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Intensification of Cement Grinding with Apply Grinding Aids with Modify Effect

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Abstract

For over 60 years technological additives used in process of grinding cement. Application of cement grinding aids can improve performance of ball mills, reduce specific energy consumption, and increase fluidity of cement during transportation and processing. Construction practice is characterized currently emergence and increasing use of so-called high-tech (effective) a new generation of concrete, suggesting the use of high quality cement. In work presents results of impact intensifiers on the grindability of cement based on different mineralogical composition of clinker. Offers original methodology for assessing of indicators intensifiers action on grinding process and qualitative characteristics of cement. Knowing positive and negative sides of each constituent component it is possible to try selection of compositions intensifiers with synergies effect considering mineralogical composition of clinker and material composition of cement. The presence of modifying component allows not only render intensifying effect in milling process, but to increase both early and late strength due to the formation of more dense and homogeneous structure of cement stone. It is shown that intensifiers with modifying additives allow not only affect on grinding process, but also on the process of hydration and morphology crystal hydrates, strength characteristics. In process of work we had determined, that among researched additives for two different cements, which differ from each other mineralogical composition, best results were obtained with used AI8 intensifier.

Keywords: intensifiers, modifying component, cement grinding process, the rate of cement hydration

1. Introduction

Relatively recently appearance a new generation of additives to improve the quality characteristics of cement (Samner, 2008). To distinguish them from grinding aids in foreign literature it is accepted call them "Quality Improvers" (QI). We use is widespread in various fields of domestic industry technical term "modifying agent" ("Modifying agent"), i.e. additive is introduced into base composition to improve physicomechanical and technological characteristics. This direction implies use of various modifying components that can change at nanoscale structural and morphological dimensionally geometric and energetic characteristics of composites (Sandberg, 2007).

Considering that main component of concrete is a cement, that optimization of particle size cement composition, and control speed of its hydration, amount and properties of the liquid phase (Unland, 2003), structural morphology of formed crystal hydrates possible already at stage of grinding cement with using surfactants (Jankovic et all., 2004). Based on these assumptions, we are carrying out research on development of composite processing aids with functions grinding aids and modifiers gripes and hardening of cement (Ghosh, 2003). The introduction of modifying additives on stage of grinding enables solve one of difficult in technological plan problems modifying composition systems - uniform distribution of additives at low concentrations in their environment polyfractional dispersed material (Perez et al., 2007).

Totality of known experimental data on effect of organic compounds on process of grinding cement validated (Adolphs, 2006). Different effects of each component is primarily due to structure of organic molecules and electronic structure of active radicals, mineralogical composition of clinker and mineral supplements in cement and considering possibilities of alloying (Aggoun, 2008). To reveal general dependence of effect of individual compounds within different classes, intensification of grinding is not possible, as grindability of cement depends on chemical and mineralogical composition of clinker, the macro-and microstructure of the clinker minerals and mineral supplements (Viviani et al., 2008). In turn, microstructure of clinker determined by the parameters of production process (the properties of raw materials, fineness of grinding and homogeneity raw mixture, firing and cooling parameters, type of fuel etc.).

2. Materials and Methods

In development of compositions of intensifiers with modifying additives assumed primarily from functional action of the intensifier. Many years of research experience milling process in laboratories of leading Russian and foreign manufacturers of grinding aids, as well as results of experimental industrial tests allowed to classify grinding aids on chemical structure of compounds, basic structure of molecules and the chemical- adsorption properties (Table1).

Table 1. Classification grinding aids

Group name (a class of chemical compounds)	International designation	Name of product	Features of the structural formula:
Amine (Amines)	TEA	triethanolamine	Monomers
	TIPA	triisopropanolamine	
Glycolic (polyhydric alcohols)	DEG	diethyleneglycol	Short unbranched chain
	PEG	polyethyleneglycol	Long unbranched chains
	PPG	polypropyleneglycol	
SAS (water and glycol solutions polymer compositions)	LS	lignosulfonates	Complicated long chain with active radicals
	PNS	polinaftalin sulfonates	Complicated long chains with active radicals and branched side chains with a strong sense of intensification, water-reducing and modifying effect of cement slurries
	PCE	polycarboxylates	
	PA	polyacrylates	

