

## Simulation of the ceramic products composition using furnace-waste filler

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**Abstract.** Modern rates of construction stimulate ceramic-bricks factories to increase volume and variety of their production. At the same time, price of production should not exceed a certain limit. It can be reached by technological process optimization and with using waste of nearby industrial plants. Last time, brick factories try to use solid waste as filler. For regional production, it can be final product of coal combustion from Kazan CHP (Combined heat and power plant). The successful experience of foreign companies in furnace-waste recycling and the production of ceramic products from them, allow us to hope in acceptable results.

The purpose of work was modeling composition of ceramic charge for Shelangovsk brick factory using Kazan TPP furnace-waste as filler. As experiment, to composition of clay gross products and working charge (75% clay + 15% sand + 10% buckwheat husks) of the Shelangovsk plant were added 10, 15, 20 and 25 percent of waste dopant. After molding of ceramic small brick, samples were fired at  $T = 980^{\circ}\text{C}$  and then the end products were tested for strength.

The results showed that addition 10, 15 and 20 percent of ash to working charge are consistently increases the strength of ceramic products in compression tests. According to the requirements of GOST (USSR Standard-Setting Authority) 530-95 for brick and ceramic stones, received products on compression match by brand not lower than M 100; by bend – not lower than M 300. The furnace-waste additive is not so effective with working natural clay. To determine specificity of reactions between waste and charge minerals was used X-ray analysis. Results are showed that ash and slag waste behaves as active fillers and forming new mineral phases.

Thus, the use of ash and slag wastes of Kazan CHP as fillers for ceramic charge improves to physical and mechanical characteristics of wall bricks. At the same time, the ash-and-slag additive actively participates in mineral formation and increasing the amount of crystallization contacts in the resulting ceramic products.

### 1. Introduction

The increasing rates of residential and public buildings construction, as well as different purposes industrial objects construction, stimulate factories to increase their production, at first of all bricks for wall [1, 2]. In this regard factories, which make red ceramic bricks, should increase volume and variety of their production. At the same time, the prime cost of finished products should not



significantly exceed a certain limit, which primarily depends from technological process optimization with using waste of nearby industrial plants [3, 4, 5, 6 and 7]. At last times, brick factories try to use bottom ash waste as filler [8]. For regional production, it can be final product of Kuznetsk coal combustion on Kazan CHP (Combined heat and power plant). The successful experience of foreign companies in solid waste recycling and the production of ceramic products from them, allow us to hope in acceptable results [9, 10 and 11]. However, change of previously used natural raw materials on synthetic mixture as like a batch, implies a comprehensive study of both bottom ash waste themselves and their influence on the clinkering processes of ceramic products.

## 2. Objects

The studies were carried out with clay raw materials used and working charge of the Shelangovsk brick factory of OJSC «Ceramics-Synthesis». Bottom ash waste was taken from the Kirov cinder dump of Kazan CHP, located on outskirts of Kazan.

The natural ceramic raw materials of the Shelangovsk open cast mines according to the fractional composition belong to polymineral loam (Table 1).

**Table 1.** Fraction composition of clay raw materials and Kazan CHP bottom ash waste, in percentage

| Size, mm           | 0.25-0.1 | 0.1-0.05 | 0.05-0.01 | 0.01-0.001 |
|--------------------|----------|----------|-----------|------------|
| Clay raw materials | 0.8      | 5.08     | 23.26     | 70.86      |
| Bottom ash waste   | 20.38    | 10.26    | 69.36     | 0.0        |

