

**The behaviour of multiple reaction fronts during iron (III)  
oxide reduction in a non-steady state packed bed for  
chemical looping water splitting**

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## Abstract

Owing to the unclear temporal and spatial variations of axial solid conversion in a packed bed using iron (III) oxide as an oxygen carrier, we directly observe these variations by means of a sub-layer approach. The results indicate that the behaviour of the multiple reaction fronts during iron (III) oxide reduction by CO or H<sub>2</sub> within a packed bed for chemical looping water splitting (CLWS) is strongly dependent on the reaction temperature. When the reaction temperature is lower than the merging temperature, three reaction fronts, i.e., Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O and Fe<sub>0.947</sub>O-Fe, and three product zones, i.e., Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>0.947</sub>O and Fe, will appear in the packed bed. In contrast, when the reaction temperature is higher than the merging temperature, the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O fronts merge, leading to the disappearance of the Fe<sub>3</sub>O<sub>4</sub> zone. As a result, only the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>0.947</sub>O and Fe<sub>0.947</sub>O-Fe fronts, as well as Fe<sub>0.947</sub>O and Fe zones will appear in the packed bed. These reduction behaviours are verified by two breakthrough curves, one for  $T < T_m$  and one for  $T > T_m$ , from the thermodynamically controlled reduction of iron (III) oxide in the packed bed. The reaction front movement model, which is proposed based on the reduction behaviour, can be used to determine the maximum solid conversion of the reduction step, i.e., the thermodynamic limitation of the reduction step, in the packed bed CLWS. The maximum solid conversion can reach 0.409 for the CO case and 0.554 for the H<sub>2</sub> case. The first discovery of both the behaviours of the reaction fronts movement and the thermodynamic limitations of the reduction step standardizes the criteria for both the oxygen carrier evaluation and the optimization of the operating conditions and provides theoretical support for scaling up the packed bed and developing new technology for packed bed CLWS.

## Keywords

chemical looping water splitting; multiple reaction fronts; merging temperature; maximum solid conversion; reduction step; iron-based oxygen carrier

## 1 Nomenclature

### 2 Abbreviations

|   |                |                                            |
|---|----------------|--------------------------------------------|
| 3 | CLC            | chemical looping combustion                |
| 4 | CLWS           | chemical looping water splitting           |
| 5 | GC             | gas chromatograph                          |
| 6 | L <sub>k</sub> | sub-layer L <sub>k</sub> (k=1, 2, ..., 10) |
| 7 | XRD            | X-ray diffraction                          |

8

### 9 Symbols

|    |                             |                                                                          |
|----|-----------------------------|--------------------------------------------------------------------------|
| 10 | $l$                         | length (m)                                                               |
| 11 | $M_{\text{Fe}_2\text{O}_3}$ | molar mass of iron (III) oxide (kg/mol)                                  |
| 12 | $P$                         | partial pressure (kPa)                                                   |
| 13 | $Q_m$                       | molar flow (mol/s)                                                       |
| 14 | $S$                         | cross-sectional area of the packed bed (m <sup>2</sup> )                 |
| 15 | $T$                         | reduction temperature (°C)                                               |
| 16 | $T_m$                       | merging temperature (°C)                                                 |
| 17 | $X$                         | solid conversion (-)                                                     |
| 18 | $y$                         | molar composition (-)                                                    |
| 19 | $\gamma$                    | reaction conversion coefficient (-)                                      |
| 20 | $\delta$                    | solid consumption coefficient (-)                                        |
| 21 | $\rho_b$                    | bulk density (kg/m <sup>3</sup> )                                        |
| 22 | $\varphi$                   | solid conversion coefficient (-)                                         |
| 23 | $\omega$                    | reaction front velocity, i.e., rate of the reaction front movement (m/s) |

24

### 25 Superscripts

|    |    |                   |
|----|----|-------------------|
| 26 | eq | equilibrium state |
|----|----|-------------------|

27

### 28 Subscripts

|    |                                                                |                                                |
|----|----------------------------------------------------------------|------------------------------------------------|
| 29 | Fe <sub>a</sub> O <sub>b</sub> -Fe <sub>i</sub> O <sub>j</sub> | reaction front                                 |
| 30 | Fe <sub>i</sub> O <sub>j</sub>                                 | product zone                                   |
| 31 | in                                                             | inlet gas of the packed bed                    |
| 32 | max                                                            | maximum solid conversion of the reduction step |

## 1 Introduction

Fossil fuel is widely used in both stationary and mobile energy systems [1] and has caused serious regional and global environment problems, such as the production of haze [2] and climate change [3]. Commonly, hydrogen is regarded as a clean energy source without a carbon footprint because it can be used as fuel in internal combustion engines and fuel cells with water as the only product [4]. However, approximately 96% of hydrogen is currently produced from fossil energy, and the CO<sub>2</sub> produced during this process has not been effectively captured [5]. Thus, fossil-based hydrogen cannot be considered to be a low-carbon energy source. Although low-carbon hydrogen production technologies, including biomass conversion and solar photolysis, have greatly progressed in recent years, hydrogen production from fossil energy with carbon capture will still share the main market for the foreseeable future due to its efficiency and commercialization issues [6, 7].

Chemical looping water splitting (CLWS) has been developed from the steam-iron scheme [8-10], in which high purity hydrogen is produced through water splitting on reduced iron oxides (Fig. S1, supplementary material). By adding an air combustion step, the Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O/Fe redox cycle in the steam-iron scheme can be extended to Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>0.947</sub>O/Fe. Through assistance by iron (III) oxide with prior thermodynamic properties (Fig. 1), the fossil fuel is completely combusted, resulting in the direct production of pure hydrogen with inherent CO<sub>2</sub> separation [11-13]. This process includes reduction, water splitting and combustion steps, which are also referred to as chemical looping gasification [14] or chemical looping hydrogen generation [15]. Owing to the use of lattice oxygen in the oxygen carrier for combustion [16, 17], less NO<sub>x</sub> and dioxins are produced [18-21] so that cleaner hydrogen can be achieved in this process.

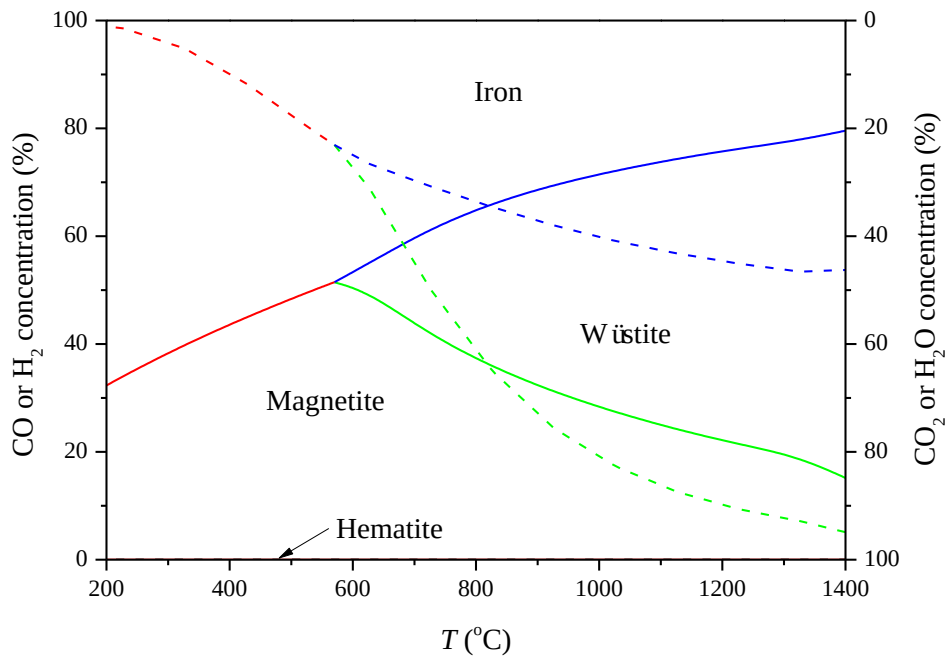
There are different reactor types for CLWS, such as a fluidized bed, a moving bed or a packed bed reactor. The fluidized bed is commonly used for the chemical looping combustion (CLC) of gaseous fuels and solid fuels [22-24]. A combustion efficiency of 96.33% has been achieved during the CLC of bituminous coal in a 5 kW<sub>th</sub> fluidized bed using hematite as the oxygen carrier [25]. With the assistance of fluidized bed CLC, the efficiency penalty for a power plant to achieve 98% of CO<sub>2</sub> capture has been reduced to 3.9%, and the additional cost of the fluidized bed CLC relative to the fluidized bed technology was 20 €/tonne CO<sub>2</sub> [26]. Considering this, a fluidized bed has also been used for CLWS [27, 28]. Rydén [27] conducted continuous operation of CLWS in a circulating fluidized-bed reactor with particles of Fe<sub>2</sub>O<sub>3</sub>(60 wt%)/MgAl<sub>2</sub>O<sub>4</sub> as oxygen carriers. Hydrogen with an average purity of 74.6% (N<sub>2</sub> free basis)

1 was obtained when the 67.0% of CO was converted. In addition, a moving bed or a packed bed  
2 is another configuration for CLWS [29-32]. Cho [31] operated the CLWS process in a moving  
3 bed configuration using carrier particles of  $\text{Fe}_2\text{O}_3$  (20 wt%) /  $\text{ZrO}_2$ , in which 99.95%  $\text{H}_2$  ( $\text{N}_2$   
4 free basis) was produced at 94.15%  $\text{CH}_4$  conversion. Hua and Zhu [30, 32] utilized a packed  
5 bed as the reactor to run CLWS, where  $\text{Fe}_2\text{O}_3$  (50-60 wt%) /  $\text{Al}_2\text{O}_3$  particles were used as the  
6 bed materials. The average purity of  $\text{H}_2$  on a  $\text{N}_2$  free basis was 98.0% when the CO or synthesis  
7 gas was fully converted.

8 In all these reactor configurations, the efficiency of CLWS was mainly determined by the  
9 reduction step and the water splitting step. The water splitting step has been widely studied in  
10 both the steam-iron scheme and the two-step water splitting process [33, 34], and the hydrogen  
11 production from the water splitting step is currently highly efficient [35]. Therefore, the key to  
12 improving the efficiency of CLWS, especially the amount of hydrogen produced per mole of  
13 the iron-based oxygen carrier, is to improve the solid conversion of the reduction step [36-40].  
14 Thus, many efforts have been made to improve the solid conversion of the reduction step.  
15 Notably, the solid conversion of the reduction step is the solid conversion of the iron-based  
16 oxygen carrier at the fuel breakthrough point [32, 41]. The fuel breakthrough point occurs when  
17 the unconverted fuel starts to escape from the oxygen carrier bed during the reduction step.  
18 Preventing the fuel breakthrough in the reduction step is necessary for carbon capture during  
19 CLWS. Rydén [27], Chen [42] and Bao [43] have found that  $\text{Fe}_2\text{O}_3$  can only be reduced to  
20  $\text{Fe}_3\text{O}_4$  in a typical fluidized bed with complete conversion of CO. The solid conversion of this  
21 reduced oxygen carrier ( $\text{Fe}_3\text{O}_4$ ) was 0.111 [11], which is not able to produce hydrogen during  
22 the water splitting step. Xiang [15, 44] raised the concept of a two-stage fluidized bed, in which  
23  $\text{Fe}_2\text{O}_3$  was further reduced to  $\text{Fe}_{0.947}\text{O}/\text{Fe}$  while CO was completely converted. Chiesa [45]  
24 reported that other types of reactors can also be used to achieve further reduction of the iron-  
25 based oxygen carrier. Sridhar [46] achieved 0.355 solid conversion of the reduction step in a  
26 counter-current moving bed using 60 wt%  $\text{Fe}_2\text{O}_3$  as the oxygen carriers. Bohn [38] gained  
27 0.254 solid conversion of the reduction step in a packed bed with pure  $\text{Fe}_2\text{O}_3$  as the oxygen  
28 carrier. Zhu [32] found that the solid conversion of the reduction step was between 0.220 and  
29 0.250 during 20 cycles in the packed bed while 60 wt%  $\text{Fe}_2\text{O}_3$  supported on  $\text{Al}_2\text{O}_3$  was used  
30 as the oxygen carrier.

31 These works achieved different solid conversions of the reduction step with complete  
32 conversion of the fuel. This result is mainly because the reduction of iron (III) oxide occurred  
33 through three steps, i.e.,  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.974}\text{O}$ - $\text{Fe}$ . According to the Baur-Glaessner phase  
34 diagram (Fig. 1) [47], the thermodynamic equilibrium properties change with these reaction

steps, which lead to various limits of the solid conversion of the reduction step in different reactors. The thermodynamic limitation of the solid conversion of the reduction step, i.e., the maximum solid conversion of the reduction step, can provide a standard for evaluating the operation results from different reactor types or to evaluate the performance of designed oxygen carriers in specific reactor types. This limitation is crucial for the development of an iron-based oxygen carrier as well as the operational optimization for CLWS. Both the fluidized bed and the moving bed are in a steady state operation. The maximum solid conversion of the reduction step during CLWS was directly confirmed by the combination of the equilibrium curve and the operating curve. As a result, the maximum solid conversion in the fluidized bed was 0.111 [15, 43], and the maximum solid conversion in the counter-current moving bed at 850 °C with H<sub>2</sub> as fuel was 0.500 [11, 48].



**Fig. 1** Thermodynamic equilibrium phase diagrams of the iron-carbon-system (solid line) and iron-hydrogen-system (dash line). The black line near the temperature axis, red line, green line, and blue line represent Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Fe, Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O, and Fe<sub>0.947</sub>O-Fe, respectively. The original data are from Barin [49].

