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### The effect of calcium aluminates on the coke analogue gasification

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## The effect of calcium aluminates on the coke analogue gasification

### Abstract

The gasification rate in CO<sub>2</sub> of the coke analogue containing calcium oxide was studied using analogues doped with alumina (corundum), calcium aluminates (CA6, CA, C3A) and lime minerals. The coke analogue is a laboratory material with simplified carbon structure that has a mineral component with a particle size, size distribution and mineral dispersion that can be controlled. The main focus of this study was to quantitatively assess the effect of calcium in the mineral on the analogue's reactivity. The analogues were reacted with CO<sub>2</sub> isothermally in the temperature range of 1173–1623 K. It was found that the reaction rate increased with increasing CaO activity/number of moles of Ca in the mineral. The relative reaction rates (from lowest to highest) of the analogues doped were alumina, CA6, CA, C3A and lime. The relative apparent activation energies of the gasification from lowest to highest was lime, C3A, CA, CA6 and alumina.

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1                   **The Effect of Calcium Aluminates on the Coke Analogue Gasification**

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8

9 Abstract

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19 from lowest to highest was lime, C3A, CA, CA6 and alumina.

20

21 Key words: Coke analogue, Calcium aluminates, TGA, Coke kinetics, Rate of reaction

22 Nomenclature

23  $X$  Carbon conversion

24  $R_C$  Initial apparent reaction rate,  $\text{g g}^{-1} \text{s}^{-1}$

25  $T$  Temperature, K

26  $dt$  Reaction time, s

27  $W_0$  Initial mass of the sample, g

28  $W$  Mass at time  $t$ , g

29  $dW$  Mass change during the reaction, g

30

## 31 1. Introduction

32 Metallurgical coke is a key reagent used in blast furnace iron production. It is the fuel for the furnace,  
33 the source of reductant for the iron ore and aids control of permeability in the furnace [1]. Coke is a  
34 complex material, composed of different forms of carbonaceous materials, minerals and has  
35 an intricate pore structure. It also is inherently heterogeneous with respect to most metrics used to  
36 characterise it.

37 The mineral component of metallurgical coke is of the order 10 to 12 mass % and comprises of  
38 elements such as O, Si, Al, Fe, Ca, S, Mg, K, Ti and Na [2-4]. Though less common, the minerals  
39 may also contain P, Mn, C, H, N, Ba, Sr, F and Cl [5]. Minerals containing oxides of alkalis [3, 6-  
40 9] and transition metals [2, 3, 7, 10, 11] can increase coke gasification/ reactivity. Calcium-  
41 bearing minerals are of particular interest in coke/coal studies. It has been shown to be  
42 particularly mobile in coal and coke [12-15] and significantly affects coke reactivity. Well-known  
43 calcium-containing minerals in coke are oldhamite (CaS), fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), akermanite  
44 ( $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ ) and diopside ( $\text{MgCaSi}_2\text{O}_6$ ) [16].

45 When exposed to high temperatures and reactive atmospheres, the inherent complexity and  
46 heterogeneous nature of coke make it difficult to isolate the effects of specific components on coke  
47 behavior and reaction kinetics [17-19]. To overcome the complexity and heterogeneity issues  
48 associated with studying the reactivity of metallurgical coke, a coke analogue has been developed.  
49 The mineral component in the analogue can be controlled with respect to phase, composition, particle  
50 size and dispersion throughout the analogue. This analogue has previously been used in studies to  
51 distinguish the relative reactivities of coke analogues doped with different minerals [18, 20], the  
52 dissolution rate of coke in liquid iron [19, 21, 22], kinetic mechanistic studies of reaction in  $\text{CO}_2$ ,  
53 isolating specific CaO/lime [15] effects on the coke analogue reactivity and demonstrating it had  
54 similar gasification reaction behaviour to that of metallurgical coke [23, 24].

55 The focus of this investigation was to assess the effects of calcium added as a simple oxide or as a  
56 calcium aluminate on the gasification kinetics of the coke analogue in  $\text{CO}_2$ . Three calcium aluminates,

57  $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$  (CA6),  $\text{CaO}\cdot \text{Al}_2\text{O}_3$  (CA) and  $3\text{CaO}\cdot \text{Al}_2\text{O}_3$  (C3A), lime (CaO) and alumina ( $\text{Al}_2\text{O}_3$ ) were  
58 used to represent the mineral (ash) component of the analogue. The choice of minerals was a  
59 compromise, dealing with minerals of some relevance to metallurgical coke but less complex than  
60 those found in metallurgical coke. This simplified mineral component of the analogue allowed the  
61 focus of the effects of Ca and Al oxides/minerals on coke reactivity in the absence of interference  
62 from other components such as Mg, F and  $\text{PO}_4^{3-}$  that have been identified to also have effects on  
63 coke gasification.

## 64 2. Experimental

65 Coke analogue samples were reacted with  $\text{CO}_2$  in a thermogravimetric analysis (TGA) set-up (Fig.1)  
66 to assess the effects of selected minerals on the coke gasification kinetics.

67 Five different coke analogue batches were prepared using either a calcium aluminate (CA6, CA or  
68 C3A),  $\text{Al}_2\text{O}_3$  or CaO. The minerals were added to give a constant concentration of 0.1 mol cations/  
69 100 g in the analogue and were sieved prior to the addition to give a constant particle size range of  
70 38 – 53  $\mu\text{m}$ . Experiments were carried out for 2 hours isothermally in the temperature range of 1173  
71 – 1623 K.

72 The calcium aluminates were chosen based on the  $\text{Al}_2\text{O}_3$ -CaO binary system (Fig. 2). The choice of  
73 minerals allowed the evaluation of the specific effects of CaO as a separate phase and of CaO  
74 bonded/complexed within a mineral.

