PRE-REDUCTION OF ILMENITE WITH NATURAL GAS – MODEL DEVELOPMENT AND USE

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ABSTRACT

TiZir Titanium and Iron AS (TTI) (formerly Eramet Titanium and Iron AS) in Tyssedal pre-reduces ilmenite using CO from partial combustion of coal in a rotary kiln. It has been shown that iron oxides in ilmenite are reduced more efficiently in H_2 than in CO. By partial replacement of CO with H_2 an increase in the reduction rate and possibly reduction at lower temperatures is expected. The possible use of syngas (CO and H_2) to reduce ilmenite is studied based on process schemes similar to those for the direct reduction of iron ores with natural gas.

The shrinking core model can be adapted to describe ilmenite reduction with syngas. An adapted model would include two solid species (iron oxides and titanium oxides) and two gaseous species (carbon monoxide and hydrogen). The iron oxides are reduced to metallic iron in stages resulting in a multi-interface model. The effects of titanium on iron oxide reduction will also need to be taken into consideration. Laboratory experiments will be used to refine and verify the model. This model could then be used to determine the feasibility of pre-reduction of ilmenite with natural gas on an industrial scale.

KEYWORDS: *Ilmenite, reduction, natural gas, modeling.*

1. INTRODUCTION

Due to dwindling sources of rutile (TiO_2), ilmenite ($FeTiO_3$) is the major mineral source of titanium. To obtain a valuable titanium product, iron must be removed. At TiZir Titanium and Iron AS 60-70% of the iron in the ilmenite is metallized in a rotary kiln using carbon monoxide (CO) from the partial combustion of coal. There have been multiple studies which show that hydrogen (H_2) is a more effective reducing agent for ilmenite than CO [1]. This work also confirms these results.

The reformation of natural gas provides a mixture of CO and H_2 which can be fed to an ilmenite pre-reduction process. In order to properly understand the mechanisms of pre-reduction, a model needs to be created to analyse the contributions to reduction from individual gas species. There will also be gas phase reactions namely the water gas shift reaction (WGSR) which will likely need to be accounted for.

The shrinking core model is widely accepted as an appropriate model for describing the behaviour during ilmenite and iron ore reduction. However, the valence state of the iron varies and the reaction typically has two distinct regions, reaction from ferric to ferrous iron and from ferrous to metallic iron. Therefore the shrinking core model must incorporate both reaction interfaces [1]. Iron ore reduction also contains a mixed ferric-ferrous phase, magnetite. Such a phase has not been reported for ilmenite reduction and will therefore not be considered in this work.

2. REDUCTION OF ILMENITE

It has been shown that oxidizing ilmenite before reduction can improve the final degree of

reduction [1-4]. Under oxidizing conditions, temperature plays a role in determining the final phases. At or below 800°C oxidation follows reaction (1) and/or (2) [5]:

$$4FeTiO_3 + O_2 \rightarrow 2Fe_2O_3 + 4TiO_2 \quad (1)$$

$$12FeTiO_3 + 3O_2 \rightarrow 4Fe_2Ti_3O_9 + 2Fe_2O_3 \quad (2)$$

Above 800°C, it has been found that ilmenite oxidizes according to reactions (3) and pseudorutile decomposes to pseudobrookite according to reaction (4) [6].

$$4FeTiO_3 + O_2 \rightarrow 2Fe_2TiO_5 + 2TiO_2 \quad (3)$$

$$Fe_2Ti_3O_9 \rightarrow Fe_2TiO_5 + 2TiO_2 \quad (4)$$

For pre-oxidized ilmenite the starting point for reduction will be ferric iron. Reduction begins by reducing this to ferrous iron and then proceeds to reduction to metallic iron:

$$Fe^{3+} \Rightarrow Fe^{2+} \Rightarrow Fe$$

The rates of reaction vary for the 1st step and the 2nd step and the reactions do not occur simultaneously over the whole course of reduction. Thus, any model of reduction must consider the intermediate ferrous iron.

It has been shown that pseudobrookite (Fe_2TiO_5) is the most desirable oxidation product [2]. Therefore, this modelling will be conducted with the initial reactant being pseudobrookite.