Compounds relating to class of amines merely modify particle size cements neutralized charges arising at rupture valence bond and catalyze hydration process to increase strength, both in initial and late periods of hardening. Glycol compositions mainly prevent agglomeration of cement particles in grinding process, and exert little effect on change in particle size. The most effective influence on processes of grinding and hardening, have intensifiers based on surfactants. Water solutions of surfactants significantly change granulometric composition of cements with increased levels of small particle size and simultaneous agglomeration neutralize surface charges as a result dissociation of the surfactant and appearance of ions, but has a negative effect on strength characteristics of cement stone. A surfactant solution in glycol merely modifies particle size of powder, but actively prevents agglomeration of fine particles.

It is known that modifying effect of surfactants in process of hydration and crystallization hydrate neoplasm is shown through chemical and physical processes at interface cement grain-liquid mixing, the cement stone - pore structure. The modification due to presence surfactants of various reactive radicals, their position in molecule chain length and shape of molecular weight polymeric surfactant.

This article outlines approaches to selection composition of complex agent with an intensifying and modifying effects and results of experiments.

The reliability of experimental investigated of effect of grinding aids in this work were achieved in study at equal conditions, kinetics of grinding investigated and an etalon materials (Domone, 2010). Thus mill loaded strictly graded materials, persisted same time of grinding and equal dosage intensifier. Clinker for investigation, were selected on enterprises in a quantity sufficient to carry out a series of grinding and reduce influence of mineralogical composition of results.

One of main purposes of grinding aids is to increase the mobility of fine powder during its transportation through the pipes of unloading silos and bins, so-called fluidity. In domestic industry fluidity determined by indirect methods, for example by filling time of vehicle or speed of transportation by pipeline (Raymond, 2010). Our flowability was determined by method of the American standard ASTM 1565-04, essence of which lies in sifting weighed cement through sieve number 05 on a shaking table Hagerman.

At observance of equal conditions of grinding can estimate resistance of material to milled in relation resulting surface area of powders standard and investigated materials, similar to so-called relative laboratory coefficient of grindability that is used to characterize the grindability of coal (GOST 15489.1-93):

$$K\ \ lo\ =\ \frac{s_{mat}}{s_{stand}} \qquad (1)$$

Here Sstand - specific surface standard powder m2/kg; Smat - specific surface of the investigated material. For standart material accepted clinker, milled without intensifier.

Action modifying additive in composition intensifier evaluated by physic-mechanical strength of standard cement samples. As strength of cement is strongly dependent primarily upon mineral composition and specific surface, then as a standard accepted strength of control without additional composition and in relation to it evaluated modifying effect of additives. By analogy with the coefficient of grindability we called it modification coefficient:

$$Kmod= \frac{R_{mod}}{R_{cont}} \qquad (2)$$

Here Rcont - value of strength control (without additional) of sample, MPa; Rmod - strength of sample with an intensifier (modifier).

It is known that increasing specific surface of grinding influence on strength. Therefore estimate of modifying effects was carried out with simultaneous evaluation an intensifying effect. Modifying effect of the complex additive occurs only when value of coefficient of the modification exceeds the value of the coefficient for grindability of same composition.

Investigations was performed on clinkers, differ in mineralogical composition, first of all on C3A content (Table 2). Data of clinker were selected on two enterprises wet process with rotary kilns one type of size. For production of clinker K-1 as a carbonate component of raw material mixture used chalk for K-2 limestone.

