

Interaction of molten salts in the systems $\text{SiO}_2\text{-Al}_2\text{O}_3$

(Interação de sais fundidos no sistema $\text{SiO}_2\text{-Al}_2\text{O}_3$)

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Abstract

The aim of this study was to realize and evaluate laboratory corrosion tests for a solution of problems such as wear of refractory materials at processing of aluminum, for example. The static crucible corrosion tests were carried out in laboratory resistive furnace at 850 °C during 2 h air atmosphere. Two standards of alumina-silica shaped refractory bricks were used as a corroding material. Pure sodium chloride and potassium chloride were applied as a corrosive media. The results of tests were evaluated by macroscopic, microscopic, chemical and semiquantitative EDX analysis. Sodium chloride shows more significant penetration and chemical interaction in penetrated area. EDX analysis confirms creation of the reaction layer between chlorides and elements of refractory lining. The products of reactions penetrate more deeply into A lining. K ions penetrate into the grains of the lining more intense than Na ions.

Keywords: chloride melts, static crucible corrosion test, alumina-silica refractory bricks.

Resumo

A finalidade deste estudo foi realizar e avaliar testes de laboratório de corrosão para a solução de problemas tais como desgaste de materiais refratários no processamento de alumínio, por exemplo. Os testes de corrosão estáticos em cadinhos foram feitos em forno resistivo de laboratório a 850 °C durante 2 h ao ar. Dois padrões de tijolos refratários silico-aluminosos foram usados como material sob corrosão. Cloreto de sódio e cloreto de potássio puros foram aplicados como meios corrosivos. Os resultados dos testes foram avaliados por análise EDX semi-quantitativa macroscópica, microscópica, química. O cloreto de sódio mostrou mais significativa penetração e interação química na área penetrada. A análise de EDX confirma a criação de uma camada de reação entre os cloretos e os elementos de revestimento refratário. Os produtos da reação penetram mais profundamente no revestimento A. Os íons potássio penetram nos grãos do revestimento mais intensamente que os íons sódio.

Palavras-chave: cloretos fundidos, teste de corrosão estáticos em cadinho, tijolos refratários silico-aluminosos.

INTRODUCTION

Aluminum is the third most abundant element in the crust of the earth. It makes up about 8% by weight of its solid surface. Aluminum does not occur in metallic form in contrast to other metals (copper, gold, silver). The technology of its production is complicated and it is energy intensive. Aluminum is extracted in two stages. First, relatively pure aluminum oxide is made, and then it is reduced to aluminum in electrolytic process. Obtained aluminum is refined to higher purity in setting furnaces as follows. The refining, covering and drossing fluxes (salts) are used for the covering the surface of melting aluminum in the furnaces in order to reduce the oxidation of melting. To minimize penetration of the atmospheric hydrogen, keep the furnace wall clean from the built up oxides, decrease the content of aluminum entrapped in the dross, remove hydrogen dissolved in the melting, provide aluminum grain refining during solidification, modify silicon inclusions in silicon containing alloys, increasing of recovery and

thermal efficiency are other function of the fluxes.

The aim of this study is monitoring the influence of melting sodium chloride (NaCl) and potassium chloride (KCl) on alumina-silica refractory bricks or lining used in refining and processing of aluminum.

MATERIALS, EQUIPMENTS AND METHODS

Two standards (A, B) of fire-clay (chamotte) aluminum-silica shaped refractory bricks or the lining with varying rate of acid oxide SiO_2 and amphoteric Al_2O_3 were used as corroded material. Their basic chemical composition is in Table I and also can be seen in Fig. 1. Some physical-mechanical properties of both standards are very similar regard to data in Table II. Both standards were analyzed by X-ray diffraction. The results are in Fig. 2. Both linings consist of mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ or $2\text{Al}_2\text{O}_3\cdot \text{SiO}_2$) and amorphous phase based on SiO_2 , generated in thermal process of refractory clay. The diffractograms present mullite as majority phase.

Table I - Chemical composition of refractory lining [1].
 [Tabela I - Composição química do revestimento refratário [1].]

