Carpathian Journal of Earth and Environmental Sciences, February 2011, Vol. 6, No. 1, p. 147 - 158

USE OF ZEOLITIC TUFFS AS CEMENT ADDITIVES, BUILDING STONE AND REMOVAL OF HEAVY METAL CATIONS

Yahya ÖZPINAR[1]
[1]*Department of Geological Engineering, Pamukkale University, 20070 Kinikli Campus, Denizli, Turkey, E-mail: yozpinar@pau.edu.tr*

Abstract: The chabazitic and phillipsitic tuffs presented in this study are located in the south of Sandıklı (Afyon-west Anatolia). In this district there are important zeolitic resources. In petrographic investigations of tuffs, optical microscopy, SEM, and XRD methods were used for mineral analysis. Trachyte/ trachyandesitic tuffs contain chabazite and tephriphonolitic tuffs contain chabazite and phillipiste. According to the XRD results, chabazite occurs in the Ca-form; phillipsite is in the Na-K, K, and K,Ca-forms. Zeolite contents of tuffs (52.41-58.59 wt. %) were determined by using a heavy liquid method.
Physical and mechanical tests of tuffs for using as building stone have been done in accordance with the Turkish Standard (TS 699). Zeolitic tuffs according to rock classification based on porosity fall in to the "very porous rock" category, and according to rock classification based on uniaxial compressive strength fall in to the "very low strength rock" category. The removal performance of heavy metal ions (Cu^{2+}, Zn^{2+} and Ni^{2+}) in aqueous solution were investigated by adsorption process on chabazitic and phillipsitic tuffs. The selectivity sequence was determined as Cu > Zn > ≅ Ni for chabazitic tuffs, and as Cu > Ni > ≅ Zn for phillipsitic tuffs. The major chemical components of the trass, along with the flexural and compressive strengths of the pozzolana mortar, conform well to the requirements of both the ASTM and the Turkish Standard TS 25 (TS EN 196-1). The chemical, physical, and mechanical properties of the blended cement mortar prepared with 15% and 30% zeolitic tuff additive are in accordance with the Turkish Standard (TS EN 197-1), and according to the results of experiments they can be mixed in the OPC and used as blended cement.
These results show that zeolitic tuffs are used as blend materials and building stone, and to remove heavy metal ions from domestic wastewater because cation exchange properties provide economical and environmental advantages.

Key words: Zeolite, Cement, Building Stone, Heavy Metal and Environmental Advantage.

1. INTRODUCTION

A huge problem is increase of heavy metal concentrations in rivers, and the other problems are groundwater pollution and soil pollution (Coppola, et al., 2003) near highways in European Countries Zeolites are most important ion exchanger. Natural zeolites frequently display selectivity for heavy metal cations, which make them valuable tools for purifications of treatment of domestic wastewater (Pansini, 1996, Inglezakis, et al., 2001, Englert, et al., 2003). On the other hand, the peculiar features of zeolites as cation exchangers make these materials potentially very interesting from a technological point of view, especially in environmental protection (Mumpton, 1999, Gomonaj et al, 2001, Langelle, et al., 2003).

Cement was used binding material in Turkey with 52 million tons of annual production in 2009. The use of high energy in the production causes high emission due to the natures and processes of raw materials. The world cement industry is responsible for 7% of the total CO_2 emission. Thus, the cement industry has a crucial role in the global warming. The use of natural and artificial pozzolans as blend materials for cement has been constantly increasing in order to reduce energy consumption and CO_2 emission without causing any degradation to cement properties. Such factors as economical and environmental advantages (Mehta, 2002, Langelle, et al., 2003, Yılmaz, et al., 2007) as well as the reduction of alkali aggregate reactions and resistance against chemical media (Yılmaz, et al., 2007, Sersale,

1987) are effective in the consumption of pozzolan blended cements (Mertens et al., 2009).

At the historical periods, zeolitic tuffs have been used in a widespread manner in Anatolia and in European Union Countries. The churches, mosques and the other historic buildings, which have been built from tuff, have been still stood since Byzantine periods. Tuffs content rich zeolite control to the moisture content of building to create healthy living space. In addition, tuff has heat insulation due to high porosity of tuff, resulted from high zeolite content. If concrete is produced by using zeolitic tuff aggregates, their heat insulation quality increases (Özkahraman & Işık, 2003, Kılınçarslan, 2007, Çobanoğlu et al., 2003).

The purpose of this paper is to determine zeolite type and zeolite contents of tuffs, as well as their mineralogical, petrographical and petrochemical properties and investigate to the tecnologycal properties such as physical and mechanical properties, and the removal performance of cationic heavy metal species from domestic wastewater, their usage as building stone, use of zeolitic tuff blended cement, and also assessment the contributions being made from the point environmental risks reduction. In accordance with this aim this study provides new data as relationship with rich chabazite and phllipsite content tuffs belonging to studied area and it is thought that these new data may be avail to the science environment of European Union Countries, because of the chabazitic and phillipsitic tuffs are found largely in Italy, Spain, Germany (in Eifel district) and the other some European Union Countries.

The chabazitic and phillipsitic tuffs presented in this study are located in the south of Sandıklı (Afyon-west Anatolia) and were discovered by the author (Fig. 1).

2. GEOLOGIC SETTING

In this study, the dispersion of the volcanites around Sandıklı was determined, and the zeolitic tuffs were mapped. The basic geological properties of the area south of Sandıklı are given below (Fig. 1). "Karatepe Formation" represented by clastic deposits at the base of the studied area, dates from Upper Triassic to Lower Jurassic period. Above that formation, "Akdağ Formation" is represented by limestone, and it dates from Upper Jurassic to Lower Cretaceous period. Above Akdağ Formation, lacustrine clastic rocks dating from Middle to Upper Miocene period are observed and are characterized by angular unconformity.

