MODELLING AND OPTIMISATION OF ANTHRACITE TREATMENT IN AN ELECTROCALCINATOR

M. M. Gasik[1], M. I. Gasik[2], O. Yu. Urazlina[3], and S. V. Kutuzov[3]

[1] TKK – Helsinki University of Technology, 02015 Espoo, Finland; mgasik@cc.hut.fi
[2] National Metallurgical Academy of Ukraine, 4, Gagarina pr., 49005 Dnipropetrovsk, Ukraine
[3] JSC “Ukrgrafit”, 20, Pivnichnoye Shose, 69600 Zaporizhzhya, Ukraine, graphite@ukrgrafit.com.ua

ABSTRACT

Electrocalcination is being used for production of thermally treated anthracite for manufacturing of electrodes for many ferroalloys processes. The quality of thermoanthracite mostly depends on its heat treatment regime at very high temperatures. The direct measurements and monitoring of an electrocalcination process are challenging and thus proper modelling is essential to predict the process control. Optimization of the electrocalcinator operation and performance requires correct knowledge of temperature distribution, electromagnetic fields, gas flow and chemical reactions kinetics. In this work, a multiphysical model of electrocalcination is presented and the results of its analysis are discussed.

1 INTRODUCTION

Manufacturing of electrodes for ferroalloys industry requires a high-conductivity carbon material, which is conventionally produced by heat treatment of anthracite at very high temperatures. Anthracite as a staring material has large variation in properties such as carbon structure, impurities and specific electrical resistance (SER), when the latter could vary of few orders of magnitude [1],[2],[3]. The primary task of a calcination of anthracite is to reduce its SER. This is achieved by transformation of amorphous structures of the anthracite into crystalline at high temperatures. Earlier, different types of furnaces have been used for this process but recently it is being mostly performed in an electrical resistive furnace (electrocalcinator).

For this thermoanthracite both chemistry and SER or specific electrical conductivity (SEC) are very important. The most important physical and chemical properties of anthracite, which vary greatly with temperature and time, are its SER, density, specific heat, degree of graphitization (crystalline size), ash and volatile organic compounds (VOC) contents. Use different sets of experimental data, the correlations of these properties with temperature and processing time have been earlier assessed.

However, due to high calcinations temperatures over 1600-2000°C, there is little possibility of making direct observations or in situ measurements within the electrocalcinator furnace. Optimization of the calcination of anthracite requires knowledge of the materials properties and the process parameters such as realistic temperature distribution, gas flow, materials movement and its interaction with the electrocalcinator (EC) lining [4],[5],[6].

These are tightly correlated with dynamically varied electromagnetic field and chemical reactions kinetics (oxidation, volatile compounds decomposition, pyrolysis, etc.). To ensure proper operation of an electrocalcinator, an adequate mathematical and multiphysical model is required. In this work, a 3D model of an electrocalcinator is presented and the effect of process parameters on EC performance and thermoanthracite quality is discussed.

2 MODELLING APPROACH

The multi-physical model for an electrocalcinator was built using the coupling of heat transfer (conduction, convection, radiation), electromagnetic fields (low-frequency AC, Ohmic heating, electromagnetic induction heating), chemical reaction (reaction kinetics between material, gas and solid lining) and fluid dynamics (gas flow in the porous solid). Materials properties were set for every computational domain. A view of an electrocalcinator used in this study is shown in Fig. 1 (dimensions in m). Anthracite is continuously charged from the feeder on the top, forming the conductive bed which is being heated by Joule heating from the current passing between electrodes and from the exothermic reactions of oxidation of volatiles and carbon. Heat-treated thermoanthracite is periodically discharged via the rotating valve at the bottom of water-cooled steel casing.

The FEM model was realized using COMSOL 3.5a Multiphysic software. Due to rotational symmetry of the problem, the mesh was build for a 2D axisymmetric case, Fig. 2 [5]. The thermal and electrical regimes of the electrocalcinator are determined by supplied power (voltage), which also depends of the inter-electrode distance (lower electrode position is fixed).

