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THE INFLUENCE OF SURFACTANTS ON THE PHYSICAL PROPERTIES OF CLINKERS

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Abstract. The influence of three types of surfactants on the following clinker properties: specific surface area, sorption behavior (hygroscopicity), water repellency, and flowability has been studied. Experimental results show that the surfactants have different influence on the grinding kinetics and properties of clinkers that mainly depend on the surfactants concentration than their origin or state of matter. Use of special surfactants as grinding aids is proposed. Molecules of these compounds should consist of a functional group and hydrocarbon chain that does not contain additional functional groups. Such surfactants provide not only grinding accelerating but also storage life prolonging. The research work demonstrates that fatty acids and organosulfur compounds satisfy these conditions and they can be successfully used as a cement grinding aid.

Keywords: clinker, grinding aids, Blaine specific surface area, hygroscopicity, water repellency, flowability.

1. Introduction

Organic admixtures are widely used as grinding aids during the processes of dry and wet grinding of raw materials, mineral additives and cements. Grinding aids help to solve the following tasks: 1) to increase significantly mill output at a determined fineness of cement; 2) to increase fineness at a constant output or increase both fineness and output simultaneously; 3) to enhance particle size distribution at a constant specific surface area; 4) to increase separation efficacy; 5) to improve cement flowability. However, even tiny amounts of grinding aids have the significant influence on the following cement properties: hygroscopicity, flowability, rheology of the fresh cement paste, kinetics of hydration [5, 13].

Organic surfactants are used as cement grinding aids. Among them alcohols and alkanolamines are the most widely used admixtures [1-4, 8, 12]. Also, the influence of monohydric alcohols, amines, fatty acids and polymers was studied and utilization of them as grinding aids was performed [7, 9-11].

Generally, the object of studying different surfactants is focused on the admixtures influence on the cement grinding kinetics. Less attention is paid to such cement properties as flowability and hygroscopicity, which have the significant impact on the cement shelf life and constancy of properties (such as strength).

Thus, the object of the present article is to study the influence of three types of surfactants on the clinker properties: specific surface area, hygroscopicity, water repellency and flowability. Herewith the influence of the molecular structure, quantity of functional groups, state of matter, and weight concentration of the surfactants on the aforementioned properties of the clinker is studied.

2. Experimental

The following chemically pure organic compounds were used for investigation:

- alcohols (2-propanol, ethylene glycol, propylene glycol, glycerol);
- alkanolamines (diethanolamine, triethanolamine);
- fatty acids (oleic and stearic acids);
- organosulfur compounds (sodium dodecylbenzenesulfonate, sodium laureth sulfate).

Stearic acid and sodium laureth sulfate are solids, the others are liquids. The surfactants were added to the clinkers at the beginning of the grinding in the lab ball mill. Admixtures concentrations were 0.05, 0.10 and 0.15 wt %. Duration of the clinkers grinding was identical.

The clinker with the following chemical and mineral composition was used for investigation. Chemical composition, wt %: SiO_2 – 21.8, Al_2O_3 – 5.3, Fe_2O_3 – 4.1, CaO – 66.8, MgO – 0.95, SO_3 – 0.63, K_2O – 0.54, Na_2O – 0.42. Mineral composition, wt %: C_3S – 57.1, C_2S – 21.3, C_3A – 6.9, C_4AF – 12.2.

Blaine specific surface area was measured with a Hiprotsement T-3 pneumatic specific surface meter.

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Hygroscopicity was evaluated by the increase in the clinkers mass during their storage in the conditions with 80–85 % relative humidity and 293–298 K. Samples of the clinkers (10 g in 1 day after grinding) were placed in a uniform thin layer on the bottom of the plastic glasses. Exposure in humid conditions lasted 16 weeks (4 months).

Contact angles were determined by two methods. Contact angles of the water-repellent clinkers (more than 90º) were measured on the pressed cement tablets using a microscope. Tablets were pressed in the metallic molds under the pressure of 100 MPa. Contact angles of the other samples were measured according to the Washburn's method of capillary suction. A force tensiometer was used. The tensiometer with a powder suction measuring module enables to obtain a square mass versus time plot. Inclination of the line to Om^2-axis means a contact angle.

