

## **EFFECT OF ALKALINE ELEMENTS ON COKE STRUCTURE UNDER BLAST FURNACE PROCESS CONDITIONS**

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### **Abstract**

Presence of alkaline elements such as sodium and potassium are highly detrimental for blast furnace operations. Even a trace amount of alkali affects the performance of raw materials considerably. The performance of coke in the process suffers significantly in presence of alkalis by the catalysis of Boudouard reaction during its descent through the shaft and subsequent deterioration of its strength in the lower zone of the furnace, leading to various furnace operating problems. The aim of this work is to investigate the impact of these harmful elements on the coke structure in micro as well as nano level. The Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) values of coke are determined for original industrial coke samples as well as the same samples artificially impregnated with alkaline elements in different amounts. The original and CRI-method treated samples (with and without added alkali) are characterized using X-Ray Diffractometry (XRD) and Transmission Electron Microscopy (TEM) to look into the lattice and crystalline structure of the constituent graphite of coke. The results demonstrate pronounced disturbance in the graphite lattice caused by alkali. An attempt has been made to explain the mechanism of the deterioration of coke properties under the influence of alkalis in terms of the difference in atomic radii of the constituent elements.

**Keywords:** Blast furnace, coke, alkaline elements, CRI/CSR tests, characterization

### **1. INTRODUCTION**

The performance of the blast furnace process is quite sensitive on the raw material properties. The quality of the raw materials affects directly the productivity and efficiency of the process. Presence of even very trace amount of alkaline elements (Na, K etc.) degrades properties of both iron and carbon carrying raw materials. The effect of alkali elements on coke has been investigated for this work. Sodium (Na) and potassium (K) have been identified as harmful for furnace operations because they catalyze the Boudouard Reaction [1, 2] and reduce the mechanical strength of coke in the lower zone of the furnace [3], which subsequently lead to furnace irregularities following lower productivity and economic loss. The major sources of these elements are coke ash and gangue materials present in the ores, which makes it impossible to eliminate them from the actual process. Different studies have shown the catalytic effect of different amounts of potassium on Boudouard Reaction under laboratory conditions [1, 2, 4]. Li et al. discussed about the modification of graphite structure under the influence of alkaline elements [5]. In the preceding study, Bhattacharyya et al. hypothesized a mechanism of the catalysis of Boudouard Reaction from the viewpoint of lattice disturbance [6]. The current study follows the aforementioned work and is focused on the investigation of the effect of alkaline elements on coke based on micro and nano level characterization.

### **2. METHODOLOGY**

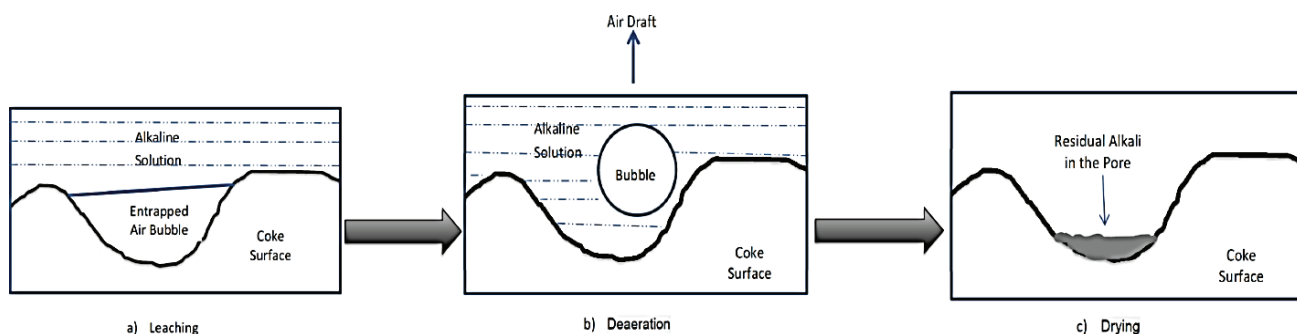
**Three types of industrial blast furnace cokes (C1, C2 and C3) were used for this work.** The proximate analysis of the coke samples are shown in **Table 1**.

**Table 1** Proximate Analysis(All values are in mass %)

	C1	C2	C3
Ash	10.70	10.10	9.35
Volatile Matter	0.19	0.37	0.65
Moisture	3.4	3.15	2.04
Fixed Carbon	85.71	86.38	87.96

## 2.1. Artificial alkali impregnation

The coke samples were artificially impregnated by alkaline elements by the method of leaching in different alkaline solutions (NaOH or KOH) containing the respective alkaline species, as mentioned by Bhattacharyya et al. [6]. Coke pieces in the size range on 19 - 22.4 mm (as described in ISO 18894) were submerged in the alkaline solution in a beaker and then placed in a vacuum chamber and deaerated until bubbling stopped. This method ensures the entry of the alkaline solution in all possible open and connected pores and removal of entrapped air. Then the excess solution was removed and the pieces were dried in a hot air oven at 125 °C for 10 hours for complete removal of water. **Figure 1** shows schematically the process of artificial alkali impregnation.



