

CARBOTHERMIC SELF-REDUCTION OF AGGLOMERATES CONTAINING MANGANESE OXYDE¹

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Abstract

Firstly, aiming to establish the thermodynamical conditions for the feasibility of the manganese oxide reduction, phase diagrams for the Mn-C-O system were drawn, considering different activities for reagents and products. Further, experiments to investigate the reduction progress were done, encompassing temperatures from 900 to 1300°C and using composite briquettes containing manganese oxides and charcoal. From the results obtained, a kinetic reduction model involving two phenomenological stages was proposed. The first reduction stage occurs in a short reaction time, up to 10 minutes. This phase is followed by a second stage, characterized by the decrease of the conversion fraction and shows a further transformation of the product generated in the first reduction stage. For the first stage the apparent activation energy was $E_a = 11.50$ kJ/mol and the frequency factor $k_0 = 57$ μ Hz. As for the second stage these parameters were $E_a = 46.50$ kJ/mol and $k_0 = 48$ Hz. The kinetic equations for these two stages fitted well the experimental data, within acceptable statistical errors.

Key words: Manganese ore; Self-reduction; Kinetics; Composite agglomerates.

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1 INTRODUCTION

Manganese is basically an ironmaking raw material, being used either in the mineral form for pig iron production or as an ferroalloy addition to the steel. Further manganese is utilized as deoxidant and desulfurization agent or also as MnO, in this case being used as micronutrient or defensive^(1,3) substance.

In the route of manganese ferroalloy production, the cost determinant main factors are the ore specific consumption and ,above all, the electric power.

Aiming mainly at the cost reduction in the high carbon manganese ferroalloy production (HC FeMn), studies focusing the carbothermic reduction of self-reducing manganese oxide agglomerates (pellets and/or briquettes) has been done.^(4,5)

Experiments using self-reacting agglomerates, besides permitting the use of ore fines and residues, exhibited no deleterious effects to the furnaces operation, also resulting in the minimization of the total energy expenditure.⁽⁵⁻⁹⁾

The essential of this work aimed to the thermodynamic studies and the kinetic of the carbothermic manganese IV self-reduction towards manganese II, one of the key stages for the formation of the manganese ferroalloy.

2 EXPERIMENTS

The samples utilized in the research were self-reducing briquettes in the shape of cylindrical disks. The constituents for these briquettes were manganese ore and charcoal as reductant, both of them finely grinded under 100 mesh, the later with a 20% of stoichiometric excess for carbon. The green agglomerates were pressed under a load of 100 kgf and then cold cured.



Figure 1 – (a) Fines blending; (b) Indeflexible steel matrix; (c) Tubular electric furnace

The briquettes reduction was performed using two electrical tubular furnaces with maximum temperatures of 1 200°C and 1 400°C, both operating under a controlled atmosphere using a flowrate of 2.5 Nm³ N₂ / min. The selected temperatures were 900°C, 1000°C, 1100°C, 1150°C, 1200°C e 1300°C, the tests being performed in a time range from 10 to 90 minutes.

After the reduction stage, every briquette was submitted to optical and electronic microscopy and thoroughly grinded for chemical analysis .

3 RESULTS AND DISCUSSION

3.1 Thermodynamical Analysis

Aiming at the determination of the predominance areas for different compounds that could be formed during the reduction process, the Mn-C-O diagram was plotted. Figure 2 shows that with low CO contents the manganese higher oxides (MnO_2 , Mn_2O_3 and Mn_3O_4) are easily reduced to MnO, considering that the charcoal reactivity is already high around 800°C.