The volcanic and volcano-sedimentary units from Middle to Upper Miocene and located in the study area are named as "Sandıklı Volcanites". K-Are ages of Sandıklı lavas were determined to be 14 ± 0.3 - 8.0 ± 0.6 million years (Ercan, 1986) (Fig. 1). "Sandıklı Volcanites" are characterized by with the presence of trachyte/trachyandesitic tephriphonolitic, basaltic andesitic, basaltic, compositions lavas, along with pyroclastic rocks. Pyroclastic rocks are composed of lapillistone, tuffaceous conglomerate tuffaceous sandstone, tuffaceous siltstone, and tuffaceous mudstone, which decrease in particle size from bottom to top. Pyroclastic rocks also contain tuffs. Tuffs have trachyte/trachyandesitic and tephriphonolitic compositions, which are named as vitric tuff and crystal vitric tuff. Trachyte/trachyandesitic tuffs contain chabazite and tephriphonolitic tuffs contain chabazite and phillipiste.

3. MATERIAL AND METHOD

3. 1. Sampling studies and determination of the mineralogical composition of the natural pozzolanas

Thin sections were prepared from the 98 lava and tuff samples collected from the study areas. The thin sections were examined with a Nikon "Alphaphot 2-YS2" polarisation microscope. Later, the X-Ray Diffraction (XRD) analyses were conducted with a Rigaku D-max 2200 instrument using a copper cathode tube. The maps were then revised according to the mineralogical compositions of the pozzolanas. Additionally, 12 tuff samples were re-examined for the zeolite minerals with a Geol JSM -6490LV scanning electron microscope.

3.2. Major element analyses

The major element oxide analysis of the samples for SiO_2, TiO_2, Al_2O_3, total Fe_2O_3, MgO, CaO, Na_2O, and K_2O were done using the wet chemical analysis method. Analyses for SO_3 and Cl were conducted at the Denizli Cement factory by using a spectrometer. The loss on ignition (LOI) was calculated after the samples were heated to 1000^0C for one hour. The chemical analyses of nine samples (the trass samples) were completed in the study. The samples were grouped according to their lithologies, and the mean values were obtained.

3.3. Physical and mechanical tests of tuffs

Zeolitic tuffs from nine locations were grouped according to their lithologies such as chaba zitic tuff, chabazitic & phillipsitic tuff and phillipisitic tuff and each group consists of seven samples.

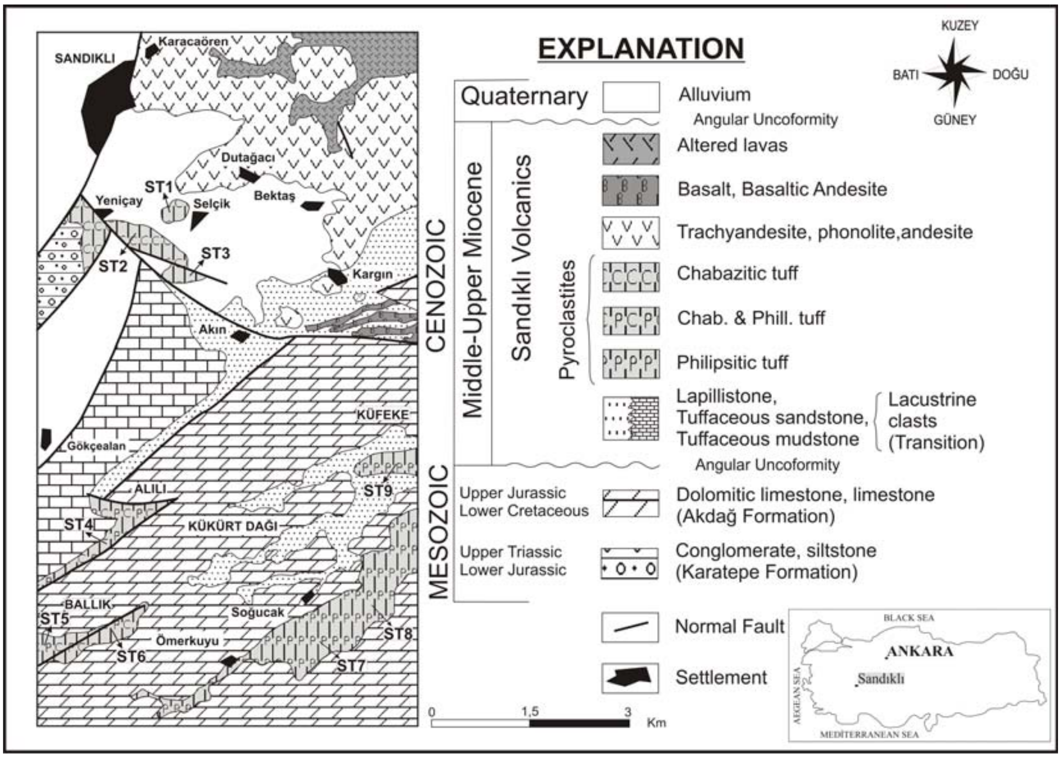

Figure 1. The geological map of the Sandıklı volcanites

The physical and mechanical properties (unit weight, specific gravity, absorption by weight and by volume, porosity and uniaxial compressive strength) of tuffs were determined according to TS 699 (Examination and observation method for building stone), and the mean values for every lithology were obtained.

3.4. Adsorption studies

Inorganic chemicals were supplied by Merck as analytical-grade reagents and deionized water was used. The metal ions (Ni^{2+}, Cu^{2+} and Zn^{2+}) were studied. It is prepared a synthetic stock solution of copper, zinc and nickel using their nitrate salts, $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2.6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$, respectively, in deionized water. The ion exchange of heavy metals on natural zeolite was carried out. Adsorption experiments were conducted by using 1 gr of adsorbent with 10 ml of solutions containing heavy metal ions of desired concentrations at constant temperatures (25^0C) in plastic bottles. Firstly zeolite particles were separated from clay mineral. The particle size of (chabazitic and phillipistic fuffs) used was in the range of 77–109 µm. The bottles containing heavy metal solutions were shaken by using VMR mark mini shaker for 2, 4, 6 and 8 hours, respectively. Later, heavy metal solution was made centrifuge (EBA 20 Hettick Zentrifugen model machine) for 10 minute, and it was taken in glass tupe with pipette. The exact concentrations of metal ions were determined by AAS (AV700, S/N7202 mark atomic absorption spectrophotometer).

