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Dolna 17, lok. A_02
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00-773

E-mail:
rsglobal.poland@gmail.com

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NATURAL ZEOLITES SATURATED WITH TECHNOGENIC GASSES, ADDITIVES OF BUILDING MATERIALS

[1]*Kordzakhia T, PhD*
[1]*Tsintskaladze G., PhD*
[2]*Skhvitaridze R., PhD*
[2]*Giorgadze I., PhD*
[2]*Verulava Sh., PhD*

[1]*Iv. Javakhishvili Tbilisi State University;*
P. Melikishvili Institute of Physical and Organic Chemistry,
[2]*Scientific Center "Nano Dugabi",*
Georgian Technical University, Tbilisi, Georgia

Abstract. *For the purpose of prevention of emission of CO2, SOx, NOx in the atmosphere and proper global problems, such as "Thermal effect" and "acid rains", there has been offered sorbent trapping with zeolites - cleaning of technogenic oxides coming out of the kiln of cement clinker and afterwards by grinding of these saturated sorbents and utilizing them as a mineral additive zeolite modifying of cement innovative BAT nanotechnology methods.*
Keywords*: natural zeolite, cement, kiln for clinker, technogenic gasses, adsorption, infrared spectroscopy.*

Introduction. Despite existing of lots of different means of neutralization of harmful components of gasses dissipated in the atmosphere (the main sources of which are energetic, chemical-metallurgical and cement enterprises) choosing of rational and effective cleaning methods is getting more and more actual. Because of becoming requirements stricter in relation to emission of stack gasses in the atmosphere [1, 2], it is necessary to develop cleaning technologies of stack gasses. One of the perspective methods of cleaning of stack gasses is a sorption method – by using natural zeolites.

Nowadays the "main source" of emission of stack gasses and their components, such as CO_2,SOx,NOx, into the atmosphere, is a kiln of clinker in cement production.

Clinker raw charge contains on average 80% limestone - $CaCO_3$. In case of using coal as fuel, as a result of burning CO/CO_2, SO_2/SO_3, and NO/NO_2 are moving to the stack gasses. Definitely: by the stack gasses of the clinker kiln emission of the following "harmful" technogenic compounds takes place: 742-825 kg/t CO_2; 1,15-9,18 kg/t SOx; 0,285-1,14 kg/t NOx [1], because of which cement production is deemed to be supporting creation of global problems "hot-house effect"/ "acid rains". The share of cement production in the emission of CO_2 in environment is deemed to be 6-8% [2]. At the same time these emitted technogenic substances are modifying mixtures of structural composition of cement-concrete and are supporting intensive solidification process. They are participating in creating crystallohydrates of complex, needle fiber habit (hydro calcium carboalluminate -C_3A $3CaCO_3$ $31H_2O$ ettringite-C_3A $3CaSO_4$ $31H_2O$, thaumasite-C_3S SO_4 $CO_3 15H_2O$) and self (nano)-reinforcement, in the decrease of anisotropicity of concrete strength [3].

In Georgia high-functional cement-concrete is in demand, satisfaction of which is hindered by fragility of its structure, less stability to bending loads, i.e. anisotropicity of mechanical strength.

Natural zeolites, which Georgia is rich of (their supply exceeds 300 mln t), are characterized with macromolecular system, having well developed surface, activity of which is due to the molecular-sieve effect of micro and nanopores and also diffusion and sorption processes, have ability to take in technogenic compounds emitted during clinker burning CO_2, SOx, NOx. These gasses are ecologically harmful, but joining with zeolite by sorption and after utilization of this modified zeolite in the composition of cement they become structural components of cement-concrete – nano-modifying compounds, because after mixing of cement they must form crystallohydrates of cement containing structural CO_2, SOx, NOx.

Earlier in production of cement there was offered by us perspectives of using zeolites as pozzolanic mineral addition [4,5]. There have been worked up technologies of different contents. Among them is the technology, which envisages drying of zeolite before grinding it together with clinker using the heat of stack gasses of the clinker kiln [6]. If we create certain conditions in the drying process of zeolite by the stack gasses, zeolite might trap CO_2, SOx, NOx by adsorption and stack gasses will be cleaned from them.

Research results. In pilot conditions an experiment was conducted, for which zeolite containing clinoptilolite of fraction 5-10 mm was prepared. For identifying adsorbed oxides CO_2, SOx, NOx in the mentioned zeolite method of infrared spectroscopy was used.