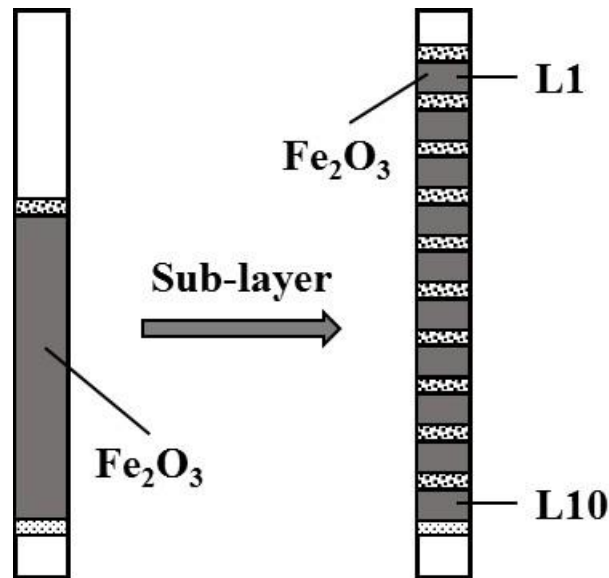
In contrast, a redox cycle in a packed bed for CLWS has been realized by gas switching [41, 50]. During this time, the packed bed is in non-steady state operation, in which the oxygen carrier conversion varies with reaction time and axial position. Thus, to obtain the maximum solid conversion of the reduction step during CLWS in the non-steady state packed bed, the

temporal and spatial variation of the iron-based oxygen carrier conversion should be known. In addition, the redox cycle of iron-based materials in a packed bed has also been used in a steam-iron scheme [8, 9], a two-step water splitting scheme for hydrogen production [36, 51], and a hybrid solar-redox scheme for hydrogen production [33, 52]. Therefore, knowledge of iron-based materials reduction in the non-steady state packed beds enables the understanding of the energy and environmental processes using the packed bed.

Current research into the temporal and spatial variation of iron-based oxygen carrier conversion in packed beds during the reduction step is still very limited. In spite of this limitation, one consensus has been reached from current research: the existence and movement of the reaction front plays a vital role in the reduction behaviour of the oxygen carrier in the packed bed. Thus, the temporal and spatial variation of the iron-based oxygen carrier conversion in a packed bed is actually the behaviour of multiple reaction fronts, mainly the relative position and the movement of multiple reaction fronts. Noorman [41, 53, 54] first used the concept of "reaction front" to explore the reaction behaviour in a packed bed chemical looping process with copper oxide as the oxygen carrier. This process only referred to one reaction front. According to the axial temperature curve and the breakthrough curve, he proved the existence of a reaction front within the gas-solid reaction in the packed bed. The breakthrough curve showed the change of the outlet gas composition with the reaction time. Heidebrecht [55] conducted a thermodynamic analysis of a cyclic water gas-shift reactor, which was a non-steady state packed bed. This process is similar to the steam-iron scheme [8, 9]. Under the assumption of chemical equilibrium, a model with five regions in the packed bed was proposed based on wave theory [56]. This model, containing three pure substance regions and two mixture regions, was used to describe the cyclic process of  $\text{Fe}_3\text{O}_4$  to Fe in the packed bed. The length of the mixture regions (reaction fronts) in the packed bed was zero due to a hypothetically high reactivity. Through qualitative analysis, changing gas compositions or reaction temperatures would lead to different operating regimes in the packed bed by influencing the movement of each reaction front. That is, the movement of the reaction fronts will definitively affect the behaviour of the packed bed. Hua [57] developed a model of a non-steady state packed bed for a cyclic system of  $\text{Fe}_2\text{O}_3$  to Fe that included three reaction fronts. The model was based on the breakthrough curve from the reduction step of CLWS.

The investigation of the behaviour of the reaction front, i.e., the behaviour of the oxygen carrier, in all these studies considered the changes in the concentration curves or the temperature curves in the packed bed. The direct change of the oxygen carrier in a packed bed has not been investigated yet. In addition, the temporal and spatial variation of the iron-based

oxygen carrier conversion in the non-steady state packed bed during the reduction step of CLWS, i.e., the relative positions and the movement of multiple reaction fronts, is not clearly understood from these indirect investigations. Thus, the maximum solid conversion of the reduction step in a packed bed reactor has remained uncertain until now.



**Fig. 2** Schematic of the sub-layer approach for the non-steady state packed bed during the reduction step of CLWS [32].

Here, we explore the real variations of the oxygen carriers in the packed bed and the maximum solid conversion by using the sub-layer method. With this method, the particle bed was evenly divided into 10 sub-layers by quartz cotton before the reaction (Fig. 2) [32], and the masses of each sub-layer before and after reduction in the non-steady state packed bed were determined directly. Combined with X-ray diffraction (XRD) analysis and mass balance, the phase distribution of the iron oxides in each sub-layer were determined. Zhu [32] used the sub-layer method to explore why the solid conversion of the reduction step was between 0.220 and 0.250 in a packed bed. The phase distribution of iron oxides in each sub-layer at the fuel breakthrough point was determined by using this method. The results indicated that two reaction fronts, i.e.,  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.947}\text{O-Fe}$ , existed in the packed bed at the fuel breakthrough point and that the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  front occupied approximately 80% of the bed length. However, the variations of the iron-based oxygen carriers in the packed bed during the reduction step and the maximum solid conversion of the reduction step remain unclear. In this study, with the assistance of the sub-layer method, the axial phase distributions of iron oxides in the packed bed at various specific reduction times were determined. The change in the axial

phase distribution with reduction time provides new insight into our understanding of the reduction behaviour of iron-based oxygen carriers in a packed bed.

This is the first direct experimental observation in which multiple reaction fronts in the packed bed move at the same time. According to the temporal and spatial variation of the iron-based oxygen carrier conversion in the non-steady state packed bed during the reduction step of CLWS, a physical model considering the movement of multiple reaction fronts is raised. The model is demonstrated by the breakthrough curves from the thermodynamically controlled reduction of iron (III) oxide in the packed bed. Furthermore, the maximum solid conversion of the reduction step in the packed bed CLWS is determined by the model. This model also provides a theoretical basis for analyzing the behaviour of the iron-based oxygen carrier reduction in a packed bed for CLWS. In summary, this paper clearly illustrates the behaviour of the reduction step in the packed bed CLWS and identifies the thermodynamic limitations of the reduction step for the first time. These new findings provide a new perspective and theoretical framework for the development of CLWS technology, especially for packed bed CLWS.

## **2 Materials and Methods**

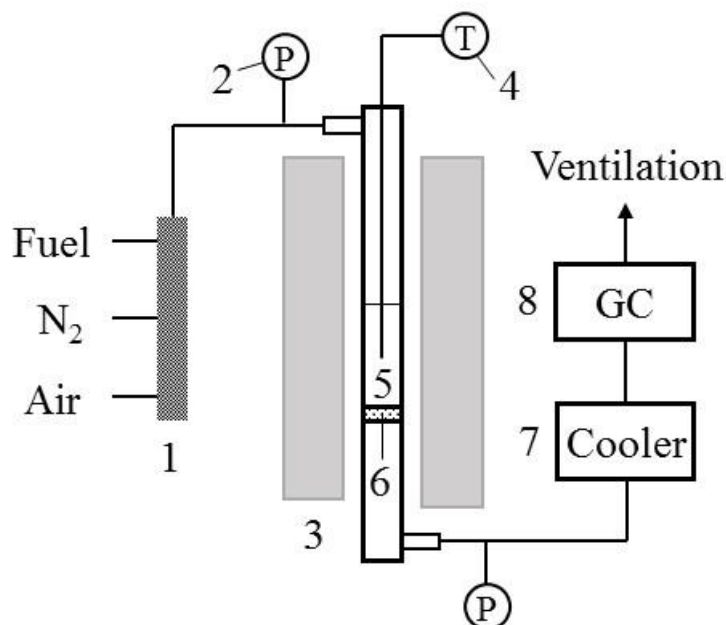
### **2.1 Oxygen carrier**

Iron (III) oxide powder ( $\text{Fe}_2\text{O}_3$ , analytical reagent, Sinopharm Chemical Reagent CO., Ltd, China) was used to prepare the oxygen carrier. This powder was calcinated in a furnace at 1200 °C for 24 hours. The heating rate was 5 °C·min<sup>-1</sup> from 25 to 1200 °C. The iron (III) oxide was then ground and sieved to 0.45-0.9 mm.

### **2.2 Packed bed system**

The packed bed system is illustrated in Fig. 3 and is made up of a quartz tube reactor with an inner diameter of 16 mm, an outer diameter of 20 mm, and a height of 1 m. A porous quartz plate is located 400 mm above the bottom of the quartz tube to support the whole oxygen carrier bed. To guarantee the gas distribution, quartz cotton fills the top of the oxygen carrier bed. The temperature of the reaction zone is maintained by a tube furnace and measured by a K-type thermocouple. The length of the constant temperature zone is 300 mm. In all experiments, the amount of the oxygen carrier is 30 g, and its height in the packed bed is approximately 100 mm. The reducing gas, purge gas (99.999%  $\text{N}_2$ ) and synthetic air (20%  $\text{O}_2$  in  $\text{N}_2$ ) are introduced to the oxygen carrier bed from the top of the reactor, and their flows are controlled by mass

flow controllers. The cooled and dry exhaust gas is measured by an on-line gas chromatograph (GC, Agilent 490). The GC contains two channels. Channel 1 is a Molecular Sieve 5A PLOT column that is used to measure  $H_2$ ,  $O_2$ ,  $N_2$  and  $CO$ . The other channel is the PoraPLOT U PLOT column, which is used to detect  $CO_2$ .



**Fig. 3** Schematic of the packed bed system. 1-mass flow controllers, 2-pressure meter, 3-tube furnace, 4-thermocouple, 5-oxygen carrier bed, 6-porous quartz plate, 7-dry unit, and 8-on-line micro GC. Fuel includes 85%  $CO$  in  $CO_2$ , 50%  $CO$  in  $CO_2$  and 50%  $H_2$  in  $N_2$ .

## 2.3 Experimental procedure

The behaviour of iron (III) oxide reduction in packed bed CLWS was investigated by conducting the following experiments. The data evaluation can be found in the supplementary material and is referred to in our previous publication [32].

### 2.3.1 Behaviour of iron (III) oxide reduction in the packed bed

The whole oxygen carrier bed was divided into 10 sub-layers by quartz cotton, with a loading of 3 g of the oxygen carrier in each sub-layer, as shown in Fig. 2. After reduction by  $CO$  or  $H_2$ , the bed was cooled to room temperature under the protection of  $N_2$  so that the reduced oxygen carrier could be further characterized and the mass of each reduced sub-layer could be weighed directly. Phase analysis of the material was conducted by XRD (Ultima IV-185). 85%  $CO$  in  $CO_2$  with a flow rate of  $100 \text{ mL}_N/\text{min}$  was used as the reducing gas for the  $CO$  case. The reduction temperatures were 850, 900, and  $1000^\circ\text{C}$ . Using 85%  $CO$  in  $CO_2$

avoided carbon deposition and guaranteed that  $\text{Fe}_2\text{O}_3$  could be reduced to Fe within certain temperature ranges (Fig. 1). At 900 °C, 50%  $\text{H}_2$  in  $\text{N}_2$  at a flow rate of 200 mL<sub>N</sub>/min was used as the reducing gas for the  $\text{H}_2$  case. The flow setting and the  $\text{N}_2$  addition were primarily to ensure that dry gas entered the GC at a rate of at least 100 mL<sub>N</sub>/min, even when all of the  $\text{H}_2$  was converted to  $\text{H}_2\text{O}$ .

According to the sub-layer approach, the characteristics of the packed bed were determined by those of all sub-layers. For example, the solid conversion of the whole bed was the average of the solid conversions of the 10 sub-layers. Thus, the uncertainties in this investigation were mainly from the sub-layer approach. The result from a blank experiment showed that the weight change of each sub-layer caused by the sub-layer approach was less than 0.09%. Thus, the corresponding solid conversion was less than 0.003 (Eq. S1, supplementary material). The oxygen carriers in the blank sub-layer experiment were heated at 900 °C for 120 min under a  $\text{N}_2$  atmosphere. In addition, by comparing the solid conversion values calculated from the breakthrough curves and the solid conversion values determined by using the sub-layer approach, it was confirmed that the sub-layer approach is accurate (Fig. 7(b)).

### 2.3.2 Thermodynamically controlled reduction of iron (III) oxide in the packed bed

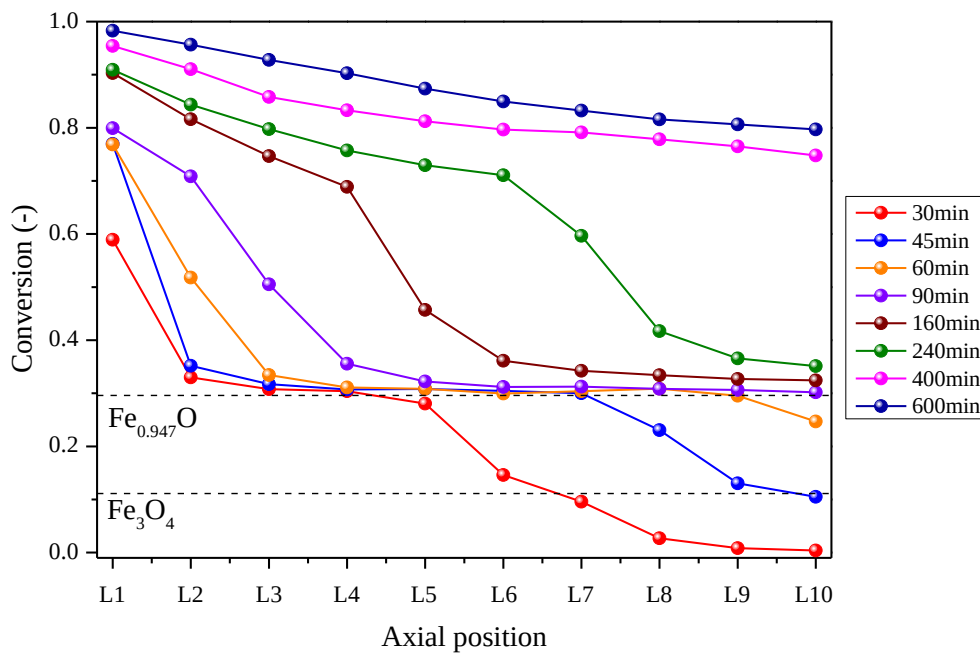
For two additional thermodynamically controlled reduction of iron (III) oxide, 30 g of iron (III) oxide was loaded in the packed bed. 50% CO in  $\text{CO}_2$  with a flow rate of 100 mL<sub>N</sub>/min was used as the reducing gas, and the reduction temperatures were 900 and 1050 °C. The reduction was not finished until the composition of the off-gas was the same as that of the reducing gas. Using 50% CO in  $\text{CO}_2$  thermodynamically ensured that the oxygen carrier ( $\text{Fe}_2\text{O}_3$ ) in the packed bed was perfectly reduced to  $\text{Fe}_{0.947}\text{O}$  but not further reduced to Fe at the two reduction temperatures (Fig. 1).

