



Effect of composition and processing conditions on the direct reduction of iron oxide pellets

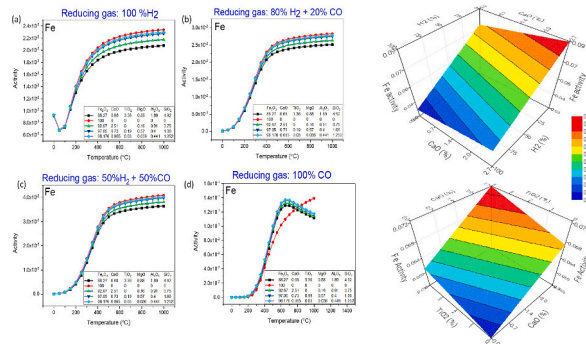
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HIGHLIGHTS

- Explored hematite's efficient reducibility and CO/H₂ performance in pellet reduction.
- Emphasized impurity impact on iron activity and overall reduction kinetics.
- Identified Gibbs free energy for iron reduction, offering thermodynamic insights.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

HSC chemistry
Iron reduction
Reduction atmosphere
Non-iron oxide impurities

ABSTRACT

In this paper, HSC software is used to estimate the effects of composition and processing conditions on the reduction behavior of iron oxide pellets, i.e., hematite (Fe₂O₃), magnetite (Fe₃O₄), wustite (FeO), pure iron (Fe), and iron carbide (Fe₃C), in a wide temperature range from room temperature (RT) to 1000°C in the presence of H₂ and CO mixtures. The reducibility of iron ores, in particular Fe₂O₃, Fe₃O₄, FeO, Fe is discussed. The choice of reducing agents CO and H₂ is explained, with CO proving to be the more effective reducing agent at high temperatures from a thermodynamic point of view. However, the free Gibbs energy of iron reduction is lowest in the presence of a 100% H₂ atmosphere. In addition, H₂ reduces tortuosity and increases porosity by reducing it at cooler temperatures and promoting diffusion. In contrast, CO increases tortuosity and reduces initial porosity because it requires higher temperatures for effective reduction and causes structural changes. The presence of impurities other than iron oxides has been shown to impair the activity of reduced pure iron by acting as catalyst poisons or participating in competing reactions. CaO accelerates the reduction of FeO, which is due to the formation of calcium ferrite, but the effect decreases at higher temperatures. MgO can either promote or hinder reduction, depending on its concentration and its influence on pellet porosity. The presence of several non-iron oxides has been shown to affect the overall direct reduction of iron ore pellets, resulting in a significant impact of the overall process.

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<https://doi.org/10.1016/j.powtec.2024.120061>

Received 22 February 2024; Received in revised form 17 May 2024; Accepted 4 July 2024

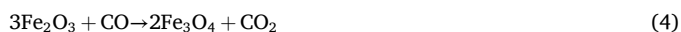
Available online 6 July 2024

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1. Introduction

The field of chemical engineering and materials science has been revolutionized by the advent of computational tools and simulations. These tools enable scientists and engineers to explore complex chemical processes and their effects with unprecedented precision and efficiency. HSC Chemistry is one of the world's most popular thermochemical software programs with a versatile flowsheet simulation module. HSC is designed for various types of chemical reactions and equilibrium calculations as well as process simulation. HSC Chemistry provides powerful calculation methods to study the effects of different variables on the chemical system at equilibrium. In many cases, it is a very cost-effective and useful tool that helps to find the optimal reaction conditions and yields for experimental investigations without expensive trial-and-error chemistry [1,2].

Iron oxide pellets are used in various industries, including hydrogen storage (H₂), direct reduced iron (DRI) production and environmental remediation. DRI research usually takes place at two scales: the pellet scale to study the reaction kinetics at the individual pellet level and the macroscopic or reactor scale to study the process in a larger reactor [3]. During the direct reduction process of iron oxide pellets, the oxygen contained in these pellets is eliminated by the reducing agents (H₂ and/or CO) as part of the subsequent series of heterogeneous chemical reactions (see below):



Achieving the desired pellet activity is a complex task that requires a deep understanding of the underlying chemical and physical processes. In fact, the composition of iron oxide pellets can vary considerably, and understanding how the different components affect their activity is a difficult task [4]. The quality of iron oxide pellets depends on various factors, such as their composition and processing conditions. In particular, studying the key factors is crucial for understanding and improving the productivity, quality control and use of H₂ in this context. The process of direct reduction (DR) is becoming increasingly complex due to successive reduction reactions and changes in the solid phase. Existing studies vary in their simplification, leading to different results [5,6]. During the direct reduction process, the reduction rate, the degree of metallization and the behavior of the iron ore vary considerably due to the ore type, atmosphere and temperature [5,7]. Studies on the reduction of iron oxide pellets show that impurities in either the pig iron oxide or the reducing gas can reduce emissions by 25–40% per ton of crude steel [8,9]. In this context, H₂ direct reduction (HyDR) of iron oxide pellets has attracted considerable attention and could potentially show a way to produce low-carbon steel that causes minimal greenhouse gas emissions and environmental problems in the production process [10,11]. Therefore, continuous efforts are being made to optimize the iron reduction process.

