New Composite Binder From Secondary Mineral Resources

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KEYWORDS: high-calcium, fly ash, burnt sand, high-alumina product, amorphous material, mechano-chemical process, planetary mill, reaction, cementless composite binder.

ABSTRACT

The Siberian State University of Industry (SSUI) in association with the institutes of the Siberian Branch of the Russian Academy of Sciences has created a new composite binder consisting of fly ash from the Abakan thermal power plant, used molding sand mixture ("burnt sand") from foundry, Abakanvagonmash, and waste product from the Yurga abrasion plant. Fly ash contains up to 40% SiO_2 and 35% CaO including above 15% free CaO. The used sand mixture includes above 90% SiO_2, mostly in the amorphous state. The waste product of the abrasion production (high-alumina product) contains 80% and more Al_2O_3.

Ash is good binder, but the presence of free CaO destroys its binding properties during service. Grinding ash, sand and high-alumina product (HAP) together by means of mechano-chemical activation in planetary ball mills to the fineness of 750 m'/kg and using thermal treatment produced a binder with a compressive strength above 50 MPa at 28 days.

It was found that during the process of mechano-chemical treatment, free CaO reacts with SiO_2 (chemistry of a solid), reduces its contents in the mixture by 60 to 80% and increases the strength by 1,5 to 2 times eliminating the process of concrete expansion.

The creation of a binder from industrial wastes and fine concretes on its basis (with slag sand as an aggregate) gives both economic (its cost is half that of Portland cement) and ecological benefits by eliminating landfills and reducing the CO_2 discharge into the atmosphere (the production of a ton of cement discharges above 0,5 ton CO_2).

INTRODUCTION

The department of civil engineering, SSUI, supported financially by the Ministry of Education of Russia, has created fine cementless ash – slag concrete from wastes of thermal power plants and ferroalloy plant [1]. Concrete has been patented (patent № 2065420). A project for the construction of the binder and silicate brick shop [2, 3] at the Abakan thermal power plant has been developed and approved. A technical certificate by the Government of Russia has been received. But as the Abakan thermal power plant is a part of the Abakanvagonmash with a large foundry which dumps used molding sand mixtures (1 ton of sand per 1 ton of founding), we thought of replacing silica fume with molding sand as a silica component of a new binder and concretes. Supported by the **Federal INTEGRATION Program**, the investigation was carried out in the laboratories of the SSUI, Associated Institute of Geology, Geophysics and Mineralogy (AIGGM) and the Institute of Chemistry of Solids and Mechanochemistry (ICSM), Siberian branch of the Russian Academy of Sciences (SBRAS).

As known, the following compounds are in composition of cement: $3CaO \cdot SiO_2$ (mass portion of 40–60 %); $2CaO \cdot SiO_2$ (15–35 %); $3CaO \cdot Al_2O_3$ (4–14 %); $3CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (10–18 %) [4]. The indicated compounds and also the initial components for their synthesis are in ashes from coals combustion, in waste products of casting and abrasives production. Therefore these wastes are used for the production of cementless binding materials from them [5]. The quality of binding materials from wastes depends on the following factors:

1) selection of composition in order to correspond to a large extant to the composition of cement;

2) mixture of composition in order to have possibly the chemical interaction between them.

Thermal method in this case are less suitable for the reason of their high energy consumption, therefore the mechanical activation of mixture is used in grinding apparatuses [6–8].

However, the mechanochemical reaction with participation of waterless oxides is not so effective. Thermodynamically, the reactions with participation of hydrated oxides are more advantageous which are formed during addition to mixtures of waterless oxides of water. So, for reaction:

$$3CaO \cdot SiO_2 = CaSiO_3$$

$$Ca(OH)_2 + SiO_2 \cdot xH_2O = CaSiO_3 + xH_2O,$$

here Gibbs energy equals to 89.4 and 117.2 kJ/mole respectively. The experiment shows that the coherence of calcium in the second case proceeds more effectively in some times than during the interaction of waterless oxides.

