The Influence of Clinoptilolite on Technological Properties of Fresh and Set Slag-Alkaline Slurries

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Vplyv Clinoptilolitu na technologické vlastnosti čerstvousadenej a alkalickej zmesi

Since 1990 the AGH-UST scientists have been working on more efficient recipes of slag-alkaline slurries for sealing the soil and rock mass with hole injection methods.

A special attention has been paid to the increasing efficiency of geoengineering works on a rational shaping of technological parameters of fresh and set slag-alkaline slurries.

The properties of slurries containing clinoptiolite zeolites from the Košice area are presented in the paper.

An addition of zeolites to the slurries increases the tightness of the set slurries. Zeolites favorably influence the course of crystallization of sodium zeolite and the hydroparameters in the slag-alkaline matrix.

Key words*: lag-alkaline slurries, klinoptiolite zealites*

Introduction

Soil and rock mass environments set high requirements for technological parameters of sealing slurries for geoengineering works and deep drilling for oil and natural gas. These environments considerably differ from their marine, offshore or onshore counterparts.

Therefore, intensive investigations have been recently carried out on the further development of new generation binders and slurries, i.e. geopolymers [1, 2, 3].

Geopolymer-based slurries are exclusively made of inorganic components. They are obtained by a modification of the composition of multicomponent cement, admixed with metakaolinite or clayey minerals and dehydration products of natural zeolite nuclei [4, 5, 6, 7].

As a result of these modifications, new generation of slurries are obtained. These highly applicable slurries are very durable and flexible as far as technological properties of fresh and set slurries used for various geological-mining conditions are concerned.

Directions of zeolites application

Zeolites are applicable in the chemical industry, microelectronics, optics, medicine, environmental protection and the agriculture. The greatest number of described zeolite applications are of industrial origin. In the construction industry, zeolite-bearing tuffs can be used for the cement production or as an additive to the Portland clinker. Zeolites are widely applied as catalyst carriers in the petrochemical industry. The adsorption properties of zeolites are commonly employed for drying and cleaning gases and water steam, as well as for the separation of gases and hydrocarbons. Clinoptilolites are used for the dehydration of alcohols and oil-freon mixtures for cooling devices. The vast applicability of zeolites is a result of their specific physicochemical properties:

- high ion exchange and selective character,
- reversible hydration and dehydration,
- high gas sorption ability,
- high thermal stability,
- resistance to aggressive environments.

In view of the standard EN 197-1, natural zeolite can be determined as natural puzzolana. Similar to other puzzolanas, it hardens in water. However, when fine by ground , it reacts with dissolved calcium hydroxide**.**

Zeolites has the following applications:

- As an anticorrosion cement admixture. By adding 15 wt. % of zeolite instead of regular Portland cement, the same sulfate resistance can be obtained as HSR cements. Zeolite is applicable

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for the aggressive sulfate environment. Being a neutral additive of sealing mixtures for ecological objects, it is used for a limiting penetration of water contaminated by chemical companies.

- Zeolite significantly increases the stability of cement slurries. It is used for making cement slurries used for underground insulation walls.
- As an additive for the production of light and insulation construction materials and puzzolana cements.

Laboratory analyses

Analyses of technological parameters of fresh and set slurries concentrated on:

- For the fresh sealing slurry:
  - Density (mass) with a Baroid scale,
  - fluidity – with a trunkated cone (AzNII),
  - viscosity (relative) with the Ford's cup No. 4,
  - sedimentation – with a measurement cylinder,
  - filtration – with the use of Baroid filtration press,
  - bonding time – with the Vicat apparatus,
  - rheological parameters (plastic viscosity, apparent viscosity, yield point, structural strength) – with a rotary viscosity meter with coaxial cylinders Chan 35 and 12 rotational speeds and a fluent regulation;

- for the set sealing slurry:
  - compressive strength – with a hydraulic press up to 200 kN,
  - bending strength – with the Michaelis apparatus.

The water-to-mixture coefficient for the analyzed sealing slurries was: 0.5 ;0.6; 0.8; 1.0. A tap water at the temperature of 293 K (± 2 K) was used for making the slurry. Inorganic hydraulic binders (Potland cement, ground blast-furnace slag grains) for making the slurries (in line with ISO 25911-1 and ISO 3310-1) were sieved through three wire sieves: 1.0; 0.20; 0.08 mm of mesh. The slurries were made only of sieved Portland cement and granulated blast-furnace slag.

Analyses were made for the Portland cement CEM I 32.5 R from GÓRAŻDŻE CEMENT S.A. [1], and the blast-furnace slag from T. Sendzimir Steel-Mills. The respective parameters are presented in Table 1 [8].

