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Mechanisms and effects of additives from the dihydroxy-compound class on Portland cement grinding

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Abstract

The present paper investigates the action and effects of wet surface active additives from the dihydroxy-compound class (ethylene glycol, propylene glycol, and polypropylene glycol) on Portland cement grinding, starting from the present knowledge of surface chemistry, with application to the solids and particularly the size reduction process. The investigations were performed using the comparative kinetic measurements of the size reduction process, aiming at the evolution in time of the specific surface of the solid; the grinding aptitude measurements, considered as specific power consumption, under comparable conditions; size distribution and flow capacity determinations of the ground cements. Within the homologous series of surfactants, the regularity of the additive's effect on the process, which is dependent on the composition of the additives, is noted. The action mechanisms of the additives are discussed. The results obtained have obvious useful implications.

Keywords: Grinding; Organic materials; Admixtures; Kinetics

The free energy of a solid material surface increases as a result of the unsatisfied surface bonds and the increase of free surface charge density during the grinding process. In this way, the thermodynamic nonequilibrium state of the dispersed system is accentuated and, consequently, its tendency to remake the equilibrium with decrease of its free energy. In the absence of other compulsions, this tendency is spontaneous and more intense with increase of the solid system dispersion, due to the mutual action between the particles or between the particles and other contact surfaces, which leads to the compensation of surface free bonds [1–7].

The mutual actions that lead to aggregation of particles and their adhesion onto the contact surfaces are favored, at the same time, by microplastic deformation at the contact interface of the particles, which is due to the striking action of the grinding media [8,9]. The aggregation process is essentially dependent on clinker nature, dispersion state of the cement, working conditions of the grinding plant, kinetic energy of the grinding media and their distribution, and the atmosphere within the mill.

Elimination or diminution of ground solid mass aggregation and adhesion effects is carried out in three main ways [1,8–11]: 1) decrease of grinding media size; 2) running of the grinding plant in a closed circuit; and 3) use of surfactants.

The use of surface active additives in the grinding process—the purpose of the present investigations, due to the surface phenomena they imply—leads to decrease of material hardness, by screening attractive surface forces and promoting fracture by the easier propagation of cracks. The effect of the surfactants is emphasized at low concentration, ranging between 0.01% and 0.5%.

Considerations based on surface science suggest the effect of surfactants is dependent on their nature and molecular structure [7].

1. Experimental conditions and procedures

To perform the investigations, surface active agents from the dihydroxy compounds: ethylene glycol [HO-H_2C-CH_2-OH], propylene glycol [OH-CH_2-CH_2-CH_2-OH (glycols), and polypropylene glycol [OH-$(CH_2)_3$-(O-CH_2-CH_2-$CH_2)_n$-O-$(CH_2)_3$-OH (ether glycol) were used. These additives were weighted as 0.03%, 0.05% and 0.10%, respectively.

The clinker used to examine the cement grinding process in the presence of the surfactants additives were industrial clinkers (D and M), which differed by the alumina modulus (for the first clinker $M_{Al} > 1.38$ and for the other clinker $M_{Al} < 1.38$), with consequences on the potential mineral

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Table 1
Chemical and mineral characteristics of the clinkers

Crt. no.	Characteristics	Clinker D	Clinker M
1	Chemical composition		
	Loss on ignition	1.16	1.87
	SiO_2 (%)	20.85	21.29
	Al_2O_3 (%)	7.03	4.84
	Fe_2O_3 (%)	3.21	5.44
	CaO (%)	64.52	62.95
	MgO (%)	1.50	1.84
	SO_3 (%)	0.55	0.55
	Na_2O (%)	0.55	0.30
	K_2O (%)	0.53	0.78
	TiO_2 (%)	0.30	0.12
	Insoluble residue (%)	0.53	0.55
	Free lime (%)	0.86	0.30
2	Modular and mineralogical composition		
	M_{si}	2.03	2.07
	M_{Al}	2.19	0.89
	Lime saturation factor	0.95	0.93
	C_3S (%)	52.86	57.11
	C_2S (%)	19.59	17.59
	C_3A (%)	13.20	3.63
	C_4AF (%)	9.76	16.54

composition (Table 1). The gypsum used in the grinding process was characterized by a content ~95% calcium sulfate dihydrate.

