

Effect of Al₂O₃ content on alkali holding capacity of blast furnace slag and related liquids

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Abstract: Alkali circulation phenomena create complex problems in the blast furnace leading to lowered production efficiency. Improving alkali holding capacity of liquid slags evolving from the cohesive zone and finally forming the blast furnace slag will reduce these problems. Effect of Al₂O₃ content on alkali holding capacity of synthetic slags in a part of system SiO₂-CaO- Al₂O₃-K₂O-FeO and modified blast furnace slag were tested with laboratory experiments. Slag samples with constant K₂O content, constant or no FeO addition, and varied Al₂O₃ contents, were heated in graphite test tubes at 1460 °C for 90 minutes in Ar gas atmosphere containing a small amount of CO gas. After rapid quenching of the liquids the usually homogenous glass samples were analyzed with SEM. The amount of K₂O retained was taken for the measure of the alkali holding capacity.

Samples with high basicity (CaO/SiO₂ ratio) had lower alkali holding capacity than those with lower basicity. Increasing the Al₂O₃ content of the slags was observed to increase the alkali holding capacity for all slags tested in the experiments. Thermodynamic calculations also indicated that higher Al₂O₃ contents will reduce alkali gasification from the liquid slags concerned. Increasing the reduction degree of the iron burden in solid state and increasing the Al₂O₃ content of the iron burden can decrease the alkali circulation related problems in the blast furnace.

Keywords: Blast furnace, slag, alkali holding capacity, laboratory tests, thermodynamic calculations

1. Introduction

Alkali circulation phenomena create complex problems in the blast furnace leading to lowered production efficiency.^[1-5] These elements are not totally captured in the liquids in the high temperature area, but released in a gas phase, blown upwards and condensed as different phases in iron burden and coke as the temperature decreases. The alkalis promote low temperature and wide interval melting of the slag-formers, which is unfavorable for the operation and productivity of the blast furnace resulting gas flow irregularities, problems in indirect reduction, thermal balance etc. in the upper shaft. Alkalis also attack on and destroy the lining materials and are one of the most impressive scaffold-building components. The scaffolds decrease the effective production volume of the furnace and also cause disturbance on the descending of the burden. One serious problem is the degradation of the coke by alkalis incorporating into the structure of the coal. This decreases the coke quality by decreasing the coke strength and reactivity.

In order to avoid the circulation, it is essential to improving alkali holding capacity of liquid slags evolving from the cohesive zone and finally forming the blast furnace slag. This requires high alkali solubilities in the slag as well as prevention of the alkali being gasified to a larger extent even in the high temperatures of the tuyere zone .

The alkali capacities and effect of composition on the capacity has been investigated widely. ^[6-9] The purpose of this study was to investigate the effect of Al₂O₃ content on the potassium holding capacity of liquid FeO containing blast furnace slag and synthetic Al₂O₃-CaO-SiO₂-K₂O-FeO slags with different basicities in contact with carbon. The influence of Al₂O₃ was investigated with laboratory experiments and computational thermodynamics.

2. Methodology

2.1 Sample preparation

Industrial blast furnace slag and synthetic slags were used as test materials. The blast furnace slag was water quenched granules from Ruukki Oyj, Raahe Steel plant (year 2003). Analyse grade oxide chemicals (Merck; CaO, SiO₂, Al₂O₃, K₂CO₃ and FeO) were used to prepare the modified blast furnace slag and synthetic slag mix for the test. As can be noticed K₂O was added as K₂CO₃. Totally 10 grams of slag (K₂O basis) was used in each laboratory test.

Chemical compositions of the blast furnace slag and modified blast furnace slags (BSF60 and BSF90) are expressed in Table 1. For the BSF60 and BSF 90 series, where 60 and 90 refer to the isothermal holding time, BF slag and K₂O tells the share of the slag and K₂O, respectively. Al₂O₃ tells the calculated content of Al₂O₃ after Al₂O₃ and K₂O additions. The share of FeO (+FeO 30 %) was ignored in the calculations, because FeO was reduced to metallic iron during the tests and the FeO content of the slags decreased typically very close to zero.