**Figure 1** Schematic representation of the impregnation of alkaline elements

An attempt was made to maintain the amount of added alkali closer to industrial values. However, exact control of alkaline content in the samples is not possible because of the heterogeneous nature of coke and different surface areas due to variable nature of porosities in the samples. Hence, the following values have been defined as a range of added alkali content (**Table 2**).

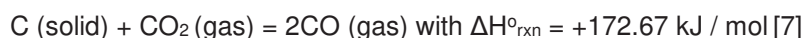
**Table 2** Alkali content ranges

Nomenclature	% of Artificially added Na or K
No added alkali	0 %
Medium alkali content	0.6 - 1 %
High alkali content	1.5 - 2 %

## 2.2. Reactivity and strength tests

Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) are internationally accepted testing standards for blast furnace cokes, described under ISO 18894 (2006). All the coke samples (with and without added alkali) are tested under standard CRI and CSR conditions. For CRI, a test portion of the dried coke sample ( $200 \pm 3$  g) having a size range between 19.0 mm to 22.4 mm is heated in a retort to 1100 °C in a nitrogen atmosphere. For the test, the atmosphere is changed to carbon dioxide for 2 hours. During this

treatment, the carbon part of the coke sample is gasified by forming carbon monoxide. This is an endothermic reaction and known as Boudouard Reaction.



After the test, the reaction vessel is cooled down to room temperature in a nitrogen atmosphere. The comparison of the sample weight before and after the reaction determines the CRI. The reacted mass is tumbled in a specially designed tumbler for 30 minutes at 20 r.p.m. After tumbling, the percentage of the mass having a particle size greater than 10 mm to the reacted mass is defined as CSR. More details about the test could be found from the corresponding standard [8].

For CRI and CSR tests, the vertical retort furnace aggregate of the Chair of Ferrous Metallurgy, Montanuniversität Leoben was used. The instrument has been constructed by Siemens VAI Metals Technologies GmbH, as well as the automation system. CSR tests have been done by a twin tumbler system (Model TB 5000 of R.B. Automazione, Genoa, Italy).

### 2.3. X-Ray Diffractometry

The samples for X-ray powder investigations were carefully ground to powders, prepared on standard sample holders and mounted on a BRUKER D8 Advance X-ray powder diffractometer with  $\theta/\theta$  geometry. All samples were measured with Cu K $\alpha$  radiation in the  $2\theta$  angle range of 5 - 110° using step width of 0.02°. The diffractograms were evaluated using the software EVA [9] (qualitative analysis) and TOPAS V4 [10] (Rietveld analyses). The lattice constants, peak profile functions as well as the quantification of the respective components were performed by whole-pattern least-squares fits.

### 2.4. Transmission electron microscopy

The TEM investigations were conducted using a monochromated TF20 TEM, Schottky cathode, operated at 200 kV, equipped for energy-dispersive X-ray spectroscopy (EDX) with a SiLi detector and an ultrathin window. For electron energy-loss spectroscopy (EELS) and energy-filtering (EFTEM), the TEM is equipped with a high-resolution Gatan imaging filter (GIF). The samples for TEM investigation were prepared by standard powder preparation method.

## 3. RESULTS AND DISCUSSIONS

### 3.1. CRI and CSR Tests

The standard CRI and CSR values of all three samples (without artificially added alkali) conform to normally required values for industrial blast furnace process. However, with the addition of very little amount of alkali, enormous increase in CRI and decrease in CSR has been observed in all cases. The CRI and CSR values under influences of Na and K are shown in **Tables 3 and 4** respectively.

