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Improvement of coke strength after reaction value (CSR) by spraying boron solutions on metallurgical coke

Metalürjik koka bor solüsyonları püskürtülerek reaksiyon sonrası kok mukavemeti değerinin (CSR) geliştirilmesi

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Abstract

In the Coke Plant of KARDEMIR, coking coal is charged to the furnaces, the hot coke is obtained after 18-21 hours of coking is discharged to the quenching wagon via the guide car with the help of the pusher machine. The hot coke is quenched by water spraying in the quenching towers and is poured into the coke ramp. The metallurgical coke is sized in the Coke Crushing and Screening Plant and sent to the blast furnaces. In the blast furnace process, the use of metallurgical coke with high CSR values obtained from high quality coking coals is preferred. In the blast furnace process, it is preferred to use metallurgical coke with CSR values in the range of 60-70% obtained from high quality coking coals. However, the reserves of high quality coal beds are decreasing day by day. In this study, it is aimed to increase the CSR value of metallurgical coke by spraying various concentrations of boron solutions in order to obtain the same efficiency from low quality coals. In this way, low quality coals in the coal blend in metallurgical coke production will be used at higher rates and raw material costs will be reduced. Solutions prepared with three different boron products and various concentrations were applied to the hot coke obtained at 1050±50 °C in coke ovens, and its effects on the alteration of coke strength after reaction (CSR) values were investigated. When the coke reactivity test results of the applications were examined, it was observed that there was a 20-48% improvement in the CSR value of the coke samples with boron solution compared to the coke samples quenched by spraying water. A 46.29% increase in CSR value and a 34.92% decrease in CRI value of the hot coke sample, which was quenched with 7 g/l concentration Disodium Octaborate Tetrahydrate solution giving the optimum value, was determined.

Keywords: Metallurgical coke, Boron, Coke reactivity, Blast furnace, Coke oven plant.

Öz

KARDEMİR Kok Fabrikalarında koklaşabilir kömür fırınlara şarj edilmekte, 18-21 sa.'lik koklaşma sonrasında elde edilen kızgın kok itici makina yardımı ile kılavuz arabası üzerinden söndürme vagonetine boşaltılmaktadır. Kızgın kok, söndürme kulelerinde su püskürtülerek söndürülmekte ve kok rampasına dökülmektedir. Metalürjik kok, kok kırma eleme tesisinde boyutlandırılarak yüksek fırınlara sevk edilmektedir. Yüksek fırın prosesinde kaliteli koklaşabilir kömürlerden elde edilen CSR değerleri yüksek metalürjik kok kullanımı tercih edilmektedir. Yüksek fırın prosesinde, kaliteli koklaşabilir kömürlerden elde edilen CSR değerleri %60-70 aralığında olan metalürjik kok kullanımı tercih edilmektedir. Fakat kaliteli kömür yataklarının rezervleri gün geçtikçe azalmaktadır. Bu çalışmada, düşük kalitedeki kömürlerden aynı verimi elde etmek için metalürjik koka çeşitli derişimlerde bor solüsyonları püskürtülerek CSR değerinin artırılması amaçlanmaktadır. Bu sayede metalürjik kok üretiminde kömür harmanı içerisinde düşük kalitedeki kömürler daha yüksek oranlarda kullanılabilecek ve hammadde maliyeti düşürülmüş olacaktır. Kok fırınlarında 1050 ± 50 °C sıcaklıkta elde edilen kızgın kok üzerine üç farklı bor ürünü ile çeşitli derişimlerde hazırlanan çözeltiler uygulanarak reaksiyon sonrası kok mukavemetindeki (CSR) değişiklikler üzerine etkileri incelenmiştir. Gerçekleştirilen uygulamaların kok reaktivite test sonuçları incelendiğinde, bor çözeltisi uygulanmış kok numunelerinin su püskürtülerek söndürülen kok numunelerine göre CSR değerinde %20-48 iyileşme olduğu gözlenmiştir. Optimum değeri veren 7 g/l derişimli Disodyum Oktaborat Tetrahidrat çözeltisi ile söndürülen kızgın kok numunesinin CSR değerinde %46.29 artış, CRI değerinde %34.92 azalış tespit edilmiştir.