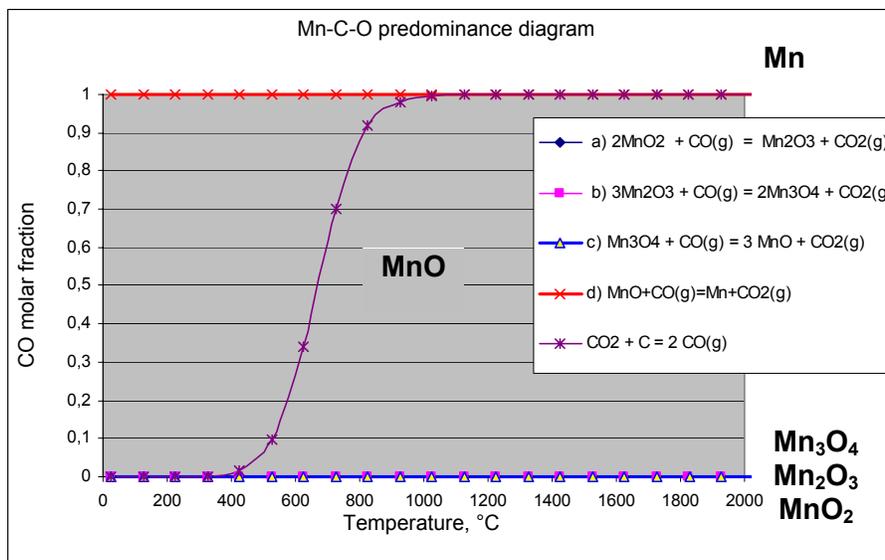
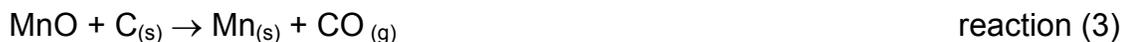
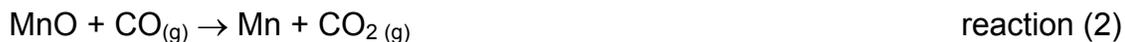


Figure 2 - Mn-C-O operational predominance diagram showing the equilibrium between the manganese oxide and CO, CO_2 and C ($P_{\text{CO}(\text{g})} + P_{\text{CO}_2(\text{g})} = 1\text{ atm}$).

As in the self-reducing briquette the Boudouard reaction also occurs:



one can represent the global reduction as the resultant of the reactions (1) and (2), that is, through gaseous intermediaries:



Taking into account the different activities for the substances present in reaction (3) Figure 3 depicts the molar fraction CO levels in equilibrium with MnO. It is to be observed that those levels are practically unitary.

Considering the experimental evidences pointing to the presence of manganese carbides coexisting with the MnO reduction by carbon, Figure 4 is presented.

In it the formation of Mn_3C from MnO is represented, showing that high activity values for MnO combined to low Mn_3C activities, widens the predominance region for the last.

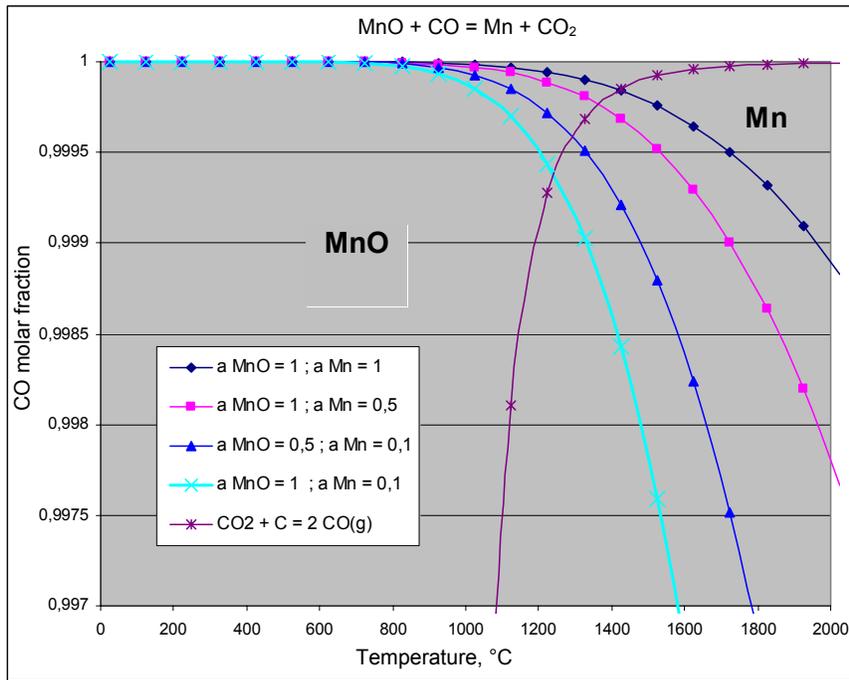


Figure 3 - Mn-C-O operational predominance diagram showing the equilibrium between MnO , Mn and the Boudouard curve. The effect of Mn and MnO activities are also shown.