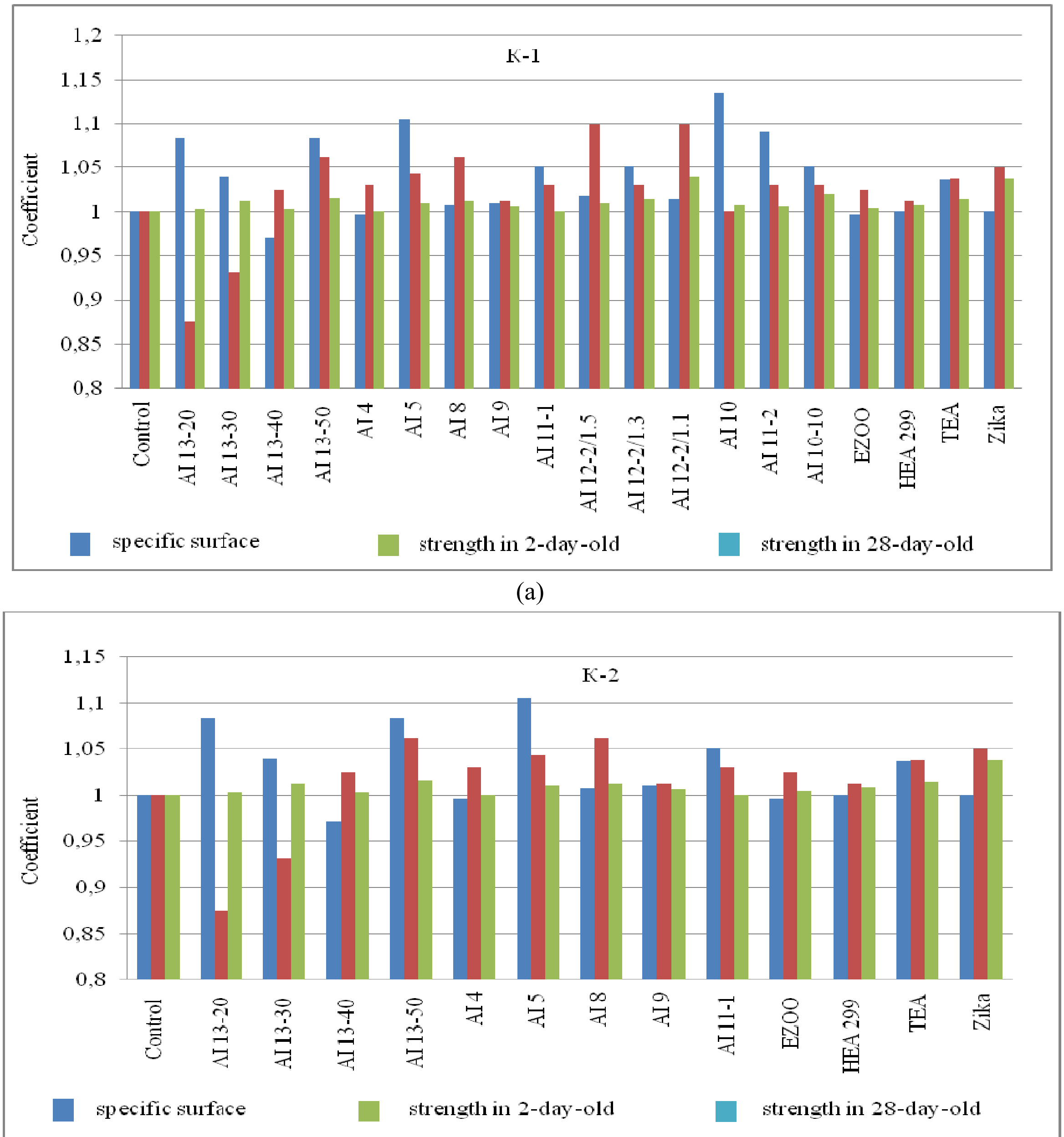
Table 2. Mineralogical composition of clinker

Index of clinker	Mineral content, mass.%				CS	Modules	
	C_3S	C_2S	C_3A	C_4AF		n	p
K-1	62,3	16,7	9,6	11,40	0,9	2,17	1,34
K-2	63,3	12,6	3,1	19,3	0,93	1,92	0,86

In course of research identified several combinations of components with a synergistic (mutually reinforcing) intensifying and modifying effect. Composition of some compositions included from 3 to 6 components belonging to different classes of inorganic compounds. As a comparison have been researched intensifiers of other companies: EZ00, HEA299, TEA and Zika.

3. Results

For clarity, results are presented in graphical form in depending coefficients, of grinding and modifying of composition of additives (Fig. 1). As seen from results, strength of control compositions has different: cement stone on clinker with minimal C3A content (K-2) is characterized by reduced strength to 2-day-old, whereas a 28-day-old the strength of control compositions is comparable.