It has had in view: 1) the Blaine specific surface variation with the nature and ratio of the additive, for the same grinding time; 2) the grinding aptitude of the cements, which is dependent on the nature and ratio of the additives; 3) the change of cement grain size distribution when using additives; and 4) the flow behavior of the cement ground with additives. The grinding was carried out in laboratory mills with 520-mm diameter and 510-mm length. The grinding media load for the first grinding stage (coarse grinding) was 26.67 kg balls with ϕ 65–75 mm; 13.32 kg balls with ϕ 55–65 mm, and 10 kg balls with ϕ 45–55 mm; the final stage was carried out with an equivalent load of dicones (~50.0 kg). The grinding was performed for 15, 30, 45, 60, 120, 180, 240, and 300 minutes. The determination of grain size distribution was performed using a Gonell granulometer with air jet. The grinding aptitude was examined by specific power consumption determinations, under comparable conditions, into a mill with electric counter, and with 540-mm diameter and 560-mm length; the grinding media load in the first grinding stage (coarse grinding) was of 144.3 kg balls (with ϕ 65–75 mm: 76.90 kg; ϕ 55–65 mm: 38.55 kg, ϕ 45–55 mm: 28.85 kg), and in the second stage (fine grinding) of 144.3 kg dicones.

The flow aptitude of the cements obtained was determined by the Imse method [12]. The flow of a powdery material is influenced by the adhesion forces between the particles. Under the action of a shear force, the adhesion forces diminish and the material on a sieve will flow. The quantity of material passing through the sieve with different size meshes, under the influence of a shear force, may represent a measure of the flow aptitude. A shaking table according to DIN 1164 and standardized sieves were used; in this way the corresponding fluidity curves were plotted.

2. Results and interpretation

2.1. Kinetics of cement grinding when using surfactants

Grinding process kinetics were observed through the evolution in time of the specific surface of the cements with additives as well as the reference clinker D. The specific surface measurements, carried out for different grinding durations and with different additive ratios, including the reference cement, are given in Table 2. The plot of the experimental data in kinetic terms for the optimum additive ratio is shown in Fig. 1.

The effect determined by the use of additives from the dihydroxy-compound class can be explained according to the Traube-Duclaux rule, under the conditions of its extension to heterogeneous adsorption, with reference to the homologous series or similar types of compounds [7].

The explanation of the superior effect, determined after the first 15 to 30 minutes of grinding cement with polypropylene glycol (hence, for specific surfaces no higher than 3000 to 3500 cm^2/g Blaine), is found only expounding the acquired results according to the fundamental concept of the Traube-Duclaux rule extended to the heterogeneous adsorption. The effect of this additive with higher molecular weight is demonstrated to be better than the effect of corresponding inferior dihydroxy compounds, but only for the early stage of the process, which corresponds to larger cement grains or larger pores, respectively. In the considered case, for high specific surfaces, the Traube-Duclaux rule, applicable to the homogenous adsorption, is inverted. Such a finding does not appear when comparing the effect of ethylene glycol and propylene glycol. For such a comparison, even if the difference between the observed effect when using ethylene glycol and propylene glycol is not high, the effect of the latter certainly is better.

When using all three additives, it was found that, for the same grinding duration, it yielded an obviously higher specific surface of cement in comparison with the specific surface of the reference (nonadditive) cement. Initial growth of the specific surface up to 28–29%, in comparison with the reference specific surface, was achieved when polypropylene glycol was used, and under 20% when the other additives were used. For longer grinding durations, when the cements have specific surfaces higher than 3500 cm^2/g Blaine, the growth of the specific surface, when using the latter additives (ethylene glycol and propylene glycol), varies between 14% and 24 %, being superior when the growth of the specific surface is due to the use of polypropylene glycol, especially when compared with propylene glycol.

The existence of an optimum additive ratio is very likely correlated with the achievement of a continuous absorption monolayer, whereas a higher ratio leads to a lubricant ef-

Table 2
Experimental results of specific surface of the reference cement and the additive cements vs. the grinding duration and the nature and the ratio of the surfactants