Flowability of clinkers was evaluated by the method of the critical angle of repose. The device for measurement consists of two adjacent vertical plates of 395x195 mm made of organic glass. These plates are mounted on the horizontal plates with the same sizes. One of the vertical plates is covered with the angle scale. Portion of the clinker (200 g) was poured carefully into the device through a metallic hopper. Critical angles of the repose were determined by means of the angle scale on the lateral surface of the device. Degree of flowability and corresponding angles of repose are given in Table 1.

3. Results and Discussion

The values of the clinker residues on the sieve No 008 are given in Table 2.

All the surfactants decrease the clinker residue on the sieve to different extents. The most efficient grinding aids are alcohols (ethylene glycol, propylene glycol and glycerol) and diethanolamine according to the values of the clinker residues on the sieve that does not exceed 1 wt %. The least efficient is 2-propanol. The others have intermediate impact. It is worth noticing that the state of matter of stearic acid and sodium laureth sulfate has not a significant influence on their efficacy as grinding aids.

So, to obtain a clearer picture of the admixtures efficacy it is necessary to study the clinker specific surface area since the admixtures can have different influence on the particle size distribution.

The values of the Blaine specific surface area of clinkers are given in Table 3.

Disregarding dependence between specific surface area and grinding aids concentration one can make conclusion that all the surfactants have almost equivalent technological effect (grinding accelerating). Specific surface area increases from 1800 up to 2000–2200 cm^2/g.

There are two cases: 1) technological effect does not depend on the surfactant concentration (for 2-propanol, ethylene glycol); 2) technological effect changes linearly or extremely with concentration changing (the other grinding aids).

Table 1

Degree of flowability and corresponding angles of repose

Degree of flowability	Critical angle of repose, grad
Very high	25–30
High	31–35
Sufficient	36–45
Insufficient	46–55
Low	56–65
Very low	more than 65

Table 2

Sieve analysis of clinkers

Grinding aid	Clinker residue on the sieve No 008 (*W*), wt %, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	7.7	6.5	7.2	7.5
Propylene glycol	7.7	0.6	0.5	0.0
Ethylene glycol	7.7	0.4	0.9	0.3
Glycerol	7.7	0.7	0.5	0.4
Diethanolamine	7.7	0.8	0.3	0.4
Triethanolamine	7.7	1.8	1.0	1.1
Stearic acid	7.7	4.7	5.3	3.7
Oleic acid	7.7	5.0	2.1	2.5
Sodium dodecylbenzenesulfonate	7.7	3.3	3.6	7.6
Sodium laureth sulfate	7.7	3.1	1.8	2.0

Hygroscopicity of control clinker and clinkers with the admixtures was evaluated with weight gain of clinker samples after 16 weeks of exposure in humid conditions. The test results are given in Table 4.

All the grinding aids can be divided into two groups: those that decrease hygroscopicity and those that don't change or increase it. Fatty acids and organosulfur acids ranks as first group grinding aids. Their molecules consist of a functional group and long hydrocarbon chain that does not contain additional functional groups. Weight gain of the clinkers with such surfactants does not exceed 3 wt %.

Molecules of the other grinding aids consist of short hydrocarbon chain (no more than 3 carbon atoms) and several functional groups. These surfactants rank as second group grinding aids.

Clearer picture of the grinding aids influence on the hygroscopicity and hygroscopicity coefficients calculated are given below in Table 7.

The values of the water contact angles are given in Table 5.

All the grinding aids increase contact angle to different extents. Fatty acids make clinker water-repellent (contact angle more than 90º). Less efficient surfactants are organosulfur compounds (40–88º) and triethanolamine (32–33º). The least efficient are alcohols (7–19º).

The values of the critical angles of repose are given in Table 6.

Almost all the grinding aids studied enhance the flowability of the clinkers at certain concentrations. On average, the critical angles of repose of the clinkers decrease from 42 to 35–38º. The most efficient surfactants are organosulfur compounds.

