Evaluation of zeolitized and vitreous tuffs located in the province of Holguín for use as a natural pozzolan in construction*

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Abstract: This work involves the evaluation of vitreous and zeolitized tuff present in the ore bodies of Sagua de Tánamo, Guaramanao, Caimanes and San Andrés, based on chemical and granulometric characterizations and flexotraction and compression resistance of mortar made with 15 percent tuffaceous material as a substitute for Portland cement by applying the methods described in the standards for those specifications for its potential use as a natural pozzolan in construction applications.

Key words: Vitreous and zeolitized tuff; natural pozzolan; construction material Holguín.

Evaluación de tobas vítreas y zeolitizadas de la provincia Holguín para su utilización como puzolana natural en la construcción

Resumen: El presente trabajo aborda la evaluación de las tobas vítreas y zeolitizadas de los yacimientos Sagua de Tánamo, Guaramanao, Caimanes y San Andrés, basado en la caracterización química, granulométrica y en la determinación de la resistencia a la flexotracción y a la compresión de morteros elaborados con adiciones de 15 % de material tobáceo como sustituto del cemento portland, a partir de los métodos indicados en las normas para tales especificaciones para su posible utilización como puzolana natural en la construcción.

Palabras clave: Tobas vítreas y zeolitizadas; material de construcción; puzolona natural; Holguín.

Introduction

Over the past several decades it has become a common practice worldwide to add solid materials mainly naturally occurring (volcanic or sedimentary) silicates and aluminosilicates or by-products from some industries (slags, etc) and even thermally activated natural minerals (calcined clays) to the Portland cement. These additions give the Portland cement certain properties of great practical importance, basically to achieve a higher chemical stability and hence increase the durability of cement and concrete (Rabilero, 1988).

Works done by Lea, F. M. (1938, 1940, 1954), Soria F. (1967), Massazza, F. (1974), Calleja, J. (1966 y 1969), Sousa Coutinho, A. (1959) and Malquori, G. (1960) have substantiated the potential for their use taking into account the benefits of these materials nature offers and a solution of great economic significance.

Natural pozzolans are an essential component for the production of mixed or Portland pozzolanic cements; which contribute to the preservation of the natural/human environment as a result of reduced emission of harmful gases such as CO_2, SO_2 and because burning in kilos of raw materials would not be required to obtain them.

Cuba has over 500 million tonnes of prospective resources in several ore bodies, at different stages of study, located around the island, containing altered, vitreous (volcanic glass) and zeolitized tuff, with the prospect of being exploited as pozzolans. In addition, the country is in possession of several hundred million tonnes of forecast vitreous tuff which requires more thorough study to make sure it can be used as pozzolan (J. De Armas, 2008).

Today's world has experienced a shortage of construction materials due to a significant increase in their demand, high costs and other factors arising at local level. In Cuba specifically, many houses have been swept away on a yearly basis by natural disasters like hurricanes, thus demanding the exploration of new construction aggregate supply sources, thereby encouraging the study of rocks such as vitreous tuff, zeolitized tuff, serpentinites, etc. Holguin is one of the most densely populated territories of Cuba. Much of its housing stock is in poor condition (nearly 40%). This is one of the areas of the country with the highest level of construction activity. Based on the above, this work is aimed at assessing the pozzolanic properties of vitreous and zeolitized tuff present in the ore bodies in Sagua de Tánamo, Guaramanao, Caimanes and San Andrés for its possible utilization in construction.

Pozzolans. Definition

According to the definition 618-78 of the ASTM Code, pozzolans are siliceous or aluminous-siliceous materials having a predominant amorphous component which in itself possesses little or no cementitious value but when ground in a finely divided form, such as a powder or liquid and in the presence of moisture, chemically react with calcium hydroxide at ambient temperature to form compounds possessing cementitious properties.

Main types of pozzolans

Natural pozzolans: are generally derived from rock materials as volcanic ash, volcanic tuffs, pumice stone, slags and obsidian, diatomaceous (diatomite), etc where amorphous silica dominates; that is, volcanic glass produced from the sudden cooling of lava. For example, volcanic ash, rocks or soils where the siliceous constituent contains opal, either by siliceous precipitation from a solution or from the residues of organisms, such as diatom earths or clays naturally calcinated from the action of heat or from a lava flow.

