

THERMODYNAMIC SIMULATION OF REDUCTION OF MIXTURES OF IRON ORE, SIDERURGICAL WASTES AND COAL

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The thermodynamic feasibility of reducing agglomerates in iron ore/carbon (ICA) from concentrate mixtures of goethite ore, siderurgical waste and carbon were performed using the HSC Chemistry for Windows V. 6.0 software. Removal by reduction and gasification of Na_2O , K_2O , ZnO and the metallization of iron oxides was performed by using a reducing atmosphere generated by heating the mixtures. Proposed mixtures generate reductions near 100 % of iron with 28 % of carbon and average removal percentages of 85 % of Na, K and Zn have been obtained.

Key words: thermodynamic simulation, reduction, iron ore, siderurgical wastes, coal

INTRODUCTION

Current steelmaking processes require a sustainable development focused on solving the problem of shortage of raw materials. Besides, the high generation of siderurgical waste (30-40 kg/ton steel) includes dusts and sludges from blast furnace and Basic Oxygen Furnace, and the materials containing high Fe and carbon contents which haven't been reused due to the presence of other elements that negatively affect the conventional fusion-reduction process in the blast furnace. Oxides of Na, K and Zn degrade the furnace refractory and generate thermal imbalances in the reduction process [1,2]. The percentages of such oxides in the dusts of BOF, sludge of cyclone and blast furnace, exceed permissible values [2], so their reuse is currently scarce.

A viable technological alternative to implement the use of unconventional raw materials in the reduction-fusion process are agglomerates based on iron ore/coal. Innovative studies [3-7] have reported that the use of other materials different than the hematite, mainly goethite, have a high degree of reduction and metallization; under specific conditions [3,4].

The use of goethite structure is restricted in the conventional sinterization and pelletization processes due to the limited metallurgical properties conferred to agglomerate. Miura et al. [3] found that sintering the goethite, a number of pores at the nanoscale are generated, which inhibits particle agglomeration. However, by combining coal goethite and using its ability as a binding agent, the resulting agglomerates show good metallurgical properties; this is because the nanopores generated in the pro-

cess of thermolysis are occupied by coal. Likewise, several types of carbonaceous materials have been implemented to generate reducing agents without the use of clays to bind the particles, resulting in pre-reduced, whose metallurgical properties are satisfactory for implementation as a raw material in foundry processes [5-7].

The aim of this research is to design optimal mixtures and determine the processing conditions for the development of ICA from the thermodynamic simulation of the behavior of mixtures of carbon with iron concentrates of goethite and steel waste contaminated with Na_2O , K_2O and ZnO . The chemical species and the concentrations were determined using techniques of characterization of materials relevant to the steel industry at the region of Coahuila north of Mexico, and they were specified in the thermodynamic calculations.

EXPERIMENTAL

Materials characterization

Selected raw materials were iron ore concentrate containing goethite, non-coking coal and waste steel with significant contents of Na_2O , K_2O and ZnO . Ferrous materials were examined by FR-X, DR-X, and atomic absorption spectrometry. The results were used to define the chemical composition and mineralogical structure of the species involved in the simulation of thermodynamic equilibrium compositions. For the same purpose a representative sample of coal, from the state of Coahuila Mexico, was selected and underwent next analysis.

Mixture design

The proportion of ferrous materials in the proposed mixtures was based on the fulfillment of the following

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criteria: a) maximization of the units of elemental iron (minimum 50 %), b) binary basicity index (BI_2) near unity, and c) maximizing the use of steel waste. Carbon as a reducing agent was incorporated in proportions in a range of 18 - 40 % regarding Fe_2O_3 content in the ferrous mixture. Table II details the proportion of ferrous mixtures based on the above criteria.

Thermodynamic simulation

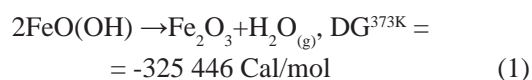
HSC Chemistry for Windows V6.0 software was used to calculate the evolution of the equilibrium composition as a function of the temperature in the range of 25 – 1 100 °C.

The equilibrium composition, amounts of prevailing phases specifying the raw material amounts, temperatures and the species of the initial unreacted system were calculated by using the software “Equilibrium Composition” module. The species can be specified by selecting the elements of the system, or typing the formulae. When the equilibrium products from an initial system are unknown, the constituent elements of the system are specified, and the resulting chemical species are determined by the software. Then, the raw materials are specified and now the system proceed to calculate the balance depending on the parameter variation [8]

Calculations can be repeated at stepwise intervals over the range of raw material amounts or reaction temperatures in order to visualize the effect of these process variables. Equilibrium calculations offer a practical way to observe the effects of process variables, such as temperature and amounts of raw materials in product composition [8].

