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HIGH - TEMPERATURE CARBOTHERMIC REDUCTION OF COAL BENEFICIATION WASTE

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ABSTRACT

This study investigates the high - temperature carbothermic reduction of coal beneficiation waste (CBW) as a sustainable approach to resource recovery and waste valorisation. Addressing the environmental burden of CBW accumulation, the inherent carbon content of the waste is utilized as a reductant to transform residual metal oxides into valuable metallurgical products. Experiments were conducted to evaluate the influence of temperature, holding time, reductant quantity, and additives on the reduction process.

Mathematical models describing the degree of carbothermic reduction and the reaction rate were developed. Results demonstrate the technical feasibility of carbothermic reduction for converting CBW into reusable materials, offering the dual benefits of waste mitigation and resource circularity. This approach aligns with circular economy principles, providing a scalable solution to minimize landfill disposal and promote sustainability within coal - dependent industries. The study highlights the potential for industrial implementation, emphasizing the economic and environmental advantages of metallurgical reprocessing of these mineral wastes.

Keywords: carbothermic reduction, coal beneficiation waste; resource recovery, mathematical modelling, circular economy, metallurgical reprocessing.

INTRODUCTION

Coal beneficiation, also known as coal preparation, encompasses the procedures employed to remove mineral impurities from unprocessed coal, resulting in fuel with enhanced combustion properties [1, 2].

These processes generate waste streams containing valuable elements for the metallurgical industry. Their recovery leads to a reduction in the volume of landfilled waste and the implementation of circular economy and sustainable development principles [3].

Our study explores the transformation of coal beneficiation waste (CBW) into valuable metallurgical products through high - temperature carbothermic reduction, emphasizing the approach's sustainability by utilizing the waste's inherent carbon content to reduce residual metal oxides [4]. The research investigates the impact of various factors, including temperature, holding time, and the addition of SiO_2 and Fe, on the efficiency of the reduction process [5]. Through the derivation of mathematical models, the study not only demonstrates the technical feasibility of this method but also its alignment with circular economy principles, offering a dual advantage of waste reduction and resource recovery.

EXPERIMENTAL

Kinetics of high - temperature carbothermic reduction of coal beneficiation waste

The kinetics study of reduction processes of coal beneficiation waste (CBW) was conducted using the

Table 1. Composition of the samples tested.

Sample	Reductant quantity, % of stoichiometrically required	Sample content, %			
		CBW	Coke fines	additives	
				SiO_2	Fe
1	CBW (70)	100	-	-	-
2	110	83.96	16.04	-	-
3	100	85.20	14.80	-	-
4	90	86.48	13.52	-	-
5	80	83.96	16.04	-	-
6	100	80.94	14.06	5	-
7	100	76.67	13.33	10	-
8	100	72.34	12.66	15	-
9	100	80.94	14.06	-	5
10	100	76.67	13.33	-	10

thermogravimetric analysis method. The experiments were carried out on a specially designed experimental setup, enabling thermogravimetric studies at temperatures up to 2673 K in a controllable gaseous working environment.

The influence of the following factors on the reduction kinetics of CEW was studied:

- Heating temperature (T = 1673 - 2273 K);
- Holding time (τ = 5 - 60 min);
- Reductant quantity (70 - 110 % of the stoichiometrically required amount for complete oxide reduction);
- Effect of SiO_2 and Fe additives.

The studies were conducted on 10 base samples with compositions shown in Table 1.

The composition of the materials used in the study is shown in Table 2, where A^c is ash content, V^c is volatile matter content, W^p is moisture content and C is carbon content, %.

The degree of progress (development) of the carbothermic process (RC) of CBW reduction is determined by the expression (Eq. (1)):

$$R_C = \frac{Y}{0Y_T} = \frac{\frac{\Delta G}{G_H}}{Y_T}.100,\ \% \quad (1)$$

where: ΔG - change in the sample mass: $\Delta G = G_{in} - G_f$ G_{in} - initial sample mass, g; G_f - final sample mass, g.

Table 2. Materials composition.