Lining	Chemical phase [wt.%]							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
A	50.00	43.61	1.54	0.82	0.55	0.23	0.20	0.82
B	63.00	26.00	2.00	1.00	1.50	1.00	0.29	1.13

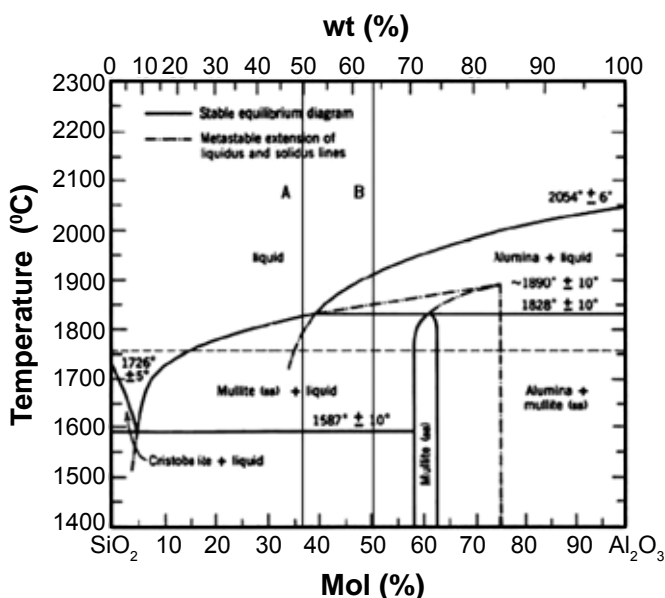


Figure 1: Phase diagram of SiO₂-Al₂O₃ [2].
 [Figura 1: Diagrama de fases de SiO₂-Al₂O₃.]

The refractory lining B consists also of dravite and cristobalite in addition to mullite. The dravite is complex magnesium-sodium borosilicate NaMg₃Al₆(BO₃)₃Si₆O₁₈(OH)₄ crystallizing in trigonal system. It can be ranked among tourmaline mineral group. The mineral cristobalite is a high-temperature polymorph of silica with the same chemical formula, SiO₂, but a distinct crystal structure.

Pure (p.a.) NaCl and KCl (producer LACHEMA, Brno) were used as the corrosive medium. The salts were dried 10 h at 110 °C before application. Some of their basic properties are in Table III.

The results of corrosion tests were evaluated by macroscopic, microscopic, chemical and semiquantitative EDX analysis. The specimens sampled from crucible's wall were observed by optic microscope Neophot 32 in reflected and polarized light and by scanning electron microscope. The penetrations were evaluated by semiquantitative local EDX element analysis using an electron microscope JEOL 35CF (SEM with a LINK AN 10,000 dispersive X-ray analyzer). The crystalline phases of lining were identified in X-ray powder diffractometer DRON 3-M using cobalt radiation.

The interaction of refractory lining and the melting of chlorides were tested by static corrosive crucible (or cup) test. The shaped refractory bricks were cut into prisms about 60 mm × 60 mm × 90 mm with diamond saw. The

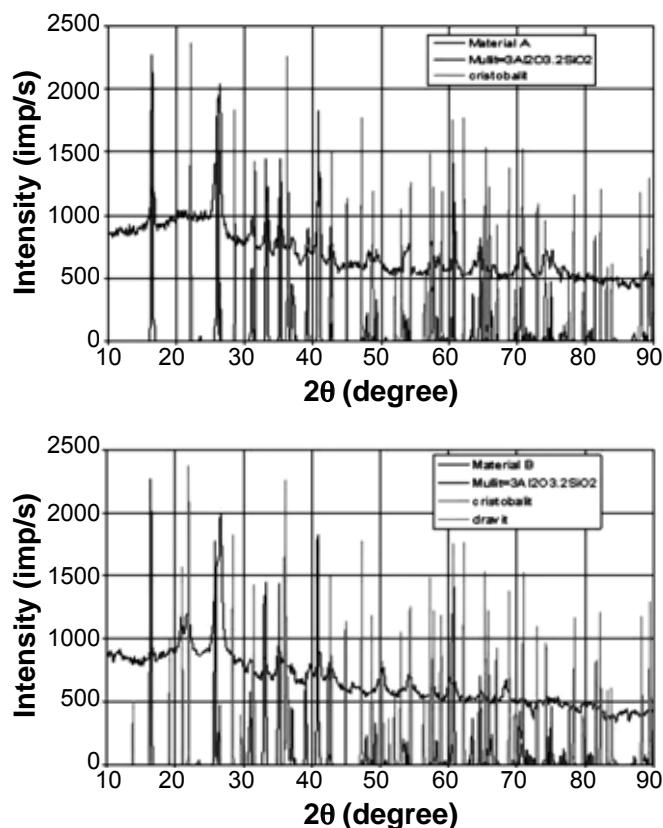


Figure 2: X-ray diffraction patterns of A and B refractory lining.
 [Figura 2: Difratogramas de raios X dos revestimentos A e B.]