(a)

(b)

Figure 1. Impact of grinding aids on grindability and strength of cement clinker based on: a) K-1; b) K-2

As seen from Fig. 1 investigation compounds of additive have ambiguous effect on process of grinding and hardening. Thus, greatest intensifying effect at grinding on clinker K-1 had compounds AI5, AI13-50 and AI10. Three ethanolamine (the TEA) increased specific surface cement by 3%. Modifying effect rendered compositions AI8, AI12-2/1.1 and AI12-2/1.5. Depending at type modifying additive early strength of some samples increased by 5-10%. In presence of TEA coefficient values of intensification at grinding and modifying was same, which confirms data of other researchers. Some modifying effect on strength exerted additive EZ00, HEA299 and Zika.

On clinker K-2-intensifying effect on grinding process noted with use compositions of AI13-20, AI13-50, AI5 and AI11-1. Increase early strength of 15-20% indicate, compositions AI13-40, AI4 and AI8. The use of additives AI13-20 and AI13-40 had negatively impact on set of early strength, although ultimate strength was comparable with strength of control composition. In presence TEA strength was also higher on 5-10%, and grindability was comparable with modifying coefficient. Available on market additives modifying effect on strength of cement-based K-2 have the compositions EZ00 and Zika. Among researched additives best results for two cements were obtained on AI8 intensifier.

Thus, our assumption about influence composition of additives on the grinding process and speed of strength development is primarily determined by mineralogical composition that was confirmed by the obtained results.

The process of hydration and hardening of cement clinker on the basis of K-1 in presence of additives AI8 studied with using X-ray fluorescence spectrometer Series 9900 ARL WorkStation with built-in diffraction system and scanning electron microscope of high resolution TESCAN MIRA 3 LMU, including energy dispersive spectrometer (EMF) X-MAX 50 Oxford Instruments Nano Analysis for electron probe microanalysis. XRD patterns of hydration products are presented on Figure 2.

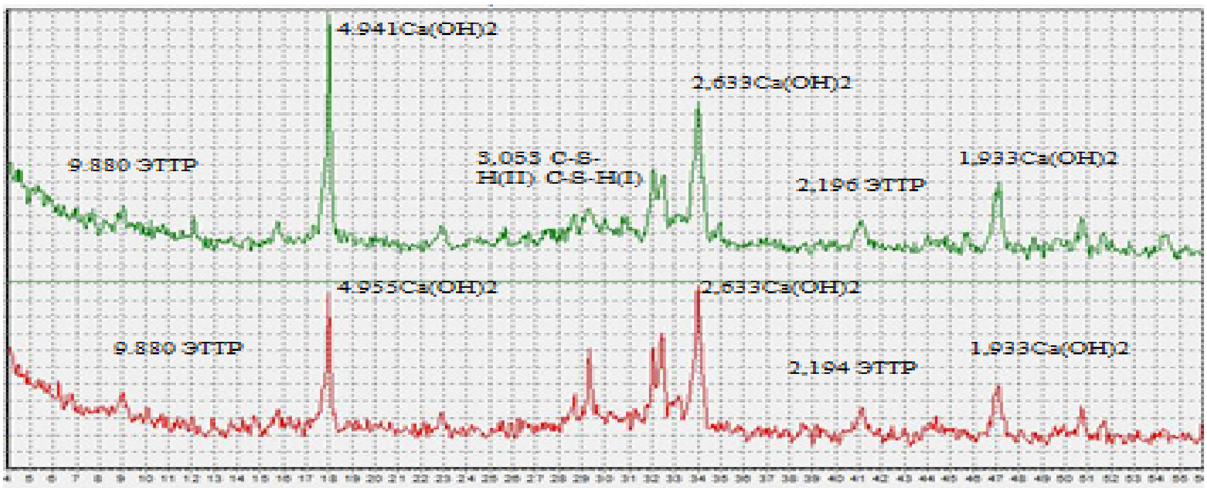


Figure 2. XRD patterns of hydration products samples in the 28-day-old

As seen from present graphical results on figure 2, composition of samples include following phases: portlandite (d / n = 4.941, 2.633, 1.933 Å); ettringite (d / n = 9.88, 5.60, 4.96 Å); C-S-H (I) (d / n = 2.8, 1.83 Å); CSH (II) (d / n = 3.055, 2.85, 2.8 Å); relicts of the original clinker phases β-C2S (d / n = 2.77, 2.609, 2.184 Å) and C-3S (d / n = 3.034, 2.776 , 2.608 Å). When entering intensifier in cement stone is marked reduction in intensity of analytical reflections of portlandite, used to evaluate relative speed of the hydration process (Table 3).