## 3 Results and discussion

### 3.1 Iron (III) oxide reduction by CO in the packed bed

Fig. 4 shows that the solid conversion of each sub-layer in the non-steady state packed bed varied over the reduction time at 900 °C. The reducing gas was 85% CO in  $\text{CO}_2$  in this case. Sub-layer L1 and L10 were located at the top and bottom of the oxygen carrier bed, respectively, presented in Fig. 2. After reduction for 30 min, the breakthrough of CO occurred. The solid conversion of L1 was 0.589, which was between the solid conversions of Fe (1.000) and  $\text{Fe}_{0.947}\text{O}$  (0.296). It can be concluded that there was mainly a mixture of Fe and  $\text{Fe}_{0.947}\text{O}$  in L1.

In L2 to L5, the solid conversion of each sub-layer was approximately 0.3, indicating that there was mainly  $\text{Fe}_{0.947}\text{O}$  (0.296) in these sub-layers. In L6 and L7, the solid conversions were 0.146 and 0.096, respectively, showing that  $\text{Fe}_3\text{O}_4$  (0.111) was mainly contained within these two sub-layers. In L8 to L10, the solid conversions of each sub-layer were less than 0.03, revealing that these sub-layers mainly contained  $\text{Fe}_2\text{O}_3$ . The XRD results (Fig. 5) for the oxygen carrier within each sub-layer of L1 to L10 after 30 min of reduction were correlated with these assertions. Our results indicated that the main phases of the iron oxides in these sub-layers could be determined by their solid conversions. This view was also validated by the XRD results of the oxygen carrier within the sub-layers after reduction at different time points, such as the XRD results of the oxygen carrier after 90 min of reduction, as shown in Fig. S2 (supplementary material).

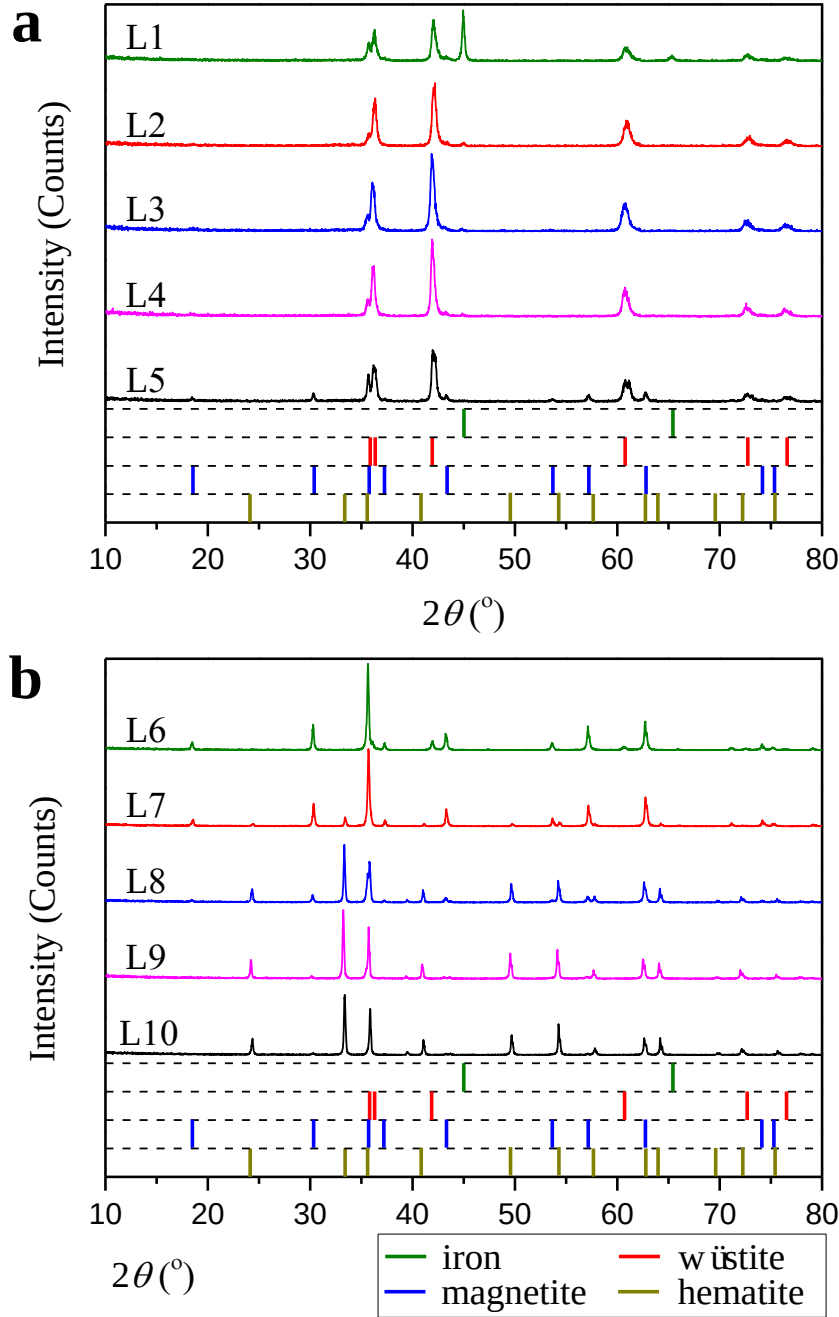


**Fig. 4** Axial solid conversion curves for different reduction times in the non-steady state packed bed with 85% CO in  $\text{CO}_2$  as the reducing gas and at 900 °C. L1 and L10, respectively, were located at the top and bottom of the oxygen carrier bed presented in Fig. 2.

From Fig. 4, it can also be inferred that the solid conversion value of any sub-layers, located at different places within the oxygen carrier bed, changes with the reduction time. The solid conversion of sub-layer L1, which is the inlet of the oxygen carrier bed, increased from 0 to 0.589 in the first 30 min, with an average reaction rate of  $0.0196 \text{ min}^{-1}$ . During this period, the  $\text{Fe}_2\text{O}_3$  in L1 was reduced to  $\text{Fe}_{0.947}\text{O}/\text{Fe}$  by 85% CO in  $\text{CO}_2$ . Monazam [58] acquired the kinetics of  $\text{Fe}_2\text{O}_3$  reduction to  $\text{Fe}_{0.947}\text{O}/\text{Fe}$  at 900 °C by 20% CO in  $\text{N}_2$ . The average reaction rate for that study over 45 min of reduction was  $0.0118 \text{ min}^{-1}$ . This rate is lower than that in L1

1 because the CO concentration in the reducing gas used in the literature was lower than that  
2 used here. Nevertheless, these rates are comparable. Over the following 15 min of reduction,  
3 the solid conversion of L1 increased from 0.589 to 0.770, and the reaction rate was  $0.0121 \text{ min}^{-1}$   
4 <sup>1</sup>, corresponding to the reduction of  $\text{Fe}_{0.947}\text{O}$  in L1 to Fe. After 45 min of reduction, the solid  
5 conversion of L1 changed slowly because of the “ceiling effect”, in which the reaction has  
6 difficulty reaching completion during real conditions. The reaction rate was only  $0.00116 \text{ min}^{-1}$   
7 <sup>1</sup> from 45 to 160 min and then decreased to  $0.00018 \text{ min}^{-1}$  from 160 to 600 min.

8 During the first 30 min of reduction, the  $\text{Fe}_2\text{O}_3$  in sub-layer L6, which is the middle part of  
9 the oxygen carrier bed, was reduced to  $\text{Fe}_{0.947}\text{O}/\text{Fe}_3\text{O}_4$ . During the following 15 min of  
10 reduction, the oxygen carriers in L6 were completely converted to  $\text{Fe}_{0.947}\text{O}$  and were almost in  
11 an equilibrated  $\text{Fe}_{0.947}\text{O}$  phase until 90 min (Fig. S2, XRD results in the supplementary  
12 material). From 90 to 160 min, the solid conversion of L6 only increased from 0.312 to 0.361,  
13 corresponding to the  $\text{Fe}_{0.947}\text{O}$ -Fe reaction. Conversely, an obvious increase in the solid  
14 conversion of L6 from 0.361 to 0.711 was observed during the reduction time of 160 to 240  
15 min. The reaction rate of  $\text{Fe}_{0.947}\text{O}$ -Fe was  $0.0044 \text{ min}^{-1}$  during this time interval, which was 8.8  
16 times that during the 45 to 160 min interval. This gap was attributed to the different  
17 compositions of the inlet gas of L6 for these two time periods. Because of the gas consumption  
18 in the sub-layers of L1 to L5, the CO concentration in the inlet gas of L6, which changed with  
19 the reduction time, was less than that in the inlet gas of the oxygen carrier bed (85%).



**Fig. 5** XRD diagrams of the oxygen carrier in different sub-layers after reduction by 85% CO in CO<sub>2</sub> at 900 °C for 30 min **(a)** L1 to L5 and **(b)** L6 to L10.

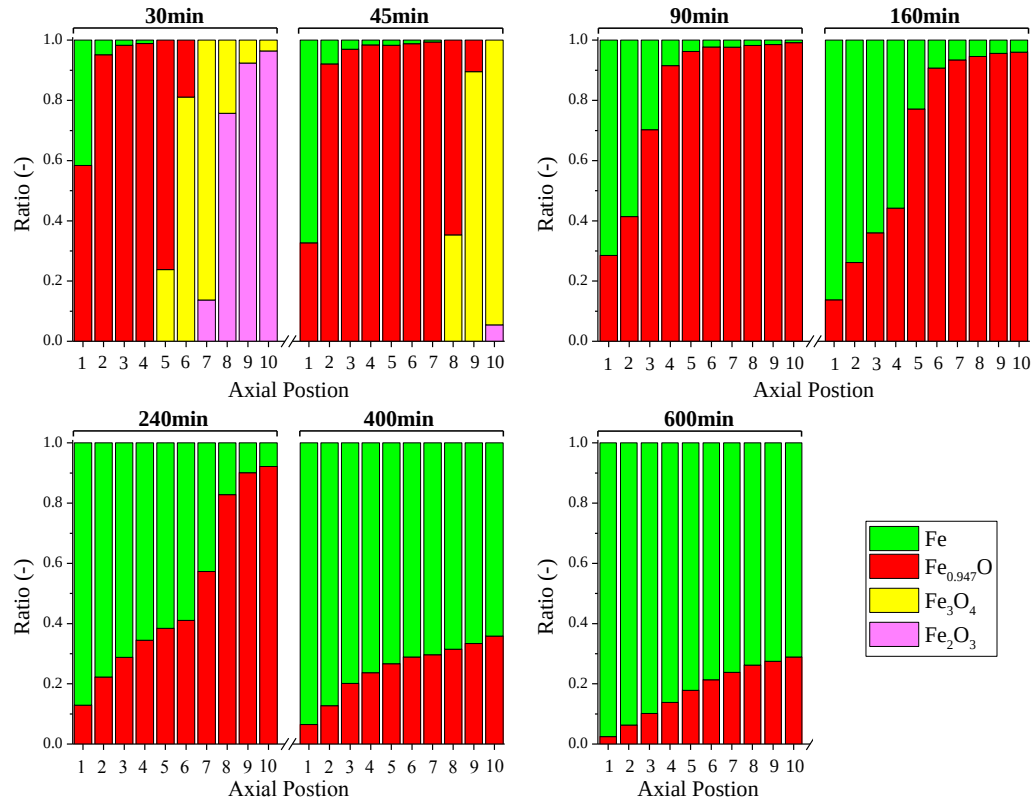
From 45 to 160 min, the solid conversion in each sub-layer from L1 to L5 was greater than 0.296, meaning that only the Fe<sub>0.947</sub>O-Fe reaction occurred in L1 to L5. At the same time, the L1 to L5 had sufficient oxidizing capacities, as observed from the contributions of the oxygen consumption by the sub-layers of L1 to L5 compared to the total oxygen consumption of L1 to L6 during this period. From 45 to 160 min, the solid conversion of the sub-layers from L1 to L5 increased from 0.411 to 0.722, corresponding to 0.0875 mole of oxygen consumption (Eq.

S1, supplementary material). Meanwhile, the solid conversion of the sub-layers from L1 to L6 increased from 0.393 to 0.662, corresponding to 0.0908 mole of oxygen consumption. That is, the sub-layers from L1 to L5 contributed 96.4% of the oxygen consumption of the L1 to L6 during this period. Thus, the sufficient oxidizing capacity in the L1 to L5 from 45 to 160 min resulted in an outlet gas composition from L5 that was close to the equilibrium of the  $\text{Fe}_{0.947}\text{O}$ -Fe reaction. This near-equilibrium gas, which is also the inlet gas of L6, could not further reduce the  $\text{Fe}_{0.947}\text{O}$  in L6 because of the thermodynamic limitation. This is fundamental for the oxygen carriers in L6 remaining in the  $\text{Fe}_{0.947}\text{O}$  phase from 45 to 160 min. Next, the solid conversion of the L1 to L5 increased from 0.722 to 0.807 over 160 to 240 min; thus, the mass ratio of the Fe phase in the sub-layers from L1 to L5 increased from 60.5% to 72.6%. During this period, the sub-layers from L1 to L5 only contributed 54.9% of the oxygen consumption of the L1 to L6, meaning that the oxidizing capacity of the L1 to L5 was insufficient. The CO concentration of the exhaust from L5 was higher than that of the equilibrium composition of the  $\text{Fe}_{0.947}\text{O}$ -Fe reaction. Hence, this gas had enough thermodynamic driving force to reduce the  $\text{Fe}_{0.947}\text{O}$  phase in L6.

The composition change of the inlet gas of L6 along with the reduction time was responsible for the variation of the oxygen carrier conversion in L6. This variation was observed when the solid conversion of L6 increased during the first 45 min and then remained as the solid conversion of the  $\text{Fe}_{0.947}\text{O}$  phase for 115 min, and subsequently further increasing. Similarly, the oxygen carriers in the other sub-layers, except L1, all remained near the  $\text{Fe}_{0.947}\text{O}$  phase for a period of time because of the thermodynamic limitations. In contrast, the inlet gas of L1, which was also the inlet gas of the packed bed, had a stable gas composition without any thermodynamic limitations. Li [48] reported that the reaction in the middle part of a counter-current moving bed is close to the thermodynamic equilibrium, leading to small changes in the gas and solid conversion. The solid conversion of the iron-based oxygen carrier increased from 0.232 to 0.321 within the middle part, which was 80% of the reactor length, and the iron oxides in the oxygen carriers within this part were mainly in the form of  $\text{Fe}_{0.947}\text{O}$ . As the author explained, the fluctuations of the solid conversion were caused by the limited amount of solid sampling.