Cement index	Additive		Specific surface (cm^2/g)	Growth of the specific surface of cements with additives	
	Symbol	Ratio (%)		(cm^2/g)	(%)
Grinding duration = 15 min					
Reference cement 1	—	—	2360	—	—
Cement 2	EG	0.03	2374	+14	+0.60
Cement 3	EG	0.05	2653	+293	+12.40
Cement 4	EG	0.10	2530	+170	+7.20
Cement 5	PG	0.03	2640	+280	+11.86
Cement 6	PG	0.05	2679	+319	+13.52
Cement 7	PG	0.10	2786	+426	+18.05
Cement 8	PPG	0.03	2560	+200	+8.47
Cement 9	PPG	0.05	2932	+572	+24.24
Cement 10	PPG	0.10	3038	+678	+28.73
Grinding duration = 30 min					
Reference cement 1	—	—	3000	—	—
Cement 2	EG	0.03	3226	+226	+7.53
Cement 3	EG	0.05	3557	+557	+18.57
Cement 4	EG	0.10	3300	+300	+10.00
Cement 5	PG	0.03	3400	+400	+13.33
Cement 6	PG	0.05	3475	+475	+15.83
Cement 7	PG	0.10	3486	+486	+16.20
Cement 8	PPG	0.03	3283	+283	+9.43
Cement 9	PPG	0.05	3430	+430	+14.33
Cement 10	PPG	0.10	3526	+526	+17.53
Grinding duration = 45 min					
Reference cement 1	—	—	3444	—	—
Cement 2	EG	0.03	3961	+517	+15.01
Cement 3	EG	0.05	4150	+706	+20.50
Cement 4	EG	0.10	3878	+434	+12.60
Cement 5	PG	0.03	4075	+631	+18.32
Cement 6	PG	0.05	4271	+827	+24.01
Cement 7	PG	0.10	3968	+524	+15.21
Cement 8	PPG	0.03	3973	+529	+15.36
Cement 9	PPG	0.05	4084	+640	+18.58
Cement 10	PPG	0.10	3886	+442	+12.83
Grinding duration = 60 min					
Reference cement 1	—	—	3820	—	—
Cement 2	EG	0.03	4479	+659	+17.25
Cement 3	EG	0.05	4626	+806	+21.10
Cement 4	EG	0.10	4158	+338	+8.85
Cement 5	PG	0.03	4567	+747	+19.55
Cement 6	PG	0.05	4710	+890	+23.30
Cement 7	PG	0.10	4363	+543	+14.21
Cement 8	PPG	0.03	4467	+647	+16.94
Cement 9	PPG	0.05	4604	+784	+20.52
Cement 10	PPG	0.10	4349	+529	+13.85
Grinding duration = 120 min					
Reference cement 1	—	—	4962	—	—
Cement 2	EG	0.03	5750	+788	+15.88
Cement 3	EG	0.05	5859	+897	+18.08
Cement 4	EG	0.10	5567	+605	+12.19
Cement 5	PG	0.03	5740	+778	+15.68
Cement 6	PG	0.05	5945	+983	+19.81
Cement 7	PG	0.10	5686	+724	+14.59
Cement 8	PPG	0.03	5700	+738	+14.87
Cement 9	PPG	0.05	5740	+778	+15.68
Cement 10	PPG	0.10	5463	+501	+10.10
Grinding duration = 180 min					
Reference cement 1	—	—	5330	—	—
Cement 2	EG	0.03	5933	+603	+11.31
Cement 3	EG	0.05	6066	+736	+13.81
Cement 4	EG	0.10	5940	+610	+11.40

(*continued on next page*)

Table 2 (*continued*)

Cement index	Additive Symbol	Additive Ratio (%)	Specific surface (cm^2/g)	Growth of the specific surface of cements with additives (cm^2/g)	Growth (%)
Cement 5	PG	0.03	6040	+710	+13.32
Cement 6	PG	0.05	6350	+1020	+19.14
Cement 7	PG	0.10	6100	+770	+14.45
Cement 8	PPG	0.03	6082	+752	+14.11
Cement 9	PPG	0.05	6035	+705	+13.23
Cement 10	PPG	0.10	5881	+551	+10.34
Grinding duration = 240 min					
Reference cement 1	—	—	5407	—	—
Cement 2	EG	0.03	6153	+746	+13.79
Cement 3	EG	0.05	6202	+795	+14.70
Cement 4	EG	0.10	6065	+658	+12.17
Cement 5	PG	0.03	6046	+639	+11.81
Cement 6	PG	0.05	6380	+973	+18.00
Cement 7	PG	0.10	6156	+749	+13.85
Cement 8	PPG	0.03	6055	+648	+11.98
Cement 9	PPG	0.05	6113	+706	+13.05
Cement 10	PPG	0.10	5943	+536	+9.91
Grinding duration = 300 min					
Reference cement 1	—	—	5306	—	—
Cement 2	EG	0.03	6092	+786	+14.81
Cement 3	EG	0.05	6224	+918	+17.30
Cement 4	EG	0.10	6059	+753	+14.19
Cement 5	PG	0.03	5978	+672	+12.66
Cement 6	PG	0.05	6218	+912	+17.18
Cement 7	PG	0.10	6061	+755	+14.23
Cement 8	PPG	0.03	6005	+699	+13.17
Cement 9	PPG	0.05	5975	+569	+10.91
Cement 10	PPG	0.10	5802	+496	+9.35

fect. This effect leads to an increase of flow aptitude, with diminution of the breakup process. The finding of an optimum proportion of additive has been noted by other researchers.

