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COMPARATIVE INTERPRETATION OF THE EFFECT OF SURFACTANTS ON GRINDING PORTLAND CEMENT WITH HIGH PROPORTIONS OF GRANULATED BLAST FURNACE SLAG

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Lucrarea aduce informații, referitoare la măcinarea cimenturilor, cu conținut ridicat de zgură, în prezența aditivilor surfactanți. Aditivii utilizati, de natură organică – din clasa etanolaminelor, se deosebesc între ei prin lungimea catenei. Sunt prezentate rezultatele obținute privind evoluția suprafețelor specifice ale cimenturilor, cu 20%, 60% şi respectiv 80% zgură granulată de furnal, măcinate la diferite perioade de timp, funcție de tipul şi proporția de surfactant. De asemenea, sunt furnizate rezultate privind influența surfactanților asupra aptitudinii la măcinare a cimenturilor.

The paper brings information on grinding cement with high proportions of blast furnace slag in the presence of surfactants employed as grinding aids. The surfactants which are organic compounds belonging to the ethanol amine group differ by the chain length. The paper presents the results regarding the evolution of the specific surface area of the cement ground with 20%, 60%, and 80% granulated blast furnace slag at various grinding times depending on the type and ratio of surfactant. The paper provides results regarding also the effect of the surfactant on the grindability of the cement.

Keywords: blended Portland cement, blast furnace slag, surfactants

1. Introduction

The power consumption in the cement industry is on the rise with more and more raw materials and binders in the manufacture of ordinary Portland cement and blended Portland cement which involve various cementitious and hydraulic materials requiring grinding. Since grinding in the cement industry is an important process for both raw materials preparation and clinker comminution, the tremendous power consumption required in grinding puts a serious burden on the overall cost of the cement. Therefore, taking into account all the economic and process engineering consequences involved in trying to reduce the electric power

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consumption in grinding, this endeavour remains one of the major reasons of concern in the industry.

The literature cumulates information at world level regarding the development and characterization of high performance blended Portland cement obtained by mixing Portland cement with various types of additions and surfactants. The information in literature [1–17] indicates that the principal roles played by the surfactant are the following:

- reducing the superficial tension of the particles undergoing grinding
- reducing the sticking tendency of the ground cement particles
- reducing or even eliminating the formation of microcrusts on the grinding media surface and the mill lining
- changing the rheological properties of the ground material.

In the first stage, the surfactant gets adsorbed on the surface of the material to be comminuted, i.e. either on the exterior surfaces or on the microcrack walls where it manages to enter. An immediate effect is a decrease in hardness accompanied by phenomena of adhesion and clogging [18].

The reason behind the surfactant's decreasing the hardness is based on Griffith's theory regarding fragile breakage, which postulates that fragile materials contain small cracks whose propagation may lead to material breakage. The Rebinder effect [20-21] concept that a compound capable of selective adsorption inside the solid particle cracks undergoing grinding would impede the attraction between any residual electric forces, and in so doing it may impede any crack closure during the inactive phase. Taking the Rebinder effect to the next level, Tanaka [12] maintains that the role played by the grinding aid on the ground material is similar to a wedge. The surfactant gets adsorbed on the surface of the material undergoing grinding and reduces the surface energy, which only leads to further breakage. Moreover, the grinding aid hampers the adherence of the fine particles on the grinding media.

All concepts suggested for the mechanism of the surfactants acting as grinding aids depend mainly on the material undergoing grinding since they get adsorbed on the respective material. The adsorption on the inner surface layers of the ground material during the first phase of the process or the active phase presents a relative exception to the Traube-Duclaux rule. The adsorption on the inner surface layers may be significantly greater with the higher porosity of the material and indirect relation to the molar volume.

The surfactant needs to act very well in the role of grinding aid and it should also feature good lubricating properties. The lubricating properties are known to depend especially on the size of the hydrocarbon chain in the surfactant molecule [23–25].

2 Experimentals

The investigations were carried out with Portland cement which included varying proportions of granulated blast furnace slag (GBFS) and surfactants employed as grinding aids. The control cement employed as reference in the experiments was prepared without any surfactant.