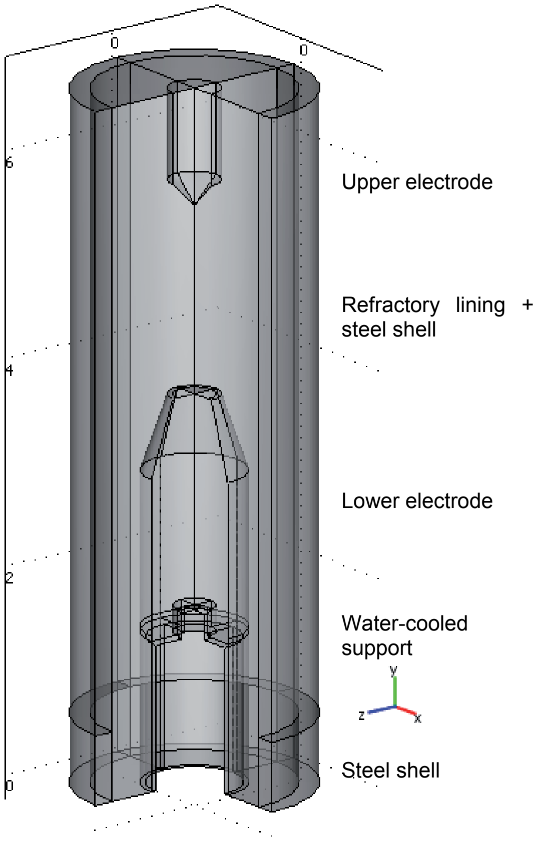

Figure 1: The 3D view of the modelling domain [5]

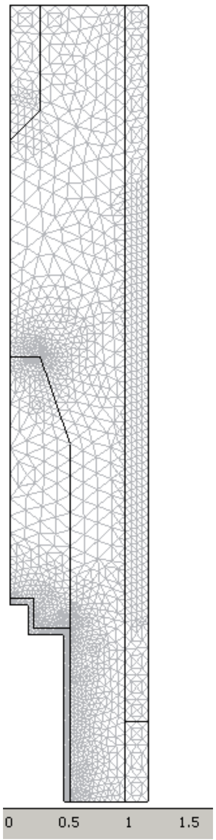

Figure 2: A FEM geometry for axial rotational symmetry of electrocalcinator [5]

All materials properties are strongly temperature-dependent so the system of differential coupled equations is non-linear. For electrical conductivity, there is also time dependence because it changes according with the anthracite processing history. For simplification, a steady-state approximation for the solution was sought with all time derivatives taken zero (with the exception of electromagnetic interaction due to 50 Hz frequency). Instead of DC Ohm law, in this case expression for current density vector **J** is written as Maxwell-Ampere law:

$$\mathbf{J} = \nabla \times \mathbf{H} = \sigma\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right) + i\,\omega\,\mathbf{D} + \mathbf{J}_{ext} \tag{1}$$

where: **H** – magnetic field strength,
E – electric field strength,
v – velocity of the media (anthracite) movement (~0.2 mm/s),
B – magnetic induction,
D - electric displacement ($\mathbf{D} = \varepsilon \cdot \varepsilon_0 \cdot \mathbf{E} + \mathbf{P}$),
ε – real part of dielectric permittivity (temperature-dependent for anthracite),

ε_0 - dielectric constant,
P – polarization vector (neglected for anthracite),
$\mathbf{J}_{ext}$ – external current density (in this case considered zero),
$i = \sqrt{-1}$,
$\omega = 2\pi f$ (f = 50 Hz).

The general Maxwell equations with use of (1) take the form:

$$\begin{aligned} &-\nabla\cdot\left(\left(i\omega\sigma-\omega^2\varepsilon\varepsilon_0\right)\mathbf{A}-\sigma\mathbf{v}\times\left(\nabla\times\mathbf{A}\right)+\left(\sigma+i\omega\varepsilon\varepsilon_0\right)\nabla\varphi-\left(\mathbf{J}_{ext}+i\omega\mathbf{P}\right)\right)=0 \\ &\left(i\omega\sigma-\omega^2\varepsilon\varepsilon_0\right)\mathbf{A}+\nabla\times\left(\left(\mu\mu_0\right)^{-1}\nabla\times\mathbf{A}-\mathbf{M}\right)-\sigma\mathbf{v}\times\left(\nabla\times\mathbf{A}\right)+\left(\sigma+i\omega\varepsilon\varepsilon_0\right)\nabla\varphi=\mathbf{J}_{ext}+i\omega\mathbf{P} \end{aligned} \tag{2}$$

where **A** – vector magnetic potential,
M - vector of materials magnetic saturation,
μ - relative magnetic permittivity (varied in anthracite as function of iron impurities content),
μ_0 - magnetic permittivity of vacuum.