Table 3. Degree of cement hydration

Index of composition	The relative intensity of the reflection 4.941Å $Ca(OH)_2$ at the age, day		
	2	7	28
Control	41	45	51
With addition of AI8	43	56	70

As seen from results present in table 3, rate of hydration K-1 in 2-day age increases slightly, but strength of the samples thus higher than control composition on 10%. In later stages rate of hydration increases significantly, but strength of samples with additives does not exceed the strength of the control composition.

For an explanation these differences in strength characteristics of samples was investigated microstructure of cement stone in different periods of hardening with using electron microscope (Fig. 3). Below presents individual differences between unmodified cement stone and modified cement stone with addition of AI8.

Stone on cement without intensifier in a 2-day-old presented a fine-fibered structure of hydration products on surface of original maternal crystals and micro nuclei of new phase. Fibrous structure at early stage of hydration has ettringite crystals, around which is formed hydrosilicate gel. By 7-days there is note fusion of individual crystals and formation of a grid structured. In a 28-day-old hydration products are presented as separate lamellar crystals as and spliced in crystallites formations with high microporosity.

For cement stone with intensifier already in initial period of hardening observed an increased quantity of new formations in form of gel products, germinated lamellar crystals of portlandite and possibly mono sulfoalyuminata calcium. With age, hydration products become more, but they have no clear crystallization and presented "fused" new formations fairly dense structure. Cement stone structure with additions through close intercalated part of crystals of ettringite, portlandite small size with gel dense hydrosilicate phases differ by more homogeneous structure, which has a positive effect on strength especially in early stages of hardening.

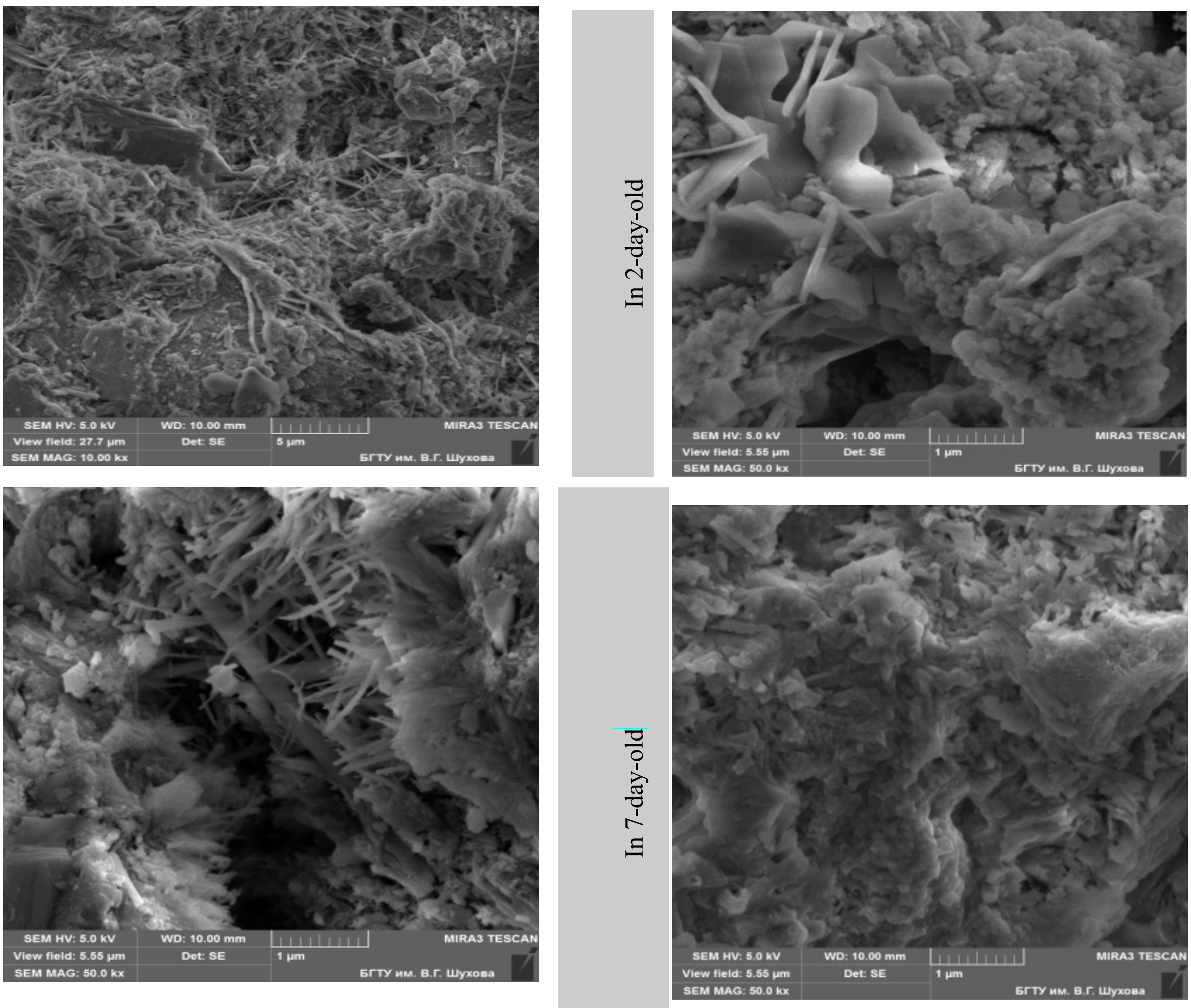
Hydration process in presence of complex additives can be presented as follows. In many works at influence of surfactants on hydration process proved in presence of small quantities of surfactants is changed degree of supersaturation by different influences on the process of dissolution of initial and appearance new phase. Changes composition of liquid phase in system "cement-water" is defined in future pace and hydration mechanism of multi component binder.

