

EFFECT OF ALKALINE ELEMENTS ON THE REACTIVITY, STRENGTH AND STRUCTURAL PROPERTIES OF BLAST FURNACE COKES

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The present study concerns itself on the adverse effects of alkaline elements like sodium and potassium on blast furnace cokes. To achieve a deeper insight on the effects of alkaline elements on coke reactivity and strength, industrial coke samples impregnated with different alkaline species in various amounts have been tested under standard conditions to find out their Coke Reactivity Index (CRI) and Coke Strength after Reaction (CSR) values. Scanning electron microscopy, petrographic and Raman Spectrometric investigations demonstrate the change of structural properties. The mechanism of catalysis has been postulated.

Key Words: blast furnace cokes, alkali elements, boudouard reaction, CRI and CSR, coke characterization

INTRODUCTION

The properties of different raw materials have great impact on the efficiency and productivity of blast furnace ironmaking process. The operational requirements of raw materials are significantly deteriorated in presence of very small amount of alkalis. Alkaline elements like sodium (Na) and potassium (K) have been marked as detrimental 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 in turn lead to furnace irregularities resulting in lower productivity and economic loss. The major sources of alkalis 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 various amounts of potassium on Boudouard Reaction under laboratory conditions [1, 2, 4].

The aim of this study is to evaluate the effect of both sodium and potassium on coke reactivity and strength under standard conditions and further investigation of the structural change of coke samples by different methods of characterization.

METHODOLOGY

Artificial Alkali Impregnation

Three different industrial coke samples (C1, C2 and C3) were used for the purpose of experiments. The

proximate analysis of the coke samples are shown in Table 1.

Table 1 Proximate analysis / 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 |

The coke samples were artificially impregnated by alkalis by leaching in different alkaline solutions (NaOH or KOH) containing the respective alkaline species.

The coke pieces submerged in the solution were 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.

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

Table 2 Alkali content ranges

| Nomenclature | Artificially added Na or K |
|-----------------------|----------------------------|
| No added alkali | 0 % |
| Medium alkali content | 0,6 – 1 % |
| High alkali content | 1,5 – 2 % |

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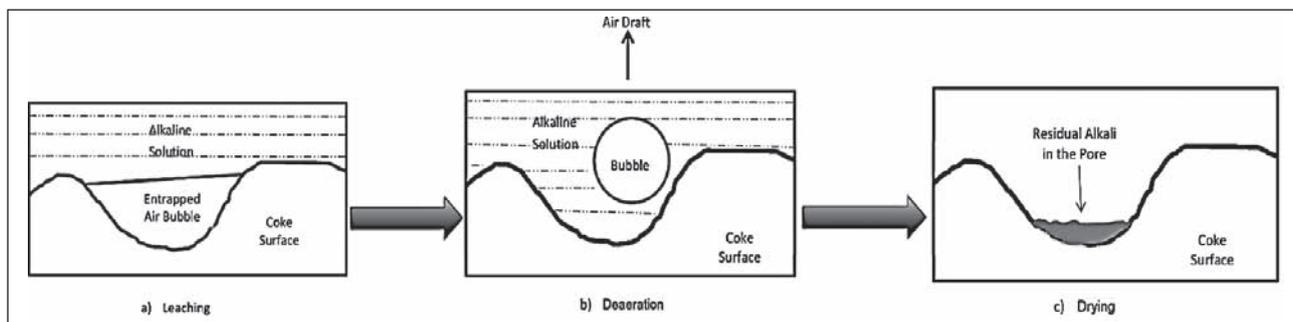
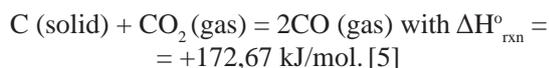


Figure 1 Steps of alkali impregnation (schematic)

CRI and CSR 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 conditions. For CRI, a test portion of the dried coke sample (200 ± 3 g) having a size range from 19,0 mm to 22,4 mm is heated in a reaction vessel to 1100°C in a nitrogen atmosphere. For the test, the atmosphere is changed to carbon dioxide for exactly 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 about 50°C 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. [6]

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).

RESULTS AND DISCUSSIONS

The CRI and CSR values of all three samples (without added alkali) agree with normally required values for industrial blast furnace operations. However, with little added alkali, enormous increase in CRI and decrease in CSR has been observed in all cases. The effect of sodium on lowering the CSR is observed to be stronger than that of potassium. The results are depicted in four separate bar diagrams in Figure 2.