3.5. Pozzolanic activity tests

The pozzolanic activity tests were conducted according to Turkish Standards TS 25, TS 24, and TS EN196-1. Pozzolanic activity test procedures are similar to those described in ASTM C 311 Standards. According to TS 25, a minimum of three mortar samples was prepared with a tuff, standard sand, and lime mixture (Table 1).

Table 1. Proportions of the ingredients of mortar specimens, as given by the TS 25 standard

Material	Weight (in gram)
Slaked lime $Ca(OH)_2$	150
Pozzolan	2 x150xN= T
Standard sand	1350
Water	0.5x(150 + T)

N = Factor obtained by dividing density of tuff by the density of lime.

The prepared mortar was placed in the moulds, and it was kept under 23 ±2^0C for 24 hours. The mortar was kept covered to reduce evaporation. Next, the moulds were kept in the drying oven at 55 ±2^0C for 7 days. The samples were taken from the oven four hours before they were broken and were kept in the room temperature for cooling. The compressive and flexural strengths of the samples on the seventh day were tested using the method described in TS 24 (Table 1).

3.7. Determination of the zeolite content in the tuffs

Zeolitic tuff was first powdered in the agate mortar. Then, the fine powder (i.e. clay minerals) was dispersed in distilled water by ultrasonic vibration in a beaker, and this dispersion was filtered using filter paper and then dried at 60 ^{0}C. Zeolite particles were separated from the quickly suspended clay mineral. Heavy liquid separation processes were carried out by using tetrabrom ethane. Purified zeolite grains were filtered by filter paper, washed by acetone, and dried. The zeolite content was determined as a weight percentage. Finally, the purified zeolite sample was analysed using the XRD method.

4. RESULTS

4.1. Petrography

The tuffs in the study area usually consist of consolidated components and/or welded volcanic ashes with fine or coarse particles. Upon microscopic examinations, they were named as vitric tuff and crystal vitric tuff. Chabazitic tuffs are beige in colour, and they can be described as welded tuffs with many cavities and pore sizes. Such tuffs are also characterised by high porosity. The surfacing of the chabazitic tuffs were found on the north of the study area (to the south and west of Selçik village) (Fig. 1).

Chabazitic & phillipsitic and phillipsitic tuffs are dark grey and brown in colour, and they are marked by extremely consolidated components and/or welded tuffs. Chabazitic & phillipsitic tuffs apper near the Ballık and Alılı locations and phillipsitic tuffs appear near the Ömerkuyu, Soğucak villages and Küfeke location. The mineralogical composition of the tuffs determined with the optical microscope and the XRD methods are given in table 2, and the microscopic and SEM views are presented in figures 2 and 3.

4.2. Zeolite content of the tuffs

The chabazite content in the tuffs (from the Selçik village location) was ST 1: 38.67 wt.%, ST2: 59.91wt.%, and ST 3:58.80 wt.%. The chabazite & phillipsite content (from the Ballık and Alılı locations) was ST 4: 49.0 wt.%, ST 5: 57.05wt% and ST 6: 60.0 wt.%. Phillipsite content (from the Ömerkuyu, Soğucak villages and Küfeke location) was ST 7: 51.53 wt.%, ST 8: 61.86 wt.% and ST 9: 62.40 wt.% respectively. According to the XRD results, chabazite occurs in the Ca-form; phillipsite is in the Na-K form K –form and K-Ca forms (Table 3 and Fig. 4).

4.3. Chemical composition of the tuffs

The total (SiO_2 + Al_2O_3 +$Fe_2O_3^T$) content of the samples was more than 70 wt% (74.33 and 86.55wt.%). The MgO contents are less than 5 wt% (0.62 and 1.38 wt.%). The SO_3 content was less than 3 wt.% (0.00 and 0.32 wt.%). LOI values were less than 10 wt.% (4.79 and 9.88 wt.%). The results of the chemical analysis are in accordance with the standards given in TS 25 (Table 4 and 5).

4 .4. Results of physico-mechanical tests of zeolic tuffs

Results of physico-mechanical test of zeolic tuffs are presented in table 6. It is shown that the porosity values of zeolitic tuffs are between 28.31% and 30.91%. The mean porosity value of chabazitic tuff from Selçik village area was 30.91%, the mean porosity value of chabazitic & phillipistic tuff from Alılı and Ballık areas was 28.76% and the mean porosity value phillipsitic tuffs from Soğucak and Ömerkuyu villages, and Kefeke areas was 28.31%, respectively.

Table 2. The mineralogical composition of the tuff samples as determined by the microscope and the XRD methods

Sample	Litology and location	Mineralogic Compositions
ST1 ST2 ST3	Chabazitic tuff (Selçik village)	Chabazite, illite glassy phase, sanidine albite quarts (± augite, biotite, chlorite, calcite, opaque mineral, iron oxide)
ST4 ST5 ST6	Chabazitic and phillipistic tuff (Alılı and Ballık)	Phillipiste, chabazite, illite, glassy phase quarts, sanidine, augite, hornblende (±calcite) opaque minerals, iron oxide
ST7 ST8 ST9	Fhillipsitic tuff (Soğucak,Ömerkuyu villages and Küfeke)	Phillipsite illite glassy phase, plagioclase, augite, biotite, chlorite opaque minerals, iron oxide