Partial derivatives of electric and magnetic energies are respectively electric and magnetic power densities, which are connected to Ohmic (active) and reactive losses [5]:

$$-\int_\Omega\left(\mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}+\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t}\right)d\Omega=\int_\Omega\mathbf{J}\cdot\mathbf{E}\,d\Omega+\oint_S\left(E\times H\right)\cdot\mathbf{n}\,dS \tag{3}$$

with **n** being the normal to the bounding surface. The first part of the right-hand side is cycle-time averaged Joule heating (Ohmic losses) and the second is reactive power (especially inductive losses). This Joule heating is the major source of the heat in electrocalcinator. Other heat sources are mostly heat of reactions (oxidation of carbon, pyrolysis and oxidation of VOC), balanced by heat losses through the walls, exhaust gases and thermoanthracite. The overall heat balance of the electrocalcinator was considered elsewhere [4],[6],[7] in more detail.

The focus of the present study was in determination of effect of electrode distance on heat flow and electrical field distribution in electrocalcinator. It is known, that shorter electrode distances (long enough not to cause arcing) lead to higher temperatures in the inter-electrode zone. This is beneficial on the quality of thermoanthracite, but may immediately lead to melting of the refractory lining locally and to excess temperature gradients in the shaft (uneven quality of thermoanthracite).

The quality of thermoanthracite is mainly expressed in forms of specific electrical resistance (SER) or conductance, measured at room temperature. It is known that SER values also depend on particle size distribution, clamping (contact) pressure and method of measurement (4 probes, DC or AC) [1]. Instead of SER, crystalline parameters of thermoanthracite related to its graphitization process – namely crystallite size, interplanar distances c/2 (d_{002}) or c (d_{004}) - are more reliable measures of the quality. They are being determined by X-ray method and they are all connected with intrinsic SER values [1]. Thus temperature distribution and time of residence of anthracite in the electrocalcinator directly affect transformation process and could be linked with the quality factor, if the transformation kinetics reliable known.

Experimental data [1],[2] of d_{002} in nm are shown in Fig. 3 as function of the treatment temperature, indicating the trend lines. The bubble size is proportional to the treatment time. Although such estimation could be used in modeling, there is uneven contribution of heating time – when heating from 2000 to 2800°C takes few hours, the transformation process already proceeds and thus holding isothermal times cannot be directly compared. To establish a formal chemical kinetic model of the process, these data have been first fitted with a non-linear regression (Fig. 4 for crystallite size L_c as an example) and extended to include time required for heating with set heating rate.

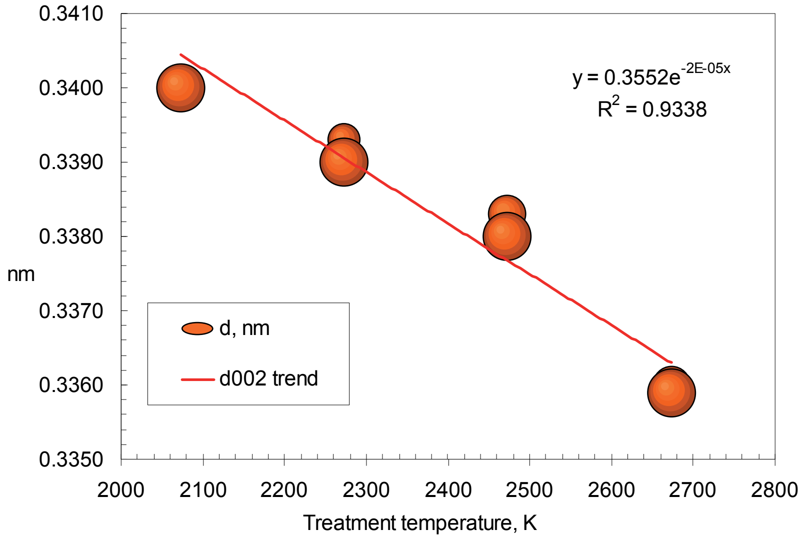

Figure 3: Dependence of d_{002} spacing of anthracite vs. treatment temperature.

