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STUDY ON THE POSSIBILITY TO UTILIZE ALUMINA INDUSTRIAL WASTE FOR
PRODUCTION OF REFRACTORIES

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Study on the Possibility to Utilize Alumina Industrial Waste for Production of Refractories: The possibility to utilize alumina industrial wastes – alumina slag and exhausted catalyst from fuel production facility was investigated. Experimental compositions were prepared at different ratios between the initial materials. The process of samples sintering and the formation of the refractory phases was studied by X-ray analysis; the physicochemical characteristics of the products obtained were determined.

Key words: Waste, Slag, Catalyst Powder, Refractories, Phase Composition.

INTRODUCTION

A key priority of many research groups around the world is the development of new technologies and methods for recycling and utilization of waste materials from process industries. The aluminum oxide industrial wastes can be used a valuable initial material for manufacturing refractory materials for industrial purposes [1-2], refractory concretes and as filler in asphalt concrete mixtures [3], synthesis of valuable construction materials – ceramic tiles, refractory and insulation bricks [4-5], initial materials for production of Portland cement [6-7] and non-plastic materials in the ceramic industry [8].

DISCUSSION

The aim of the present work is to study the possibility to utilize waste aluminum slag and waste powdery catalyst for synthesis of refractory materials.

The aluminum slag used is a waste materials from the roll mill and press department of the aluminum production facility of “Alumina” Co., city of Shumen. The powdery catalyst is a waste product from petrol production unit of oil processing industry. As intermediate technological binding, 3% PVA was introduced as 8% aqueous solution. The chemical compositions of the initial materials are shown in Table 1.

Table 1. Chemical composition of the initial materials, mass.%

Materials	Al ₂ O ₃	SiO ₂	MgO	Na ₂ O	Fe ₂ O ₃	K ₂ O	CaO	TiO ₂	MnO	P ₂ O ₅	La ₂ O ₃	REO	Mass loss by heating
Slag	67,70	5,93	2,95	2,23	1,88	1,69	1,36	0,75	0,69	0,35	-	-	14,36
Catalyst	37,24	57,46	-	0,31	0,58	-	-	0,98	-	-	1,69	1,74	-

It can be seen from the data presented in Table 1 that the Al₂O₃ contents in the initial materials was high enough which is a prerequisite for their use as components in compositions for synthesis of ceramic refractory products. The high content of SiO₂ (57,46 %) observed in the chemical composition of the powdery catalyst was considered enough to assume that refractory crystalline phases can be obtained by high temperature sintering.

The formulations of the initial blends are presented in Table 2.

Table 2. Formulations of the sample blends, mass. %

Composition	K1	K2	K3	K4
Slag	90	80	70	50
Catalyst	10	20	30	50

The calculated chemical compositions of the sample blends are shown in Table 3.

Table 3. Chemical compositions of blends K1 – K4, mass. %

	Mass loss by heating	Na ₂ O	MgO	MnO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	La ₂ O ₃	REO
K1	12,93	2,05	2,67	0,63	64,67	11,11	0,32	1,53	1,23	0,79	1,76	0,17	0,17
K2	11,50	1,85	2,37	0,56	61,62	16,24	0,29	1,36	1,09	0,80	1,63	0,34	0,35
K3	10,06	1,66	2,07	0,49	58,58	21,40	0,25	1,19	0,96	0,82	1,49	0,51	0,52
K4	7,18	1,27	1,49	0,35	52,47	31,70	0,18	0,85	0,68	0,87	1,24	0,85	0,87

The samples were prepared by hydraulic pressing at pressure of 100 MPa. The sintering was carried out in a super kanthal chamber furnace „Naber“ equipped with program regulator „EVROTERM“ 822 at temperatures 1250, 1350 and 1500 °C. The isothermal period was 1 h and the heating rate - 10 °C/min.

Figs.1 and 2 show the diffractograms of the initial materials taken on a powder X-ray diffractometer D2 Phaser. It was found from the XRD analysis of the slag (Fig.1) that the main crystalline phases were corundum, bayerite, residual metal aluminum and AlN. The Al₂O₃ contained in the slag was γ -phase with cubic crystal lattice which transforms into α -modification (corundum) at temperatures 800-1000°C with hexagonal lattice. These crystalline phases are initial materials for wear- and heat-resistant technical ceramics. The most intense reflexes observed in the diffractogram of the catalyst (Fig.2) were registered from the crystalline phase zeolite Y and amorphous phase. The specific area determined by the BET method was 87 m²/g. The catalyst used was finely dispersed and no additional grinding was necessary. The effect of the introduction of finely dispersed components in the ceramic blends is that an additional partitioning boundary is formed which facilitates the increase of the volume of the water bound by adsorption and chemisorption which. In turn leads to increased plasticity of the ceramic blends and better tensile properties.