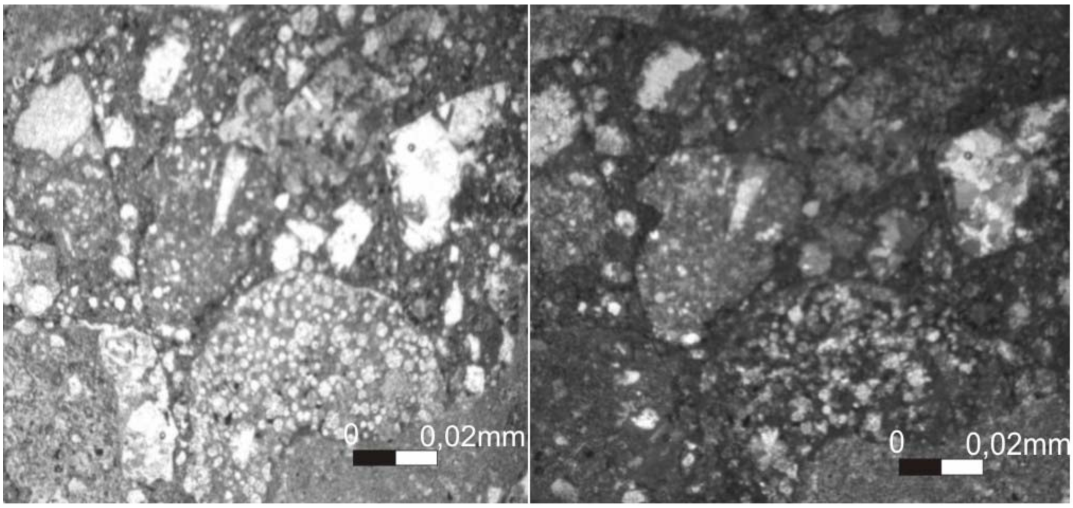

Figure 2. Thin sections of the tuffs viewed with the microscope (right, single nicol; left, double nicol) showing coarse pyroclasts and dense zeolite minerals (sample no: 17, enlargement 4x).

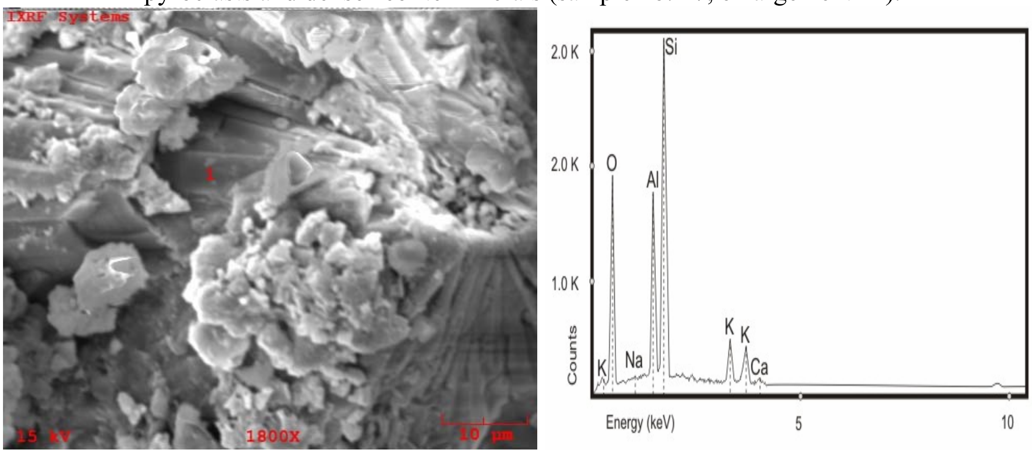

Figure 3. SEM image and EDS spectrum of the phillipsite in the phillipsitic tuff sample

It is indicated that zeolitic tuff according to rock classification based on porosity (Tarhan, 1996) fall into the "very porous rock" category. The mean uniaxial compressive strength values are shown to change between 8.57 Mpa and 18.14 Mpa The mean uniaxial compressive strength values from Selçik, Alılı- Ballık and Soğucak-Ömerkuyu-Küfeke areas were 8.57 Mpa 18.14 Mpa, and 17.87 Mpa, respectively. The zeolitic tuffs according to rock classification based on uniaxial compressive strength (Tarhan, 1996) fall in to the "very low strength rock" category.

4.5. Adsorption of metals on natural zeolite

The results of this study contribute to knowledge of the cation-exchange properties of phillipsitic and chabazitic tuff widespread in Sandıklı volcanic area. According to the XRD results, chabazite occurs in Ca-form; phillipsite is in Na-K, K, and K-Ca forms (Table 3 and Fig. 4). The chabazitic tuff sample using for tests was occurred by mixing of samples taken from three locations belonging to Selçik village area. The phillipsitic tuff sample using for tests was occurred by mixing of samples taken from three locations belonging to Soğucak, Ömerkuyu areas and Küfeke areas. The percent adsorption (%) and distribution ratio (K_d) were calculated using the following equations.

Adsorption % $= C_i - C_f / C_f \times 100$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, and respectively, and

Kd = [amound of metal in adsorbant/ amount of metal in solution] x V/m xml/gr

where V is the volume of the solution (ml) and m is the weight of the adsorbent (gr). The percent adsorption and Kd (ml/gr) can be correlated by the following equation (Khan et al 1995, Erdem et al 2004)

adsorption% = 100 x Kd /Kd + V/m

The uptake (%) of heavy metal ions from solutions is presented in figure 5. Heavy metal ions are immobilized by zeolite by means of an ion-exchange adsorption. Cu^{+2} ions immobilized by chabazite and phillipiste are higher.

Table 3. The mineral content (determined with the XRD method) and average zeolite content (weight %) of the samples purified using the heavy liquid method (A: albite; S: sanidine; Q; quartz, Ca: calcite; Cha: chabazite, phil: phillipsite (KN: K, Na-form, K: K-form, KC: K,Ca-form)

Sample	Location and lithology	According to XRD, mineralogic composition								Average of zeolite (wt%)
		Minerales determined little amount				Chabazite and phillipsite form				
		Alb	San	Q	Cal	Cha	Na-K Form	K form	K, Ca Form	
ST 1, 2, 3	Cha. Tuff, (Selçik)	±	±	±	±	+				52.41
ST 4, 5, 6	Cha. & Phil. Tuff (Alılı and Ballık)	±	±	±	±	+	+	+	+	55.35
ST 7, 8, 9	Phil. Tuff, (Soğucak, Ömerkuyu and Küfeke)	±	±		±		+	+	+	58.59