By comparing the axial solid conversion curves at different reduction times within 30 to 400 min (Fig. 4), the reaction front movement was clearly observed in addition to the product zone formation from the reaction front movement, especially the Fe-rich and  $\text{Fe}_{0.947}\text{O}$  zone. The results indicate that the order of the reaction front velocities should be  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4 > \text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O} > \text{Fe}_{0.947}\text{O-Fe}$ , which is necessary to form these product zones. The reaction

front velocity is the rate of the reaction front movement. Fig. 5 shows that each sub-layer was made up of no more than two iron oxides. Notably, the XRD results for the oxygen carrier after reduction for other durations also show that each sub-layer was made up of one or two iron oxides.

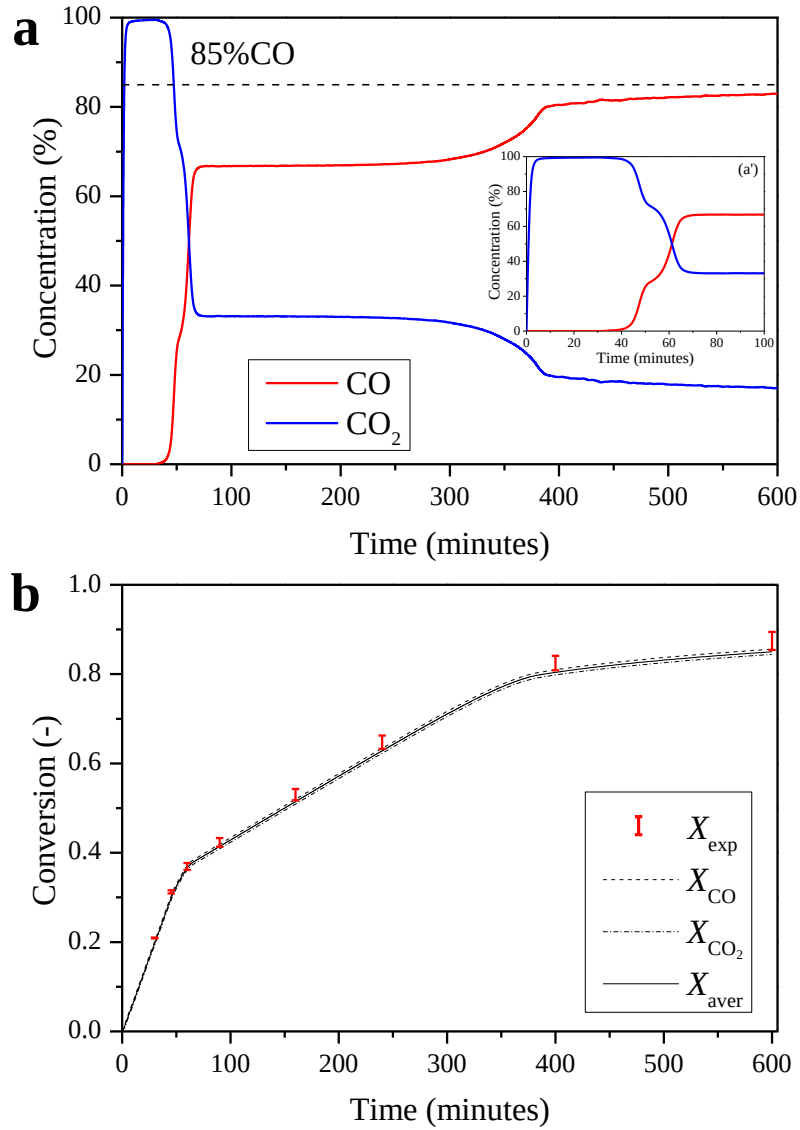


**Fig. 6** Mass ratios of the iron oxides in each sub-layer at different reduction times with 85% CO in  $\text{CO}_2$  as the reducing gas at 900 °C. The masses of the different iron oxides, which were normalized to  $\text{Fe}_2\text{O}_3$ , were used to calculate the ratios. The axial positions 1 to 10 refer to sub-layer L1 to L10.

According to the mass balance and the iron element balance [32], the mass ratios of the iron oxides in each sub-layer at different reduction times were determined (Appendix B in supplementary material), as shown in Fig. 6. After 30 min, three reaction zones (mixtures of iron oxides), i.e.,  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.947}\text{O}$ -Fe, appeared simultaneously in the packed bed as well as the  $\text{Fe}_{0.947}\text{O}$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  zones. As a result of the reaction front movement, the  $\text{Fe}_2\text{O}_3$  zone almost disappeared at 45 min, and the  $\text{Fe}_{0.947}\text{O}$  zone became more apparent within the packed bed. After 90 min, only the  $\text{Fe}_{0.947}\text{O}$  and Fe phases remained in the bed. Then, the  $\text{Fe}_{0.947}\text{O}$ -Fe front mainly moved in the bed and outflowed from the bed until 400 min. Next, the Fe zone almost occupied the whole packed bed while there was still a small amount of  $\text{Fe}_{0.947}\text{O}$ . The existence of  $\text{Fe}_{0.947}\text{O}$  was the result of the "ceiling effect". While

further increasing the reduction time to 600 min, the ratio of  $\text{Fe}_{0.947}\text{O}$  decreased slightly but at an extremely low rate. It was determined from the solid conversion in Fig. 4 that the average reaction rate in the whole bed from 400 to 600 min was only  $0.00025 \text{ min}^{-1}$ . It can also be seen from the breakthrough curve for the oxygen carrier reduction by 85% CO in  $\text{CO}_2$  for 600 min (Fig. 7(a)) that the CO concentration in the outlet gas of the bed increased slowly after 400 min. However, the CO concentration in the outlet gas did not reach the CO concentration in the inlet gas of the packed bed (85%), even after 600 min. In addition, Fig. 6 clearly shows that the  $\text{Fe}_{0.947}\text{O}$  zone grew from 30 to 45 min because the velocity of the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  front was significantly faster than that of the  $\text{Fe}_{0.947}\text{O-Fe}$  front. The change of the  $\text{Fe}_3\text{O}_4$  zone was not significant, indicating that there was no distinct difference between the velocities of the  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  fronts. These velocity differences at  $900^\circ\text{C}$  can be seen in section 3.2 (Fig. 10).

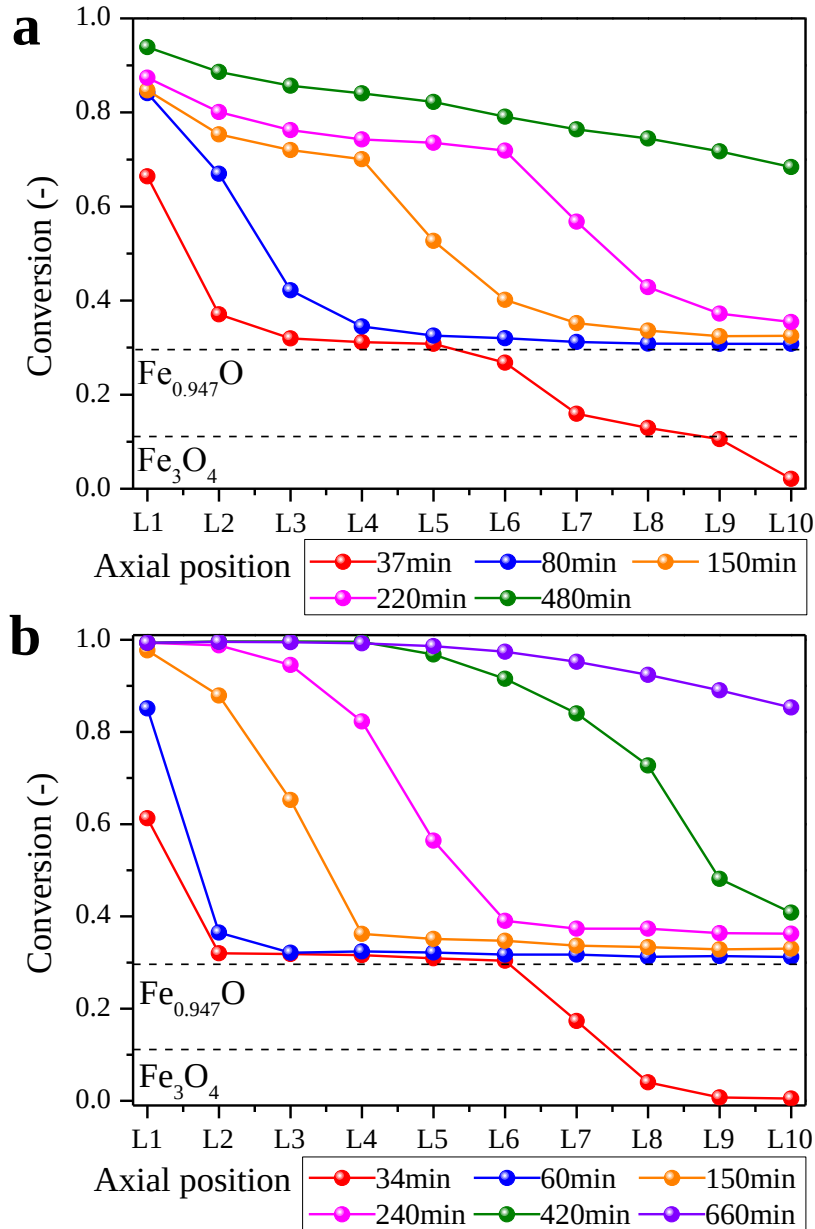
Fig. 7(a) shows the change of the composition of the outlet gas when  $\text{Fe}_2\text{O}_3$  was reduced by CO in the packed bed at  $900^\circ\text{C}$ , which represents the breakthrough curve of the reduction step. This curve can be fully explained by the reaction fronts movement (referring to Fig. 9(a)). During 0-39.5 min, the  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$  reaction front moved in the packed bed, and the CO was completely converted to  $\text{CO}_2$ . During 39.5-50.3 min, the  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$  reaction front started to flow out of the packed bed, leading to an increased CO concentration in the breakthrough curve. When the  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$  reaction front completely flowed out of the packed bed, the breakthrough curve was controlled by the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  reaction front, which still remained in the packed bed. The CO concentration of the breakthrough curve remained almost the same from 50.3 to 55.7 min, but from 55.7 to 73.8 min, the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  reaction front started to flow out of the packed bed, leading to an increase of the CO concentration. When the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  reaction front completely flowed out of the packed bed, the breakthrough curve was controlled by the  $\text{Fe}_{0.947}\text{O-Fe}$  reaction front, which remained in the packed bed. The CO concentration of the breakthrough curve remained stable from 73.8 to 284.5 min, but from 284.5 to 400.0 min, the  $\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}$  reaction front began to flow out of the packed bed, resulting in a further increase in the CO concentration of the breakthrough curve that was almost equal to the composition of the inlet gas of the packed bed. This result demonstrates that the reaction fronts movement proposed based on the temporal and spatial variation of the axial solid conversion in the packed bed can be used to explain the changes of the outlet gas concentration from the packed bed well. A similar phenomenon was also found in our previous work [57].



**Fig. 7** Breakthrough curve for iron (III) oxide reduction by 85% CO in CO<sub>2</sub> at 900 °C in the non-steady state packed bed **(a)**, and the comparison between the calculated solid conversions of the whole bed based on the breakthrough curve and the results from sub-layer experiments with an error analysis **(b)**.

In addition, by using mass balance and the integral of the CO or CO<sub>2</sub> concentration from the breakthrough curve (Eqs. S2-S5 in the supplementary material), the solid conversions of the whole bed at various reduction times were confirmed, as shown in Fig. 7 (b). The solid conversions from the breakthrough curve are in excellent agreement with the results from sub-layer experiments, which also provides evidence for the validity of the sub-layer approach.

Fig. 8 indicates that the solid conversion of each sub-layer changed with the reduction time at 850 and 1000 °C. Similar to the behaviours at 900 °C, the reaction fronts moved and the oxygen carriers of several sub-layers remained in the  $\text{Fe}_{0.947}\text{O}$  phase for a period, which also occurred at these two reduction temperatures. The mass ratio of the iron oxides in each sub-layer at different reduction times can be seen in Figs. S3-S4 (supplementary material). The temperature mainly affected the thermodynamic equilibrium and the reaction kinetics and further affected the details of the reaction front movement in the packed bed. After reduction for 150 min, the solid conversions of L1 at 850, 900, 1000 °C were 0.847, 0.888 and 0.977, respectively. Notably, the solid conversion of L1 after reduction for 150 min at 900 °C was equal to the linear interpolation of that between 90 and 160 min (Fig. 4). It was obvious that the reaction rate could be promoted by increasing the temperature. However, the solid conversions of the whole bed after reduction for 150 min at these temperatures were 0.529, 0.515 and 0.490, respectively. Temperature increases led to decreases in the solid conversion of the whole bed because the  $\text{Fe}_{0.947}\text{O}$  and Fe phases were mainly in the packed bed after 150 min of reduction (Fig. 6, and Figs. S3-S4 in the supplementary material). When the reduction temperature increased from 850 to 1000 °C, the number of sub-layers almost exclusively containing the  $\text{Fe}_{0.947}\text{O}$  phase increased from 4 to 7. The increasing proportion of the  $\text{Fe}_{0.947}\text{O}$  zone gave rise to a decreased solid conversion in the whole bed. The proportion of the  $\text{Fe}_{0.947}\text{O}$  zone increased with the reduction temperature, which was due to the change of the thermodynamic equilibrium with temperature. This change increased the difference between the velocities of the  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.947}\text{O}$ -Fe fronts (Fig. 10). Thus, the length of the  $\text{Fe}_{0.947}\text{O}$  zone in the packed bed at the same period increased with temperature (Eq. S15 in the supplementary material). These results will be discussed in more detail in the model section.