The blended Portland cements with 20%, 60% and 80% slag were prepared with industrial Portland cement, gypsum, and granulated blast furnace slag. Table 1 shows the oxide composition of the raw materials, whereas Table 2 shows the calculated mineralogical composition (Bogue) of the Portland cement, as well as the modular properties.

Table 1

Chemical composition of the raw materials

Properties, %	Clinker	GBFS	Gypsum
Los on ignition	1.43	2.47	–
SiO_2 + Ins. in HCl	19.92	34.60	18.50
Al_2O_3	6.79	11.87	5.82
Fe_2O_3	4.27	0.6	2.16
CaO	64.62	42.24	24.63
MgO	0.7	4.71	1.79
Insolubles in HCl	0.20	0.8	–
SO_3	0.49	0.84	26.91
Free CaO	0.16	–	–
$CaSO_4.2H_2O$	–	–	57.74
$CaSO_4$	–	–	0.09
Clayey matter	–	–	28.84

Table 2

Mineralogical composition and modular characteristics of the Portland cement clinker

Properties	Content, %	Modular composition	Calculated ratios
C_3S	60.79	S_K *)	0.98
C_2S	11.92	SM	1.78
C_3A	10.78	AM	1.59
C_4AF	12.98		

*) The lime saturation factor was calculated on the basis of the Kühl equation:

$$S_k = \frac{\% CaO}{2.8\ \%SiO_2 + 1.1\ \%Al_2O_3 + 0.7\ \%Fe_2O_3}$$

Note: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, SM = silica modul, and AM = alumina modul.

The Portland cement clinker corresponded to ordinary Portland cement.

The granulated blast furnace slag complied with the requirements in the standard SR 648, i.e. (%CaO + %MgO + %SiO_2), min 66%; (%CaO +

%MgO)/%SiO_2), min. 1; %CaO/%SiO_2 = 1.1–1.4; %MgO, max. 7%; SO_3, max 2.5%.

The blast furnace slag belongs to the melilite–C_2S–C_3S_2 system.

The setting regulator employed in all the experiments was gypsum with the content of $CaSO_4.2H_2O$ in a ratio of 57.74%.

As surfactants, monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) were employed in ratios of 0.03%, 0.5%, and 0.1%.

Grinding was carried out in laboratory mills and the grindability was monitored by determining the specific power consumption in grinding in a laboratory mill equipped with an electricity meter.

3. Results and discussion

3.1. Fixed grinding times. Correlations between the dispersion parameters (specific surface area), the grinding time, and the surfactant type and ratio

Table 3 presents the evolution of the specific surface area of the Portland slag cement prepared with GBFS ground at various grinding times in relation to the surfactant type and ratio.

Table 3

Specific surface area at the same grinding times, function of surfactant proportion

Grinding time, min	Blaine specific surface area, cm^2/g									
	Control sample	Surfactant ratio, %								
		MEA			DEA			TEA		
		0.03	0.05	0.1	0.03	0.05	0.1	0.03	0.05	0.1
Cement CEM II/A–S with 20% GBFS										
15	2610	2780	3000	2800	2870	2900	3380	2810	2810	2840
30	3280	3410	3810	3620	3600	3710	3900	3560	3610	3580
45	3720	3850	4250	4000	4100	4050	4380	3900	4000	3900
60	4200	4400	4670	4620	4710	4690	5010	4400	4510	4420
120	5260	5650	5720	5780	5870	5950	5700	6010	6200	5500
180	5720	6170	6120	6000	6400	6320	5230	6520	6480	5790
240	6420	6690	6560	6350	6830	6750	5970	7010	6940	6170
300	6780	6900	6800	6620	6970	6800	6310	7200	7310	6980
Cement CEM III/A with 60% GBFS										
15	3350	3290	3570	3010	3250	3480	3400	3850	3900	3710
30	410	4000	4100	3800	4020	4080	4070	4440	4510	4480
45	4320	4410	4400	4250	4500	4480	4680	4680	4800	4720
60	4820	5140	5280	5210	5200	5350	5310	5380	5510	5200
120	5190	5310	5450	5340	5240	5380	5270	5510	5680	5450
180	6400	6800	6880	6820	6710	6780	6750	6800	7000	6700