Reduction with CO/H_2

Reduction of iron oxides to metal takes place in a number of stages. First, ferric iron is reduced to ferrous iron. Pseudobrookite reacts with CO or H_2 to form synthetic ilmenite according to reaction (5) at 1000°C [6]:

$$Fe_2TiO_5 + TiO_2 + CO\ (H_2) \rightarrow 2FeTiO_3 + CO_2\ (H_2O) \quad (5)$$

Hematite may either be present in the natural ilmenite, or formed after oxidation. The reduction of hematite can be assumed to proceed according to reaction (6)[1]:

$$Fe_2O_3 + CO\ (H_2) \rightarrow \text{“FeO”} + CO_2\ (H_2O) \quad (6)$$

The synthetic ilmenite then reacts further with CO or H_2 between 1000°C-1200°C as shown in reaction (7):

$$FeTiO_3 + CO\ (H_2) \rightarrow Fe + TiO_2 + CO_2\ (H_2O) \quad (7)$$

Remaining wüstite is metallized according to reaction (8).

$$\text{“FeO”} + CO\ (H_2) \rightarrow Fe + CO_2\ (H_2O) \quad (8)$$

The formation of metal from ferrous iron is expressed by reactions (7) and (8). The mechanisms of iron metallization from ilmenite are not simple. The above reactions do not take into account the presence of a mixed valence phase containing both Fe^{2+} and Fe^{3+}. If such a phase is present then it would need to be accounted for in the model. It can be seen that many special

considerations are needed to effectively model the whole reduction process.

3. THEORY

The shrinking core model is used to describe the kinetics of reduction of ilmenite. Sun and colleagues used the two interface model and the schematic is shown in figure 1 [1].

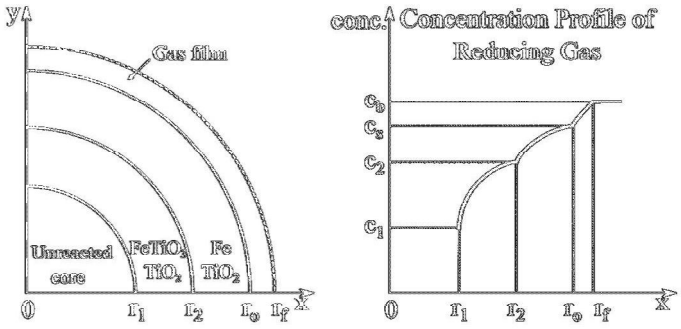


Figure 1: Redrawn schematic diagram of a two-interface reaction system for ilmenite reduction along with the reducing gas composition profile [1]

Studies have shown that this process is controlled by diffusion of the reactants and the products through the solids [1,7]. The concentrations are approximated as steady-state and the activities of the solids are assumed to be unity.

The model should be described by time dependent equations which are able to adapt based on changing conditions. Kolbeinsen and Onshus have developed an electric circuit analogy which describes the dynamic behaviour during iron ore reduction [8-10].

The circuit analogy uses the shrinking core as a basis and each controlling step is a resistance. That is, diffusion (both gas film and solid product layer) and chemical reactions are resistant to the "current". In this model the "current" is the flow of oxygen in the "circuit". Figure 2 shows the circuit used by Kolbeinsen and Onshus:

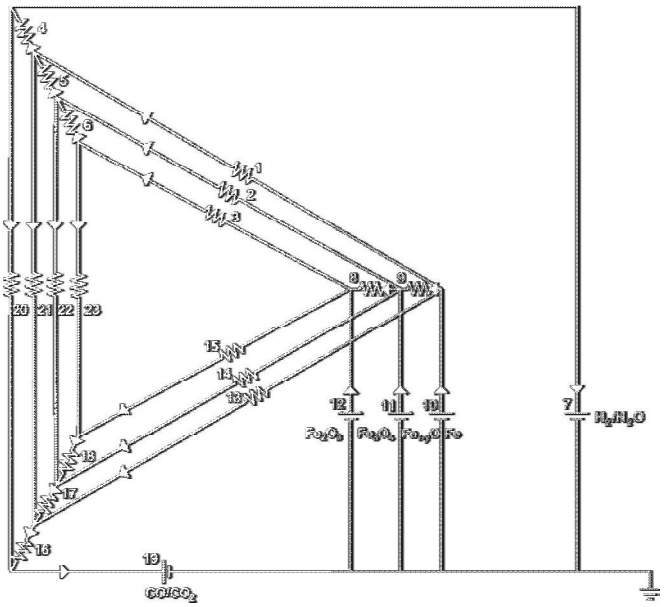


Figure 2: Electric circuit analogy for iron ore shrinking core model [9, 10]

