

## Assessment of the Suitability of the Opal-Cristoballite Rocks of Korkinsk Deposit in the Construction Industry

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**Abstract:** The work carried out a comprehensive assessment of physicochemical and technological properties of the waste coal of Korkinsk coal deposit in the form of opal-cristobalite rocks flask. Installed that the main rock-forming mineral flask is amorphous silica. Economic feasibility of the flask instead of quartz sand is high grindability to obtain high dispersion of the particles. Thermally activated flask in the structure with composite cement binder thin grinded cement-50 shows physic-chemical activity to the lime and exchange reactions that in complex effects on the structure and phase formation at hydration and hardening with the increase of strength characteristics. Peculiarities of phase formation are in the binding of calcium of hydration and hardening of binding in the hydrate connection with the primary content of high-strength of  $\text{Ca}(\text{OH})_2$  at hydration and hardening of the binder in the hydrate compounds with a primary high content of calcium hydrosilicate of calcium as CSH (I). Economically profitable use of baked goods and flasks in thin grinded cement 50 and concretes on their base, which will increase the strength characteristics of concrete, lead to energy and resource conservation, reduced environmental pressures.

**Key words:** Flask · Grinded cement · Composite binder · Thermal activation

### INTRODUCTION

Rational use of mineral raw materials in the construction industry is one of the major questions in solving the problems of energy and resources. At the same time, the construction industry can be a unique utilizer of wastes of other industries to produce new composite binders and a wide range of high-performance materials based on them.

Every year the world is extracted from the bowels of the planet about 26 billion tons of rock, processed about 4.5 billion tons of mineral resources, of which only 2 to 10% is a useful product, 2.7 billion tons go to the category of industrial waste rational use of which as a rule is not defined [1]. Mineral development is accompanied by the accumulation of billions of cubic meters of overburden, which take hundreds of thousands of hectares of land. As a result of the accumulation on the surface of our planet powerful of technogenics formations are environmental pressure.

The rational solution to the problem of industrial waste depends on a number of factors, but the most effective solution is the introduction of non-waste technology. With the integrated use of natural resources, industrial waste some industries may be the source of other raw materials. Rational use of mineral complex of natural resources, involvement in the production of man-made materials and secondary products of various industries for the production of building materials will significantly reduce the burden on the environment and lead to the resource-and energy-saving.

One way to increase the volume of mineral binders is to obtain composite binders. The use of composite binders using waste industry will lead not only to a reduction in consumption of clinker component in the binder, but also to the high-performance building materials based on them.

Preparation of composite binding accompanied by using complex multi-component in order to produce high quality concretes different functionality with

improved properties and a predetermined specified structure. The foundation of such binding on the principle of goal-oriented control technology in all its phases: the use of active components, the development of optimum structures, the use of chemical modifiers, the use of mechanical activation of components and some other techniques.

Traditionally, as the silica component for thin grinded cement, fine concrete and binders low water consumption using natural sands, quartz content which is about 95% [1-5].

In this situation, an acute shortage of not only binding, but also high-quality aggregates, a significant importance of utilizing man-made structures as an active mineral supplements.

Solve some of the social and ecological problems, to create waste-free technology is possible using waste coal Korkinsk coal mine, which is one of the largest in Europe [6].

For the extraction of coal in a coal mine in Korkinsk waste contains a sufficient amount of silica-containing raw materials, which can be a potential reserve of mineral resources base of industrial industry. Among a variety of mineral particle size and composition of the waste flasks and flasks-like clays are allocated which can be used in the preparation of cement, pozzolanic additives as active components binders.

## MATERIALS AND METHODS

Grinding of quartz components and composite binding was carried out in a porcelain laboratory mill. Determination of the specific surface of the materials was provided by the air permeability of the on the device

PSH according to GOST 310.1-76 [7]. This determination method is based on measuring resistance air sucked through the layer thickness and installed cross-sectional area of compacted powder.

The presence of  $\text{CaO}_{\text{free}}$  in the binder determined by ethyl-glitserratnym method [8].

X-ray diffraction analysis of the samples was carried out on a DRON-4 with radiation using Cu-anode (Ni-filter to attenuate [beta]-radiation components). Scanning step 0,05 °, the measurement of the intensity in the scanning points-1.

X-ray diffraction analysis of flaks breed was carried out in an automated way using a DRON-3M using the program PELdos.

Test of composite binding Ground cement 50 on the compressive strength was carried out according to GOST 310.4-81 [9].

**The Main Part:** For the experiment in this work we used materials: Portland cement CEM I 42,5 N of PJSC "Belgorod cement" (Russia); flask of Korkinsk coal deposit (Russia) - quartz sand Lower- Olshansky deposit (Russia).

Chemical composition of siliceous rocks is shown in Table 1.

