Estudio de dos materiales volcánicos y efecto del tipo de molienda en su reactividad

Study of two volcanic materials and the grinding effect on the reactivity of these materials

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Resumen

En este estudio se presenta la caracterización y evaluación de la actividad puzolánica de dos materiales volcánicos procedentes de dos depósitos volcánicos Colombianos (Volcán Puracé y Nevado del Tolima). Estos materiales fueron analizados mediante diversas técnicas de caracterización, la aptitud de los materiales volcánicos como puzolanas y el efecto de la molienda en su reactividad, se evaluó por medio del Índice de Actividad Puzolánica (IAP), ensayo de Frattini. Los resultados indican que el MVP presenta un IAP de 77,51% y se ubica en la zona reactiva de la curva de Frattini, características que permiten clasificar este material como una puzolana natural. En cuanto al MVT los resultados indicaron que químicamente no reaccionó, pero generó un índice de resistencia de 92,36% respecto a la muestra patrón, características de un material inerte que por efecto filler permite el desarrollo de resistencias mecánicas. Por otra parte, también se evidenció que no existe un efecto significativo del proceso de molienda en la reactividad de estos materiales.

Palabras claves: Puzolanas naturales, materiales volcánicos, actividad puzolánica, efecto de molienda

Abstract

This study presents the results of characterization and evaluation of pozzolanic activity of two Colombian volcanic materials from different sources (Puracé volcano and the snowy of Tolima). These materials were analyzed by scanning electron microscope, X-ray fluorescence, X-ray powder diffraction, thermal analysis, and petrographic study, among others. The ability of volcanic materials as pozzolans and the grinding effect were evaluated by pozzolanic activity index, Frattini's test and calorimetry test. The results of this research showed that the Puracé volcanic material has physical and chemical characteristics to be considered as natural pozzolan; while the Tolima volcanic material does not react chemically, but this material generates an increase in the mortars strength due to the filler effect. On the other hand, there are not differences of the grinding process on the reactivity of the volcanic materials.

Keywords: Natural pozzolans, volcanic materials, pozzolanic activity, grinding effect

1. Introduction

Over the years, the search of alternative materials to be used as cement replacement has been developed finding economical, technological and ecological alternatives for the construction industry. As example we may point out the natural pozzolans of volcanic origin, which are originated by magma explosive eruptions, which easily get cold thus turning into a micro-porous glass, mainly containing SiO_2 , Al_2O_3 y Fe_2O_3 (Massazza, 1993) When adding such materials to the cement paste, they react with the $\text{Ca}(\text{OH})_2$ released during its hydration process forming calcium silicates (H-C-S) of stable, hydraulic and non-soluble phases (Rosell-Lam, Villar-Cociña, & Frías, 2011), thus providing different benefits from different points of view, such as mechanical, durability and reduction of heat release in cementitious elements (Alp et al., 2009; J. L. Costafreda, Calvo, & Parra, 2011; Hossain & Lachemi, 2007, 2010; Hossain, 2005, 2006; Kaid, Cyr, Julien, & Khelafi, 2009; Ramezaniapour, Samadian, & Mahdikhani, 2012; Siad, Mesbah, Kamali, Khelafi, & Moulli, 2010). However, there are several factors determining the potential of these volcanic materials to react and form cementitious composites; among them the chemical composition, mineralogical composition, the particles physical structure and the surface area of such materials.

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These factors vary in accordance to their nature and origin; that is why the evaluation and comparison between different sources becomes so difficult (Valdez et al., 2004). Calvo et al., (2005) studied pozzolanic properties of volcanic materials, in Spain. They found that although the chemical composition of these materials was suitable to classify them as pozzolans, some of them did not show high reactivity with the calcium hydroxide. Therefore, they were classified as low quality pozzolans. On the other hand, Vargas et al. (2005) investigated the pozzolanic activity of tuffs in Guadalajara. They found that these materials showed high pozzolanic activity, which was proven by the production of tobermorite gel, which is a phase that increases with curing time. Furthermore, they found that when increasing grinding level, the reaction with hydrated lime increased. Therefore the mechanical strength and durability also increased.

