The 52[nd] International October Conference on Mining and Metallurgy
November 29[th] – 30[th], 2021
www.ioc.tfbor.bg.ac.rs

KINETIC STUDY OF SOLID-PHASE REDUCTION OF POLYGRADIENT IRON-CONTAINING MATERIAL

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ABSTRACT

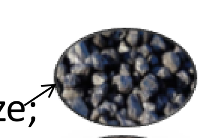
The kinetics of the direct reduction of iron-containing material with increased content of manganese, barium, and lead was studied.
Coke breeze and brown coal/ lignite were used as reducing agents. The mechanism and kinetics of the reduction reaction were systematically studied by means of thermogravimetric analysis.
The apparent activating energy of the dissociation and solid-phase processes that took place when heating pellets without a reducer was E= 98,62 kJ/mol. The reduction processes were significantly influenced by the Boudoir reaction. It was found that when using coke breeze, the speed of the processes was higher due to their higher reactivity. When using coke breeze in the pellets, the activating energy was 240 kJ/mol, and when using brown coal – 158 kJ/mol. The reduction processes took place in the kinetic region. Brown coal can be successfully used as a reducing agent.

Keywords*: kinetics, TGA analysis, activation energy, rate of reaction*

EXPERIMENTS

Table 1 - Chemical composition of initial iron-containing material, %.

Fe (total)	SiO_2	Al_2O_3	Cu	CaO	Zn	MgO	S	Mn	P	Pb	Ba
50,100	7,067	1,157	0,142	1,64	0,071	0,915	0,599	7,687	0,014	0,416	3,163

Pellets 1- consisted of iron ore material
Pellets 2- consisted of a homogenized mixture of iron ore material and crushed coke breeze;

Pellets 3- consisted of a homogenized mixture of iron ore material and brown coal/lignite.


Green pellets of size 9-16 mm were prepared in a laboratory disc pelletiser of 1 m diameter with 0,6% bentonite as a binder. A strength level of 180 kg/pellet was achieved. The pellets were heated up to 1473 K. A STA PT1600 TG-DTA/DSC thermogravimetric apparatus was used in the experiments.

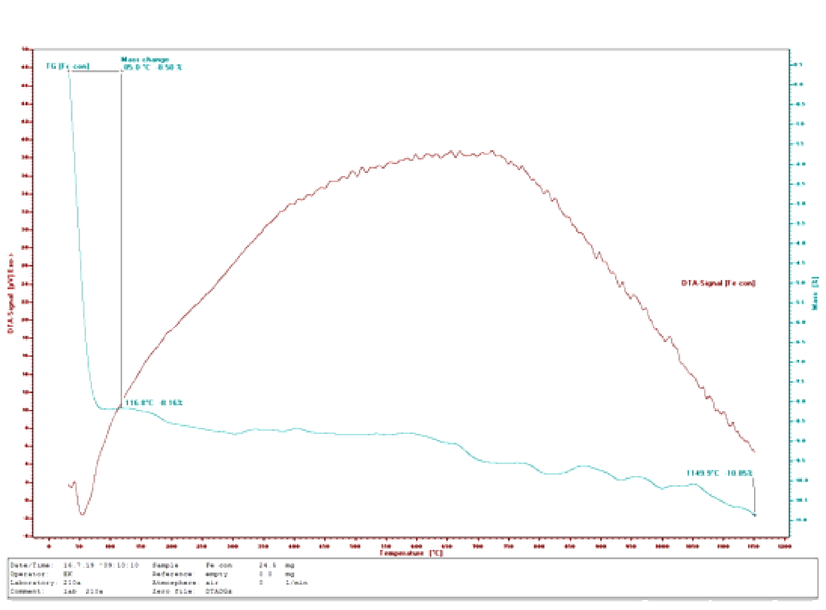


Figure 1. TG/ DTA analysis of pellets 1.