Roentgenamorphic hydrosilicates relating to tobermorite group ($Ca(OH)_2 \cdot Si_6O_{16} \cdot 4H_2O$) are the products of mechanical activation in relation of components $Ca(OH)_2 : SiO_2 \cdot H_2O = 1 : 1$; during their scaling the pure wollastonite β-$CaSiO_2$ [9] is obtained.

It is possible to get bicalcium silicate by indicated method. In work [10] the activation of calcium oxide and amorphic silica gel was being carried out in presence of water, the quantity of which was larger than calculatedš on theoretical composition of $2CaO \cdot SiO_2 \cdot 2H_2O$. After activation during 14 hours in vibration mill the roentgenamorphic product is obtained, in which the former of bicalcium silicate is contained. After heating upto 550 ^{0}C, the peak appears belonging to β-$2CaO \cdot SiO_2$, but during heating till 1000 ^{0}C the product is already crystallized well.

By analogy during mechanical activation of calcium hydrooxides mixtures and of aluminium the hydroaluminates of calcium $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $2CaO \cdot Al_2O_3 \cdot 4H_2O$ are formed, which during heating till temperature of 700–1000 ^{0}C are decomposed with formation of $12CaO \cdot 7Al_2O_3$ and $2CaO \cdot Al_2O_3$ having viscous properties [11–13].

In this work the use of mechanical activation for synthesizing of composite binder from industrial waste containing the oxides of calcium, silicon and aluminium.

MATERIALS

Fly Ash

According to Ivanov [14], high – calcium fly ash from the electrostatic filters of the Abakan thermal plant is a coarse polydispersed ash with the surface area below 250 m^2/kg.It consists mostly of irregular agglomerated particles (Fig. 1). The bulk density, absolute density and effective specific activity of the ash are 1120, 2680 kg/m^3 and 118,9 Bq/kg, respectively. Chemical analysis of the ash is given in Table 1.

As can be seen from the data, the ash has to be ground to break its agglomerated particles and bind free CaO, the presence of which would induce expansion and fracture of concrete. Furthermore, the method of Ovcharenko [15] showed that 58% free CaO was in a glass phase which prevented it from hydration prior to strength gain.

Molding Sand Mixture

The molding sand mixture consists of 92% quartz sand, 6% bentonite and 2% water glass. After its use in foundry and removing gritty scale from the mixture, it has a form of a black sand ("burnt" sand) with the fineness modulus of 1,91 (Fig. 2). The bulk density, absolute density and the effective specific activity of the sand are 1450, 2380 kg/m^3 and 98 Bq/kg, respectively. Chemical analysis of the burnt sand is given in Table 2.

The burnt sand has high content of silicon oxide in the amorphous state (thanks to a high – temperature treatment) which enhances the possibility of chemical binding free CaO in the ash into calcium silicates.

High – Alumina Product (HAP)

High – alumina product, the waste from the Yurga abrasion plant, is a grey powder (Fig. 3). Its chemical analysis is shown in Table 3.

This powder is used to enhance strength and fire resistance a binder and concrete.

TESTING PROCEDURES

The following test series were undertaken.

Determining Optimum Mixture Proportions of a Binder

Correlation of the two components (fly ash and burnt sand) were determined. Fly ash was ground in a laboratory ball mill to the fineness of 400 m^2/kg, and the burnt sand was ground to a powder with the residue of 15% on the sieve № 008. Strength and waterproofness of a binder versus fly – ash – to – burnt sand ratios are in Table 4.

The results of the initial investigation showed that a cementless binder can be produced from the above wastes of thermal power plant and foundry. The optimum components ratio as determined by a computerized analysis was 85 to 90% fly ash and 10 to 15% ground burnt sand. However, long – term testing in water and a chemical analysis of the binder showed that below 50% free CaO interacted with SiO_2 with the resulting cracks in specimens.

