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Pore characterization of volcanic tuffs used as building stone in Afyonkarahisar (Turkey)

Afyonkarahisar'da yapıtaşı olarak kullanılan volkanik tüflerin gözenek özellikleri

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Pore Characterization of Volcanic Tuffs Used as Building Stone in Afyonkarahisar (Turkey)

Araştırma Makalesi / Research Article

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ABSTRACT

The tuffs have been used as a building material for hundreds of years. The physical and mechanical properties of tuffs are affected by the amount of pore and its geometry. The pore characteristics of the building natural stone of Seydiler and Ayazini (Afyonkarahisar-Turkey) tuffs were investigated in this article. For determination of the mineralogical and petrographical properties of the tuff; a polarizing optical microscope, X-ray diffractometry and scanning electron microscope (SEM) were used. Tuffs are composed of a mineral assemblage of various crystals including quartz, feldspar; mafic mineral is biotite and rock particles with glass cement. SEM images show the presence of numerous voids in tuffs. The mean value of effective porosity of the Ayazini and Seydiler tuffs was 37.3% and 36.0%. Mercury porosimetry was used to determine the pore size distribution. Ayazini tuffs have pore sizes ranging from about 200.000 to 10 nm and Seydiler tuffs ranging from about 7.000 to 10 nm.

Keywords: Tuff, porosity, pore-size distribution, mercury porosimetry, building stone.

Afyonkarahisar'da Yapıtaşı Olarak Kullanılan Volkanik Tüflerin Gözenek Özellikleri

ÖZ

Tüfler yüzlerce yıldır yapı malzemesi olarak kullanılmaktadır. Tüflerin fiziksel ve mekanik özellikleri, gözenek miktarı ve geometric özelliklerinden etkilenmektedir. Bu makalede, doğal yapı taşı olarak kullanılan Seydiler ve Ayazini (Afyonkarahisar-Türkiye) tüflerinin gözenek özellikleri araştırılmıştır. Tüflerin mineralojik ve petrografik özelliklerinin belirlenmesi için; polarize optik mikroskop, XRD analizi ve taramalı elektron mikroskobu (SEM) kullanılmıştır. Tüfler kuvars, feldispat kristallerinin yanı sıra; mafik mineral olarak biyotit ve kayaç parçacıkları içermektedir. SEM görüntüleri, tüflerde çok sayıda boşluk bulunduğunu göstermektedir. Ayazini ve Seydiler tüflerinde gözenek liliğin ortalama değeri % 37.3 ve % 36.0'dır. Gözenek boyut dağılımını belirlemek için cıva porozimetresi kullanılmıştır. Gözenek boyutları, Ayazini tüflerinde yaklaşık 200.000 - 10 nm ve Seydiler tüflerinde yaklaşık 7.000 - 10 nm arasında değişmektedir.

Anahtar Kelimeler: Tüf, gözeneklilik, gözenek boyut dağılımı, civa porozimetresi, yapı taşı.

1. INTRODUCTION

Tuff is a type of rock consisting of consolidated volcanic ash ejected from vents during a volcanic eruption. Tuff rocks can be used at construction sector and in landscape architecture. Tuff stones used in masonry are welded tuffs and the masonry walls made of tuff stone is more durable than concrete and brick walls. After application on building, tuff stones have been sticked together firmly each day due to their consolidation characteristic. Tuff stones were used densely in many buildings constructed in Ottoman and Seljuk Turks era in central Anatolia [1].

Great part of the Afyon region is covered by volcanic tuff so it is easy to carve out stones to build temples and monument. There are many open-air temples, monuments, natural rock formation, fairy chimneys and rock-cut churches. It is known to be used as a settlement since the Phyrigian period. The village of Ayazini has many cave settlements, also an early Christian church and tombs dating from antiquity and the Byzantine period which is carved in the volcanic tuff stone (Fig 1). The churches have been well preserved despite all atmospheric effects which may damage to the tuff constructed. Ayazini tuffs have been traditionally used as a building material in many areas in local building construction in the region since prehistorical times. Most of the major building stone quarries working today are located in the Ayazini region.

The most of the historical buildings such as mosques and fountains in Afyon (Turkey) were made of tuffs by Ottoman civilizations. This tuff rock was produced in the stone quarries nearby Ayazini, Afyon. The parts of the many fountains and mosques were constructed of Ayazini tuffs which are carved easily due to being moister inside the tuffs. After the vaporization of the moister they became hardened. However, due to having very high ratio of porosity in tuffs, which is the reason of the high-water absorption feature, it's weathered very easily.