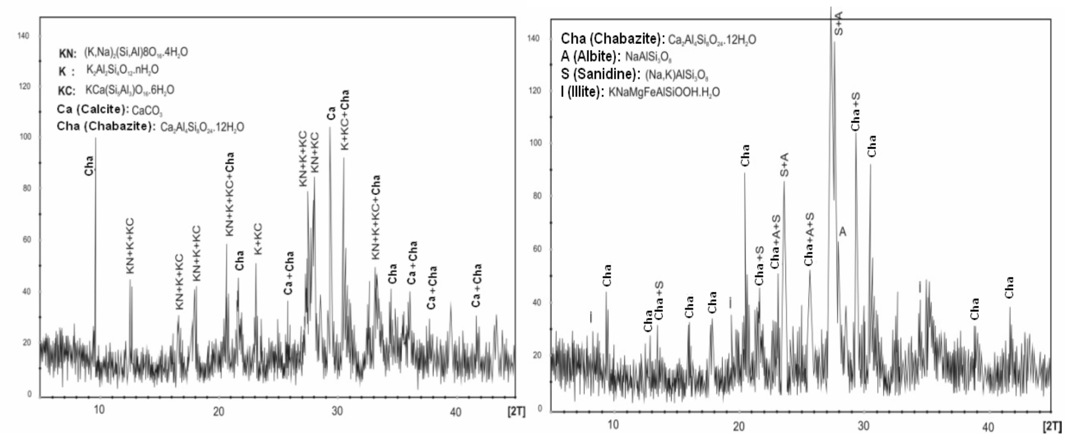

Figure 4. Mineralogical composition of the samples determined by using X-ray diffraction (A: albite; S: sanidine; I; illite, Ca: calcite; Cha: chabazite, phillipsite (KN: K, Na form, K: K form, KC: K,Ca form)), after separation with heavy liquid.

Table 4. The average chemical properties of the pozzolana samples

Sample	Lithology and locations	Chemical analysis (%mass)									
		SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	LOI.	TOTAL
ST 1, 2, 3	Chabazitic Tuff ,Selcik V.	58.29	17.19	4.12	0.80	5.53	2.72	3.99	0.27	5.83	98.74
ST 4, 5, 6	Shabazitic & Phillipsitic tuff (Alılı &Ballık)	51.05	18.07	5.76	0.62	5.45	1.58	6.06	0.32	9.88	99.74
ST 7,8, 9	Phillipsitic tuff (Soğ., Ömer.Küf.)	1.86	17.59	5.93	1.23	5.57	3.41	5.86	0.16	7.29	99.87

Table 5. TS 25 standard requirement

SiO_2 $+Al_2O_3+$ $^TFe_2O_3$(%)	MgO (%)	SO_3 (%)	LOI (%)	7th day Flex.st. (Mpa)	7th day comp. st. (Mpa)
>70	<5	<3	<10	>1	>4

Immobilization of the other heavy metal ions (Zn^{+2}, Ni^{+2}) is weaker (Fig. 5).The chabazite and the phillipsite selectivity with respect to the investigated metal ions, determined on the basis of the per cent removal of a given ion from the solution follows order: For the chabazite; Cu > Zn > ≅ Ni, for the phillipisite; Cu > Ni > ≅ Zn.

4.6. Pozzolanic activity

The physical properties of the tuff samples and the mechanical properties of the pozzolana mortar are given in table 6. The seventh-day compressive strength of the pozzolana mortar was between 11.05 and 13.2 Mpa, and these values are higher than the limit value, 4 Mpa. Flexural strengths were between 3.3 and 4.44 Mpa, and these values are higher than the limit value, 1 Mpa. The flexural and compressive strengths of the tuff samples are in accordance with TS 25; therefore, they can be used as pozzolana and as an additive material in the blended cement (Table 7).

4.6.1. Pozzolanic activities and their relationship with the chemical composition

There is a linear, positive relationship between the total (SiO_2+Fe_2O_3+Al_2O_3) wt%, the (SiO_2+Al_2O_3) wt%, the (Na_2O+K_2O) wt%, and the compressive strength of the trass samples.

Additionally, there is a negative, linear relationship between the total (CaO+Na_2O+K_2O) wt% and total Fe_2O_3 wt% and total (Fe_2O_3T+MgO) wt.% the compressive strength. The increase in the CaO wt.% of the trass is related to the secondary calcite and epiclast (limestone) content. The increase in the total Fe_2O_3 and MgO values are related to the crystallization process of the magma. Excess Fe_2O_3 and MgO in the magma will decrease the cavities in the magma and will increase the crystallization tendency. Also, it will cause the Fe-Mg mineral content to increase and it will cause the glassy material (glass shard and pumice) content to decrease.

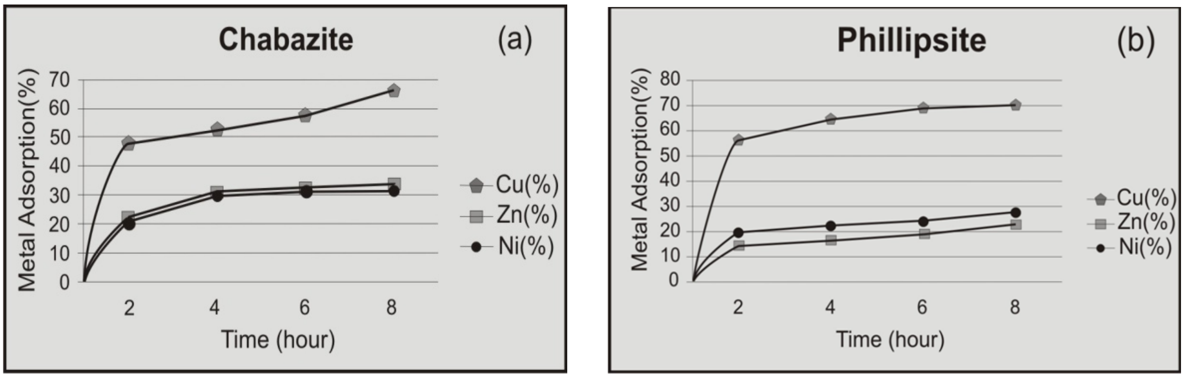

Figure 5. Adsorption (%) of metal ions by chabazite (a) and phillipsite (b) sample as a function of initial concentration.