### 75 2.1. Reaction rate measurements

76 An unreacted coke analogue sample was weighed and placed in the furnace hot zone on an alumina pedestal  
77 suspended from a balance. This was then heated at 10 K/min to the desired temperature under Ar flowing  
78 at 1 L/min. Once the reaction temperature was reached, the gas was changed from Ar to  $\text{CO}_2$  and set  
79 at a flow rate of 4.5 L/ min. The changing over of the gas was defined as the start of the experiment.  
80 The flow rate was chosen/ established to ensure the reaction kinetics were independent of gas flow  
81 (i.e. eliminate gas film diffusion control) [23]. The gases used were 99.99% pure and passed

82 through ascarite and drierite prior to entering the TGA. When running with Ar, the gas was also  
83 passed through Cu turnings at 573 K to minimise oxygen entering the furnace.

84 The recorded weight change during the reaction as measured by the TGA was used to calculate the  
85 carbon conversion,  $X$  (eq. 1), and initial apparent reaction rate,  $R_C$  (eq.2).

$$86 \quad X = \frac{W_0 - W}{W_0} \quad (1)$$

$$87 \quad R_C = \frac{1}{(1-X)} \frac{dX}{dt} \quad (2)$$

88

## 89 2.2. Preparation of coke analogue

90 The coke analogue was prepared using carbonaceous materials (laboratory grade graphite, phenol-  
91 formaldehyde resins (Bakelite and Novolac resin in propylene glycol) and hexamethylenetetramine  
92 (HTMA)) and minerals (CA6, CA, C3A, alumina or lime). The ingredients were mixed and pressed to  
93 form a cylinders of ~30 mm height and 18 mm diameter samples. These cylindrical samples were then  
94 cured for 24 hours in an oven at 443 K and then fired in a two-stage process. In stage 1, the analogue  
95 was fired at 1273 K for 1 hour. In stage 2, the analogue was fired at 1473 K for 1 hour.

96 A fired coke analogue sample from each batch was cross-sectioned, mounted in epoxy resin, polished  
97 and carbon coated for SEM analysis. The CA6, CA, C3A and lime doped coke analogue samples were  
98 treated as water sensitive and prepared using, water-free alcohol based polishing lubricants. These  
99 samples were used in optical porosity and SEM/EDS characterisation.

100 The initial porosity of all the coke analogue samples was measured using an optical porosity  
101 method (detailed elsewhere [20]). The initial porosities of the samples (10 – 500  $\mu\text{m}$  pore  
102 diameter range) prior to the gasification in the TGA were in a narrow range of 30 – 33 %. This  
103 technique had a pore diameter lower limit of ~10 $\mu\text{m}$ . It is desirable to maintain the initial porosities  
104 in a narrow range to minimise the effect of porosity on the measured analogue reactivity. This should



105 aid elucidation of the specific effects of mineralogy on reactivity.

### 106 2.3. Preparation of the mineral phase

107 High purity (+ 99.9 %) laboratory grade  $\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$  powders obtained from Sigma Aldrich  
108 were used in the production of the mineral phases.

109 The calcium aluminates were prepared by mixing  $\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$  powders in appropriate  
110 proportions and fired to produce pellets of calcium aluminates.  $\text{CaCO}_3$  was used instead of  $\text{CaO}$  to  
111 overcome issues associated with  $\text{CaO}$  moisture absorption, allowing accurate weighing of the  
112 carbonate. The powders were first mixed with 500 ml of deionised water to make a slurry. They were  
113 then filtered using a 75 mm Büchner funnel and a Filtech 2850 – 70 filter paper equivalent to  
114 Whatman #6 (pore size 3  $\mu\text{m}$ ). The resulting filter cake was then oven dried at 373 K for 24 hours.  
115 Deionised water (2 mass %) was added as a binder to the dried filter cake prior to pressing into  
116 pellets. Approximately 8 g of the mixture was pressed in a 25 mm diameter steel die under a  $1.3 \times 10^8$  Pa  
117 pressure. The pellets were then fired in a muffle furnace at the temperatures listed in Table  
118 1. The firing temperatures for the calcium aluminates were chosen based on the phase diagram  
119 given in Fig.2. The pellets were then crushed and sieved to get the particle size of 38 – 53  $\mu\text{m}$ .

120  $\text{CaO}$  was prepared by heating  $\text{CaCO}_3$  in the air to 1273 K in a muffle furnace. To minimize the  
121 moisture pick-up the calcined  $\text{CaO}$  was cooled and stored in a vacuum desiccator. The  $\text{CaO}$  was  
122 sieved to get particle size of 38 – 53  $\mu\text{m}$  and added to the coke analogue as quickly as possible to  
123 reduce the potential moisture pick-up.

124 Alumina particles in the size range of 38 – 53  $\mu\text{m}$  were prepared by sintering the  $<10 \mu\text{m}$  as received  
125 alumina powders from Sigma Aldrich. The as-received alumina powder was mixed with 2 %  
126 deionized water prior to pressing into pellets. The pellets were made by pressing approximately 8 g  
127 of alumina powder + deionized water mixture in a 25 mm diameter steel die under  $1.3 \times 10^8$  Pa  
128 pressure. These pellets were heated to 1973 K for 12 hrs. The pellets were then crushed and sieved to  
129 get the particles sizes required.

130 Post-mineral preparation of all minerals phases was confirmed by XRD prior to the addition to, and in  
131 the fired state of, the coke analogue. No significant change in the mineral was observed, see Fig. 3 for  
132 the XRD patterns of the added minerals.