According to the data obtained, the intensity of bands of adsorbed ions in zeolitic filters from the clinker kiln is gradually increasing and reaches its maximum.

In the laboratory conditions we conducted adsorption of CO_2, N_2O and SO_2 separately on zeolites. Infrared spectra of these samples confirmed the results of the experiments performed in the pilot conditions.

In the laboratory and pilot conditions from adsorptive zeolitic tuff of CO_2, SOx, NOx oxides were prepared 6 samples, which in the amount of 20 mass% were mixed with cement composition. For the purpose of comparing the prepared 6 samples of “modified” cement there were prepared initial without additive CEM I 52, 5 type and 20 mass% cements containing unmodified and modified zeolites. Testing was carried out by EN 196 method, Results are represented in Table 1.

Table 1. Testing results of plain cements of CEM I 52, 5 type 20 mass% containing unmodified and modified zeolites

#	Cement composition, mass%									Weight / cement	Physico-mechanical properties				
	Clinker	Plaster	Initial	CO_2	SOx	NOx	CO_2 + NOx	CO_2 + SOx	CO_2 + SOx + NOx	%	Binding time hr-min		Strength bending/compaction, mPa		
											Start	Finish	Day 2	Day 7	Day 28
1	95	5	-	-	-	-	-	-	-	36.0	2-00	3-05	25.6	34.3	7.0/54.8
2	75	5	20	-	-	-	-	-	-	40.8	2-30	3-10	26.2	34.4	7.7/52.6
3	75	5	-	20	-	-	-	-	-	37.0	2-40	3-40	29.4	39.4	9.3/59.0
4	75	5	-	-	20	-	-	-	-	38.4	1-15	2-20	18.8	24.8	4.7/33.7
5	75	5	-	-	-	20	-	-	-	38.4	3-00	4-10	32.0	43.2	8.2/60.7
6	75	5	-	-	-	-	20	-	-	37.6	2-50	4-40	24.4	30.6	7.1/47.8
7	75	5	-	-	-	-	-	20	-	38.4	1-00	2-35	29.6	35.2	6.2/49.4
8	75	5	-	-	-	-	-	-	20	42.0	1-35	2-40	28.0	27.6	8.1/47.9

Initial cement under study was serial “HeidelbergCement Georgia “of type CEM I 52,5R. It was mixed with 20mass% of initial natural zeolitic and adsorbed tuffs, by means of which it was turned into modified cement of CEM II type.

Mixing of the cement under study with 20 mass% zeolitic tuff is increasing water demand by 4.80%, slowing down the binding speed and is increasing cement strength (initial 2-7-day strength) by 0,50-2,30%, also is increasing 28-day strength under binding by 10% and decreasing 28-day strength under compaction by 4%;

Mixing of the cement under study with 20 mass% CO_2 adsorbed zeolitic tuff is increasing its water demand only by 1%, is slowing down the binding speed, is increasing the cement strength under compaction by 7,60-14,80% and under bending by 32,80% at all stages;

Mixing of the cement under study with 20 mass% SOx adsorbed zeolitic tuff is increasing its water demand only by 2,40%, is quickening the binding speed sharply, and is decreasing mechanical strength under bending/compaction by 26,50- 38,50%;

Mixing of the cement under study with 20 mass% NOx is increasing its water demand only by 2,40%, is slowing down the binding time sharply at all stages, at all stages –most sharply by10,70-25,00 is increasing strength on compaction by 17,14% - strength on bending;

Mixing of the cement under study with 20 mass% CO_2+NOx adsorbed zeolitic tuff, only by 1,60% is increasing its water demand, is slowing down binding speed, by 12,70%-is decreasing strength on compaction and by 1,40% is increasing strength on bending;

Mixing of the cement under study with 20 mass% CO_2+SOx adsorbed zeolitic tuff, only by 2,40% is increasing its water demand, is increasing binding speed by 2 times, by 2,60-15,62% is increasing the initial strength and by 9,80% is decreasing 28- day strength;

Mixing of the cement under study with 20 mass% CO_2+SOx+NOx adsorbed zeolitic tuff, is sharply increasing by 6% as its water demand, as well as binding capacity, by 9,37% is increasing 2-day strength and 12,60% is decreasing 28-day strength;

Cements of CEM II type containing zeolitic tuffs adsorbed with CO_2 and NOx are of the highest strength!

On all samples of studied cement was performed X-ray diffractometric analysis. Results are given in Table 2.