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In the Afyon – İscehisar – Bayat – Kırka –Şuhut areas, potassic and ultrapotassic alkaline magmatism followed Upper Eocene - Middle Miocene calc-alkaline volcanism, which was related to the northward subduction of the African Plate beneath Eurasia. The alkaline volcanism lasted from 14.8 Ma (in the north) to 4 Ma (in the south) and was associated with a presently still active extensional tectonic regime [2, 3]. Around the Kırka-Afyon region, a thick sequence of acid tuff interlayered with subordinate calc-alkaline lava flows

A considerable amount of work has been done by Metin et al [6], Kavas and Çelik [7], Kuşçu and Yıldız [8], Demir et al [9] studied the geology, industrial, physical and engineering properties aspects of Ayazini tuffs in Afyonkarahisar region.

Tuff stone is very porous in nature so its density, uniaxial compressive strength and P-wave velocity is lower than other rocks. Porosity is one of the important physical properties that govern physical attributes of rocks such as



Fig 1. Ancient civilizations carved great caves and underground cities out of the soft volcanic rock (a). One great example the Oyma Church made of tuffs by the Early Christians in Ayazini (Afyon, Turkey) (b).

and breccia crops out. It is covered by a continental sedimentary succession containing subordinate tuffs. The tuff sequence yielded K/Ar ages between 21 ± 0.4 Ma and 15.4 ± 1.7 Ma [4] and is overlain by basic K-alkaline lavas. The tuffs in the north of Afyon cover an area of about 2000 km² (Fig 2). They overlie a marked relief in Paleozoic schist and marbles. They are laterally intercalated with Neogene lacustrine sediments. Their stratigraphic position is Pliocene. The tuff unit has a maximum thickness of 300 m and consists of a basalt main flow unit of about 200 m and 2-3 following minor flow units [5].



Fig 2. Map of the Ayazini and Seydiler rhyolitic tuff in the region of Afyon-Turkey [5]

strength, deformability and hydraulic conductivity [10]. Effective porosity does not necessarily reflect the durability of the tufts, and water absorption is a better indicator. However, the sensitivity of the tuff to weathering can be approximately estimated by analyzing pore-size distribution; focusing on the presence of small capillary pores or micro pores [11].

Weathering processes cause progressive changes in rock porosity due to alterations in pore size distribution, pore geometry, pore connectivity, pore infilling and new pore formation. Interactions between mechanical, lithological and pore properties of rocks, and the nature of the weathering processes affecting them, create a complex system [10]. Several investigators have studied weathering of tuffs [11, 12, 13, 14, 15, 16, 17] also they show that rock fabric characteristics, especially pore geometry, affecting rock susceptibility to weathering.

Various investigators have studied the effect of weathering on the engineering properties of tuffs [18,19, 20, 21, 22] many investigators have studied the effect of porosity and weathering on the engineering properties of different types of rock [23, 24, 25, 26, 27, 28] several investigators have reported pore size and its distribution of the rocks [29, 30].

Mercury intrusion characterizes a material's porosity, its pore size and pore volume. The test instrument typically uses a non-wetting fluid with a high surface tension, such as mercury, to characterize the material's porosity. Since the mercury porosimetry study of Ritter and Drake [31], it has been widely used in industry. Its applications have varied from the study of pore structure and fluid distributions by Pickell et al [32], studied by Klavetter and Peters [33] regarding hydrologic properties of volcanic tuff [34]. Many investigators have reported pore size and its distribution with using mercury intrusion of the rocks [34, 35, 36, 37, 38, 39, 40, 41] they also describe general concepts of mercury porosimetry measurements and determination pore size distribution and its characterization. Vacchiano et al, [42] measured the pore-size distribution by mercury porosimetry of yellow and grey tuff stones of the historic buildings in Salerno (Italy). Their purpose was treating yellow and grey tuff stones with different polymeric materials. Scanning electron microscope (SEM) and image processing technologies provide new scopes for researching the internal structure of rocks, soils and concrete [43, 44, 45, 46, 47, 48, 49].

2. MATERIAL and METHOD

The physical and mechanical properties of tuffs are affected by the amount of pore and its geometry. The pore characteristics of the building natural stone of Seydiler and Ayazini (Afyonkarahisar) tuffs were investigated in this article. Samples from the tuff quarries of Ayazini and Seydiler region were analyzed by using several analytical techniques. For determination of the mineralogical and petrographic analyses of the tuff, a polarizing optical Method of the high pressure porosimetry is based on phenomenon of the mercury capillary depression, where the wettability angle is $>90^{\circ}$ and mercury leaks into pores by the effect of pressure. Mercury volume infiltrated into a pore system (Fig 3) is generally interpreted as total pore volume in measured specimen. Relationship between actual pressure p and cylinder pore radius D is expressed by Washburn equation (1):

$$p = -4 \gamma \cos\theta/D \tag{1}$$

where p [Pa] is an actual pressure, D [nm] half-length distance of two opposite walls of a pore expressed by an effective radius, γ surface tension of mercury [480.10⁻³ N·m⁻¹] and θ contact angle of mercury [141.3°] [39].