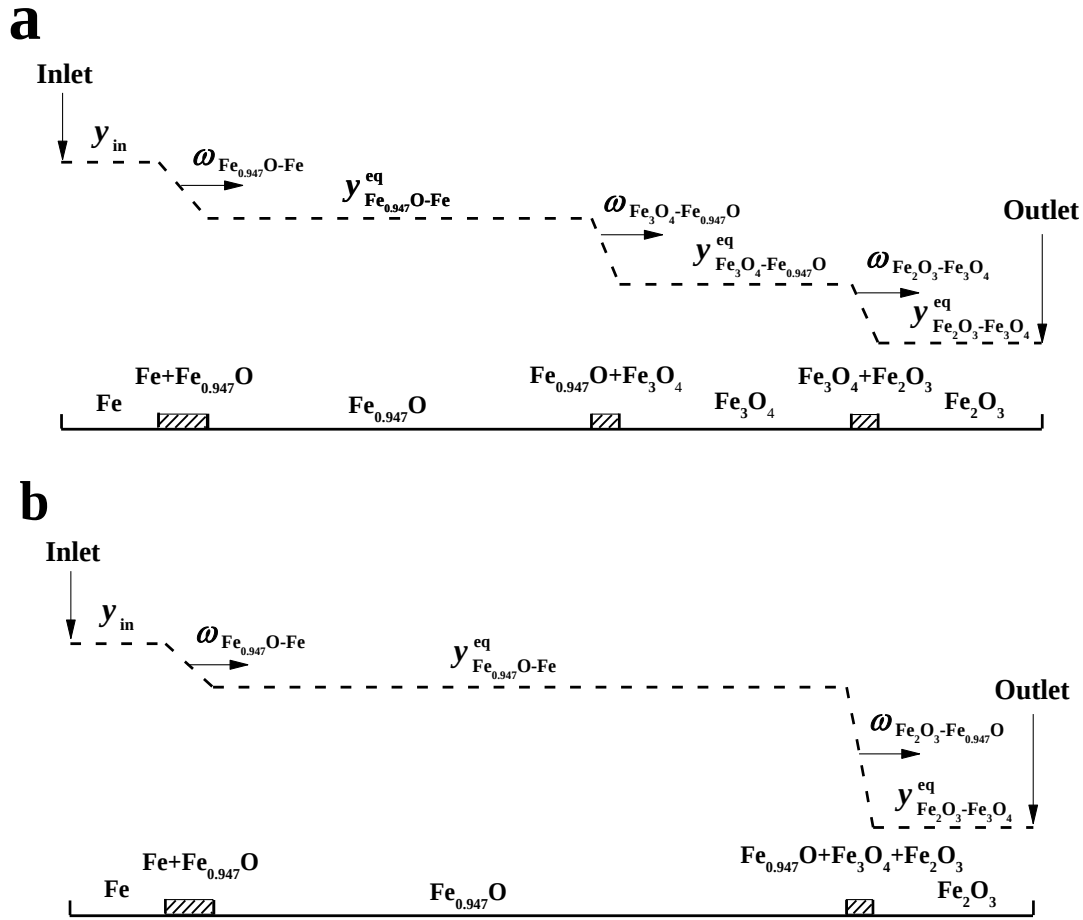


**Fig. 8** Axial solid conversion curves at different reduction times in the non-steady state packed bed with 85% CO in CO<sub>2</sub> as the reducing gas at **(a)** 850 °C and **(b)** 1000 °C. L1 and L10, respectively, were located at the top and bottom of the oxygen carrier bed, as shown in Fig. 2.

### 3.2 Model of iron (III) oxide reduction in the packed bed

By using the sub-layer approach to determine the changes of the oxygen carrier conversion in each sub-layer with reduction time, the behaviour of the iron (III) oxide reduction in the non-steady state packed bed has been essentially understood. Assuming that the gas-solid reaction had reached equilibrium in each reaction front, a physical model for the iron (III) oxide reduction in the non-steady state packed bed, which has enough length to form all the reaction

fronts and the product zones, was proposed and referred to as the tri-front model, as shown in Fig. 9(a).



**Fig. 9** Physical model for iron (III) oxide reduction by CO or H<sub>2</sub> in the non-steady state packed bed. **(a)** Tri-front model of 727-1032 °C for the CO case and **(b)** dual-front model of 1032-1377 °C for the CO case. For the H<sub>2</sub> case, (a) 727-945 °C and (b) 945-1377 °C. Solid lines denote the axial position in the packed bed, and the shadow zones in the solid lines represent the mixture of two iron oxides, i.e., the reaction fronts. The dash lines above the solid lines represent the gas compositions in different zones corresponding to the solid lines. The lower limit of the temperature, 727 °C (1000 K), was used to inhibit the carbon deposition and to ensure the reduction pathway involving the Fe<sub>0.947</sub>O phase from thermodynamics. Meanwhile, it also guaranteed effective reaction kinetics and maintains an exhaust gas with a high temperature. Fe<sub>0.947</sub>O liquefaction was avoided by limiting the maximum temperature to 1377 °C (1650 K) [49].

Each reaction front velocity was obtained through the mass balance based on the tri-front model:

$$\omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}} = Q_m \left( y_{\text{in}} - y_{\text{Fe}_{0.947}\text{O}-\text{Fe}}^{\text{eq}} \right) \gamma_{\text{Fe}_{0.947}\text{O}-\text{Fe}} \frac{M_{\text{Fe}_2\text{O}_3}}{\rho_b S} \quad (1)$$

$$\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}} = Q_m \left( y_{\text{Fe}_{0.947}\text{O}-\text{Fe}}^{\text{eq}} - y_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}^{\text{eq}} \right) \gamma_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}} \frac{M_{\text{Fe}_2\text{O}_3}}{\rho_b S} \quad (2)$$

$$\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4} = Q_m \left( y_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}^{\text{eq}} - y_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4}^{\text{eq}} \right) \gamma_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4} \frac{M_{\text{Fe}_2\text{O}_3}}{\rho_b S} \quad (3)$$

4

5 where  $\omega$  is the reaction front velocity and the subscripts indicate the corresponding reaction  
6 fronts. The variable  $Q_m$  is the molar flow of the reacting gas during the reduction step. Since  
7 the main reactions in the CO case are equimolar,  $Q_m$  is a constant. The variable  $y$  is the molar  
8 composition of CO in the reacting gas. The subscript “in” indicates the inlet gas of the packed  
9 bed, and the rest of the subscripts indicate the outlets of the corresponding reaction fronts. The  
10 superscript “eq” indicates the equilibrium state. The variable  $M_{\text{Fe}_2\text{O}_3}$  is the molar mass of the  
11 iron (III) oxide. The variable  $\rho_b$  is the bulk density of the oxygen carrier in the packed bed. The  
12 variable  $S$  is the cross-sectional area of the packed bed. The variable  $\gamma$  is the reaction  
13 conversion coefficient, which stands for the amount of  $\text{Fe}_2\text{O}_3$  consumption corresponding to 1  
14 mole of CO consumption, and the subscripts indicate the reactions that consume CO. Its  
15 formula is shown as follows:

$$\gamma_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j} = \delta_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j} \varphi_{\text{Fe}_a\text{O}_b-\text{Fe}_2\text{O}_3} \quad \left( \begin{smallmatrix} b & j \\ a & i \end{smallmatrix} \right) \quad (4)$$

17 Among these variables,  $\delta_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}$  indicates the solid consumption coefficient, which is the  
18 amount of  $\text{Fe}_a\text{O}_b$  consumed in the  $\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j$  reaction corresponding to 1 mole of CO  
19 consumption. The variable  $\varphi_{\text{Fe}_a\text{O}_b-\text{Fe}_2\text{O}_3}$  is the solid conversion coefficient, which denotes the  
20 amount of  $\text{Fe}_2\text{O}_3$  consumed with 1 mole of  $\text{Fe}_a\text{O}_b$  consumption based on the iron element  
21 balance. The reaction conversion coefficients are shown in Table 1.

22

23 **Table 1** Conversion coefficients for different reduction reactions

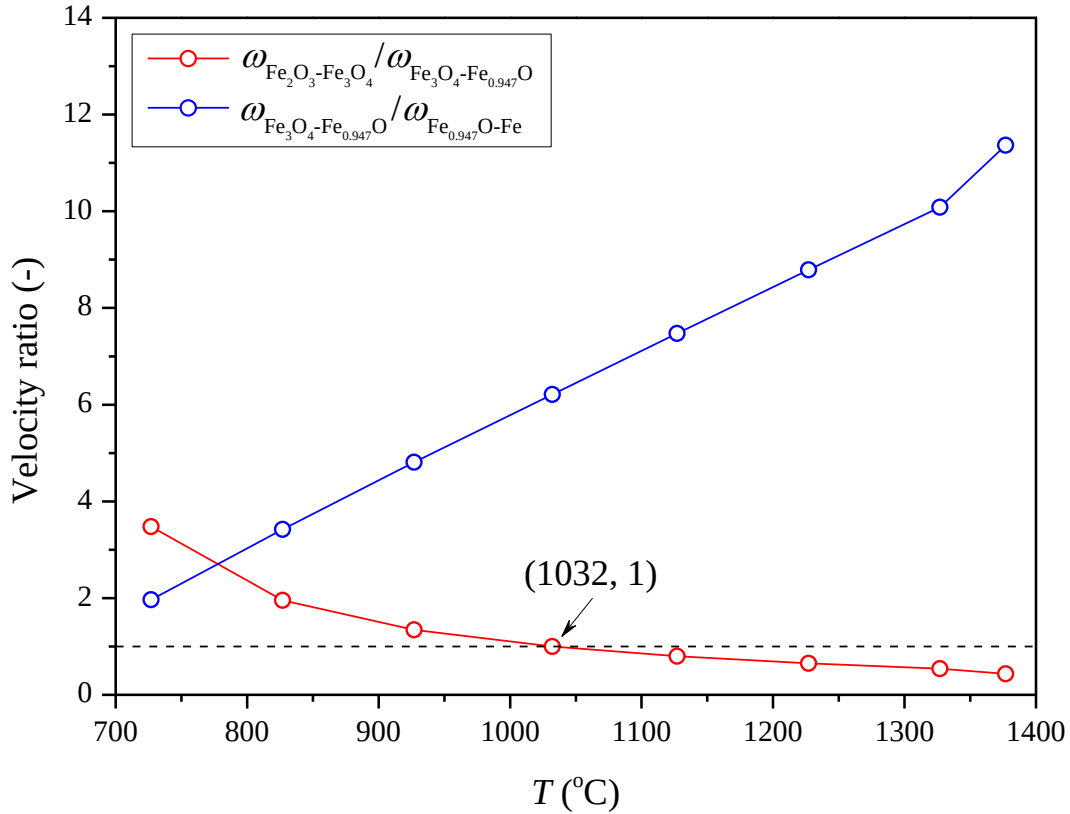
| Reaction                                          | Equation                                                                                                | Coefficient* |
|---------------------------------------------------|---------------------------------------------------------------------------------------------------------|--------------|
| $\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4$     | $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$                   | 3.000        |
| $\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}$ | $0.947\text{Fe}_3\text{O}_4 + 0.788\text{CO} \rightarrow 3\text{Fe}_{0.947}\text{O} + 0.788\text{CO}_2$ | 1.803        |
| $\text{Fe}_{0.947}\text{O}-\text{Fe}$             | $\text{Fe}_{0.947}\text{O} + \text{CO} \rightarrow 0.947\text{Fe} + \text{CO}_2$                        | 0.474        |
| $\text{Fe}_2\text{O}_3-\text{Fe}_{0.947}\text{O}$ | $0.947\text{Fe}_2\text{O}_3 + 0.841\text{CO} \rightarrow 2\text{Fe}_{0.947}\text{O} + 0.841\text{CO}_2$ | 1.126        |

24 \* These coefficients were also the same when  $\text{H}_2$  was used as the reducing gas.

25

26 From the above equations, the velocity ratios of the adjacent reaction fronts at different

reduction temperatures were easily obtained, namely  $\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4}/\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}$  and  $\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}/\omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}}$ , as shown in Fig. 10. The behaviour of the iron (III) oxide reduction by 85% CO in CO<sub>2</sub> in the non-steady state packed bed from 850 to 1000 °C mentioned in section 3.1 indicated that the order of the reaction front velocities was  $\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4 > \text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O} > \text{Fe}_{0.947}\text{O}-\text{Fe}$ . This was also the precondition for the tri-front model, so the two ratios of the reaction front velocities should have been greater than 1.

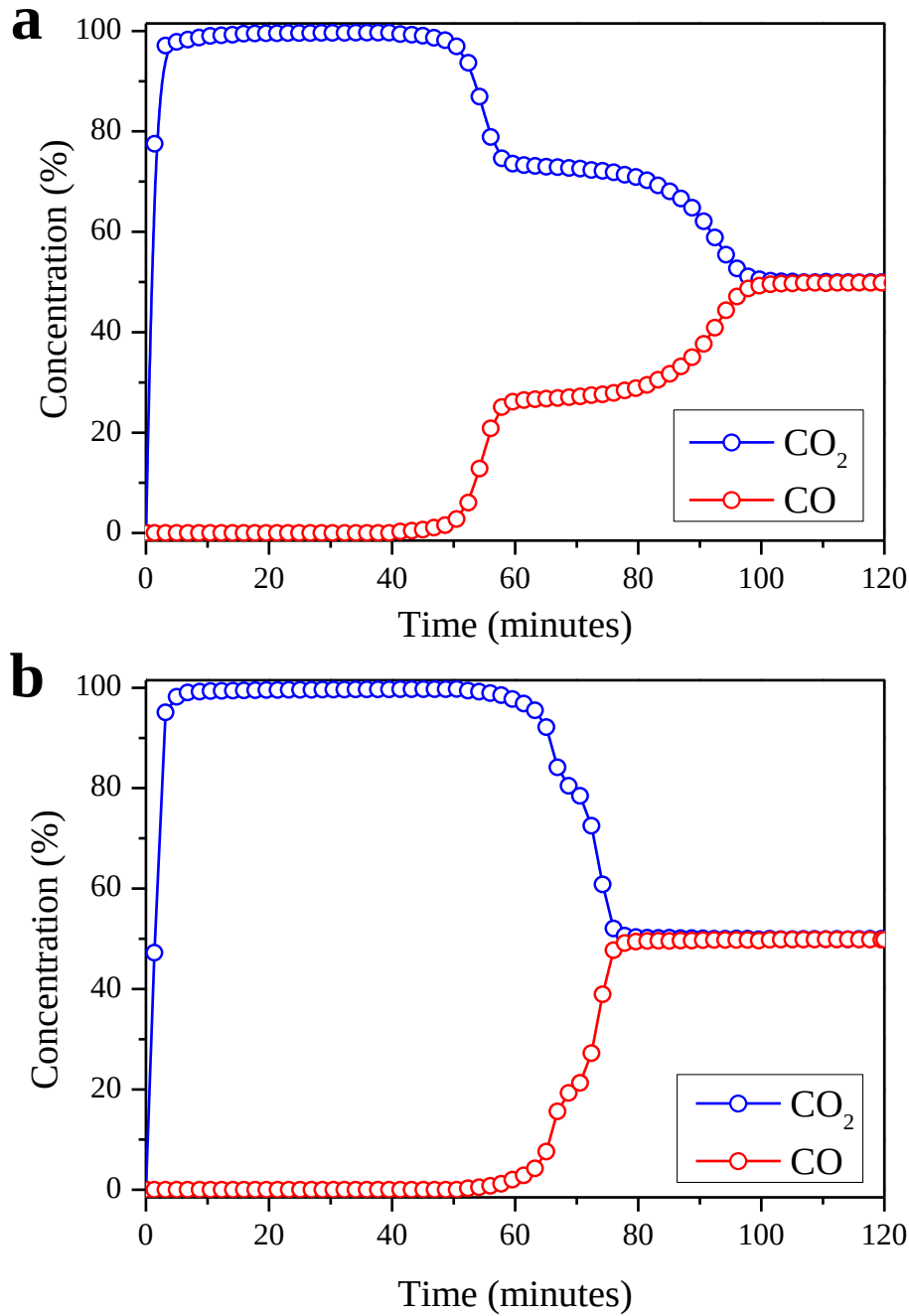


**Fig. 10** Ratios of the reaction front velocities at different reduction temperatures according to the tri-front model. The value of  $y_{\text{in}}$  in these calculations is 1.

