Journal Homepage: -www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
Article DOI:10.21474/IJAR01/5758
DOI URL: http://dx.doi.org/10.21474/IJAR01/5758

RESEARCH ARTICLE

SCIENTIFIC FUNDAMENT, INNOVATION, PRACTICE AND BENEFITS TO USE ZEOLITE TUFF IN CEMENT MANUFACTURING IN GEORGIA.

Rajden Skhvitaridze[1],Teimuraz Kordzakhia[2],Giorgi Tsintskaladze[3],Irakli Giorgadze[1] and Shalva Verulava[1].

1. Ph.D., Scientific Center "NanoDugabi", Georgian Technical University, Tbilisi, Georgia.
2. Ph.D. Leading Scientist, Ivane Javakhishvili Tbilisi State University, P.Melikishvili Institute of Organic and Physical Chemistry, Tbilisi, Georgia.
3. Ph.D. Leading Scientist, Ivane Javakhishvili Tbilisi State University, P.Melikishvili Institute of Organic and Physical Chemistry, Tbilisi, Georgia.

Manuscript Info

Manuscript History

Received: 03 September 2017
Final Accepted: 05 October 2017
Published: November 2017

Key words:-
Zeolite tuff, additive, cement, emission, technology.

Abstract

Georgia and the Georgian cement producers are pioneers of using Zeolite Tuff (ZT) in the cement grinding process. ZT reserves in Georgia reach 300.0 million tons. Formally, EN standards regulates that it is allowed to use a material which contains more than 25% SiO2 in its composition as a mineral pozzolanic cement additive. ZT meets the formal requirement of EN standards, because it contains at least 40% SiO2. ZT - without reducing the technical properties of cement and concrete, cement can be introduced in an amount of up to 40% by weight of the clinker, which is very important from an economic point of view, because the share of the most expensive and energy-intensive component in cement, clinker, decreases. This will also reduce the emission of harmful gases into the atmosphere by 40%: the CO2 emission will decrease from 0,585-0,640 t/t.kl. – up to 0,351-0,384 t/t.kl.; Emission of SOx from 1,150-9,180 kg/t.kl – up to 0,690-5,508 t/t.kl.; Emission of NOx from 0,285-1,140 kg/t.kl. – up to 0,171-0,684 t/t.kl., which is very important from an ecological point of view. There are given results of experiments on the basis of ZT and technics & possibilities it's using in cement technology.

Introduction:-

After the investment from "HEIDELBERGCEMENT", the quantity of cement produced in Georgia increased. There were produced 1.2 million tons of cement in Georgia in 2007 and 1.5 million tons in 2011. In 2016, HEIDELBERGCEMENT GEORGIA produced up to 2.0 million tons of cement. It should be noted that the increase in cement production aggravates the global-ecological and local-economic problems of cement production.

Global-ecological problem - emission of harmful substances. During the production of cement technogenic harmful oxides are emitted from clinker furnaces into the atmosphere: CO_2 in (calculated-theoretical / practical) quantity: 0,585/0,640 t / t.kl which promotes the formation of "greenhouse effect" and "acid rain"; 1,150/9,180kg/t.klSOx and 0,285/1,140 kg/t.klNOx – which promote the formation of "acid rain".

Corresponding Author:-Rajden Skhvitaridze.
Address:-Ph.D., Scientific Center "NanoDugabi", Georgian Technical University, Tbilisi, Georgia.

Local economic problem. Deficiency and high durability of mineral cement additives. Since 1926 cement plants of Georgia used Ani (Armenia) pumice as a mineral additive in the process of cement grinding, and since 1956 also the granulated blast furnace slag of the Rustavi Metallurgical Combine. After the collapse of the Soviet Union, starting from 1991 the pumice import from Armenia had been shut down due to the appearance of customs duties on the import of materials and a rise in the cost of transportation, and blast furnaces and slag granulation in Rustavi stopped functioning. There was a shortage of materials used as a mineral additive. Cement manufacturers had to look for alternative materials for use in production. The way out of the situation was an innovative technical solution: - using non-traditional for the cement industry of the former USSR's mineral additives in the production of cement, for example zeolite tuff.