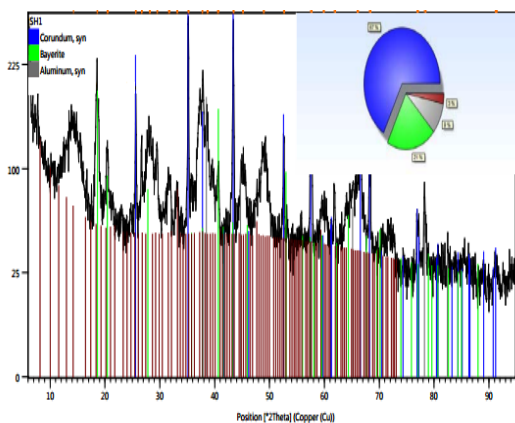


Fig.1. Diffractogram of waste slag

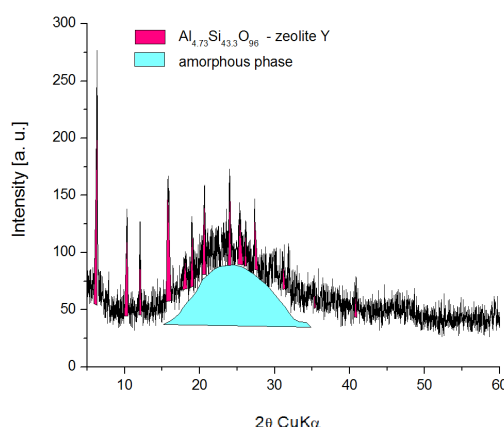


Fig.2. Diffractogram of waste catalyst

The samples sintered in the temperature interval 1250-1500°C were characterized for their water absorption (WA), apparent density (ρ_{app}), apparent porosity (P_{app}) and linear shrinkage (LS). The physicochemical characteristics of the materials synthesized are shown in Table 4.

Table 4. Physicochemical characteristics of samples K1-K4

	LS, %			WA, %			P_{app} , %			$\rho_{app} \cdot 10^{-3}$, kg/m ³		
	1250	1350	1500	1250	1350	1500	1250	1350	1500	1250	1350	1500
K1	2	4	6	29,58	25,43	23,11	49,75	49,19	43,18	1,68	1,73	1,87
K2	2	4	8	29,46	24,62	13,84	49,18	44,46	28,84	1,67	1,81	2,08
K3	4	8	10	29,47	19,72	8,45	48,68	37,99	17,15	1,65	1,93	2,03
K4	4	8	8	26,87	22,45	16,82	45,08	40,35	33,08	1,68	1,80	1,97

The dependencies of the apparent density and water absorption of the samples on temperature prepared are presented in Figs.3 and 4. It was found that the degree of sintering of all the compositions increased with the increase of sintering temperature from 1250 to 1500°C while the water absorption and apparent porosity decreased. For composition K2, ρ_{app} reached value of $2,08 \cdot 10^3$ kg/m³ at sintering temperature 1500°C.

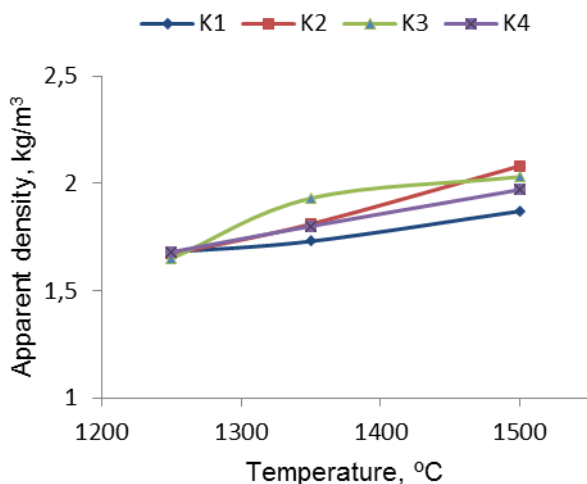


Fig.3. Dependence of apparent density on synthesis temperature for compositions K1-K4

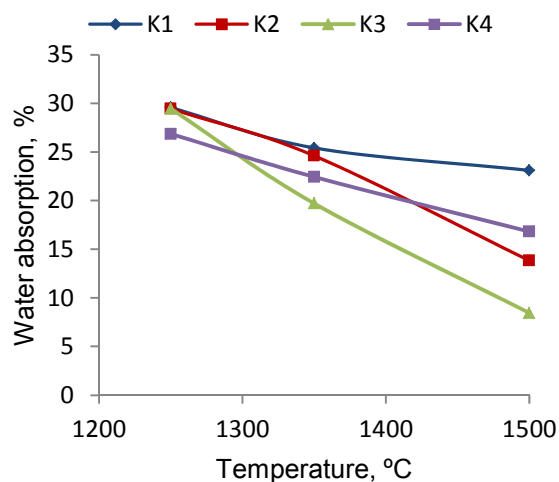


Fig.4. Dependence of water absorption on synthesis temperature for compositions K1-K4

The samples from all the compositions sintered at 1500°C did not show signs of defects and overheating. The increase of the apparent density is accompanied by significant increase of the mechanical strength of the sintered samples. The linear shrinkage was low for the samples sintered at lower temperatures which indicates for insufficient shrinkage of the material. It increased with the sintering temperature but remained auspiciously low (Table 4).