The study of ash and slag wastes showed that they are characterized by a relatively uniform fractional and material composition. The predominant phase is an amorphous substance represented by spherical particles of silica and alumina. The crystalline phases are in a smaller amount. They include quartz, mullite, hematite, magnetite, calcite, microcline and albite. According to the results of ash particles chemical analysis in their composition predominate silica ( $\text{SiO}_2$ ) and alumina oxides ( $\text{Al}_2\text{O}_3$ ), accounting for 60.35% and 28.03%, respectively. In appreciable quantities there are  $\Sigma \text{Fe}_2\text{O}_3 + \text{FeO}$  - 7.17%,  $\Sigma \text{Na}_2\text{O} + \text{K}_2\text{O}$  - 2.10%,  $\text{CaO}$  - 1.08%,  $\text{TiO}_2$  - 0.75%,  $\text{SO}_3$  - 0.28%,  $\text{P}_2\text{O}_5$  - 0.24 %. All study mineral phases belong to the class of low-hazard substances that do not pose a threat to human health. Therefore, ash and slag waste can be used as a secondary raw material.

## 3. Methods

The main methods of study were X-ray, synchronous thermal analysis (STA) and SEM analysis.

X-ray phase analysis. The X-ray phase analysis was performed on the diffractometer D2 Phaser (Bruker, Germany) used for measuring the powder products in the Bragg-Brentano geometry, with the use of monochromatic  $\text{CuK}\alpha$ -radiation ( $\lambda = 1.54178 \text{ \AA}$ ), in the step-scan mode. Measuring and recording modes: X-ray tube voltage-30 kV, current-30 mA. Scanning step –  $0.02^\circ$ ; speed –  $1 \text{ deg/min}$ . The range of scanning angles in the Bragg-Brentano geometry  $3\text{--}40^\circ$ .

At the same time was a studied quantitative change of the amorphous phase at different temperatures. Qualitative and quantitative analyzes were taken using a computer international database PDF-2.

Also, the STA was used as an additional method of investigation. Sample analysis was carried on Netzsch STA 449 F3 Jupiter device (Germany), witch allowing measurements of mass changes and thermal effects at temperatures up to  $1200^\circ\text{C}$ . We fixed changes using thermogravimetric measurements (TG) and curves of differential thermal analysis (DTA).

Electron microscopic analysis of the samples conducted on the scanning electron microscope XL-30 ESEM.

#### 4. Results and Discussion

To assess the effectiveness of bottom ash waste for ceramic batch was conducted series of model experiments. In some experiments were used natural clay raw materials, from which ceramic bricks are made at the Shelangovsk brick factory of OJSC «Ceramics-Synthesis», in others - the work batch consisting of 75% of clay raw, 15% of sand and 10% of buckwheat husks. In this mixture were added 10, 15, 20 and 25% of the ash additive. After molding of ceramic small brick, samples were fired at  $T = 980^{\circ}\text{C}$  and then the end products were tested for strength. During the process of manufacturing ceramic products tested changes of their unit-weight and heat setting degree. The results of the studies are given in Tables 2 and 3.

**Table 2.** The physical and mechanical properties of ceramic products, made from natural clay with different content of ash filler

| Clay, % | Furnace bottom ash, % | Strength, kg/cm <sup>2</sup> | Unit-weight, g | Heat setting, % |
|---------|-----------------------|------------------------------|----------------|-----------------|
| 100     | 0                     | 248.32                       | 114.0          | 6.6             |
| 90      | 10                    | 220.0                        | 113.0          | 6.4             |
| 85      | 15                    | 203.0                        | 105.0          | 4.8             |
| 80      | 20                    | 192.3                        | 104.4          | 3.6             |
| 75      | 25                    | 180.3                        | 102.0          | 3.5             |

**Table 3.** The physical and mechanical properties of ceramic products, made from working batch with different content of ash filler

| Batch, % | Furnace bottom ash, % | Strength, kg/cm <sup>2</sup> | Unit-weight, g | Heat setting, % |
|----------|-----------------------|------------------------------|----------------|-----------------|
| 100      | 0                     | 110.56                       | 112.0          | 2.5             |
| 90       | 10                    | 125.0                        | 102.0          | 3.6             |
| 85       | 15                    | 128.0                        | 102.0          | 4.2             |
| 80       | 20                    | 150.0                        | 100.0          | 5.1             |