Zeolite tuff (ZT). "HEIDELBERGCEMENT GEORGIA", "EVROCEMENT" and other companies began to produce cement of the types EN 197-1: CEM II / B 32.5; CEM IV / B 32.5 and EN 413-1 - MC 22.5X, which contain 5 - 40% ZT of the Dzegwi or Khandaki fields. It should be noted that they do not use ZT in the production of cement in other countries. Georgia and the Georgian cement producers are pioneers of using ZT in cement grinding process, which has several grounds. Let’s consider them:

Economic grounds. Obtaining high-tech and competitive systems based on local raw materials is one of the priority directions of Georgia's economy. ZT reserves in Georgia reach 300.0 million tons. It is an easily processed rock (Mohs hardness 3-5); It is extracted by open method; The distance from the existing ZT deposits to cement plants is only 15 - 70 km; ZT in the cement "replaces" the most expensive component - clinker. All this is a precondition for the low cost of the produced cement.

Legal grounds. The agreement on Georgia's association with the European Union has created the need to develop technologies to protect the environment in Georgian cement plants. One of the ways to reduce the emission of harmful compounds into the environment is the decrease in the proportion of clinker during cement grinding, and correspondingly an increase in the proportion of mineral additives [1,2,3]; Formally, EN 197-1 [4] regulates that it is allowed to use a material which contains more than 25% SiO_2 in its composition as a mineral pozzolanic cement admixture. ZT meets the formal requirement of EN 197-1, because it contains at least 40% SiO2. Starting from 2014, the inclusion of ZT in cement is regulated in accordance with GOST R 56196-2014 [5], which must be carried out in accordance with the criteria (GOST 24640-91. [6]): "decrease in the proportion of clinker is greater than the decrease in cement activity" (All these normative documents are valid for the territory of Georgia).

Physical-chemical, and scientific grounds. Based on many years of research [7], we have been convinced that using a mineral additive of any type in the structure of the cement in an amount of up to 7%, increases its activity (strength), and above this limit - decreases. This dependence is represented by hyperboloid curves for various types of additive and cement (Fig. 1).

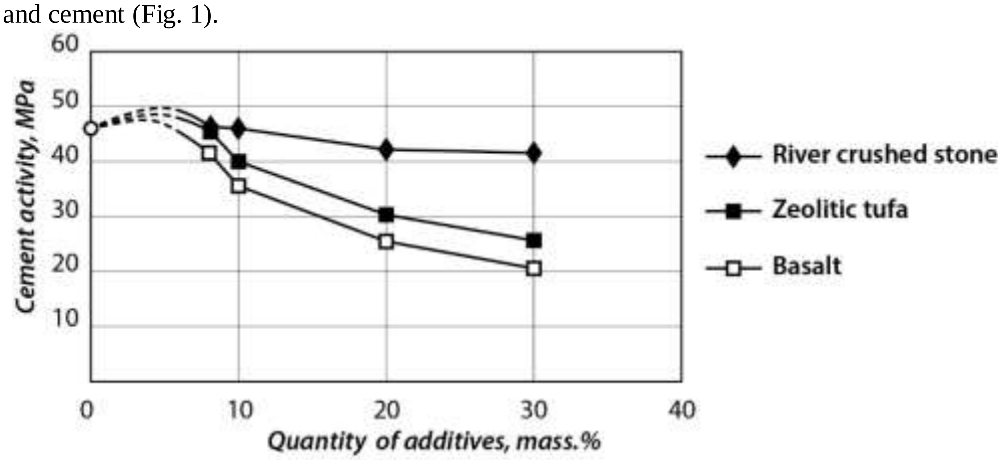

Fig.1:-The curves of the dependence of the cement activity (strength) on the amount and activity of the mineral additive