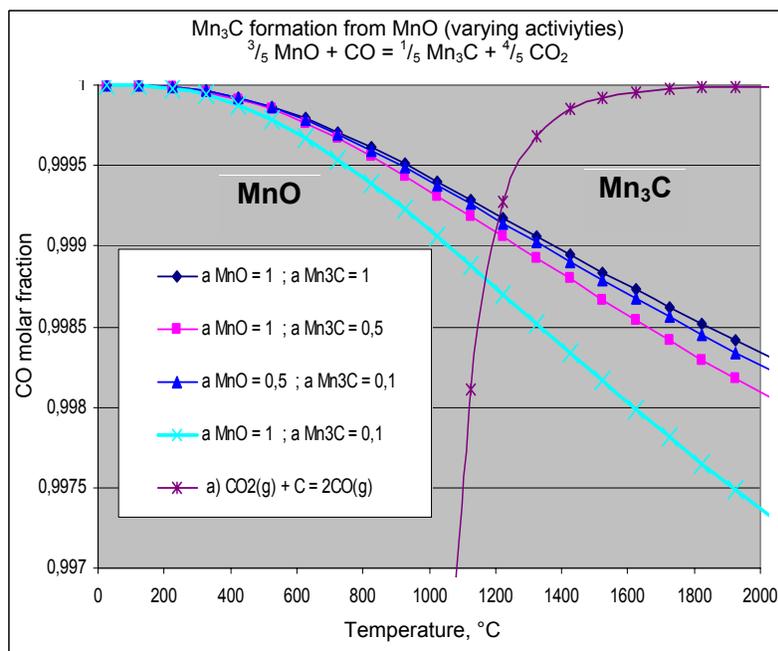


Figure 4 - Mn-C-O operational predominance diagram showing the equilibrium between MnO and Mn_3C and the Boudouard curve. The effect of MnO and Mn_3C activities are also shown.

Figure 5 shows the temperature range where the formation of Mn₃C is thermodynamically predominant with respect to the formation of metallic manganese, for activities from 1 to 0.1 for both substances. It should be noted that the formation of Mn₃C will only be predominant with respect to Mn, for activities 0.1, at temperatures below circa 1420°C. These behavior suggests that the production of Mn₃C will precede the formation of metallic manganese.

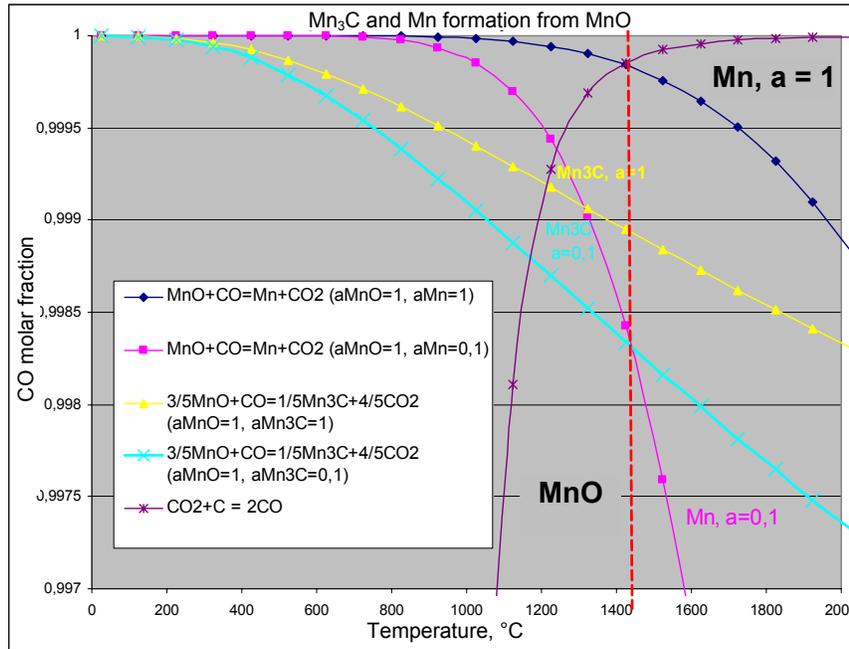


Figure 5 - Mn-C-O operational predominance diagram showing the equilibrium between MnO, Mn₃C, Mn and the Boudouard curve, for various activities of Mn₃C and Mn.