Simplifications

Closed system to the atmosphere has been assumed and the carbon in the form of amorphous carbon species has been specified despising the coal rank. Goethite phase becoming unstable at low temperatures (see Figure 1) has been specified in the form Fe_2O_3 as a product of decomposition according to the following reaction:



RESULTS AND DISCUSSION

Table I shows the analysis of ferrous materials; it can be appreciated that the blast furnace sludge contains higher concentrations of alkalis and zinc which preclude reuse in conventional sintering and pelletization processes. However, the iron content is considerable for recovery. Ore of Durango city and the remaining residues contain alkali and zinc at tolerable concentrations and the percentage of Fe_2O_3 is considerable so that the mixture of these constituents is a good source of Fe.

Table 1 also includes the proximate analysis of a representative sample of non-coking coal from Coahuila Mexico, which could eventually represent a viable reducing agent.

Table 1 **Chemical composition of raw material / wt. %**

Ferrous materials				
Chemical species, wt. %	Durango concentrate one	Cyclone dust	Blast furnace sludge	BOF sludge
Fe_2O_3	88,68	76,47	55,32	75,36
K_2O	0,24	0,43	2,01	0,49
CaO	1,9	4,24	8,19	3,21
TiO_2	0,78	/	/	0,44
MnO	0,11	0,28	0,37	0,22
Al_2O_3	1,24	0,97	2,96	1,02
SiO_2	5,43	5,78	8,35	5,38
S	0,005	0,32	1,61	0,36
P_2O_5	0,57	1,12	/	/
Na_2O	0,13	0,2	1,4	0,26
MgO	0,83	/	1,45	1,02
ZnO	/	0,26	1,06	0,14
C	/	15,3	13,9	13,61
Bituminous Coal from Coahuila, (Proximate analysis)				
Fixed carbon	Ash	Volatile Matter	Sulfur	FSI(a)
50,63	16,06	33,31	1,69	5,0

(a) Free Swelling Index

Table 2 shows the main parameters of four samples designed for the study, the concentration of pollutants (K, Na and Zn oxides), the basicity index and the contribution of iron units represent a special interest.

Table 2 **Chemical composition of the formulated mixtures/ wt.%**

Mixture Components(b)	M1 25-25-30-20	M2 30-5-35-30	M3 22-30-35-13	M_{Avg} (M1+M2+M3) 3
Fe_2O_3	72,96	72,4	71,61	72,32
K_2O	0,873	0,948	0,954	0,925
CaO	4,64	4,61	4,98	4,74
TiO_2	0,286	0,369	0,231	0,295
MnO	0,258	0,247	0,271	0,259
Al_2O_3	1,646	1,764	1,735	1,715
SiO_2	6,39	6,46	6,56	6,47
S	0,642	0,695	0,713	0,683
P_2O_5	0,426	0,23	0,465	0,374
Na_2O	0,558	0,621	0,616	0,598
MgO	0,848	1,065	0,824	0,912
ZnO	0,417	0,432	0,473	0,441
C	10,76	9,75	11,27	10,59
Fe_{Tot}	51,07	50,68	50,13	50,63
B_2 index	0,726	0,714	0,759	0,733
Fe_2O_3	72,96	72,4	71,61	72,32

(b) Respectively, (wt. %): Durango concentrate ore – cyclone dust – blast furnace sludge –BOF sludge

The thermodynamic stability diagram of goethite is shown in Figure 1. The initial component of the system is pure goethite and can be seen that from room temperature an equilibrium exists between the $FeO(OH)$ and Fe_2O_3 phases. By increasing the temperature, goethite decomposition occurs at concentrations of 10 % and at temperature close to 150 °C, disappearing almost

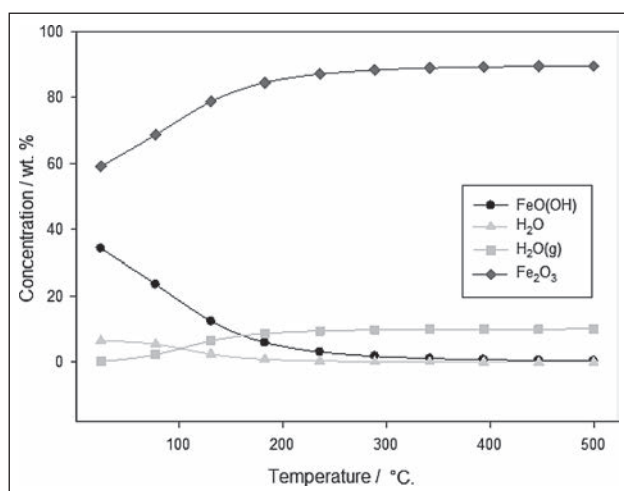


Figure 1 Goethite decomposition as a function of the temperature

completely at temperatures around 350 °C. This behavior allows assuming the initial iron in the form of Fe_2O_3 phase.