Table 1. Chemical composition of the blast furnace slag and BSF60 and BSF90 mixtures used.

Component	K ₂ O	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	Ti	Mn	V	S	SUM	B
w-%	0,70	0,82	9,79	8,72	36,20	39,80	1,14	0,50	0,05	1,43	100	1,10
BSF 60	BF Slag	Al ₂ O ₃	K ₂ O	+FeO	BSF 90			BF Slag	Al ₂ O ₃	K ₂ O	+FeO	
w-%	90,00	7,85	10,00	30,00				w-%	90,00	7,85	10,00	30,00
w-%	90,00	11,43	10,00	30,00				w-%	90,00	11,43	10,00	30,00
w-%	90,00	13,05	10,00	30,00				w-%	90,00	13,05	10,00	30,00
w-%	90,00	14,67	10,00	30,00				w-%	90,00	14,67	10,00	30,00

Chemical compositions of the synthetic slag mixtures are expressed in Table 2. The share of FeO (+FeO) was ignored, because of FeO reduction to metallic iron in test conditions leading to the decrease of the FeO content of the slags close to zero.

Table 2. Chemical composition of the synthetic slags used.

Sample	SiO ₂	CaO	Al ₂ O ₃	K ₂ O	SUM	B	+FeO
A10	56,70	24,30	9,00	10,00	100	0,43	0
A15	53,55	22,95	13,50	10,00	100	0,43	0
A20	50,40	21,60	18,00	10,00	100	0,43	0
B10	48,60	32,40	9,00	10,00	100	0,67	0
B15	45,90	30,60	13,50	10,00	100	0,76	0
B20	43,20	28,80	18,00	10,00	100	0,67	0
C10	44,55	36,45	9,00	10,00	100	0,82	0
C15	42,08	34,43	13,50	10,00	100	0,82	0

C20	39,60	32,40	18,00	10,00	100	0,82	0
E10F	40,50	40,50	9,00	10,00	100	1,00	30,00
E15F	38,25	38,25	13,50	10,00	100	1,00	30,00
E17F	37,35	37,35	15,30	10,00	100	1,00	30,00
E20F	36,00	36,00	18,00	10,00	100	1,00	30,00
E24F	34,20	34,20	21,60	10,00	100	1,00	30,00
F16F	34,02	41,58	14,40	10,00	100	1,22	30,00
F20F	32,40	39,60	18,00	10,00	100	1,22	3,00

2.2 Experimental tests

Each slag sample was put in a test tube made of pure microcrystalline graphite. The height and inner diameter of the tubes were 60 mm and 12 mm, respectively. Four graphite tubes were put in a time inside a sample container made of Mg-Al-spinel. The bottom of the container had holes to allow gas flow. The container was covered with a spinel plate having hole for gas outlet and thermocouple inlet enabling temperature measurement between the graphite tubes. This part of the experimental arrangement is seen in the Figure 1.

A vertical high temperature tube furnace having 75 mm inner diameter corundum tube was used for the tests. Inside the tube at the high temperature zone of the furnace a perforated corundum plate was mounted for a stable resting level for the sample container. The sample container with four graphite test tubes at a time was laid down on the resting level. The furnace was heated with a heating rate of 10 °C per minutes up to 800 °C, 6 °C per minutes up to 1150 and 3 °C per minutes up to the target temperature, 1460 °C, and kept isothermal for the targeted time, 60 or 60 minutes. 3 l/min gas flow, containing 99 % Ar (purity 99.9996) and 1 % CO from bottom to top was used during the experiments.

When the targeted holding time was reached, the sample container was quickly elevated out of the furnace and exterior of each graphite tube was quickly water quenched. The quenching took typically 20-30 seconds leading in most cases to completely glassy structure for the slag.