The absolute value of the specific surface growth, corresponding to the optimum ratio of additive, increases obviously when increasing the grinding duration and with discontinuity at a grinding duration of between 180 and 240 minutes, when the specific surface of the cement exceeds 6000 cm^2/g Blaine. This behavior must be correlated essentially with the increased intensity of the adhesion phenomenon, accompanied by aggregation of particles and their adherence to the grinding media and walls of the grinding mill, leading to diminution of the effect of the surface active additives on the size reduction.

2.2. Grinding aptitude of cements with surfactants

The examination of cements with additives from the grinding aptitude point of view was carried out using clinker D. The electric power specific consumptions for an additive ratio of 0.05% (proportion that proved to be optimum in almost cases) were measured and related to the power specific consumptions for the reference (nonadditive) cement. The results are given in Table 3.

The plotting of specific power consumption against achieved specific surface (Fig. 2) suggests the essential features of the effect determined by the additives used, which is in agreement with information concerning time evolution of Blaine specific surface of ground cements, as shown in Table 2 and Fig. 1. A better effect when using propylene glycol is observed for 3200–4400 cm^2/g Blaine specific surface; for lower values of specific surface of cement, the additive polypropylene glycol shows comparable effects, whereas the effect of ethylene glycol is somehow better only for high values of specific surface of the cements obtained.

According to the dependencies suggested in Fig. 2, it seems that the effect of additives on reduction of power consumption in the grinding process is achieved mainly through the attenuation of adhesion and adherence phenomena. In the final stage of grinding, when specific surface values are high and these phenomena become important, the decrease of power consumption is emphasized if related to grinding to reference cement (additive free). The relative value of power consumption ranges between 20% and 35%, depending on desired specific surface and grinding additive.

2.3. Changes in grain-size distribution of cements ground with additives

The increase of the dispersion degree of the additive cements under comparable grinding conditions causes simultaneous narrowing of the grading spectrum. In this context, for quasicomparable specific surfaces, an increase of the ratio of grain-size fractions smaller than 30 μm,, with the de-

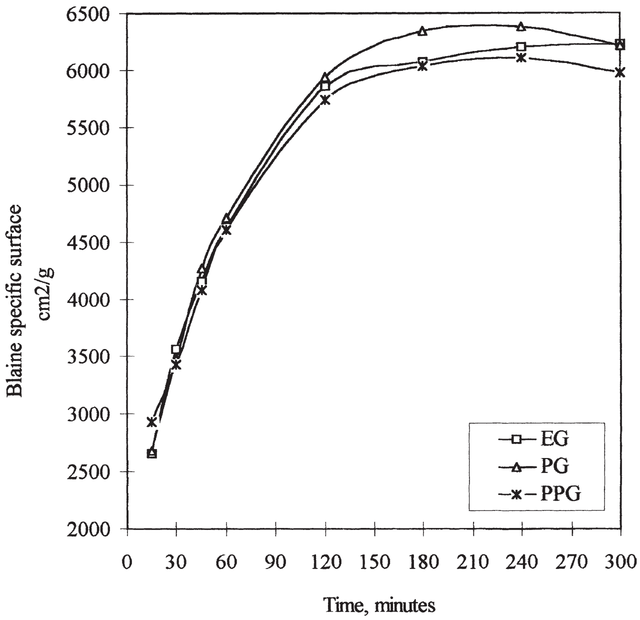

Fig. 1. Development in time of the specific surface of the cements ground with surfactant additives.