Analysis of the data obtained reveals following trends. Addition 10, 15 and 20 percent of ash to working charge are consistently increases the strength of ceramic products in compression tests. The maximum value of strength is achieved when introducing into the working charge 20% of the ash additive. Simultaneously with the increase in mechanical strength by 12-13%, unit-weight is decreases, which is an important factor for wall materials. According to the requirements of GOST (USSR Standard-Setting Authority) 530-95 for brick and ceramic stones, received products on compression match by brand not lower than M 100 (withstand a load of not less than 100 kg per 1 cm<sup>2</sup>); by bend - not lower than M 300 (withstand a load of not less than 100 kg per 1 cm<sup>2</sup>).

The furnace-waste additive is not so effective with working natural clay as with batch. Ceramic products which made from natural clay without filler have greater strength, compared with products containing ash additive. But they exhibit high shrinkage during thorough burning, which in mass production will lead to an increase in the proportion of defective bricks. The introduction of ash additive reduces the burning shrinkage by two times, and the strength characteristics significantly exceed the minimum values specified in GOST 530-95.

Solid mineral leaner additives, mixed with natural clay raw materials, are traditionally considered as inert components of ceramic batch. Their function is only to reduce air shrinkage and prevent mechanical deformations of molded greenware raw materials during drying. In the process of burning molded batch natural mineral additives practically do not participate in phase transformations. Bottom ash waste, characterized by a high content of amorphous silica and alumina, obviously can be not only as nonplastic material, but also as a catalyst for various thermal transformations, performing the function of a fusible matter. After carrying out physical and mechanical tests, the ceramic products

were examined with an electron microscope and an X-ray diffractometer. The aim of the research was to establish how the ash additives affect the processes of phase transformations occurring in the batch. The analysis of ceramic crocks sheared surface using electron microscopy showed that the aluminosilicate microspheres of the ash waste are relatively evenly distributed in the volume of the batch during the molding of articles (Figure 1a and b).