### 133 3. Results and Discussion

#### 134 3.1. Reactivity studies using minerals doped coke analogues

135 The initial apparent reaction rates,  $R_C$ , were calculated for the analogues and plotted against  $1/T$  and  
136 the results are given in Fig. 4. From this figure, it can be seen that over the temperature range  
137 tested (1173 – 1623 K),  $R_C$  increased with increasing temperature. Further, similar to that  
138 previously reported for the base analogue with no mineral addition, [23, 25] lime doped coke  
139 analogue [15] and that of metallurgical coke [26, 27], two reaction zones were identified. These  
140 zones were established using the method developed by Walker et al [26]. In this method, the  
141 linearity of the curves in the plot given in Fig. 4 are used to define the reaction zones. The transition  
142 from zone I (chemical reaction control) to zone II (Chemical reaction + pore diffusion control) was  
143 in the range of 1330 – 1400 K. There was no strong correlation between the transition temperature  
144 and the calcium content in the coke analogue.

145 Fig. 5 shows the comparison of  $\ln R_C$  and  $1/T$  of the coke analogue samples studied. From this  
146 figure it can be seen that  $R_C$  increases with increasing Ca content of the mineral, i.e.  $R_C$  for alumina  
147  $< CA6 < CA < C3A < lime$ .

148 To assess the effect of Ca on the reactivity plots of the total number of moles of Ca ( $n_{Ca}$ ) versus  $R_C$   
149 (Fig. 6) and the chemical activity of CaO ( $a_{CaO}$ ) versus  $R_C$  (Fig. 7) were made. MTDATA [28] was  
150 used to evaluate  $a_{CaO}$ . The reference state used for CaO was halite (monoxide). The  $n_{Ca}$  and the  $a_{CaO}$   
151 for the respective minerals at the different temperatures are given in Table 2. Temperatures  
152 representative of zone I (1223 K) and zone II (1623K) have been considered in this comparison.  
153 The solid line in the Fig.s represent the best fit linear regression of the data.

154 From the Figure, it can be seen that there is a stronger correlation with  $R_C$  and  $n_{Ca}$  than that for  $a_{CaO}$  as

155 indicated by the higher  $R^2$ . This would tend to indicate that the Ca effect is simply a mass effect rather  
156 than a chemistry effect associated with the bonding in the mineral phase. Both approaches show that  
157 their effect is greater at higher temperatures as indicated by the increased slope of the regression lines  
158 at higher temperatures.

159 Notwithstanding the distinction between  $n_{Ca}$  and  $a_{CaO}$  on  $R_C$ , the data shown in Figs 6 and 7 are in  
160 general consistent with that reported in the literature [29-32] on the effects of Ca in the ash on the rate  
161 of coke gasification. It is not clear why the  $R_C$  is a linear function with the Ca content. This will be  
162 discussed in more detail in the mechanistic section 3.3.

163 The effect of temperature was further analysed by calculation of activation energies for zones I and II  
164 (see Table 3). The activation energies for both zones decrease with the increasing Ca content of the  
165 mineral in the analogue. This is indicative of the strong catalytic effect of Ca on the gasification and is  
166 consistent with what others have reported for Ca effects on gasification for metallurgical coke [18, 29,  
167 31-34].

### 168 3.2. Mineral dispersion in the coke analogues – SEM studies

169 Fig. 8 shows SEM backscattered images and EDS maps for the coke analogues in their fired condition  
170 prior to the gasification reaction. In the micrographs in Fig.8a (alumina) and Fig. 8b – d (calcium  
171 aluminates) the shape and size of the particles in the coke analogue were of similar nature (size and  
172 morphology) to those added to the green analogue i.e. the particles have not changed significantly on  
173 firing. With the lime addition (Fig 8e), the particles were reduced in size and more dispersed  
174 throughout the analogue. In a previous study focused on the effects of lime addition to the analogue  
175 it was found that the lime had reacted with the analogue during preparation [15]. The reaction of  
176 lime on firing was explained in terms of an acid-base reaction [15] similar to that found in low  
177 ranked lignite coals [35-37]. More specifically, the strongly basic lime is reacting with the weakly  
178 acidic phenolic (Novolac) resin. This resulted in a greater dispersion of the lime throughout the  
179 analogue compared to the other minerals added to the analogue, a significant reduction in the lime  
180 particle size and a significantly increased contact area between the lime and the carbon in the

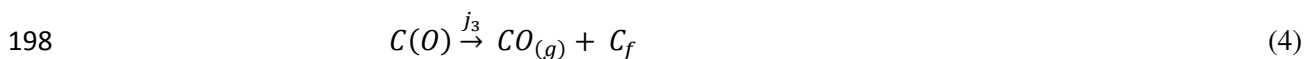
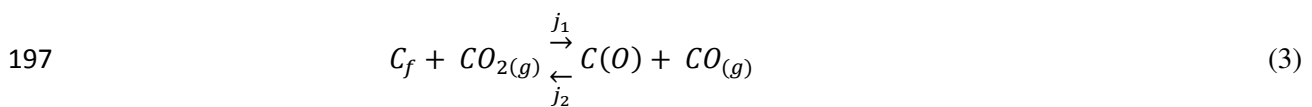
181 analogue. There was no apparent increase in the analogue porosity from the lime addition.

182 Why does the lime show significantly different behaviour in the analogue to the other calcium-bearing  
183 minerals (CA6, CA, and C3A)? While the answer is not clear it is likely related to the relatively  
184 higher acidity of alumina compared to the acidic entities (phenolic groups) present in the phenolic  
185 resins. This may result in a stronger bond with the alumina than the phenolic resin.