Chemical composition of the flask is different from naturally occurring quartz. Flaks - are siliceous sedimentary rocks, more than half composed of silica minerals. As a consequence of rock-forming processes catagenesis silica in the mold formed silica in the form of free  $\text{SiO}_{2\text{free}}$  water and silica  $\text{SiO}_{2\text{free}} \cdot n\text{H}_2\text{O}$ .

To prepare ground cement-50 produced 50% of the joint grinding clinker with 50% of silica-containing rocks.

Table 1: The chemical composition of minerals, wt. %

oxide content	SiO <sub>2</sub>	SiO <sub>2free</sub>	SiO <sub>2free</sub> •nH <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	SO	Igniting lossers
casting-box	80,96	70,61	67,81	7,33	4,95	1,30	0,76	0,1	4,8	3,8	5,3	-	4,62
quartz sand	92,4	90,03	-	2,36	0,77	1,88	0,2	-	-	-	-	0,05	1,95

Table 2: The phase composition of the investigated species

formula	name	amount		no ICDD
		casting-box natural	casting-box thermally activated	
SiO <sub>2</sub>	Quartz	****	****	46-1045
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Halloysite	***	*	29-1487
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Anorthite	*	*	12-301
Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	Gehlenite	*	*	35-755
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Kaolinite	**	*	6-221
Ca <sub>0,3</sub> (Al,Mg) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> •4H <sub>2</sub> O	Montmorillonite	**	traces	13-135
x-qla 3a	Amorphous silica	***	***	-

Table 3: Kinetics of grinding components

Material	The specific surface area, m <sup>2</sup> /kg with milling time, min			
	0	30	60	90
casting-box				
thermally activated	170	698	1319	1760
Quartz sand	170	390	565	660

Table 4: Strength of the composite binder (thin-ground cement-50)

no composition	composition	Hardening time, days			
		3	7	14	28
		Compressive strength, MPa			
1	cement + Quartz sand	10	15	21	32
2	cement + casting-box natural	8,5	13	18	27
3	cement + casting-box thermally activated	13	17	24	37

**Phase-structural Analysis of Flaks-cristobalite Rocks:**

The microstructure of the flask Korkinsk coal deposit is mainly composed of tiny (less than 0.005 mm) particles of opal-cristobalite silica. Opal is meant by the term of reactive silica (soluble in weak alkalis) which have a biogenic origin. Table 2 shows the studied species, which is present in varying amounts detritus (mainly quartz) and clay material. Organic residues (shells of diatoms, radiolarians sink, sponge spicules) are rare and poorly preserved.

For the active component of the binder opal-cristobalite rocks (flask) was fired (thermal activation) at 600 °C for 20 min. Low thermal treatment was optimized experimentally [10].

During the heat treatment is modified amorphous silica flasks with polymorphic transformations to form the most active silica. Identification of mineral components was based on database diffraction data PDF-2 [11].

The main study of the natural minerals are quartz flask, halloysite and about 70% amorphous clay. Accessory minerals are kaolinite, montmorillonite, anorthite and gelnite. Thermal processing changes the phase while maintaining the concentration of the amorphous clay.

**The Study of the Grindability of Silica-containing Component:**

The main component of the silica-used in the composition of the composite binder is silica sand, activation of which is carried out by the fine grinding with large amounts of energy. When considering the flask as silica-component composite binder established experimentally that different high grindability flask

compared with the quartz sand, the surface of which is increased in 90 minutes to 10 times (Table 3).

Due to the fact that the flask consists mainly of individual grains, the strength of the contact zone between them is much lower than the strength of the individual monocrystals quartz with close hardness rockforming minerals. When grinding the destruction of the flask is precisely the contact areas, so it has the greatest grindability.

**The Kinetics of Curing Composite Binders:** To assess the management of thermally activated flask in the composite binder thin ground cement -50 molded samples, hardening of which took place in natural environment. As a control sample was chosen composition thin ground cement-50 on the quartz sand. For comparison molded compositions based on natural flask without thermal activation. Activity of binders was determined at 3, 7, 14 and 28 days. Samples of the composite binder using flasks untreated inferior in strength parameters composite binders with baked flask (Table 4). At all stages of hardening of the material strength of the samples with the use of heat-treated flask above.

The difference of strength characteristics of these samples can be attributed to the high activity of interaction with components of the heat-activated silica binder that is present in the flask. Fineparticles of thermally activated flask in in compound with thin ground cement-50 gives additional filling of intergranular space, increasing the strength of the binding complex. On this basis one can conclude that the heat treatment has a positive effect on the kinetics of the compressive shear strength [12-14].