Mixture Activation

The preliminary researches were being carried out in laboratory planetary mill AGO-2 [16] with samples of 10 gr. processed mixtures and in large planetary mill AGO-3 [17] with total 1 kg mixture loading.

Power characteristics of mills are close between each other. The mixtures made ofš chemically pure oxides of calcium, silicon and aluminium and also the mixtures composed from wastes were undergone by activation. Roentgenphase analysis is carried out on device DRON-3 (radiation of CuKa). Determination of content of incoherent calcium oxide was made by method described in work [15]. The measurement of basic indices of binder and manufactured articles from it was made in accordance with State Standard 310 "Cement".

The experiments influence of mechanical activation on interaction in mixture of oxides CaO, Al_2O_3, SiO_2 made. Mixtures were activated during 10 minutes. Data of roentgenphase analysis of mixture are presented in Fig. 4. In absence of water the chemical interaction, as seen from Fig. 4, are practically absent (i.e. the dispersion and amorphisation of oxides are carried out).š In adding water the reflexes of $Ca(OH)_2$ and also the reflexes corresponding to formation of calcium aluminate $3CaO \cdot Al_2O_3 \cdot 6H_2O$ appear. Thermodynamic calculations of hydrosilicates and hydroaluminates formation by reactions

$$5Ca(OH)_2 + 6SiO_2 = Ca(OH)_2 \cdot Si_6O_{16} \cdot 4H_2O$$

$$6Ca(OH)_2 + 2Al_2O_3 + 6H_2O = 2(3CaO \cdot Al_2O_3 \cdot 6H_2O)$$

show that the probabilities of forming the products mentioned above are approximately the same.

Gibbs energy for the first reaction equals to 303 kJ/mole [18] and for the second one it is equal to 303.2 kJ/mole [19]. It means that hydrosilicates of calcium also may present in product but, probably they are less oxitallized and do not give diffraction picture.

For obtaining the composite binder the fume high-calcium ash from Abakan TPS (Thermal Power Station), wasted mould mixture (burnt ground) of casting production AO "Abakanwaggonmachine" and high-alumina product, i.e. the wastes from Yurginsk abbrasive production were taken.

For mechanical activation the mixture of 80% ash and 20% of burnt ground were selected and 5% high-alumina product were added into it.

To enhance the activity of the binder components, the blend of 80 % fly ash, 10% burnt sand and 10% HAP was ground in a planetary activator mill AGO-3 (0,1–100 μm) designed by the ICSM, Siberian branch oh the RAS (Fig. 5).

The composition mentioned above was being processed different time in mill AGO-3. It should be noted that water was not added to mixture, but nevertheless one cannot consider that the process was carried out without water. One can believe that water adsorbed on the surface of initial products, the content of which, as it follows from data on losses during scaling, is at the level of 2%, will take part.

Grinding in this mill is performed in the field of three inertia forces (two centrifugal forces and the Koriolis force), due to which fact the electric tension of AGO-3 is 2 to 3 times higher than that of gravity ball mills (Fig. 6). Mechanochemical activation of the components (chemistry of solids) and partial interaction of the amorphous silica and CaO takes place during the process. The data on the free CaO content and the degree of the blend dispersity with respect to the duration of grinding in a planetary mill are shown in Table 5. In Fig. 7 the structure of mixture after grinding is shown.

Casting and Testing of Specimens of a New Binder

2 – cm cube of specimens were cast once again from the activated mixture of the normal consistency. The test results are given in Table 6.

From the data shown in Table 6, it can be seen that the best results were obtained with the activator mill during minutes (the dispersity of the blend was 750 m^2/kg). The binder exhibitedš high compressive strength and waterproofness. It was found thatš with further treatment (above 10 min, the dispersity of 1000 m^2/kg), water demand and setting time of the mixture sharply increased, and a drop in the compressive strength was observed.