Table 2. Results of X-ray structural analysis on the studied samples of cement

#	Composition of cement mass%	diffraction peaks of compounds in cement stone revealed by X-ray structural analysis d=Å						
		Alite C_3S	Portlandite CH	Stratlingite C_2ASH_8	Ettringite $C_2AS_3H_{32}$	Taumassite $C_3SC_3S_3$ 14,5H_2O	Calcium carbo-aluminate C_3ACaCO_3 12H_2O	Calcium nitrate $Ca(NO_3)_2$
1	95Clinker+5 Gypsum	3,03;2,98; 2,75;2,61; 2,32;2,03; 2,06;1,93; 1,82;	4,90; 3,11; 2,618; 1,80	-	9,70; 5,60; 4,70; 2,75; 2,58; 2,18	-	-	-
2	75 Clinker +5 Gypsum +20zeolite	3,03; 2,98; 2,76; 2,74; 2,61; 2,18	4,90; 2,618	12,5; 3,037; 2,613; 2,40.	9,70; 5,60; 4,70; 3,88; 2,75;2,58;2,16	-	-	-
3	75 Clinker +5 Gypsum +20zeolite +CO_2	3,03; 2,98; 2,76; 2,75; 2,61; 2,44; 2,40; 2,18; 1,98	4,90; 3,10; 2,618	12,3; 3,037; 2,79; 2,613; 2,404.	9,70; 5,61; 4,70; 3,88; 3,04; 2,75; 2,183.	-	3,97; 3,04; 2,86.	-
4	75 Clinker +5 Gypsum +20zeolite+ SO_x	3,03; 2,98; 2,75; 2,61; 2,31; 2,18; 2,09; 2,05; 1,92	4,90; 3,10; 2,618	12,10; 3,037.	9,70; 5,61; 4,70; 3,89; 3,24; 2,75; 2,58; 2,18.	3,62; 3,26; 2,98; 2,75; 2,10.	-	-
5	75 Clinker +5 Gypsum +20zeolite + NO_x	3,03; 2,08; 2,31; 2,18; 2,15.	4,90; 3,10; 2,618	12,20; 4,28; 3,037.	9,70; 5,61; 4,71; 3,88; 3,23; 2,77; 2,22.	-	-	2,45; 2,18.
6	75 Clinker +5 Gypsum +20zeolite+ CO_2/NO_x	3,03; 2,98; 2,76; 2,75; 2,61; 2,03.	4,90; 3,10; 2,618	12,20; 3,037; 2,40.	9,70; 5,61; 4,71; 3,88; 3,17; 2,75; 2,57; 2,183.	4,88; 3,18; 2,98; 2,75; 2,18.	-	2,18
7	75 Clinker +5 Gypsum +20zeolite+ CO_2/SO_x	3,03; 2,98; 2,76; 2,75; 2,61; 2,18;	4,90; 3,10; 2,618	12,60; 3,037.	9,7; 5,60; 4,70; 3,88; 3,46; 3,21; 2,83.	5,53; 3,42; 2,98; 2,75; 2,59; 2,18.	-	-
8	75 Clinker +5 Gypsum +20zeolite+ $CO_2/NO_x/SO_x$	3,03; 2,98; 2,76; 2,75; 2,61; 2,32; 2,03; 1,76.	4,90; 3,10; 2,618	12,47; 3,037; 2,40.	9,75; 5,63; 5,58; 4,70; 3,69; 3,46; 3,23; 2,76; 2,70; 2,56; 1,75.	3,62; 3,42; 2,98; 2,56; 2,21; 2,18; 2,15.	3,04; 2,86.	2,56; 2,18.

Apart from the first sample all the other samples of cement alongside with Alite, Portlandite, Ettringite must contain mineral stratlingite C_2ASH_8, which is caused because of mixing and existing of zeolitic tuffs in cement;

№3 sample of cement unlike others contains calcium carbo aluminate $C_3ACaCO_312H_2O$, which can be caused by mixing in cement zeolitic tuff adsorbed with CO_2;

№5 unlike the rest of cement samples contains Calcium Nitrate $Ca(NO_3)_2$, which might have been caused by mixing in cement zeolitic tuff adsorbed with NOx.

Conclusions. The performed work enables us to solve such global ecological problems as "thermal effect" and "acid rains" in the atmosphere by using zeolitic sorbents. Also by grinding such saturated sorbents and utilizing them as a mineral additive and further by zeolitic modifying of cement we can get cement-concrete of high strength

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