According to Fig. 10,  $\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}/\omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}}$  was greater than 1 under the reduction temperatures ranging from 727 to 1377 °C and increased with temperature. This result indicates that there was a  $\text{Fe}_{0.947}\text{O}$  zone in the packed bed (Fig. 6), and the length of the  $\text{Fe}_{0.947}\text{O}$  zone in the bed increased with temperature within the same period. This is also the reason why the proportion of the  $\text{Fe}_{0.947}\text{O}$  zone in the oxygen carrier bed increased after 150 min of reduction as the temperature increased, which decreased the solid conversion of the whole bed, as discussed in section 3.1. In the temperature range from 727 to 1032 °C,  $\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4}/\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}$  was also greater than 1, revealing that the  $\text{Fe}_3\text{O}_4$  zone existed in the

packed bed (30 min in Fig. 6). Thus, the tri-front model is applicable in this temperature range. In addition, this velocity ratio decreased with the reduction temperature, which was responsible for the lessening the  $\text{Fe}_3\text{O}_4$  zone in the packed bed at the breakthrough point with the reduction temperature (Fig. 6 and Figs. S3-S4 in the supplementary material). However, from 1032 to 1377 °C,  $\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4}/\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}}$  was less than 1 because the movement of the  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  front was faster than the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  front. In this case, the  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  fronts in the tri-front model merged, resulting in the disappearance of the  $\text{Fe}_3\text{O}_4$  zone. Thus, only two reaction fronts, i.e.,  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.947}\text{O}$ -Fe, existed in the packed bed, and the tri-front model evolved into a dual-front model, as shown in Fig. 9(b).

Two behaviours during the iron (III) oxide reduction by CO in the packed bed were deduced from the ratios of the reaction front velocities. First, there were three reaction fronts and three product zones in the packed bed when the reduction temperature was below the merging temperature ( $T_m$ , 1032 °C). Conversely, only two reaction fronts and two product zones existed in the packed bed when the reduction temperature was above  $T_m$ . The differences between them included the existence of an  $\text{Fe}_3\text{O}_4$  zone and the number of reaction fronts in the interval from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_{0.947}\text{O}$ . To verify this inference, the variation of the breakthrough curves at two designed temperatures ( $T > T_m$  and  $T < T_m$ ) when the iron (III) oxide was reduced by 50% CO in  $\text{CO}_2$ , were observed. As mentioned above, the 50% CO in  $\text{CO}_2$  helped to control the iron (III) oxide reduction to  $\text{Fe}_{0.947}\text{O}$  rather than being further reduced to Fe. Subsequently, only two reactions, i.e.,  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$ , occurred in the packed bed. It was easy to define the relationship between these reactions, as shown in Fig. 11. From Fig. 11(a), there were two distinct CO concentration plateaus over both 0 to 40 min and 60 to 80 min at 900 °C. This result indicated that these two reactions, i.e.,  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$ , occurred at two spatially separated reaction fronts. In contrast, there was only one CO concentration plateau within 0 to 50 min at 1050 °C (Fig. 11(b)), indicating that these two reactions occurred within one reaction front (the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_{0.947}\text{O}$  front). Further, an obvious change in the slope of the breakthrough curve at 1050 °C appeared at approximately 70 min. This was further evidence that the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_{0.947}\text{O}$  front involved two distinct reactions.



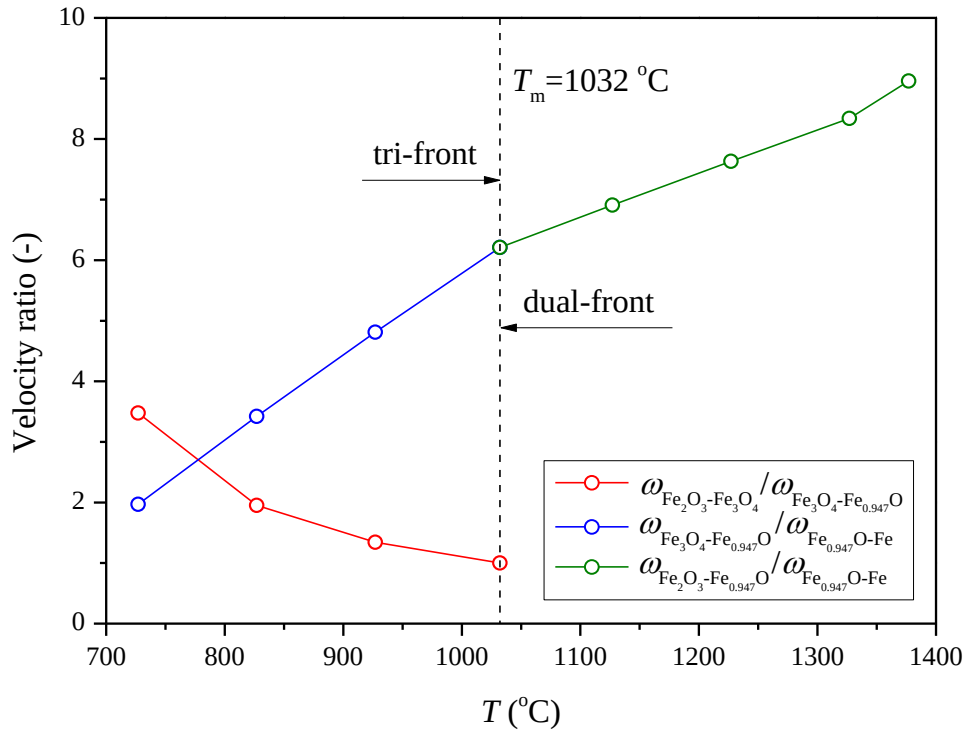
**Fig. 11** Breakthrough curves at 900 °C (a) and 1050 °C (b) with 50% CO in CO<sub>2</sub> as the reducing gas.

The breakthrough curves from the thermodynamically controlled reduction process (Fig. 11) demonstrated that the reduction of iron (III) oxide by CO in the packed bed exhibited two behaviours, and their physical models can be seen in Fig. 9. When the reduction temperature was lower than  $T_m$ , there were three reaction fronts, i.e., Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O and Fe<sub>0.947</sub>O-Fe, and three product zones, i.e., Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>0.947</sub>O and Fe, in the packed bed. The model

is shown in Fig. 9(a), referred to as a tri-front model. The reaction front velocities were calculated by Eqs. 1-4. However, when the reduction temperature was higher than  $T_m$ , there were only two reaction fronts, i.e.,  $\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}$  and  $\text{Fe}_{0.947}\text{O-Fe}$ , and two product zones, i.e.,  $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}$ , in the packed bed. The model is shown in Fig. 9(b), referred to as a dual-front model. The  $\text{Fe}_{0.947}\text{O-Fe}$  front velocity was also obtained by Eq. 1, while the  $\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}$  front velocity followed:

$$\omega_{\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}} = Q_m \left( y_{\text{Fe}_{0.947}\text{O-Fe}}^{\text{eq}} - y_{\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4}^{\text{eq}} \right) \gamma_{\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}} \frac{M_{\text{Fe}_2\text{O}_3}}{\rho_b S} \quad (5)$$

where the value of  $\gamma_{\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}}$  is shown in Table 1, and the meanings of the other symbols can be found previously. The velocity ratios of the adjacent reaction fronts under different reduction temperatures were calculated on the basis of the physical model in Fig. 9. From Fig. 12,  $\omega_{\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4} / \omega_{\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}}$  and  $\omega_{\text{Fe}_3\text{O}_4\text{-Fe}_{0.947}\text{O}} / \omega_{\text{Fe}_{0.947}\text{O-Fe}}$  were greater than 1 within the range of 727 to 1032 °C, and  $\omega_{\text{Fe}_2\text{O}_3\text{-Fe}_{0.947}\text{O}} / \omega_{\text{Fe}_{0.947}\text{O-Fe}}$  was also greater than 1 in the range of 1032 to 1377 °C. The ratios of these reaction front velocities in Fig. 12 are all greater than 1, proving that the physical model in Fig. 9 is applicable.



**Fig. 12** Ratios of reaction front velocities at different reduction temperatures according to the physical model in Fig. 9. The value of  $y_m$  in these calculations is 1.

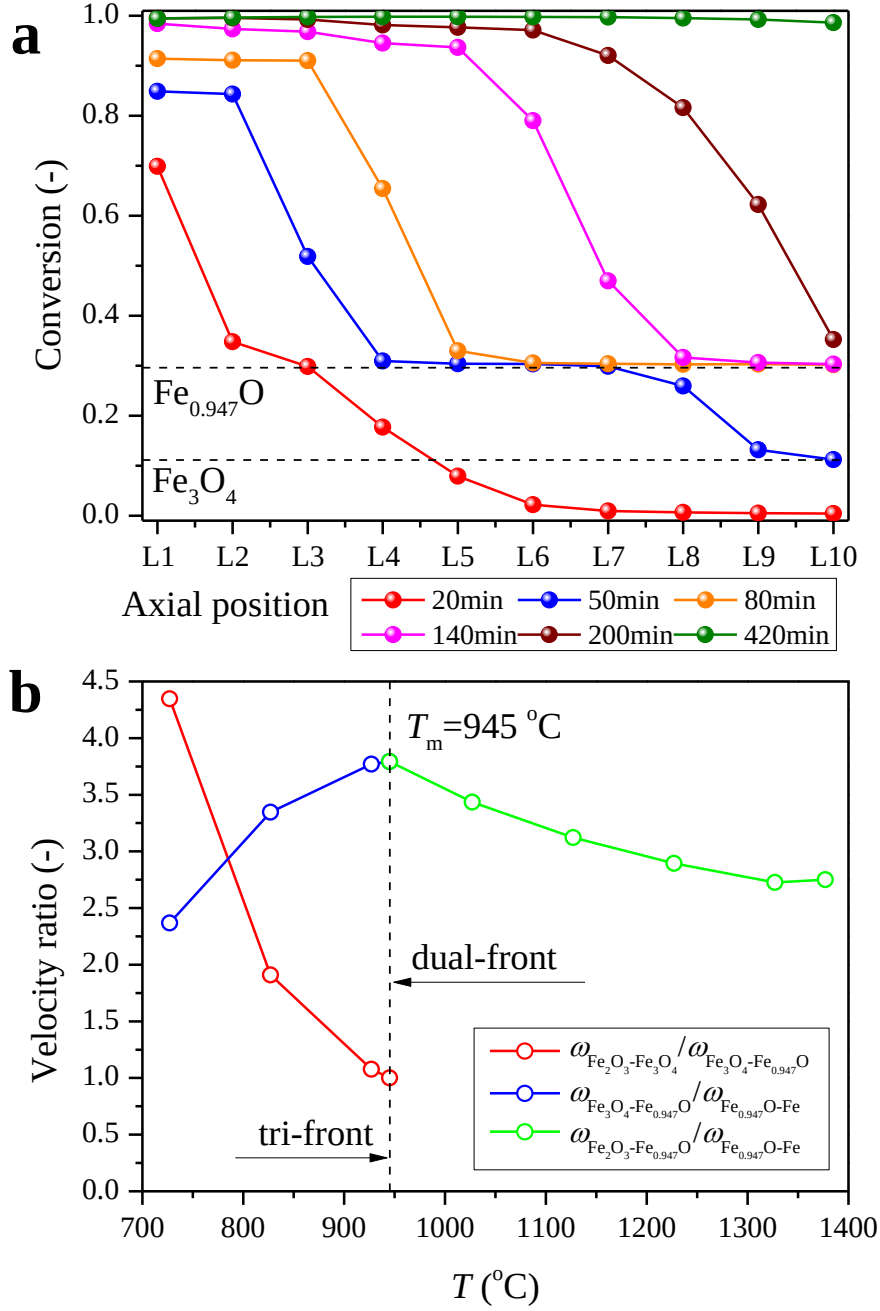
### 3.3 Iron (III) oxide reduction by H<sub>2</sub> in the packed bed

The behaviour of iron (III) oxide reduction by CO in the non-steady state packed bed is now understood. Since H<sub>2</sub> is the other main component in the common fuel for CLWS, such as syngas, understanding the behaviour of iron (III) oxide reduction by H<sub>2</sub> is also essential.

Fig. 13 (a) presents the solid conversion of each sub-layer in the non-steady state packed bed at different reduction times, with 50% H<sub>2</sub> in N<sub>2</sub> as the reducing gas at 900 °C. Similar phenomena to the CO case were also observed during H<sub>2</sub> reduction, indicating that the reaction fronts moved and the oxygen carriers in several sub-layers remained in the Fe<sub>0.947</sub>O phase for a period. The mass ratios of the iron oxides in each sub-layer during this process are shown in Fig. S5 (supplementary material).

Compared to the CO case, the different thermodynamic and kinetic characteristics of the reaction between H<sub>2</sub> and the iron oxides had an effect on the reaction front movement in the packed bed. In the case of CO vs. H<sub>2</sub>, the solid conversion values of L1 after 80 min of reduction were 0.789 and 0.914, respectively, indicating that H<sub>2</sub> had a higher activity than CO. In the H<sub>2</sub> case, the oxygen carrier in L1 was almost converted within 200 min, with the solid conversion up to 0.995. In the CO case, the solid conversion of L1 only reached 0.909 after 240 min of reduction and 0.982 after 600 min of reduction. This result was observed because, compared to CO, H<sub>2</sub> had a higher reactivity with iron oxides and could completely convert iron oxides, even at lower reaction temperatures [59].