240	7025	7310	7250	7150	7100	7230	7100	7380	7280	7080
300	7240	7350	7380	7220	7280	7310	7180	7440	7520	7250
Cement CEM III/B with 80% GBFS										
15	3510	3670	3710	3600	3540	3600	3540	3580	3650	3560
30	4220	4220	4280	4200	4250	4300	4200	4280	4320	4280
45	4810	4950	5030	4910	4870	5100	4930	5000	5150	5000
60	5340	5670	5900	5800	5600	5810	5750	5780	5870	5740
120	6490	6710	6950	6740	6750	6850	6700	6800	7040	6730
180	7030	7420	7560	7480	7380	7500	7420	7450	7680	7420
240	7430	7550	7520	7500	7490	7500	7480	7580	7540	7450
300	7465	7600	7620	7500	7540	7580	7480	7650	7720	7550

The investigations regarding the influence of the surfactants belonging to the amino alcohol group (mono-, di-, and triethanolamine) in the process of grinding the cement with granulated blast furnace slag have clearly highlighted the role of the surfactants in grinding.

The best behaviour highlighted by an increase in the specific surface area at short grinding times of 60 minutes at the most was exhibited by a proportion of 0.1% DEA. At grinding times longer than 120 minutes, the fineness was greater in the case of employing TEA, particularly in a ratio of 0.05%.

The justification of the above behaviour may be viewed as a correlation between the phenomenon of adsorption of the surfactant, the molecular weight of the surfactant, and the condition of the granular material. MEA gets adsorbed far easier onto the grain pores at short grinding times with its low molecular volume when compared to DEA and TEA. Then again, at longer grinding times the surfactants will rather get adsorbed on the grain surface layers. The finer the cement, the better the adsorption. An increase in surfactant proportion influences the cement behaviour in grinding. The best results were obtained with 0.05% TEA.

3.2 Determination of grindability

The specific power consumption in grinding is a measure of the grinding aptitude of the material. In comparing the results obtained upon grinding with and without the aid of the grinding aids, yet under overall similar conditions, there is inherent information regarding the effect of the surfactants on the grindability and their capability to decrease the specific power consumption in obtaining the same fineness for a certain type of material.

Figures 1–3 show the obtained results as far as the grindability is concerned at a fineness value of approx. 4500 cm^2/g and by the help of additives belonging to surfactants.