Artificial pozzolanas: The main sources of artificial pozzolanas are industrial by-products and thermally-treated materials; such as: ashes produced during the combustion of mineral carbon, bitumens and hydrocarbons in thermal, electrical power plants, etc; ashes from burning organic matter such as rice husk, sugarcane straw and thermally activated clays known as microsilica (or the Anglicism "silica fume"), etc. The pozzolanic properties of these materials are found in the amorphous or vitreous portion and also in altered or decomposing minerals.

Pozzolanic activity: The properties of pozzolanas depend upon the chemical composition and the internal structure. It refers to pozzolanas with a chemical composition in which the presence of the three main oxides (SiO2, AL2O3, Fe2O3) is greater than 70%. The objective is to have pozzolanas with an amorphous structure. It is essential that pozzolanas be in a finely divided state as it is only then that silica can combine with calcium hydroxide (liberated by the hydrating Portland Cement) in the presence of water to form stable calcium silicates which have cementitious properties. Addition of pozzolans to the Portland cement may range from 3% to over 35%. The addition of pozzolan gives Portland cement certain properties that are of practical importance; such as increased chemical stability; which hence provides greater durability to concrete, less amount of heat liberated during hydration resulting in a reduction in permeability in concrete. The assessment of the pozzolans is based on both chemical and physical requirements which are classified into three types: N, F and C, according to the ASTM Standard C 618-01.

Sampling and sample preparation

To carry out the research, samples were taken from the regions of Caimanes (Farallones), Sagua de Tánamo (El Picao), San Andrés and Guaramanao (San Andrés). These are made up of tuffs consisting largely of volcanic glass and zeolite as a product of alteration of these rocks. The amount of material used in each case was determined based on the Cuban Standard (NC 178 2002).

Methods used during the investigation

The analysis and experiments were carried out using methods of granulometric characterization by dry and wet sieving conforming to the American Society for Testing and Materials (ASTM) Standard C 897–00 and the wet analysis was corroborated by a particle size analyzer HORIBA LA –910. The mechanical strength was determined according to ASTM C-31 1 "*Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for use as a Mineral Admixture in Portland-Cement Concrete*". Chemical testing was carried out by Inductively Coupled Plasma (ICP) and X-ray fluorescence. The characterization techniques and methods used were applied to certified circuits and equipment in order to allow reliable results to be obtained.

Mortar preparation

The mix was prepared using a mixer. Six mixtures of mortars with sand from the Jobo´s plant located in Sagua de Tánamo were prepared for the vitreous tuffs from Sagua de Tánamo and zeolitized tuffs from Caimanes, as well as six mixtures of mortar with sand from the "Doscientos Mil" mill located in Holguin for the Guaramanao´s vitreous tuffs and San Andrés zeolitized tuffs in each case. Also, six standard mortar mixes (with no tuff addition) were prepared, three mixtures for each type of sand, using Portland cement (P350) and water based on normal consistency test and 15% percent replacement of cement with tuffaceous material, in weight. The dosage for each one of the cases can be observed in Table 4 of the attachments. Normal consistency was determined for dosage of tuffaceous material taking into account the type of sample (vitreous and zeolitized tuffs) in compliance with the Cuban Standard NC 54-207:1980. In all cases, 3:1 sand-cement ratio was used, while changing water-cement-tuff ratios based on the test results of normal consistency of each material.

Equipment used during the Investigation

Jaw crushers TQ (320 x 165 mm) and TQ (150 x 75 mm) are included among the key pieces of equipment used. These machines were used to reduce the size of the studied samples, with the help of mechanical crackers. Particle size analysis was carried out using dry sieving for sand based on the mesh scales (9,52; 4,76; 2,36; 1,18; 0,59 and 0,15 mm) and wet sieving for tuff based on (0,09; 0,075, 0,053 and 0,045 mm) and for this a mechanical vibrator was used and a EUROPE digital scale for weighing samples. A mixer and a compactor were used for the preparation of mortars. A hydraulic press was used to conduct flexotraction resistance and compression resistance test works. Other equipment used during the investigation includes: stove, digital camera, etc.

Analysis and discussion of results

This chapter presents and describes the analysis and discussions with regard to the test works conducted and comparing them to other previous investigations on natural pozzolans as well as the suitability of using vitreous and zeolitized tuffs in construction as natural pozzolans.

Results of granulometric analysis of tuffaceous material

Vitreous and zeolitized tuffs were characterized from the granulometric point of view and the results are shown in Figure 1. it could be observed that the vitreous tuffs are the thickest, d80 of the material sieved is within mesh diameter of 0,070 mm and the mean particle diameter is 0,045 mm, followed by the zeolitized tuffs from Caimanes and the vitreous tuffs from Sagua de Tánamo with d80 of the material sieved within a mesh diameter of 0.051 mm and particle mean diameters of 0.041 and 0.033 mm; respectively. While the zeolitized tuff from San Andrés is thinner, d80 of the material sieved is 0.050 mm and a particle mean diameter of 0.042 mm; which demonstrates the behavior of these materials is very similar. These characteristics provide these materials with what it takes to be used as pozzolanic additions to the cement.