The graph shows with dotted line the change in cement activity (strength) when including and increasing the amount of the mineral additive of river crushed stone, ZT or basalt in the range of 5-7%; after increasing the amount of mineral additive above 7% - the activity (strength) of cement begins to decline. All this is explained by the fact that small amounts of mineral additives stimulate the formation of crystalline hydrate-ettringite [7] during hardening of cement, which is confirmed by the well-known Dr. H. F. W. Taylor [8]. A question arise: - In what quantity is it possible to add mineral additives in cement composition? The answer: - During the production of cement, it is necessary to observe the criteria: "the decrease in the proportion of clinker in cement is greater than the decrease in cement activity (strength)" [6]. Inclusion of 5-7% of activated ZT in the composition of cement will allow to obtain cement with a strength of 62.5 MPa.

Since 1926 they used the Khandaki tuff in the grinding of cement at the Kaspi cement plant in Georgia, as a pozzolanic mineral additive, along with pumice stone, which required drying. Its humidity was in the range of 13-20%, which increased the cost of production and prime cost of cement and therefore, it's not been used from the 60s of the 20th century. Then they did not know that it contains 50-85% zeolitic mineral clinoptilolite {$(Na, K)_6$ $[Al_6Si_{30}O_{72}]$ $24H_2O$}, which has a crystalline structure consisting of nanopores with diameters of 0.4-3.0 nm. The calcium tosilmorite-CSH calcium hydrosilicate gel formed during hardening of cement is a dispersed (3d) reinforced material with nano sizes.

Hypothesis: interaction of ZT with CH, i.e. the reaction of pozzolanization will promote the formation of water-resistant nanoscale compounds with a fibrous-acicular plate habit: tobermorite CSH, stratlingite C_2ASH_8, and externgite C_3A $3CaSO_4$ $31H_2O$, which leads to their wreath, (3d) self-nano reinforcement of the cementitious cement structure and a sharp increase in its strength (activity) [1.8.9]. To use ZT, it is necessary to know not only its chemical composition and structure, but also its behavior when grinding cement and making concrete, because during cement grinding the temperature in the mill reaches 200 ° C and ZT is being heated. Fig. 2 shows a derivatogram of ZT containing 60% clinoptilolite, from which it is evident that it is dehydrated at 130 ° C - (Hypothesis), this will lead to its activation - water found in the nano (0.4-3.0 nm) pores of clinoptilolite releases space - for example, for $Ca\ (OH)_2$, i.e. to intensify the reaction "pozzolanization" [1,9], which will further contribute to an increase in the stability of the structure and durability of concrete.

On the diffractogram of crude ZT (Fig. 3), except for clinoptilolite peaks 2.01; 2.35; 2.44; 2.52; 2.70; 2.80; 2.98; 3.34; 3.43; 3.56; 3.92; 3.96; 4.07; 5.14; 5.26; 5.37; 5.63; 6.68 Å, there are peaks of feldspar 3.20Ao and calcite 3.03 are observed; 2.03; 1.96; 1.877 Å. Heating ZT at 200 ° C does not change the diffraction pattern, which confirms that when ZT is heated to 200 ° C, the main process is only its dehydration at 130 ° C.

Technological grounds. During milling in tube ball mills, the cement heats up. It happens because, according to the data [10], the energy consumed at the grinding process (400 kWh) is used directly for grinding only partially, and 87% (390 kWh) is converted to heat, which causes dehydration of the water-containing components of the ground mixture - for example ZT. This heat can be used for drying a wet component (e.g. ZT) milled cement mixture. The theoretical dehydration temperature of ZT according to DTA is 130 ° C. ZT with grain sizes of 32 μm will be more easily and more rapidly dehydrated than with grain sizes of 80 μm, which leads to its Nano activation by absorption of $Ca(OH)_2$. Proceeding from this, it can be assumed that the higher the temperature of thermal activation and the surface area of ZT, the higher will be its activity in the absorption of $Ca(OH)_2$ and the cement purity.