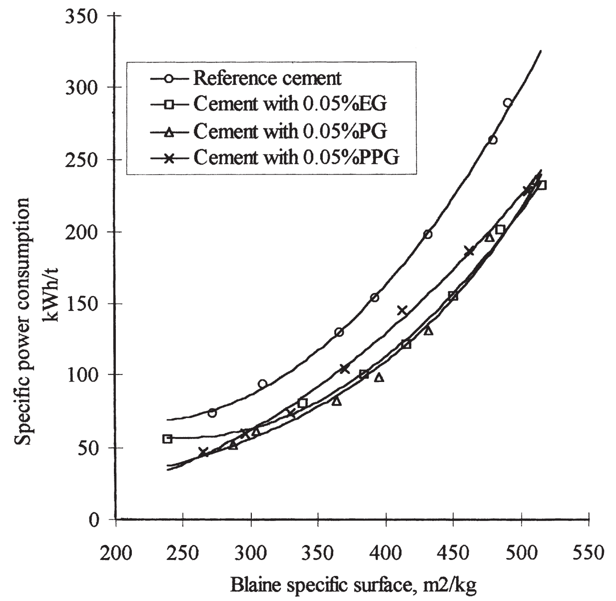

Fig. 2. Dependence of the specific power consumption vs. specific surface.

crease of the fractions corresponding to particles larger than 45 μm was found.

The experimental data are given in Table 4. For the cements manufactured with clinker D as well as for the cements made with clinker M, the increases of the 30-μm smaller grain-size fractions, with 3–9% for the optimum additive ratio, was observed. These increases are more significant for the cements manufactured with clinker M (which, as shown previously, has $M_{Al} < 1.38$, i.e., $M_{Al} = 0.89$, which differs from clinker D, especially by the increase of the potential content of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and by the drastic decrease of the potential content of $3CaO \cdot Al_2O_3$).

In this context, the poor behavior from the point of view of the 30-μm smaller grain-size fraction content of the reference cement, manufactured with clinker M in comparison with the cement made with clinker D, is to be noted—natural behavior if taking into account the higher grindability of the tricalcium aluminate in comparison with the tetracalcium ferroaluminate. A lower porosity of the clinker M is to be expected.

The higher effect determined by the use of the propylene glycol with regard to grain size distribution of the manufactured cements, with obviously higher increases of the fractions smaller than 30 μm has been found, which is in agreement with the results shown and analyzed previously.

2.4. Flow aptitude of cements ground with additives

For a higher dispersion degree, the powder systems will show better behavior with regard to their flow aptitude, when having a narrow size distribution and in the presence of the adsorbed layers by the surface active additives. Under these circumstances, the tendency of ground powders to form aggregates (through the adhesion of small particles on

Table 3
Dependence of power specific consumption vs. the obtained specific surface for reference cement and cements with addidtives

Reference cement		Cement with 0.05% EG		Cement with 0.05% PG		Cement with 0.05% PPG	
Power specific consumption (kWh/t)	Specific surface (m^2/kg)	Power specific consumption (kWh/t)	Specific surface (m^2/kg)	Power specific consumption (kWh/t)	Specific surface (m^2/kg)	Power specific consumption (kWh/t)	Specific surface (m^2/kg)
73.4	271.7	55.9	238.6	51.8	287.0	47.3	264.3
94.1	309.1	80.0	338.5	60.8	303.7	59.3	296.4
129.7	365.8	100.5	383.8	81.8	364.0	73.3	329.0
154.4	392.5	121.3	415.2	98.4	395.0	103.9	370.0
198.3	431.2	154.9	450.0	131.4	431.5	144.9	412.2
262.8	480.4	201.1	485.0	192.6	477.0	186.1	461.7
288.6	491.8	231.8	516.0	235.2	511.6	227.5	505.1

EG: ethyleneglycol, PG: propylene glycol, PPG: polypropylene glycol.

Table 4
Grain-size distribution of the reference cement and of the additive cements

Cement index	Additive Symbol	Additive Ratio (%)	Specific surface (cm^2/g)	Size distribution (%) for the fraction 0–19 (μm)	19–30 (μm)	30–45 (μm)	>45 (μm)	0–30 (μm)
Cements manufactured with clinker D								
Reference cement 1	—	—	3998	56.1	14.4	16.8	12.6	70.5
Cement 2	EG	0.03	4020	—	—	—	—	71.2
Cement 3	EG	0.05	4050	—	—	—	—	72.1
Cement 4	EG	0.10	4060	58.2	17.4	16.8	7.6	75.6
Cement 5	PG	0.03	4020	—	—	—	—	71.2
Cement 6	PG	0.05	4000	—	—	—	—	76.1
Cement 7	PG	0.10	4090	60.2	16.9	16.3	6.6	77.1
Cement 8	PPG	0.03	4100	—	—	—	—	71.5
Cement 9	PPG	0.05	4050	—	—	—	—	72.7
Cement 10	PPG	0.10	3990	55.6	17.8	17.2	9.4	73.4
Cements manufactured with clinker M								
Reference cement 1	—	—	3950	57.1	10.9	17.6	14.3	68.0
Cement 2	EG	0.03	4120	—	—	—	—	73.5
Cement 3	EG	0.05	4230	59.0	15.9	18.0	7.2	74.9
Cement 4	EG	0.10	4150	—	—	—	—	76.2
Cement 5	PG	0.03	4290	—	—	—	—	73.1
Cement 6	PG	0.05	4360	—	—	—	—	77.1
Cement 7	PG	0.10	4120	60.0	17.2	18.2	4.6	77.2
Cement 8	PPG	0.03	4030	—	—	—	—	70.8
Cement 9	PPG	0.05	4300	—	—	—	—	72.5
Cement 10	PPG	0.10	4360	58.6	17.2	18.1	6.1	75.8