Component		Coal beneficiation waste	Coke
Technical analysis, %	A^c	74.3	13
	V^c	10.37	2
	W^p	1.36	1.6
	C	13.97	83.4
Chemical composition, %	SiO_2	62.5	38.27
	Al_2O_3	24.86	13.88
	Fe_2O_3	7.25	FeO 26.9
	CaO	1.19	7.82
	MgO	1.69	5.08
	MnO	0.97	-
	P	0.03	0.12
	S	0.54	SO_3 2.03

The theoretical mass losses (Y_t) are determined by the losses associated with the interaction of the entire amount of O_2 from the metal oxides of the mineral part of the studied samples and the reducer - C according to the reaction (Eq. (2)):

$$MeO + C \rightarrow Me + CO \quad (2)$$

The process rate (V_{RC}) is determined by the

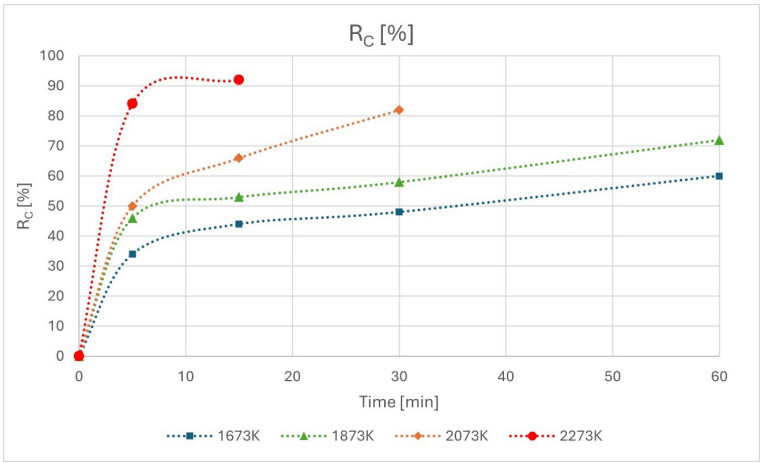

Fig. 1. Influence of temperature and holding time on the degree of carbothermic reduction of CBW (R_C).

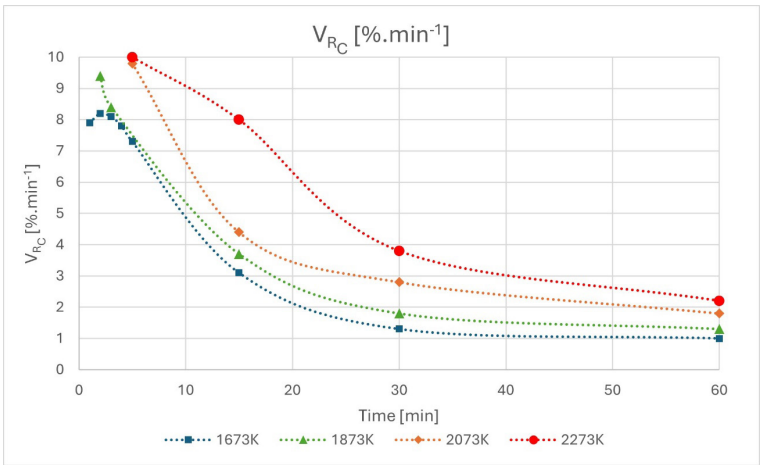

Fig. 2. Influence of temperature and holding time on process rate (V_{RC}).

expression in Eq. (3):

$$V_{RC} = Y'_C = \frac{\Delta R_C}{\Delta \tau},\ \%.min^{-1} \quad (3)$$

where: $V_{RC} = Y'_{RC}$ - process rate, % min^{-1}; ΔR_C - interval of change in R_C, %; $\Delta\tau$ - interval of change in τ, min.

RESULTS AND DISCUSSION

Influence of temperature and holding time

The influence of temperature in the range of 1673 - 2273 K and the sample holding time (0 - 60 min) on the degree of process progress (R_C) is shown in Fig. 1 and its rate (V_{RC}) - in Fig. 2 (sample 1 - CBW).