In initial period, presence of certain anionic surfactants increases number of passing into solution ions Ca2+, Al3+. Such supersaturation mixing water determines high rate of hydration of clinker minerals and reduces period of structure formation, decreases solubility of ettringite, which consequently increases part of it in the crystal phase.

On the other side presence of cationic surfactants leads to an accumulation of excess amounts of SO42-, OH-ions, which are activators of the liquid phase, i.e. accelerators of hydration.

Cement stone without intensifier

Cement stone with intensifier



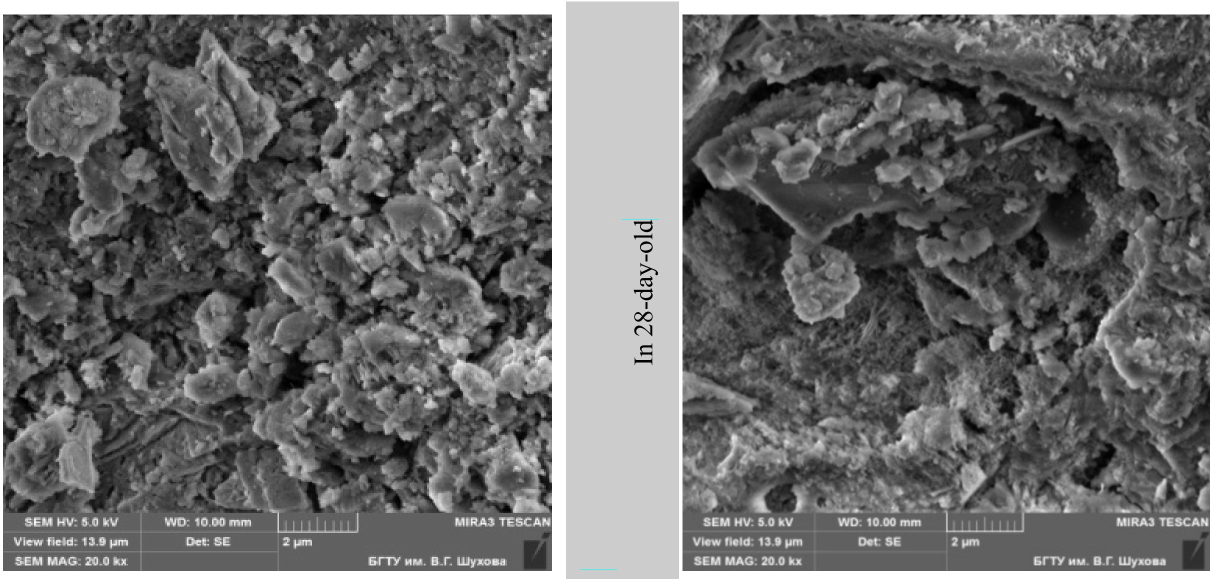


Figure 3. Characteristic pictures cleavage surface samples of cement stone at different periods of hardening without addition and in presence of the modifying additive

Synergetic effect of complex additives were used in selection of the composition and dosage intensifier based on clinker K-1 (Table 4).

Table 4. Influence of type intensifier and its dosage on physico-mechanicall properties of cement based on clinker K-1

Index of composition	Dosage, g / t	S, m^2/kg	Fluidity%	Strength, MPa on compression, aged, days	
				2	28
Control	0	298	38	14,3	46,6