Table 5: The content of free form a calcium oxide (CaO<sub>free</sub>),%

The composite binder thin ground cement-50	raw	3 day	7 day	14 day	28 day
cement + casting-box natural	1,70	1,65	1,62	1,60	1,55
cement + casting-box thermally activated	0,89	0,84	0,81	0,79	0,76

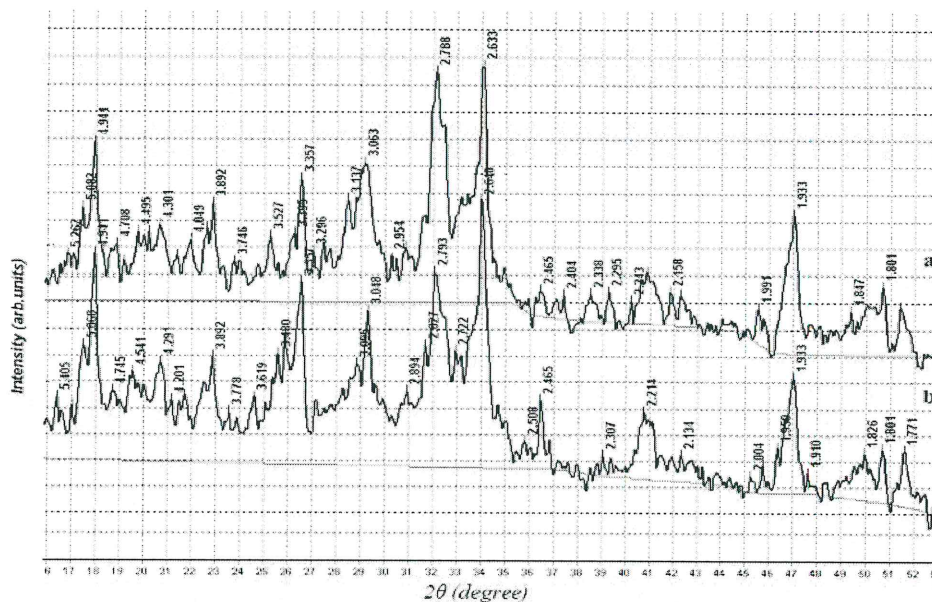


Fig. 1: Radiographs thin ground cement-50 after 28 days of hardening a - part 2; b - part 3 (Table 2).

**Determination of Unbound Calcium Oxide in the Composite Binder:** Completeness of the chemical reactions between the components of the binder with formation of calcium hydrosilicates when measured by hydration of the calcium oxide content in free form. An important factor in obtaining high bonding quality intrusion of calcium oxide in the free form no more than 1%.

Content of unbound calcium oxide in the test composite binder is shown in Table 5.

The use of heat-treated opal-cristobalite flask useful in the development of composite binders, since the content CaO<sub>free</sub> in it no more than 1%. Thermally activated silica in the flask, as well as clay components exhibit a high physic-chemical activity with respect to the lime adsorption capacity and exchange reactions in the binder to form a hydro-silicate ligament.

**RFA of Thin Ground Cement-50:** Confirmation of a complete binding of Ca(OH)<sub>2</sub> in the crystal neoplasms is reflected on XRD, differential intensity of the reflections characteristic of Ca(OH)<sub>2</sub> (1.933, 2.404, 2.295, 3.063 Å), in the binder is reduced by using heat-treated flasks, indicating that the binding portland in substantially crystalline hydrosilicates of low type (Figure 1 b).

The high intensity of the diffraction peaks of portland and alite (2.788, 2.158, 1.771 Å) and a smaller number of hydrated phases indicates a low degree of interaction in the hydrated system using natural flask (Fig. 1a). On the RFA presence opal-cristobalite phase is diagnosed by an amorphous background in the range of 18-26° angles 2θ (distance between planes 4.90-3.40 with a maximum near 4.05.) Wide smeared bands in the sample binder based on natural flask indicate the formation of hydrates low degree of cristallisation with less structural order of amorphous silica phase. Thermally activated flask vigorously interact in chemical reactions of hydration with the transition of the active part of the crystalline silica hydro-silicates, the bulk of which is a high-strength calcium hydro-silicates CSH (I) (5.405, 4.291, 2.465, 2.722, 3.357, 1.826 Å).

**CONCLUSION**

Rational comprehensive utilization of mineral resource is possible due to involvement in the production of industrial waste coal-flask.

Economic and technological feasibility of the flask is to reduce the grinding due to the high grindability compared with quartz sand.

**Conclusions:** Obtained by firing an active phase comprising silica with the flask vigorously reacts hydration alkaline mixtures with a reduction of free lime. The results of XRD binding of Ca (OH) 2 occurs mainly in the high crystalline calcium of hydro-silicates of calcium. Fine particles of thermally activated flask in binder fill intergranular space, creating a tight packing by increasing the number of contacts in each of the high-strength hydrate phases contribute to the strength thin ground cement -50 by 37% in comparison with composition binder on natural flask and 16% in comparison with composition binders astringent on quartz sand.

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