Using methods (cut-set analysis) from electric circuit analysis the model can be solved with oxygen flow acting similarly to current and Gibbs free energy providing a driving force.
The following calculations show how the Gibbs free energy is used to determine the potential for the reactions. The reduction of ilmenite can be expressed by the following reaction:

$$FeO_x \cdot TiO_2\,(s) + R\,(g) \rightarrow FeO_{x-1}\,(s) + TiO_2\,(s) + RO\,(g) \quad (9)$$

R represents the reducing agent (CO or H_2) and RO is the oxidized gas product (CO_2 or H_2O). Reaction (9) can be split into two reactions one involving solids and one involving gases:

$$FeO_x \cdot TiO_2\,(s) \rightarrow FeO_{x-1}\,(s) + TiO_2\,(s) + \tfrac{1}{2}\,O_2\,(s) \quad (10)$$

$$\tfrac{1}{2}\,O_2\,(s) + R\,(g) \rightarrow RO\,(g) \quad (11)$$

The Water Gas Shift Reaction (WGSR):

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \quad (12)$$

must also be taken into account when both H_2 and CO are the reducing gases.

The Gibbs free energy of reaction (9) is given by

$$\Delta G_9 = \Delta G_9^\circ - RT \ln \frac{p_R}{p_{RO}}$$

and for reactions (10) and (11)

$$\Delta G_{10}^\circ = RT \ln \frac{1}{p_{O_2(s)}^{1/2}}$$

$$\Delta G_{11}^\circ = RT \ln \frac{p_R \cdot p_{O_2(g)}^{1/2}}{p_{RO}}$$

since reactions (10) and (11) combine to form reaction (9), the Gibbs free energy of reaction (9) can be expressed by the following:

$$\Delta G_9 = (\Delta G_{10}^\circ + \Delta G_{11}^\circ) - RT \ln \frac{p_R}{p_{RO}}$$

$$\Delta G_9 = \left(RT \ln \frac{1}{p_{O_2(s)}^{1/2}} + RT \ln \frac{p_R \cdot p_{O_2(g)}^{1/2}}{p_{RO}} \right) - RT \ln \frac{p_R}{p_{RO}}$$

$$\Delta G_9 = RT \ln \frac{1}{p_{O_2(s)}^{1/2}} + RT \ln \frac{p_R}{p_{RO}} + RT \ln p_{O_2(g)}^{1/2} - RT \ln \frac{p_R}{p_{RO}}$$

$$\Delta G_9 = RT \ln \frac{1}{p_{O_2(s)}^{1/2}} + RT \ln p_{O_2(g)}^{1/2}$$

$$\Delta G_9 = \frac{RT}{2}\left(-\ln p_{O_2(s)} + \ln p_{O_2(g)} \right)$$

A similar consideration can be used for the water gas shift reaction (12), giving a driving force of the difference in the $\ln p_{O_2}$ of the CO/CO_2 and H_2/H_2O fractions of the gas. This allows us to calculate reaction rates for both gases simultaneously, with the gas compositions linked through the water gas shift reaction.

The electrical analogy allows for much simpler calculations of the reaction rates. Resistance terms are arranged into a matrix, called the G-matrix and the driving force, oxygen potentials form the e-vector. The reaction rates can be calculated using the following:

$$i = G (u + e)$$

the u - vector is an unknown describing the potential drop in each branch. It can be expressed, using Kirchhoff's law and the Q-matrix from the cut-set method. Further details can be found in previous work [8-10].

4. REDUCTION OF TITANIUM SPECIES

While the electric circuit analogy has been shown to accurately describe reduction of iron ore, it has not been proven for ilmenite. Reduction of titanium oxides would add oxygen to the "circuit". If this is a simple reaction like so:

$$TiO_x + R \rightarrow TiO_{x-1} + RO \qquad (13)$$

then another "battery" can be added to the shrinking core model and the oxygen potential of this reaction would be accounted for. However, if the reactions proceed with intermediate phases and possible solid-solid phase changes this further complicates the oxygen equilibrium.

The Fe-Ti-O system has multiple possible phases. Those relevant to oxidation and reduction of ilmenite are indicated in figure 3.