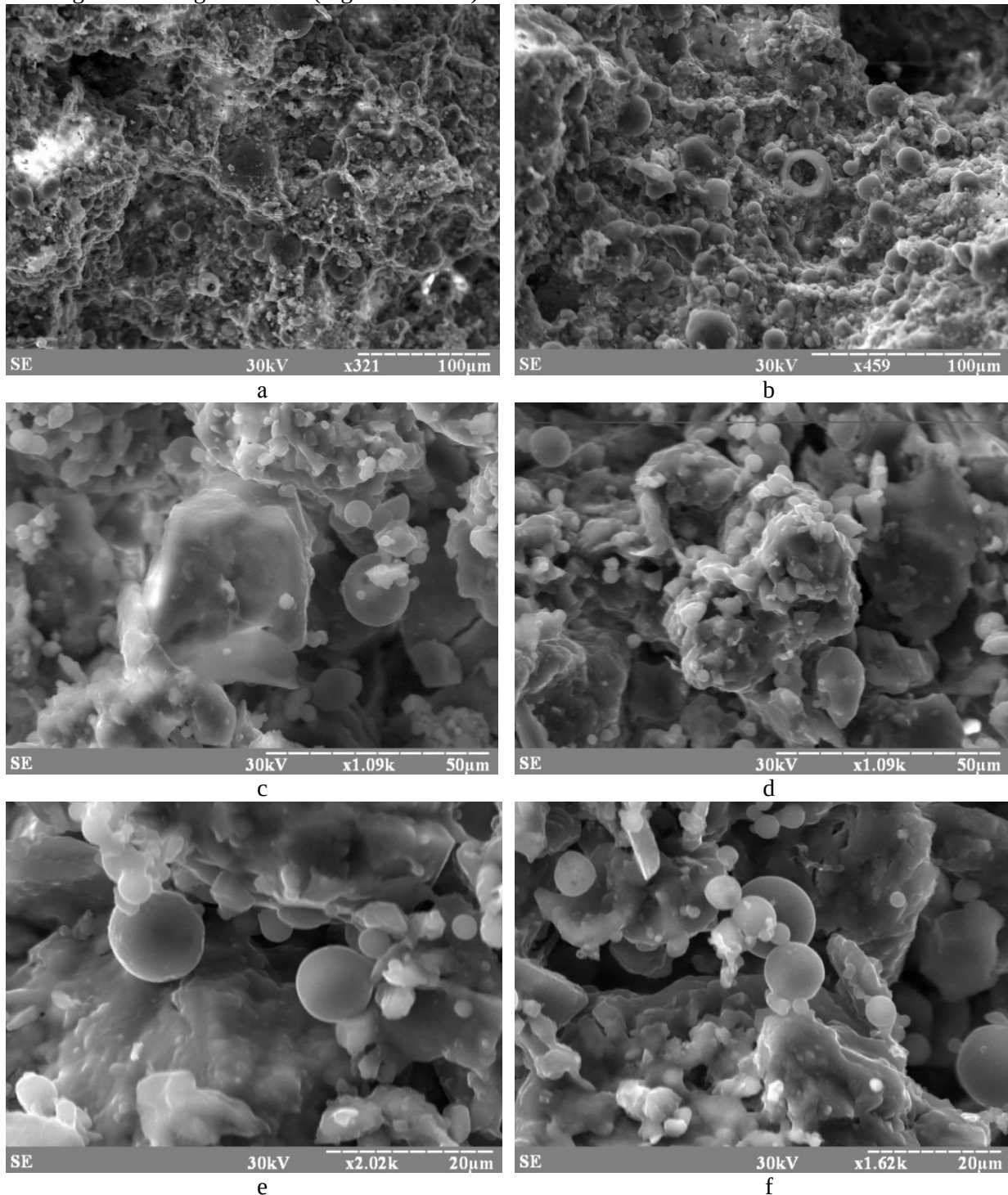


**Figure 1.** SEM photos of ceramic crocks sheared surface with ash filler

Some of them are concentrated in a clay suspension, some - on the minerals solid fragments surface. Regardless of localization place, all the particles to a greater or lesser extent interact with the surrounding components. In this case, the reactivity of microspheres is entirely determined by their size. Particles with a diameter of less than  $4.0\ \mu\text{m}$  are subject to more intense melting, compared to their larger counterparts. It is interesting that the batch minerals which are in contact with the alumino-silicate microspheres also influence their reactivity. On contact zone with quartz fragments microspheres form melting surfaces point on the whole retaining their spherical appearance. In contact zone with the surfaces of K-feldspar and Na-feldspar, microspheres begin to melt more intensively, often deforming into hemispheres. Depending on the size the microspheres in the clay mass can either remain spherical, or partially melt and spread with the formation of hemispheres (Figure 1c, d, e and f). The different reactivity of spherical alumino-silicate aggregates is due to the chemical composition and the melting point of the minerals in contact with them. In the presence of low-melting elements in the mineral composition such as sodium and potassium in feldspars and micas, the microspheres intensively melt. If there are not fluxing elements in the composition of minerals, then the melting of the microspheres is only at points on contact zone. Often on the ceramic crocks sheared surface it is possible to observe the fusion of alumino-silicate aggregates with each other. In this case the microspheres form peculiar bridges between the mineral components of the ceramic batch (Figure 1e and f). Melting of ash and slag additives on the one hand leads to an increase in burning shrinkage of products, on the other - to the growth of the amount of crystallization contacts in their volume. This explains the tendency to increase the strength and volume reduction (burning shrinkage) of ceramic products as the content of the ash additive increases in the working batch (see Table 3). In the batch using only the initial clay raw material, an inverse relationship is observed (see Table 2). Apparently, in this case the ash-and-slag additive behaves like an inert leaner. The different behavior of the alumino-silicate microspheres during the clinkering of the ceramic batch may be due to the structure of the pore space acquired by the products during burning. The burning buckwheat husks and the additionally introduced quartz grains into the working batch probably improve the thermal conductivity in the products volume. The result of this is a more intense flow of melting reactions on the minerals surfaces.