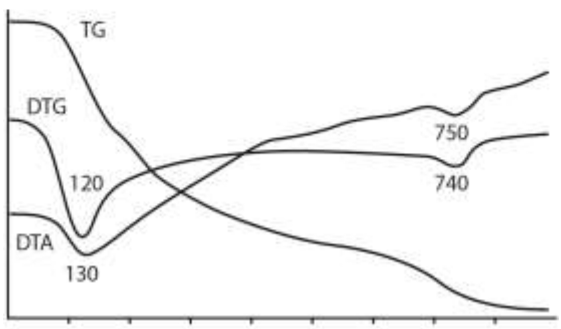

Fig.2:-Derivatogram of clinoptilolite

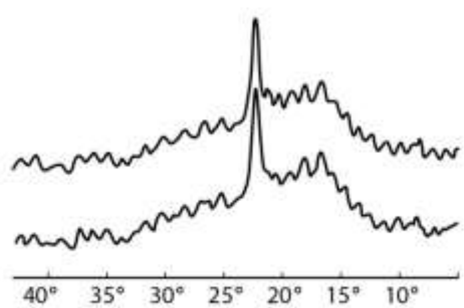

Fig.3:-Diffraction pattern of clinoptilolite

The chemical composition of ZT used in the cement industry of Georgia is presented in Table 1, and the mineralogical composition and expected neoplasms in cement stone are shown in Table 2.

Table 1:- Chemical composition and origin of mineral additives

Name	Chemical composition of the mass%									Origin
	Pp.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	R_2O	SO_3	
Zeolite tuff of Khandaki	14.06	43.80	14.83	6.87	12.80	2.45	0.44	4.72	0.02	Sedimentary
Zeolite tuff of Dzegvi	11.56	57.45	16.06	3.75	5.49	1.70	0.01	3.65	0.22	Sedimentary

Table 2:- Mineralogical composition of additives and expected neoplasms in cement stone

Name	Basic minerals	Neoplasms after reaction with $Ca(OH)_2$ in hardening cement stone
Zeolite tuff	Volcanic glass; SiO_2; $Al_2O_3{\cdot}SiO_2{\cdot}OH$; $R_2O(RO)Al_2O_{3m}SiO_2{\cdot}nH_2O$; Clinoptilolite $(Na,K)_6[Al_6Si_{30}O_{72}]24H_2O$	CSH(B); C_2AH_8; C_4AH_x; C_2ASH_6; $C_3AS_xH_{6-2x}$

LAB Experiment. The average size of grains of any material is connected with a surface by the ratio Dm = 600,000 / h, x s cm; Hence, S = 600,000 / γ x Dm cm^2 / g. Here: S-ud.p. Cm^2 / g; Dm is the average particle size in microns; γ - uid weight of the material. ZT of the Dzegvi field was milled to the full passage through sieves №008 (80 μm) и №0032 (32 μm). Then the surface of the experimental ZT powders will be:
S80 μm = 600000/2.1x 80 = 3571 cm^2/g. S32 μm = 600000/2.1x 32 = 9523 cm^2/g.
The surface of the ZT at a grain size of 32 μm is 2.66 times larger than at 80 μm.

The crushed ZT was divided into 3 parts. 1- part before displacement with cement for 24h was held in a desiccator – at 20^0C; 2- part before displacement with cement for 1 h dried at 100^0C; 3 – the part before displacement with cement was also dried for 1 hour at 130^0C. Thus, 6 tested ZT were prepared: ZT-1 (80 μm-20^0C); ZT-2. (80 μm -100^0C); ZT-3.(80 μm -130^0C); ZT-4.(32 μm -20^0C); ZT-5.(32 μm -100^0C); ZT-6.(32 μm -130^0C).