Gamisch et al. [12] investigated the kinetic mechanisms of the reduction/oxidation reactions (redox) of iron oxide/iron pellets under different operating conditions. They used a single pellet consisting of 90% Fe₂O₃ and 10% stabilizing cement and reduced it with different H₂

concentrations at temperatures between 600 and 800 °C. The redox reactions were measured experimentally in a thermogravimetric analyzer (TGA). They found that the measured kinetic results can be described excellently with the so-called shrinking core model. Using the geometric contraction sphere reaction mechanism model, the concentration- and temperature-dependent reduction and oxidation rates can be reproduced with a maximum deviation of <5%. In another study by Ghadi et al. [3], the authors reviewed the main models in the literature in relation to direct reduction reactions at the pellet scale together with new approaches developed more recently. They presented a critical evaluation of the previously proposed models in terms of which models are applicable under which conditions and for which types of solid structure. The weaknesses and pitfalls of some of these models are also pointed out. The authors emphasize that the kinetic parameters used in the reactor modeling come from the study on single pellets and that these two aspects are not independent of each other. From a thermodynamic point of view, the activity of each component involved in the reduction process is not independent as it depends on a number of operating conditions such as temperature, pressure, flow rate, gas composition and parameters of the solid pellet such as size, morphology, porosity, pore distribution and mineralogical composition [5,13]. In addition, the activity parameter, a fundamental thermodynamic factor, serves as a crucial variable in modeling and simulation, providing information on the behavior of iron and its different phases during the reduction process [14]. This understanding is essential to achieve high-quality iron production, increase productivity and optimize resource utilization.

To the best of our knowledge, the process of direct reduction is complex and hierarchical, i.e. it is composed of several chemical reactions and physical phenomena that take place on different length and time scales [14,15]. Direct reduction technology has been continuously developed to improve the understanding of the kinetics of the reduction process and the control steps in the reaction–transport process that takes place in the pellet [14,16]. However, the complexity lies in the different (possible) mechanisms that iron undergoes when exposed to the different non-ferrous oxides with different contents, the adjacent iron layers and the different reducing gas under stoichiometric or non-stoichiometric conditions. Despite numerous studies on the reduction behavior of iron oxide pellets, the effects of iron ore impurities have not been extensively studied [17–19].

Among the many experimental efforts that have been made in the field of direct regeneration of iron oxide pellets, there is not much and extensive experience in the field of simulation and estimation of the direct reduction behavior of iron oxide pellets. To the authors' knowledge, only a few works [10,20] have been devoted to the use of HSC software to predict the thermodynamics of iron oxide pellets during the direct reduction process and indirect reduction [21,22]. Jabbour et al. [10] have shown that direct reduction of Fe₂O₃(s) to Fe(s) is not possible, but that a series of H₂-induced reduction steps take place together with other side reactions, resulting in partially reduced iron oxide species. It should be noted that there is not much research work estimating and optimizing the effects of different non-ferrous oxides on the DRI process. Therefore, considering the importance of the behavior of iron compounds during the reduction process, there is an urgent need for a clear and detailed investigation. In this context, the composition of the pellets used in this study is of industrial quality and contains a wide range of non-ferrous oxides that are likely to have a remarkable impact on the activity behavior of iron compounds.

Traditionally, empirical and experimental approaches are used, which can be time-consuming, costly and less environmentally friendly. However, when the user specifies the raw materials, quantities and other conditions for almost any chemical process, the HSC program provides the quantities of the product as a result. So, this is where computer simulations come into play, especially those supported by HSC software, revolutionizing the approach. The field of chemical engineering and materials science has been revolutionized by the introduction of

computational tools such as HSC, which allow scientists and engineers to study complex chemical processes and their effects with unprecedented precision and efficiency. HSC is designed for various types of chemical reactions and equilibrium calculations as well as process simulation. It also provides powerful computational methods to study the effects of different variables on the chemical system at equilibrium. In many cases, it is a very cost-effective and useful tool that helps to find the optimal reaction conditions and yields for experimental investigations without expensive trial-and-error chemistry. To overcome these challenges, the article proposes the use of HSC Chemistry software to simulate the effects of composition and processing conditions on pellet activity. The software provides a powerful tool for predicting the behavior of materials under different conditions, which can help optimize pellet production and improve pellet quality.

This article aims to bridge the gap between challenges and solutions. Here it is proposed that HSC chemistry simulations may be the key to understanding the complex interplay between composition and processing conditions in pellet production. The present work focuses on estimating the overall activity of different iron compounds, namely Fe_3O_4 , FeO , Fe and Fe_3C , from room temperature to 1000°C in the presence of H_2 and CO mixtures. Furthermore, this study aims to understand how variations in the composition of these pellets, especially in terms of non-ferrous oxide content, interact with different compositions of H_2 and CO in the reduction process. Thus, the main purpose of this article is to demonstrate the effectiveness of HSC chemistry simulations in predicting pellet activity and to provide insights into the factors that influence pellet quality. In other words, by addressing the challenges in this area, we aim to show how the activity of iron oxides and iron phases changes as a function of non-ferrous oxides, temperature and gas composition during reduction to provide researchers and engineers with the in-depth understanding needed to optimize pellet properties efficiently and sustainably. Ultimately, optimizing pellet activity can lead to higher efficiency, better product quality and reduced environmental impact across numerous industries. In addition, the ability to tailor the properties of pellets can open the doors to innovative applications and novel materials. Furthermore, by using HSC chemistry simulations, we can save time and resources and reduce the need for extensive experimentation.