186 In addition to the amount/concentration of minerals, the reactivity is also a function of particle size  
187 and the distribution of the mineral phase [2]. In this study, attempts were made to fix particle size and  
188 distribution to elucidate the effects of mineral type on the reactivity of the analogue. The fact that the  
189 lime particle behaviour was significantly different during the preparation from the other minerals,  
190 reducing in size, makes this problematic. It is likely the lime effects on reactivity at the nanoscale are  
191 more complex than simple particle size-contact area analysis allows. In spite of this, the results  
192 excluding lime, and focusing on only the alumina and calcium aluminates, still indicate that  
193 increasing the Ca level in the analogue increases reactivity.

### 194 3.3. Discussion of rate controlling mechanism

195 Generally, the carbon – carbon dioxide gasification reaction mechanism can be expressed as Eq. 3 and  
196 4 [39-45].



199 where;  $C_f$  = active carbon site

200  $C(O)$  = surface oxygen complex

201  $j_1, j_2$  and  $j_3$  = rate constants

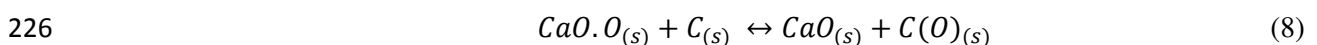
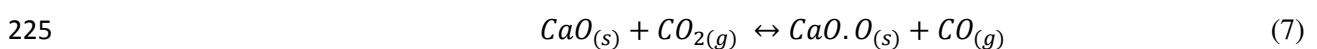
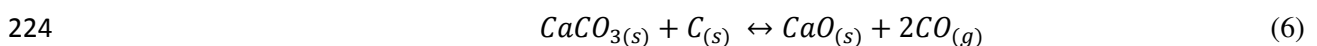
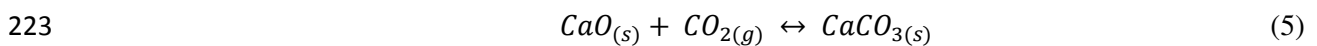
202 In the first step (Eq.3),  $CO_2$  dissociates into CO forming a surface oxygen complex C(O). In the

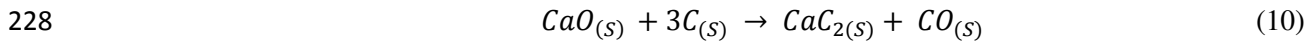
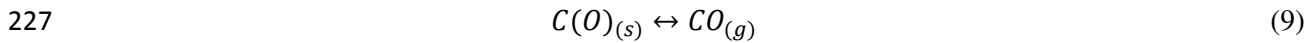
203 second step (Eq.4), the surface oxygen complex produces another CO molecule leaving a free C  
204 active site for further reaction. The second step is considered as the rate controlling step [41, 46].

205 There are two widely accepted mechanisms to explain the increasing reactivity of gasification  
206 reactions, an oxygen transfer mechanism and an electron transfer mechanism [8, 47, 48]. The  
207 electron transfer mechanism is suggested for the transition metals bearing systems. It is based on the  
208 ability of transition metals to accept an electron to influence the distribution of  $\pi$  electrons in the  
209 carbon surface [49]. The oxygen transfer mechanism is suggested for the reactions that are affected  
210 by metals and metal oxides where the catalytic surface chemisorbs an oxygen atom from  $\text{CO}_2$  to  
211 transfer to the carbon site later on [8, 50].

212 Ca, as a non-transition metal, most probably followed an oxygen transfer mechanism. Some  
213 researchers have suggested different reactions for Ca catalysis in carbon gasification. Those  
214 involve formation of  $\text{CaCO}_3$  (reaction 5 and 6) or  $\text{CaO}\cdot\text{O}$  (reaction 7-9) or  $\text{CaC}_2$  (reaction 10) [51-  
215 54]. The formation of these species at the high temperatures used in this study was  
216 thermodynamically assessed by consideration of the  $\Delta G^\circ$  of reactions 5, 7 and 10 over a range of  
217 temperatures (see Fig. 9). The  $\Delta G^\circ$ 's were calculated using the reaction module of FactSage 7.0  
218 [55]. In the FactSage calculations,  $\text{CaO}\cdot\text{O}$  is represented by  $\text{CaO}_2$ . Reactions 5 to 9 were  
219 thermodynamically assessed in a previous publication [15]. To aid clarity and understanding this  
220 assessment has been included here for comparison with reaction 10.

221 It was found that the reactions all had a  $\Delta G^\circ > 0$  for the temperature ranges evaluated in this study. It  
222 is therefore unlikely that these reactions occurred during the gasification experiments.





229 It is known that the presence of Ca in coke ash can increase the amount of active sites ( $C_{(f)}$ ) [45]. The  
230 enhanced reaction rate is attributed to the increased number of active sites ( $C_{(f)}$ ) that favour carbon  
231 dioxide dissociation. From a molecular modeling study, it was found that calcium interacts  
232 exothermically with the carbonaceous lattice [56]. These interactions are thought to cause the increase  
233 in the electron density of carbon, increasing the number of active carbon sites (Eq.3). This increase in  
234 active sites ( $C_{(f)}$ ) offers a plausible explanation of why Ca increases the reactivity of the coke  
235 analogues in this study.

236 This catalytic mechanism may explain the increasing reactivity with increasing Ca content. It may  
237 also explain why the  $R_C$  is a linear function with the Ca content (Fig. 6). The contact area between  
238 the minerals and the carbon in the analogue is, with the exception of lime, reasonably controlled  
239 due to the control of particle size addition of the minerals. Therefore, the Ca in the mineral  
240 associated with this surface is likely proportional to the mineral Ca content. This could explain the  
241 linear effect, though more work is required to confirm this possibility.

