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RESEARCH ARTICLE

PERSPECTIVES OF USAGE OF NATURAL ZEOLITE SATURATED WITH KILN GASSES OF CEMENT CLINKER.

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Abstract

For the purpose of prevention of emission of CO_2 , SO_x , NO_x 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.

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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.

Matter point of the problem

Nowadays the "main source" of emission of stack gasses and their components, such as CO_2 , SO_x , NO_x , 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: **742-825kg/tCO₂; 1,15-9,18kg/tSO_x; 0,285-1,14kg/tNO_x** [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 carboaluminate - $\text{C}_3\text{A} \cdot 3\text{CaCO}_3 \cdot 31\text{H}_2\text{O}$ ettringite- $\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$, thaumasite- $\text{C}_3\text{S} \cdot \text{SO}_4 \cdot \text{CO}_3 \cdot 15\text{H}_2\text{O}$) and self (nano)- reinforcement, in the decrease of anisotropy 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. anisotropy of mechanical strength.

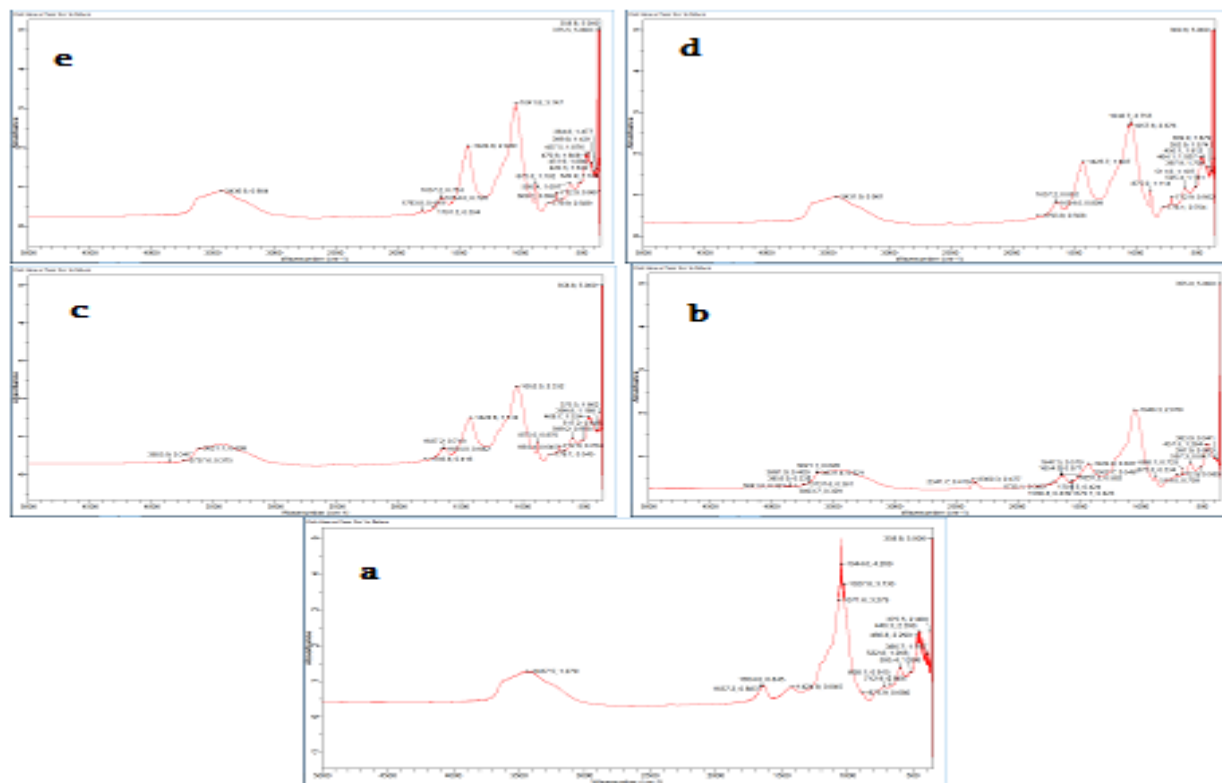
Natural zeolites, which Georgia is rich of (their supply exceeds 300 mln t), are characterized with macromolecular system, having well developed surface, activity of which is due to the molecular-sieve effect of micro and nanopores and also diffusion and sorption processes, have ability to take in technogenic compounds emitted during clinker burning CO_2 , SO_x , NO_x . 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 , SO_x , NO_x .

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 , SO_x , NO_x by adsorption and stack gasses will be cleaned from them.