Çavdar & Yetgin (2007) studied the pozzolanic activity of volcanic materials in Turkey. They found that the pozzolanic activity is directly related to the SiO_2 component, while components such as Al_2O_3 , Fe_2O_3 , MgO and K_2O decreased this activity. Türkmenoğlu & Tankut (2002) reported that although pozzolanic activity of volcanic materials is mainly affected by SiO_2 and Al_2O_3 , the presence of secondary minerals in the amorphous phase, such as caolinite and zeolites also influenced the material reactivity. The ability of such materials to act as natural pozzolans has led to several research studies in areas where there are huge amounts of volcanic deposits, and where the pozzolan production is quite limited. For example, Ozgunler & Ozgunler (2011) used a composite binder, with volcanic tuffs from Turkey and hydrate lime, for mortars fabrication to restore historical structures, thus obtaining a mortar of adequate strengths made of materials available in the area. By considering above and the fact that there are many active volcanoes in Colombia, which have generated huge sources of volcanic materials throughout the times, this research job proposes the assessment and evaluation of Colombian volcanic materials, such as natural pozzolans in the production of cementitious materials.

2. Experimental methodology

2.1 Materials and Methods

For the experimental development of this study, samples were taken from two volcanic material sources, which are located in the Cauca and Tolima departments, specifically Puracé Volcano and Tolima snow-capped volcano. Once the samples were collected, such materials were subjected to a modification process. They were grinded by using a balls mill during two hours and later they were grinded using an attrition mill during 15 minutes, thus obtaining two average particle sizes for each volcanic material **21 and 17.2 μm** for Puracé Volcanic Material (PVM) and **20.2 and 12.3 μm** for Tolima Volcanic Material (TVM). The two particle sizes were employed to evaluate the grinding effect on the volcanic materials reactivity.

2.1.1 Characterization methods of volcanic materials

The characterization consisted in analyzing the grinding capacity of both volcanic materials. Consequently, samples were taken every 30 minutes, during the whole grinding process. Afterwards, the average particle size was determined by using the laser particle size analysis. When grinding processes were completed, size and distribution of particles were determined by means of the same laser technique. Besides, the specific density of volcanic materials was determined by means of the regulation NTC 221. A scanning electron microscope SEM was also employed to observe particles morphology. The fire-loss per ignition percentage was determined by following the regulation NTC 184. A scanning electron microscope was also employed to observe particles morphology. The chemical and mineralogical composition was determined by means of x-ray fluorescence XRF, x-ray powder diffraction XRD and petrographic study on the thin sections and, finally, a thermal-gravimetric analysis was performed on volcanic materials.

2.1.2 Evaluation methods of pozzolanic activity on volcanic materials

- **Mechanical Method:** A random design was performed using a 2x2 Factorial Structure (two factors with two levels each). The first factor was the volcanic material type and its levels are Puracé (PVM) and Tolima (TVM). The second factor was the grinding process and its levels were grinding by balls mills for 2 hours (Balls 2h) and grinding by balls mill for 2 hours + grinding by attrition mill for 15 minutes (Balls 2h + Attrition). The response variable of design experiments was the pozzolanic activity index (PAI), which was determined in accordance with ASTM C311. The experimental units corresponded to mortars specimens in cylindrical shape, of 25.4 x 50.8 (x10⁻³) m. For the elaboration of these mortars standardized Ottawa sand was employed, as well as non-blended Portland cement type III, and 20% percentage of constant addition of volcanic material (Puracé and Tolima) as mass cement replacement. Although this value is recommended by the regulation ASTM C311, we shall take into account that this percentage might not be the optimal volcanic material addition percentage (providing the best strengths). Therefore, the PAI will only serve as a benchmark on the reactivity of materials studied. So as to reach the optimal percentage, we suggest developing mechanical tests with different addition percentages. The ratio water/cement was 0.5 for mortars with TVM, and 0.55 for mortars with PVM (ratios in accordance with requirements of each volcanic material and keeping the same fluidity). Table 1 shows the design treatment (4 treatments and 2 repetitions for each one). Such combinations were originated from each value factor, which were randomly run by using the software MINITAB 16.
- **Chemical method:** The Frattini's test was employed at 28 curing days following the regulation NTC 1512.