Tab. 1. Properties of granulated blast-furnace slags

Component	**Type and composition of slag** [wt. %]	
	„Katowice" Steel-Mills	**T. Sendzimir Steel-Mills**
CaO	44.20	42.90
SiO_2	38.60	39.70
Al_2O_3	8.48	8.15
MgO	6.13	5.97
Fe_2O_3	0.90	0.82
SO_3	2.01	1.97
Ilość fazy szklistej [%]	>90	>85
CaO+MgO+SiO_2 [%]	88.93	88.57
(CaO+MgO)/SiO_2 [%]	1.30	1.23

The analyses were made for klinoptilolite zeolite from ZEOCEM (Slovakia). The zeolite mainly consists of SiO_2 (65.0 to 71.3 %) and Al_2O_3 (11.5 to 13.1 %).

Tap water was used for making the slurries.

Results of analyses of fresh and set sealing slurries

The influence of klinoptilolite zeolite concentration (1 %; 3 %; 5 %) in technological parameters of 5 % Portland cement activated slag-alkaline slurry, for various water-to-mixture ratios is presented in Tab. 2 to 4. Rheological parameters for various models [9] are listed in Tab. 6. The influence of zeolites on strength parameters of slag-alkaline slurries after 7 days of maturing in water environment are presented in Tab. 5.

Tab. 2. Technological parameters of 5 % CEM I 32.5R activated slag slurries for w/s = 0.5;„----" – unmeasurable because of the measurement principle

Slurry recipe w/s=0/5		5% CEM I 32.5 R			
		95% slag 0% zeolite	94% slag 1% zeolite	92% slag 3% zeolite	90% slag 5% zeolite
Filtration	Filtrate [ml]	85	63	69	53
	Filtration time [s]	12	12	13	13
Baroid scale [g/cm^3]		1.76	1.79	1.79	1.78
Ford's cup [s]		----	----	34	----
Fluidity [mm]		200	190	190	160
Sedimentation after 2 hrs. [%]		1.4	----	1.4	1
CHANN	Φ 600	163	260	270	----
	Φ 300	101	155	190	210
	Φ 200	78	118	139	165
	Φ 100	53	80	94	116
	Φ 60	41	63	73	92
	Φ 30	31	47	54	64
	Φ 20	26	39	45	50
	Φ10	20	27	32	33
	Φ 6	14	20	23	25
	Φ 3	10	15	16	18
	Φ 2	8	12	13	14
	Φ 1	6	9	9	11
Bonding time [h:min]		2:40	6:50	10:05	5:10
Beginning of bonding [h:min]		11:35	9:25	17:15	8:00
End of bonding [h:min]		14:15	16:15	27:20	13:10

Tab. 3. Technological parameters of 5% CEM I 32.5R activated slag slurries for w/s=0.8

Slag recipe w/s = 0.8		5% CEM I 32,5 R			
		95% slag 0% zeolite	94% slag 1% zeolite	92% slag 3% zeolite	90% slag 5% zeolite
Filtration	Filtrate [ml]	100	83	106	97
	Filtration time [s]	15	12	17	15
Baroid scale [g/cm^3]		1.57	1.56	1.56	1.57
Ford Cup[s]		11	11	13	28
Fluidity [mm]		----	----	----	----
Sedimentation after 2 hrs. [%]		4	24	13.6	5.6
CHANN	Φ 600	42	35	30	32
	Φ 300	22	21	16	23
	Φ 200	16	15	12	16
	Φ 100	10	9	8	11
	Φ 60	8	7	6	8
	Φ 30	6	5	4	6
	Φ 20	5	4	3	5
	Φ10	4	3	3	5
	Φ 6	3	3	2	4
	Φ 3	3	2	2	3
	Φ 2	2	2	1	3
	Φ 1	2	2	1	2
Bonding time [h:min]		4:20	8:30	14:50	15:30
Beginning of bonding [h:min]		27:10	15:10	9:10	15:40
End of bonding		21:30	23:40	24:00	31:10

Tab. 4. Technological parameters of 5% CEM I 32.5R activated slag slurries for w/s = 1.0.

Slag recipe w/s = 1.0		5% CEM I 32.5 R			
		95% slag 0% zeolite	94% slag 1% zeolite	92% slag 3% zeolite	90% slag 5% zeolite
Filtration	Filtrate [ml]	168	122	118	120
	Filtration time [s]	13	14	15	16
Baroid scale [g/cm^3]		1.44	1.47	1.49	1.48
Ford cup [s]		9	10	10	10.4
Fluidity[mm]		----	----	----	----
Sedimentation after 2 hrs. [%]		46	48	21.4	19
CHANN	Φ 600	12	20	20	20
	Φ 300	6	11	12	12
	Φ 200	4	8	9	8
	Φ 100	3	7	5	6
	Φ 60	2	7	4	4
	Φ 30	2	5	3	3
	Φ 20	1	5	3	3
	Φ10	0	5	2	3
	Φ 6	0	4	2	3
	Φ 3	0	3	2	2
	Φ 2	0	2	2	2
	Φ 1	0	1	2	2
Bonding time[h:min]		18:00	18:50	21:20	19:30
Beginning of bonding [h:min]		22:10	19:00	17:10	18:20
End of bonding [h:min]		40:10	37:50	38:30	37:50