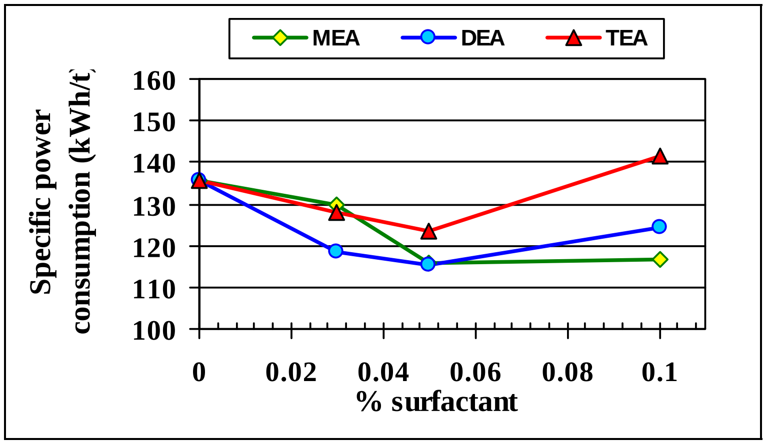

Fig. 1. Grindability of the Portland slag cement with 20% GBFS

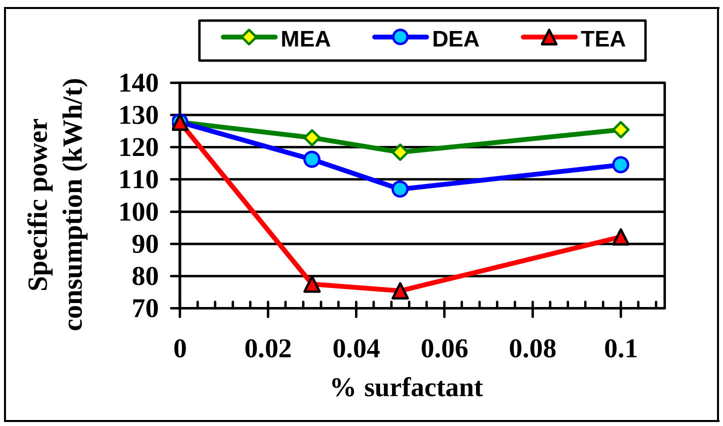

Fig. 2. Grindability of the Portland slag cement with 60% GBFS

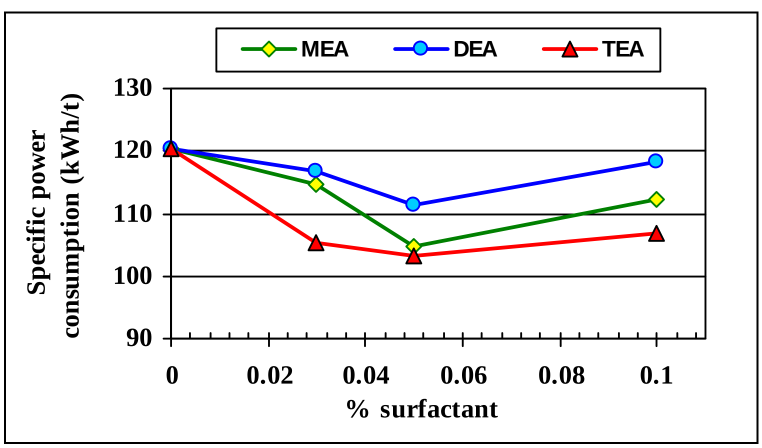

Fig. 3. Grindability of the Portland slag cement with 80% GBFS

An analysis of the grindability results revealed that the best proportion of surfactant with respect to reducing the specific power consumption in grinding was of 0.05% for all the Portland slag cement sorts, taking into account only the surfactants employed in the investigation.

An analysis of the specific power consumption in grinding when employing the optimal ratio of surfactant (i.e. 0.05%) for the Portland slag cement with 20% GBFS revealed that DEA had the best effect on lowering the specific power consumption in grinding. The behaviour is illustrated in Fig. 1 and is supported by the Rebinder effect (i.e. the wedge effect) which is also correlated to the active and inactive phases during the grinding process.

The lowest values of specific power consumption in grinding the Portland slag cement with high proportions of GBFS were associated with the use of TEA.

Table 5 presents the results of the calculation of the specific power consumption in grinding for different fineness values.

Table 5

The variation of the specific power consumption in relation to the specific surface area

Surfactant ratio, %		Specific power consumption calculated in relation to the specific surface area					
		Specific surface area, cm^2/g					
		2500	3000	3500	4000	4500	5000
		Specific power consumption, kWh/t					
Cement CEM II/A–S with 20% GBFS							
	0	47.46	62.84	83.20	110.16	145.86	193.13
MEA	0.03	44.79	58.70	76.91	100.78	132.06	173.05
	0.05	34.73	45.98	60.87	80.59	106.69	141.25
	0.1	41.95	54.22	70.08	90.58	117.08	151.32
DEA	0.03	43.71	56.48	72.99	94.31	121.88	157.49
	0.05	43.94	56.08	71.58	91.36	116.61	148.84
	0.1	38.13	52.33	71.82	98.56	135.27	185.66
TEA	0.03	43.99	57.55	75.29	98.50	128.86	168.58
	0.05	44.56	57.21	73.47	94.34	121.15	155.56
	0.1	40.30	54.39	73.40	99.07	133.71	180.47
Cement CEM III with 60% GBFS							
	0	33.61	46.65	64.75	89.86	124.72	173.10
MEA	0.03	37.60	50.41	67.58	90.59	121.44	162.80
	0.05	29.14	41.39	58.77	83.46	118.51	168.29
	0.1	42.01	56.33	75.53	101.27	135.78	182.05
DEA	0.03	42.59	54.90	70.76	91.21	117.57	151.54
	0.05	32.04	44.25	61.11	84.41	116.58	161.02
	0.1	33.55	45.40	61.44	83.16	112.54	152.31
TEA	0.03	37.91	45.08	53.60	63.75	75.80	90.15
	0.05	37.63	44.64	52.94	62.80	74.49	88.35
	0.1	35.55	44.82	56.51	71.25	89.83	113.25
Cement CEM III with 80% GBFS							