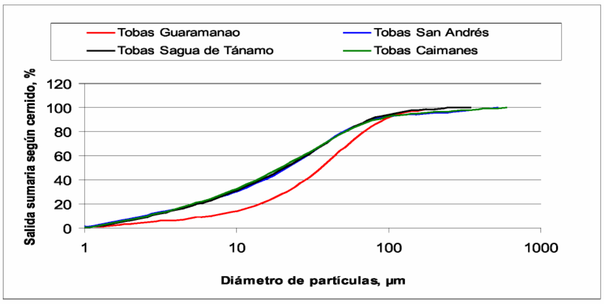

Figure 1. Size characteristics of vitreous and zeolitized tuffs.

Results of chemical characterization of vitreous and zeolitized tuffs

The tuffaceous material from the Sagua de Tánamo ore body is characterized for being vitreous-clastic and vitreous-crystal-clastic, grayish white in color, with particle size ranging from fine to medium, generally abrasive to the touch, porous, acid with a high content of SiO_2 (60,84 %) and over 50% content of volcanic glass. On the other hand, the Guaramanao tuff deposits consist of vitreous clastic tuffs of acid composition (67,6 % SiO_2), with volcanic glass content above 87 %, which represents the useful rock or ore body. These tuffs generally contain 11,10% of montmorillonite on the average; as demonstrated by the montmorillonite content, they have low degrees of alteration to clay minerals.

The zeolitized tuffs in the Caimanes ore body are mainly composed of zeolites of Clinoptilolite-Heulandite type, with calcium and potassium content ranging from approximately 80 to 85%, containing quartz in the shape of chalcedony and up to 14% montmorillonite; while iron oxide does not constitute a mineralogical phase due to its low content. It contains an amorphous uncrystallized volcanic glass. On the other hand, the San Andrés ore body is characterized by the presence of zeolitized tuffs with Heulandite and Clinoptilonite types being predominant, with zeolite content of more than 60 up to 85%. Lithologically, useful raw materials are present in vitreous clastic and vitreous crystal clastic tuffs; which are light green or green in color.

Table 1 Average chemical composition of vitreous and zeolitized tufos

Composición química, %	MnO	FeO	K_2O	MgO	Na_2O	Fe_2O_3	CaO	$CaCO_3$	Al_2O_3	SiO_2	PPI
Sagua de Tánamo	-	0,48	1,4	2,56	2,68	3,82	4,5	5,02	14,22	60,8	12,1
Guaramanao	0,08	0,5	2,2	1,11	2,6	2,35	2,7	2,78	12,44	67,6	8,1
Caimanes	1,25	0,58	0,91	4,79	1,28	2,57	0,58	2,95	12,38	62,27	13,17
San Andrés	-	0,87	1,2	1,38	2,05	2,24	3,51	-	11,33	64,5	11,98

The results shown in Table 1 have demonstrated that the overall content of silica, aluminum and iron oxides in the tested materials exceeds minimum values, which are to be 70% minimum and with a smaller amount of alkaline and terrous alkaline components. The amorphous structure of these materials is attributable to the presence of volcanic crystal; hence increasing their pozzolanic activity. In this sense, the Guaramao and San Andrés tuffs have certain qualities that make them more suitable for use as natural pozzolanic additives.

Flexotraction resistance test results

In figure 2 it is observed that at 7 and 28 days the flexotraction resistance of tuffaceous materials is below average and increases at 28 days. The materials showing a better behavior are the Guaramanao vireous tuffs and San Andrés zeolitized tuffs.

However, this does not mean that Sagua de Tánamo vitreous tuffs and Caimanes zeolitized tuffs do not have a positive behavior, which is reflected on the % increase in resistance at 28 days. Based on previous works consulted and past experience, these materials have had good results during resistance tests.