holes with diameter 25 mm and depth 30 mm were drilled into prisms and filled with 15 g of dried NaCl or KCl. The crucibles were heated in laboratory resistance furnace under air atmosphere ($p_{O_2} \sim 212.78$ kPa) at 850 °C with dwell time 2 h. Experimental temperature 850 °C was chosen pursuant to the melting temperature of corrosive medium (Table III) to ensure the homogeneity of the melting for a period of the test.

The crucibles were chilled in furnace, dry cut into two halves and photographed. The penetration depth of corrosive medium was evaluated by visual observation and then by use argentometry. The modifications of lateral sections of the crucible's potsherd were also evaluated.

The following chemical equations can be used for reviewing the ability of chemical reactions pursuant to thermodynamic analysis of corrosive system NaCl-(SiO₂-Al₂O₃) between 0 °C and 1000 °C:

Table II - Comparison of the properties of refractory lining A and B [3].

[Tabela II - Comparação entre as propriedades dos revestimentos A e B [3].]

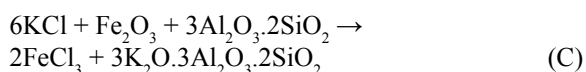
Properties	Lining A	Lining B
Cold compression strength [MPa]	60	60
Volume weight [kg.m ⁻³]	2250	2150
Apparent porosity [%]	12	14
Heat strain resistance [°C] *	1440	1100

* Standard Test used

Table III - Comparison of the properties of salts NaCl and KCl [4].

[Tabela III - Comparação entre as propriedades dos sais NaCl e KCl [4].]

	NaCl	KCl
Molar weight M [g.mol ⁻¹]	58.43	74.55
Density ρ [g.cm ⁻³]	2.165	1.984
Melting temperature t _{top} [°C]	800.4	771.0
Boiling temperature t _{var} [°C]	1413	1420
Surface tension σ [mN.m ⁻¹]	113.8	97.4
Diameter - anion [Å]	1.81	1.81
Diameter - cation [Å]	0.98	1.33



The process of fire-clay refractory lining corrosion can be characterized also by chemical reactions A-C. The existence of ion pairs K⁺:Cl⁻ is possible in regard to thermodynamic stability of KCl in this system.

NaCl and KCl show high stability in oxidizing atmosphere and structure of ion pairs remains after melting. KCl looks to be more stable phase in regard to thermodynamic stability in connection which oxide system SiO₂-Al₂O₃-X (X = K₂O, Na₂O, CaO, Fe₂O₃, TiO₂, MgO) and in conditions of crucible test [5].

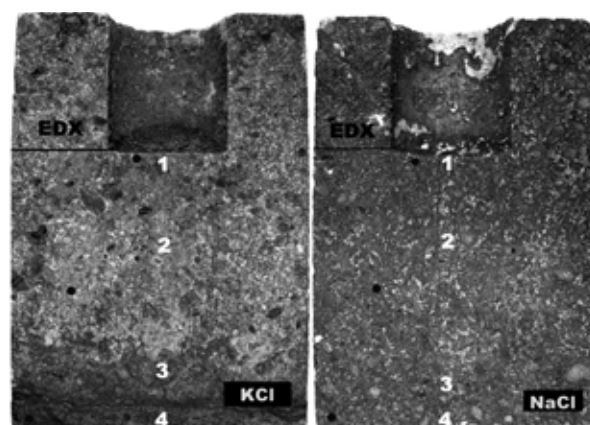
RESULTS AND DISCUSSION

The weight reduction of corrosive medium was calculated as the difference between the weight of crucible with corrosive medium and crucible after the test. It equals to evaporation corrosive medium into the atmosphere during the test. Table IV shows different weight reduction of corrosive medium. More intense evaporation of both

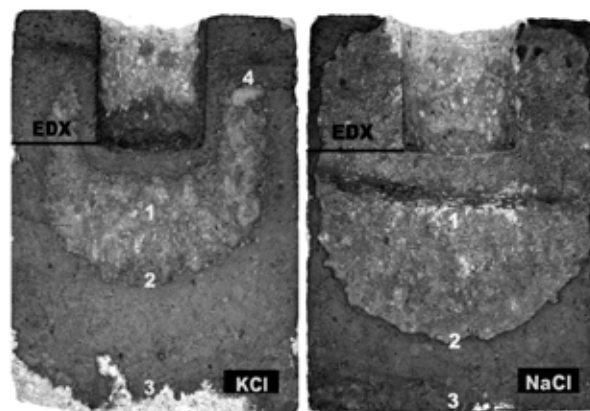
Table IV - The weight reduction of corrosive medium during crucible test.