1.1. Experimental and methodology

The numerical estimates presented in this paper build on our previous experimental results, which are described in detail in references [6, 15, 23]. To ensure a comprehensive understanding, a systematic approach was used in the experimental design. Specifically, iron oxide pellets of different compositions were tested under controlled laboratory conditions. These pellets were predominantly composed of iron, with total iron content ranging from 82.92 to 100 wt%. The pellets also contained non-iron oxides such as CaO , MgO , Al_2O_3 , SiO_2 and TiO_2 with weight percentages in the ranges 0–2.65%, 0–4.69%, 0–2.93%, 0–7.69% and 0–3.36%, respectively. In order to investigate the reduction behavior over a wider temperature range, experiments were conducted from room temperature (approx. 25°C) up to 1000°C . This wide range allowed detailed observation of phase changes and reduction dynamics at different thermal points. The basicity index of the pellets was varied between 0 and 2.15 to evaluate its influence on the reduction process. All experiments were conducted at a constant pressure of 1 bar using HSC version 6 software in equilibrium calculation mode to simulate the atmospheric conditions of H_2 and CO mixtures. This setup provided a controlled environment to study the specific activities of various iron oxides, including Fe_3O_4 , FeO , Fe and Fe_3C . The pellets used in these experiments were supplied by VALE. The detailed production processes are described in reference [6]. These pellets were well shaped, spherical with a diameter of 1.36 cm, a density of 3.6 g/cm^3 and an average pore size of $2\ \mu\text{m}$, as shown in Fig. 1. A full breakdown of the chemical composition of these industrially produced iron ore pellets used in all

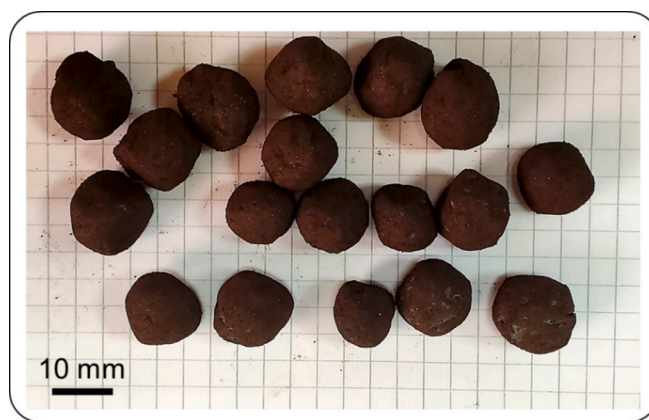


Fig. 1. Pellets employed in the present study.

simulations can be found in Table 1. With this rigorous experimental setup, we aim to elucidate the complex interplay between the composition of iron oxide pellets and their processing conditions, providing valuable insights that could improve industrial applications.

Table 1 shows the chemical composition of the pellets, which consist mainly of Fe_2O_3 . The main simplifications include: (1) pellet and grain shape are assumed to be spherical; (2) temperature and pressure within and around the pellet are assumed to be constant; (3) H_2 and H_2O are treated as ideal gasses; (4) the average diameter of the pellet is assumed to be constant and no cracks form in the pellet. These simplifications make the mathematical model more solvable and allow a basic understanding of the direct reduction process. In addition to the HSC software, a commercial multi-objective optimization tool, namely Mode Frontier, was used to precisely define the weight that each individual parameter has on the reduction behavior of the pellets. For this purpose, according to the objective of this work, different non-iron oxides were defined as input data and the activity of iron compounds as output, as shown in Fig. 2. The scatter plots are located at the top right of the matrix and the univariate histograms appear on the diagonal. The lower left part shows the correlation coefficients. The green circles indicate how well the design space is fulfilled and how the inputs influence the outputs. A numerical index of +1 indicates a direct effect, while -1 indicates an inverse relationship.

2. Results

The reduction process of iron oxide with 100% Fe_2O_3 under different reducing gas atmospheres proceeded in the following order: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, as shown in Eqs. (1) to (6), with different stages in which different forms of iron compounds coexisted. Fig. 3, which represents the equilibrium amount (in log) of different iron compounds such as Fe , Fe_3C , FeO and Fe_3O_4 , shows the evolution of each stage as a function of temperature for different compositions of reducing gas.

Fig. 3 (a) shows the equilibrium amount of Fe as a function of temperature in different gas mixtures. The curves show that the equilibrium amount of Fe increases with increasing temperature for all reducing gasses. It can also be observed that in an atmosphere with 100% H_2 as the reducing gas, the equilibrium amount of Fe is much greater than that of 100% CO . This is consistent with the principle that the equilibrium of a reaction has a significant temperature dependence and the equilibrium constant increases with increasing temperature [24–26]. The reducing gas 100% H_2 has the highest equilibrium amount of Fe at all temperatures. This could be due to the fact that H_2 has a strong reducing power that promotes the formation of Fe . On the other hand, 100% CO shows the lowest equilibrium amount of Fe . The presence of CO in the reducing gas significantly reduces the equilibrium amount of Fe , and this is more pronounced the higher the CO content. This could be due to the fact that CO also acts as a reducing agent, but less effectively than H_2 .

Table 1
Composition of the industrial iron ore pellet used in HSC software.