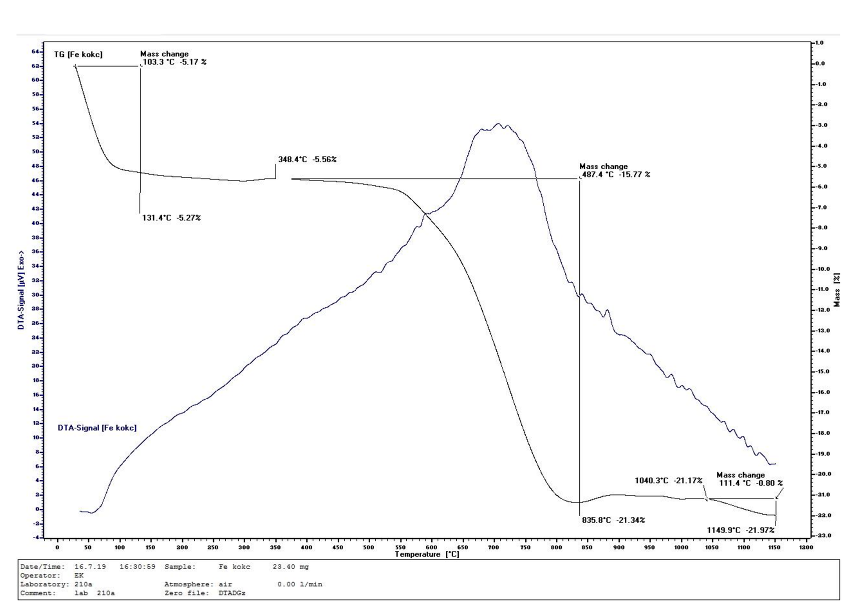


Figure 2. TG/ DTA analysis of pellets 2.

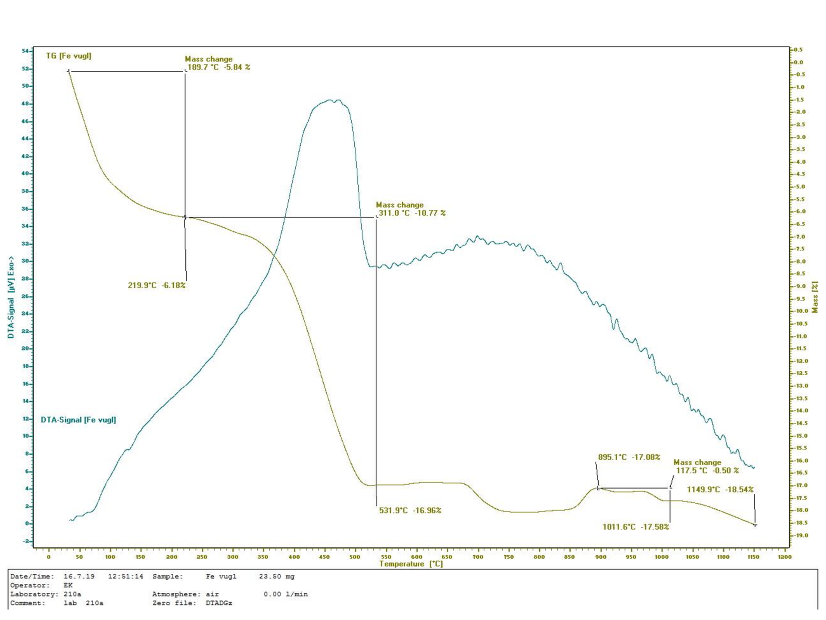


Figure 3. TG/ DTA analysis of pellets 3.

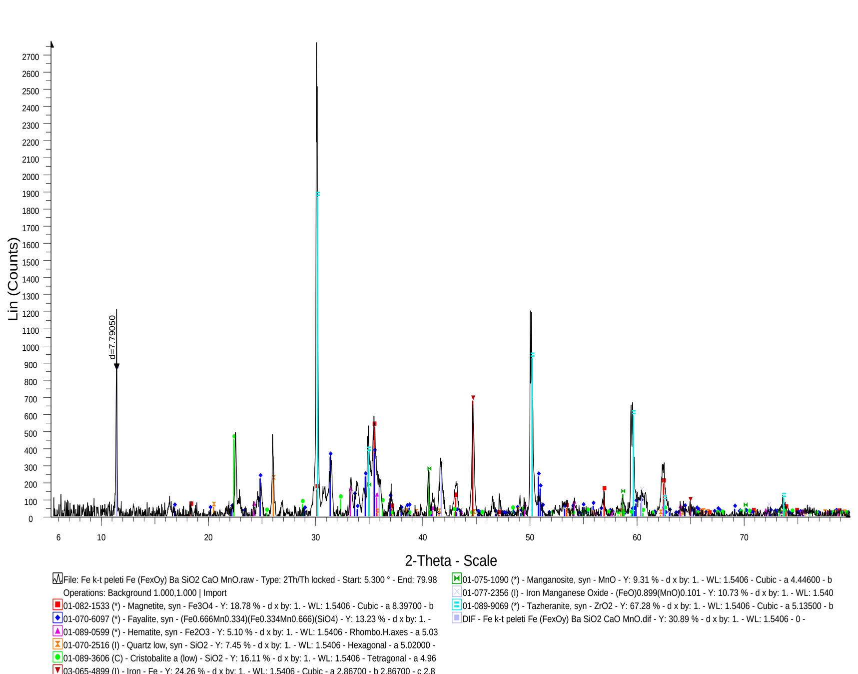


Figure 4. XRD analysis of pellets 3 after heat treatment.