242 The catalytic mechanism does not explain the observed decreased apparent activation energy. At  
243 this point, there is no clear understanding of the reason for the decreasing activation energy.

244 Further studies will focus on testing the possibilities of the changing reaction mechanism from both a  
245 theoretical and experimental perspective. The effect of other minerals commonly available with Ca in  
246 metallurgical cokes, such as  $SiO_2$  and  $MgO$ , will also be considered.

#### 247 4. Conclusion

248 The effect of calcium aluminates (CA6, CA and C3A) on the coke analogue gasification kinetics was  
249 studied. The results were compared with lime doped and alumina doped coke analogues gasification.  
250 Calcium aluminates were observed to increase the reaction rates with increasing CaO activity/number

251 of moles of Ca. The relative reaction rates (from lowest to highest) of the analogues doped with  
252 minerals were alumina, CA6, CA, C3A and lime. The relative apparent activation energies of the  
253 gasification vary, from lowest to highest, lime, C3A, CA, CA6 and alumina.

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375

376 List of figures

377 Fig. 1: A schematic diagram of the TGA set up used for reactivity experiments.

378 Fig. 2: A phase diagram of the  $\text{Al}_2\text{O}_3 - \text{CaO}$  binary system (from MTDATA [28]). The dashed lines  
379 represent single-phase calcium aluminates.

380 Fig.3: XRD patterns of the minerals prior to adding to the coke analogue.

381 Fig.4: Plots of  $\ln R_C$  Vs  $1/T$  for the coke analogues studied

382 Fig.5: A plot of  $\ln R_C$  Vs  $1/T$  for the coke analogues

383 Fig 6: A plot of reaction rates Vs number of moles of CaO ( $n_{\text{Ca}} =$  number of moles of Ca)

384 Fig.7: A plot of reaction rates Vs CaO activity ( $a_{\text{CaO}} =$  activity of CaO)

385 Fig.8: SEM backscattered images and EDS maps of the cross sections of the coke analogues.

386 Fig.9: A plot of  $\Delta G^\circ$  Vs temperature for the reactions 5, 7 and 10

- 387 List of tables
- 388 Table 1: The firing temperatures of the calcium aluminates.
- 389 Table 2: The number of moles of CaO and calcium activities in coke analogue samples.
- 390 Table 3: Activation energies for the coke analogues gasification in CO<sub>2</sub>.

Table 1:

Calcium aluminate type	Firing temperature / K
CA6	1898
CA	1823
C3A	1623

Table 2:

Mineral	Number of moles of Ca in 100 g of base coke analogue	Activity of CaO at 1223 K	Activity of CaO at 1623 K
Alumina	0.000	0.0000	0.0000
CA6	0.007	0.0015	0.0012
CA	0.031	0.0400	0.0800
C3A	0.055	0.6720	0.6000
Lime	0.100	1.0000	1.0000

Table 3

Coke analogue	Apparent activation energy / kJ mol <sup>-1</sup>	
	Zone I	Zone II
Alumina doped coke analogue	231.3 ± 1.8	63.1 ± 0.3
CA6 doped coke analogue	204.4 ± 1.5	39.5 ± 0.4
CA doped coke analogue	159.9 ± 1.7	37.8 ± 0.3
C3A doped coke analogue	146.3 ± 1.8	34.5 ± 0.3
Lime doped coke analogue	119.8 ± 1.5	20.7 ± 0.3

Fig.1.

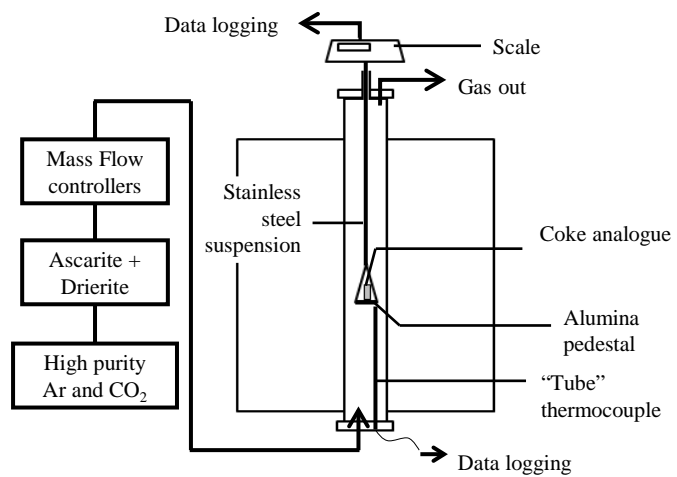
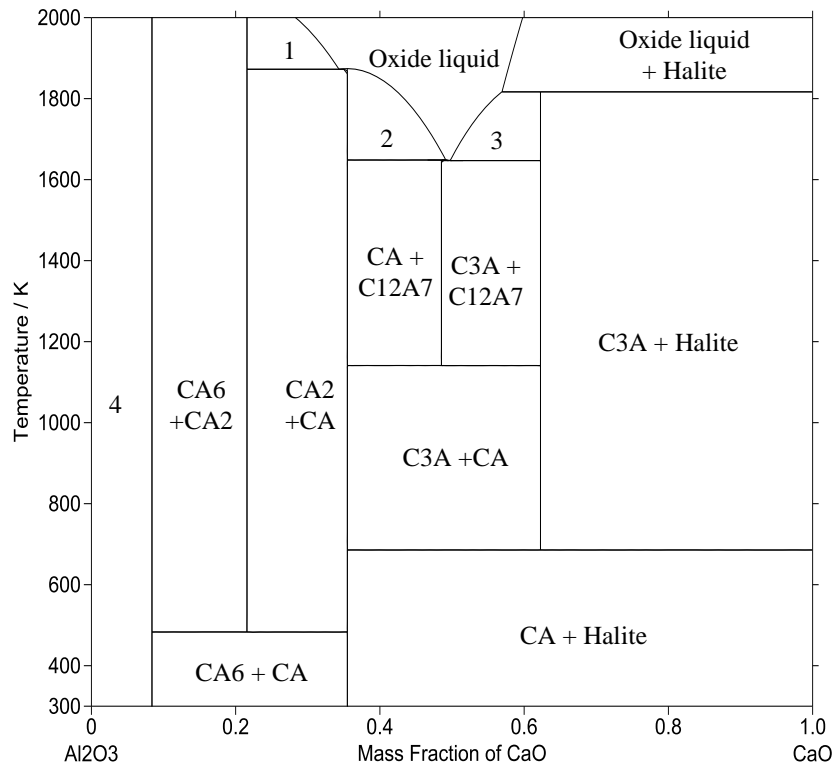