The obtained X-ray data show that in all ceramic products regardless of the presence and amount of the ash additive, the same processes of phase transformation go. The thermal decomposition of clay minerals is dominant - smectite, vermiculite and illite, which actually leads to the formation of a ceramic crock. As a result of sequential departure of different chemical elements from the structure of layered silicates, occurs their amorphisation which is fixed by an increase in the background component of the X-ray spectra. At the same time with the growth amorphous phase on the X-ray diffractograms, the appearance of new minerals growth, such as hematite ( $\text{Fe}_2\text{O}_3$ ) and wollastonite ( $\text{Ca}_3[\text{Si}_3\text{O}_9]$ ), is observed (Figure 2).

However, despite the identity of the phase transformations processes, the intensity of their manifestations is, to some extent, controlled by ash additive amount. First of all, control is manifested in the newly formed crystallochemical compounds. When comparing the absolute values of the peak intensities of the hematite ( $d = 0.269\ \text{nm}$ ) and wollastonite ( $d = 0.296\ \text{nm}$ ) reflexes of ceramic products with different amounts of the ash additive, the tendency of their increase with increasing content of the filler in the batch is well traced. It is important to remember, that the peak intensities of the reflexes actually reflect the amount of mineral in the investigation object. In fact we note that the ash additive leads to processes intensification of hematite and wollastonite formation.

The obtained results show that the use of ash wastes of Kazan CHP as mineral fillers of ceramic batch is quite acceptable. They introduce improved for physical and mechanical characteristics of wall bricks while reducing their weight. At the same time, the ash additive takes an active part in mineral formation processes, increasing the amount of crystallization contacts in ceramic products.