Id	Basicity	Fe ₂ O ₃	CaO	TiO ₂	MgO	Al ₂ O ₃	SiO ₂	Basicity
0	0.43	96.63	1.02	0	0	0.38	1.97	0.52
1	0.60	82.93	1.63	0.19	4.69	2.93	7.63	0.21
121	0.23	88.27	0.68	3.36	0.88	1.89	4.92	0.14
133	1.14	95.46	1.8	0.04	0.6	0.5	1.6	1.13
149	1.54	97.03	1	0.18	0.69	0.2	0.9	1.11
165	0.49	89.59	2.65	0	0.78	1.25	5.73	0.46
357	0.47	96.6	1	0.09	0.06	0.53	1.72	0.58
565	0.16	95.39	0.25	0	0.39	0.3	3.67	0.07
703	0.00	100	0	0	0	0	0	0.00
767	1.51	97.253	1.62	0.02	0.02	0.334	0.753	2.15
863	0.57	92.67	2.51	0	0.16	0.91	3.75	0.67
894	1.00	96	1	0	1	0	2	0.50
920	0.13	96.65	0.19	0	0.19	0.29	2.68	0.07
1065	0.30	97.65	0.4	0	0.14	0.08	1.73	0.23
1132	0.06	97.71	0.08	0	0.05	0.7	1.46	0.05
1188	0.47	97.8	0.7	0	0	0	1.5	0.47
1200	0.89	97.05	0.73	0.19	0.57	0.4	1.06	0.69
1205	0.31	93.61	1.43	0	0.07	1.32	3.57	0.40
1225	0.03	94.99	0.09	0	0.05	1.32	3.55	0.03
1242	0.00	96.88	0	0.92	0	0.7	1.5	0.00
1251	0.13	96.65	0.19	0	0.19	0.29	2.68	0.07
1331	0.06	98.176	0.065	0.03	0.036	0.441	1.252	0.05
1335	0.35	87.09	1.29	0.23	2.02	1.68	7.69	0.17
1425	0.99	96.4	1.5	0	0.29	0.47	1.34	1.12

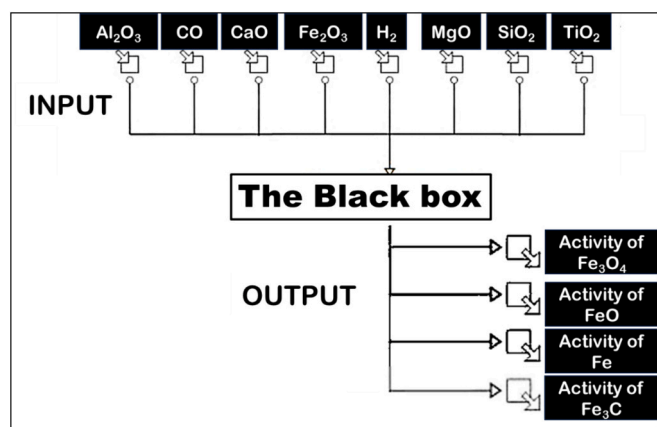


Fig. 2. Workflow of analysis describing the input–output correlation.

According to Fig. 3(b), the equilibrium amount of FeO in different atmospheres varies with temperature. At higher temperatures, the equilibrium value of FeO increases in atmospheres with a higher proportion of CO. The presence of H₂ in the reducing gas mixture can significantly influence the process of FeO reduction. In an atmosphere with 100% CO, the equilibrium amount of FeO reaches its highest value at a temperature of 600° Celsius. Conversely, in an atmosphere with 100% H₂, a lower amount of FeO is available. This indicates that atmospheres containing more H₂ have a higher reduction behavior at temperatures above 600° Celsius. On the other hand, atmospheres with a higher CO content show a higher reduction behavior for FeO at temperatures below 600 °C. According to a study by Jozwiak et al. [27], the presence of H₂ in the reducing gas mixture can promote the reduction of iron oxide. The study found that the reduction rate of iron oxide increased with increasing H₂ content in the reducing gas mixture. Similarly, a study by Ling et al. [24] found that the reduction of iron oxide was enhanced in the presence of H₂. The study attributed this behavior to the fact that H₂ can react with oxygen to form water vapor, which can react with iron oxide to form iron and water vapor [23,28].

As shown in Fig. 3(c), the reduction behavior of Fe₃O₄ was found to be similar to that of FeO. The reduction behavior of atmospheres containing more H₂ increases with increasing temperature. However, there

is a threshold temperature (here around 300 °C) at which the reducing power of atmospheres containing larger amounts of CO is significant when the temperature is lower. This indicates that the reduction behavior of Fe₃O₄ is influenced by the composition of the reducing gas mixture and the temperature. Taheri et al. [29] found that the reduction of iron oxide to Fe₃O₄ is faster in a CO atmosphere than in H₂. This behavior was attributed to the reaction of CO with iron oxide, during which iron and carbon dioxide are formed, reducing the amount of iron oxide available for reduction. In addition, Jiang et al. [30] observed that the addition of a carbon coating to the Fe₃O₄ powder improved the reduction rate, further supporting the inhibitory effect of CO on Fe₃O₄ reduction.