	0	43.85	55.76	70.90	90.15	114.63	145.76
MEA	0.03	36.74	48.47	63.95	84.38	111.34	146.91
	0.05	36.46	47.13	60.91	78.74	101.77	131.54
	0.1	32.00	43.97	60.43	83.04	114.12	156.82
DEA	0.03	35.74	47.52	63.17	83.98	111.65	148.43
	0.05	29.92	41.62	57.89	80.53	112.01	155.81
	0.1	36.34	48.27	64.12	85.17	113.13	150.27
TEA	0.03	29.46	40.85	56.64	78.52	108.87	150.95
	0.05	34.44	45.71	60.69	80.56	106.95	141.98
	0.1	38.02	49.34	64.02	83.06	107.77	139.83

The calculated values of the specific power consumption in grinding have revealed the following:

- The best surfactant in grinding the Portland slag cement with 20% GBFS was MEA in a ratio of 0.05% for all the fineness values.
- The best surfactant in grinding the Portland slag cement with 60% GBFS was MEA in a ratio of 0.05% when the grinding was restricted to fineness values lower than 3000 cm^2/g. When the fineness exceeded 3000 cm^2/g, the most significant reduction in the specific power consumption was recorded for the TEA surfactant employed in a ratio of 0.01%.
- In grinding the Portland slag cement with 80% GBFS, the use of MEA in a ratio of 0.1% led to the lowest values for the specific power consumption in grinding at fineness values below 3500 cm^2/g. When the cement grinding went up to fineness values of 4000 cm^2/g, the best results, as far as the specific power consumption in grinding was concerned, pertained to MEA in a ratio of 0.05% and TEA in a ratio of 0.03%. The same remark holds for the higher fineness value of 4500 cm^2/g. The specific power consumption in grinding with respect to the fineness of 5000 cm^2/g was the lowest of all at the use of 0.05% MEA, or 0.1% TEA.

4. Conclusions

A comparison between the results obtained in grinding cement with granulated blast furnace slag as far as the effect of the amino alcohol surfactants employed as grinding aids in the process and their mechanism of action were concerned, led to the following conclusions:

- The surfactants act in general by means of the basic surface phenomena in which they are involved, i.e., adsorption and adhesion.
- Grinding at similar grinding times the Portland slag cement with 20% GBFS led to a differentiation between the proper surfactant ratio to be employed in grinding in relation to the grinding duration and the type of surfactant. The best behaviour belonged to DEA employed in a ratio of

0.1% at short grinding times of 60 minutes at the most, as revealed by the specific surface area increase. At longer grinding times, i.e. above 120 minutes, the fineness was higher with the use of 0.05% TEA.

A higher proportion of granulated blast furnace slag addition in cement will definitely have an apparent effect on the grinding behaviour of the cement. In this respect, it was TEA in a ratio of 0.05% that brought out the best results in reducing the specific power consumption in grinding.

As far as the grindability was concerned, the Portland slag cement including 20% granulated blast furnace slag recorded the best results in terms of reducing the specific power consumption in grinding when employing 0.05% DEA. In what concerns the Portland slag cement with higher proportions of granulated blast furnace slag, the lowest specific power consumption values recorded in grinding were at using 0.05% TEA.

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