Testing the activity of ZT cement with grain sizes of 32-80 μm, according to ASTM C 311-05 [10], showed that the cement activity index with natural ZT of the Dzegvi field is higher than 75 and is 2days - 76.7 (ZT-1) and 90.0 (ZT-1); after 28days -88.8 (ZT-1) and 100.9 (ZT-1); i.e. it is a hydraulic active material (Table 3). The activity test according to ASTM C 311-05 procedure of the same ZT, but ground to particle sizes of 80 μm and 32 μm, and heat treated at 100^0C and 130^0C showed that grinding ZT to 32 μm in size and heat treatment at 100-130^0C sharply increases the ZT activity index to 93.3 - 118.5 respectively (ZT-2 - ZT-6).

Table 3:-ASTM C 311-05. Strength activity index

constituents	Control mix	Test mix					
		ZT-1	ZT-2	ZT-3	ZT-4	ZT-5	ZT-6
Portland cement	450	420	420	420	420	420	420
Test sample	-	30	30	30	30	30	30
Standart sand, g	1350	1350	1350	1350	1350	1350	1350
Water, g	225	225	225	225	225	225	225
A.Average compressive Strength of the test mixture in MPA, after **2** days	-	23,0	28.0	30,0	27,0	31,0	33,0
B.average compressive strength of the control mixture in MPA after **2** days	30,0	-	-	-	-	-	-
Strength activity index= A/B *100	-	76,7	93,3	100,0	90,0	103,3	110,0
A.Average compressive Strength of the test mixture in MPA, after **28** days	-	48,0	50,0	56,0	54,5	62,0	64,0
B.average compressive strength of the control mixture in MPA after **28** days	54,0	-	-	-	-	-	-
Strength activity index= A/B *100	-	88,8	95,6	103,7	100,9	114,8	118,5

Innovative nanotechnology. The interaction of the constituents of thermally activated **ZT** with **CH** (portlandite), i.e. The reaction of pozzolanization promotes the intensive formation of water-resistant nanoscale connections with a fibrous-acicular plate habit: tobermorite **CSH**, stratlingite **C_2ASH_8**, externgite **C_3A $3CaSO_4$ $31H_2O$**, which causes them to weave, **(3d**) self-nano-reinforcement of the cementitious cement structure and sharply increase its strength (activity) [1.16.22].

The practice of applying ZT with the use of energy efficient innovative technology. Since 2001, "Eurocement" uses Khandaki ZT as a mineral additive for grinding cement (Table 1). It is characterized by high humidity (13 - 20%;), and requires drying - which is economically impractical at the current energy situation. Based on the situation, we have developed a highly economical way of drying mineral additives. The essence of the method is that the mineral additive is fed to the clinker conveyor for drying, and for the time the hot clinker, which has a temperature of 50 - 300 ^{0}C, is fed to the conveyor - onto a layer of moist mineral additive (Fig. 4). The technology is patented in the former USSR and in Georgia [12].

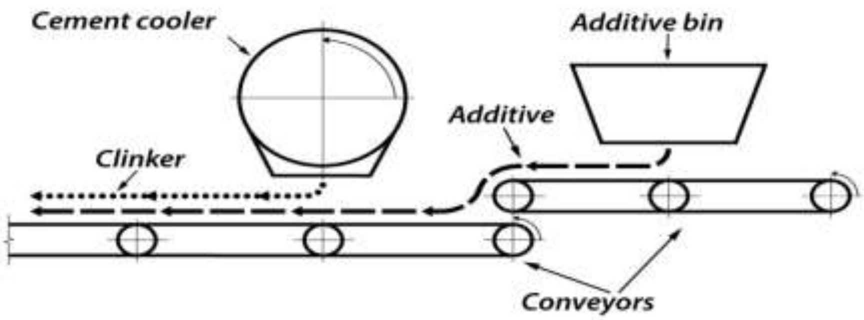

Fig.4:-Scheme of simultaneous cooling of clinker and drying of the additive - ZT

Grinding in a separator mill. The moisture of the clinker before feeding to the milling is 0%, gypsum 2-6%, Dzegvi ZT 13 - 17%. Composition of cement: clinker 55%, gypsum 5%, ZT 40%. Then the estimated expected moisture content of cement mixture will be: (0.55 x 0) + (0.05 x 2-6) + (0.4 x 13-17) = 5.3 - 7.1%. The moisture content of cement MC 22.5X, emerging from the separator mill, is 0.0-0.2%. Question arise: Where goes the moisture content of the mixture is in the amount (5.3-7.1) - (0.0-0.2) = (5.1- 6.9)% ?.