Fig. 3(d) shows a plot of the equilibrium amount of Fe₃C as a function of temperature. At higher temperatures, the equilibrium amount of Fe₃C decreases in all atmospheres. This can be related to Le Chatelier's principle, which states that when a dynamic equilibrium is disturbed by a change in conditions, the equilibrium position changes to compensate for the change [31]. In addition, Fe₃C production was found to increase when more CO is present in the reducing atmosphere. In agreement with these results, Ho et al. [32] found that the carbonization rate increased with a decrease in CO gas fraction and was highest at a gas fraction of 0.5. Cohn et al. [33] observed that the carburization of iron oxide with CO resulted in Hagg Fe₃C with a higher Curie point. Wang et al. [34] described the kinetic behavior of producing Fe₃C in a fluidized bed and found that the reduction rate and production components changed with time. Therefore, the presence of higher amounts of CO in the reducing atmosphere is associated with an increase in Fe₃C production [32].

The thermodynamic stability of different compositions of iron oxide as the function of the temperature are given in Fig. 4.

The first inspection shows that for all Fe₂O₃ compounds a rapid increase in the reduction of Fe activity with increasing temperature up to about 500 °C is observed for all atmospheres. It can be observed that after this temperature, regardless of the reducing atmosphere, the Fe activity for all iron oxide compounds reaches its maximum value with increasing temperature. At a given temperature, the maximum Fe activity is reached in an atmosphere of 100% CO, regardless of the composition of the primary iron oxide. On the other hand, the Fe activity decreases at all temperatures when the H₂ content in the reducing atmosphere increases and reaches its minimum value in an atmosphere with 100% H₂.

To further investigate the effects of the individual oxide impurities

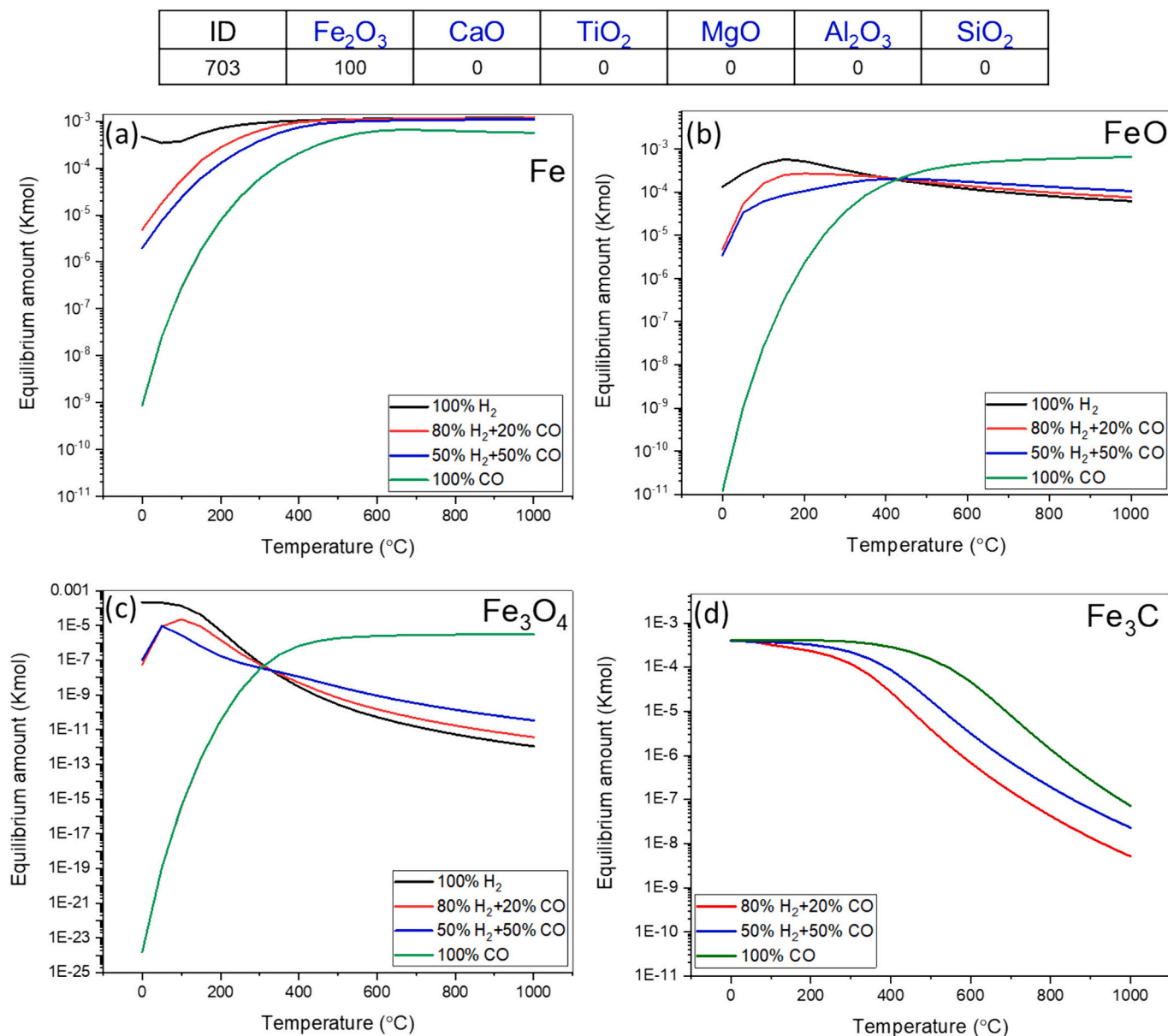


Fig. 3. Evolution of chemical composition of the pure pellet of iron oxide without any other oxides impurities.

such as CaO, SiO₂, TiO₂, MgO and Al₂O₃, Fe₂O₃ pellets with different proportions of impurities are examined in more detail. Fig. 5 shows the effects of TiO₂ impurity on Fe activity as a function of temperature in different atmospheres. In one particular atmosphere, the presence of TiO₂ decreased the activity of Fe, which increased with increasing temperature. The maximum activity of Fe in all atmospheres containing H₂ is reached in the case where the sample contains no oxide impurity (Fig. 5a-c). It can be seen that the activity of Fe in all atmospheres decreases significantly with the gradual increase of TiO₂ in Fe₂O₃ pellets. In addition, it is known that in the absence of TiO₂, the presence of other oxide impurities such as CaO, MgO, Al₂O₃ and SiO₂ also has a significant effect on reducing the activity of Fe in atmospheres with H₂.