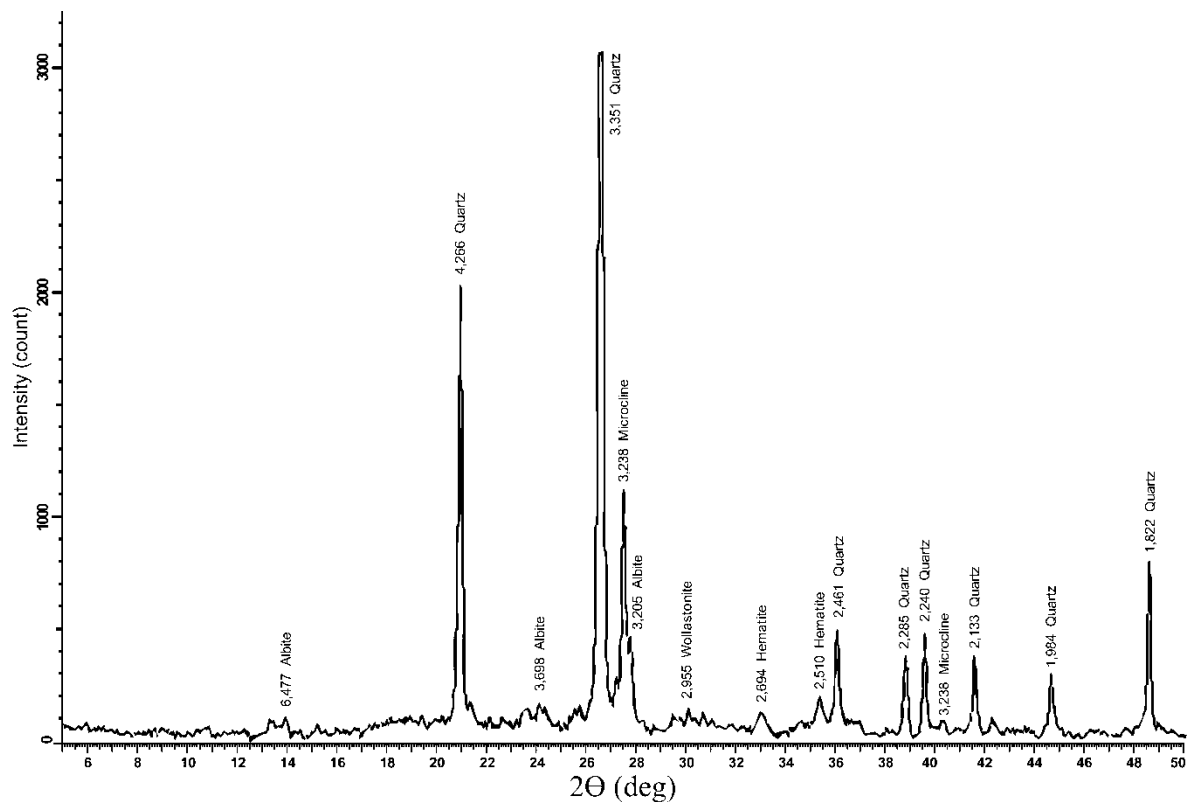


**Figure 2.** X-ray diffraction pattern of a ceramic crock with an ash additive

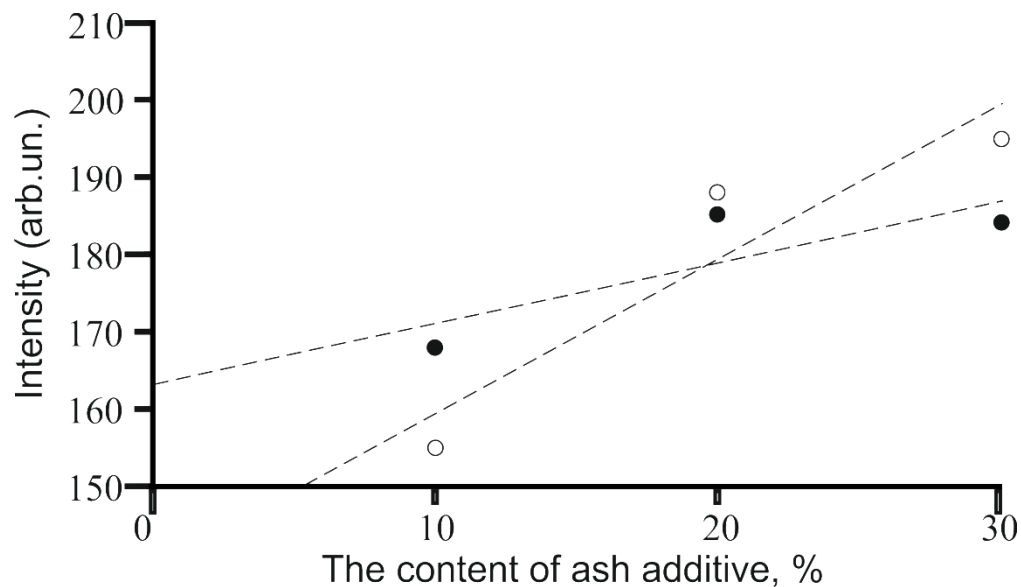


**Figure 3.** Change in the intensity of diagnostic reflexes of hematite (light circles) and wollastonite (black cups) with an increase in the content of the ash additive to the ceramic batch. The trend is shown by the dotted lines of the trend

## 5. Conclusion

Based on the results obtained, the following conclusions can be drawn:

- The ash additive to the working ceramic batch of the OJSC «Ceramica-Synthesis» Shelangovsk brick factory helps to increase the products strength. The introduction of an ash additive into the clay raw material reduces the strength characteristics of the finished products.
- The optimum amount of ash additive to the working batch and in the initial clay raw materials is 15-20%.
- Ash in the part of working batch is active additive, contributing to an increase in the amount of crystallization contacts in ceramic products.
- In final ceramic product the alumino-silicate microspheres of the ash additive participate in the formation of the spatial crystallization skeleton and contribute to the appearance of new crystalline phases, hematite and wollastonite.

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