The decrease in mass in the first sample-pellets 1 was due to the release of moisture and volatile substances; above the temperature of 845 K, it was due to the decomposition of iron oxides according to the scheme $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$. The exothermic effect, accompanied by mass loss, was observed in pellets using reducing agents. This effect was due to the combustion of carbon from coke and coal, as well as from the completed reduction processes, mainly of iron and partly of manganese oxides. At temperatures above 850 K, solid-phase interactions between Fe_2O_3 and SiO_2 took place until the formation of Fe_2SiO_4 (fayalite).

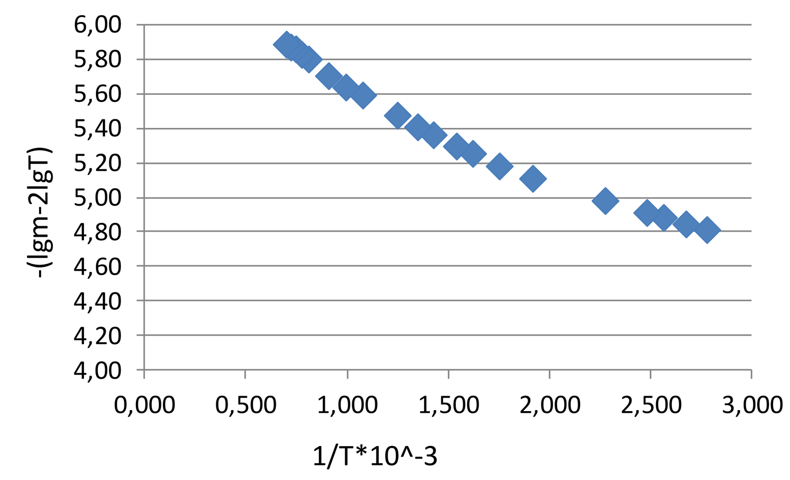


Figure 5. The dependence of lgm - 2lgT = f (1/T) of **pellets 1**.

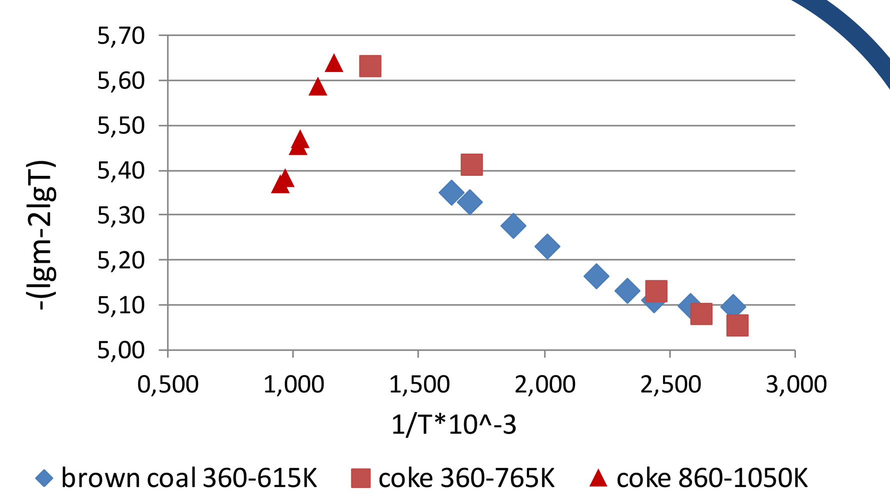


Figure 6. The dependence of lgm - 2lgT = f (1/T) of **pellets 2 and 3** up to temperature 1050 K.

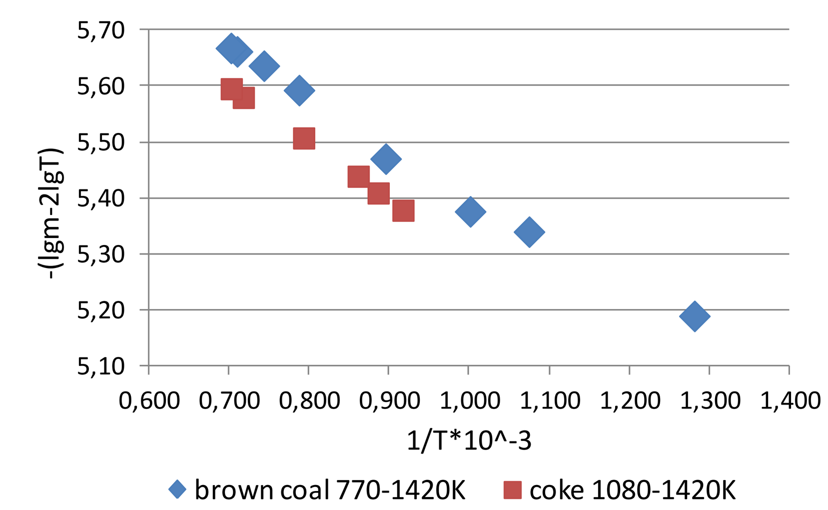


Figure 7. The dependence of lgm - 2lgT = f (1/T) of pellets 2 and 3 up to temperature 1420 K.