The chemical composition of the unreacted system introduced in the software was: $\text{Fe}_2\text{O}_3 = 72,32$, $\text{SiO}_2 = 6,47$, $\text{CaO} = 4,74$, $\text{K}_2\text{O} = 0,925$, $\text{Na}_2\text{O} = 0,598$, $\text{ZnO} = 0,441$ (wt. %), including initial carbon content of 10,59 wt. %. The evolution of the concentration of ferrous species and reducing agents as a function of temperature is shown on Figure 2. The sequence of the iron oxides reduction was: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, showing intervals where different ferrous species coexist. The temperature ending to temperature near 600 °C accompanied by the simultaneous generation of FeO and Fe_3O_4 . The maximum concentration of Fe_3O_4 and FeO takes place at 260 and 500 °C, respectively. It is noteworthy that the degree of metallization (metallic Fe, wt. %) begins from 400 °C, and above 750 °C minimal variation occurs (close to 100 %). Another important result was the activation of the reduction reactions of the iron oxides at a temperature around 400 °C, accompanied by carbon consumption and the simultaneous formation of $\text{CO}_{2(g)}$ and $\text{CO}_{(g)}$, yielding an almost complete reduction at temperatures above 800 °C.

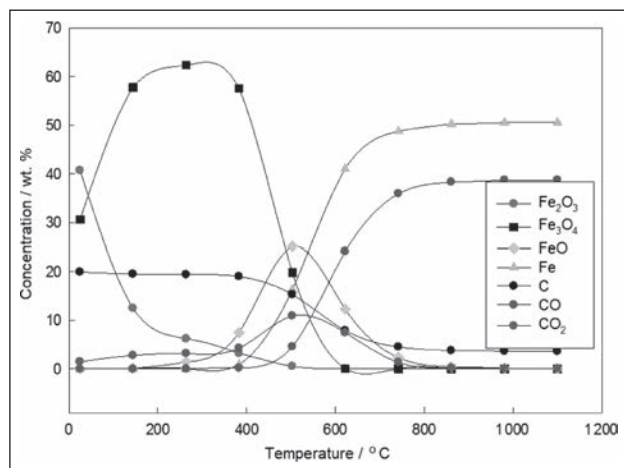


Figure 2 Evolution of chemical composition of the initial system M_{Avg} as a function of the temperature using a rate $C/\text{Fe}_2\text{O}_3 = 28\%$

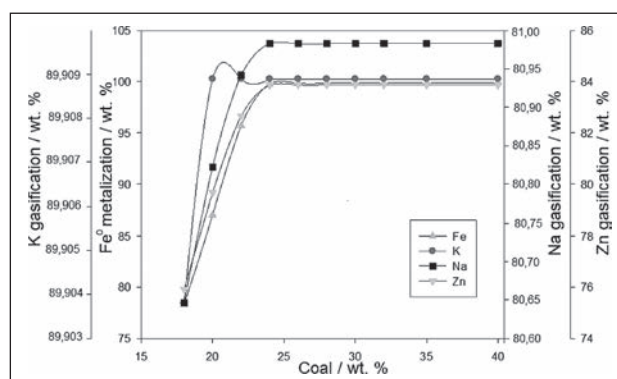


Figure 3 Evolution of the Fe° concentration and the proportion of Na, K and Zn removed by gasification as a function of the carbon concentration for the mixture M_{Avg} at temperature of 1 100 °C

Figure 3 shows the percentages of metallized iron as well as zinc and alkalis gasified as a function of the carbon concentration at a temperature of 1 100 °C for M_{Avg} mixture. It can be appreciated that the carbon concentration has a significant effect on iron metallization and gasification of alkalis and zinc. In the case of iron, a metallization of nearly 100 % with 24 % of carbon was obtained in the mixture. The K reached its gasification limit close to 89 % with carbon concentrations of 20 % while Na and Zn were 24 % C gasifying 81 % and 84 %, respectively. It was concluded that a mixture of 20 % of carbon is optimal to achieve a high degree of metallization of iron, and also reduces zinc and alkalis in considerable quantities. 20% carbon in the mixture corresponds to a $C/\text{Fe}_2\text{O}_3$ ratio close to 28 %, and it was obtained by adding carbon to the M_{Avg} mixture which initially contained a $C/\text{Fe}_2\text{O}_3$ ratio close to 14 %, equivalent to 10,59 % of carbon.

Figure 4 shows the evolution of the concentration of metallic iron (Fe°) as a function of the temperature for M_{Avg} mixture added with carbon at a ratio of $C/\text{Fe}_2\text{O}_3 = 28\%$. It can be seen that the reduction of the iron oxide to produce metallic iron starts at 400 °C is completed at about 900 °C. The effect of temperature is negligible above 900 °C, according to reduction process design, this temperature range is very important for energy optimization.