3.2 Kinetic Parameters Evaluation

Based on the experimental results, that showed initially crescent conversion curves followed by a further decreasing behavior, a two stage process mechanism was proposed. The first stage, valid for short reaction times, up to circa 10 minutes, essentially involving the reduction of MnO₂ to MnO, was followed by a second step, characterized by the transformation of the generated MnO, probably to the Mn₃C. Aiming at the description of the process as a whole, that is, the formation of the MnO for the first stage and a second stage where the transformation of the previously generated MnO takes place, the following equation was utilized:

$$\chi_{\text{MnO}} = \chi_1 [1 - e^{-t/\tau_1}] - \chi_2 [1 - e^{-t/\tau_2}] \quad \text{equation (1)}$$

in which the first parcel in the right side of the equation models the MnO formation and the second the consumption of this same species.

3.3 Temperature Effect

In Figure 6 the kinetic curves for the experimental and calculated reduction degrees for the first stage of the model are presented.

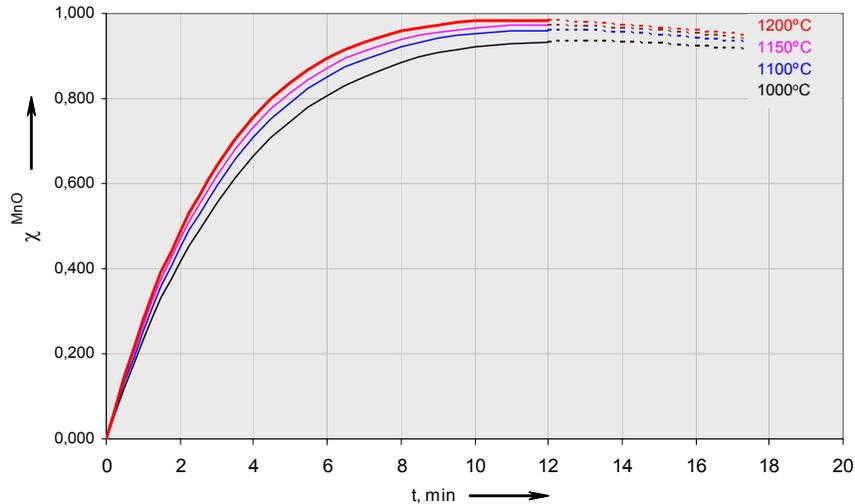


Figure 6 - MnO_2 to MnO conversion for short times and MnO transformation under 1000, 1100, 1150 and 1200°C. Briquette : manganese ore with charcoal (C in excess of 20%).

This figure shows that the self-reduction of the briquettes exhibited high conversions for Mn^{+4} towards Mn^{+2} , being increased for higher temperatures, mainly for that one above the reductant reactivity (800°C).

It was also determined that the adopted kinetic model described with accuracy the briquettes reduction (correlation of 94.4% for the short times step and 96.1% for the second step).

The jointly analysis of Figures 6 and 7 permits the conclusion that for temperatures above 900°C the MnO_2 to MnO conversion is maximal (1000°C in this work).