Tests for expansion (State Standard 310.3-76* Cements, Methods for Determining Normal Consistency, Setting Time and expansion) were carried out by boiling cakes in a bath with the hydraulic date and in an autoclave. Cakes made from the mixture № 1 had fractures and radial cracks while cakes from the mixture № 2 had smaller defects but with some warping. The remainder mixtures (nos 3 to 6) sustained both boiling and an autoclave tests. The test results showed that the new binder was in accordance with the requirements of the State Standard 310 Cement.

CONCLUSIONS

1. Previous investigation shows that wastes from thermal power plants burning brown coals of the KATPC in combination with silica by – products from other industries can be used for composite high – class binders (up to 60 MPa) and concretes on their basis which are equivalent to the traditional binders and concretes.

2. To bind free CaO in brown coal ashes, mechanochemical activation of the components has to be made their combined grinding in the planetary activator mills. This assists interaction of above 50% CaO and SiO_2 and prevents from destructive processes in concretes with a cementless binder.

3. Creation of binders from secondary mineral resources contributes much to the environment protection and also helps towards the solving of economic and social problems (construction of dwellings from concretes with cementless binders).

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Table 1. Chemical analysis of ash

Component	Compound, %								
	SiO_2	Cao total	including free CaO	MgO	Al_2O_3	Fe_2O_3	$Na_2O + K_2O$	TiO_2	LoI
Fly ash from Abakan TPP	40.47	34.94	15.75	7.28	4.87	10.32	1.1	0.80	1.02

Table 2. Chemical analysis of burnt sand

Component	Compound, %						
	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	$Na_2O + K_2O$	LoI
Burnt sand	92.28	1.80	0.2	2.71	2.38	1.02	-

Table 3. Chemical analysis of HAP

Component	Compound, %							
	SiO_2	TiO_2	Al_2O_3	$FeO + Fe_2O_3$	MgO	CaO	$K_2O + Na_2O$	LoI
HAP	4.51	2.36	34.00	5.17	1.64	1.14	0.34	0.12

Table 4. Compressive strength and waterproofness of a composite binder

Components, % by weight		Compressive strength, MPa		Coefficient of softening	Notes
sand	ash	R dry	R sat		
40	60	24.85	5.45	0.22	non-waterproof
30	70	34.4	6.70	0.13	non-waterproof
20	80	41.4	21.55	0.52	non-waterproof
10	90	21.2	31.75	1.5	higher waterproofness

Table 5. Free CaO content of the blend versus duration of treatment in AGO-3 mill

Blend no	Duration of treatment, min	Dispersity, m^2/kg	Free CaO content, %
1	without treatment	200	12.60
2	1	400	6.33
3	3	500	4.82
4	6	600	3.92

5	10	750	2.80
6	15	1000	2.02

Table 6. Strength and waterproofness of a composite binder

Mixture no	Compressive strength, MPa		Coefficient of softening	Notes
	R dry	R sat		
1	27.82	6.36	0.49	non-waterproof
2	35.63	9.87	0.57	non-waterproof
3	41.35	25.73	0.88	non-waterproof
4	52.48	47.65	1.59	higher waterproofness
5	56.76	49.98	1.85	higher waterproofness
6	43.54	40.54	1.34	higher waterproofness