3. EXPERIMENTAL INVESTIGATION and RESULTS

3.1. Mineralogical and Petrographic Analysis

Mineralogical and petrographic properties of the Ayazini and Seydiler tuffs were studied using a polarizing optical microscope, X-ray diffractometry (XRD), and scanning electron microscope (SEM).

3.1.1. Polarizing optical microscope analyses

Standard thin sections were prepared for mineralogical and petrographic descriptions. For determination of the



Fig 3. Schematic representation of pores [50]

microscope and scanning electron microscope (SEM -LEO 1430 VP in TUAM Laboratory in Afyon Kocatepe University) were used. During the preparation of samples, each sample was covered by a thin carbon film. In this study, mercury porosimetry was employed for the determination of porosity and pore-size distribution. Mercury porosimetry relies on capillary theory and the non-wetting property of mercury to determine porosity, pore-size distribution and pore surface area by forcing mercury into matrix samples under pressure. A "Quantachrome Corporation Poremaster 60" in the Central Laboratory of Middle East Technical University (Ankara-Turkey) was used for the mercury intrusion porosimetry measurements with the test conditions of a surface tension mercury-vacuum of 480.00 erg/cm² and a contact angle mercury-tuff of 140°.

mineralogical composition of the tuffs, a polarizing optical microscope was used. The Ayazini tuff contains crystals of quartz, feldspar, biotite and opaque minerals (Fig 4). Various rock fragments and pumice are also present. The crystals, rock fragments and pumice are embedded in a tuffaceous matrix. In the tuffaceous matrix, volcanic glass shards are rather common. The optic-microscope data of these tuffs that are examined petrographically, also conform with XRD data. The Seydiler tuff is composed of a mineral assemblage of various crystals including quartz, feldspar; mafic mineral is biotite and rock particles with glass cement (Fig 5). Physical weathering causes fracturing of feldspars, especially along their cleavage planes, within the both tuffs.



Fig 4. Thin section photomicrographs of Ayazini tuffs illustrating various pyroclasts (F) feldspar, (Q) quartz, (B) biotite, various size of pore and (P) pumice grain. Photomicrographs of 4a, b, and c taken with crossed nicols, 4d with plane polarized light



Fig 5. Photomicrographs of Seydiler tuff, feldspar (F), quartz (Q) and hornblende (H) minerals settled in glassy matrix, various size of pore and (P) pumice grain. Photomicrographs of 4a, c, and d taken with crossed nicols, 4b with plane polarized light

3.1.2. XRD analyses

X-ray diffraction analysis was performed on Ayazini and Seydiler tuff samples in order to determine the mineralogical nature of their crystalline phases. XRD analyses of the Ayazini tuff reveal that feldspar, quartz, cristobalite and illite (mica) are present within the tuff. XRD analyses for the Ayazini tuff indicated illite (mica)type clay minerals. A typical XRD pattern for an Ayazini tuff samples are depicted in Fig. 6a. The Seydiler tuff samples are composed of feldspar, quartz, hornblende and illite (mica) (Fig. 6b). Cristobalite is present only in Ayazini tuff samples and is the dominant silica phase. In addition to these minerals, an important component of amorphous materials (volcanic glass) constitutes the both tuffs. Erguler [16] have indicated that volcanic glass is

3.1.3. SEM analyses

Photomicrographs of the minerals and texture identified using the SEM is shown in Fig 7 and 8. Presences of feldspar, quartz are smectite are detected in the Ayazini tuffs. The Seydiler tuffs are composed of feldspar, quartz, smectite and illite. It was determined that flaky morphology smectite is the main clay mineral in both tuffs. In general, smectite develops in fissures, fractures and dissolution voids of the volcanic glass. Alteration of feldspars results in formation of smectites. Formation of smectite is closely related to hydrolysis of volcanic glass and alteration of feldspar. In all tuff samples, smectite develops on and along the edges of feldspar as well as volcanic glass.



Fig 6. X-ray diffraction (XRD) diffractogram of Ayazini (a) and Seydiler (b) tuff samples. The figures show also the assignation of peaks to the main minerals identified in the analyzed tuffs samples

the least stable component of tuffs and decomposes more readily than the other associated minerals phases. Overall evaluations of the findings show that chemical weathering produces a small amount of clay minerals, namely illite within the Ayazini and Seydiler tuffs. Summarizing, the characterization performed on the samples of Ayazini and Seydiler tuff collected in different quarries show that the stones have a similar composition to that of the original materials.