Table 6. Results of physico-mechanical tests of zeolic tuffs

Sample	Lithology and location	Unit weight gr_f/cm^3	Spesific gravity	Absorbtion by weight %	Absorbtion by volume %	Apparent Porosity %	Compressive strength Mpa
ST 1, ST 2 ST 3	Chabazitic tuff (Selçik village)	1.49	1.74	21.89	31.18	30.91	8.57
ST 4, ST 5 ST 6	Chabazitic & phillipistic tuff (Alılı and Ballık)	1.74	1.98	17.23	28.78	28.76	18.14
ST7, ST 8 ST 9	Phillipsitic tuff (Soğ.,Ömer., and Küfeke)	1.74	1.96	16.76	28.38	28.31	17.87

Table 7. The amount of additional water demand of the pozzolanic mortar and the average pozzolanic activity results from the tuff samples.

Samples	Locations	Specific mass (g/cm^3)	Specific surface area cm^2/gr	Water added in mortar (ml)	Compressive strength, 7 th. days (Mpa)	Flexural strength, 7 th. days (Mpa)
ST 1,2,3	Chabazitic tuff (Selçik village)	2.41	5129	35.1	11.05	3.4
ST 4,5.6	Chabazitic & hillipsitic tuff (Alılı and Ballık)	2. 79	5021	55.0	12.1	3.44
ST17, 8, 9	Phillipsitic tuff soğ., Ömer. and Küfeke)	2.4	4650	60.0	13.2	3.46

4.6.2. The consistency of the pozzolana mortars and additive water demand

Excess water is added to adjust the consistency of the prepared mortars. The quantity of additional water is related to the specific surface area of the pozzolana, and it is also related to the zeolite type and zeolite content of the tuff. Additional mixture water is required in the mortars with large amounts of zeolite and small amounts of illite. Additional mixture water demand is related to the framework structure of the zeolite and its external surface area. Pozzolanic minerals adsorb the mixture water and cause the mixture water to be used properly in time (Fig. 6).

4.7. Determination of the tuff ratio to be added to the Portland cement (OPC)

Turkish Standard TS 26 (TS EN 197-1) defines the limit values of the natural pozzolana (tuff) used to make additions to the Portland cement. In these experiments, zeolitic tuff was mixed with the Portland cement at 15% and 30%. The physical and mechanical properties of the mortar prepared with zeolitic tuff and Portland cement are given in table 8. The experimental results are compatible with the Turkish Standards.

4.7.1 The specific surface area (Blaine), compressive strength, and volume expansion of 15% and 30% mixtures

In the OPC, the specific surface area of the mixture increased as the zeolitic tuff additive increased. The increase in the specific surface area is compatible with the zeolite content in the tuffs. As the fineness module value increases, the compressive and flexural strengths increase. Also the additive water in the blended cement mortar increases, while the volume enlargement decreases. The tuffs with high zeolite content significantly contribute to the improvement of the physical and mechanical properties of the blended cement mortar.

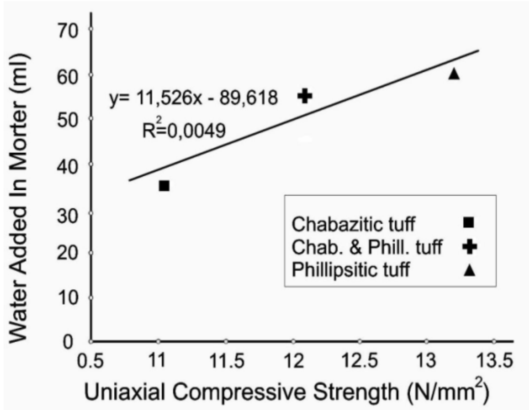

Figure 6. The relationship between the water demand of the pozzolanic mortar (ml) and the compressive strength.

Table 8. The physical and chemical properties of the OPC with 15% and 30% tuff additives and the compressive and flexural strengths of the blended cement. Each is in compliance with Turkish Standards. (Cha.:chabazitic, phil:phillipsitic).

TS EN 197-1 (TS 26) standard requirement		Lithology, sample number and admixture					
		Cha. Tuff (ST 1, 2, 3)	Cha.& Phil. Tuff (ST 4,5, 6)	Phil.. (ST7,8, 9)	Cha. Tuff (ST1,2,3)	Cha.& Phil. Tuff (ST 4,5 , 6)	Phil. tuff (ST7,8, 9)
Amounts of trass additives (%)	19-40	15	15	15	30	30	30
SO_3 (%)	3.5<	2.03	2.11	2.08	2.43	2.32	2.38
LOI (%)	5.0<	2. 64	2.43	2.48	1.93	1.83	1.74
MgO (%)	5.0<	2.54	2.77	2.72	2.53	2.76	2.66
Chlorium (%)	0.1<	-	-	-	-	-	-
Fineness modulus (cm^2/gr)	>2000	3393	3431	3446	4015	4200	4112
Comprehensive strength (2th days, Mpa	>10	12.6	14.2	16.4	9.5	10.1	10.4
Comprehensive strength (7th days, Mpa	>21	25.5	27.0	29.3	19.0	20.9	23.7
Initial of settling time(minutes)	>60	205	205	207	150	170	162
Final of setting time (Hours)	10<	4.35	4.55	4.45	3.45	4.00	4.00

Table 9. Physical and chemical properties of mixtures with 15% and 30% additives (Cha: cahabazite, phil:Phillipsite)

Sample and lithology	Content of Zeolite (wt.%)	Admixture (15%)				Admixture (30%)			
		Specific mass g/cm^3	Water %	Litre wt%	Volume expansion mm	Specific mass g/cm^3	Water %	Litre W%	Volume expansion mm
Cha.,Tuff (Selcik) (ST 1,2, 3)	52.41	2.99	29	995	2	2.9	32	947	1.3
Cha..& Phil. tuff (Alılı and Balllık) (ST4,5, 6)	55.35	3.03	29	1015	2	2.8	33	930	1
Phill. Tuff (Ömer. Soğ. and Küfeke) (ST 7, 8, 9)	58.59	3.03	30	1025	1	2.9	33	978	1

4.7.2. The beginning and the end of the setting processes

When the additive amount is 15%, the beginning of the setting process is the same for the blended cement mortar, but the ending of the setting process is short for the chabazitic tuffs and longer in the phillipsitic tuffs. When the additive amount is 30%, the setting process of the blended cement mortar starts and ends earlier for the chabazitic tuffs than for the phillipsitic tuffs (Table 9).