All the surfactants studied increase specific surface area in comparison with the control clinker at all concentrations. It is worth noticing that the surfactant concentration has the major impact on the specific area. The organic compound type and state of matter have far less influence. This statement is proven by the value of the specific area of the clinkers with a stearic acid (1900–2000 cm^2/g) and sodium laureth sulfate (1900–2000 cm^2/g). Also the grinding aids studied can not be divided into more and less efficient.

Along with fineness enhancement, however, the admixtures influence the hygroscopicity significantly. Since the clinkers obtained have different values of the specific surface area and hygroscopicity, coefficient of hygroscopicity ($G \cdot 10^{-5}$ g^2/cm^2) is used to simplify the comparative analysis. The coefficient is calculated as a ratio of the moisture content of 10 g of the clinker (g) to the specific area (cm^2/g). The higher the coefficient, the higher the clinker hygroscopicity. The coefficients calculated are given in Table 7.

Table 3

The influence of grinding aids on the Blaine specific surface area of clinkers

Grinding aid	Blaine specific surface area (S), cm^2/g, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	1800	2000	2000	2000
Propylene glycol	1800	2100	1900	1800
Ethylene glycol	1800	2100	2100	2000
Glycerol	1800	1900	2000	1800
Diethanolamine	1800	2100	1900	1900
Triethanolamine	1800	2200	2100	2100
Stearic acid	1800	1900	2000	2000
Oleic acid	1800	1900	2000	2000
Sodium dodecylbenzenesulfonate	1800	2100	2200	1900
Sodium laureth sulfate	1800	1900	2000	2000

Table 4

Hygroscopicity of clinkers

Grinding aid	Weight gain (δ_m), wt %, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	5.64	6.76	6.81	6.30
Propylene glycol	5.64	6.17	6.26	6.93
Ethylene glycol	5.64	6.38	6.60	6.86
Glycerol	5.64	9.95	11.45	13.56
Diethanolamine	5.64	5.05	5.46	6.03
Triethanolamine	5.64	6.15	6.54	6.86
Stearic acid	5.64	2.04	1.92	2.09
Oleic acid	5.64	2.01	2.42	2.55
Sodium dodecylbenzenesulfonate	5.64	1.68	1.61	1.28
Sodium laureth sulfate	5.64	2.98	3.18	3.20

Table 5

Water repellency of clinkers

Grinding aid	Water contact angle (θ), degree, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	6	10	9	9
Propylene glycol	6	8	15	13
Ethylene glycol	6	17	16	19
Glycerol	6	10	8	7
Diethanolamine	6	17	16	15
Triethanolamine	6	33	32	32
Stearic acid	6	74	131	126
Oleic acid	6	115	128	132
Sodium dodecylbenzenesulfonate	6	86	88	88
Sodium laureth sulfate	6	40	41	44

Table 6

Flowability of clinkers

Grinding aid	Critical angle of repose (α), degree, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	46	46	46	40
Propylene glycol	46	42	35	35
Ethylene glycol	46	44	44	42
Glycerol	46	42	42	43
Diethanolamine	46	40	40	36
Triethanolamine	46	35	35	35
Stearic acid	46	41	35	36
Oleic acid	46	35	37	43
Sodium dodecylbenzenesulfonate	46	35	35	27
Sodium laureth sulfate	46	35	31	33

Table 7

Coefficient of hygroscopicity of clinkers

Grinding aid	Coefficient of hygroscopicity ($G \cdot 10^{-5}$), g^2/cm^2, at grinding aid concentration, wt %			
	0.00	0.05	0.10	0.15
2-Propanol	3.1	3.4	3.4	3.4
Propylene glycol	3.1	2.9	3.3	3.9
Ethylene glycol	3.1	3.0	3.1	3.4
Glycerol	3.1	5.2	5.7	7.5
Diethanolamine	3.1	2.4	2.9	3.2
Triethanolamine	3.1	2.8	3.1	3.3
Stearic acid	3.1	1.0	1.0	1.0
Oleic acid	3.1	1.1	1.2	1.3
Sodium dodecylbenzenesulfonate	3.1	0.8	0.7	0.7
Sodium laureth sulfate	3.1	1.6	1.6	1.6

There are two general trends: 1) an increase of the hygroscopicity with an increase of the admixtures concentrations, in other words, the storage life of the clinkers is deteriorated at high amounts of the admixtures; 2) constant hygroscopicity at all the concentrations. As with the specific surface area the surfactant concentration has the major impact on the hygroscopicity.