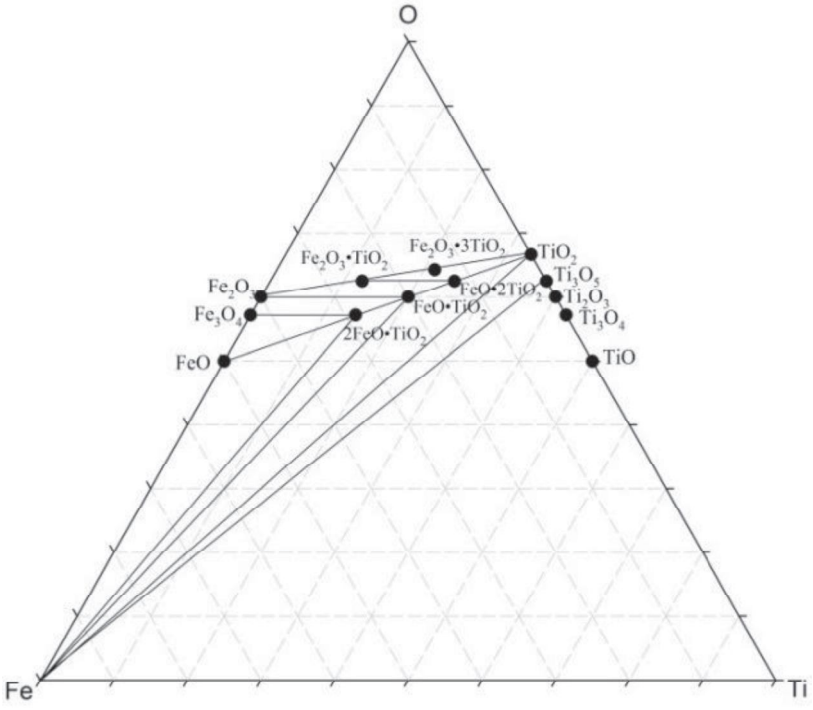


Figure 3: Fe-Ti-O system

While TiO_2 itself might not be reduced, it does "move" within the system. For example, pseudobrookite can be transformed into pseudorutile as shown below (reaction (4) in reverse):

$$Fe_2TiO_5 + 2TiO_2 \rightarrow Fe_2Ti_3O_9 \quad (Fe_2O_3 \bullet TiO_2 \rightarrow Fe_2O_3 \bullet 3TiO_2) \tag{4}$$

It can be seen that the oxidation state of the metals is not changed, however the oxygen potential could be due to the change in the metal-oxygen ratio. Therefore the representation of batteries controlling the oxygen potential might need to be altered.

The oxidation path in pure oxygen is realized by a line from the original composition ($FeO \bullet TiO_2$ in the case of pure ilmenite) up to pure oxygen. Reduction can follow different paths based on the partial pressure of oxygen in the system [11].

The presence of magnesium and manganese in the raw material has also shown to affect the reduction behaviour. The associated oxides are not reduced and migrate inward during reduction. The concentration of Mg and Mn build up in the unreduced material and eventually the iron activity is lowered to such an extent that it cannot be reduced [12]. In many cases, the Mn or Mg is dissolved into the pseudobrookite phase or form a new phase with iron, titanium and oxygen.

5. EXPANSION OF THE SHRINKING CORE MODEL

The shrinking core model (SCM) is a well-developed model which expresses the kinetics of fluid-particle reactions. The conventional SCM deals with one solid reacting in an atmosphere of a one-reactant fluid. This reaction has one gaseous product and one solid product. This means there is only one reaction interface. Figures 4 and 5 show how the basic shrinking core model can be modified to include multiple reactant gases and multiple solid products.