3.2. Pore-Size Distribution of Tuffs

3.2.1. The influence of porosity and its importance

Total porosity is the ratio of the total void volume to the total bulk volume. Porosity ratios traditionally are multiplied by 100 and expressed as a percent. Total porosity can be classified as primary or secondary. Primary porosity is the porosity that forms when the tuff is deposited, whereas secondary porosity is formed after the tuff was deposited. Secondary porosity includes



Fig 7. SEM images of Ayazini tuff, SEM images show the presence of numerous dissolution voids (P), quartz (Q) and feldspar (plagioclase) (F) minerals in Ayazini tuffs. Platy and honeycomb textured smectite (S) developing around on the feldspar minerals

cavities produced by the solutioning of some minerals and by fractures.

micropores, materials with pores between 2 and 50 nm are called mesopores, and material with pores greater



Fig 8. Scanning electron micrograph of tuff sample from Seydiler, the SEM image shows smectite (S) developing around on the feldspar (F) minerals and illite (I) minerals in Seydiler tuffs

Several methods have been developed for determining the surface area and the pore size distribution in porous systems. The operations of these different methods are generally based on different physical principles. It should be expected, therefore, that they effectively represent probes of different sizes and, hence, that the pore size ranges in which they are most reliable are necessarily different. Figure 9 compares the ranges of validity of a selection of methods commonly used for pore characterization [51].

Porous material is classified according to the size of pores: material with pores less than 2 nm are called

than 50 nm are macrospores [52]

Solid particles from crushing or grinding operations and weathering or leaching processes often will be found to have cracks, cavities, and holes (collectively called pores) within their structure. As well as many natural stone especially tuffs pore structure influence the physical properties of building stone, including porosity, unit weight, absorption water by weight, ultrasonic pulse velocity, strength, and failure behavior. Some physical and mechanical test results of the Ayazini and Seydiler tuffs are given in Table 1.



Fig 9. Measuring ranges of methods for pore size determination [51]

| Tests | Ayazini Tuff | | | Seydiler Tuff | | |
|---|--------------|-------|-------|---------------|-------|-------|
| | Min | Max | Av. | Min | Max | Av. |
| Dry unit weight (kN m ⁻³) | 1.81 | 1.88 | 1.85 | 1.66 | 1.80 | 1.74 |
| Density | 2.39 | 2.44 | 2.42 | 2.27 | 2.31 | 2.29 |
| Absorption by weight (%) | 16.73 | 17.18 | 16.93 | 17.93 | 19.56 | 18.51 |
| Absorption by volume (%) | 26.59 | 27.42 | 27.00 | 23.68 | 25.24 | 24.21 |
| Porosity (%) | 34.30 | 39.50 | 37.30 | 33.60 | 38.70 | 36.00 |
| Uniaxial compressive strength (MPa) | 21.61 | 23.68 | 22.21 | 17.14 | 20.76 | 19.07 |
| Flexural strength (MPa) | 1.28 | 1.50 | 1.37 | 0.99 | 1.12 | 1.07 |
| Dry ultrasonic pulse velocity (km s ⁻¹) | 1885 | 2168 | 1990 | 2505 | 2848 | 2675 |

Table 1. Average physical and mechanical properties of tuffs rocks [53]

Mercury porosimetry is probably the most commonly indirect technique used to characterize the pore space allowing to calculate the total connected porosity and its pore size distribution. But mercury porosimetry only measures pores access and real pore size was usually misestimated. Determination of the total open porosity used to helium pycnometers method. The mean value of effective porosity of the Ayazini and Seydiler tuffs was 37.3% and 36.0%. A "Quantachrome Corporation Poremaster 60" mercury porosimetry was used to determine the pore size distribution. Incremental intrusion volumes are used to predict the pore-size distribution range from atmospheric pressure to 200 MPa.

3.2.2. Pore-size distribution of Ayazini tuffs

The pore size distribution study was carried out with mercury intrusion porosimetry (MIP) testing. The cumulative intruded pore volume curves for Ayazini tuffs, obtained from MIP, are provided in Fig 10. Ayazini tuffs have pore sizes ranging from about 10 nm (0,010 μ m) to 20.000 nm (20 μ m) (Fig 11). Fig. 12 illustrates the results of pore-size distributions, as relative cumulative volume. Thus, the size of pores varies widely from nanometer to micrometer. Mercury porosimetry results show that most of the pores (>80%) have a pore access diameter of between 200.000 and 10 nm, mega pores reaching up to 200.000 nm in diameter were also observed.