After the quenching, each graphite tube, having the slag inside, was enclosed in epoxy, longitudinally cross-sectioned and polished for microscope studies and scanning electron microscope (SEM) analysis. Two examples of cross-sectioned, but not polished graphite tubes are seen in Figure 2.

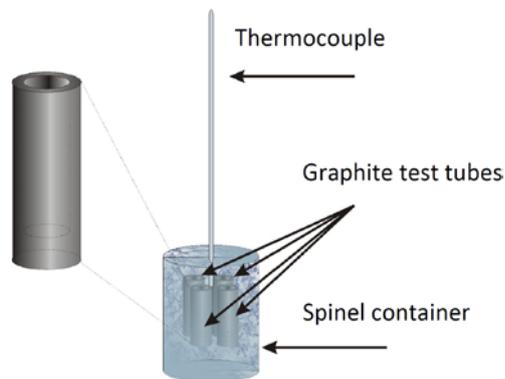


Figure 1. A part of the test arrangement. Four graphite test tubes inside a sample container made of spinel. Temperature measurement arranged with thermocouple between the test tubes.

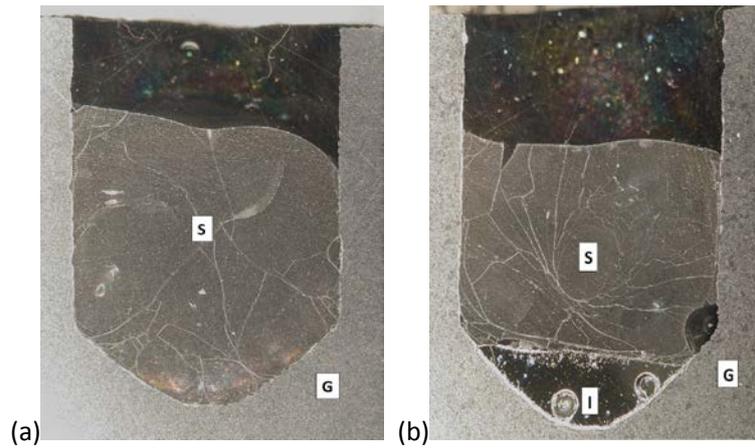


Figure 2. Longitudinal cross-sections of two blast furnace slag samples before polishing. Slags solidified as glass (a) and glass and metallic iron (b) formed in the contact with graphite. Glass (S), metallic iron (I), and graphite (G).

2.3 Thermodynamic calculations

The equilibrium compositions of the molten slag in contact with either Ar or CO/CO₂ -gas were calculated using a computational thermodynamic software FactSage Version 5.5 and its databases^[10]. The software, its database and its possibilities and restrictions are presented thoroughly elsewhere by the authors of the software^[11], thus making it unnecessary to present the software here. The phases that were considered in the calculations were a gas phase that was assumed to behave ideally, stoichiometric solid compounds from the FactSage's database and a molten slag phase that was considered as a solution containing CaO, Al₂O₃, SiO₂ and K₂O and which was described by models included in the FactSage databases^[10]. The amount of components in the gas phase as well as the amount of stoichiometric compounds were understandably determined by the elements that were considered in the calculations in question. The maximum amounts of the possible components in the system were 32 components for the gas phase and 78 stoichiometric compounds that were considered as invariant phases. Total pressure was constant at 101,3 kPa (1 atm) in all the calculations. The compositions of the systems as well as temperatures for the calculations are presented in Table 3.

Table 3. The compositions of the systems considered in the first part of calculations.