Tabla 2. Tratamientos propuestos por el diseño para la selección del Material Volcánico

Table 2. Treatments proposed by design for the selection of Volcanic Material

OrdenEst/ Est. Order	OrdenCorrida/ Run order	PtType	Bloques/ Blocks	Tipo de Material volcánico/ Volcanic Material type	Proceso de molienda/ Grinding process
7	1	1	1	Puracé	Bolas 2h/ Balls 2hrs.
1	2	1	1	Tolima	Bolas 2h/ Balls 2hrs.
8	3	1	1	Puracé	Bolas 2h +Atrición/ Balls 2hrs.+Attrition
5	4	1	1	Tolima	Bolas 2h/ Balls 2hrs.
6	5	1	1	Tolima	Bolas 2h Atrición/ Balls 2hrs. Attrition
3	6	1	1	Puracé	Bolas 2h/ Balls 2hrs.
2	7	1	1	Tolima	Bolas 2h Atrición/ Balls 2hrs. Attrition
4	8	1	1	Puracé	Bolas 2h Atrición/ Balls 2hrs. Attrition

2.1.3 Calorimetric study on cement pastes with 20% addition of volcanic materials

The evolution of heat release speed was performed in accordance with ASTM C1679, by using a paste conductive calorimeter. Basis temperature for measurements was fixed at 25 °C. Recordings were completed during the first 24 hours of the hydration process.

3. Results and discussion

3.1 Physical characteristics of volcanic materials

3.1.1 Grinding ability and grain size ability

Figure 1 shows the grinding ability of volcanic materials. The graph depicts that PVM tends to reduce its size at shorter grinding time. Although PVM begins with a greater particle size (57.6 μm), compared to TVM (34.5 μm) this can be clearly observed after 90 minutes of grinding by the balls mill, as PVM reaches the average particle size of TVM. This might be translated into a cheaper transformation process when comparing the incorporation of both materials in cement elaboration.

On the other hand, when comparing the grinding process performed by balls mill 2 hours to the balls mill 2 hours + attrition, Figure 2 shows that the distribution of particle sized obtained by both processes were similar. Therefore, there are no significant differences between the grinding processes. However, the attrition process is the one involving more energy and it was expected to significantly increase the fine aggregates fraction. This result allows us to deduce that volcanic materials reached their limit particle size with the grinding process balls 2h, which suggests that from an economical point of view it would be unnecessary to consider a longer grinding time or involving a higher energy process without considering the future mechanical strength behavior.

Figura 1. Aptitud de molienda de los materiales volcánicos
Figure 1. Grinding ability of volcanic materials

Figura 2. Curvas de distribución granulométrica de los materiales volcánicos sometidos a los dos procesos de molienda
(Bolas 2h y Bolas 2h+Atricion)

Figure 2. Grain size distribution curves of volcanic materials subjected to both grinding processes (Balls 2h and Balls 2 h + Attrition)

3.1.2 Particles morphology

Figure 3 shows the micro-images of volcanic materials subjected to different grinding processes. The micro-images (a) and (b) show Puracé and Tolima volcanic materials obtained from balls mill grinding process in 2 hrs. Images show some particles of irregular morphology produced by grinding effect. Besides, there is a great amount of lower particles sizes, thus confirming the results obtained by laser grain particle size study. On the other hand, micro-images (c) and (d) show the volcanic materials additionally subjected to a grinding process, performed by an attrition mill during 15 minutes, indicating that there are no significant morphological changes in comparison to the previous samples. However, some small particles tend to agglomerate over the higher size particles. This factor can alter the materials strength resistances.

Figura 3. Microfotografías MEB de los materiales volcánicos de Puracé y Tolima a un aumento de 1000X
Figure 3. SEM micro-images of Puracé and Tolima's volcanic materials at 1000X magnification

3.2 Chemical and mineralogical characterization

3.2.1 Chemical composition

Table 2 shows the chemical analysis of volcanic materials and non-added Portland cement. The analysis shows that the addition of composites SiO_2 , Al_2O_3 and Fe_2O_3 for TVM and PVM exceeds the 70% established by the ASTM C618-12 regulation for natural origin pozzolans. It is worthwhile mentioning that this regulation does not specify the structure nor the morphology these composites should have (Çavdar & Yetgin, 2007). The PVM is of acid nature, since its SiO_2 content is higher than 65% and, the TVM is of an intermediate nature, since its SiO_2 content ranges from 55% to 65%. Consequently, both materials are able to achieve great similarity due to water lime content in water at room temperature (Valdez et al., 2004). However, other factors shall be taken into consideration so as to guarantee their reactivity, such as the materials' grain size and mineralogical composition. As far as the fire-loss in both materials is concerned (8.35% for PVM and 0.4% for TVM), it is understood they are within the limit established by the same regulation for natural pozzolans ($\approx 10\%$). Differences between these two values are basically produced because PVM fire-loss comprises elemental sulfur and other volatile elements