the extended surface of large particles) is decreasing. The surfactants are actually favouring factors of flow aptitude both through formation of adsorption superficial layers and through the effect upon the narrowing of grading spectrum.

The results of measurements regarding the flow aptitude of cements D and M—with and without additives—are presented in Fig. 3. Fig. 3 was plotted after processing the experimental data, based on the Imse.

According to information collected from other investigations, it was found that propylene glycol offers the best flow aptitude to manufactured cement.

3. Conclusions

The results of the effect and mechanisms of action of the surfactants from the hydroxy-compound class lead to the following essential conclusions:

1. The action of surface active additives, particularly those from the dihydroxy-compound class, is expressed through the fundamental surface phenomena, which determine their adsorption and adhesion. It was found that the action of dihydroxy compounds is governed by their adsorption onto the surfaces of the

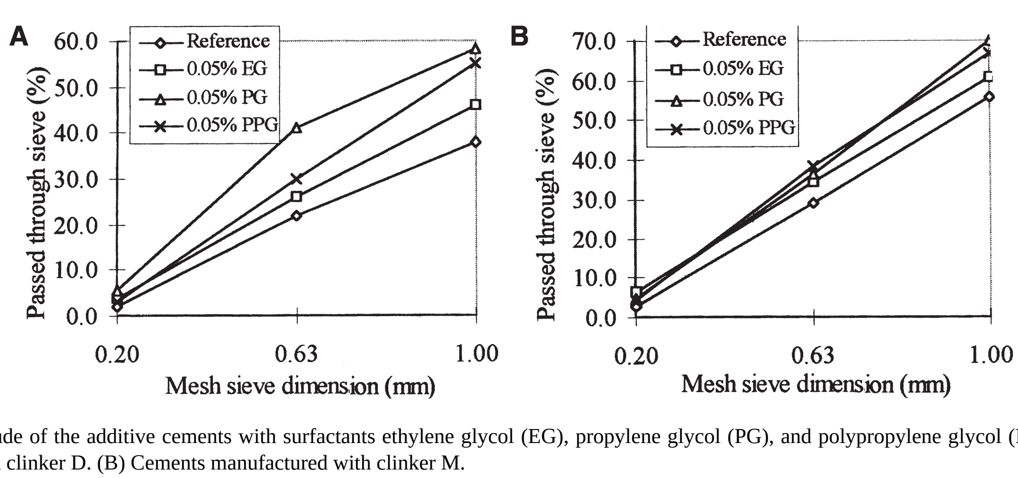

Fig. 3. Flow aptitude of the additive cements with surfactants ethylene glycol (EG), propylene glycol (PG), and polypropylene glycol (PPG). (A) Cements manufactured with clinker D. (B) Cements manufactured with clinker M.

strongly microfractured solid particles to be ground, according to the Traube-Duclaux rule. For high specific surfaces, was found that this rule is inverted for the superior term of the used surfactants series, which is plausible for heterogeneous adsorption. In the grinding process, propylene glycol has the most significant positive effect of the three dihydroxy compounds examined. The changes of the specific surface—for the same grinding duration, as well as those regarding the power specific consumptions—i.e., their reduction when using additives, suggest the action mechanisms of the surfactants with special implication of the Rebinder effects, especially in the first stage of grinding, as well as the decrease of the adhesion forces prevalent in the second stage of the process.

2. The additive ratio used emphasizes an optimum value motivated by the suggested action mechanisms. For the additives used, this value is regularly 0.05%.
3. The use of additives has consequences not only to the specific surface growth for the same grinding durations and the power consumption reduction for the same obtained specific surface, but also to the improvement of the grading spectrum (its narrowing and its shifting toward smaller grain-size fractions) and flow aptitude. According to the other results, the use of propylene glycol has also a better effect.

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