Sample	K ₂ O [w-%]	Al ₂ O ₃ [w-%]	CaO/SiO ₂	Atmosphere	T [°C]
1	10	0 ... 20	The rest with B of 0.8/1.0/1.2	Ar	1450
2	10	0 ... 20	The rest with B of 0.8/1.0/1.2	Ar	1500
3	10	0 ... 20	The rest with B of 0.8/1.0/1.2	Ar	1550
4	10	0 ... 20	The rest with B of 0.8/1.0/1.2	CO and CO ₂ (90%/10%)	1450
5	10	0 ... 20	The rest with B of 0.8/1.0/1.2	CO and CO ₂ (90%/10%)	1500
6	10	0 ... 20	The rest with B of 0.8/1.0/1.2	CO and CO ₂ (90%/10%)	1550

2.4 Scanning electron microscopy

Compositions of the slags were analyzed from the polished samples with Jeol JSM-6400 Scanning electron microscope (SEM-EDS). 10 point analyses, 5 from the central part and 5 from the upper part of each slag sample were

analyzed with 10 μm electron beam spot radius. The samples were carbon coated before SEM analyzing to ensure the electrical conductivity.

3. Results and discussion

Results of the experimental tests are presented in Figure 1 and Figure 2. The contents of K_2O and Al_2O_3 are averages of 10 SEM point analyses from each slag. 5 point analyses were taken from the central part and 5 analyses and from the upper part of each slag sample with 10 μm spot radius. In most cases the content of K_2O was a little bit lower in the central part of the slag possibly indicating, that the slag systems did not reach full equilibrium during the tests.

The content of K_2O was analyzed to be highest in the most acid slag with highest Al_2O_3 content and lowest in the most basic slag with the lowest Al_2O_3 content. It can be seen from Figure 3, that slag basicity is the most affecting factor on the alkali capacity of the synthetic slags tested. Also, the content of K_2O seems to increase as the content of Al_2O_3 increases. The effect is much less intense when compared to the effect of basicity. It must be noticed, that the results of the most basic slags ($B=1.22$, and 1.00) are not directly comparable with the more acid ones ($B=0.82$, 0.67 , and 0.43), because they contained initially 30 % FeO , and were finally equilibrated in contact with iron and carbon.

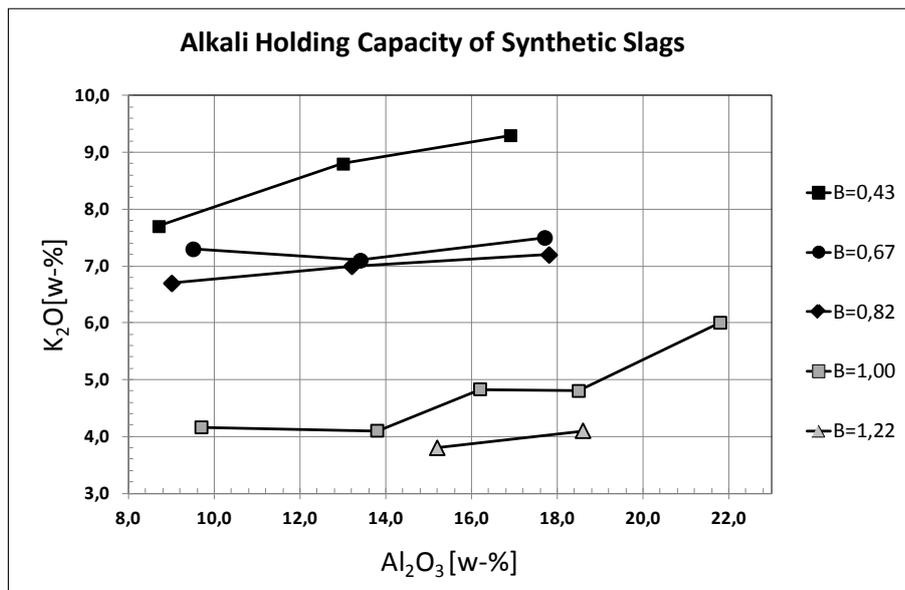


Figure 3. Alkali holding capacity of the synthetic slags. Black markers refers to slags without FeO addition and grey ones to slags containing initially 30 % FeO .

For the blast furnace slags (Figure 4) the content of K_2O seems to increase as a function of Al_2O_3 increase. The slags from experiments with 60 minutes holding times had higher K_2O contents. All tests for blast furnace slag were made for systems contained initially 30 % FeO .