The obtained results from the study of the influence of t and τ on the degree of carbothermic reduction of CBW show that the reduction process of MeO proceeds completely (100 %) at 2273 t = K ± 15K for τ = 20 - 30 min.

The results obtained for the Rc and the rate of the carbothermic process (V_{RC}) were processed using mathematical analysis methods. Equations for the relationships were derived: $R_C = f(T, \tau)$ and $V_{RC} = f(T, \tau)$, which are described by Eqs. (4, 5):

$$y_1 = c + b_0 x + b_1 \sqrt{x} \quad (4)$$

$$y_2 = c + \frac{b_0}{x} + b_1 x \quad (5)$$

where $R_C = y_1;\ \tau = x$ and $V_{RC} = y_2;\ \tau = x$

The values of the parameters c, b_0, and b_1 are given in Table 3.

Fig. 3 shows a comparison between the models for Rc (left) and V_{RC} (right) at 1873 K and the experimental data. From the values of the coefficient of determination, as well as from the two graphs, the adequate description of the process from the mathematical models is clearly visible.

A generalized model of R_C encompassing the four experimental configurations was developed. This involved performing quadratic regression on each coefficient as a function of temperature (T). The Python code written for this purpose is listed on Fig. 4.

The resulting surface area of carbothermic reduction of CBW (y = RC) as function of temperature and time is presented in Fig. 5.

Effect of reductant amount

At lower temperatures (up to 1873 K), the effect of the reductant amount is comparatively small. Under these conditions, the reduction processes mainly occur with iron oxides and partially with SiO_2 (leading to the formation of iron silicide's and SiC) [1]. As the carbon content in the samples increases, the carbo -

Table 3. Values of mathematical models' parameters.

samples \ T [K]		$R_C = y_1 = c + b_0x + b_1\sqrt{x}$				$V_{RC} = y_2 = c + \frac{b_0}{x} + b_1x$			
		1673	1873	2073	2273	1673	1873	2073	2273
CBW	c	1.98	2.37	2.02	2.55	23.14	18.92	12.24	50.97
	b_0	-0.91	-1.05	-1.19	-0.87	822.55	408.37	368.75	30.67
	b_1	14.31	20.75	21.65	13.81	-0.28	-0.13	-0.11	-0.83
	R^2, [%]	97.4	99.2	99.1	98.9	99.2	99.9	99.7	90.6
CBW + 100 % reductor	c	-0.66	-0.49	0.09	-0.01	44.73	42.78	31.55	22.34
	b_0	-1.15	-0.45	-0.84	-0.40	291.38	36.91	41.95	8.62
	b_1	25.5	14.52	12.3	8.25	-0.54	-0.56	-0.45	-0.31
	R^2, %	99.8	99.9	99.5	99.9	99.8	97.8	98.1	95.1