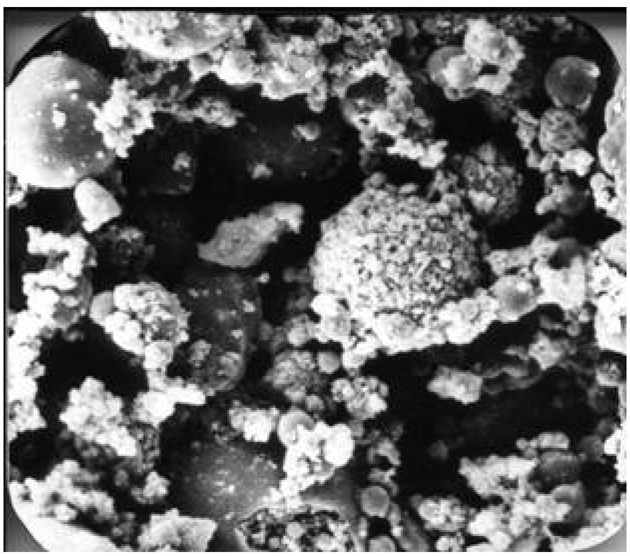


Fig. 1. Structure of fly ash from the Abakan thermal power plant x 1000

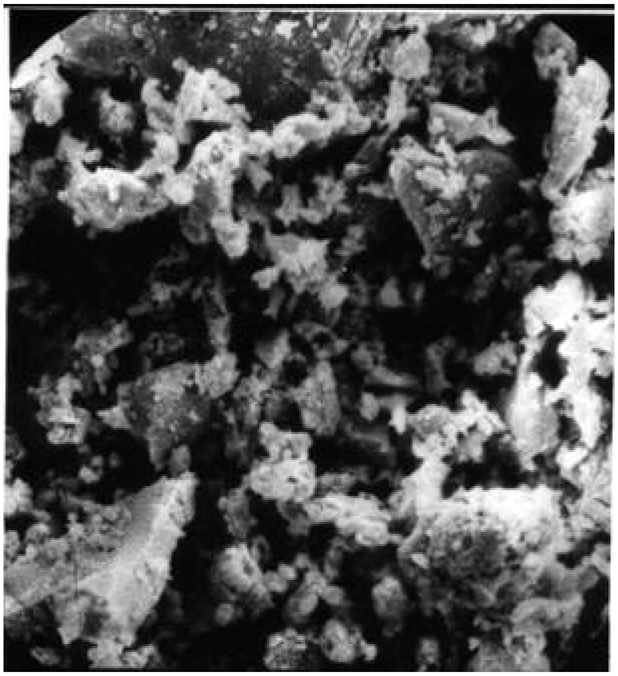


Fig. 2. Structure of burnt sand x 1000

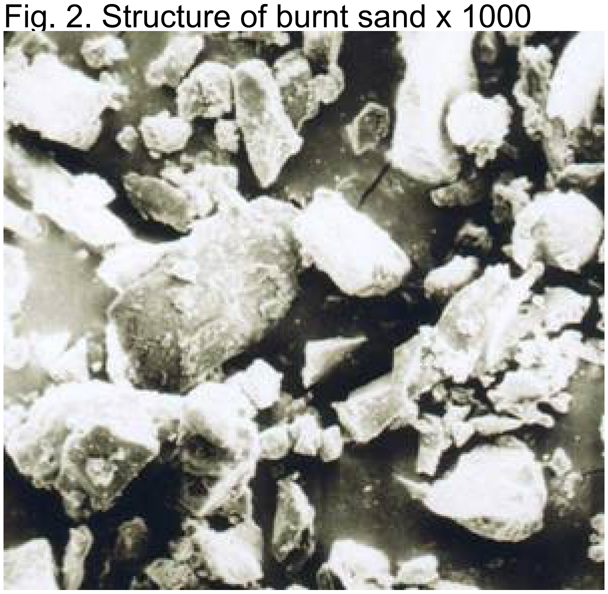


Fig. 3. Structure of HAP x 400

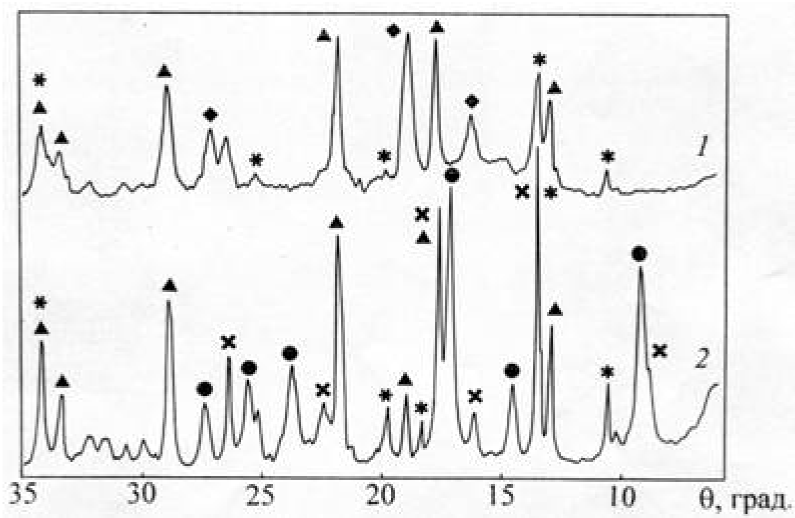
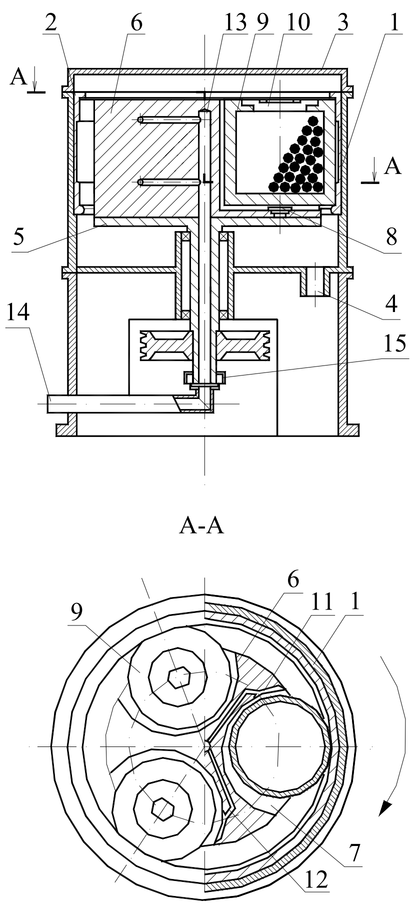


Fig. 4. Diffractogrammes of activated mixtures CaO + Al_2O_3 + SiO_2 :
1 – waterless oxides; 2 – mixture contains 20 % H_2O