[Tabela IV - Redução de peso dos meios corrosivos durante o teste em cadinho.]

Lining	Corrosive Lmedium	The weight reduction of corrosive medium [wt.%]
A	NaCl	16.10
	KCl	24.36
B	NaCl	33.34
	KCl	40.00



Refractory lining A



Refractory lining B

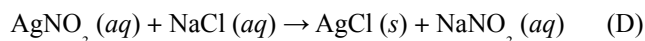
Figure 3: The penetration depth of NaCl and KCl - macroscopic analysis.

[Figura 3: Nível de penetração de NaCl e de KCl - análise microscópica.]

corrosive media was obtained if the crucible of lining B was used. Obviously, the corrosive medium preferentially reacts with lining A. The macroscopic analysis (Fig. 3), and evaluation of individual corrosive medium penetration depth confirm this fact.

The quality of macroscopic analysis can be improved by using argentometry. It is a method based on the use of silver nitrate, AgNO₃. One half of cut crucible is painted with a dilute solution of the AgNO₃. It reacts with chlorine ions, and white coagulation of silver chloride AgCl is formed. The

coagulation step by step became brown, until turn nearly black due to sunlight. The following chemical reactions can be expected for reviewing the penetration depth [6].



The results of macroscopic analysis confirm different ways of the penetration of corrosive medium into a wall of crucible. The penetration of NaCl is more significant as it of KCl (Table V). The modifications in not penetrated structure of the crucible were not observed by optic microscope analysis. Compact reaction layer occurs on the boundary line crucible - corrosive medium. The layer is saturated with melting corrosive medium and also potentially with the product of reaction between the melting and oxide components of the crucible. The compactness of penetrated area with closed pores is below it of the layer on the boundary line crucible - corrosive medium. The compactness of external border of the crucibles is also low with bigger and connected pores.

Table V - Macroscopic evaluation of penetration depth into lining.

[Tabela V - Avaliação macroscópica do nível de penetração no revestimento.]

Lining	Corrosive medium	The place of measurement	Mean penetration depth [mm]
A	NaCl	side wall	17.8
		bottom	50.5
	KCl	side wall	17.8
		bottom	47.5
B	NaCl	side wall	16.0
		bottom	29.0
	KCl	side wall	12.0
		bottom	22.0

The chemical analysis of three areas was carried out: 1 - boundary line - the layer between corrosive medium and crucible, about 2 mm from the hole of crucible; 2 - penetrated area, about 20 mm from the hole; 3 - the area of crucible unaffected by penetration, about 48 mm from the hole.

Figs. 4 and 5 show different process of the corrosion of refractory lining A and B, respectively. Fig. 4 shows the concentration of Na and Cl in both standards of refractory lining (A, B) with NaCl as corrosive medium. The concentration of both elements is stable with linear course in lining A or uniformly decreases in lining B from the hole to external wall of the crucible. Fig. 5 shows the concentration of K and Cl in both standards of refractory lining with KCl as corrosive medium. The concentration of both elements moderately decreases from the hole to external wall of the

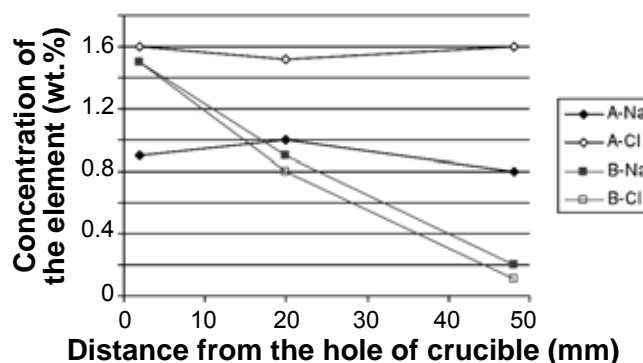


Figure 4: Penetration of the elements Na and Cl into linings A and B (corrosive medium 100% NaCl).