The answer: when grinding cement in a separator mill, the temperature inside the mill rises to 70-150^{0}C. If the moisture content of the milled material does not exceed 6% [10], intensive heat exchange takes place, and therefore, simultaneously with grinding, with the help of the heated medium of the mill, drying or evaporation of water occurs, or dehydration or dehydration of the deformable material-that is, dehydration and activation of ZT, and the temperature of the cement upon leaving the mill is 40-60 ° C. Thus, grinding cement with the inclusion of ZT in a separator mill is an innovative energy-efficient technology!

As a result, the strength of the cement obtained is higher, compared to cement in a mill without a separator.

Results and Recommendations:-

- **ZT** - without reducing the technical properties of cement and concrete, cement can be introduced in an amount of up to 40% by weight of the clinker, which is very important from an economic point of view, because the share of the most expensive and energy-intensive component in cement, clinker, decreases. This will also reduce the emission of harmful gases into the atmosphere by 40%: the CO_2 emission will decrease from 0,585-0,640 t/t.kl. – up to 0,351-0,384 t/t.kl.; Emission of SOx from 1,150-9,180 kg/t.kl – up to 0,690-5,508 t/t.kl.; Emission of NOx from 0,285-1,140 kg/t.kl. – up to 0,171-0,684 t/t.kl., which is very important from an ecological point of view.
- Introduction of Dzegvi **ZT** into the cement composition in an amount of 5 - 7%, after grinding in a separator mill, will allow to obtain cement with a strength more than 62.5 MPa.

Acknowledgement:-

The work was prepared with the support of the Ministry of Education and Science of Georgia and ShotaRustaveli National Science Foundation. Grant № AR 216800.

References:-

1. Skhvitaridze R., Giorgadze I.. (2011). Scientific and Technical basis for HPC usage and dispersive (3d) reinforcement necessity on the construction market of Georgia. "INNOVATIVE TECHNOLOGIES AND MATERIALS". 24-27 october. PROCEEDINGS. Tbilisi.. p. 279-285;
2. Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. http://www.ifc.org
3. European Commission. (2010) "Integrated pollution Prevention and Control. Reference Document on Best Available Techniques in the Cement and Magnesium Oxide Manufacturing Industries. May 2010". http://eippecb.jrc.ec.europa.eu;
4. EN 197-1:2011. Cement – Part 1: Composition, specifications and conformity criteria for common cements;
5. GOST R 56196-2014. Active mineral additives for cements. General specifications (RU);
6. GOST 24640-91. Additions for cements. Classification (RU);
7. Skhvitaridze R. (2005). "Cement Chemistry and Rapid Methods Of Determination Of Cement Activiti With Mineral Additives And Concrete Strength". J.: "Beton I Jelezobeton". (RU). 3(534). 06.2005. p..6-11;
8. H.F.W.Taylor (1990).CementChemistry. Academic Press.London;
9. Skhvitaridze R., Keshelava B., Giorgadze I., Tsintskaladze G., Verulava Sh.. (2014) "THE INNOVATIVE CONCRETE NANOTECHNOLOGY IN GEORGIA". Journal "NANO STUDIES", 3-4. Proceedings of the 3rd International Conference "Nanotechnologies" (October 20-24, 2014, Tbilisi, Georgia);
10. W.H.Duda. (1981). Cement Data-Book. Bauverling GmbH. Wiesbaden and Berlin (Translate in Ru.) M.:"Stroiizdat". 1981.p.242.
11. ASTM C 311-05. "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland – Cement Concrete";
12. Skhvitaridze R. E., Gabadadze T. G. (1982). Patent of USSR № 973498. "Way of receiving additive to portland-pozzolana cement".