Fig.2.



- 1 – CA<sub>2</sub> + Oxide liquid
- 2 – CA + Oxide liquid
- 3 – C<sub>3</sub>A + Oxide liquid
- 4 – CA<sub>6</sub> + Corundum

Fig.3.

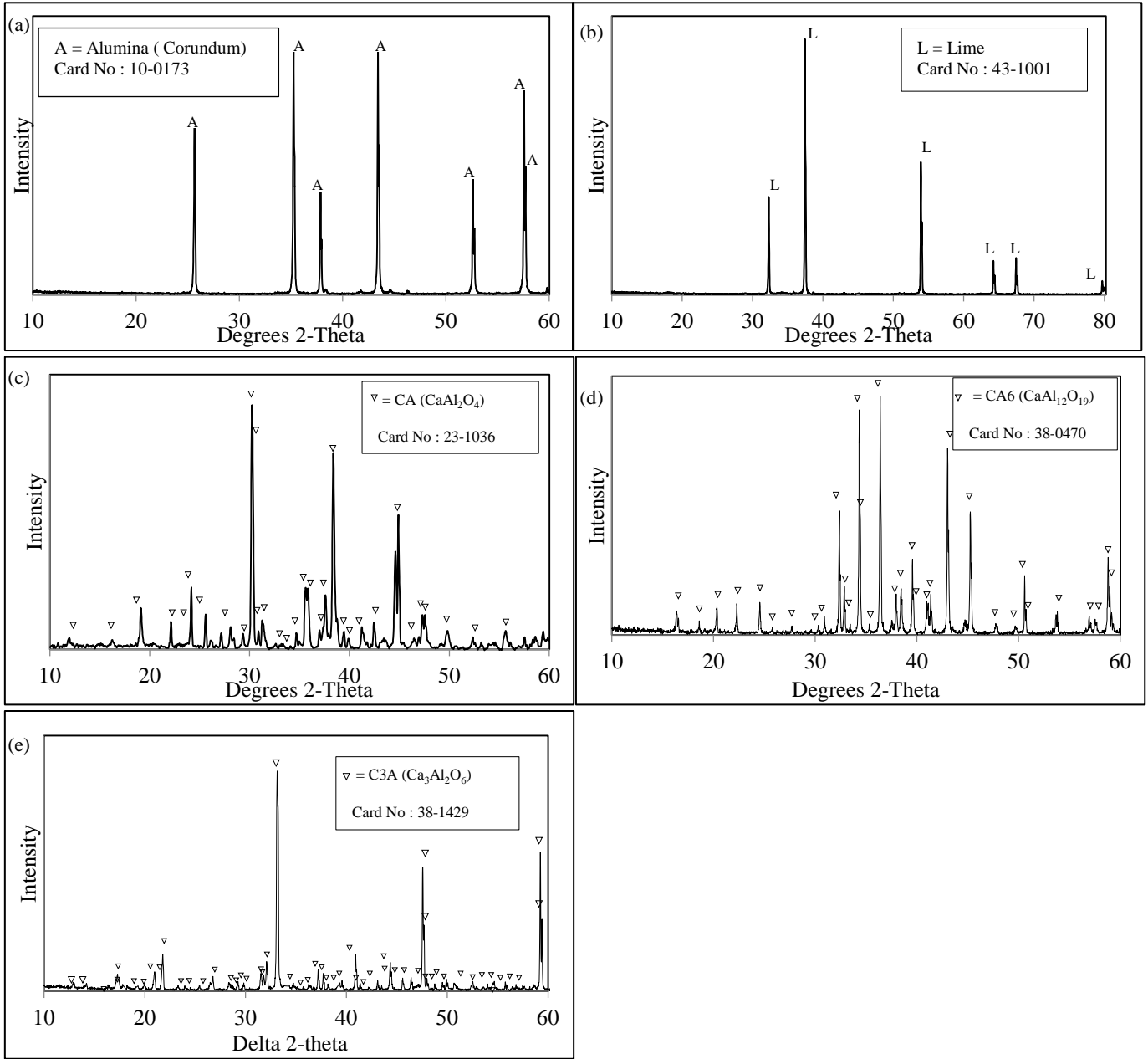


Fig.4.