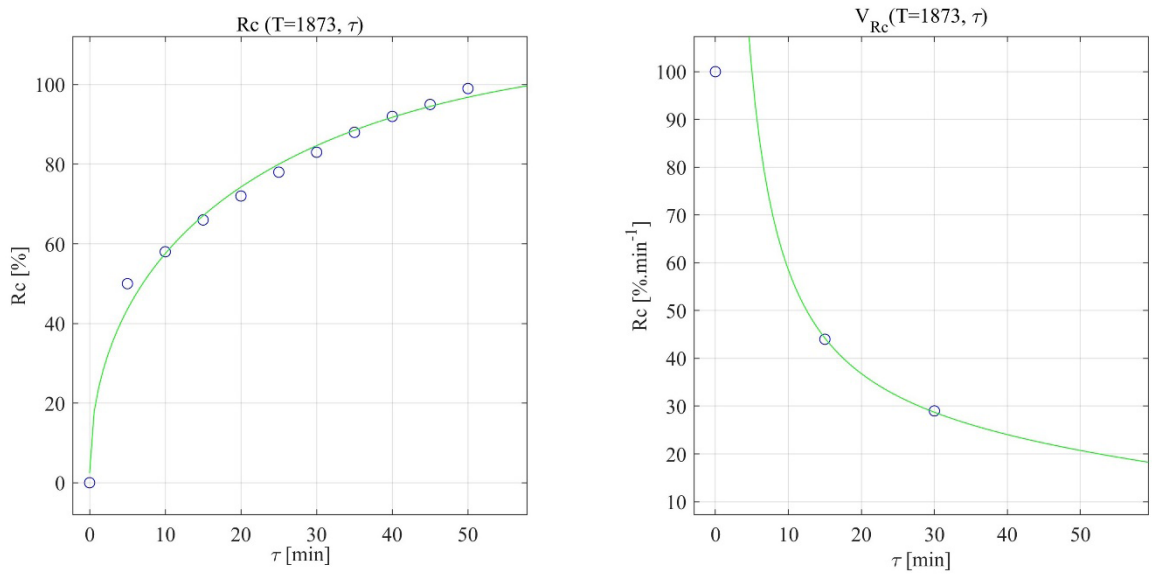

Fig. 3. Experimental data fitting, with derived equations at temperature 1873 K.

```python
T_data = np.array([1673, 1873, 2073, 2273])
c_data = np.array([1.98, 2.37, 2.02, 2.55])
b0_data = np.array([-0.91, -1.05, -1.19, -0.87])
b1_data = np.array([14.31, 20.75, 21.65, 13.81])

c_coeffs = np.polyfit(T_data, c_data, 2)
b0_coeffs = np.polyfit(T_data, b0_data, 2)
b1_coeffs = np.polyfit(T_data, b1_data, 2)

def c_T(T):
return np.polyval(c_coeffs, T)

def b0_T(T):
return np.polyval(b0_coeffs, T)

def b1_T(T):
return np.polyval(b1_coeffs, T)

x = np.linspace(0, 60, 200)
T = np.linspace(1673, 2273, 200)
X, TT = np.meshgrid(x, T)

Y = c_T(TT) + b0_T(TT)*X + b1_T(TT)*np.sqrt(X)
```

Fig. 4. Python code for model of Rc.

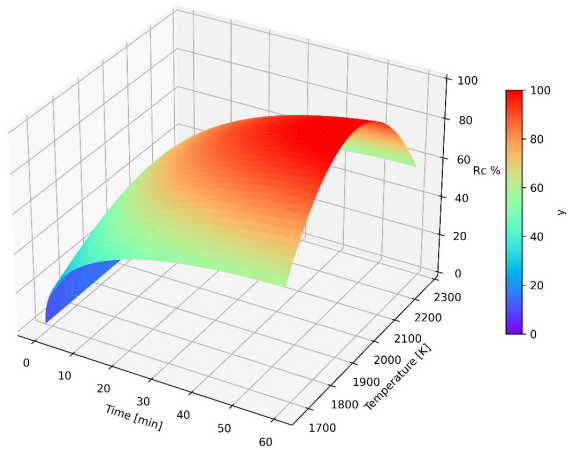

Fig. 5. Surface area of carbothermic reduction of CBW.

reduction process rate (Rc) decreases. This effect is most prominent at T = 2271 K. The difference between the maximum (for sample 1 - CBW 70 % reductant) and minimum (for sample 2 - CBW 120 % reductant) Rc values is 35 %.

Influence of SiO_2 and Fe addition

The influence of additives 0 - 15 % SiO_2 and 0 - 10 % Fe on the carbo-reduction degree of CBW was investigated. Up to 2073 K, the addition of SiO_2 resulted in a decrease in Rc values by 10 - 15 % on average. At 2273 K, Rc values increased by approximately 20 %. The optimum Fe addition to the samples was determined to be 5 %. At temperature 2273 K Rc values are increased by 10 %.

Composition of Condensed Products from Carbothermic Reduction

The high - temperature carbothermic reduction process of CBW proceeds with the formation of several main phases according to the scheme in Eq. (6):

$$CBW \rightarrow metal + metal\ oxides + metal\ carbides + gas\uparrow \quad (6)$$

The relative amounts of these phases vary depending on the carbo - reduction degree. Up to certain temperature and time values, the amount of the metal phase increases at the expense of the oxycarbide phase content. As temperature and time increase, the amount of the metal phase decreases due to increased gas phase losses from volatile suboxides of Si and Al (SiO, Al_2O, AlO) formed under these conditions, as well as dissociation and evaporation of some elements and compounds [6].

