STRUCTURIZATION OF CERAMICS BASED ON FUSIBLE CLAYS WITH THE ADDITION OF WASTES OF CHROMIA-ALUMINA CATALYST

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Abstract

In this work are represented results of research of impact of waste of chromia-alumina catalyst (hereinafter CAC) on ceramic samples structure formation. It is established that with increase of CAC dose from 1.5 to 12%, general quantity of pores decreases, structure became denser. Increasing of samples burning temperature from 960 to 1160°C reduces defectiveness of structure, porosity decreases by cost of more complete filling of inter-grain space, increases the degree of ingredients packing. Results of roentgen-phase analysis and electronic microscopy show that increase of density is stipulated by larger volume of crystalline new growths that are forming in space between grains at high temperature burning, and also by increase of density of glass phase by cost of its armoring by crystals.

Keywords: Waste of chromia-alumina catalyst (CAC), disposal, burning, and structure.

Introduction

Chrome in form of hexavalent oxide is counted one of seventeen of the most toxic chemicals hazardous for health. Hexavalent chrome is contained in ammonia dichromate, chromic acid, sodium dichromate, sodium chromate and potassium dichromate. In USA, in accordance to the law on universal protection of environment, compensation and responsibility at its contamination, all chrome compounds are counted dangerous substances. Their content in drinkable water should not exceed 0.5 mg per liter. All chrome containing waste should be labeled as dangerous. There are directives in EC directed at protection of water environment. This refers to internal surface waters, territory waters, internal coast waters, ground waters. Disposal of chrome-containing waste is one of the major directions for industry, because non-solution of this issue can result in significant ecological loss in connection to mobility of toxic elements [1,2]. For burying of particularly toxic waste and concentrated solutions is anticipated their preliminary
solidifying. This type of procession is used for toxic waste. For example, at open storage of cyanide waste, in atmosphere is evaporating approximately 90% of cyanide hydrogen (approximately 3% stays in waste and approximately 3% blooms out into ground waters). Storage of waste containing arsenic, chrome, mercury at landfill results in occurrence of heightened concentrations of these elements in ground waters. In process of solidifying are received insoluble compounds that are formed in blocks. At storage of such blocks the toxic impurities are not washed out of them. For performance of solidifying process to waste are added cementing components. As cementing addition is most frequently used cement or lime.

This method is distinguished by its simplicity, accessibility and low cost of materials. But received mixtures are unstable to acid components and are gradually decomposing in acid soils. Domestic scientists had developed diverse effective methods of disposal of chrome containing waste of enterprises of oil-chemical branch and acre receiving on their basis of the following products, mostly of construction intention: unburned refractory composites for refractory material [3]; heat resistant foamed concrete on basis of ion modified chrome and silicone alum-phosphate cementing [4].

Effectiveness of CAC disposal by their use at manufacturing of diverse construction materials is also shown in a whole range of works of domestic and foreign scientists. Below is shown the technical rationality is their use for different branches of industry as: pigment and base paint with anti-corrosion properties [5]; absorbent for oil products purification [6]; additions that increase strength of natural cementing materials (substitutes of cement) in manufacturing of construction materials [7-9]; unburned refractory composites (heat resistant solution and cements with increased service life as refractory, fire-proof glues [10]; mineral fillers that improve properties and composition of bitumen [11], geo-polymers [12] etc.

In foreign works can be also found researches of impact of chrome-containing waste on ceramics structure [13-18]. In this work are represented results of research of impact of introduction of waste of chromia-alumina catalyst (hereinafter CAC) on structure formation of ceramics based on fusible clays.

**Materials And Methods Used In Researches**

As addition-regulator of ceramics properties was used waste of chromia-alumina catalyst and CAC enriched with 10%Na₂O - (CAC+10%Na₂O).

Na₂O was applied to CAC by vacuum soaking by water absorption from water solution of NAOH. CAC characteristics are shown in table 1.
Table 1: CAC characteristics.

<table>
<thead>
<tr>
<th>CAC parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>-</td>
<td>Powder of bluish-green or grayish-green color</td>
</tr>
<tr>
<td>Chemical composition:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Cr₂O₃</td>
<td>%</td>
<td>10-25</td>
</tr>
<tr>
<td>- γ-Al₂O₃</td>
<td>%</td>
<td>73-89</td>
</tr>
<tr>
<td>- K₂O</td>
<td>%</td>
<td>1-2</td>
</tr>
<tr>
<td>- SiO₂</td>
<td>%</td>
<td>0-6</td>
</tr>
<tr>
<td>- impurities of iron</td>
<td>%</td>
<td>up to 0.5-0.7</td>
</tr>
<tr>
<td>- impurities of nickel, copper, zinc, titanium</td>
<td>%</td>
<td>up to 0.2</td>
</tr>
<tr>
<td>Poured density</td>
<td>g/sm³</td>
<td>1.3-1.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>%</td>
<td>0.9-5.0</td>
</tr>
<tr>
<td>Concentration of Cr (VI)</td>
<td>mg/g</td>
<td>25</td>
</tr>
</tbody>
</table>