Experimental part

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 , SO_x , NO_x in the mentioned zeolite method of infrared spectroscopy was used. Infrared spectra were taken in far infrared and middle infrared bands on spectrophotometer „Agilent Technologies Cary 630 FTIR”.

Probes were taken from the grid, which was placed in the pipe of the stack gas on the 7th, 14th, 21st and 27th day of working of the zeolitic filter. In the drawing below are given infrared spectra of these samples and initial zeolites.



Drawing:

Infrared spectra of aluminosilicate carcass of the taken probes from the initial (a) and zeolitic filters in far and middle infrared bands on the 7th(b), 14th (c), on the 21st(d) and 28th day (e) of working.

As it is seen from the drawing the spectrum of the initial sample fully corresponds to the data given in literature [7,8], accordingly these are bands of tetrahedral deformational vibration inside aluminosilicate at 466 cm^{-1} and valence vibration at 1044.6 cm^{-1} , also bands of vibration between tetrahedrons accordingly are at $522.8, 595.4, 668.1, 712.9\text{ cm}^{-1}$. Characteristic bands of natural minerals are: deformational of water at 1654.2 cm^{-1} and valence at 3437.5 cm^{-1} and vibration band of adsorbed carbon-ions at 1424.8 cm^{-1} . In infrared spectrum taken on the 7th day and especially on the 14th day the picture is changing –intensity of bands at 1424 cm^{-1} , 875 and 712 cm^{-1} , which correspond to CO_3^{2-} , NO_2^- , NO_3^- , SO_3^{2-} and SO_4^{2-} ions accordingly [9,10]. Vibration frequencies of these ions are very close to each other and often their corresponding bands are overlapped. Also valence vibration band of Si-O-Si aluminosilicate at 1044 cm^{-1} coincides with vibration bands of SO_4^{2-} and NO_2^- ions [10], hence it is hard to fix absorbed ions exactly, though the general picture is clear. Intensity of bands of adsorbed ions in zeolitic filters from the clinker kiln is gradually increasing and reaches its maximum in the spectrum of the sample taken after the 28th day (drawing).

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 **CO₂, SO_x, NO_x** 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 196-1** 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%									w/c	Physico-mechanical properties					
	Clinker	Plaster	Initial	CO ₂	SO _x	NO _x	CO ₂ + NO _x	CO ₂ + SO _x	CO ₂ + SO _x + NO _x		%	Binding tems hr-min		Strengthbending/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 20 mass % 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 % SO_x 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% NO_x is increasing its water demand only by 2,40%, is slowing down the binding timesharply at all stages, at all stages–most sharply by10,70-25,00 is increasing strength on compactionby 17,14% -strength on bending;

Mixing of the cement under study with 20 mass% CO₂+NO_x 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% CO₂+SO_x 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% CO₂+SO_x+NO_x adsorbed zeolitic tuff, is sharply increasing by 6% as its water demand, as well as binding capacity,by9,37% is increasing 2-day strength and 12,60% is decreasing 28-day strength;

Cements of CEM II type containing zeolitic tuffs adsorbed with CO₂ and NO_x 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 cementmass%	diffraction peaks of compounds in cement stone revealed by X-ray structural analysis d=Å						
		Alite C ₃ S	Portlandite CH	Stratlingite C ₂ ASH ₈	Ettringite C ₂ AS ₃ H ₃₂	Taumasite C ₃ SC ₃ S ₃ 14,5H ₂ O	Calcium carbo-aluminate C ₃ ACaCO ₃ 12H ₂ O	Calcium nitrate Ca(NO ₃) ₂
1	2	3	4	5	6	7	8	9
1	95clinker+5gypsum	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	75clinker+5gypsum+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	75clinker+5gypsum+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	75clinker+5gypsum+20zeolite	3,03;	4,90;	12,10;	9,70;	3,62;	-	-

	+ SO _x	2,98; 2,75; 2,61; 2,31; 2,18; 2,09; 2,05; 1,92	3,10; 2,618	3,037.	5,61; 4,70; 3,89; 3,24; 2,75; 2,58; 2,18.	3,26; 2,98; 2,75;2,1 0.		
5	75clinker+5gypsum+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	75clinker+5gypsum+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	75clinker+5gypsum+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	75clinker+5gypsum+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 **C₂ASH₈**, which is caused because of mixing and existing of zeolitic tuffs in cement;

№3 sample of cement unlike others contains calcium carbo aluminate **C₃ACaCO₃12H₂O**, which can be caused by mixing in cement zeolitic tuff adsorbed with **CO₂**;

№5 unlike the rest of cement samples contains Calcium nitrate **Ca(NO₃)₂**, which might have been caused by mixing in cement zeolitic tuff adsorbed with **NO_x**.

Conclusion:-

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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