Based on extensive research on the influence of temperature and residence time on the chemical and phase composition of metallic and oxycarbidic products from the carbothermic reduction of coal waste beneficiation [7] samples with varying reductant amounts, a reaction scheme for the probable course of CBW carbo - reduction processes has been developed (Fig. 6) [3, 8, 9].

The developed scheme allows for the elucidation of the probable mechanism of CBW carbothermic reduction processes conducted with or without a minimal addition of 20 - 30 % supplemental reductant, at the established optimum residence time of τ = 30 min. The following key observations and trends are noted across the various experimental temperatures:

T = 1873 K

The reduction of iron oxides is complete. The metallic phase consists mainly of intermetallic compounds of Fe and Si, primarily $FeSi_2$ and FeSi in approximately equal proportions. The oxycarbidic phase is mainly composed of SiC and mullite (Al_2O_3. SiO_2) phases with a negligible amount of magnetite and free carbon - graphite. When the reduction process is carried out with a stoichiometric amount of reducing agent, the carbide and oxide phases are in approximately equal proportions (1 : 0.96).

T = 2073 K

The composition of the metallic phase is analogous

to that obtained at 1873 K. The high degree of Si extraction (ηSi > 95 %) indicates that under these conditions, the reduction of Si is practically complete. In the slag phase, a slight change in the ratio between the oxide and carbide phases is observed. The increase in the relative proportion of aluminium compounds (Si / Al = 1 : 0.57) indicates that under these conditions, processes of both SiO_2 reduction and SiC decomposition have developed according to the scheme (Eq. (7)):

