33.7±2.0	73.3±1.2

- ✓ The final reduction degree of **Ore A (Carajas)** was measured to be **89% as the highest**.
- ✓ **Ore B(MAC)** and **Ore C(Royhill)** showed similar reduction degrees of **81 %**. **Ore D (Yandi)** exhibited the lowest degree of final reduction of **73 %**.

⇒ Difference in reduction behavior of four iron ores become noticeable starting from R2 reduction stage.

3. Results and discussion

❑ Reduction behavior at R4 stage



Reduction behavior of four iron ores at R4

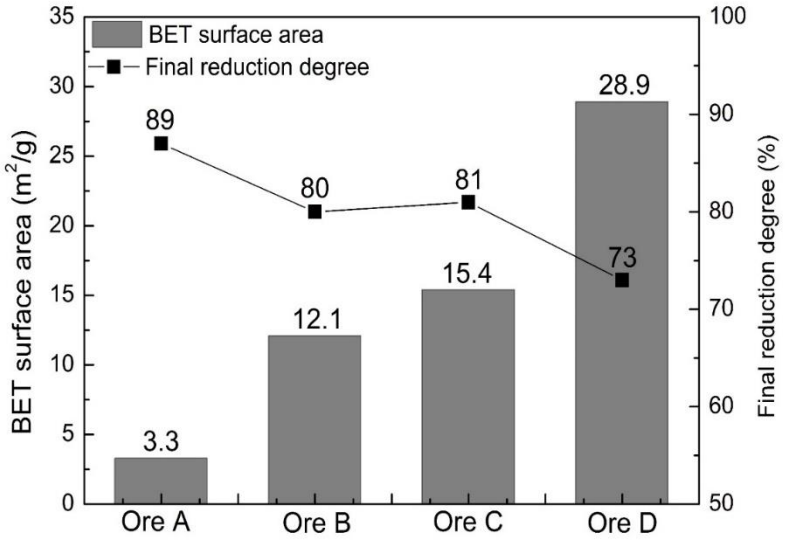
Specific surface areas after dehydration (m^2/g)			
Ore A	Ore B	Ore C	Ore D
2.8	11.9	12.3	27.7

- ✓ At **R4** stage, **Ore A(Carajas)** showed not only the **smallest reduction degree,** but also **lower reduction rate** at R4 while **Ore D(Yandi) showed the highest** reduction rate.
- ✓ The iron ores containing **$Fe_2O_3 \cdot H_2O$ and FeO(OH) showed higher surface areas**, which indicates the **formation of pores** due to dehydration. A slower reduction rate was observed for lower surface area, suggesting that the **reduction reaction at R4 might be diffusion control**.

3. Results and discussion

3.1. Reduction behavior of four kinds of iron ores and their kinetic analyses

❑ Reduction behavior during R2 and R1 stage



Relationship between surface area after R3 reduction and final reduction degree

Model		R^2 value for each model		
		R4	**R2**	**R1**
Phase-Boundary control Geometrical Contraction	Mass Transport	0.9096	0.9938	0.8406
	Contracting Area	0.9125	0.9966	0.8914
	Contracting Volume	0.9134	0.9968	0.9064
Diffusion Control	1-D Diffusion	0.9811	0.9918	0.8790
	2-D Diffusion	0.9820	0.9863	0.9121
	3-D Diffusion – Jander	0.9829	0.9784	0.9466
	3-D Diffusion – Ginstling	0.9823	0.9838	0.9255
Reaction Control	First Order	0.9152	0.9971	0.9326
	3/2 Order	0.9180	0.9951	0.9619
	Second Order	0.9206	0.9909	0.9791
	Third Order	0.9259	0.9759	0.9835
Nucleation	Avrami 1.5	0.8704	0.9943	0.9137
	Avrami 2	0.8432	0.9901	0.9029
	Avrami 3	0.8130	0.9839	0.8911
	Avrami 4	0.7968	0.9801	0.8848

✓ The **surface area is not clearly correlated** with the final reduction degree. Conversely, **Ore D(Yandi) showing the highest surface** area was measured to reach the **lowest final reduction degree**.