Anahtar kelimeler: Metalürjik kok, Bor, Kok reaktivite, Yüksek fırın, Kok fabrikaları.

1 Introduction

The process of heating bituminous coal in an airless environment, losing its volatile substances, leaving a solid and well-cooked hard product is called coking. The product with a hard, porous sponge structure and high carbon content remaining after the volatile substances are removed from the coal is called coke [1].

Due to its chemical and mechanical properties, coke is one of the most important and expensive raw material inputs among the charging materials used as a reductant during iron production in blast furnaces.

Chemical and physical properties of coke affect blast furnace operating conditions, hot metal quality and fuel consumption. Coke constitutes 55% of the total volume of the blast furnace and 75% of the reaction zone [1]-[4].

The main functions of coke in the blast furnace;

- *Calorific*; to provide some of the heat required for the melting of iron ores and slag as well as the reduction of iron ore by reacting with the O_2 in the hot air blown from the tuyeres,

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- *Chemical*; to produce reducing gases in the furnace by reacting with O_2 and CO_2,
- *Mechanical*; to create a permeable zone to allow iron and slag to descend to the lower zone of the furnace and at the same time to allow the flow of reducing gases towards the upper zone of the furnace [1],[2],[5]-[7].

Coke is a very important energy input in the blast furnace process. With the improvement in the CSR values of coke; the resistance of coke to combustion in the blast furnace will be increased, the combustion reaction will be slowed down and the amount of coke to be charged in the furnace will decrease. As the amount of coke consumed per ton of hot metal produced in the blast furnace decrease, production and consumption costs will also be reduced.

In Blast Furnace operation, it is always preferred to use metallurgical coke, which is obtained from quality coals and has high CSR values. In order to obtain the same efficiency from lower-quality coals, the CSR value of the metallurgical coke should be improved.

Tamko VA. et al. found that quenching coke with sodium tetraborate solution ($Na_2B_4O_7{\cdot}5H_2O$) led to a good improvement in qualitative properties (CRI and CSR). In this case, they observed that coke strength after reaction (CSR) increased by 18.8%, while the reactivity index (CRI) decreased by 13.2% [8].

Musiiwa A. focused on evaluating coke qualities from blends that contained increased proportions of Grootegeluk blend coking coal (GG), ranging from 31% and incrementally up to 40 %. In each case, samples of the resultant coke products were split into separate sub-samples, with one sub-sample quenched using normal water. In contrast, another sub-sample was quenched with water containing sodium tetraborate solution. Results showed that for each blend with an incrementally increased proportion of GG coal, the coke strength properties improved by 17% when the borate solution quenched the sub-sample [9].

Alekseevich YY, it becomes obvious that the most simple and cheap method of improving coke quality is post-furnace treatment with borate solutions. An analysis of the data showed that during the processing of blast furnace coke with a solution of tetraborates, the coke strength after the reaction (CSR) increased by 5-11.2% abs. or 26.5% rel. about the CSR of the original coke. The reactivity index (CRI) at the same time decreased by 3-6.7% abs. or 17.5% rel. [10].

Viktorovich SP. proposed a process for preparing high-quality coke from different blends that coke with a temperature of 1050±50 °C after issuing the furnaces is quenched in the quenching car with the aqueous solution containing 3-10 g/dm^3 borate. The coke strength after the reaction (CSR) increased by 9.4-13.1% rel. and the reactivity index (CRI) at the same time decreased by 5.3-11.9% rel. about the original coke [11].

Zolotaryov IV. et al. study results, show that after post-furnace processing of samples of blast-furnace coke with water solution of $Na_2B_4O_7$ containing SAC, CRI index decreases by 3.8-6.8%, and CSR index increases by 7.5-10.6% [12].