$$SiC + SiO_2 \rightarrow Si_{(Fe)} + CO \quad (7)$$

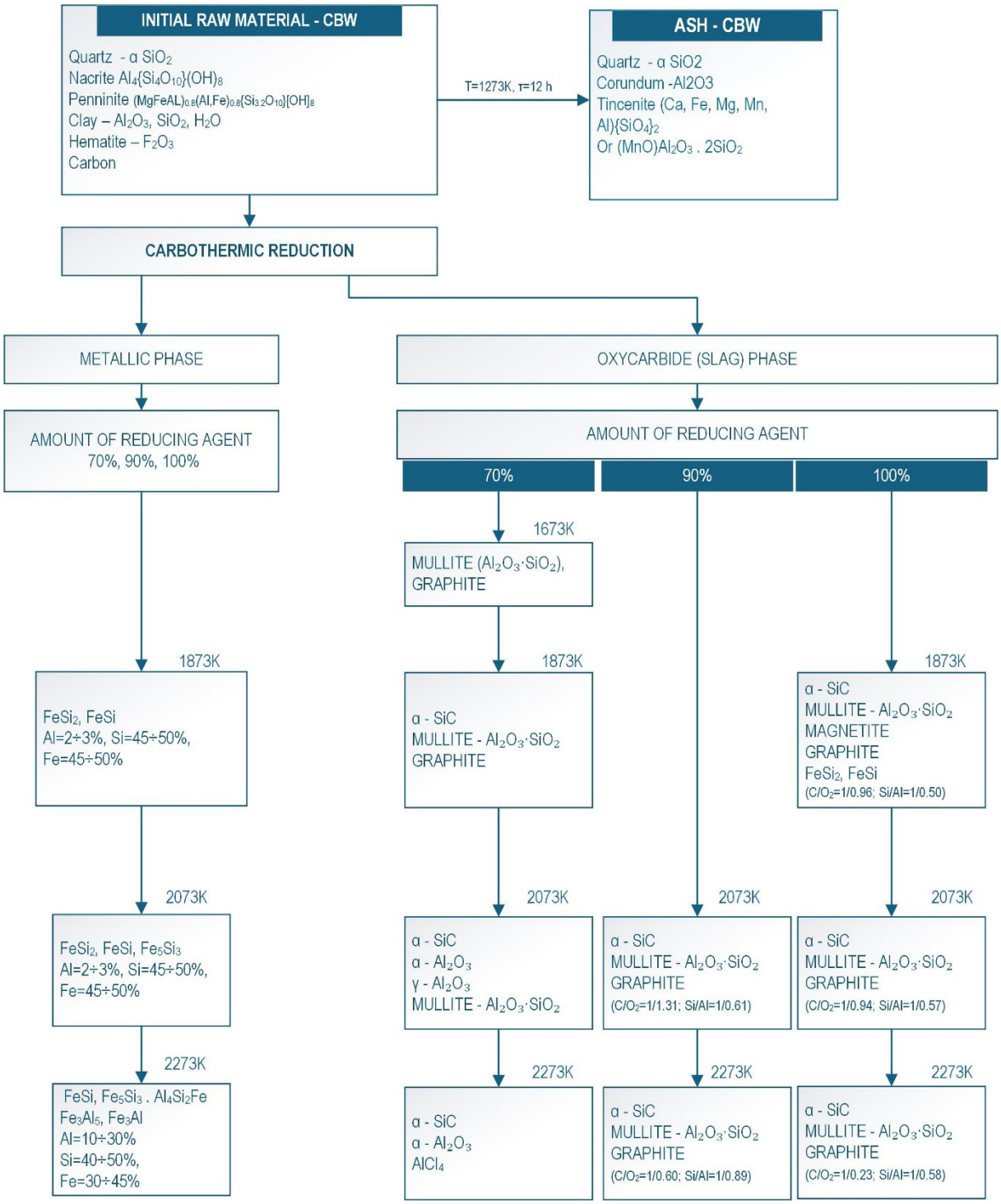

Fig. 6. Reaction scheme for the probable course of CBW carbo - reduction processes.

The reduction of Al under these conditions is practically undeveloped.

T = 2273 K

Processes mainly involve the reduction of Al from Al_2O_3 and mullite. The metallic phase is composed of the compounds FeSi, Fe_5Si_3, Al_4Si_2Fe, Fe_3Al_5, and Fe_3Al. A redistribution of Fe in the intermetallic compounds is observed - depletion of Si in the ferrosilicon phases and the formation of iron aluminides (Fe_3Al_5 and Fe_3Al) and mixed iron silicide aluminides of the Al_4Si_2Fe type. Under these conditions, the reduction of CBW proceeds mainly due to the reactions shown on Eq. (8 - 10) [6, 7]:

$$Al_2O_3 + C \rightarrow AlC_x + CO \quad (8)$$

$$Al_2O_3.SiO_2 + C \rightarrow AlC_{(SiFe)} + AlC_x + CO \quad (9)$$

$$Al_2O_3 + SiC \rightarrow AlC_{(Si)} + CO \quad (10)$$

The amount of the oxide phase decreases sharply ($C / O_2 = 1 : 0.23$) at the expense of the carbide phase. The amount of free carbon - graphite, in the oxycarbidic phase increases, due to the processes of recrystallization (graphitization) of carbon and a decrease in its reactivity, as well as the release of inactive C (graphite) from the supersaturated metal solution, occurring at high temperature (2000 - 2100°C).

CONCLUSIONS

The basic kinetic dependencies of the carbothermic reduction of coal enrichment waste have been investigated. The dependence of the degree of reduction processes and their rate on the change in temperature, residence time, the amount of reducing agent, and the influence of SiO_2 and Fe additives has been established. Using mathematical analysis methods, equations have been derived describing the change in the investigated quantities (R_C and V_{RC}) in the range of T = 1873 - 2273 K and τ = 0 - 60min.

Based on the generalized results from the analysis of the composition (chemical, phase) of the condensed products, a scheme of the probable course of carbo - reduction processes of CBW have been developed. The limiting conditions determining the course of reduction processes have been established.

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In memory of Metodi Ivanov, whose mentorship, inspiration and deep knowledge in metallurgical processes has greatly impacted this work. Though he is no longer with us, his dedication to using metallurgy science for resource recovery and waste reduction continues to inspire and guide our research.

Authors' contributions: *V.M.: Data collecting, Modelling and Analysis, Writing - Original draft and editing, Submission.*

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