Tabla 2. Composición química de los materiales volcánicos por medio de la técnica de FRX

Table 2. Chemical composition of volcanic materials by means of XRF technique

	SiO_2	S	Fe_2O_3	TiO_2	Al_2O_3	Ba	CaO	Na_2O	MgO	P_2O_5	K ₂ O	Zr	Cr	Cu	Sr	Pérdida por Ignición
MVT/TVM	64,36	0,00	4,92	0,54	15,9	0,08	4,71	5,38	1,80	0,17	1,49	0,01	0,00	0,00	0,09	0,40
MVP/PVM	87,45	0,04	1,89	1,16	0,23	0,13	0,07	0,05	0,05	0,03	0,02	0,02	0,01	0,01	0,00	8,35
Cemento Portland/Portland Cement	21,70	1,02	4,39	0,31	5,44	0,00	63,99	0,31	1,52	0,18	0,30	0,14	0,00	0,00	0,14	0,60

3.2.2 Mineralogical composition

Figure 4A shows the micro-images obtained from thin sections of PVM, which evidence that this material is mainly composed of amorphous volcanic vitreous phase and some opaque crystals dispersed on the vitreous matrix. Regarding the micro-images obtained from the thin sections of TVM (Figure 4B), they evidence that this material is composed of dispersed phenocrysts of tubular plagioclases and subhedral quartz of small size, floating on a hypo-crystalline amorphous vitreous matrix, where small plagioclase crystals are dispersed showing no preferred orientation. These results support the analysis developed on volcanic materials grinding ability, as they confirm that TVM is mainly crystalline, which justify that this material decreased its particle size along grinding period compared with PVM that has a vitreous matrix in accordance with the petrography analysis.

Figura 4. Secciones delgadas de los materiales volcánicos. A. Puracé y B. Tolima
Figure 4. Thin sections of volcanic materials. A. Puracé and B. Tolima

Figure 5. The TVM diffraction pattern supports the petrography analysis results demonstrating this is predominantly a crystalline material, mainly composed of Albite with max peak intensity $2\theta \approx 28,059$ and lower intensity peaks corresponding to Anorthite and Andesine, which are plagioclase minerals. Furthermore, it also has minerals such as Zeolite, Quartz, Corderite and Diopside. On the other hand, the PVM diffraction pattern showed a higher intensity peak corresponding to Alpha Cristobalite with a diffraction angle equal to 21.9361° ; this phase crystallizes at high temperatures and faster than quartz (Prado et al., 2007). Some lower peaks can be observed corresponding to Albite, Zeolite and Sulfur S8. The presence of the latter material is explained by the PVM origin, which comes from a hydrothermal flow circulation area rich in sulfur

Figura 5. Patrones de difracción de rayos X de los materiales volcánicos del Puracé y Tolima
Figure 5. X-ray diffraction patterns of Puracé and Tolima volcanic materials

Table 3 shows the actual densities of volcanic materials. They demonstrate that TVM has a lower density than PVM; this behavior is mainly explained by the minerals available in each material. As shown in the TVM mineralogical analysis, this material is composed by plagioclases, which is a group that generally shows high porosity thus having low density. Albite density is 2.65 g/cm^3 and Anortite 2.76 g/cm^3 (Delgado, 2006).

Tabla 3. Densidades reales de los Materiales Volcánicos de Puracé y Tolima
Table 3. Actual densities of Puracé and Tolima Volcanic Materials

	MVT	MVP
Densidad Real (g/cm^3)	2,09	2,18

The results obtained for mineralogical composition indicate that TVM is produced by non-explosive volcanic eruptions gradually getting cold resulting into a predominantly crystalline structure. This factor may affect the reactivity of this material towards the lime stone (Siddique, 2008) when compared to natural pozzolans produced by volcanic eruptions, as the case of PVM, which petrographic analysis showed it has a vitreous matrix with some small crystals. However, some researchers such as Çavdar & Yetgin (2007) state that crystalline minerals or semi-crystalline minerals, such as quartz and cristobalite, might collaborate in the pozzolanic activity.