Fig 10. Mercury intrusion porosimetry of tuff from Ayazini tuff, plots report pore-size distributions, as relative pore volume



Fig 11. Mercury intrusion porosimetry of tuff from Ayazini tuff, since the size of pores varies widely from 10 nm (0,010 μm) to 20.000 nm (20 μm)



Fig 12. The cumulative intruded pore volume curves obtained from MIP for Ayazini tuff

3.2.3. Pore-size distribution of Seydiler tuffs

Mercury intrusion porosimetry of tuff from Seydiler, plots report pore-size distributions, as relative pore volume is provided in Fig 13. Seydiler tuffs have pore sizes ranging from about 10 nm (0,010 μ m) to 4.000 nm (4 μ m) (Fig 14). Fig. 15 illustrates the results of pore-size distributions, as relative cumulative volume. Since the size of pores varies widely from nanometer to micrometer. Mercury porosimetry results show that most of the pores (>80%) have a pore access diameter of between 3.000 and 10 nm, mega pores reaching up to 10.000 nm in diameter were also observed. Seydiler tuffs have a smaller porosity compared to that of the Ayazini tuffs.



Fig 13. Mercury intrusion porosimetry of tuff from Seydiler tuff, plots report pore-size distributions, as relative pore volume



Fig 14. Mercury intrusion porosimetry of tuff from Seydiler tuff, since the size of pores varies widely from 10 nm (0,010 μm) to 4.000 nm (4 μm)



Fig 15. The cumulative intruded pore volume curves obtained from MIP for Seydiler tuff

4. PORE CHARACTERIZATION OF TUFFS

The accuracy of pore diameter measurements by mercury porosimetry when the pores are right circular cylinders is exceptionally good, agreeing to at least 0.008 µm openings. However, true circular cross-section pores or pores of any regular geometry are rarely encountered in real materials. On the contrary, shapes of typical pores are slits, cracks, fissures, or highly irregular interstitial voids between particles. In order for the mathematics of pore characterization to be manageable, it is convenient to treat the filling of these complex pores as if they were right circular cylinders. This means that pore data from mercury porosimetry should be understood and used as equivalent cylindrical dimensions, just as the particle size determined by sedimentation of nonspherical particles is an equivalent spherical diameter. How pore shape alters basic pressure-volume curves is illustrated in Figure 16a. Figure 16b shows a typical intrusion/extrusion curve (volume vs. pressure curve) of a porous glass with a hysteresis loop that is typical for cylindrical pores [51, 54].

Cylindrical pores are observed for microporous solids having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites, and certain porous oxides). The limiting uptake is governed by the accessible micropore volume rather than by the internal surface area. Fig. 17 shows volume vs. pressure curve of Ayazini tuffs (a) and Seydiler tuffs (b). The mercury porosimetry analysis of Ayazini and Seydiler tuffs are observation the pore geometry as cylindrical holes in Fig 16a.

SEM images of Ayazini tuffs show the presence of numerous pores. SEM image of the slightly collapsed pumice fragments showing irregular vesicle shapes from pipes to pods. Slot pores comprise a honeycomb like structure, bounding the surfaces of flanking grains. Micro channels exhibit elongated shapes; in general, the walls of the micro channels appear to be irregular (Fig 18).



Fig. 16. Characteristic hysteresis loops for cylindrical holes and for pores formed within aggregates (a), intrusion/extrusion curve (volume vs. pressure curve) of a porous glass (b) [51]

Spherical shapes are associated with platy minerals (clays). This pore type has different sizes which are distributed within the Seydiler tuff sample (Fig 19). Pores are present mainly in volcanic glass matrix, which makes up the intergranular cement of the tuff rock.

and opaque minerals. Seydiler tuff is composed of a mineral assemblage of various crystals including quartz, feldspar; mafic mineral is biotite and rock particles with glass cement. The optic-microscope data of these tuffs that are examined petrographically, also conform with



Fig 18. SEM photo-micrograph of Ayazini tuffs is showing irregular pore shapes and flaky form. (scale (a): 10 microns, (b): 1 microns). This kind of welded tuffs with pores tuff (ignimbrite) is called



Fig 19. SEM photo-micrograph of Seydiler tuffs showing volcanic glass porosity (a), SEM image of the slightly collapsed pumice fragments showing irregular vesicle shapes from pipes to pods (b), (scale 10 microns)

5. CONCLUSIONS

Physical properties such as porosity and water absorption are good indicators of mechanical and weathering behavior of tuff rocks. Natural materials pore structure influence the physical and mechanical properties of building stone, including elastic module, compressibility, thermal conductivity, poroelastic parameters, strength, and failure behavior. Both of Ayazini and Seydiler tuffs are highly porous. The Ayazini and Seydiler tuffs the mean value of effective porosity was 37.3% and 36.0%. The pore-size distribution was measured by means of a mercury porosimetry on all the specimens examined. Mercury porosimetry is a very widely accepted method for determining total volume and pore size distribution in the mesopore and macropore ranges.