Additionally, for the CO and H<sub>2</sub> cases, the solid conversion values for the whole bed after 80 min of reduction were 0.405 and 0.524, respectively. This result was due to the presence of only the Fe<sub>0.947</sub>O and Fe phases in the packed bed at this time (Fig. 6 and Fig. S5 in the supplementary material). After 80 min of reduction, in the CO case, approximately seven sub-layers existed that almost exclusively contained the Fe<sub>0.947</sub>O phase; whereas, in the H<sub>2</sub> case, only approximately six sub-layers with this phase were observed. In the H<sub>2</sub> case, the Fe<sub>0.947</sub>O-Fe front was shorter, and the average solid conversion of the Fe product zone was higher (Fig. 6 and Fig. S5 in the supplementary material). Therefore, the solid conversion of the whole bed after 80 min of reduction in the H<sub>2</sub> case was higher than that of CO.



**Fig. 13** Axial solid conversion curves at different reduction times in the non-steady state packed bed with 50%  $\text{H}_2$  in  $\text{N}_2$  as the reducing gas at  $900^{\circ}\text{C}$  **(a)** and ratios of the reaction front velocities at different reaction temperatures during  $\text{H}_2$  reduction **(b)**.

The behaviour of iron (III) oxide reduction by  $\text{H}_2$  in the packed bed was similar to that in the CO case, and the thermodynamic equilibrium phase diagram of the iron-hydrogen-system was also similar to the iron-carbon-system, as shown in Fig. 1. In light of this observation, it was considered reasonable to apply the physical model in Fig. 9 to the behaviour of the iron (III) oxide reduction by  $\text{H}_2$  in the packed bed. With the help of Eqs. 1-5, the velocity ratios of

the adjacent reaction fronts in the  $H_2$  case were acquired. From Fig. 13(b),  $\omega_{Fe_2O_3-Fe_3O_4}/\omega_{Fe_3O_4-Fe_{0.947}O}$  and  $\omega_{Fe_3O_4-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  were greater than 1 below 945 °C ( $T_m$ ), conforming to the tri-front model. Meanwhile,  $\omega_{Fe_2O_3-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  was greater than 1 above 945 °C ( $T_m$ ), obeying the dual-front model. Hence, the behaviour of the iron (III) oxide reduction by  $H_2$  in the packed bed was similarly described using the physical model in Fig. 9, only with different merging temperatures. Unlike the CO case in which  $\omega_{Fe_2O_3-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  increased with the reduction temperature, this velocity ratio for the  $H_2$  case first decreased and then increased with the reduction temperature. In other words, the length of the  $Fe_{0.947}O$  zone in the packed bed first decreased and then increased with the reduction temperature in the same period (Eq. S17 in the supplementary material). This is due to the equilibrium composition of the reaction between  $H_2$  and  $Fe_{0.947}O$ , which changes differently than that of the CO case, as shown in Fig. 1. From Eqs. 1 and 5,  $\omega_{Fe_2O_3-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  was proportional to  $(y_{Fe_{0.947}O-Fe}^{eq} - y_{Fe_2O_3-Fe_3O_4}^{eq})/(y_{in} - y_{Fe_{0.947}O-Fe}^{eq})$ . Since  $y_{Fe_2O_3-Fe_3O_4}^{eq} \approx 0$  and  $y_{in} = 1$ , this velocity ratio was proportional to  $y_{Fe_{0.947}O-Fe}^{eq}$ . For the  $H_2$  case, the equilibrium composition ( $y_{Fe_{0.947}O-Fe}^{eq}$ ) first decreased and then increased with the reaction temperature, as observed in Fig. 1. However, for the CO case, this equilibrium composition increased with the reaction temperature (Fig. 1). It led to different changes in the velocity ratios with the reduction temperature in the  $H_2$  case compared to the CO case.

In addition,  $\omega_{Fe_3O_4-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  was 3.656 at 900 °C for the  $H_2$  case, while it was 8.581 at 900 °C for the CO case (Fig. S6 in the supplementary material, 85% CO in  $CO_2$ ). This indicates that the  $Fe_{0.947}O$  zone in the CO case was longer during the same period, explaining the difference between the solid conversion of the whole bed after 80 min of reduction for  $H_2$  or CO as fuel.

### 3.4 Maximum solid conversion of the reduction step in the packed bed CLWS

The reduction of iron (III) oxide by CO or  $H_2$  in the non-steady state packed bed exhibited different behaviours at different reduction temperatures. When the reduction temperature ( $T$ ) was higher than the merging temperature ( $T_m$ ), the three reaction fronts turned into two. From the physical model in Fig. 9, the solid conversion of the whole bed at the fuel breakthrough point, which is the moment when the  $Fe_2O_3$  zone disappears in Fig. 9, can be calculated from Eq. 6. This solid conversion is also called the solid conversion of the reduction step, as stated in the introduction.

$$X = \frac{\sum X_{\text{Fe}_i\text{O}_j} l_{\text{Fe}_i\text{O}_j} + \sum X_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j} l_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}}{\sum l_{\text{Fe}_i\text{O}_j} + \sum l_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}} \quad (6)$$

where  $X_{\text{Fe}_i\text{O}_j}$  represents the solid conversion of  $\text{Fe}_i\text{O}_j$  [60] and  $l_{\text{Fe}_i\text{O}_j}$  is the length of the  $\text{Fe}_i\text{O}_j$  zone in the packed bed.  $X_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}$  and  $l_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}$ , respectively, express the solid conversion and the length of the  $\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j$  front. When  $T < T_m$ ,  $\text{Fe}_i\text{O}_j$  stands for Fe,  $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_3\text{O}_4$  and the corresponding  $\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j$  front represents the  $\text{Fe}_{0.947}\text{O}-\text{Fe}$ ,  $\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4$  front. When  $T > T_m$ ,  $\text{Fe}_i\text{O}_j$  stands for Fe and  $\text{Fe}_{0.947}\text{O}$ , and the corresponding  $\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j$  front expresses the  $\text{Fe}_{0.947}\text{O}-\text{Fe}$  and  $\text{Fe}_2\text{O}_3-\text{Fe}_{0.947}\text{O}$  front. The solid conversions of Fe,  $\text{Fe}_{0.947}\text{O}$  and  $\text{Fe}_3\text{O}_4$  were 1.000, 0.296 and 0.111, respectively. The solid conversion of the reaction front was between the solid conversions of the two iron oxides in this reaction front, and the lengths of the reaction fronts in the packed bed were determined by the compositions of their inlet and outlet gases as well as the reaction rate in the reaction fronts (Eqs. S10-S13 in the supplementary material).

From the physical model in Fig. 9, each product zone in the packed bed was formed by the movement of the corresponding reaction front. For example, the Fe zone was generated from the movement of the  $\text{Fe}_{0.947}\text{O}-\text{Fe}$  front. The  $\text{Fe}_{0.947}\text{O}$  zone was formed by the movement of the  $\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}$  front ( $T < T_m$ ) or the  $\text{Fe}_2\text{O}_3-\text{Fe}_{0.947}\text{O}$  front ( $T > T_m$ ). At the fuel breakthrough point, the product zone and relevant reaction front only appeared in combination. Compared to the product zones, the solid conversions of the corresponding reaction fronts were relatively lower. Thus, if the lengths of the reaction fronts could be ignored as compared to the product zones, the solid conversion of the whole bed at the fuel breakthrough point could reach the maximum value. However, the reaction rate in each reaction front was not quick enough [32, 58]. In other words, each reaction front had a certain length, which can also be seen from the previous results in the sub-layer experiments.

In this case, only when the product zones in the packed bed were long enough could the lengths of the reaction fronts be ignored as compared to the product zones, achieving the maximum solid conversion of the reduction step. To achieve sufficiently long product zones, the length of the oxygen carrier bed should be infinite, leading to the infinite time of the reaction front movement. The maximum solid conversion of the reduction step can be calculated when the length of the oxygen carrier bed is infinite in Eq. 6, as shown in Eq. 7.

$$X_{\max} = \lim_{l \rightarrow \infty} \frac{\sum X_{\text{Fe}_i\text{O}_j} l_{\text{Fe}_i\text{O}_j} + \sum X_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j} l_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}}{\sum l_{\text{Fe}_i\text{O}_j} + \sum l_{\text{Fe}_a\text{O}_b-\text{Fe}_i\text{O}_j}} = \frac{\sum X_{\text{Fe}_i\text{O}_j} l_{\text{Fe}_i\text{O}_j}}{\sum l_{\text{Fe}_i\text{O}_j}} \quad (7)$$

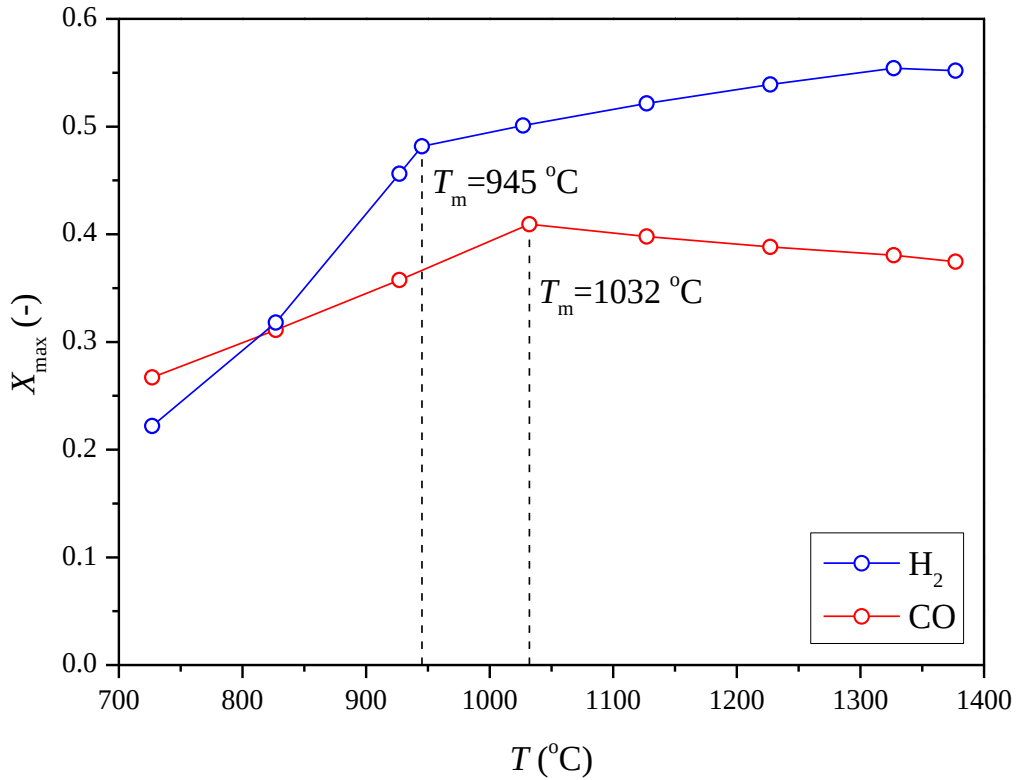
According to the expression of each product zone length (Eqs. S14-S17 in the

supplementary material), the maximum solid conversions of the reduction step, when the reduction temperature was below or above the merging temperature, could be obtained (Eqs. 8-9).

$$X_{\max} = \frac{X_{\text{Fe}}\omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}} + X_{\text{Fe}_{0.947}\text{O}}(\omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}} - \omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}}) + X_{\text{Fe}_3\text{O}_4}(\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4} - \omega_{\text{Fe}_3\text{O}_4-\text{Fe}_{0.947}\text{O}})}{\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4}} \quad T < T_m \quad (8)$$

$$X_{\max} = \frac{X_{\text{Fe}}\omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}} + X_{\text{Fe}_{0.947}\text{O}}(\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_{0.947}\text{O}} - \omega_{\text{Fe}_{0.947}\text{O}-\text{Fe}})}{\omega_{\text{Fe}_2\text{O}_3-\text{Fe}_{0.947}\text{O}}} \quad T > T_m \quad (9)$$

Combined with Fig. 12 and Fig. 13 (b), the maximum solid conversions of the reduction step at different reduction temperatures were acquired, as shown in Fig. 14. In the CO case, the maximum solid conversion first increased and then decreased with the reduction temperature. The extremum of 0.409 was achieved at the merging temperature (1032 °C). For the H<sub>2</sub> case, with the increasing reduction temperature, the maximum solid conversion also first increased and then decreased. The extremum was 0.554, and all the maximum solid conversions in the range of 827 to 1377 °C were higher than those of the CO case.



**Fig. 14** Maximum solid conversions of the reduction step with pure CO or H<sub>2</sub> as the reducing gas at different reduction temperatures.

The distinct difference between the H<sub>2</sub> and CO cases is that the maximum solid conversions

of the reduction step changed with the reduction temperature when  $T > T_m$ . The maximum solid conversion in the  $H_2$  case first increased and then decreased when  $T > T_m$ , while the maximum solid conversion in the CO case declined directly because the maximum solid conversion was determined by the relative ratio of the Fe and  $Fe_{0.947}O$  zone in the packed bed when  $T > T_m$ . It was explained in section 3.3 that  $\omega_{Fe_2O_3-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  was proportional to  $y_{Fe_{0.947}O-Fe}^{eq}$ . From Fig. 1, the equilibrium composition in the  $H_2$  case first decreased and then increased with the reaction temperature. However, for the CO case, this equilibrium composition increased with the reaction temperature. Thus, the change of  $\omega_{Fe_2O_3-Fe_{0.947}O}/\omega_{Fe_{0.947}O-Fe}$  with the reduction temperature was different for  $H_2$  and CO cases, which was responsible for the various tendencies of their maximum solid conversions to change with the reduction temperature when  $T > T_m$  (Eq. 9).

From Fig. 14, the merging temperature was not necessarily the extremal point of the maximum solid conversion of the reduction step. The merging temperature was the temperature at which the  $Fe_2O_3-Fe_3O_4$  and  $Fe_3O_4-Fe_{0.947}O$  fronts began to merge, i.e., the two fronts had the same velocity. According to Eqs. 2-3, the velocity ratio of the  $Fe_2O_3-Fe_3O_4$  and  $Fe_3O_4-Fe_{0.947}O$  fronts was decided only by the thermodynamic equilibrium composition. Thus, the merging temperature, corresponding to the velocity ratio being equal to 1, was permanent. This temperature is a basic thermodynamic property of the gas-solid reaction, namely iron (III) oxide reduction by CO or  $H_2$  in a packed bed, and it was not affected by the pressure quotients of the inlet gases of the bed during the reduction step ( $P_{CO}/P_{CO_2}$  or  $P_{H_2}/P_{H_2O}$ ). In the case that the pressure quotient could reduce  $Fe_2O_3$  into Fe, the physical model in Fig. 9 was still applicable for the reducing gases with different pressure quotients. The ratios of the reaction front velocities, when 85% CO in  $CO_2$  or 85%  $H_2$  in  $H_2O_{(g)}$  were used as the reducing gases, were always greater than 1, regardless of whether the reduction temperature was below or above the merging temperature (Fig. S6 in the supplementary material).