Optical methods of research were conducted by autoemission scanning electronic microscope Merlin of CARL ZEISS company. Microscope is combined with spectrometer of energetic dispersion AZtec X-MAX. Resolution of spectrometer - 127 eV. Detection limit 1500-2000 ppm. Accuracy of measuring is 0.01-1% and depends on condition of researched object. Survey of surface morphology was conducted at accelerating voltage 5keV for improvement of depth of image focus. Element analysis was conducted at accelerating voltage 20keV and flange focal distance 9 mm that allows to avoid minimal faults. Penetration depth is less than 1 micron.

Computer processing of images received with electron microscope was conducted on PC "STRUKTURA" [19].

Roentgen-phase analysis (hereinafter RPA)

Roentgen-diffraction powder experiments were conducted on automatic roentgen diffractometer Bruker D8 Advance equipped by detachable device Vario and linear coordinate detector Vantec.

There was used CuKα irradiation, monochromatized (λ(Cu-Kα)=1.54184 Å) be germanium bent monochromator of Johansen, operation mode of roentgen tube 40 kV, 40 mA. Experiments were conducted at room temperature in geometry of Bragg-Brentano with flat sample. Building and analysis of diffractograms were conducted using the program Bruker Diffrac Eva.

Experimental Part

In order to determine impact of waste on physically-mechanical characteristics of ceramics from fusible clays were researched samples of flux of compounds shown in table 2.
Table 2: Researched compounds of fluxes on basis of fusible S-Ch clay

<table>
<thead>
<tr>
<th>No. of compound</th>
<th>Consumption of flux ingredients, mas. %</th>
<th>Burn temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S-Ch clay</td>
<td>CAC</td>
</tr>
<tr>
<td>1 (control)</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>98.5</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>92</td>
<td>6.0</td>
</tr>
<tr>
<td>5</td>
<td>88</td>
<td>12.0</td>
</tr>
</tbody>
</table>

The maximum strength of samples is provided at introduction of 0.5% CAC - 87.41 MPa and at 12%(CAC+10%Na₂O) – 89.52 MPa. This is higher than strength of control samples for 83.17% and 87.59% respectively. At introduction of CAC in interval of 1.5-12% the strength of samples stays higher than of control ones for 28.72%-56.81% and equals 61.4-74.8 MPa, and at introduction of (CAC+10%Na₂O) in interval of 0.5 to 6% it is higher than control for 31.01-45.35% and is equal to 62.52-69.36 MPa. Depending on burn temperature and amount of sand content in clay solid, the major crystalline phases of ceramic shard can be mullite, cristobalite and β-quartz, at this in hydromicaceous clays prevails the process of mullitization, and cristobalization in montmorillonite ones. In course of burning products of decomposition of clay constituent of flux are interacting with oxides of aluminium, calcium, iron and magnesia that could be present, for example, in additional materials and waste. This promotes partial expression of pyroplastic phase that accelerates progress of solid phase reactions with prevailing formation of mullite, hematite, anorthite, augite etc., that is confirmed by results of roentgen-phase analysis shown below. Besides, a certain role in solid-phase reactions at burning of ceramic items made of fusible clay would be played by oxides of alkaline (Na₂O, K₂O) and alkali earth (CaO, MgO) metals comprised in clay. Oxide of alkali earth metals are present in fusible clays in small quantities in composition of non-clay minerals – carbonates in form of calcite and dolomite. At relatively high temperatures CaO enters into reaction with clay loam Al₂O₃ and silicon earth SiO₂ and, forming eutectic fusion in form of alumina-calcium-silicate glasses, drastically decreases temperature of clays melting. At burning temperatures up to 1160°C CaO promotes aeration of shard [20]. Disperse alkali earth components stipulate formation of calcium containing crystalline phases like anorthite (CaO·Al₂O₃·2SiO₂) [21,22]. That's why we can suppose that fine-disperse carbonates in conditions of low-temperature burning, along with alkaline oxides, would promote achievement of necessary strength of ceramic shard. Figure 1 represents data of RPA of samples formed from fusible Saray-Chekurchinsk clay and burned at temperature of 960°C, 1060°C and 1160°C. After comparing of
Roentgenograms of samples on pure S-Ch clay without CAC burned at temperature of 960°C (a), 1060°C (b) and at 1160°C (c)
On order to confirm the RPA data were additionally conducted researches of sample shard structure by method of electronic microscopy, which results are shown in figure 2.