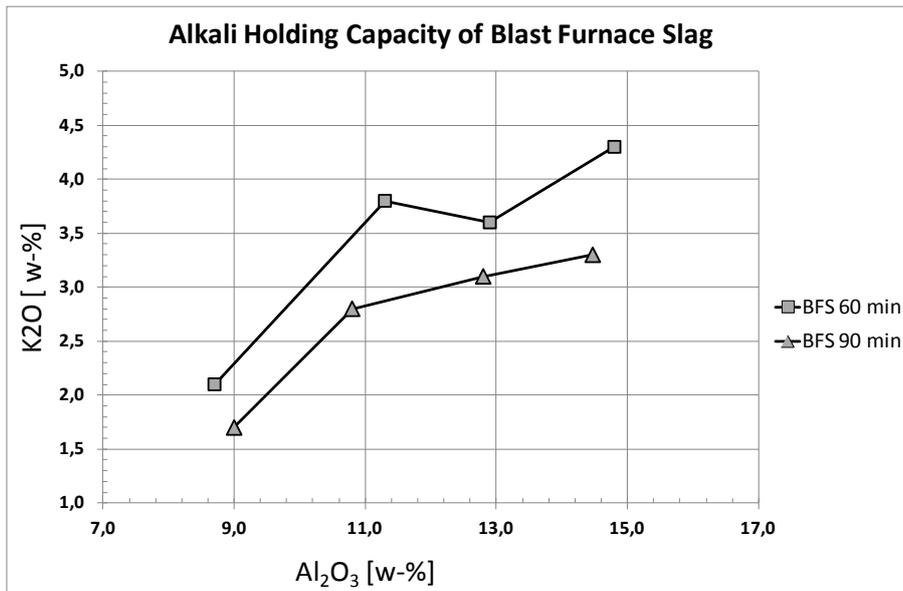


Figure 4. Alkali holding capacity of blast furnace slag. All slags contained initially 30 % FeO.

The results of the thermodynamic calculations in equilibrium with Ar and CO/CO₂-gas with a ratio of 90/10 are presented in Figures 5 and 6, respectively. In both cases, it seems, that the equilibrium amount of K₂O in the slag is decreased with increasing temperature and increasing slag basicity. Effect of Al₂O₃ content seems to be much less intense when compared to the effect of basicity and temperature. As a whole the results are in good accordance with the experiments. It is also seen from the Figures 5 and 6 that the amounts of K₂O in equilibrium with CO/CO₂ -gas are approximately one tenth of the amounts of K₂O in equilibrium with argon.

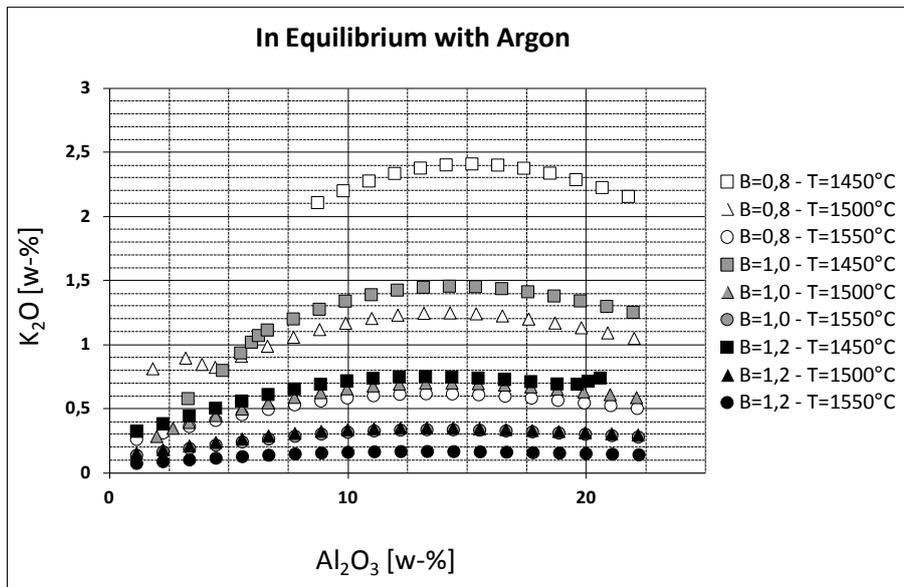


Figure 5. The amount of K₂O as a function of Al₂O₃ content in equilibrium with argon gas.