In this study, solutions prepared with three different boron products and various concentrations were applied to the hot coke obtained at 1050 ± 50 °C in coke ovens, and its effects on the alteration of coke strength after reaction (CSR) values were evaluated.

2 Experimental studies

2.1 Preparation of solutions

Boron solutions were prepared in the laboratory of KARDEMIR R&D Center using different pure boron products obtained from ETİ MADEN (Sodium Tetraborate Decahydrate, Disodium Octaborate Tetrahydrate, Sodium Tetraborate Pentahydrate) and pure surfactants obtained from BASF Chemistry (Fatty Alcohol Alkoxylate).

Boron products were weighed on precision scales with a concentration of 5 g/l, 7 g/l and 10 g/l in the solution content and added to 1 liter of water together with the surfactant (Figure 1). For the solution to be homogeneous, the boron products were mixed at a certain temperature in a heated magnetic stirrer until dissolved.

Three different boron products were used for each solution with different concentrations.

The required amount of solution was calculated according to the coke-spraying water ratio used in the quenching towers of the KARDEMIR Coke Plant.

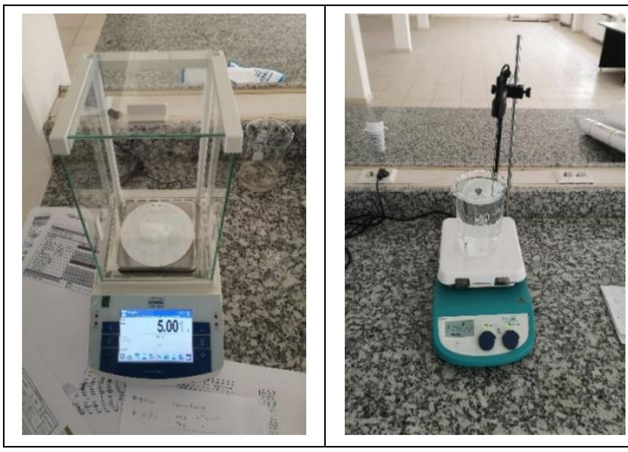


Figure 1. Preparation of solutions; weighing on precision balance and mixing on magnetic stirrer with heater.

2.2 Quenching of hot coke

Coking coal is charged to the furnaces. The hot coke is obtained after 18-21 hours of coking and is discharged to the quenching wagon via the guide car with the help of the pusher machine.

The determined amount of hot coke was taken on the sheet metal for the application of solutions (Figure 2). The hot coke sample was divided into four parts; one part of the hot coke was quenched with water and the other parts with a solution prepared with different boron products (Figure 3).

2.3 Preparation of samples

During operation at the KARDEMIR Coke Crushing and Screening Plant, the metallurgical coke was sized and sent to the Blast Furnaces. In order to simulate the same conditions; Test samples, which were prepared in the quality laboratory at the crushing-screening facility with a size of +19-22.4 mm (Figure 4), were sent to the laboratory for reactivity tests.


Figure 2. The hot coke was taken on sheet metal.


Figure 3. The moment of application of boron solution to the hot coke.


Figure 4. Preparation of coke samples for reactivity tests.

2.4 Coke quality and CSR/CRI tests

The quality of coke is determined by various physical and chemical tests. In addition, CSR and CRI tests are used for reactivity determination.

In addition to the determination of moisture, ash, volatile matter, sulfur in coke, particle size, calorie, swelling index and fluidity tests are also carried out.

The CSR test is a laboratory test designed to determine an indicator of coke strength after exposure to the reducing atmosphere of a blast furnace. After the coke is exposed to the high temperature and carbon dioxide atmosphere of the reactivity test, 600 cycles are performed at 20+1 rpm in the drum specified in the ASTM D5341M-19 Standard [14] to determine its strength. The resulting coke is sieved through a 9.5 mm sieve and its ratio to the CSR of the sample on the sieve is calculated. The CSR value is between 55-60% and it is preferred over 60% [14]. The CSR value is affected by three main factors: coke surface area, coke chemistry and coke carbon structures [15].