Figure 2: Microstructure (enlargement 10000 folds) of samples on pure S-Ch clay without CAC burned at temperature of 960°C (a), 1060°C (b) and of 1160°C (c)

Analysis of figure 2 shows that with increase of burning temperature from 960 to 1160°C of samples based on fusible S-Ch clay the defectiveness of structure reduces, porosity lessens due to more complete filling of space between grains, and therefore the degree of ingredients packing increases. Such structure is more advantageous for reduction of Cr (VI) blooming out at introduction of CAC in composition of fluxes on basis of fusible S-Ch clay.

With taking into account of the fact that the best physical-mechanical properties of shard on base of Saray-Chekurchin clay were received at temperature of 1160°C, processes of structure formation of samples modified by CAC and burned at this temperature were further researched in more detail.

Addition of CAC in amount of 1.5; 6.0 and 12% and 12% (CAC+10%Na₂O) from clay mass to S-Ch clay allows to regulate phase composition of crystalline phase of shard burned at temperature of 1160°C (figure 3).
Analysis of roentgenograms (figure 3, a, b, c) of samples made of fusible S-Ch clay burned at temperature of 1160°C and modified by addition of CAC in amount of 1.5; 6 and 12 mass % shows the following:

- a shard of all three samples is mostly represented by β-SiO₂ (4.267; 3.35; 2.46; 2.284; 2.13; 1.819), mullite (3.43; 2.686; 2.24; 2.13; 1.544), spinel (2.894; 2.46; 2.02; 1.982; 1.544), hematite (2.686; 2.505), FeO·Cr₂O₃ (4.82; 2.505; 1.159); β-CaO·Cr₂O₃ (2.284; 1.982; 1.383), corundum Al₂O₃ (2.505; 1.982; 1.376) and γ-Cr₂O₃ (1.675).

- as can be seen, by comparison to compositions without addition, at introduction of CAC an additional crystalline phase in form of anorthite and γ-Cr₂O₃ is formed.

- as can be seen, intensity of mullite peaks at d equaling 5.436; 2.686 and 2.21 for samples of 291-294 composition of fusible S-Ch clay with addition of CAC from 1.5 to 6.0 and 12.0 mass %  is increasing extremely and has a maximum value at addition of 12% CAC. Replace of CAC with 1.5 mass % (CAC+10%Na₂O) promotes a certain decrease of peak intensiveness, but at this it is higher than at 1.5% of CAC and approximately matches composition with 6 mass % of CAC.

Formation of mullite-like phase and crystallizing of anorthite after burning at temperature of 1160°C provide firmness at compression of vitrified samples in limits up to 90...110 MPa, which corresponds to results of work [29].
In order to confirm RPA results of samples based on fusible (S-Ch) clay modified by addition of CAC and (CAC+10%Na₂O), researches of structure of samples burned at temperature 1160°C by electronic microscope were conducted. Structures of samples with addition of 1.5; 6.0; 12% of CAC and with 12% (CAC+10% Na₂O) are shown below in fig. 4.

Figure 4: Microstructure of samples burned at temperature of 1160 ºC with enlargement by 1000 and 5000 folds, of following compositions: a, b - Composition [98.5%(S-Ch) + 1.5% CAC], c, d - Composition [94%(S-Ch) + 6% CAC], e, f - Composition [88%(S-Ch) + 12% CAC], j, h - Composition [88%(S-Ch) + 12%(CAC+15% Na₂O)]
PC "STRUCTURA" that allows to measure indexes of porosity, sizes of separate crystalline new growths, degree of their filling of space between grains, degree of packing or concentrations of new growths per unit of volume of selected material volume at different scale levels was used for analysis of micro-photographs.

Analysis of photographs in fig. 4 shows that with increase of CAC dose from 1.5 to 12%, general quantity of pores decreases, structure became more dense. So, at absence of CAC addition, the average density of shard burned at temperature of 1160ºC, equals 2.05 g/cm³, at 0.5% of CAC – 2.07 g/cm³, at 1.5% of CAC – 2.09 g/cm³, at 6% of CAC reaches 2.17 g/cm³. This is connected, first if all, with a large volume of crystalline new growths formed at high-temperature burning of fusible flux in presence of CAC addition, second, with more complete filling of space between grains by new growths, third, with increase of glass phase density by cost of its reinforcement with crystals.

It should be noted that further increase of CAC up to 12% reduces density to 2.06 g/cm³.

Different picture is observed at introduction of 12% of modified addition (CAC+10%Na₂O) into composition of fusible flux. At the the total amount of pores increases. All samples with addition (CAC+10%Na₂O) have lesser density than with addition of CAC, although at 12%(CAC+10%Na₂O) these indexes are matching and equal to 2.06 g/cm³.

**Conclusion**

Therefore it can be stated that one of the reasons of increase of firmness of samples burned at 1160ºC and composed of fusible clay modified by CAC or (CAC+10%Na₂O), is formation of crystalline phase in form of mullite and anorthite that by armoring of glass-phase creates in it a continuous firm crystalline carcass.

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**References**