Furthermore, in the presence of 100% CO, it can be observed that the activity of Fe increases with increasing temperature (Fig. 5d). The presence of oxidic impurities in the Fe₂O₃ pellets in the reducing atmosphere of 100% CO has a significant effect on the changes in Fe activity, such that an increase in temperature up to about 650 °C causes a parabolic increase in Fe activity. In contrast, Fe activity decreases at temperatures above 650 °C. It is also observed that in the absence of

oxidic impurities, i.e. at a composition of 100% Fe₂O₃, the activity of Fe increases continuously with increasing temperature. It is noteworthy that the rate of increase in Fe activity is high up to a temperature of about 650 °C and that the rate of increase in Fe activity gradually decreases with the increase in temperature to higher values.

Fig. 6 shows the behavior of activity of FeO (FeO) as a function of temperature in various reducing atmospheres.

The activity of FeO in H₂-containing atmospheres first increases strongly with increasing temperature (up to ~100, 190 and 425 °C for 100% H₂, 80% H₂ + 20% CO and 50% H₂ + 50% CO of the reducing gas, respectively) and then decreases with increasing temperature after these temperatures. It is clear that for all Fe₂O₃ compositions used in this study, as the amount of H₂ in the reducing atmosphere increases, the maximum activity of FeO shifts to higher values that can be obtained at lower temperatures. Furthermore, it is clear that the activity of FeO in the reducing atmosphere with 100% CO is highest at a higher temperature than in other reducing atmospheres with H₂. At a certain temperature, the presence of impurity oxides in Fe₂O₃ can lead to a decrease in the activity of FeO from about 1.35×10^{-1} to 7.5×10^{-2} .