The CRI test is a laboratory test designed to simulate the loss of coke through reaction in a reducing atmosphere as metallurgical coke travels down the blast furnace. The coke is heated to 950°C in an inert atmosphere and kept at this temperature in an atmosphere of carbon dioxide. The coke is cooled under an inert atmosphere and the weight loss rate expressed as a percentage gives the reactivity index [14].

2.5 Scanning electron microscopy (SEM)

After the metallographic preparation of the quenched cokes, their microstructure analyses have been conducted by using Zeiss Ultra Plus model SEM device. Energy-Dispersive X-ray Spectroscopy (EDS) analyses and mapping processes have been conducted from certain zones during the SEM analyses.

3 Results and discussion

Experimental studies were carried out by blending coals taken from different regions. The coal blend distribution in which the site application was carried out is given in Table 1.

Table 1. Coal blend distribution.

Coking Coal (Country)	Blend Distribution (%)
Türkiye	10
Russia	25
Australia	30
USA	35

- Comparison of hot coke samples quenched by spraying water and 5 g/l boron solutions,
- Hot coke sample quenched with Sodium Tetraborate Decahydrate solution; 33.87% increase in CSR value and 26.10% decrease in CRI value,
- Hot coke sample quenched with Disodium Octaborate Tetrahydrate solution; 25.59% increase in CSR value, 22.96% decrease in CRI value,
- Hot coke sample quenched with Sodium Tetraborate Pentahydrate solution; 28.71% increase in CSR, 23.62% decrease in CRI value.

When the results in Figure 5 were evaluated, optimum % CSR and % CRI values were reached with Sodium Tetraborate Decahydrate solution.

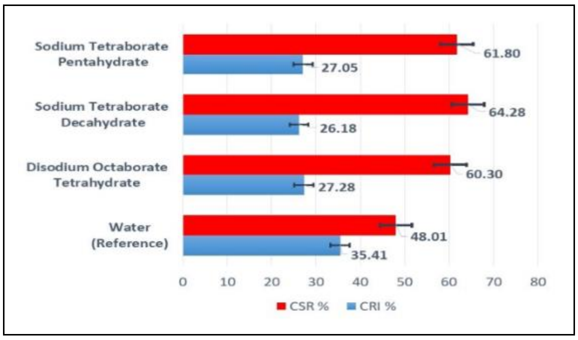


Figure 5. % CSR and % CRI values of solutions prepared using different boron products with a concentration of 5 g/l and water-quenched coke samples.

Comparison of hot coke samples quenched by spraying water and 7 g/l boron solutions;

- Hot coke sample quenched with Sodium Tetraborate Decahydrate solution; 37.54% increase in CSR value and 31.96% decrease in CRI value,
- Hot coke sample quenched with Disodium Octaborate Tetrahydrate solution; 46.29% increase in CSR value, 34.92% decrease in CRI value,
- Hot coke sample quenched with Sodium Tetraborate Pentahydrate solution; 31.71% increase in CSR, 29.36% decrease in CRI value.

When the results in Figure 6 were evaluated, optimum % CSR and % CRI values were reached with Disodium Octaborate Tetrahydrate solution.

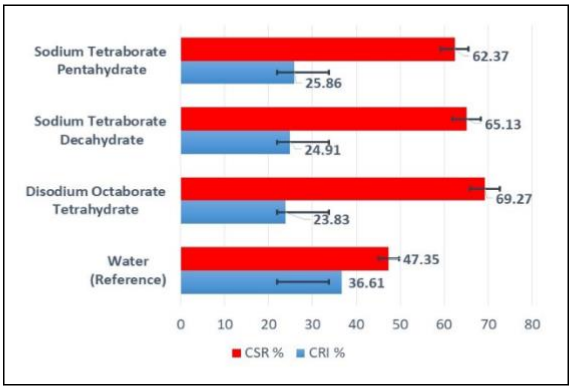


Figure 6. % CSR and % CRI values of solutions prepared using different boron products with a concentration of 7 g/l and water-quenched coke samples.