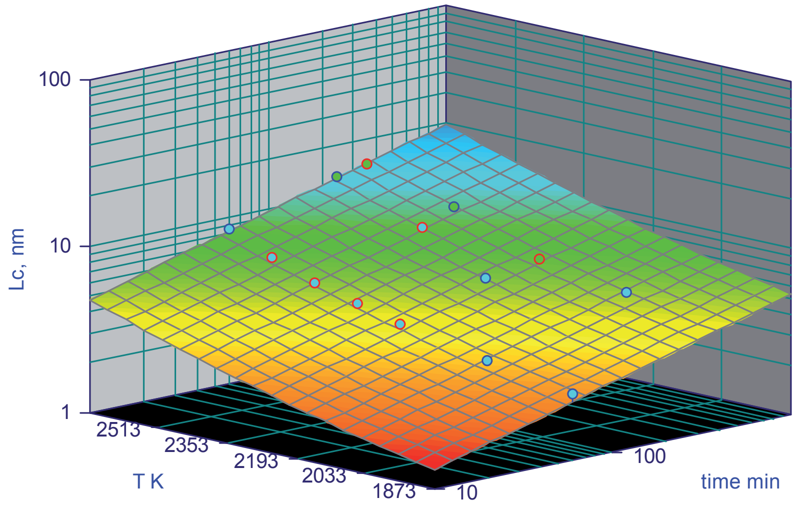

Figure 4: Dependence of L_c of anthracite vs. treatment temperature and isothermal treatment time. Points are experimental data from [1],[2].

Overlaying different experimental curves to the single initial value of d_{002}^0 = 0.344 nm, smoothing and scaling to 100% of initial distance, have given a possibility of presenting of the whole process timeline in the single plot, Fig. 5. With such data it is possible to apply a formal kinetic analysis [8] and a non-linear regression [9] to establish kinetic equation of the process for further predictions and optimisations. A model-free analysis using dedicated software (Netzsch Thermokinetics 3) has indicated that the process cannot be adequately represented by a single stage reaction (there is a strong, 2-3-fold dependence of activation energy vs. reaction degree).

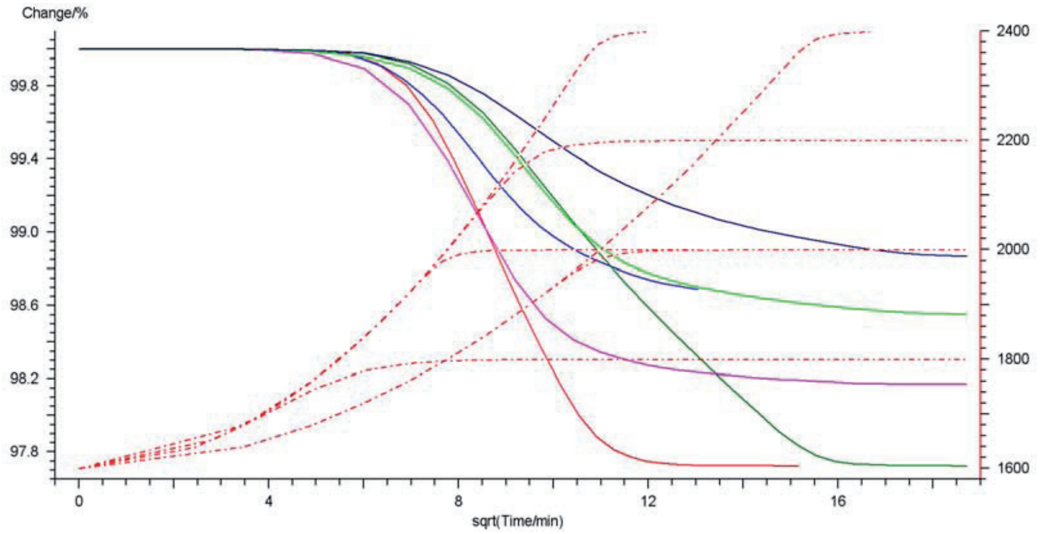

Figure 5: Kinetics of change of d_{002} distance (% to original; solid lines to the left axis scale) for anthracite vs. square root of time for different heating rates and treatment temperatures in °C (dash-dotted lines to the right axis scale).