The increased apparent density of the samples synthesized from blends K1-K4 was due to the increased content of SiO₂ in the initial materials (Table 3) which facilitates the formation of mullite structure. This was confirmed by the diffractograms shown in Figs.5-7.

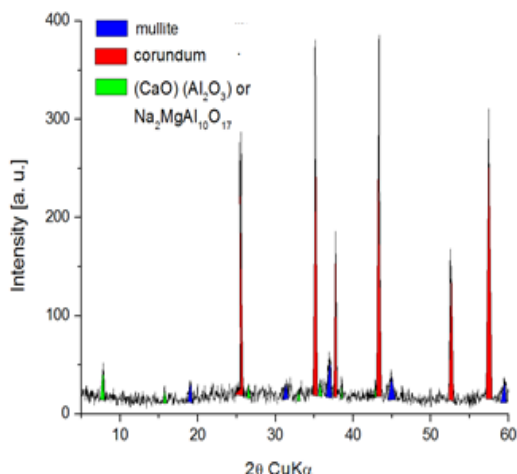


Fig.5. Diffractogram of composition K1

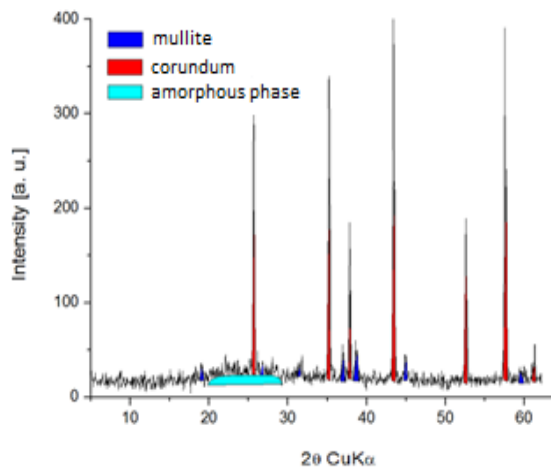


Fig.6. Diffractogram of composition K3

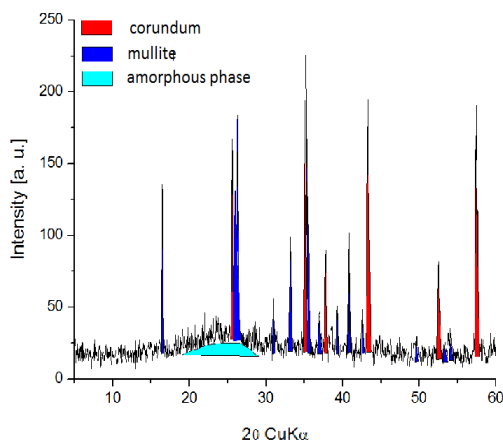


Fig.7. Diffractogram of composition K4

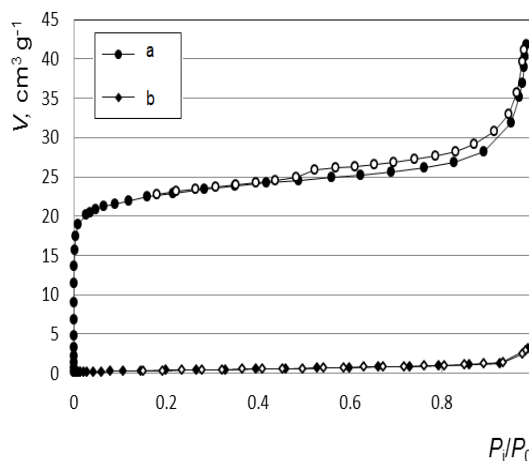


Fig.8. Nitrogen adsorption isotherms of catalyst powder (a) and composition K4 (b)

The determination of the texture characteristics was carried out by recording N₂ adsorption isotherms at -196 °C using Surfer (Thermo Scientific) sorption analyzer. The specific area (S_{BET}) was measured by the method of Brunauer-Emmett-Teller (BET).

The N₂ adsorption isotherms of pure catalyst powder and composition K4 are presented in Fig.8. According to the IUPAC classification, the adsorption isotherm of the sample of pure catalyst was type I which is characteristic for microporous structures. The isotherm has a hysteresis section type H-4 which indicates for the presence of mesopores.

The adsorption isotherm of sample K4 (Fig.8) reveals that the sample is macroporous or finely dispersed material with specific area about 2 m²/g.

Since the materials obtained contained the crystalline phases corundum, mullite and spinel, they can be classified as refractory materials. The latter are known to have good refractory properties in the temperature interval 1350-1500 °C.

The refractory materials synthesized can be classified as alumina refractory ones.

According to the experimental data, the optimal composition were K2 and K3 thermally treated at 1500°C in which mullite phase was formed with high apparent density.

CONCLUSION

Blends containing various amounts of waste catalyst and foundry slag were developed. It was found that the phase composition of the sintered samples consisted of the refractory phases mullite, spinel and corundum. The physicochemical parameters of the products correspond to these of refractory materials.

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