Comparison of hot coke samples quenched by spraying water and 10 g/l boron solutions;

- Hot coke sample quenched with Sodium Tetraborate Decahydrate solution; 31.20% increase in CSR value and 29.03% decrease in CRI value,
- Hot coke sample quenched with Disodium Octaborate Tetrahydrate solution; 33.13% increase in CSR value, 28.80% decrease in CRI value,
- Hot coke sample quenched with Sodium Tetraborate Pentahydrate solution; 39.14% increase in CSR, 30.55% decrease in CRI value.

When the results in Figure 7 were evaluated, optimum % CSR and % CRI values were reached with Sodium Tetraborate Pentahydrate solution. It is thought that borate solutions form a film layer covering the coke surface and delay the reaction by clogging the surface pores, thus providing improvements in CSR value. [3],[10]-[17].

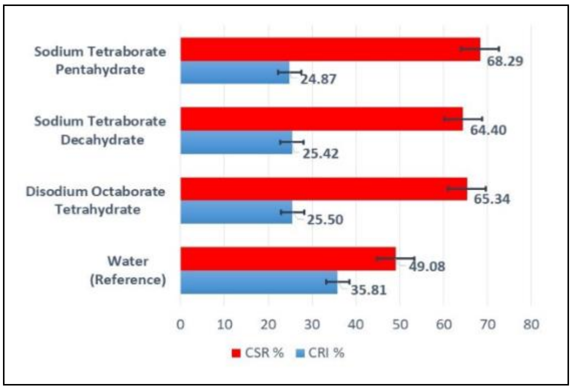
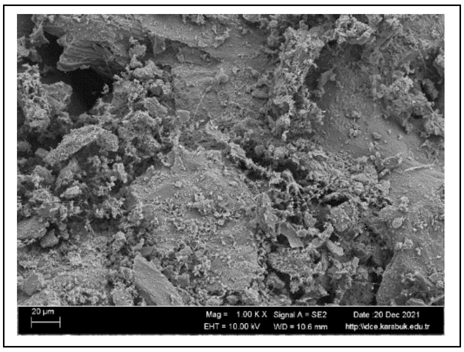
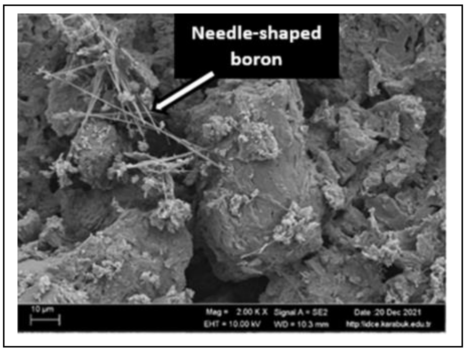


Figure 7. % CSR and % CRI values of solutions prepared using different boron products with a concentration of 10 g/l and water-quenched coke samples.

SEM images of the coke sample quenched with 7 g/l Disodium Octaborate Tetrahydrate solution are given in Figure 8. When the SEM images have been examined, it is seen that the boron is homogeneously dispersed and covers the pores in the coke samples quenched with 7 g/l Disodium Octaborate Tetrahydrate solution.



(a)



(b)

Figure 8. Different magnification SEM image of the coke sample quenched with Disodium Octaborate Tetrahydrate solution at a concentration of 7 g/l. (a): 1000X and (b): 2000X.

SEM and EDS analyzes were performed to examine the elemental distribution on the coke sample treated with the 7 g/l Disodium Octaborate Tetrahydrate solution. EDS (Table 2) and mapping analysis (Figure 9) prove the homogeneous distribution of boron elements.