Tab. 5. Strength parameters of 5 % CEM I 32.5R activated slag slurries after 7 days

	5% CEM I 32.5 R															
	95% slag 0% zeolite				**94% slag 1% zeolite**				**92% slag 3% zeolite**				**90% slag 5% zeolite**			
w/s	**0.5**	**0.6**	**0.8**	**1.0**	**0.5**	**0.6**	**0.8**	**1.0**	**0.5**	**0.6**	**0.8**	**1.0**	**0.5**	**0.6**	**0.8**	**1.0**
Bending strength [MPa]	2.50	2.43	1.76	----	2.17	2.11	1.24	----	1.79	1.58	1.17	----	2.16	1.53	1.17	----
Compressive strength [MPa]	12.23	8.87	5.25	----	10.68	6.68	4.53	2.98	7.75	6.62	3.50	3.50	6.43	5.20	3.33	1.97

Tab. 6. Rheological parameters of 5 % CEM I 32.5R activated slag slurries admixed with 1. 3.5 % zeolite for specific w/s

Recipe / Rheological parameters		94% slag binder 5% CEM I 32.5 R 1% klinoptilolite zeolite				92% slag binder 5% CEM I 32.5 R 3% klinoptilolite zeolite				90% slag binder 5% CEM I 32.5 R 5% klinoptilolite zeolite			
		w/s=0.5	w/s=0.6	w/s=0.8	w/s=1.0	w/s=0.5	w/s=0.6	w/s=0.8	w/s=1.0	w/s=0.5	w/s=0.6	w/s=0.8	w/s=1.0
Newtonian Model	Newtonian dynamic viscosity [Pa*s]	0.1429	0.0593	0.0190	0.0109	0.1566	0.0490	0.0158	0.0109	0.2412	0.0809	0.0249	0.0117
	Correlation coefficient [-]	0.9445	0.9522	0.9655	0.7553	0.9152	0.9206	0.9721	0.9419	0.8997	0.8310	0.8831	0.6220
Bingham Model	Plastic viscosity [Pa*s]	0.1232	0.0512	0.0167	0.0081	0.1321	0.0408	0.0141	0.0092	0.1978	0.0622	0.0197	0.0081
	Yield point [Pa]	12.68	5.22	1.44	1.78	15.82	5.27	1.08	1.06	14.65	6.33	1.76	1.22
	Correlation coefficient [-]	0.9883	0.9954	0.9960	0.9682	0.9741	0.9907	0.9960	0.9974	0.9721	0.9734	0.9929	0.9855
Ostwald de Waele Model	Consistency coefficient [Pa*s^n]	3.26	1.87	0.53	0.67	3.49	1.77	0.33	0.53	3.19	2.16	0.81	0.71
	Exponential coefficient [-]	0.5107	0.4449	0.4555	0.3581	0.5243	0.4324	0.5101	0.3564	0.5297	0.4420	0.3856	0.2764
	Correlation coefficient [-]	0.9855	0.9451	0.9363	0.9413	0.9976	0.9671	0.9564	0.8834	0.9996	0.9949	0.9564	0.9338
Casson Model	Casson/s viscosity [Pa*s]	0.0874	0.0325	0.0113	0.0040	0.0969	0.0255	0.0100	0.0053	0.1400	0.0373	0.0108	0.0034
	Yield point [Pa]	5.40	2.70	0.68	0.14	6.34	2.76	0.47	0.62	6.01	3.33	1.04	0.85
	Correlation coefficient [-]	0.9967	0.9969	0.9996	0.9724	0.9875	0.9981	0.9984	0.9960	0.9860	0.9895	0.9964	0.9913
Herschel-Bulkley Model	Yield point [Pa]	5.37	0.26	-1.62	-0.53	7.98	0.63	-1.57	-1.27	8.94	1.77	-0.93	-1.06
	Consistency coefficient [Pa*s^n]	1.00	0.99	0.99	0.99	1.00	0.99	0.99	0.99	1.01	1.00	0.99	0.99
	Exponential coefficient [-]	0.6967	0.5682	0.4096	0.3135	0.7079	0.5372	0.3855	0.3266	0.7421	0.5762	0.4004	0.3158
	Correlation coefficient [-]	0.9982	0.9828	0.9663	0.9360	0.9961	0.9894	0.9575	0.9354	0.9922	0.9951	0.9808	0.9151
*Apparent viscosity at 1022.04 [s^{-1}] [Pa*s]*		*0.1300*	*0.0560*	*0.0175*	*0.0100*	*0.1350*	*0.0445*	*0.0150*	*0.0100*	----	*0.0575*	*0.0160*	*0.0100*

Conclusions

The clinoptilolite zeolite admixture (5 wt. %) to slag-alkalize slurries results in:

- lowering the sedimentation,
- slightly lower fluidity,
- elongated bonding time,
- lowered proper filtration quantity,
- minimal increase of density of analyzed sealing slurries,
- lowering the mechanical bending strength after 7 days of maturation.

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