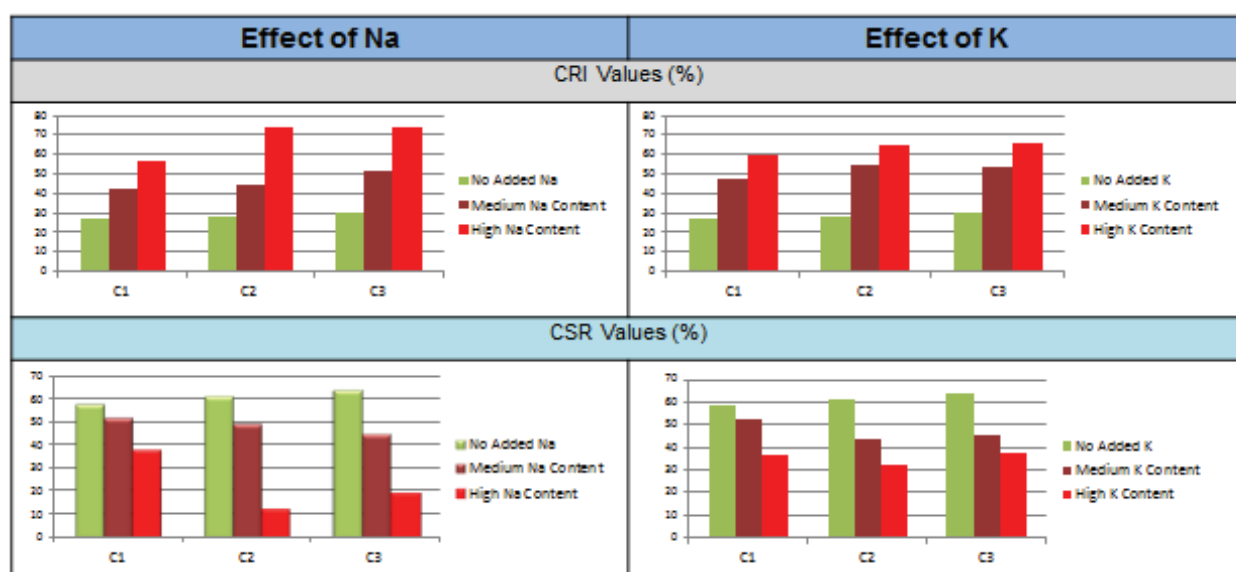
**Table 3** Effect of Na on CRI and CSR

Sample	Property (CRI/CSR)	No Added Na	Medium Na Content	High Na Content
C1	CRI	26.6	42.0	56.2
	CSR	58.3	52.3	38.2
C2	CRI	28.2	44.8	73.7
	CSR	61.0	49.7	12.9
C3	CRI	30.2	51.4	73.8
	CSR	64.0	44.7	19.8

**Table 4** Effect of K on CRI and CSR

Sample	Property (CRI/CSR)	No Added K	Medium K Content	High K Content
C1	CRI	26.6	47.5	59.6
	CSR	58.3	52.2	36.4
C2	CRI	28.2	54.8	65.0
	CSR	61.0	43.3	32.4
C3	CRI	30.2	53.7	66.1
	CSR	64.0	45.0	37.3

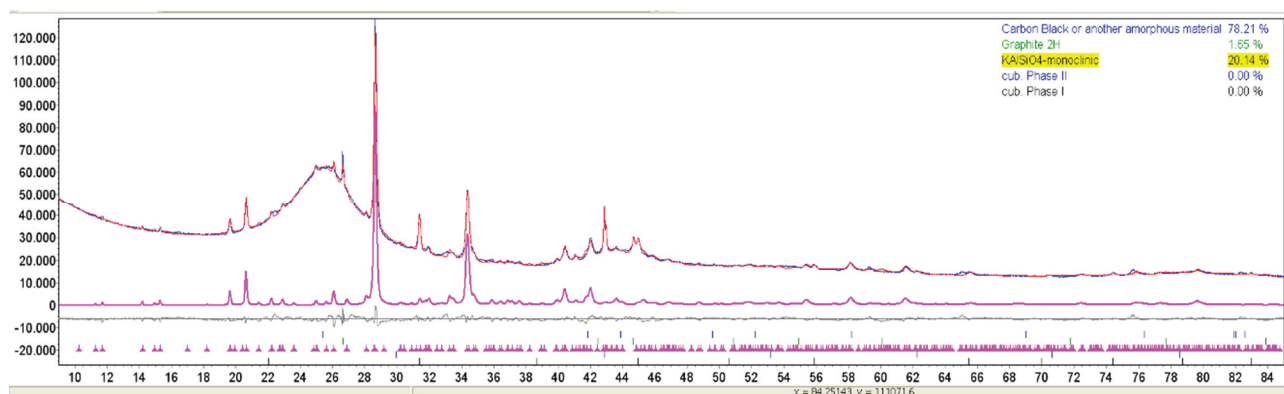
The effect of sodium on lowering the CSR is found to be stronger than that of potassium. The results are depicted as bar diagrams in **Figure 2**.



**Figure 2** Effect of alkaline elements on CRI and CSR

Sample C3 has been chosen for further characterization tests such as TEM analysis and XRD.