Above is supported by Valdez et al. (2004), who stated that crystalline phases, partially disorganized or under a meta-stability condition, show some kind of pozzolanic activity, such is the case of cristobalite. However, cristobalite reactivity depends on dissolving ions contained in its atoms structure, because such ions create a structural stability for the material.

3.3 Thermal Analysis

Figure 6 presents the thermal gravimetric analysis results, developed on the PVM and TVM, in the presence of oxygen. Figure 6 a) corresponds to MPV, where the curve TG (weight loss in regards to temperature) shows a huge weight loss (8.89%w) within a temperature range from 25 to 1000°C, where two slope changes take place. In the first slope shown by the curve (range 25-150 °C with weight loss of 0.84%w) two processes take place, which can be clearly observed in the DSC curve (temperature difference). Such curve shows that from 70 to 112°C, peaks of endothermic nature take place, which correspond to the material dehydration reaction and the transformation phase of sulfur contained by PVM, which turns from rhombic into monoclinic form (αS_8 - βS_8). According to literature the rhombic sulfur is the steadiest condition at low temperature and it is transformed into monoclinic sulfur at a temperature close to 95.5°C. The transformation rhombic $\leftrightarrow$ monoclinic form consists in the change of the crystalline structure without modifying the molecular structure (Ríos, 1984). In the second slope change shown by TGA curve between 150 and 420 °C the greatest weight loss takes place (7.12%w) and in accordance with DSC curve (fuchsia line) it corresponds to an exothermal reaction, at a maximum temperature of 242.6 °C, due to a combustion process that oxidizes sulfur, thus producing sulfur dioxide (SO_2) and sulfur trioxide (SO_3).

Figure 6 b) corresponding to TMV we observe a small TGA curve slope within a temperature range from 25 to 300°C, which is mainly attributed to TVM's dehydration (approximated weight loss 0.70%w). Normally, this material does not undergo huge transformations when faced to temperature increases, in comparison to PVM, since its chemical composition does not include elements to be affected by volatile transformations.

Figura 6. Resultados del análisis térmico diferencial. a) Material volcánico Puracé (MVP); b) Material volcánico del Tolima
Figure 6. Results from differential thermal analysis a) Puracé's volcanic material; b) Tolima's volcanic material

3.4 Pozzolanic Activity Assessment

3.4.1 Frantini's Chemical Method

Frantini's chemical method represents the maximum calcium hydroxide amount allowed by a pozzolan combination. This reaction depends on different factors, such as the nature and ratio of pozzolanic material active phases and its specific surface, as well as the lime-pozzolan ratio and the reaction temperature. Samples located under the saturation curve are likely to react with calcium hydroxide Ca(OH)_2 . However, this method does not indicate the material ability to develop mechanical resistances, or to decrease hydration heat, among other characteristics to be developed by a pozzolanic material (Guzmán, Gutiérrez, Amigó, Mejía de Gutiérrez, & Delvasto, 2011). From results obtained by TVM and PVM, subjected to different grinding processes (Figure 7); it can be generally observed that PVM has a greater ability to generate pozzolanic reactions. Since at 28 days, it is located under the saturation curve independently on the grinding process it was subjected to. Such behavior can be attributed to the higher amount of amorphous phase contained by PVM compared to the TVM.

On the other hand, in the same graph (Figure 7) it can be observed that the grinding process involving higher energy consumption (Balls 2hrs + Attrition) does not have a significant effect on the volcanic materials reactivity. Such behavior is contrary to the one expected, since the method involving high energy consumption was expected to deliver higher specific surface and, consequently, higher materials reactivity. This behavior may be attributed to the agglomeration of small size particles over the big size particles (observed on the SEM micro-images), thus affecting the reactivity on both materials.