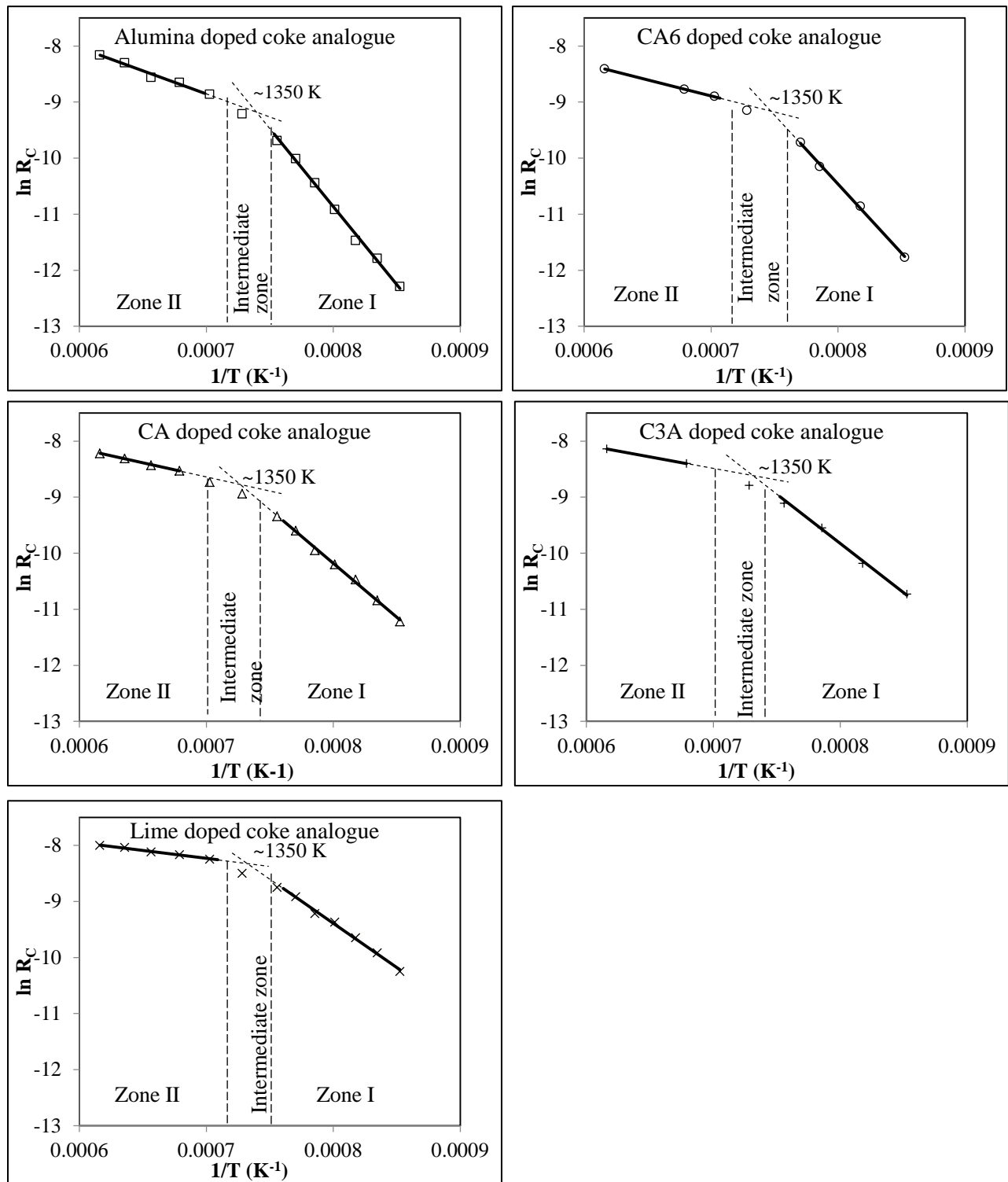


Fig.5.

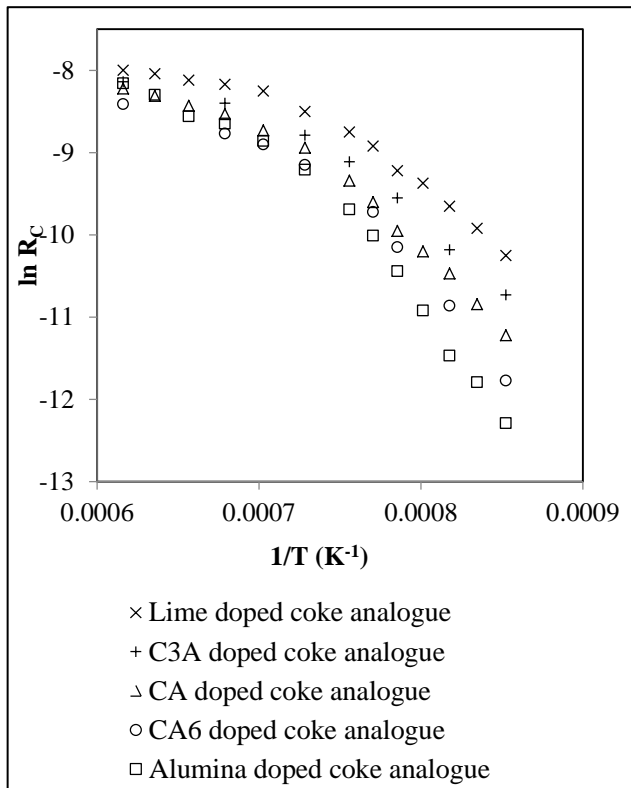


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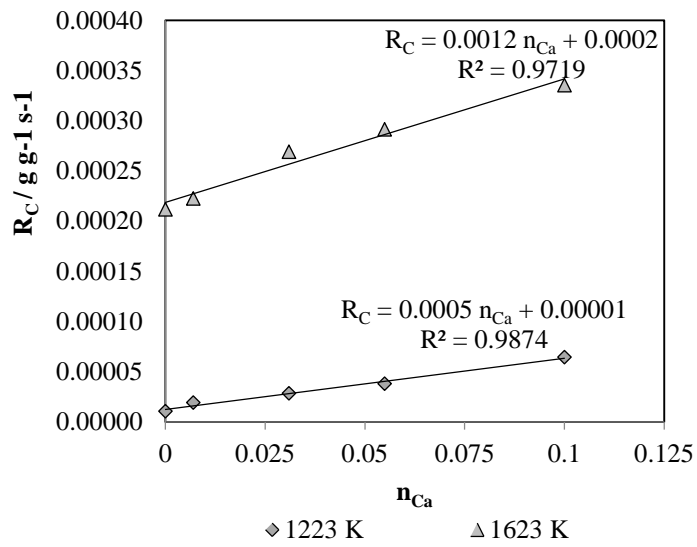


Fig.7.