Fatty acids and organosulfur compounds decrease the hygroscopicity to the most due to their molecular structure. The hydrocarbon chains of the molecules form a screen adsorbed layer around the clinker particle. This layer is electrically neutral. The hygroscopicity of the clinkers with these surfactants is constant and does not depend on the concentration.

The molecules of the other grinding aids have several functional groups that are oriented inwards and outwards on the clinker surface. Thus the adsorbed layer is electrically charged. Functional groups that contain

highly electronegative elements bond water molecules from air and form a hydrogen bond. That is why the layer is not a screen and the hygroscopicity increases with the concentration increase.

Regarding the resistance to the short-term water action, only the clinker with fatty acids has water repellent properties. The others are not water repellent but in comparison with control clinker organosulfur compounds have 7.5–14.5 times higher values of the contact angles, and triethanolamine has 5.5 times higher values. The efficacy of alcohols depends on their concentration, and the values of the contact angles are 2–3 times higher.

Initial degree of flowability of the clinker is "insufficient". All the surfactants enhance the clinkers flowability. The most efficient are organosulfur compounds and their technological effect (flowability enhancing) is not dependent on the concentration. Organosulfur compound changes the degree of flowability to "high" and "very high". The technological effect of the other surfactants strongly depends on the concentration. Propylene glycol, diethanolamine and fatty acids enhance the degree of flowability to "high". Other alcohols and diethanolamine are the least efficient.

4. Conclusions

The experimental data confirm the aforementioned statement that even tiny amounts (up to 0.1 wt %) of grinding aids have significant impact on the properties of the clinkers. Rational choice of the grinding aid depends not only on its influence on grinding kinetics but also on the physical properties of the material such as hygroscopicity and flowability. These characteristics have the significant impact on the cement physical properties during all stages of the manufacturing process and marketing. Thus, the rational choice of the grinding aid may improve the clinker and cement flowability and, accordingly, simplify its transport and storage in the silos.

Based on the laboratory experiments conducted one can make the following conclusions:

- the surfactants can be used as grinding aids regardless their state of matter;
- the influence of the surfactants on the clinker fineness and particle size distribution strongly depends on the surfactant concentration and far less on the type of the organic compound and molecular structure;
- for the purpose of the enhancing of the groups of clinker properties (enhanced fineness and flowability, decreased hygroscopicity or water-repellent properties) it is rational to use surfactants with special molecular structure that consists of a functional group and long hydrocarbon chain that does not contain additional functional groups.

Thus, fatty acids and organosulfur compounds satisfy aforelisted requirements can be successfully utilized as grinding aids and quality improvers.

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ВПЛИВ ПОВЕРХНЕВО-АКТИВНИХ РЕЧОВИН НА ФІЗИЧНІ ВЛАСТИВОСТІ КЛІНКЕРІВ

Анотація. *Досліджено вплив трьох видів поверхнево-активних речовин на наступні властивості клінкерів: питому поверхню, гігроскопічність, водовідштовхувальні властивості та сипучість. Результати експериментів показують, що поверхнево-активні речовини мають різний вплив на кінетику помелу та властивості клінкерів, що, головним чином, залежить від концентрації поверхнево-активної речовини, у порівнянні з її природою або агрегатним станом. Запропоновано застосування окремих поверхнево-активних речовин. Молекули цих сполук повинні містити функціональну групу та довгий карбоновий ланцюг, який не містить додаткових функціональних груп. Такі поверхнево-активні речовини забезпечують не лише прискорення помелу, а також збільшення тривалості зберігання. Дослідженнями встановлено, що жирні кислоти та органічні сульфосполуки задовольняють приведеним умовам і можуть знайти успішне застосування як інтенсифікатори помелу.*

Ключові слова: *клінкер, інтенсифікатор помелу, питома поверхня за Блейном, гігроскопічність, водовідштовхувальні властивості, сипучість.*