For determination of the mineralogical composition of the tuffs, a polarizing optical microscope was used. Ayazini tuff contains crystals of quartz, feldspar, biotite XRD data. XRD analyses of the Ayazini tuff reveal that feldspar, quartz, cristobalite and illite (mica) are present within the tuff. XRD analyses for the Ayazini tuff indicated illite (mica)-type clay minerals.

Seydiler tuff samples are composed of feldspar, quartz, hornblende and illite (mica). Cristobalite is present only in Ayazini tuff samples and is the dominant silica phase. Chemical weathering produces a small amount of clay minerals findings namely illite within the Ayazini and Seydiler tuffs.

Photomicrographs of the minerals and texture are identified using the SEM images. In all tuff samples, smectite develops on and along the edges of feldspar as well as volcanic glass.

Several methods have been developed for determining the surface area and the pore size distribution in porous systems. Mercury porosimetry is probably the most commonly indirect technique used to characterize the pore space allowing calculating the total connected porosity and its pore size distribution. The pore size distribution study was carried out with mercury intrusion porosimetry (MIP) testing. Fig. 20 shows pore volume (%) versus pore radius of tested tuff stone. Ayazini tuffs have pore sizes ranging from about 10 nm (0,010 μ m) to 20.000 nm (20 μ m). Mercury porosimetry results show that most of the pores (>80%) have a pore access diameter of between 200.000 and 10 nm (Fig. 20). Seydiler tuffs have pore sizes ranging from about 10 nm (0,010 μ m) to 4.000 nm. Mercury porosimetry results show that most of the pores (>80%) have a pore access diameter of between 3.000 and 10 nm (Fig. 20). Seydiler tuffs have a smaller porosity compared to that of the Ayazini tuffs.

The mercury porosimetry analysis of Ayazini and Seydiler tuffs are the observation of the pore geometry as cylindrical holes. SEM images of Ayazini tuffs show the presence of numerous pores. SEM image of the slightly collapsed pumice fragments show irregular vesicle shapes from pipes to pods. Slot pores comprise a honeycomb like structure, bounding the surfaces of flanking grains.

- [7] Kavas T. and Çelik M.Y., "Usability of the Ayazini (Afyon) tuffs as trass material for cement production", *Madencilik*, 40(2-3):39-46. (in Turkish), (2001).
- [8] Kuşçu M. and Yıldız A., "Usability of the Ayazini (Afyon) tuffs as building stone", *Turkey III. Marble Symposium* Afyon, 85-98, (in Turkish), (2001).
- [9] Demir İ., Başpınar M.S. and Görhan G., "Mechanical properties of the natural construction stone of Ayazini Tuffs-Afyonkarahisar", *MERSEM'2006 Turkey V. Marble and Natural Stone Symposium*, 31-38. (in Turkish), (2006).
- [10] Tuğrul A., "The effect of weathering on pore geometry and compressive strength of selected rock types from Turkey", *Eng Geol*, 75:215-227, (2004).
- [11] Torok A., Forgo L.Z., Vogt T., Lobens S., Siegesmund S. and Weiss, T. "The influence of lithology and pore-size distribution on the durability of acid volcanic tuffs, Hungary", *Spec Publ Geol Soc Lond*, 271:251-260, (2007).
- [12] Topal T. and Doyuran V. "Analyses of deterioration of the Cappadocian tuff, Turkey", *Environ Geol*, 34(1):5-20, (1998).
- [13] Topal T. and Sözmen B. "Deterioration mechanisms of tuffs in Midas Monument", *Eng Geol*, 68:201-223,



Fig 20. Pore volume (%) versus pore radius of Ayazini and Seydiler tuff stone

REFERENCES

- Yasar E., Tolgay A. and Teymen A., "Industrial usage of Nevsehir-Kayseri (Turkey) tuff stone", *World Appl Sci J*, 7(3):271-284, (2009).
- [2] Francalanci L., Innocenti F., Manetti P. and Savaşçın M.Y., "Neogene alkaline volcanism of the Afyon – Isparta area, Turkey: petrogenesis and geodynamic implications", *Miner Petrol*, 70:285-312, (2000).
- [3] Yıldırım D. and Altunkaynak Ş., Geochemistry of Neogene-Quaternary alkaline volcanism in western Anatolia, Turkey and implications for the Aegean mantle, *Int Geol Rev*, 52:579-607, (2010).
- [4] Besang C., Eckhardt F.J., Harre W., Kreuzer H. and Muller P. "Radiometricshe altersbestimmungen an Neogenen eruptivgesteinen der Turkei", *Geol Jb B*, 25:3-36, (1977)
- [5] Keller J. and Villari L., "Rhyolitic ignimbrites in the region of Afyon (Central Anatolia)", *Bull Volcan*, 36:342-358, (1972).
- [6] Metin S., Genç Ş. and Bulut V., "The geology of Afyon", MTA Report Nu: 8103, (not Published) (in Turkish), (1987).