Fig. 5. The laboratory activator mill AGO-3



1. Body
2. Lug for a guided drum movement
3. Cover
4. Water outlet
5. Driver bottom
6. Driver
7. Recess for drum
8. Bearing
9. Drum
10. Drum cover
11. Water pocket
12. Water outlet
13. Water conduit
14. Branch pipe
15. Gland packing

Direction of the driver revolution

Fig. 6. The scheme of activator mill AGO-3

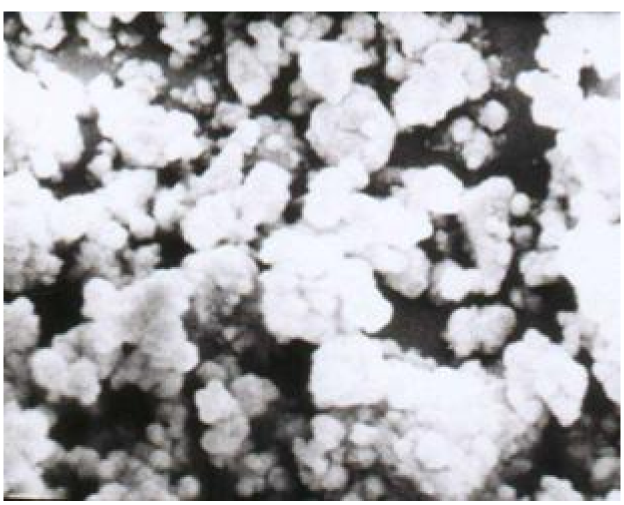


Fig. 7. Structure of grinded mixture of th