3 RESULTS AND DISCUSSION

The multiphysical calculations were performed for electrode distances from 1 to 2 m and these two borderline cases are shown in Fig. 6 and 7 respectively. Here surface color represents temperature (°C), contours – potential (-28 V at lower and +28 V at upper electrode at phase zero), arrows – current flow and closed streamlines – magnetic potential (Wb/m). All pictures shown here are for phase zero for the case of unloading of the portion of thermoanthracite, when potential of lower electrode is being short-cut to the water-cooled steel shell at the lower part of electrocalcinator, Fig. 1. It may be seen that smaller distance (1 m) leads to higher density of potential lines there and thus to higher currents and higher Joule heat release since electrical conductivity of thermoanthracite is non-linear. This also changes distribution of magnetic field.

In the case of 2 m distance, maximal temperature is about 2650°C and acting current 10 kA. For 1.5 m distance this temperature rises to 2850°C (and current to 17 kA), for 1 m – to 3200°C and 20.8 kA respectively. In terms of applied total power, it also rises from 620 kVA (for 2 m) to 969 kVA (1.5 m) and 1040 kVA (1 m), which agree well with the plant experimental data. At smaller distances however reactive losses (capacitance losses in anthracite and inductive losses in steel parts) are also increased, although their change is not directly proportional to the total power rise.

Since the maximal temperatures of over 2500°C are occurring between the electrodes and near their edges, it is difficult to perform exact temperature measurements using thermocouple technique. Thermocouple signal is also significantly disturbed by induction current and by increasing electrical conductivity of the thermocouple shield at these conditions.

To validate model, direct measurements of electrical potential were performed at electrocalcinator of JSC “Ukrgrafit” (Zaporizhzhya, Ukraine) by inserting a probe through the specially made holes in the wall at different heights. Measurement of electrical potential is considered to be more reliable than temperature, which might be varied significantly due to gas flow or local stagnations zones. The potential was measured on the distance of 100-200 mm off the lining to minimize effect of the carbonized refractory material.

From Fig. 6 and 7 it is seen that in the centre of the electrocalcinator (4-5 m) the radial component of the electrical potential gradient is minimal and thus in this region immersion depth of the probe should affect the least obtained signal. In Figure 8 calculated potential distribution (starting form the lower electrode back as zero) is shown for three radial distances (at the axis, 0.5 m from the central line and near the lining) when the electrode distance is 2 m (Fig. 7). The exception to the shown calculated data was the applied acting potential was ±31 V as during the measurements, i.e. about 6 V higher than in Fig. 7. Experimental points shown here are for R = 0.92 m, i.e. near the internal lining surface of the electrocalcinator. From Fig. 8 it can be seen that experimental data are in a very good agreement with calculated ones, which gives confidence of the developed model.