[Figura 4: Penetração dos elementos Na e K nos revestimentos A e B (meio corrosivo 100% NaCl).]

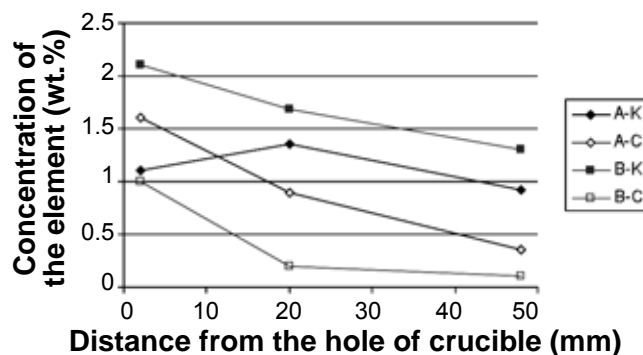


Figure 5: Penetration of the elements K and Cl into linings A and B (corrosive medium 100% KCl).

[Figura 5: Penetração dos elementos K e Cl nos revestimentos A e B (meio corrosivo 100% KCl).]

crucible in both standards of refractory lining.

After microscopic analysis, the specimens were analyzed by semiquantitative local EDX with the view of exact study of the corrosion process. The selected surface (100 \times 100) μm^2 was used for analysis of composition of the matrix in intergranular space and the grains of the opening material. The analysis confirmed marginal diffusion of Na, Cl and K ions into the grains of mullite in accordance with literary sources [7]. The penetration of melted corrosive medium into the lining went per matrix in intergranular space. The EDX analysis was also used to provide the evaluation of possible diffusion of corrosive medium into the grains of the fire-clay lining. Fig. 6 shows microstructure of lining B after corrosive test about 5 mm from the boundary line with the marking of the surface, selected for evaluation.

The results of EDX analysis indicated the possibility of chemical reactions A-C between SiO_2 - Al_2O_3 system of refractory lining of crucible and melted corrosive medium NaCl or KCl. The thermodynamic analysis of this mixed system suggests some possible reactions. The run of reactions depends on their kinetics, however. It is assumed that, in general, occurs adsorption of chloride ions on the surface of oxide phases in the event of interactions of chloride melting

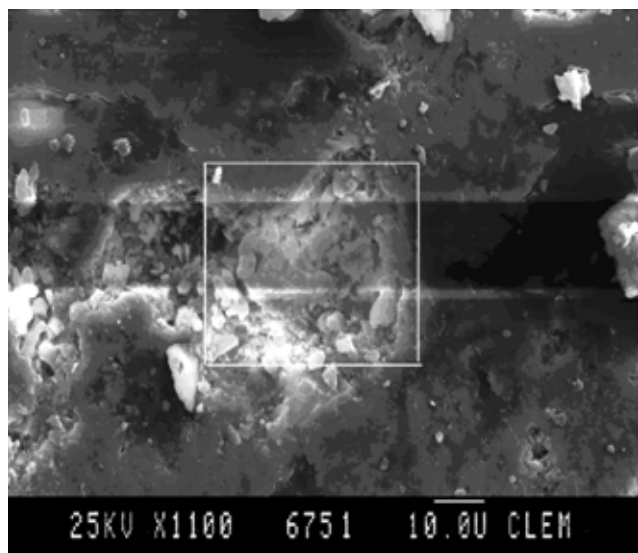


Figure 6: SEM micrograph of lining B in penetrated area after corrosive test about 5 mm from the boundary.

[Figura 6: Micrografia obtida em microscópio eletrônico de varredura do revestimento B na área penetrada após teste de corrosão a 5 mm da borda.]

on the interface of solid-solid phases [8].

The possibility of the diffusion of melted corrosive medium into volume of fire-clay grains was evaluated. The results of semiquantitative EDX analysis, presented in Table VI confirm diffusion in the surface layer of the grains. The diffusion of Cl and Na ions into grain in the event of interaction with NaCl can be expected. Only surface layer of the grain is penetrated with Cl and K ions if KCl melting is used. The ions of Na or K could get into grains also in the production process (first of in manufacturing operations of raw material at high temperature). The soothing of grains with chlorine ions is improbable in that way. The diffusion of ion pairs Na^+Cl^- through the pores and cracks is supposed during crucible tests. The literary sources [9] relate to dimensions of ion pairs Na^+Cl^- and K^+Cl^- confirm this supposition. Theoretical internuclear radius of NaCl is $r_{\text{NaCl}} = 0.276$ nm, and it of KCl is $r_{\text{KCl}} = 0.314$ nm. Higher activity of ion pair Na^+Cl^- is supposed during corrosion tests.