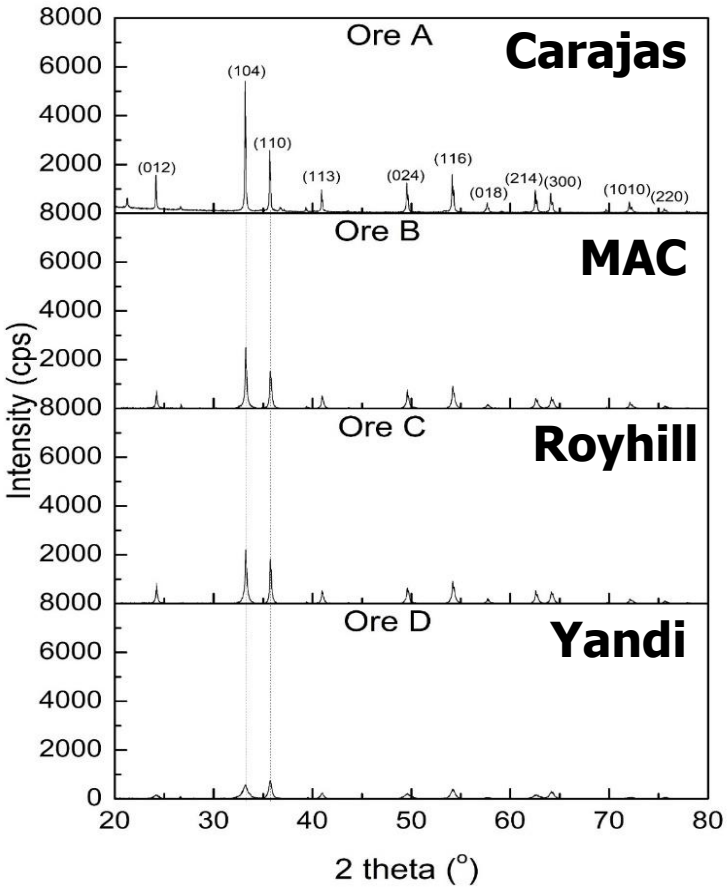
⇒ This might indicate that **different reduction mechanisms** might apply to the reduction in **wustite to metallic iron at R2 and R1**.

⇒ The reduction mechanism was measured to be **1st order and 3rd order chemical reaction for R2 and R1**, respectively.

3. Results and discussion

3.2. Effect of crystallite size and lattice constant on the reduction behavior of iron ores

❑ Crvstallite size and lattice constant after dehydration (Fe_2O_3)



Phase analyses of iron ores after dehydration

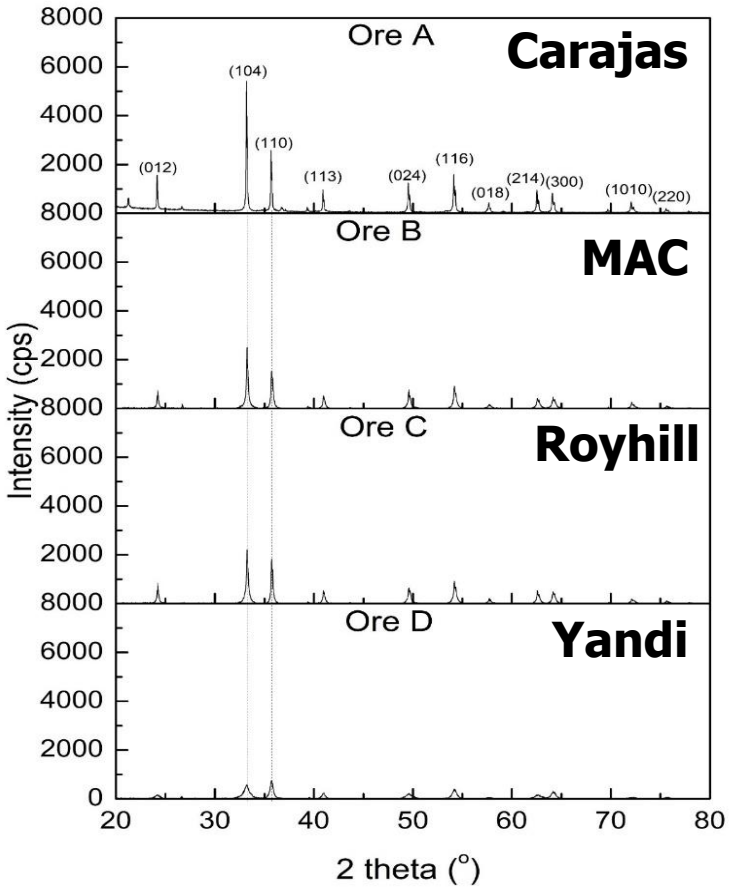
Iron ores	Lattice constant (Å)		Crystallite size (Å)
	a=b	c	(104)
Ore A (Carajas)	5.026	13.752	18.293
Ore B (MAC)	5.018	13.713	8.651
Ore C (Royhill)	5.018	13.713	7.946
Ore D (Yandi)	5.018	13.713	2.559