4AI -10	100	304	50	17,7	48,5
4AI -14	140	309	54	17,2	48,4
5AI -10	100	310	48	15,2	49
5AI -14	140	310	50	15,9	49,1
8AI -10	100	289	50	16,3	51,3
8AI -14	140	295	52	18,3	52,1

As seen, different components of additive influence not only on specific surface, but change fluidity of cement powder. Modify components of additive allow increase initial strength on 20-25% (figure 4). Increase dosage of additive in some cases lead to increase initial strength and specific area, in another – on contrary. As seen from figure 4, change ratio between intensifiers and modifying components allow reinforced that or another effect.

Also was studied influence type of additive at grinding without additional cement K – 1 and with additive of 20 mass % of furnace slag (figure 4).

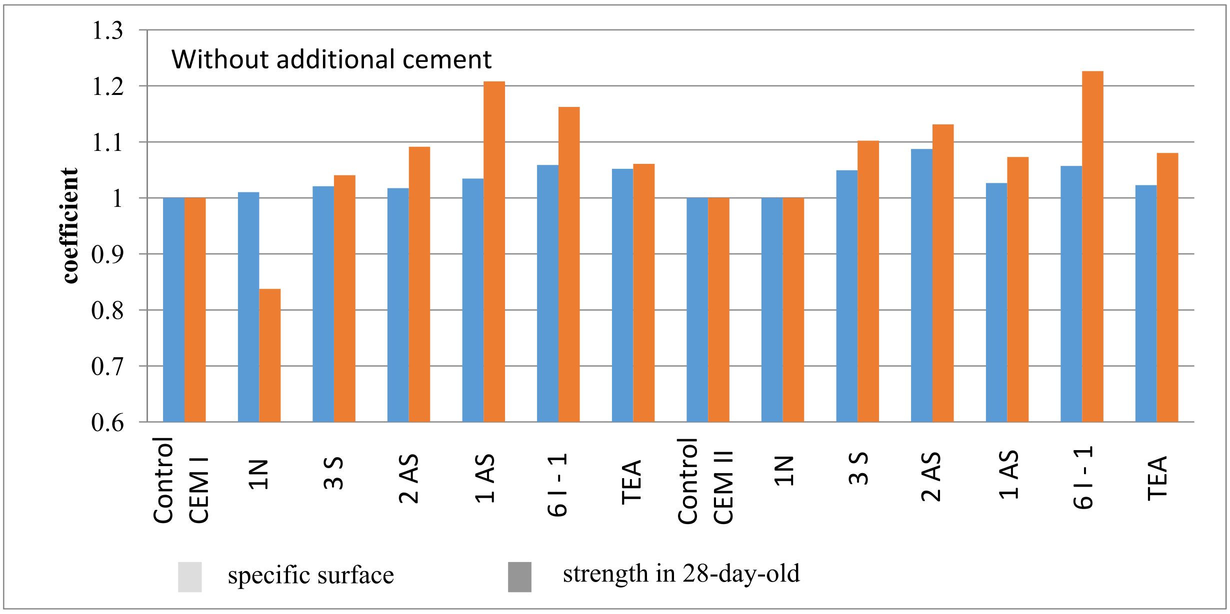


Figure 4. Influence of type additive on intensifiers and modifying effect on without additional cement and cement with 20% of slag

As seen from figure 4 action of technological additive on different type of cement differ. At same time additive 6 I – 1 almost similar increase specific area and strength in 2 – day-old as without additional, so and cement with mineral additive.