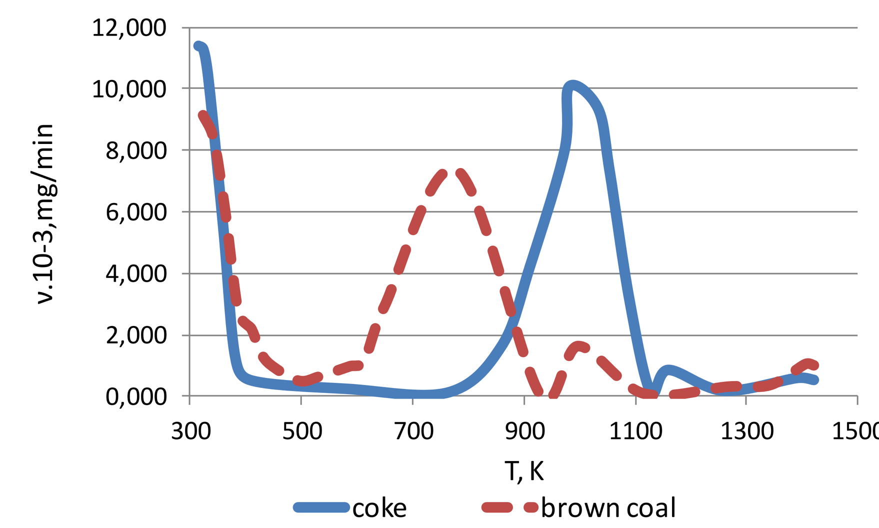


Figure 8. Rate of the processes depending on the temperature of the pellets containing reducer agent.

Dissociation and solid-phase interactions are the main processes occurring in pellets 1; the processes take place in the external diffusion region. In the case of pellets 2 using coke breeze, the processes take place in three sub-stages. When using brown coal (pellets 3), the processes take place in two stages: the first is limited in the external diffusion region, and the second in the kinetic region. The activating energy in the reduction of $Fe_2O_3 \rightarrow Fe_3O_4$ is 69- 100 kJ/mol; $Fe_3O_4 \rightarrow FeO$ = 64-78 kJ/mol; $Fe_xO \rightarrow Fe$ = 100-116 kJ/mol. The apparent activating energy in the reduction of zinc oxide pellets is between 165-242 kJ/mol. The activating energy of the thermal dissociation of MnO_2 is 175 kJ/mol. Ea of the reduction of Mn_2O_3 - 226 kJ/mol, and Mn_3O_4 is 289 kJ/mol, which is almost equal to that for the reaction of carbon gasification. The gasification reaction is catalyzed by Mn_3O_4

Table 2 - Activation energy and reaction rate equation of the studied pellets.

Pellets	lnK	R²	Activation energy (Ea)	T, K
1	lnK = 521/T – 6,17	0.974	98,62 kJ/mol (23555 cal/mol)	355-1400
2	lnK_1 = 395/T – 6,12	0.988	75,51 kJ/mol (18040 cal/mol)	88-492
	lnK_2 = -1342/T –4,09	0.988	241,32 kJ/mol (57641 cal/mol)	587-780
	lnK_3 = 1009/T – 6,31	0.999	193,48 kJ/mol (46138 cal/mol)	816-1147
3	lnK_1 = 251/T – 5,74	0.948	43,36 kJ/mol (10356 cal/mol)	360-613
	lnK_2 = 853/T – 6,26	0.989	158,03 kJ/mol (37744 cal/mol)	780-1150

CONCLUSIONS

Based on the experimental data, the apparent activating energy for the processes occurring during heating of pellets 1, 2, and 3 was determined. Equations for determining the rate constant lgK = f (1/T) were derived. It was found that at higher temperatures the processes took place in the kinetic region. The reduction of iron oxides took place with activating energy of 193,48 kJ/mol (coke breeze) and 158,03 kJ/mol (brown coal). The reduction of Mn_2O_3 at a temperature of about 700 K has Ea = 241,32 kJ/mol. At a temperature of 780 K, a rate of 7,4. 10^{-3} mg/min was reported for the sample using brown coal, while in the sample containing coke breeze the maximum was drawn at a temperature of 980 K at a rate of 10,05 10^{-3} mg/min. During this period, the combustion and gasification of carbon took place, as well as the reduction of some oxides, such as zinc, iron, and manganese. The results show that brown coal can be successfully used as a reducing agent, achieving lower activating energy and high metallization.

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