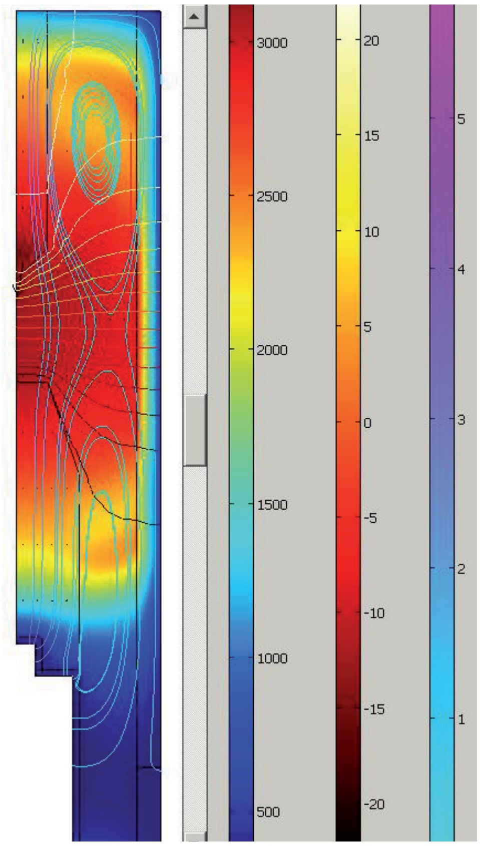

Figure 6: Results for electrode distance of 1 m

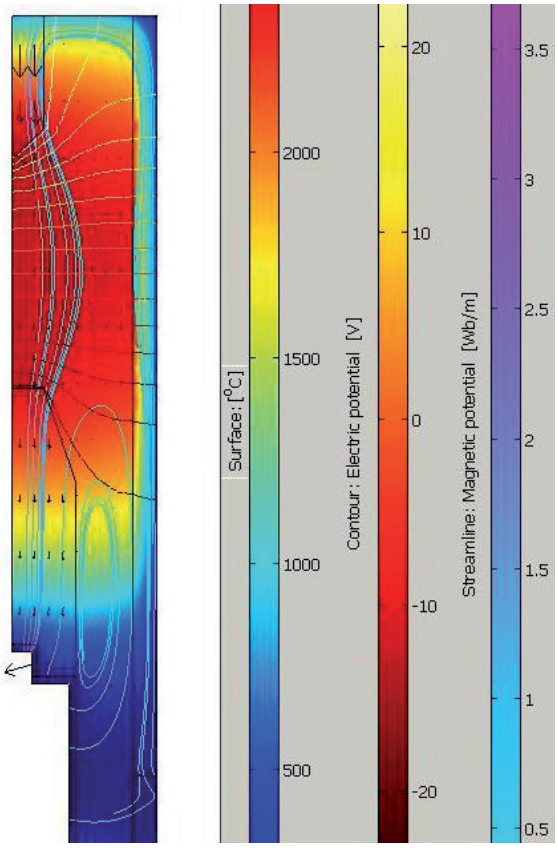

Figure 7: Results for electrode distance of 2 m

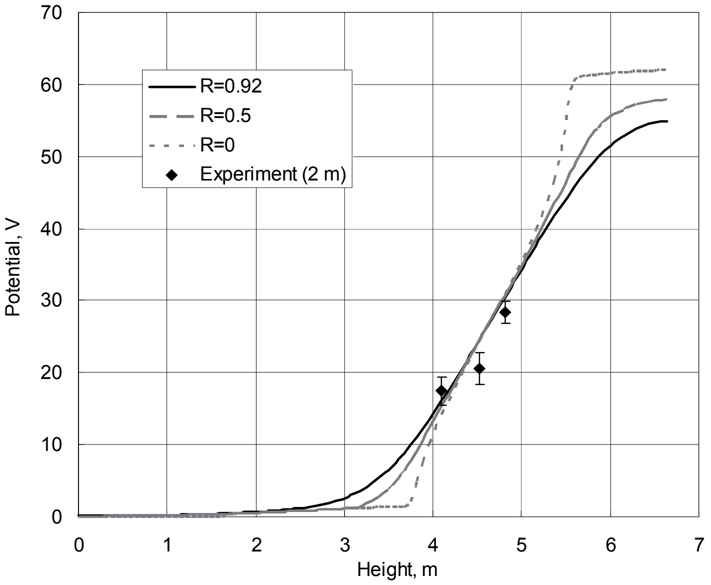

Figure 8: Distribution of electrical potential (relative to the lower electrode as zero) along the electrocalcinator height (m) at inter-electrode distance of 2 m (see text for details).

A formal kinetic analysis of data Fig. 5 has shown that it is possible to describe the process of anthracite heat treatment with two parallel reactions of the n-th order:

$$Ant \rightarrow \begin{cases} \xrightarrow{1} TAntA \\ \xrightarrow{2} TAntB \end{cases};$$

$$\frac{1}{[Ant]_0}\frac{\partial [Ant]}{\partial \tau} = -A_1 \exp\left(-\frac{E_1}{RT}\right)[Ant]^{n_1} + A_2 \exp\left(-\frac{E_2}{RT}\right)[Ant]^{n_2} \tag{4}$$

where [*Ant*] – fraction of anthracite in the charge,
[*Ant*]$_0$ – initial fraction of anthracite,
A_1, A_2 – kinetic pre-factors for each reaction, 1/s,
E_1, E_2 – activation energy of each reaction, kJ/mol,
n_1, n_2 – reaction power factors for each reaction,
TAntA and *TAntB* – respective fractions for thermoanthracite.