Recent reviews show that, despite much interest, the cause of corrosion mechanism between melting chloride corrosive medium and oxide refractory lining is published only on a small scale. The examples in the literature are

Table VII - Physical properties of pure chlorides NaCl at KCl at 850 °C [9].

[Tabela VII - Propriedades físicas dos cloretos puros NaCl e KCl a 850 °C [9].]

Composition/ Melting temperature [°C]	Physical property		
	Dynamic viscosity [mPa.s]	Surface tension [mN.m ⁻¹]	Density [g.cm ⁻³]
NaCl/800	1.211	110.8	1.532
KCl/771	0.931	93.0	1.484

restricted to physical influences, affecting the course of interactions: porosity of masonry (bricks, lining), adsorption, wetting power and other physical properties of the melting. Obtained results suggest that we can regard to chemical reactions. However, it will be necessary to review their kinetics. In general, the wetting power of the oxide refractory lining with chloride corrosive medium is very strong. Their adsorption on the surface of the oxide lining is mostly taken in account. The references regarding physical properties of melting chloride corrosive medium are infrequent and out-of-date [10]. The density, surface tension and viscosity of melting medium are determining factors for their intensive penetration. Selected physical properties of pure melting of NaCl and KCl at temperature 850 °C are in table VII.

Fig. 7 shows the results of semiquantitative EDX analysis of the elements K, Na and Cl reduced to chlorides NaCl and KCl. Different penetrations of both compounds

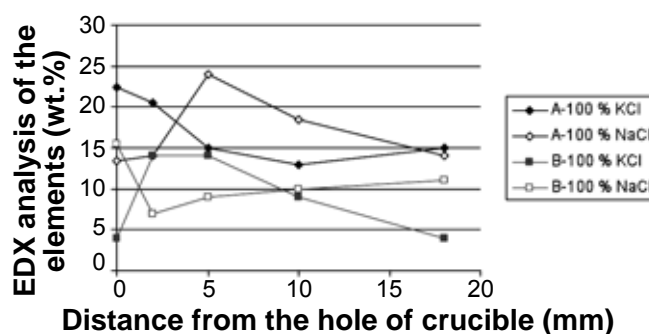


Figure 7: Penetration of chlorides KCl and NaCl into linings A and B - semiquantitative EDX analysis.

[Figura 7: Penetração dos cloretos KCl e NaCl nos revestimentos A e B - análise EDX semi-quantitativa.]

Table VI - Semiquantitative EDX analysis of crucible (lining B) grains after crucible test.

[Tabela VI - Análise semi-quantitativa EDX dos grãos do cadinho (revestimento B) após o teste no cadinho.]

	Analyzed part of grain	Semiquantitative EDX analysis [wt.%]								
		Al	Si	Mg	Na	Cl	K	Ca	Ti	Fe
100 %	edge	12.0	68.1	0.0	0.1	0.9	13.3	0.0	2.2	3.3
KCl	middle	14.9	67.4	0.0	0.0	0.0	15.3	0.1	0.7	1.6
100 %	edge	16.6	75.9	0.0	0.7	1.3	1.2	0.2	2.3	1.9
NaCl	middle	16.1	70.9	0.0	0.4	0.5	0.6	0.2	9.1	2.2

into refractory lining are visible. The variation in content of particular elements was obtained in all four combinations of lining and melting (A-NaCl, A-KCl, B-NaCl, B-KCl) measured about 2 mm from the hole of crucible according to plot in Fig. 7. This area is apparently the layer of reaction. The chlorides with elements of refractory lining can react there, for example, in accordance with equations A-C.

CONCLUSIONS

The weight reduction-evaporation of KCl is more significant for both linings in comparison with NaCl. Both chlorides penetrate into linings A in preference. NaCl shows more significant penetration and chemical interaction in penetrated area. The variance of structure of crucible walls were not obtained by microscopic analysis. The concentration of observed elements is stable without significant variations. The ions of K penetrate into the grains of the lining more intense than the Na ions. EDX analysis confirms creation of the reaction layer between chlorides and elements of refractory lining.

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