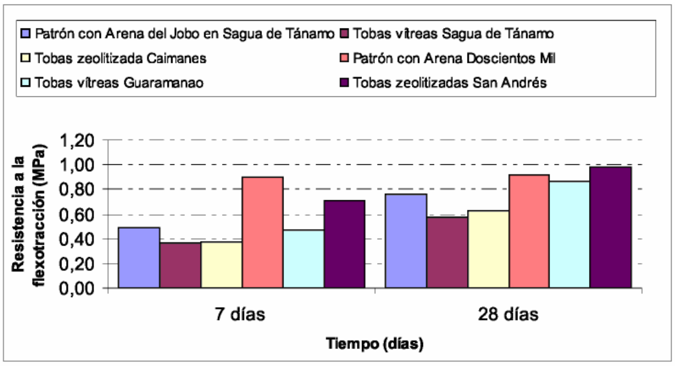

Figure 2. Resistance to the flexotraction of the patron mortars and with 15% of tufas.

It can be observed a similar increase at 7 and 28 days except for zeolitized tuffs where a more perceptible growth is noticeable despite having the highest resistance values in each case. The results obtained at 28 days show a tendency to have a flexotraction strength with different doses of tuffs (pozzolans) close to that of a standard mix: this is even higher for San Andrés tuffs. In all the cases, the strength is prone to increase above average; which indicates the pozzolanic activity of the tested tuffaceous materials.

Compressive strength test results

As shown in figure 3, the materials from San Andrés and Guaramana yielded the best results; which can be attributable to their granulometric and chemical characteristics, being fine materials with a high content of silica, aluminum and iron oxides (SiO_2, Al_2O_3 and Fe_2O_3) and their high content of amorphous material. Based on the resultd, it is recommended to use these materials as natural pozzolans.

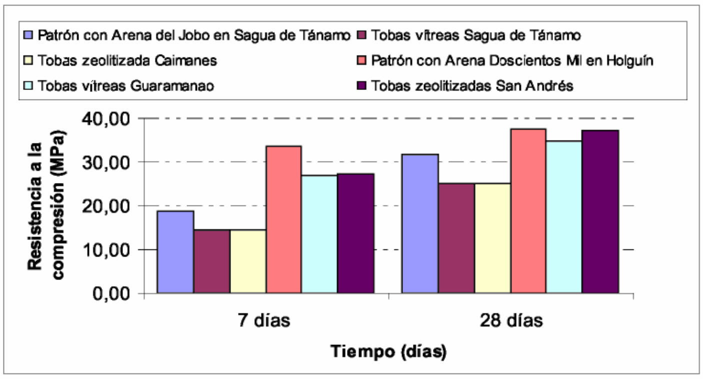

Figure 3. Resistance to the compression of the patron mortars and with 15% of tufas.

Compliance with the requirements for use of materials as natural pozzolans

The resistance to compression at day 28 is generally used as a key parameter to select the type of mortar as it is relatively easy to measure and is commonly related to other properties, such as adherence and absorption of the mortar. According to the results obtained from the compressive strength test shown in figures 9 and 10 when comparing them with the type of mortar used in masonry; which must have a compressive resistance of 12,4 Mpa at day 28 for a sand–cement ratio of 3:1 (ratio used during the investigation) in accordance to the Cuban Standard (NC 175: 2002). It can be stated that adding 15% vitreous and zeolitized tuffs results in higher resistance values in all the cases, which proves the suitability of the materials tested in this investigation. In addition, it is proven their potential to be used as natural pozzolans in accordance with the standards for use of these materials to this end.

Table 2. Standardized requirements met by tested materials

Test	Requirements	Results			
		Tuffs	Tuffs	Tuffs	Tuffs
Pozzolanity index	At day 7	77%	78%	80%	81%
	At day 28	79%	79%	93%	99%
Chemical analysis	Silica, aluminun and iron oxides	78,88%	77,22%	82,41%	78,07%
	Loss on ignition, max	11,2	13,17%	8,10%	11,98%

Conclusions

All the tested materials conform to the requirements established for material used as a natural pozzolan.

The mortars with 15% vitreous and zeolitized tuffs have greater strengths than the masonry mortar (NC 175: 2002), which demonstrates that the materials tested in this investigation are suitable for use in the construction materials industry.

The flexotraction and compressive strengths of the mortars prepared with tuffaceous material increase in 7 to 28 days compared to that of standard mortars. This demonstrates their pozzolanic activity accentuated for zeolitized tuffs, San Andrés and vitreous tuff, Guaramanao.

Recommendations

Determining the Bond index for the Sagua de Tánamo vitreous tuffs and Caimanes zeolitized tuffs to propose a technology to exploit these materials.

Investigate the implementation of a technology to exploit vitreous and zeolitized tuffs in order to contribute to savings on cement by eliminating shortages of construction materials in addition to the local development.

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