Organic Petrology

The microstructures (investigated for C1 and C3) show a large variety (Figure 3). During the experiments, vitrinite fuses to diverse mesophase structures. The presence of mesophase particles in untreated samples demonstrate that this transformation has already started

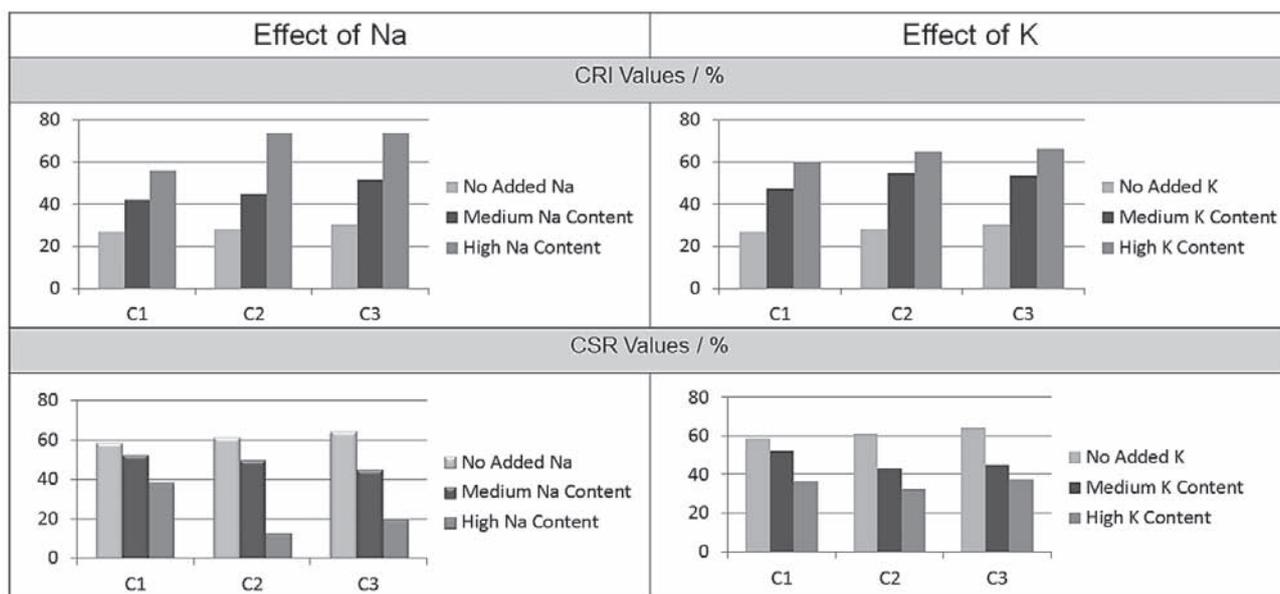


Figure 2 CRI and CSR Values

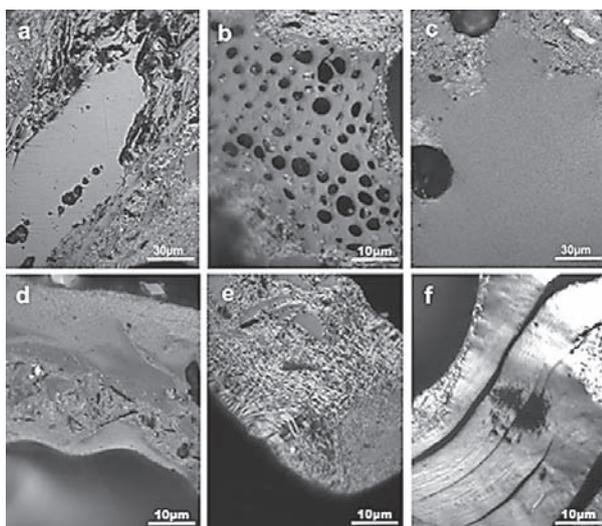


Figure 3 Microstructure of the investigated coke samples (a= large fused (isotropic) particle in fine and lenticular anisotropic matrix, b= fused vitrinite with degassing pores, c= fused vitrinite with degassing pores, c= incipient anisotropy, d= decomposition of vitrinite into an anisotropic matrix at a pore contact, e= lenticular anisotropy developing out of a circular Anisotropy, f= graphitized lamella with undulose darkening)

during coking. During the experiment, coke porosity increases by the disintegration of the coke matrix. Simultaneously the microstructural composition of the carbonaceous matter changes independently from the parent samples. Homogeneous particles evolve to granular and lenticular particles.