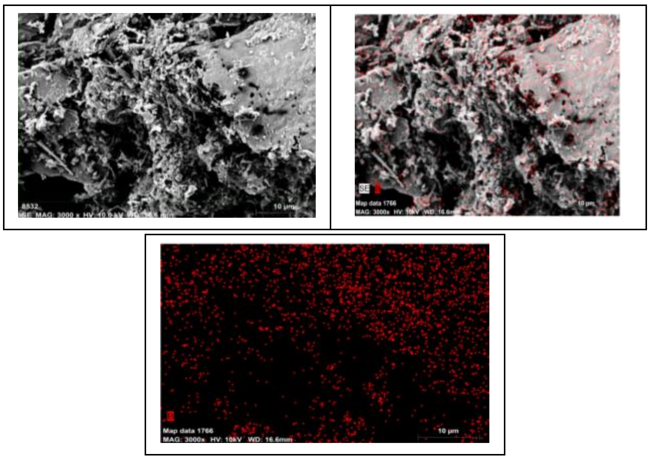


Figure 9. Mapping analysis of the coke sample quenched with Disodium Octaborate Tetrahydrate solution at a concentration of 7 g/l.

That is, the boron ratio at 3 points taken over the microstructure was measured as 11.95%, 13.07% and 14.93%, respectively (Figure 10 and Table 2). It is thought that the needle-shaped boron structure seen in Figure 8b penetrates the coke pores and provides a more resistant structure against the applied loads.

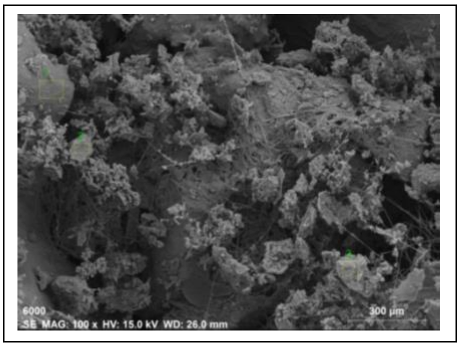


Figure 10. Three different EDS points of coke sample quenched with 7 g/l Disodium Octaborate Tetrahydrate solution.

Table 2. EDS distributions of coke sample quenched with 7 g/l Disodium Octaborate Tetrahydrate solution.

Spectrum (%mass)	B (%) Boron	C (%) Carbon	O (%) Oxygen
1.	11.95	74.92	13.13
2.	13.07	72.08	14.85
3.	14.93	56.48	28.59
Mean Value	13.32	67.83	18.86

4 Conclusions

In this study, the solutions were prepared at 5 g/l, 7 g/l, and 10 g/l concentrations using three different boron products. The analysis of water and boron solution quenched coke samples were made and analysis was done according to ASTM D5341M-19 [13]. As a result, the optimum value was reached with the "Disodium Octaborate Tetrahydrate" solution with a concentration of 7 g/l.

In the SEM and EDS analyses, it was considered that the sprayed boron solutions penetrated the coke pores in needle form, thus providing a more resistant structure against the applied loads. Therefore, these improvements in the CSR value were realized.

As an alternative to quenching with water, an increase was observed in the %CSR values of all of the coke samples quenched with boron solutions. It is predicted that this increase will improve the coke strength and contribute to reducing the problems arising from the coke movements in the blast furnace, coke wear, coke cracking, and the physical properties of coke, which are closely related to the blast furnace regime.

5 Acknowledgment

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6 Author contribution statements

In the scope of this study, Fatih ESİN and Engin ÇEVİK in the formation of the idea, the design, the literature review, SEM-EDS analysis and evaluation; Onur ACUR, Fatih ESİN, Berkman İŞÇİ, Caner CANTÜRK and Cansu BESUN have been involved in the application of experimental steps for both bench-scale and semi-pilot stages in order to obtain coke samples, supplying the materials used in the study, discussed the results and contributed to the writing of the paper.

7 Ethics committee approval and conflict of interest statement

There is no need to obtain permission from the ethics committee for the article prepared.

There is no conflict of interest with any person / institution in the article prepared.

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