4.7.3. The relationship between the zeolite content, the type of the mixture prepared, and the compressive strength

Due to the zeolite content, an increase was observed in the mechanical strengths (measured from the second to seventh day) of blended cement mortars prepared with the 15% zeolite/zeolitic tuff addition. Similarly, mechanical strengths of blended cement mortars with 30% zeolite additive increase according to the zeolite content (Fig. 7) As the additive ratio increases, the mechanical strength of the blended cement mortars decreases. The mechanical strength of the 30% blended cement mortar is 25.49% less than the value obtained for the 15% blended cement mortar using chabazitic tuffs. These decreases were noted as 22.59% for the chabazitic & phillipsitic tuffs, and 19.11% for the phillipsitic tuffs (Fig. 7). According to the OPC mortars, the mechanical strength of the 15% and 30% blended cement mortars are higher.

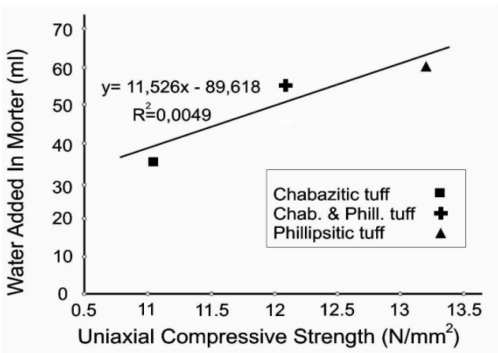

Figure 7. The relationship between the zeolite contents and seventh day comprehensive strength of blended cement mortars of the 15% and 30% zeolitic tuff additive.

5. DISCUSSION

Tuffs of investigated area are zeolite rich tuffs according to zeolite content (wt %). Tuffs which have high zeolite content control the moisture content of buildings for create healthy living spaces. In addition, tuffs have heat insulation property due to porosity of tuffs which caused by high zeolite content. Chabazitic tuffs are used in different localities of world for heating and air conditioner of small houses. Compressive strengths of zeolitic tuffs of study area are between 8.57 Mpa and 17.87 Mpa as average. It may be used for air conditioner of small houses at this district and settlements located its surroundings. It is indicated that the tuffs of study area, despite their high porosity and low compressive strength, can be used to form both concrete and satisfactory building stone (Çobanoğlu, et al, 2003). If concrete is produced by using zeolitic tuff aggregates, their heat insulation quality increase (Özkahraman & Işık, 2003, Kılınçarslan, 2007).

The values of absorption as weight % are between 16.76 % and 21.89 % and the value of absorption as volume % are between 28.38% and 31.18 % were determined. Because of their high absorption properties, they may be used for garden plant cultivation. It is thought that zeolitic tuff of this region will do important contribution for garden plant cultivation.

There are widespreadly shelters of cattles and goats at this district and its surrounding area. Because of these sitituation, they have dispersed dirty smells to the environment. Zeolite absorbs dirty smells because of urine, fecal matter and ammonium. So, zeolitic tuffs may be used for shelters of cattles and goats. In addition, in last years, using of zeolite in place of clay has increased for garbage dump. It is shown that they may be used for prevent to the leaking harmful ions to the water from the surface to undergroud. Beside, if they use, they will reduce dirty smells and will decrease to cost of making dump.

Using of nitrogenous manure, the groundwater of this region cause to inrease amound of nitrate (NO_3) and ammonium (NH_4). In this region, there is an interference from hot groundwater to cold groundwater. So, the amount of ammonium is too high in groundwater of this region. The chabazitic tuff may be used to decrease ammonium contamination of groundwater used as drinking water for some settlements. Because of ammonium exist inside of selective series of chabazite (Özpınar, 2008, Tsitsishvili et al.,1992) ammonium ions are easily concentrated on chabazite from solutions, and zeolitic tuff may be used for removal of ammonium.

Many toxic heavy metals have been discharged in to the environment with domestic wastewaters, causing serious water pollution in Afyon district (near the Sandıklı region) and surrounding areas. The adsorption behavior of Sandıklı zeolitic tuffs with respect to Cu^{2+}, Zn^{2+}, and Ni^{2+} has been studied in order to consider its application to purity with heavy metal removal from domestic wastewaters. The selectivity sequence was determined as Cu > Zn > ≅ Ni for chabazitic tuffs, and as Cu > Ni > ≧ Zn for phillipsitic tuffs. This study revealed that chabazitic and phillipsite tuff that selectivity and efficiency for the different heavy metal cations are related to some factors such as ionic size, ionic valence, as well as hydration energy (Ibrahim et al., 2002, Colella, 1996). Accourding to Ibrahim et al. (2002) the selectivity sequence of the chabazite-phillipsite tuff were obtained as Cr^{+3} > Cu^{+2} >Zn^{+2}> Ni^{+2}, and this preference increase with the decrease in total ionic concentration of solution. If the ions have similar valence, selectvity increase with the free dimentions of phillipsite and chabazite channels. Hydrated ions can pass though the channels if the radii are smaller than the channels (Ibrahim et al., 2002). Presence of competing ions, such as K^{1+} and Ca^{2+} is another major factor controlling the selectivity of the zeolite. Na-loaded phillipsite is more selective for K than any other cation (Collella et al. 1998, Ibrahim et al, 2002). Generally, pretreatment consist of washing with solutions contain cation, mainly sodium and cacium and in some cases potassium. Supplementary washing with alkali or acid solutions are also used. Efective capasity for chabazite and clinoptilolite for heavy metal is increase by using higher solution temperature during the pretreatment. Treatment of natural zeolite (chabazite and clnoptillolite) samples with sodium chlorite and sodium hydroxide solutions was found to improve their effctive exchance capacity for several cations including Pb^{2+} and Cd^{2+}, Cu^{2+}, Zn^{2+} (Mumpton 1999, Kesraoui - Quki, et al,.1993 Englert & Rubio, 2005) Acid and thermal treatments are frequently applied on zeolites in order to modify their physical and chemical properties (Kallo, 1988). Acid treatment causes dealumination of zeolites through removal of Al from the zeolite framework and replacement of exchangeable cations by H^+ (Christidisa et al., 2003). The adsorption of lead(II) ions on the natural forms of Transcarpathian zeolite under static and dynamic conditions was investigated by Gomonaj et al., 2009. Partial conversion of inactive calcium ions in the zeolite into relatively more mobile sodium or ammonium ions resulted in an increase in the adsorption of Pb^{2+}. Similarly, partial removal of aluminium oxide from the zeolite changed its physicochemical properties and led to the maximum adsorption of lead(II) ions (Gomonaj et al., 2009). On the other hand the Na^+ concentration released by the Na-exchanged chabazite and phillipsite tuffs owing to exchange with Cu^{2+} and Zn^{2+} were reported by Colella et al., 1998 as a function of time. The removal of Zn, Cu and Ni ions, from diluted solutions, by the adsorptive particulate flotation process was studied by Rubio & Tessele (1997), at laboratory scale and the sorption of Ni, Cu and Zn was found to be very efficient (>90%) at pH values higher than 5.5, although the metal uptake started at pH 3.5. These results show that zeolitic tuffs hold great potential to remove cationic heavy metal species from domestic wastewater. However, it is belived that efective capasity for chabazitic and phillipsitic tuffs in this region for heavy metal must investigate for some factors that influence both selectivity and efficiency of chabazite and phillipisite.