For data of Fig. 5 the best fit was obtained with the following values: A_1 = 13615 1/s, $A_2 = 1.473 \cdot 10^{-29}$ 1/s, E_1 = 327.98 kJ/mol, E_2 = 226.95 kJ/mol, n_1 = 2, n_2 = 0.88 (correlation coefficient 0.993416, Durbin-Watson factor 2.921). Note these values represent mathematical fit and should not be used for making conclusions about the exact mechanism of the process [8],[9]. With these numerical data iso-conversion rates have been calculated as shown in Fig. 9. Here it could be estimated that residence time of 2 h at 2200°C will lead to about 90% of transformation of anthracite into thermoanthracite.

When a proper correlation between d_{002} and SER are known, calculated temperature fields of Fig. 6 and 7 might be converted into the “quality iso-lines”, reflecting the local SER, which could be expected at normal temperature. This immediately might be integrated over the electrocalcinator volume to define whether non-homogeneities in temperature and mass flow variation will affect SER data scatter of thermoanthracite.

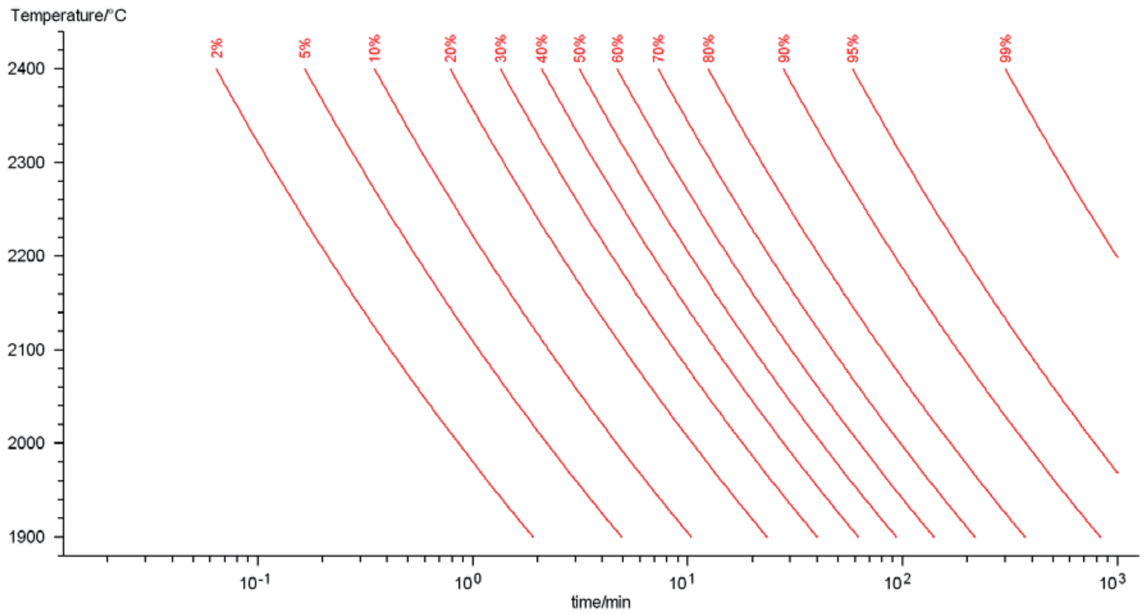

Figure 9: Temperature-time transformation (TTT) diagram for anthracite calculated using reactions (4). Iso-conversion lines indicate time and temperature required to achieve set degree of transformation.

4 CONCLUSIONS

The multiphysical combined model of an electrocalcinator for heat treatment of anthracite was developed and realized with COMSOL software. Coupled partial differential equations were solved for heat, momentum, electromagnetic field and chemical reaction kinetics. The model results were validated by measurements of electrical potential in real electrocalcinator for thermoanthracite production. Kinetic equation was obtained from experimental data by fitting interplanar distance values (d_{002}) to temperature, time and heating regime, but this also could be linked with crystalline size (L_c) and specific electrical resistance of thermoanthracite, which reflects its quality.

With such a modeling it is possible to evaluate not only temperature and potential distributions but also to assess variables, which are difficult to measure in situ (magnetic flux, volumetric Joule heating, etc.). This approach demonstrates the possibilities for such complex modeling and provides an additional insight for understanding the process. It was noticed that even for low frequency AC case electromagnetic coupling might be significant due to very high currents and this effect should not be neglected when designing metallurgical equipment and process.

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