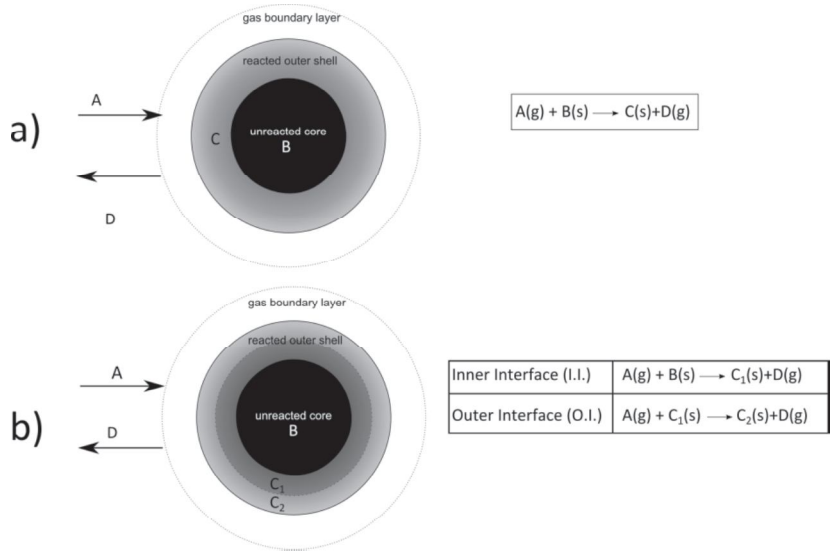
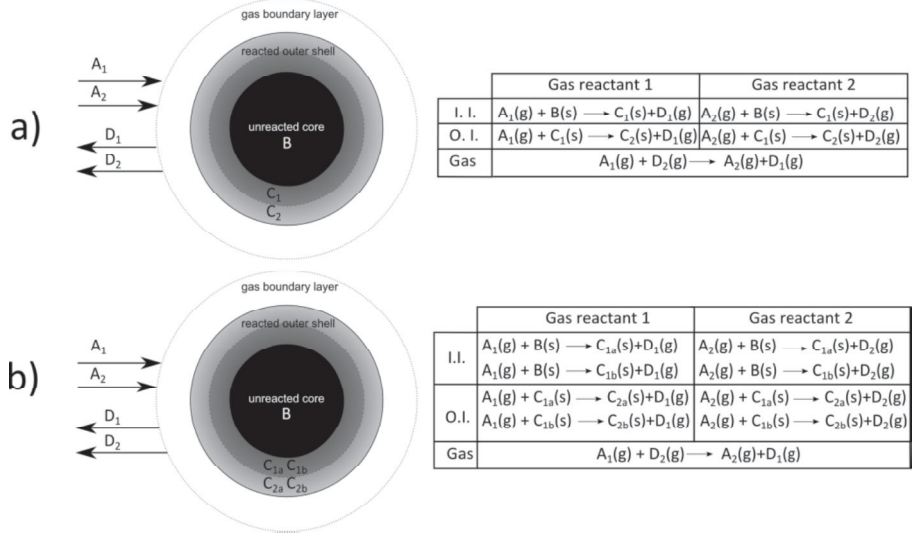


Figure 4: Development of the shrinking core model (SCM)
a) basic SCM b) SCM with intermediate product

Further refinement of the basic model has included the expansion to two or more interfaces due to intermediate reaction products as discussed previously [1]. Further still, work has been done to create a shrinking core model with multiple interfaces and multiple gas phases [9, 10]. In each of these cases only one solid species takes part at each of the reaction interfaces. The modelling of solid state reduction with multiple solid species being reduced in parallel has not been thoroughly

investigated. Sun and colleagues used figure 4 b) as the basis for their investigation in reducing ilmenite [1]. This disregarded any effects of TiO_2 reduction. Kolbeinsen and colleagues have developed the model for iron ore reduction in syngas (one solid, two gas species) according to figure 5 a) [8, 10]. To consider both iron oxides' and titanium oxides' reduction of ilmenite in an atmosphere of CO and H_2 would require developing a model according to figure 5 b). In this case, products Cxa and C_{xb} (x=1, 2) are the iron reduction products and titanium reduction products respectively and A_1 and A_2 are CO and H_2.



	Gas reactant 1	Gas reactant 2
I. I.	$A_1(g) + B(s) \rightarrow C_1(s) + D_1(g)$	$A_2(g) + B(s) \rightarrow C_1(s) + D_2(g)$
O. I.	$A_1(g) + C_1(s) \rightarrow C_2(s) + D_1(g)$	$A_2(g) + C_1(s) \rightarrow C_2(s) + D_2(g)$
Gas	$A_1(g) + D_2(g) \rightarrow A_2(g) + D_1(g)$	

	Gas reactant 1	Gas reactant 2
I.I.	$A_1(g) + B(s) \rightarrow C_{1a}(s) + D_1(g)$ $A_1(g) + B(s) \rightarrow C_{1b}(s) + D_1(g)$	$A_2(g) + B(s) \rightarrow C_{1a}(s) + D_2(g)$ $A_2(g) + B(s) \rightarrow C_{1b}(s) + D_2(g)$
O.I.	$A_1(g) + C_{1a}(s) \rightarrow C_{2a}(s) + D_1(g)$ $A_1(g) + C_{1b}(s) \rightarrow C_{2b}(s) + D_1(g)$	$A_2(g) + C_{1a}(s) \rightarrow C_{2a}(s) + D_2(g)$ $A_2(g) + C_{1b}(s) \rightarrow C_{2b}(s) + D_2(g)$
Gas	$A_1(g) + D_2(g) \rightarrow A_2(g) + D_1(g)$	

