

# **Modelling the mechanisms that govern the oxidation of graphite**

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# **Modelling the mechanisms that govern the oxidation of graphite**

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## **Synopsis**

The Pebble Bed Modular Reactor (PBMR) design is one of the High Temperature Gas Cooled Reactors (HTGR) under the Generation IV initiative. These designs incorporate numerous inherent passive safety features. Graphite is an important material of construction for the reactor core and the fuel pebbles. Knowledge of the high temperature oxidative behaviour of the graphite materials utilized in such reactors is important for design and accident modelling purposes.

Despite large amounts of research into the oxidation of graphite, a coherent framework for the comparison and assessment of the relative reactivity's of graphite samples from different origins has not yet been established. This is mainly due to a lack of clarity regarding the relative contribution of different factors which influence the overall behaviour of a given sample. The objective of this work was to identify and isolate the key factors which influence the oxidation of graphite and understand their operation across the entire range of conversion. Based on this understanding a comprehensive model for the oxidation can be established. The framework of this model will allow the sensible comparison of samples from different origins, based on the relative contribution of the relevant mechanisms. The work focused purely on the



kinetic factors which influence the oxidation and extreme care was taken to avoid mass transfer limitations where possible.

Through a carefully established experimental methodology three key factors were found to influence the progression of oxidation in a given sample:

- First and foremost, the development of the active surface area of a given sample
- Secondly, the presence of catalytic impurities
- Thirdly, the influence of inhibiting impurities

Based on these three effects, a finite element type, Monte Carlo simulation was developed. In this simulation virtually any geometry can be easily represented and the progression of the active surface area as the oxidation proceeds can be monitored. Furthermore, catalytic impurities could be easily incorporated into the simulation in a clear, consistent manner. This leads to an overall simulation which produces results that visually reflect the observed behaviour as well as accounting for the kinetic aspects of the experimentally determined conversion behaviour.

This work provides a starting point for assessing samples from different origins to first determine differences in the three basic governing effects, followed by a relative assessment of their reactivity's on a common basis. Future work should focus on refining the understanding of the mechanistic aspects of each of the individual governing effects, especially the influence of surface complexes and different reaction pathways. In addition, the work should be extended to cover a more comprehensive selection of graphite samples from different origins and a wider variety of impurity behaviours.

**Keywords:** Graphite; Oxidation; Catalysed reaction; Finite element; Monte Carlo simulation; Conversion function



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## Nomenclature

Symbol	Description	Units
$A$	Reaction rate constant at isokinetic temperature	$s^{-1}$
$A_C$	Catalysed reaction rate constant	$s^{-1}$
$A_U$	Uncatalysed reaction rate constant	$s^{-1}$
$ASA$	Active surface area	$m^2$
$ASA_{cube}$	Active surface area of infinitesimal cube	$m^2$
$a(\alpha, T, P, \dots)$	Accommodation function	-
$a, b, c$	Dimensions of crystallographic unit cell	$\text{\AA}$
$C(\lambda)$	Correlation co-efficient: Eq. (2.5)	nm
$C_{A\dots n}$	Concentration of reactant A through n	$mol.m^{-3}$
$C_f$	Active site concentration	kg reactive carbon. (kg carbon at $t$ ) $^{-1}$
$C_g$	Bulk gas concentration	$mol.m^{-3}$
$C_F$	Vacant/unoccupied surface area	$m^2$
$C_S$	Surface area occupied by the stable surface complex	$m^2$
$C_U$	Surface area occupied by the unstable surface complex	$m^2$
$D$	Diameter of ideal disc	m
$d$	Thickness of ideal disc	m
$d'$	Spacing between diffracting planes	nm
$dr, dx, dy$	Dimensions of infinitesimal cube	m
$E_A, E_a$	Activation energy	$J.mol^{-1}$
$E_{app}$	Apparent activation energy	$J.mol^{-1}$
$E_C$	Catalysed activation energy	$J.mol^{-1}$
$E_U$	Uncatalysed activation energy	$J.mol^{-1}$
$f(\alpha)$	Dimensionless conversion function	-
$f^0(\alpha)$	Normalised dimensionless conversion function	-
$g(\alpha)$	Integral form of reaction rate	-
$g^0(\alpha)$	Normalized integral form of reaction rate	-
$\Delta G^0$	Standard Gibbs energy change of reaction	$J.mol^{-1}$