Figure 5 shows the evolution of alkalis and Zn removal by gasification as a function of the temperature for M_{Avg} mixture with carbon added to a ratio of $C/\text{Fe}_2\text{O}_3 = 28\%$. The figure shows the thermodynamic instability of K, Na and Zn oxides as a function of the temperature.

Three temperature ranges occur during heating of the sample in the closed system: 1) the oxides are stable, 2) reduction of such oxides occurs generating liquid and gaseous metal, 3) the liquid phase reaches a maximum concentration and decreases when temperature increases, at the maximum heating temperature (1 100 °C), the equilibrium in which the gas phase dominates and the remaining amounts of the liquid phase is established. Evidently, alkalis and Zn vapors are generated from the

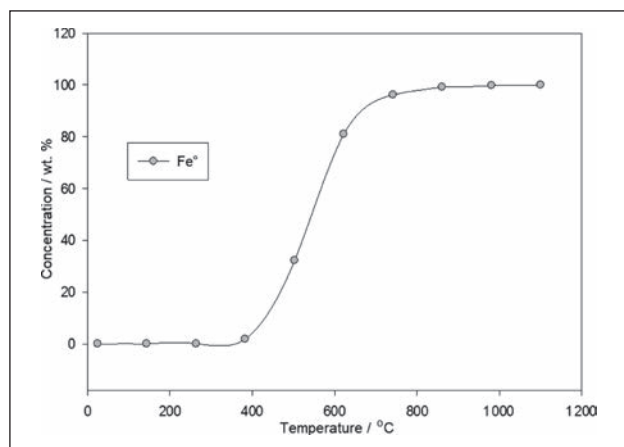


Figure 4 Evolution of Fe^0 concentration as a function of the temperature for the mixture (M_{Avg}), using a ratio of $\text{C}/\text{Fe}_2\text{O}_3 = 28\%$

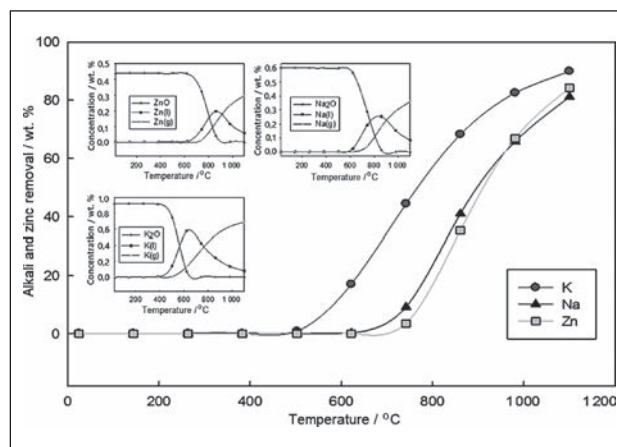


Figure 5 Evolution of alkalis and of Zn removal by gasification as a function of the temperature, using a ratio of $\text{C}/\text{Fe}_2\text{O}_3 = 28\%$ wt. %, for the mixture M_{Avg}

solid mixture. In consequence, a significant removal of these contaminant elements is feasible. The initiation temperatures of gasification were: 500, 620 and 750 °C, for K, Na and Zn, respectively. The removal percentages were: 90, 80 and 84 % for K, Na and Zn, respectively.

CONCLUSIONS

The use of steel waste with significant contents of Na_2O , K_2O and ZnO , for generating iron ore/coal agglomerates is thermodynamically feasible. This can be achieved when mixing with carbon as reducing agent and heated nearly 1 100 °C, which produces a self-reducing atmosphere capable to obtain completely metallized iron, besides reducing and gasifying the Na, K and Zn to about 86 %.

The mixture design that maximizes the use of siderurgical waste with B_2 almost equal to 1, adding carbon to obtain a ratio of $\text{C}/\text{Fe}_2\text{O}_3$ ratio close to 28 % and thermolysis temperatures close to 1 100°C, are optimal for the complete Fe metallization and also to obtain a substantial gasification of alkalis and Zn.

The siderurgical wastes (Cyclone dust, Blast furnace sludge, and BOF sludge) contain significant percentages of carbon 13 – 15wt.%, so by using low additions of this element can lead us to obtain a self-reducing mixture.

The thermodynamic feasibility of removing alkali and Zn, and the high percentage of reduction of Fe, makes promising the recycling of siderurgical waste by generating a pre-reduced from the thermolysis of iron/carbon agglomerates at temperatures of 1 100 °C

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Note: The responsible translator for English language is Ph. D. Leticia González Valdez, Mexico.