Figure 5: SCM with two gaseous reactants and products and consideration of gas phase reaction
a) one intermediate solid product and one final product
b) two intermediate solid products and two final solid products

6. EXPERIMENTAL

Thermogravimetic analysis can be used to verify the pellet behaviour. Equipment at the Department of Materials Science and Engineering at NTNU can run experiments over a wide range of temperatures and gas compositions. If the mass change corresponds to the model then the accuracy of the model is verified.

Preliminary tests on reduction of oxidized ilmenite with CO and H_2 have been completed. Ilmenite pellets were reduced at approximately 1000°C in three separate tests according to the conditions in table 1.

Table 1: Experimental conditions

Test Number	Gas Flow Rate	Time
1	5 L/min CO	4 hr
2	2.5 L/min CO 2.5L/min H_2	2 hr
3	5 L/min H_2	2 hr

The metallization degree corresponding to the weight loss is shown in the plot in figure 6.

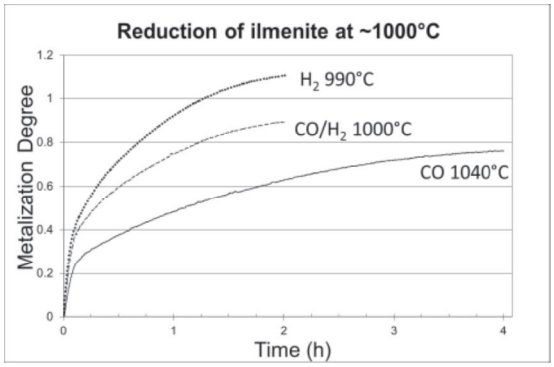


Figure 6: Difference in reaction rate based on gas composition

This clearly shows that both gases need to be considered when building a model as the reaction rate is significantly increased with increasing amounts of hydrogen compared to CO alone. The pure hydrogen reduction exhibits a reduction degree greater than one meaning the mass lost was greater than the mass associated with oxygen in the iron oxides. It is therefore likely that other oxides were reduced and any model should include the possiblity of other oxides being reduced.

To verify a future model, simulations can be run and the computed mass loss can be compared with experimental mass loss to check the validity of the model. One model should be able to fit the results within a wide range of experimental conditions.

7. MULTI-SCALE MODELLING

The shrinking core model describing a single pellet during reduction will form the basis for larger or smaller scale modelling. Smaller scale modelling would describe the grain behaviour during reduction. Larger scale modelling would describe the collective behaviour of many individual models, for example pellets in a shaft furnace or grains in a fluidised bed.

A "micro" model, shown in figure 7, will give an indication of how reduction progresses on a small scale. This could be either a grain or a pellet, not necessarily microscopic scale. Reducing gas (R) migrates to the pellet and the product gas(RO) leaves the pellet.

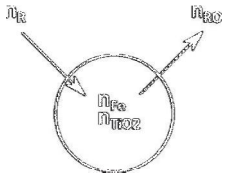


Figure 7: "Micro" model

The behaviour will, in turn, provide information about how much of each gas species is produced and consumed and this determines the gas atmosphere in the furnace. The rate of solid conversion will also be given based on this. The model can be manipulated to show how the behaviour changes based on different inputs such as different gas compositions and temperatures. A dynamic model is better able to illustrate exactly how changing conditions in the furnace affect the pellet.

The combined "micro" behaviour can be collectively modelled to form a larger scale "macro" model. The combined effects from evolution and consumption of gas will directly determine the atmosphere. Figure 7 shows the inputs and outputs of a shaft furnace model, individual pellet behaviour would determine the gas atmosphere at different points in the furnace. With a particle

model, a fluid bed process could be modelled instead of a shaft furnace. The feed gas composition is an important variable that will be determined by the large scale model.