$\Delta H^0$	Standard enthalpy change of reaction	J.mol <sup>-1</sup>
$i$	Imaginary unit number	-
$I(D)$	Raman D-band intensity	-
$I(G)$	Raman G-band intensity	-
$h,k,l$	Crystallographic Miller indices	-
$\hbar$	Reduced Planck constant	J.s
$\hat{H}$	Hamiltonian operator	-
$K$	Equilibrium constant	-
$K^h$	Shape factor	-
$k$	General gas phase reaction rate constant	atm <sup>-1</sup> .s <sup>-1</sup>
$k_0$	Pre-exponential factor	s <sup>-1</sup>
$k(T)$	Temperature dependent reaction rate constant	kg carbon reacted. (kg carbon at $t=0$ ) <sup>-1</sup> .s <sup>-1</sup>
$k_A(T)$	Intrinsic reaction rate constant	kg carbon reacted. (kg reactive carbon) <sup>-1</sup> .s <sup>-1</sup>
$k'_{O_2}$	Reaction rate constant based on TSA	m <sup>-2</sup> .s <sup>-1</sup>
$k_{O_2}$	Reaction rate constant based on ASA	m <sup>-2</sup> .s <sup>-1</sup>
$k_f$	Reaction rate constant based on active sites	kg carbon reacted. (kg reactive carbon) <sup>-1</sup> .s <sup>-1</sup>
$k_{ASA}(T)$	Reaction rate constant based on ASA	kg carbon reacted. (m <sup>2</sup> ASA) <sup>-1</sup> .s <sup>-1</sup>
$k^0_{ASA}(T)$	Normalised reaction rate constant based on ASA	kg carbon reacted. (kg carbon at $t=0$ ) <sup>-1</sup> .(m <sup>2</sup> ASA) <sup>-1</sup> .s <sup>-1</sup>
$k_1, k_2, k_3, k_4$	Reaction rate constant based on surface complex reactions	kg carbon reacted. (m <sup>2</sup> ASA) <sup>-1</sup> .s <sup>-1</sup>
$L$	Crystallite domain size	nm
$L_a$	Crystallite domain size in a direction	nm
$L_c$	Crystallite domain size in c direction	nm
$m$	Mass	kg
$m_{cube}$	Mass of infinitesimal cube	kg
$m_{edge}$	Mass of edge (reactive) carbon atoms	kg reactive carbon



$N_A$	Number of moles of reactant A	mol
$n$	Any integer	-
$n_{total}$	Total number of carbon atoms	-
$n_{edge}$	Total number of edge carbon atoms	-
$P_{O_2}$	Oxygen partial pressure	atm
$P_{cube}$	Probability an infinitesimal cube reacts in time step	-
$R$	Ideal gas constant	J.mol <sup>-1</sup> .K <sup>-1</sup>
$R_R$	Dimensionless reaction rate	s <sup>-1</sup>
	Defined as: change in mass at time $t$ divided by mass at time $t$	
$R_{T0}$	Dimensionless reaction rate	s <sup>-1</sup>
	Defined as: change in mass at time $t$ divided by mass at time $t=0$	
$r_t$	Radius of ideal disc at time $t$	m
$r_{t=0}$	Radius of ideal disc at time $t=0$	m
$s$	Fraction of carbon surface under catalysed reaction	-
$T$	Absolute temperature	K
$T_S$	Isokinetic temperature	K
$t$	Time	s
$\Delta t$	Time step	s
$U$	Arbitrary distance less than particle radius	m
$V$	Reactor volume	m <sup>3</sup>
$V(r)$	Time-independent potential energy at the position $r$	J
$v$	Edge recession rate	m.s <sup>-1</sup>
$x,y,z$	Cartesian co-ordinates	-
$X_F$	Fraction of vacant/unoccupied surface area	-
$X_S$	Fraction of surface area occupied by the stable surface complex	-
$X_U$	Fraction of surface area occupied by the unstable surface complex	-

**Subscript Description**

0	At start of experiment, i.e. at time $t=0$
$t$	At time $t$
$\infty$	At end of experiment

**Superscript Description**

n	Reaction gas order
m,n,p	Arbitrary fitting constants in Eq. (2.47)

<b>Greek Symbol</b>	<b>Description</b>	<b>Units</b>
$\psi$	Wave function (probability amplitude)	-
$\nabla$	Gradient operator	-
$\alpha$	Dimensionless degree of conversion	-
$\alpha', \beta', \gamma'$	Internal angles of crystallographic unit cell	$^{\circ}$
$\beta$	Experimental temperature ramp rate	$^{\circ}\text{C} \cdot \text{min}^{-1}$
$\beta^h$	Peak width at half maximum intensity	$^{\circ}$
$\theta$	Angle of incident X-ray beam	$^{\circ}$
$\lambda$	Wavelength of incident X-ray beam	nm
$\delta$	Stagnant boundary layer depth	m
$\eta$	Effectiveness factor	-
$\Omega$	Surface coverage fraction	-
$\tau$	Generalised time	s
$\tau'$	Gas change time constant	s
$\kappa$	Ratio of channel depth to exterior half-width	-
$\rho_c$	Crystalline graphite density	$\text{kg} \cdot \text{m}^{-3}$
$\rho_{ASA}$	Active site density	kg reactive carbon. $(\text{m}^2 \text{ASA})^{-1}$
$\chi_0$	Specific active surface area at time $t=0$	$\text{m}^2 \cdot \text{kg}^{-1}$
$\sigma$	Particle size distribution standard deviation	m