4. Discussion

The most laborious and energy-intensive processes of manufacture cement is crushing and grinding (Bogdanov and Romanenko, 2013). In manufacture of finished product units grinding consumes only 60 to 85% of energy. Grinding in cement industry has a significant material costs. For grinding raw materials and clinker grinding on average spent three-quarters, and sometimes more, of total cost of electricity. Grinding materials has a decisive influence on quality of produced clinker and cement, as well as economy of entire production process in general. Cement production begins and ends grinding (Sirchis, 1990). To intensify production process and increase the rate of chemical reactions necessary to increase specific surface area of materials by grinding them. This, along with the improvement and improvement of the existing production processes becomes possible to obtain qualitatively new properties that are not possible without fine grinding for this use different grinding aids. At fine grinding of the clinker smallest particles milled cement stick to grinding bodies and internal surface of mill is quite durable layer and aggregate with each other to form clumps, flakes and plates (Klassen, 2012).

These conditions are so sharply worsen the condition of clinker grinding that further grinding becomes just economically inexpedient. Great scientific interest and practical importance has grinding intensifiers of cement (Kryhtin and Kuznetsov, 1993). Their main goals are to reduce energy required to grind clinker in this subtlety and therefore increase efficiency of cement mill. Furthermore, to increase performance efficiency of mill, grinding aids provide some important positive effects on final stage of grinding, such as cement, cement paste rheology of fresh or enhanced strength development of concrete (Gan, 1997). Milling is carried out at present time mainly in drum-ball mill. Because of disadvantages: the high specific energy consumption and metal in recent times beginning to apply also other mill types, but for fine grinding of cement clinker, drum mill still indispensable (Shevchenko et all., 2008).

Is known that with increasing dispersion of cement is growing its activity, that allowing reduces specific consumption of cement at manufacturing concrete specified strength (Luginina, 2004). Moreover, the intensification of cement grinding helps save energy and improves performance of existing equipment (Katsioti, 2009). At the same time reducing wear metal grinding bodies and reduces gild expenses.

Various grinding aids have different effects on the grindability of clinker (Bravo, 2003), so at present time it is expedient study the effect of different, complex compositions intensifiers on grindability and clinker quality of different mineralogical composition.

5. Conclusions

Mechanism of action of grinding aids in crushing various materials to date still not sufficiently studied, a result of work concluded that:

Greatest intensifying effect at grinding on clinker K-1 had compounds AI5, AI13-50 and AI10. Modifying effect rendered compositions AI8, AI12-2/1.1 and AI12-2/1.5. Depending at type modifying additive early strength of some samples increased by 5-10%.

On clinker K-2-intensifying effect on grinding process noted on compositions of AI13-20, AI13-50, AI5 and AI11-1. Increase the early strength of 15-20%, indicate the compositions AI13-40, AI4 and AI8.

Among the researched additives best results for two cements were obtained on AI8 intensifier.

Thus, knowing positive and negative aspects of each component is possible to carry out selection of composition intensifiers with synergetic effect considering mineralogical composition of clinker and cement material composition.

Presence of modifying component allows not only provide intensifying effect in milling process, but also to improve both early and late strength by formation of more dense and homogeneous structure of cement stone.

In this work used grinding aids of largest company for production chemical additives that are widely used in the manufacture of construction products a wide range of destination by domestic enterprises, OLC "Polylayer Novomoskovsk" and other companies to compare the effect of the action. Considering that in laboratory conditions, the amount of materials and time is limited, studies have been conducted on a limited number of additives. In future it is planned conduct research on the new series of additives, which results as obtained in the present work will be implemented in production at leading domestic cement plants.

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