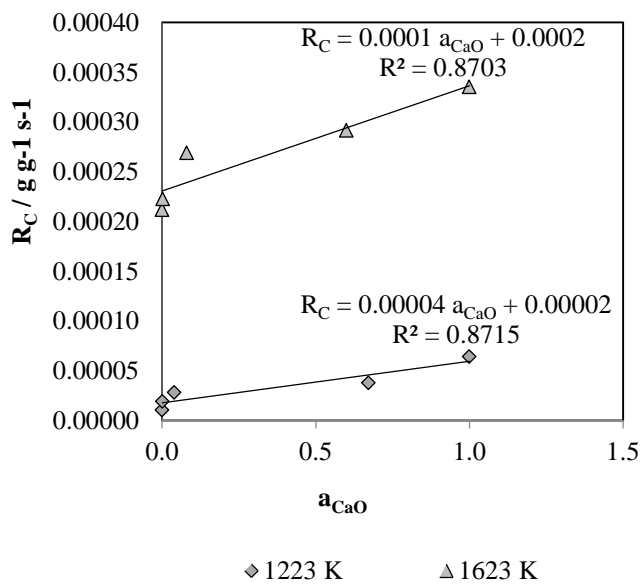


Fig.8.

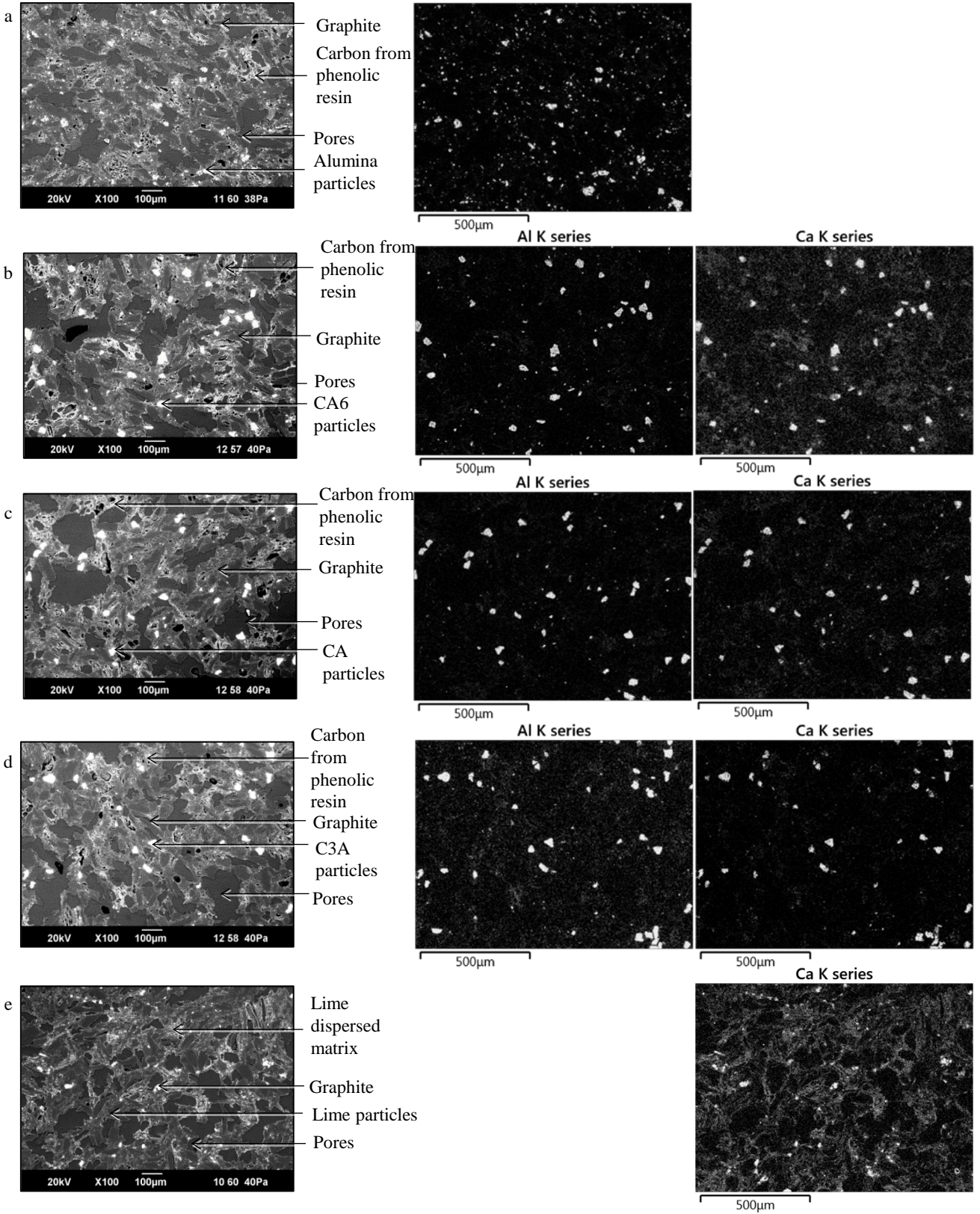


Fig.9.