The difference was that when the pressure quotient of the reducing gas became lower, the maximum solid conversion of the reduction step dropped as well. For example, when the reducing gas was changed from pure CO or  $H_2$  (an infinite pressure quotient) to 85% CO in  $CO_2$  or 85%  $H_2$  in  $H_2O_{(g)}$  (the pressure quotient was 5.667), the extremum of the maximum solid conversion dropped from 0.409 to 0.348 in the CO case and it dropped from 0.554 to 0.469 in the  $H_2$  case (Fig. S7 in the supplementary material). A decrease in the pressure quotient of the reducing gas led to a lower reaction rate in the  $Fe_{0.947}O-Fe$  front and enlarged the length of this front. However, the length of the other reaction fronts did not change, owing to the fact

that the inlet gases of the other reaction fronts remained at the equilibrium composition of the reaction in the previous fronts. At the same time, the maximum solid conversion was obtained in the case of the infinite bed length. The change of the  $\text{Fe}_{0.947}\text{O}$ -Fe front length did not affect the maximum solid conversion of the reduction step (Eqs. 8-9). Therefore, the decrease of the maximum solid conversion, caused by the decreasing pressure quotient of the reducing gas, had no relationship with the declining kinetic driving force. Essentially, the pressure quotient of the reducing gas affected the  $\text{Fe}_{0.947}\text{O}$ -Fe front velocity, which further changed the maximum solid conversion. From Eq. 1, when the pressure quotient of the reducing gas decreased, the  $\text{Fe}_{0.947}\text{O}$ -Fe front velocity was slower. In contrast, the velocities of the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  fronts ( $T < T_m$ ) or the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_{0.947}\text{O}$  front ( $T > T_m$ ) were not affected by the pressure quotient of the reducing gas (Eqs. 2 and 5). This resulted in a decrease in the maximum solid conversion of the reduction step in the packed bed CLWS (Eqs. 8-9).

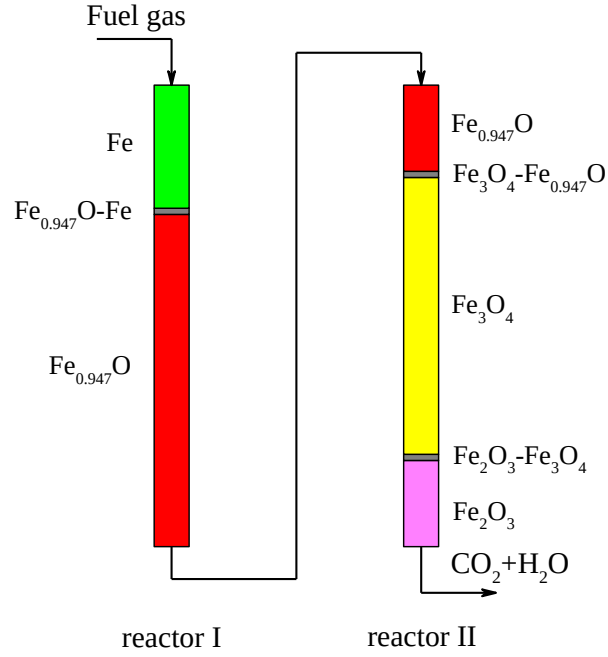
### 3.5 Application of the reaction fronts movement model

In the above discussion, we observed that three reaction fronts moved at the same time during iron (III) oxide reduction in the the packed bed CLWS and found that the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_{0.947}\text{O}$  front merged while the reaction temperature was above the  $T_m$ . After that, the thermodynamic limitation of the reduction step in the packed bed CLWS was confirmed for the first time. This new knowledge will provide some insights and theoretical support for the development of CLWS, especially packed bed CLWS.

First, it offers a standard for both the evaluation of the iron-based oxygen carrier and the operational optimization. A packed bed has always been used to evaluate the iron-based oxygen carrier, where the solid conversion at the breakthrough point is also an index. Formerly, the thermodynamic limitation of the fluidized bed or moving bed has been used as a reference to evaluate the performance of the iron-based oxygen carrier in the packed bed or the operation conditions. For example, Zhu [32] found that the solid conversion of the reduction step was between 0.220 and 0.250 during 20 cycles in the packed bed while 60 wt%  $\text{Fe}_2\text{O}_3$  supported on  $\text{Al}_2\text{O}_3$  was used as the oxygen carrier at 900 °C, and they compared this performance with the results in a fluidized bed to show the performance of the oxygen carrier and operating conditions, but the exact performance of the oxygen carriers or operating conditions in the packed bed still remained unknown. Thus, the confirmation of the thermodynamic limitation of the reduction step in packed bed CLWS provides criteria for the evaluation of the oxygen carrier or the operating conditions. Fig. 14 shows that the maximum solid conversion when

1  $\text{Fe}_2\text{O}_3$  was reduced by CO at 900 °C was 0.345, meaning that for the operating conditions used  
2 in Zhu's study, the conversion of the iron-based oxygen carrier had reached 72.5% of the  
3 maximum solid conversion. This indicates that the performance of the oxygen carrier was  
4 impressive, but the iron-based oxygen carrier or operating conditions are still able to be further  
5 optimized.

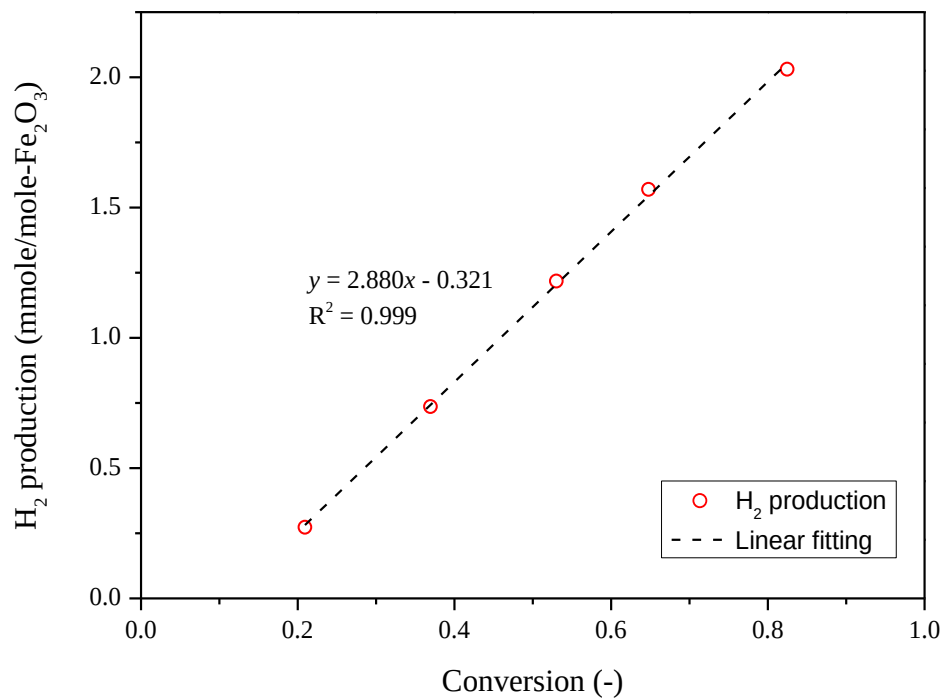
6 Second, these new findings provide a theoretical support for the scale-up of the packed bed  
7 reactor for CLWS technology. In addition to being used as an experimental facility, the non-  
8 steady state packed bed is also a main technique for CLWS because it not only offers the  
9 possibility of deep reduction of the iron-based oxygen carrier but also enables the reduction of  
10 the required mechanical strength of the oxygen carrier. To realize the commercial applications  
11 of packed bed CLWS, the scale-up of the packed bed is vital. In our previous study [30], we  
12 found that the experimental results from the scaled-up packed bed were similar to those from  
13 the bench scale packed bed. The solid conversion of the reduction step in the pilot-scale packed  
14 bed was 0.250 (the maximum solid conversion at 800 °C was 0.299, as observed in Fig. 14),  
15 which is close to the solid conversion of 0.220-0.240 in the bench scale test. The reasons why  
16 the two packed bed reactors of different scales have close solid conversion values during the  
17 reduction step are as follows: As seen from Fig. 9, the solid conversion of the reduction step is  
18 mainly determined by the relative proportions of the product zones and reaction fronts. The  
19 discussion in section 3.4 revealed that the relevant lengths of these zones are mainly affected  
20 by the thermodynamic equilibrium composition (Eqs. 1-5 and Eqs. S10-S17), but the  
21 thermodynamic equilibrium composition is not subject to the scale of the device; thus, the pilot  
22 test and bench test obtained close results. In addition, the change of the axial temperature curve  
23 during the air combustion step in the pilot unit also indicated that there was a reaction front in  
24 the pilot packed bed, and obvious reaction front movement was also observed. These results  
25 all indicate that the behaviour of the reaction front was prevalent in the packed beds at different  
26 scales, and the reaction front movement model can describe the relationship between the gas  
27 conversion and solid conversion in the packed bed, which functions similarly to the operating  
28 curves for the fluidized bed and the moving bed. Combined with the thermodynamic  
29 equilibrium phase diagram, these results can provide a theoretical basis for the scale-up design  
30 of packed beds for CLWS technology.



**Fig. 15** Schematic of the deep reduction process for CLWS at 900 °C. Reactor I serves as the deep reduction reactor, and reactor II ensures the complete conversion of the outlet gas from reactor I. The three gray parts represent three reaction fronts and the other parts represent the reactant and product zones.

Finally, these new discoveries provide new insights into developing new technologies for CLWS. It can be seen from Fig. 14 that the maximum theoretical solid conversion of the whole bed was only 0.345 at 900 °C when CO was used as the reducing gas, but Fig. 9 shows that the distribution of the phases along the packed bed reactor led to a higher reduction conversion at the inlet part than that of the whole bed. For example, the solid conversion of the Fe-rich zone, located at the inlet part of the packed bed, was quite close to 100% (Fig. 4). Based on this phenomenon, we propose a new technology, i.e., deep reduction CLWS technology. The difference from the traditional packed bed chemical looping technique [41], where only a single packed bed is operated during the reduction step, is that during the deep reduction process, multiple packed beds operating in series are considered for the reduction step. For example, Fig. 15 describes using two packed beds as the reduction reactors, from which it can be seen that reactor I guarantees the deep reduction of the iron-based oxygen carrier, and reactor II ensures the complete conversion of the outlet gas from reactor I. Compared to using a single reactor, the solid conversion of reactor I increased from 0.312 to 0.411 (Fig. 4 and 9), representing an increase of 31.7% at the end of the reduction step, and the theoretical hydrogen

production could be increased by 49.3% if reactor I was used for producing hydrogen. In addition, we also found that the actual hydrogen production was very close to the theoretical value with the error being less than 8%, and the relationship between the actual hydrogen production and reduction degree is positive and linear (see Fig. 16). Thus, the deep reduction CLWS technology can significantly improve the efficiency of CLWS, especially the amount of hydrogen produced per mole of the iron-based oxygen carrier. Some details about the deep reduction technology are still under study.



**Fig. 16** The relationship between the actual hydrogen production at 900 °C and the solid conversions of the reduction step. The experimental methods for hydrogen production were referenced from Zhu [32].

#### 4 Conclusions

Basing on the sub-layer approach, a direct experiment investigation of the reduction step during packed bed CLWS was conducted for the first time. From the axial solid conversion curves in the non-steady state packed bed when iron (III) oxide was reduced by CO at 900 °C, there were three reaction fronts and three product zones in the packed bed. These product zones were formed by the movement of the corresponding reaction fronts. The iron (III) oxide reduction reactions by CO at 850 and 1000 °C, as well as by H<sub>2</sub> at 900 °C, had similar behaviours. This was the first experimental observation that multiple reaction fronts move in a

packed bed at the same time as iron (III) oxide is reduced by CO or H<sub>2</sub>. From this, a model to characterize the reaction front movement was devised. By observing the change in the velocity ratios of adjacent reaction fronts with the reduction temperature, it was found that the reduction of iron (III) oxide in the packed bed presents two different behaviours upon different reduction temperatures. First, when the reduction temperature ( $T$ ) is lower than the merging temperature ( $T_m$ ), there are three reaction fronts, i.e., Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O and Fe<sub>0.947</sub>O-Fe, and three product zones, i.e., Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>0.947</sub>O and Fe, in the packed bed. Contrariwise, when  $T > T_m$ , the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O fronts merge, leading to the disappearance of the Fe<sub>3</sub>O<sub>4</sub> zone, and therefore, only the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>0.947</sub>O and Fe<sub>0.947</sub>O-Fe fronts appear in the packed bed as well as the Fe<sub>0.947</sub>O and Fe zones. The merging temperature is the temperature at which the Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>0.947</sub>O fronts start to merge. This temperature is a basic thermodynamic property of the gas-solid reaction, namely the iron (III) oxide reduction by CO or H<sub>2</sub> in the packed bed. These observations were verified by the two breakthrough curves, one for  $T < T_m$  and the other for  $T > T_m$ , of the iron (III) oxide reduction by 50% CO in CO<sub>2</sub> in the packed bed. The interesting phenomenon that the solid conversion of the whole bed after 150 min of reduction decreased with the increasing reduction temperature within the range of 850 to 1000 °C, can be well explained by the behaviour of the reaction front movement.

In addition, the physical model representing the reaction front movement was used to calculate the maximum solid conversion of the reduction step at different reduction temperatures in the packed bed CLWS. According to the results, the maximum solid conversions were only affected by the thermodynamic equilibrium alongside the pressure quotient of the reducing gas. The extremums of the maximum solid conversion were, respectively, 0.409 and 0.554, when pure CO or H<sub>2</sub> was used as the fuel. In addition, the velocity of the Fe<sub>0.947</sub>O-Fe front decreased with the declining pressure quotient of the reducing gas, leading to a drop in the maximum solid conversions of the reduction step. Thus, for the non-steady state packed bed containing multiple reaction fronts, the velocity difference of the reaction fronts definitively influences its performance.

Finally, the new findings in this work help the development of packed bed CLWS, such as standardizing the criteria for both the oxygen carrier evaluation and the optimization of the operating conditions and providing theoretical support for the scale-up of the packed bed as well as the development of new technology for the packed bed CLWS.

## Appendices

The supplementary material includes supplementary Figs. S1-S7 and Eqs. S1-S17.

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