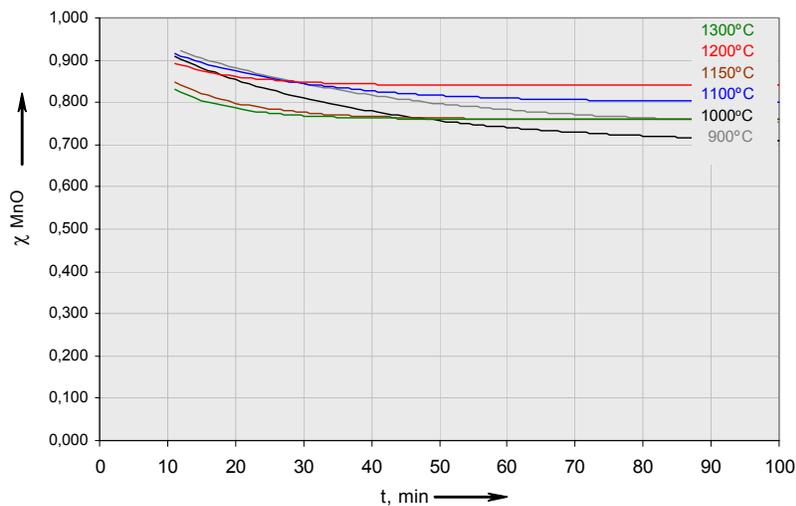


Figure 7 – Decrease of the conversions from MnO_2 to MnO for long times in the temperatures of 900, 1000, 1100, 1150 e 1200 e 1300°C. Briquette: manganese ore with charcoal (C in excess of 20%).

The Tables 1 and 2 show the χ_i values (proportionality factors) and τ_i (temporal factors) determined for the kinetic model for each test temperature and for the two proposed reaction stages ($i = 1, 2$). The values for k_o (pre-exponential frequency factor) and E_a (apparent activation energy) are also presented for both of processes steps.

Table 1 – Kinetic parameters for short reaction times.

T °C	$10^3 / T$ $10^3 \times K^{-1}$	χ_1	τ, s	$\Delta\varepsilon\%$		$\ln \chi_1 / \tau$	Model (short reaction times)	
				(Mn_{Tot})	fitting deg		k_o	$E_{ativação}$
1000	0,79	1,4700	4,60	4,62%	5,35%	-1,1408	k_o	$E_{ativação}$
1100	0,73	1,4400	4,20	5,70%	10,31%	-1,0704	mHz	$\text{kJ} \times \text{mol}^{-1}$
1150	0,70	1,4250	4,00	5,13%	9,57%	-1,0321	0,057	11,50
1200	0,68	1,4100	3,80	5,13%	4,40%	-0,9914	$\pm 0,004$	$\pm 0,952$
				$\Delta\varepsilon_{\%glob} = 6,28\%$				
				$r^2 = 0,944$				

Table 2 – Kinetic parameters for long reaction times.

T °C	$10^3 / T$ $10^3 \times K^{-1}$	χ_2	τ, s	$\Delta\varepsilon\%$		$\ln \chi_2 / \tau$	Model (long reaction times)	
				(Mn_{Tot})	fitting deg		k_o	$E_{ativação}$
900	0,85	0,2600	33,00	8,86%	8,28%	-4,8436	k_o	$E_{ativação}$
1000	0,79	0,3000	30,00	4,62%	6,08%	-4,6052	Hz	$\text{kJ} \times \text{mol}^{-1}$
1100	0,73	0,2000	20,00	5,70%	9,78%	-4,6052	48,045	46,10
1150	0,70	0,2400	11,00	5,13%	4,25%	-3,8250	$\pm 3,067$	$\pm 2,942$
1200	0,68	0,1600	10,00	5,13%	4,24%	-4,1352		
1300	0,64	0,2400	9,00	6,18%	5,68%	-3,6243		
				$\Delta\varepsilon_{\%glob} = 6,16\%$				
				$r^2 = 0,961$				

With the values calculated in Table 1 and aiming at the estimation of the kinetic parameters that govern the reduction process, the Arrhenius equation (5) was utilized and $\ln(\chi_i / \tau)$ was considered as a function of the temperature reciprocal ($1 / T$). The graph in Figure 8 presents a curve that characterizes the mechanism occurring in the reduction process for short reaction times.