Figura 7. Curva de saturación del método Frattini para los materiales volcánicos sometidos a diferentes procesos de molienda a 28 días de ensayo
Figure 7. Saturation curve in Frattini's method for volcanic materials subjected to different grinding processes, at 28 days

3.4.2 Mechanical Method

Figure 8 shows pozzolanic activity indexes, at 28 curing days, for mortars with 20% addition of two volcanic materials subjected to different grinding processes. These results were analyzed by the software MINITAB 16, as the validation of the design assumptions was accurate. This analysis enabled us to deduce that there is no interaction between factors (volcanic material type and grinding process) with an importance level of 20%; for this reason the effect of factors on the API shall be examined independently. Figure 8 shows that for the grinding process Balls 2 h, both materials, TVM and PVM, exceeded the limit established by the regulation ASTM C618 ($API > 75\%$ to consider a material as pozzolanic addition). Therefore, if we only consider this limit, then both materials will be considered as natural pozzolans from a mechanical point of view, with an importance level of 30.9%. However, API is clearly affected by the grinding process Balls 2h + Attrition, with an importance level of 2.1%, since it decreased in 30% app for the TVM and in 15% for the PVM. Consequently, both materials did not reach the established API. This behavior may be attributed to the agglomeration of great amount of small size particles over the big size particles. This phenomenon was observed by SEM micro-images from both materials, thus affecting the material reactivity, as well as particles dispersion and distribution in the cementitious matrix. Therefore, it is concluded that the most effective grinding process is Balls 2h.

On the other hand, it is necessary to complement and compare the two methods to evaluate the reactivity of both materials, in order to reach a concluding analysis for both materials behavior, by only employing the grinding process balls 2 h. We shall take into account that the mechanical method demonstrated that TVM showed an API higher than PVM. However, the results obtained by the chemical method (Frattini) demonstrated that TVM is located in the non-reactive area (non-pozzolanic), while PVM is located in the reactive zone (pozzolanic). Such difference between the two evaluation methods for pozzolanic ability enables us to deduce that TVM might be acting as an inert addition, that in spite of not having pozzolanic activity and not chemically reacting with cement hydration products, it could be working as a catalyzer in the hydration process. TVM particles would serve as a nucleation center for the growth of hydration products, thus contributing to develop mechanical properties on cementitious materials. Poppe & Schutter (2005) evaluated the effect an inert addition has and demonstrated that Portland cement hydration reactions were clearly influenced by the incorporation of such addition, based on calorimetric results that showed increases of induction periods and new and pronounced hydration peaks. Other explanation for the differences of mechanical strengths on mortars with additions of TVM and PVM could be related to the water/cement ratios employed, which were selected in accordance with water requirements of each volcanic material. In the case of TVM the ratio was 0.5 and 0.55 for PVM. The rise of water amount could have increased material porosity and also could have affected the mechanical performance of mortar with PVM addition

Figura 8. Gráfico de interacción de efectos principales (diseño de experimentos)
Figure 8. Main interaction effects graph (Experiments Design)

3.5 Calorimetric study for pastes with 20% addition of volcanic material

Figure 9 presents calorimetric curves for the pattern cement paste and the ones having TVM and PVM additions and subjected to different grinding processes. The test period was established in 24 hours; therefore, this analysis shows the effect during the first reaction hours. The calorimetric curve in the pattern specimen shows the first stage at 15 minutes, where there is a great heat release, caused by the initial hydrolysis and the reaction of cement phase C_3A with water. As from this phase the precipitation of first hydration products take place (CH, ettringite and CSH). Hydrolysis continues decreasing without stopping until showing the first minimum point of the curve, at 30 minutes. This is attributed to the fact that hydration products make up a layer on the non-hydrated binder grains thus delaying their hydration evolution, in this case during two hours approximately (dormant period). By the end of this period, the layers of the first hydration products break up leading to the process progress. After completing two hours, acceleration stage takes place, where there is a second peak at 8 hours of reaction and more products start to crystallize and progressively they fill the spaces between cement grains and create contact points that harden the paste. This is the beginning of cement paste setting process. As time goes by, reactions decrease once again thus producing the second minimum and later the speed increases thus producing the third peak at 12 hours of reaction. This is where the superposition of the formation period of CSH gel and the transformation period of phase AFT to AFM takes place. By increasing time, there is a greater amount of hydration products and the contact points are also increased. They finally limit the paste mobility and final setting is achieved, thus commencing the hardening period, where the paste improves its resistance and the reactions are decelerated (ASTM C1679).