- ✓ For all the iron ores, the **lattice constant of Fe_2O_3 showed similar values**, which matched the results mentioned in the previous study. However, the **crystallite size are significantly different** for the iron ores.
- ✓ **Ore D** showed the **lowest degree of final reduction** showed the **smallest crystallite size**. These **results are in opposite to those reported** in the previous investigation.
  - The **previous study** explained the reduction **mechanism of nickel oxide by diffusion control**, which **suggested that smaller crystallite size would prefer to be reduced.**

3. Results and discussion

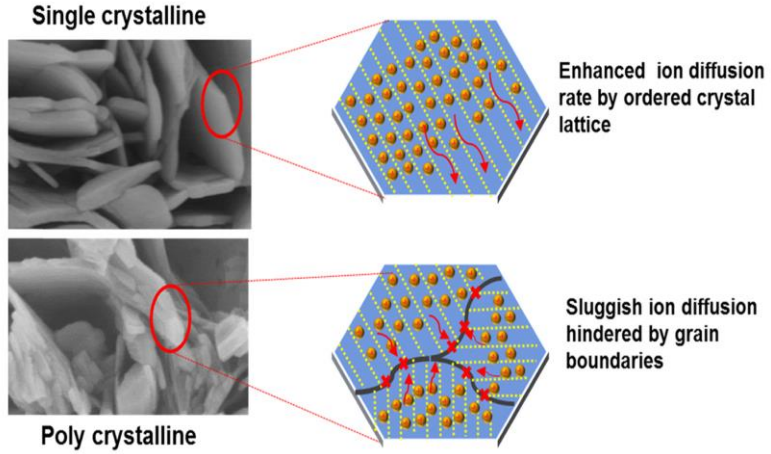
3.2. Effect of crystallite size and lattice constant on the reduction behavior of iron ores

❑ Crystallite size and lattice constant after R3 (Fe_3O_4)



Phase analyses of iron ores after dehydration

Iron ores	Lattice constant (Å)	Crystallite size (Å)
	a=b=c	(311)
Ore A	8.376	6.809
Ore B	8.341	3.471
Ore C	8.341	3.339
Ore D	8.341	2.983