### 3.2. X-Ray Diffractometry



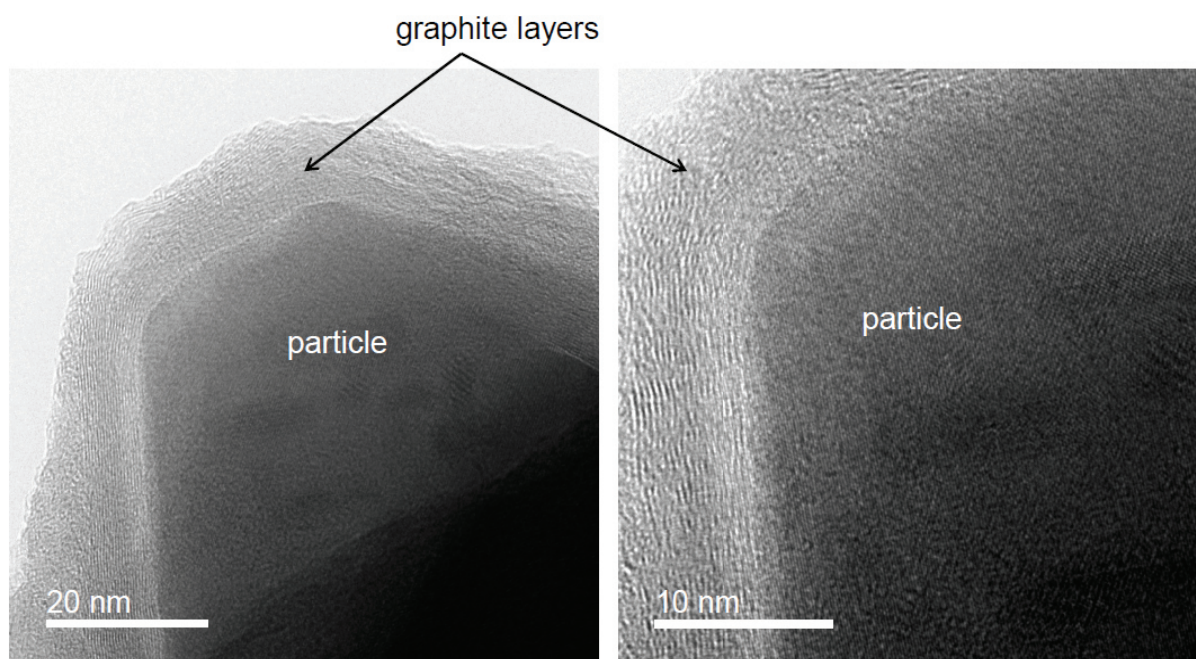
**Figure 3** - Diffractogram showing matching peaks of  $\text{KAlSiO}_4$

The X-Ray diffractograms of the treated samples do not show any stable or metastable intermediate catalytic phases. Instead, the results indicate peaks corresponding to complex oxides in the form of  $\text{KAlSiO}_4$  and

NaAlSiO<sub>4</sub> (respectively for K and Na treated samples), which might have resulted by the interaction between the ash phases in coke and alkaline oxides at high temperature. These peaks are not observed in samples without added alkali. A diffractogram of C3 treated with K is shown in **Figure 3**.

### 3.3. TEM Analysis

TEM analysis was also performed to investigate the effect of alkaline elements on the lattice structure of coke. The untreated coke structure consists of turbostratic graphite which is comparatively disorientated by normal CRI treatment (without added alkali). However, the reacted and alkaline treated samples show a significantly distorted graphitic structure around alkali bearing particles (**Figure 4**). The EDX data confirm the presence of alkaline particles in the structure.



**Figure 4** TEM images of C3 treated with K showing misaligned graphite layers oriented around an alkali bearing particulate component in the structure in two different magnifications. Note the turbostratic nature of the graphite lattice.

## 4. CONCLUSION

In the previous work, Bhattacharyya et al. hypothesized a possible mechanism of the catalysis of Boudouard reaction on the theory of ionic radii. The ionic radius of carbon is much smaller than that of sodium or potassium (**Table 5** [11]).

**Table 5** Effective ionic radii

Elements	Effective Ionic Radii (in Å)		
	Na <sup>+</sup>	K <sup>+</sup>	C <sup>4+</sup>
Ionic Radii	1.02	1.38	0.16

The TEM analysis depicted significant structural distortion of graphite layers under the influence of alkaline elements. It can be explained in terms of pronounced lattice disturbance at higher temperatures (1100 °C and above), which is possibly caused by the rapid diffusion of Na or K in the graphite crystal system (which has



much lower atomic radius) followed by consequent expansion and distortion of the unit cells. This process of distortion caused by rapid diffusion of alkali atoms is likely to cause the higher reactivity and weakening of the carbon structure. This work is an important step to establish the theory of ionic radii as the reason behind the deterioration of coke properties under the influence of alkaline elements. Further research will be performed in future with a much broader scope for the advancement of understanding in this domain.

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