$$\ln(\chi_i / \tau) = \ln k + [-E_a / RT] \quad \text{equation (2)}$$

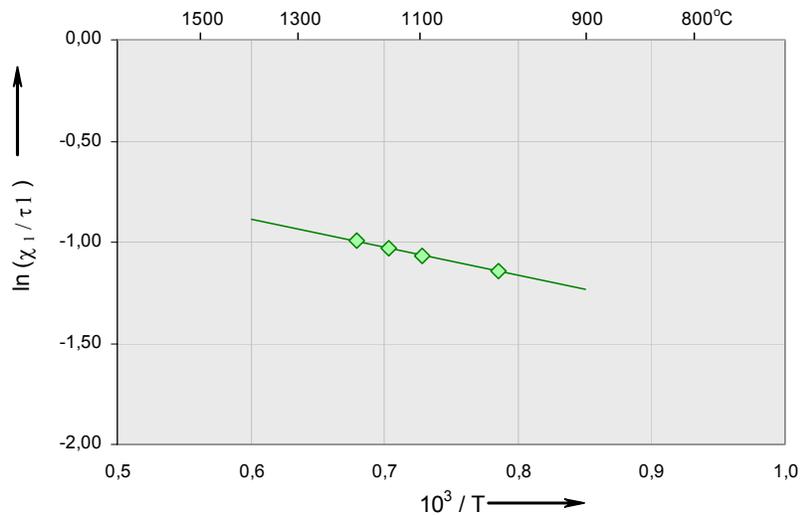


Figura 8 - Arrhenius plot for the mechanism for short reaction times.

The value for the apparent activation energy (E_a) presented in Table 1, for the short reaction times periods, showed a value consistent with a diffusion process, this value being $E_a = 11,50$ kJ/mol. The pre-exponential frequency factor for this stage was $57 \mu\text{Hz}$.

For the long reaction times, related to Figure 9, that is above 10 minutes from onset, the apparent activation energy measured $E_a = 46,10$ kJ/mol and the pre-exponential frequency factor 48 Hz. This value of activation energy is coherent with mix control, that is, intermediary to diffusion and chemical controls.

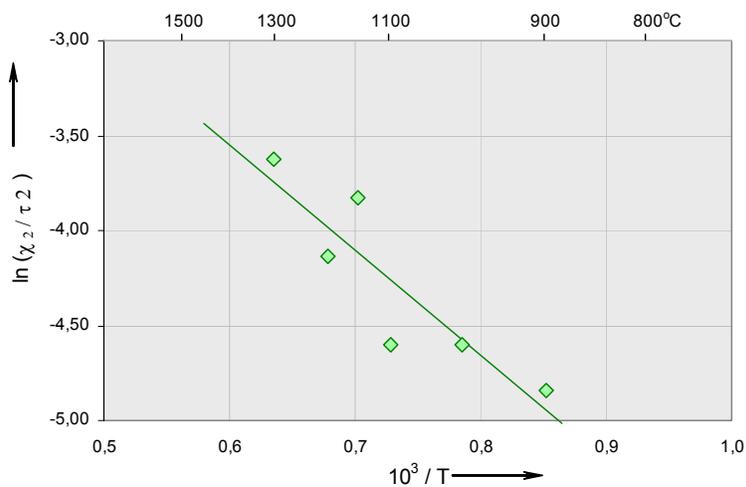


Figure 9 - Arrhenius graph for the mechanism for long reaction times.

4 CONCLUSIONS

Based on the obtained results the following conclusions can be drawn:

- The self-reduction process in the temperature range utilized in this work exhibited two distinct phases. The first phase was characterized by high reduction rates of MnO_2 to MnO . In the second phase, a decreasing in the reaction rate was

observed, this occurred simultaneously with lower conversions levels in comparison with the first stage.

- The proposed kinetic model belonged to the semi-empiric nature and fitted very consistently the experimental results. For the first 10 minutes of reaction (first stage) the model presented 94% of correlation, and further, for the second stage the correlation measured 96%.
- For the first stage, the calculated apparent activation energy valued as 11.50 kJ/mol and the pre-exponential frequency factor 57 μ Hz, these values suggesting a diffusion control. For the second stage the apparent activation energy amounted to 46.10 kJ/mol and the pre-exponential frequency factor 48 Hz, values consistent with a mix control.

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