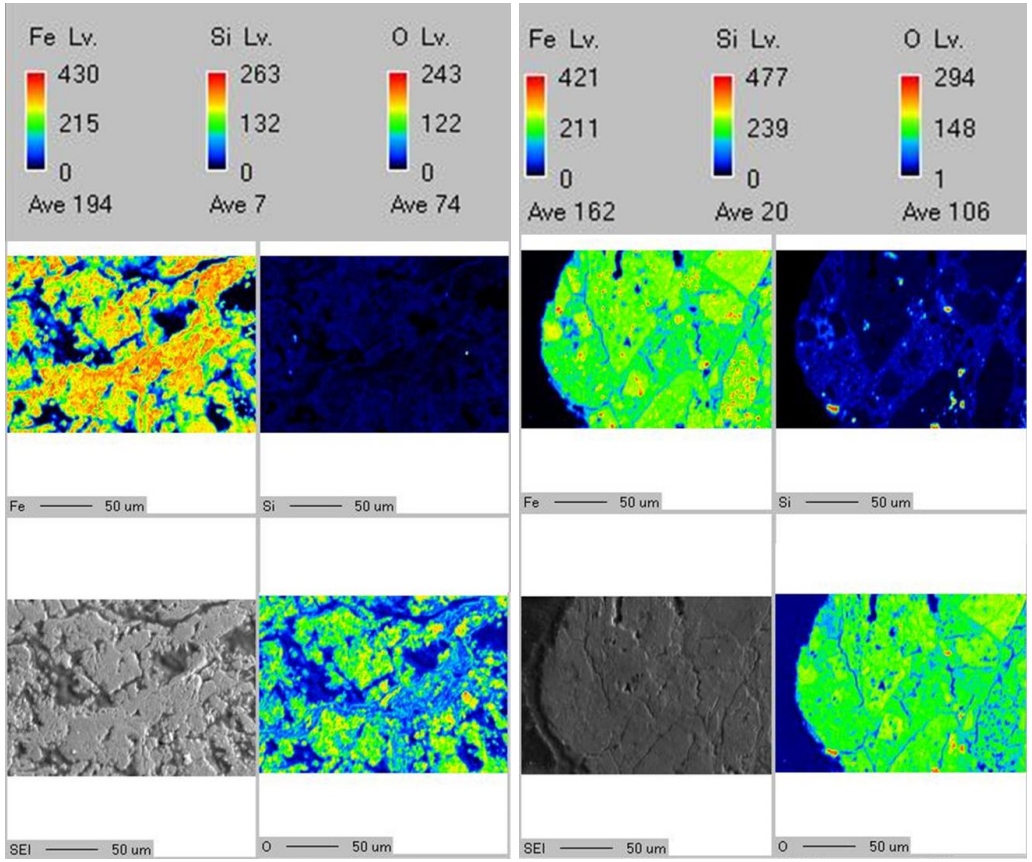


- ✓ Lattice size of magnetite was consistently estimated to be similar within all iron ores while the **crystallite size of the iron ores showed different** values.
- ✓ The **order of crystallite size** in magnetite showed **the similar trend** to those in hematite.
  - This might be attributed to **impurities such as SiO_2 and MgO**, as mentioned in previous studies.
  - Previous studies mentioned that **impurities induce defects and distortions** of crystal **structure**.

  ⇒ The current study observed the variation in SiO_2 content for the iron ores, and the **crystallite size was found to be inversely proportional** to **SiO_2 content** in the iron ores.