Raman Spectrometry

As shown by Raman Spectroscopy [7], there is a major change of the bulk microstructure of the alkali treated samples during CRI test, whereas the untreated sample shows only minor changes. This is accompanied by the evolution of the coke porosity. The data of this study suggests that the microstructural evolution of the coke components (macerals) remains unaffected by alkali treatment. The transformation of these components is more probably temperature controlled.

Scanning Electron Microscopy

The scanning electron microscopy (SEM) of representative untreated and treated samples was performed using Quanta 200 Mk2 (Manufacturer – FEI Company) and an attached Energy Dispersive X-Ray spectroscopy (EDX) device (INCA Energy 200, Oxford Instruments). SEM/EDX analyses of various alkali treated samples (after reaction) show fused aggregates (complex oxides) of alumina and silica containing Na and K, frequently scattered over the coke matrix. This type of structure is not observed in reacted samples without additionally added alkali. These aggregates have been

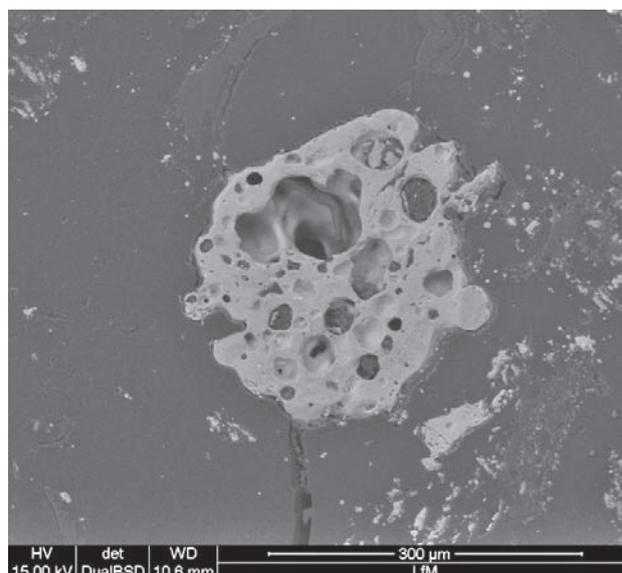


Figure 4 SEM image showing fused aggregate of $KAlSiO_4$ on the dark coke matrix

generated by local fusion of the ash (which consists of basically alumina and silica) caused by alkaline oxides (by lowering the melting point). The phases ($NaAlSiO_4$ and $KAlSiO_4$) have been confirmed by X-Ray Diffraction (XRD) of reacted alkali treated samples. Figure 4 shows a microscopic image of reacted and potassium treated coke sample.

Apart from mechanical weakening, alkali treated and reacted coke samples generate a lot of fines during tumbling. All of these phenomena can be explained as a result of local fusion caused by lowering of the melting temperature of the ash phase by alkaline elements which may generate internal stress in the structure and subsequently make the structure weak.

Catalysis of Boudouard Reaction: Hypothesis on the Theory of Ionic Radii

No chemically stable (or metastable) intermediate catalytic phase was found by SEM/EDX and XRD analysis. However, various literatures confirm XRD peak broadening, i.e. change of lattice parameters of organic crystals treated with alkali [3, 8]. On the other hand, the degradation of hematite pellets under alkaline influence has been explained in terms of the ionic radii of the concerned elements [9]. Table 3 demonstrates effective ionic radii of Na^+ , K^+ and C^{4+} .

Table 3 **Effective Ionic Radii / nm [10]**

| Elements | Na+ | K+ | C4+ |
|-------------|-------|-------|-------|
| Ionic Radii | 0,102 | 0,138 | 0,016 |

The ionic radius of carbon is much smaller than that of sodium or potassium. At higher temperatures (1 100 °C and above), pronounced lattice disturbance 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.

CONCLUSIONS

Both sodium and potassium, when present in very little amounts, bring a tremendous change to the CRI and CSR. On one hand, reactivity increases steeply and on the other hand, the coke becomes more and more weak. In actual blast furnace process, higher alkali input increases the coke consumption rate, causing economic loss and also lower the stability of the burden resulting in various operational irregularities. The effect of sodium on lowering the CSR is somewhat stronger than that of potassium. Cokes with higher porosities pick up more alkali when leached. Also in industrial process cokes with more porosity will pick up more alkali from the system, hence making it weaker. Local fusion caused by lowering of the melting temperature of the ash phase by alkaline elements is likely to generate internal stress in the structure and subsequently make the structure instable.

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