(2003).

- [14] Chen T.C., Yeung M.R. and Mori N., "Effect of water saturation on deterioration of welded tuff due to freezethaw action", *Cold Reg Sci Technol*, 38:127–136, (2004).
- [15] Steindlberger E., "Volcanic tuffs from Hesse (Germany) and their weathering behavior", *Environ Geol*, 46:378-390, (2004).
- [16] Erguler Z.A., "Field-based experimental determination of the weathering rates of the Cappadocian tuffs", *Eng Geol*, 105:186-199, (2009).
- [17] Yavuz A.B., "Durability assessment of the Alaçatı tuff (Izmir) in western Turkey", *Environ Earth Sci*, 67:1909-1925, (2012).
- [18] Topal T. and Doyuran V., "Engineering geological properties and durability assessment of the Cappadocian tuff", *Eng Geol*, Vol.47(1-2):175-187, (1997).
- [19. Chigira M., Nakamoto M. and Nakata E., "Weathering mechanisms and their effects on the landsliding of ignimbrite subject to vapor-phase crystallization in the Shirakawa pyroclastic flow, Northern Japan", *Eng Geol*, 66:111-125, (2002).

- [20] Entwisle D.C., Hobbs P.R.N., Jones L.D., Gunn D. and Raines M.G., "The relationships between effective porosity, uniaxial compressive strength and sonic velocity of intact Borrowdale volcanic group core samples from Sellafield", *Geotech Geol Eng*, 23:793-809, (2005).
- [21] Emir E., Konuk A. and Daloğlu G., "Strength enhancement of Eskischir tuff ashlars in Turkey", *Constr Build Mater*, 25(7):3014-3019, (2011).
- [22] Pola A., Crosta G.B., Fusi N., Barberini V., Norini G. and Pola Villasenor A., "Influence of alteration on physical properties of volcanic rocks", *Tectonophysics*, 566– 567:67-86, (2012).
- [23] Palchik V., "Influence of porosity and elastic modulus on uniaxial compressive strength insoft brittle porous sandstones", *Rock Mech Rock Eng*, 32(4):303–309, (1999).
- [24] Vásárhelyi B., "Influence of the water saturation on the strength of volcanic tuffs", *ISRM International Symposium - EUROCK 2002*, November 25 - 27, 2002; Madeira, Portugal, (2002).
- [25] Palchik V. and Hatzor Y.H., "The influence of porosity on tensile and compressive strength of porous chalk", *Rock Mech Rock Eng*, 37(4):331–341, (2004).
- [26] Kahraman S., Gunaydin O. and Fener M., "The effect of porosity on the relation between uniaxial compressive strength and point load index", *Int J Rock Mech Min Sci*, 42(4):584-589, (2005).
- [27] Vasarhelyi B. and Van P., "Influence of Water Content on the Strength of Rock", *Eng Geol*, 84:70–74, (2006).
- [28] Ju Y., Yang Y.M., Song Z.D. and Xu WJ., "A statistical model for porous structure of rocks", *Sci China Ser E*, 51:11:2040-2058, (2008).
- [29] Nimmo J.R., "Porosity and pore size distribution". in: Hillel D, ed. *Encyclopedia of soils in the Environment*, London: Elsevier, 3:295-303, (2004).
- [30] Fakhimi A. and Alavi Gharahbagh E., "Discrete element analysis of the effect of pore size and pore distribution on the mechanical behavior of rock", *Int J Rock Mech Min Sci*, 48(1):77-85, (2011).
- [31] Ritter H.L. and Drake L.C., "Pore-size distribution in porous materials: pressure porosimeter and determinations of complete macropore-size distribution", *Ind Eng Chem Anal Ed*, 17:782, (1945).
- [32] Pickell J.J., Swanson B.F. and Hickman W.B., "Application of air mercury and oil-air capillary pressure data in the study of pore structure and fluid distribution", *Soc Petrol Eng, J*, 237:55-61, (1966).
- [33] Klavetter E.A. and Peters R.R., "An evaluation of the use of mercury porosimetry in calculating hydrologic properties of tuffs from Yucca Mountain, Nevada", *SAND86-0286, Sandia National Laboratories*, Albuquerque, NM, (1987).
- [34] Vogt G.T., "Porosity, pore-size distribution and pore surface area of Apache Leap Tuff near Superior, Arizona using mercury intrusion", Unpublished master's thesis, *Department of Hydrology and Water Resources, University of Arizona*, Tucson, 130 p. (1988).
- [35] Nwaubani S.O., Mulheron M., Tilly G.P. and Schwamborn B., "Pore-structure and water transport properties of surface-treated building stones", *Mater Struct*, 33:198-206, (2000).