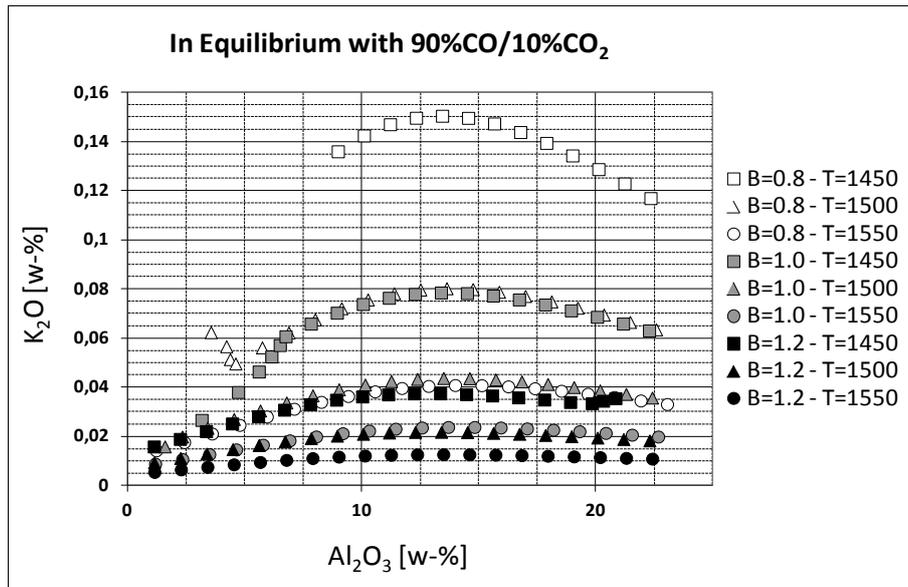


Figure 6. The amount of K_2O as a function of Al_2O_3 content in equilibrium CO/CO_2 -gas with a ratio of 90/10.

Although the experimental tests of this research do not fulfill the strictest requirements of scientific research arrangements, the result show certain general trend which seems to be reasonable and correct. The positive effect of Al_2O_3 increase on the alkali capacity is clear, but not as prominent as the effect of basicity increase. It can be assumed that part of the $(AlO_4)^{5-}$ anions and the charge balancing K^+ cations will couple and act as network formers in the silicate liquid structure partially preventing the gasification of the alkalis and increasing the alkali holding capacity. More testing with longer test times and at different temperatures must be done for samples with or without FeO.

4. Conclusions

Experimental test for synthetic slags and blast furnace slag were made to determine the effect of basicity and Al_2O_3 content on the amount of K_2O remaining in the liquid slags in contact with carbon or iron and carbon at 1460 °C. The amount of K_2O retained was taken for the measure of the alkali holding capacity.

The highest alkali holding capacities were analyzed for the most acid synthetic slag with highest Al_2O_3 content and lowest capacities for the most basic slag with the lowest Al_2O_3 content. The effect of Al_2O_3 increase on the alkali holding capacity was noticed to be less prominent as the effect of basicity increase. For the blast furnace slags the alkali holding capacity seemed to increase as a function of Al_2O_3 increase.

It can be assumed that in the silicate liquids, at least part of the $(AlO_4)^{5-}$ anions and the charge balancing K^+ cations will couple and act as network formers thus preventing the gasification of alkalis and increasing the alkali holding capacity. Increasing the reduction degree of the iron burden in solid state and increasing the Al_2O_3 content of the iron burden and blast furnace slag can decrease the alkali circulation related problems in the blast furnace.

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