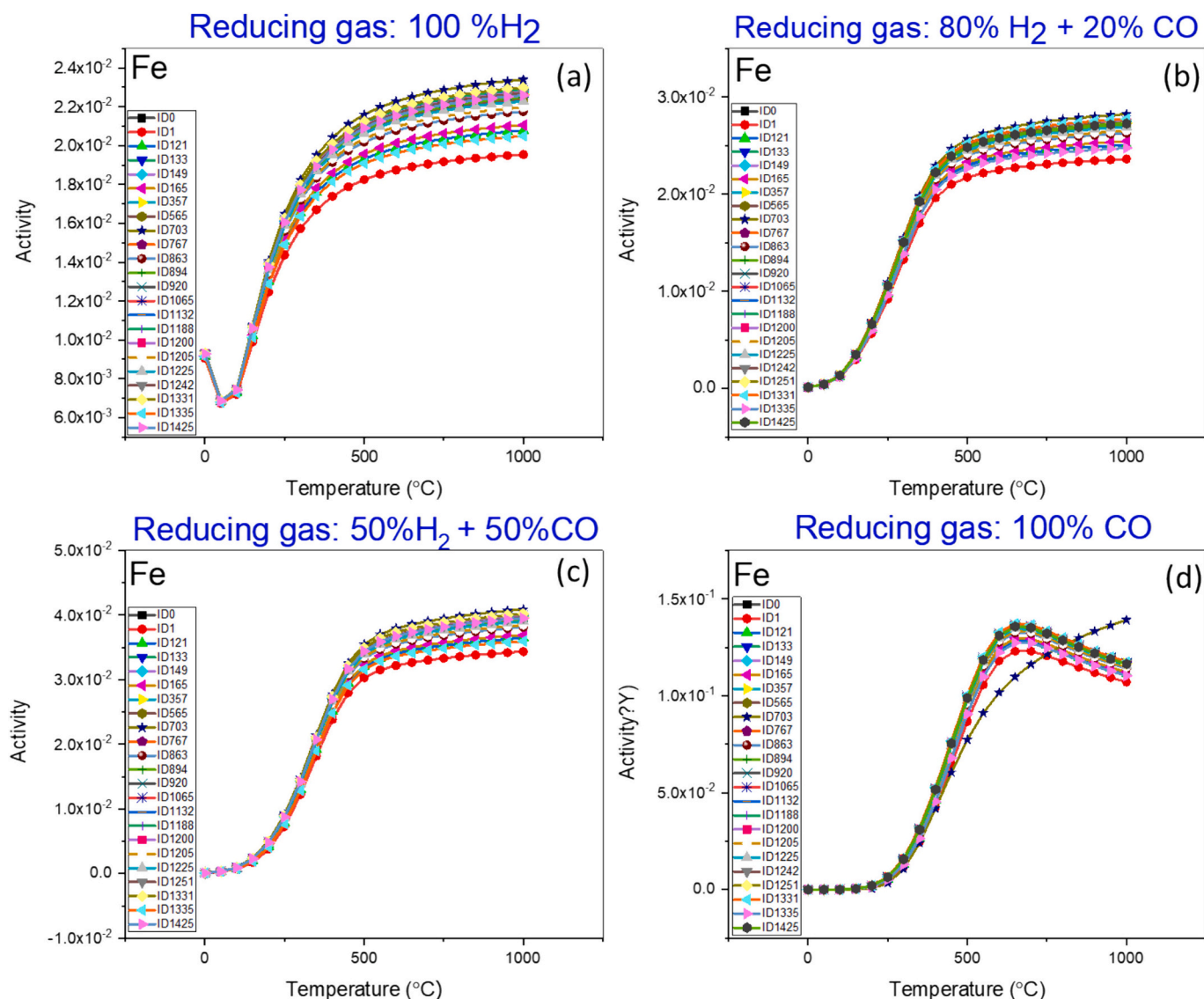


Fig. 4. Evolution of activity of Fe as function of the temperature in reducing gas atmosphere (a) 100% H_2 , (b) 80% H_2 + 20%CO, (c) 50% H_2 + 50%CO, (d) 100% CO.

In general, the increasing trend observed in the FeO profile is an indication of its formation below 500 °C. However, from a thermodynamic point of view, it cannot be stable below 570 °C. Therefore, the presence of FeO is associated with a non-reducing reaction that consumes (some) iron oxides (Fe_3O_4 or pure iron) already present in the medium. It seems that among the non-ferrous oxides, the role of MgO and CaO in the reduction of FeO is much more pronounced in the presence of a higher percentage of H_2 in the reducing gas. In addition, the activity maximum of FeO shifts with increasing H_2 content in the reducing atmosphere to higher values that can be achieved at lower temperatures. This can be attributed to the fact that an increase in the H_2 concentration in the reducing gas promotes a more efficient reduction of FeO.

Fig. 7 depicts the effect of CaO impurity on the evolution of FeO activity as function of the temperature in different reducing gas atmosphere.

It is obvious that the activity of FeO depends not only on the temperature but also on the presence of CaO. At a certain temperature, an increase in CaO leads to a decrease in the activity of FeO. The maximum activity of FeO is reached in an atmosphere of 100% CO. It was also found that the presence of the impurity CaO has a greater influence on the activity of FeO in an atmosphere with 100% CO than in an

atmosphere with H_2 .

In an atmosphere with H_2 , the activity of FeO depends on the amount of H_2 present. The maximum activity of FeO is reached when the highest possible amount of H_2 is present in the reducing gas, i.e. 100% H_2 . However, the presence of CO can increase the temperature required to reach the maximum activity of FeO from about 100 to 190 °C in an atmosphere with 20% CO to about 420 °C in an atmosphere with 50% CO and to about 600 °C in an atmosphere with 100% CO.

The development of Fe_3O_4 activity as a function of temperature in different reducing atmospheres is shown in Fig. 8. In the atmosphere with 100% H_2 , it can be observed that the Fe_3O_4 activity decreases very sharply with increasing temperature and reaches the minimum at a temperature of around 190 °C for all the compositions used here. In the presence of 100% CO, however, the process of change in Fe_3O_4 activity is completely opposite, so that after increasing the temperature to about 330 °C, the reduction process of Fe_3O_4 increases dramatically and reaches its maximum value at a temperature of about 950 °C.

A closer examination of the graphs in reducing atmospheres containing both H_2 and CO shows that the activity of Fe_3O_4 for all compositions increases very sharply with increasing temperature up to about 100 °C for 80% H_2 + 20%CO and up to about 50 °C for 50% H_2 + 50%CO and then drops sharply. Moreover, the presence of non-ferrous oxides