- [36] Roels S., Elsen J., Carmeliet J. and Hens H., "Characterisation of pore structure by combining mercury porosimetry and micrography", *Mater Struct*, 34(2):76-82, (2001).
- [37] Schoelkopf J., Gane P.A.C., Ridgway C.J. and Matthews G.P., "Practical observation of deviation from Lucas-Washburn scaling in porous media", *Colloid Surface Physicochem Eng Aspect*, 206:445-454, (2002).
- [38] Yang C.C. and Chiang C.T., "On the relationship between pore structure and charge passed from RCPT in mineralfree cement-based materials", *Mater Chem Phys*, 93(1):202-207, (2005).
- [39] Šperl J. and Trčková J., "Permeability and porosity of rocks and their relationship based on laboratory testing", *Acta Geodyn Geomater*, 5(149):41-47, (2008).
- [40] Angeli M., Benavente D., Bigas J.P., Menéndez B., Hébert R. and David C., "Modification of the porous network by salt crystallization in experimentally weathered sedimentary stones", *Mater Struct*, 41(6):1091–1108, (2008).
- [41] García-Del-Cura M.A., Benavente D., Martínez-Martínez J. and Cueto N., "Sedimentary structures and physical properties in travertine and carbonate tufa building stone", *Constr Build Mater*, 28:456-467, (2012).
- [42] Vacchiano C.D., Incarnato L., Scarfato P., Acierno D., "Conservation of tuff-stone with polymeric resins", *Constr Build Mater*, 22(5):855-865, (2008).
- [43] Anselmetti F.S., Luthi S. and Eberli G.P., "Quantitative characterization of carbonate pore systems by digital image analysis", *AAPG Bulletin*, 82(10):1815–1836, (1991).
- [44] Abell A.B., Willis K.L. and Lange D.A., "Mercury Intrusion porosimetry and image analysis of cementbased materials", *J Colloid Interf Sci*, 211:39-44, (1999).
- [45] Atzeni C., Sanna U. and Spanu N., "Some mechanisms of microstructure weakening in high-porous calcareous stones", *Mater Struct*, 39:525–531, (2006).
- [46] Lu S., Landis E.N. and Keane D.T., (2006) "X-ray microtomographic studies of pore structure and permeability in Portland cement concrete", *Mater Struct*, 39:611–620,
- [47] Loucks R.G., Reed R.M., Ruppel S.C. and Jarvie D.M., "Morphology, genesis and distribution of nanometerscale pores in siliceous mudstones of the Mississippian Barnett shale", *J Sediment Res*, 79:848-861, (2009).
- [48] De La Fuente S., Cuadros J., Fiore S. and Linares J., "Electron microscopy study of volcanic tuff alteration to illite-smectite under hydrothermal conditions", *Clays Clay Miner*, 48:339–50, (2000).
- [49] Liu C., Shi B., Zhou J. and Tang C., "Quantification and characterization of microporosity by image processing, geometric measurement and statistical methods: application on SEM images of clay materials", *Appl Clay Sci*, 54(1):97-106, (2011).
- [50] Giesche H., "Mercury porosimetry: A general (Practical) overview", *Part Syst Char*, 23:1-11, (2006).
- [51] Klobes P., Meyer K., Munro R.G., "Porosity and specific surface area measurements for solid materials", *NIST Recommended Practice Guided*, Special Publication, 960-17, (2006).

- [52] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A. and Rouquerol Jiemieniewska T., "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity", *Pure Appl Chem*, 57(4):603-619, (1985).
- [53] Ergül A., "Investigation of the effect on physicomechanic characteristics of the water content dependent upon porosity in the tuffs used as a building stone in

Afyonkarahisar", Master of Science Thesis, *Afyon Kocatepe University, Graduate School of Natural and Applied Science, Mining Engineering Department,* 117p. (Unpublished). (2009).

[54] Webb P.A. and Orr C., "Analytical methods in fine particle technology", *Micromeritics Instrument Corporation, Norcross*, 303 p. (1997).