Since volcanic materials were added at the same cement replacement percentage (20%), we can prove the effect of each material on the hydration heat compared to the benchmark Portland cement. Therefore, when analyzing the first stretch of the curve where the first heat release takes place (C_3A hydration available in cement), it is observed that TVM (no matter the grinding process) registered a decreased of speed for the evolution of hydration heat. Such decrease was expected due to the reduction of C_3A amount produced by the weight replacement of cement by volcanic materials. Contrarily, the PVM addition produced a higher evolution speed. This behavior could be attributed to the origin of PVM, which is an area of hydrothermal flow circulation rich in sulfur; therefore it could be polluted with some traces of sulfuric acid that contacting the mixing water releases a great amount of heat. Other explanation for the presence of sulfuric acid in the PVM, according to Hossain & Lachemi (2007), could be that volcanic eruptions also contain water vapor, carbon dioxide (CO_2), sulfur dioxide (SO_2), hydrochloric acid (HCL) among others,

when they are dissolved with water; they form acid rain in the case of HCL. In the case of SO_2 it would be slowly turned into sulfuric acid (H_2SO_4). On the other hand, in the dormant period great changes were not observed when adding volcanic materials. However, in the acceleration stage, we observe that there is a delay in hydration reactions and setting times in PVM curves compared to the pattern curve, thus finding that setting time increased in app 2 hours for the PVM sample with Balls 2h and, approximately 4 hours for the PVM sample Balls + Attrition, proving our statements that reactions are slower when employing a grinding process that involves higher amount of energy. As far as the TVM curve is concerned, it shows a behavior quite similar to the pattern sample, without registering significant changes for setting time. This behavior is explained because PVM acts as a pozzolan; therefore, it requires longer time to react, while the TVM produced acceleration in hydration reactions. This demonstrates that this material is not completely an inert material, but it also participates in hydration reactions by acting as a heterogeneous nucleation center promoting the development of hydration products (Poppe & De Shutter, 2005). These results support our findings on the pozzolanic activity index; the TVM promoted hydration reactions and had a great influence on the mechanical properties of added mortars, as previously demonstrated.

Finally, Table 5 shows the total heat amount developed by the samples, during the first 24 hydration hours. The results obtained prove that when hydration reactions are delayed due to the PVM effect, bigger curves are generated for the time analysis, which is translated into a greater amount of total hydration heat in comparison with TVM. Meanwhile, the TVM decreased the total hydration heat in 16.31% regarding the total heat of the pattern sample. This behavior can be useful when selecting a material for the elaboration of cement with low hydration heat and adequate mechanical strength (Sánchez de Rojas & Rivera, 2010). As far as grinding processes are concerned, significant changes were not observed in regards to total hydration heat reported for both processes.

Figura 9. Curvas calorimétricas de pastas de cemento adicionadas con materiales volcánicos sometidos a diferentes procesos de molienda
Figure 9. Calorimetric curves for cement pastes with volcanic material additions, subjected to different grinding processes

Tabla 4. Calor total de hidratación liberado por las pastas de cemento adicionadas con los materiales volcánicos a 24 horas de reacción
Table 4. Total hydration heat released by cement pastes with addition of volcanic materials, at 24 hours of reaction

Material Volcánico	Calor Total de Hidratación (J/g)
Patrón	179,53
MVT Bolas 2h	145,83
MVT Bolas 2h + Atrición	154,64
MVP Bolas 2h	175,03
MVP Bolas 2h + Atrición	170,75

4. Conclusions

The results from this research job demonstrated that PVM showed adequate physical and chemical characteristics to be considered as natural pozzolan, since it was located in the pozzolanic curve in Frattini's test and it exceeded the PAI established by the regulation ASTM C311. Meanwhile, the TVM acted as an inert addition, not showing reactivity (according to Frattini's test), but it had the best mechanical behavior with a PAI of approximately 92%. This behavior is attributed to the filler effect produced by the best allocation and distribution of its particles in the cementious matrix.

Such particles may also work as nucleation centers for the development of hydration products by accelerating the hydration process of pastes with TVM additions, as demonstrated by the calorimetric test. This test also demonstrated that PVM, which is a natural pozzolan, tends to delay the hydration process for added pastes proved by their setting times.

As far as the grinding type effect on the materials reactivity is concerned, significant changes were not observed when implementing a higher energy grinding process (balls 2 hrs + attrition). On the contrary, the pozzolanic activity index decreased the performance of both volcanic materials in comparison with the results obtained from the grinding process Balls 2 h. This behavior was attributed to a potential agglomeration of small size particles over the bigger size ones, which might have hidden the performance of both materials. For this reason, it was concluded that the most adequate grinding process for both materials is Balls 2h, which achieved the best results for both materials.

5. Referencias/References

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