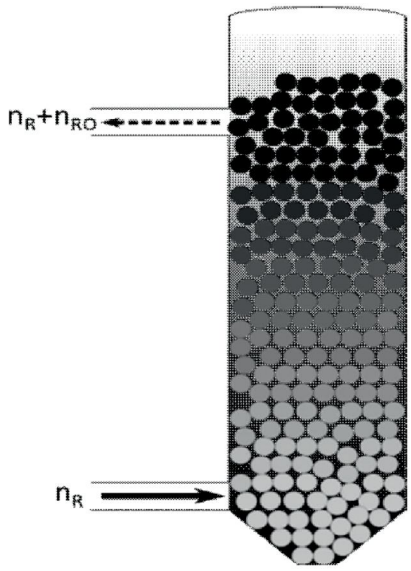


Figure 7: "Macro" model

An industrial process model of ilmenite pre-reduction is proposed based on the MIDREX® Process for direct reduced iron in a shaft furnace. Figure 8 shows a flowsheet for such a process, however, instead of iron ore and iron entering and leaving, it is oxidized ilmenite and pre-reduced ilmenite.

Natural gas enters the process and is reformed to a blend of CO and H_2 (syngas). The exact composition of syngas can be varied within limits based on the temperature in the reformer. Reformation takes the natural gas (mainly CH_4) and forms syngas according to reactions (14) and (15). The syngas is fed into the shaft furnace as reducing gas.

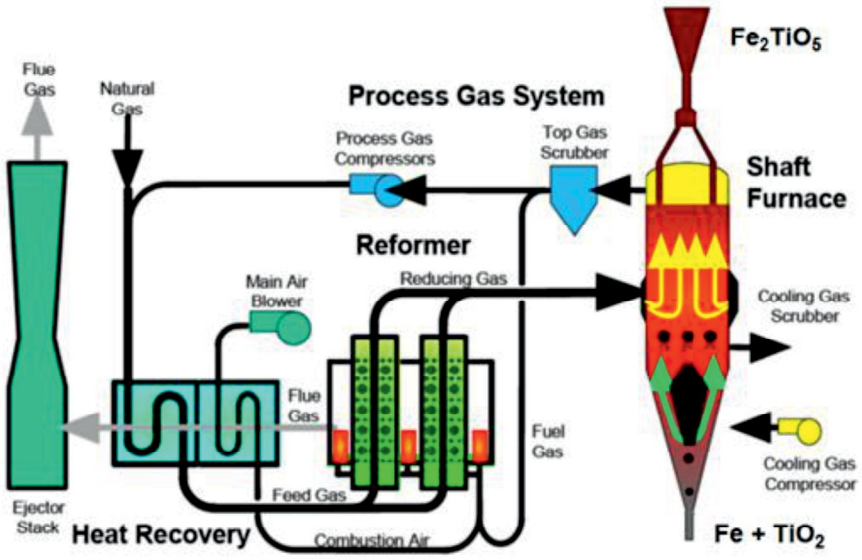


Figure 8: MIDREX® flowsheet adapted for pre-reduction of ilmenite

$$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2 \qquad (14)$$

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \quad (15)$$

In addition to the temperature, the balance between the two reforming reactions also relies on the gas recycling ratio. The CO_2 and H_2O supplied to the reformer come from the recycled off gas and the heat needed for the reformation reactions comes from burning unused CO and H_2.

The important conditions in the model such as natural gas feed to the process, gas recycle ratio and the temperature of the reformer all need to be determined from modelling. These variables are inevitably tied to the pellet behaviour.

8. CONCLUDING REMARKS

Studies in the reduction of ilmenite generally only take into account the reduction of the iron species. The titanium dioxide is assumed to only be a spectator to the reduction of iron oxides. There are many studies which confirm this behaviour in certain conditions. However, a more complete model should include the behaviour of the titanium species. The titanium oxides have been shown to form alternate phases and solid solutions with iron oxides which will influence the overall reduction. One possible way of including titanium is by expanding the shrinking core model to include multiple reactions at different interfaces. This forms the small scale “micro” model.

A “micro” model which can express the reaction progression demonstrates how ilmenite is reduced based on changing atmospheres. Using these results the model can be used in developing large scale, “macro”, processes. A pellet “micro” model forms the basis for a shaft furnace “macro” model and a grain forms the basis for a fluidised bed.

The challenges in the future work will be to incorporate the effects of titanium oxides into the shrinking core model for iron reduction. This means the calculation of oxygen potentials will have to be expanded to include the titanium-iron, and titanium-oxygen effects. A robust shrinking core model will ensure that scaling up or down from a base model will produce accurate results.

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