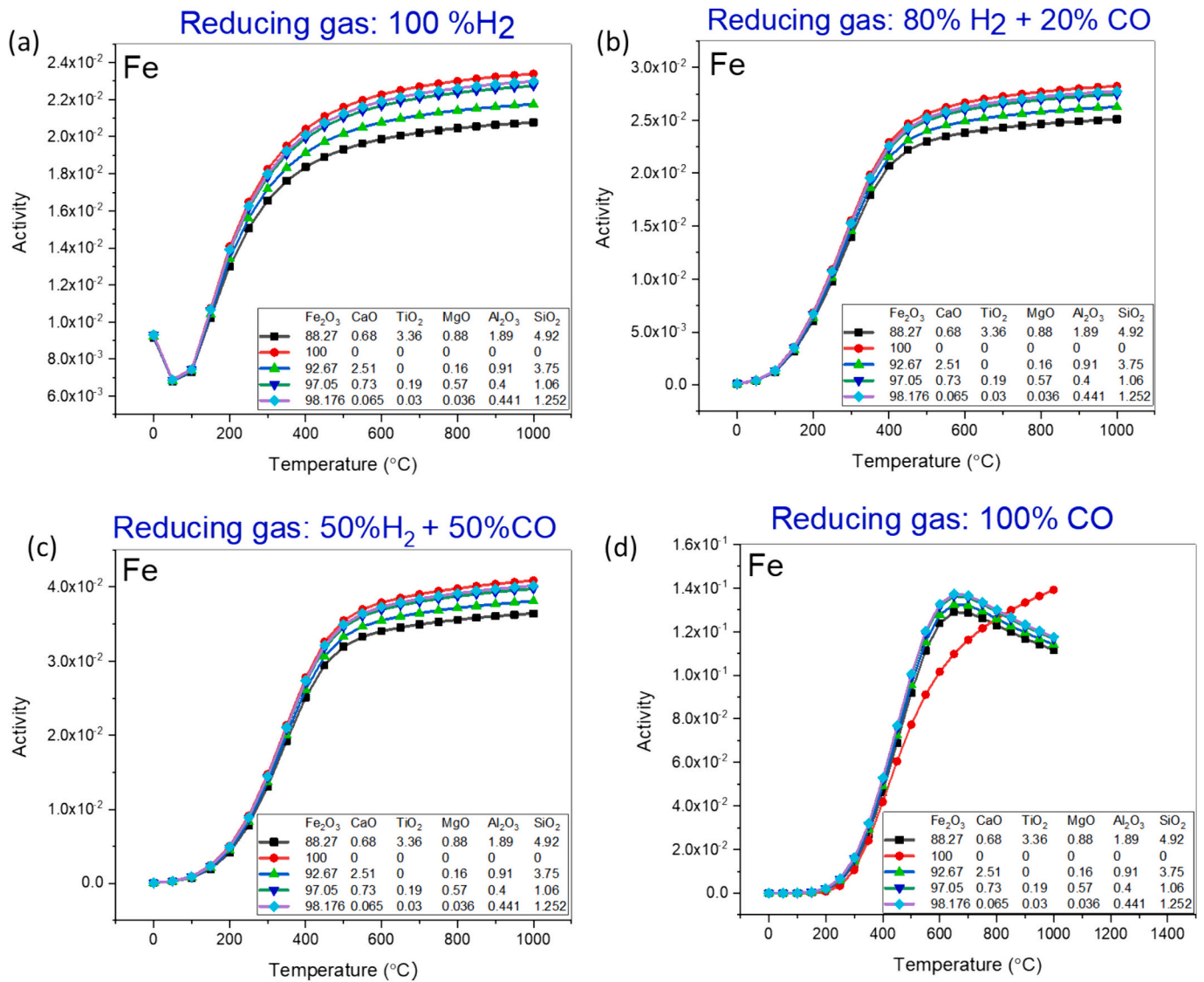


Fig. 5. The effect of TiO_2 impurity on the evolution of Fe activity as function of the temperature in reducing gas atmosphere (a) 100% H_2 , (b) 80% H_2 + 20% CO, (c) 50% H_2 + 50% CO, (d) 100% CO.

seems to have less influence on the Fe_3O_4 activity in the presence of H_2 in the reducing gas. On the other hand, it can be observed that the Fe_3O_4 activity in the presence of CO was significantly influenced by the non-ferrous oxides.

Fig. 9 shows how different oxides influence the process of changes in Fe_3O_4 activity. It was found that the maximum activity of Fe_3O_4 in atmospheres with 100% H_2 and 100% CO decreases as the amount of CaO and MgO in the initial pellets increases. This decrease in activity has its lowest value in an atmosphere with 100% H_2 and its highest value in an atmosphere with 100% CO.

Moreover, the presence of oxidizing oxides such as SiO_2 and Al_2O_3 significantly decreases the activity of Fe_3O_4 , while the presence of reducing oxides such as CaO and MgO increases the activity of Fe_3O_4 . It is found that regardless of the reducing atmosphere, the presence of TiO_2 also significantly reduces the activity of Fe_3O_4 . It is found that regardless of the reducing atmosphere, the presence of TiO_2 also significantly reduces the activity of Fe_3O_4 . In an atmosphere containing 80% H_2 , the effect of oxidizing oxides on the activity of Fe_3O_4 can be more pronounced than that of reducing oxides such as CaO and MgO.

As can be seen from Fig. 10, the activity of Fe_3C can only be formed in the presence of CO, and the activity of this carbide increases as the amount of CO in the reducing gas increases. Regardless of the type of

reducing atmosphere, the activity of Fe_3C decreases with increasing temperature and reaches its lowest value at temperatures of 430 °C, 550 °C and 730 °C for the atmospheres of 80% H_2 , 50% H_2 and 100% CO, respectively. In general, it was found that the presence of impurity oxides reduces the activity of Fe_3C , which at a given temperature depends significantly on the amount of H_2 in the reducing gas.

Fig. 11 shows that regardless of the type of reducing atmosphere, the presence of oxidic impurities in iron ore pellets can lead to significant changes in the activity of Fe_3C . It appears that in reducing atmospheres with higher H_2 content, the presence of TiO_2 plays a greater role in reducing the activity of Fe_3C than in atmospheres with higher CO content. On the other hand, the activity of Fe_3C decreases in reducing atmospheres with a CO content of at least 50 when the strength of reducing oxides such as CaO and MgO increases. In other words, as the amount of oxides increases with the oxidizing power of Al_2O_3 and SiO_2 in the pellets, the activity of Fe_3C increases significantly, and this effect is even more pronounced in a reducing atmosphere with 100% CO.

Fig. 12 shows how iron and iron oxides behave in different H_2 and CO atmospheres at 950 °C with different compositions. At the given temperature, the highest activity of Fe, FeO and Fe_3C in H_2 -containing atmospheres shows very little change for all compounds. The presence of oxides such as SiO_2 and Al_2O_3 has a stronger effect on the activity of