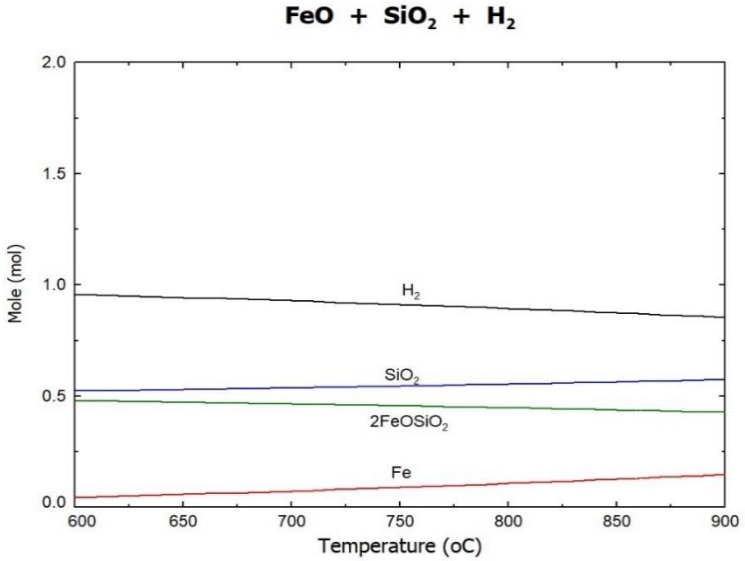
3. Results and discussion

❑ Distribution of Si and Fe (EPMA) after R2 reduction



Ore A (Carajas) **Ore D (Yandi)**

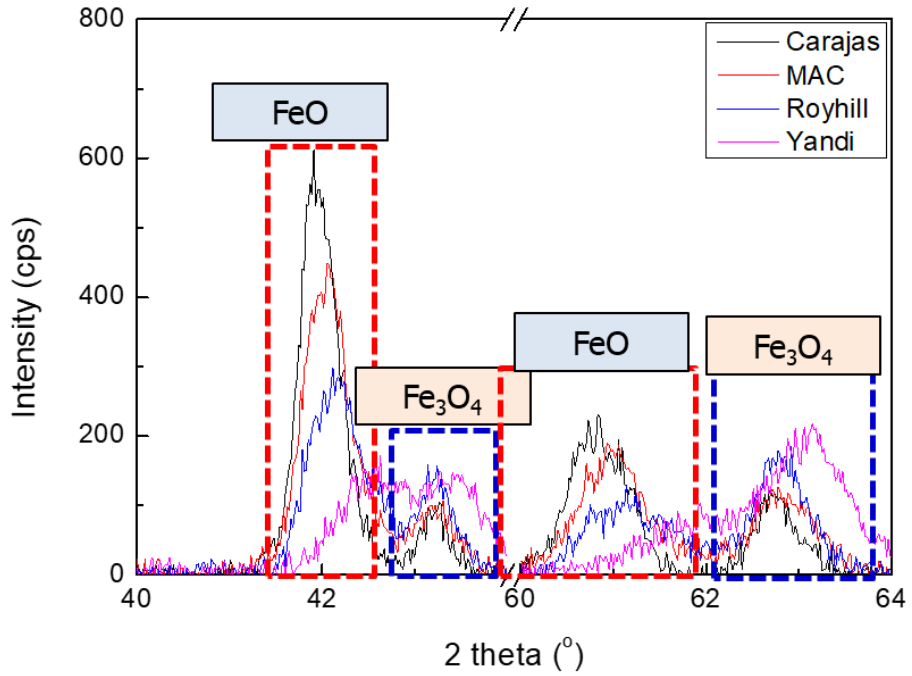
3.3. Effect of SiO_2 on the reduction behavior of iron ores



- ✓ It was observed that there was more **overlapping** area in the distribution of **Fe and Si in Ore D(Yandi) compared with Ore A(Carajas)**.
  ⇒ It is believed that **SiO_2 reacts with wustite** to **form fayalite** during reduction.
- ✓ Thermodynamic calculation was performed using FactSage to confirm whether **fayalite might form in the reducing atmosphere** in the temperature range of **600 to 900 °C**.

3. Results and discussion

❑ XRD analysis of wustite after reduction



Comparison of XRD peaks for reduced iron ores:

(a) In the range of 41 to 44 degree

(b) In the range of 60 to 64 degree

- ✓ As the content of **SiO_2 within the iron ores increases**, it could be observed that XRD peaks shift **towards the right side**.
- ✓ Shift in peak positions was observed, suggesting that **gangue components react with FeO, leading to the change in structure**.

4. Conclusions

- ✓ As the **surface area increased** due to the **dehydration** of iron ore, the **reduction rate in R4 increased**.
  - This result was consistent with the reaction mechanism of R4 stage, which was analyzed to be **controlled by diffusion**.
- ✓ However, **no correlation** was observed between the **final reduction degree** and **surface area** of iron ore.
  - This suggests that **reduction mechanism other than diffusion** operates in the later stage of reduction.
- ✓ The **final reduction degree decreased** as the **gangue content** in iron ore **increased** and **crystallite size** of iron oxides **became smaller**.
  - As the **crystallite size decreases**, the **diffusion of hydrogen within lattice** is expected to be **hindered**, leading the reduction reaction less favorable.
  - **Increase in gangue** content **promotes the formation** of phases such as **fayalite**, which are **challenging to reduce**, thereby **suppressing the reduction** reaction.