The increase in the total CaO wt% in the zeolitic tuffs corresponds to an increase in the secondary calcite and epiclast “limestone”. Also, the increase in the total Fe_2O_3 wt% and MgO wt% demonstrates that glassy phase (glass shard and pumice) and secondary mineral zeolite, clay (illite) content is low in areas where pyrogenic mineral and phenocrystal content is high. The increase in the Fe_2O_3 wt% and MgO wt% values may have negative effects on the pozzolanic activity.

Although the additional consistency water in the pozzolana mortar is related to the specific surface area of the tuff, it is primarily related to the zeolite type and content in the tuff along with the smaller clay mineral (illite) content. External surface areas of the zeolites increase their adsorption properties.

The increase in the additive water amounts decreases the Blaine value of the blended cement. As the additive ratio increases, the Blaine value decreases and the volume expansion decreases. This decrease in volume expansion indicates that zeolite content is high and that the residual glassy phase (e.g. pumice and glass shard) is small.

High zeolite content in the tuff decreases the specific mass of blended cement with added tuff. Additionally, the consistency water demand increases as the zeolite content increases. When the additive amount is 15%, the onset of the blended cement’s mortar setting is nearly the same, but the end of the setting occurs earlier for the chabazitic tuffs and later for the phillipsitic tuffs. On the other hand, when the additive amount is 30% the setting period of the blended cement mortar starts and ends earlier for the chabazitic tuffs and later for the phillipsitic tuffs.

When compared to those for the 15% blended cement mortar, the mechanical strengths of the 30% blended cement mortar are 25.49% lower for the chabazitic tuffs, 22.59% lower for the chabazitic & phillipsitic tuffs, and 19.11% lower for the phillipsitic tuffs.

The forms of the zeolite used in the experiments are the Ca-form of chabazite and K-

Na-form, K-form and K-Ca-forms of phillipsite. In the phillipsite samples for different forms, the selectivity occurs as K^{1+} >Na^{1+} >Ca^{2+} over a temperature range of 35-70 ^{0}C in the 0.1 M salt solutions. It is noted that this selectivity is not dependent on temperature (Shibue, 1981). For the phillipsite containing high amounts of siliceous and aluminous compounds, the thermodynamic affinity can be ordered as K^{1+} > Na^{1+} > Ca^{2+}. During the hydration of the OPC, there is a lag in the first days' reactions of the chabazite when compared with the phillipsite (Caputo, et al., 2008). Phillipsite reacts with nearly 50% of the lime at early times (Sersale,1987). The dissolution of the $Ca(OH)_2$ occurs as $Ca(OH)^{1+}$, OH^{1-}, and $Ca(OH)^{1+}$ dissociate into the Ca^{2+} and $(OH)^{1-}$ ions in solution. At low temperatures, Na^{1+} that is found in the K,Na-form of the phillipsite is subject to cation exchange because Ca^{2+} acts selectively. Thus, Na^{1+} passes to the solution and causes an alkalinity increase in the solution in contact with zeolite (Caputo et al., 2008).

The dissolution of the portlandite and alkali solution in contact with the zeolite causes the zeolite to be transformed into an amorphous material. The zeolite's breakdown and/or conversion into the amorphous material is followed by the formation of hydrated calcium aluminates and hydrated calcium silicates. In fact, the alkaline alumino- silicate magmas, rich in Ca^{2+}, are more prone to form silicates and aluminates than aluminium-silicates (framework silicates). First, non-permanent aluminosilicate gels are formed, and hydrated calcium aluminates and hydrated calcium silicates are settled. Non-permanent gels and unknown non-crystalline material plays an important role in the continuation of the pozzolanic effect after the zeolite's breakdown (Caputo et al., 2008).

6. RESULTS

It is shown that zeolitic tuffs according to rock classification based on porosity fall in to the "very porous rock" category, and according to rock classification based on uniaxial compressive strength fall in to the "very low strength rock" category. It is indicated that the tuffs of investigataed area, despite their high porosity and low compressive strength, can be used to form both concrete and satisfactory building stone.

The adsorption behavior of Sandıklı zeolitic tuffs with respect to Cu^{2+}, $Zn^{2+,}$ and Ni^{2+} has been studied in order to consider its application to purity with heavy metal removal from domestic wastewater. The selectivity sequence was found as Cu > Zn > ≅ Ni for chabazitic tuff, and as Cu > Ni > ≅ Zn for phillipsitic tuff. These results show that zeolitic tuffs hold great potential to remove cationic heavy metal species from domestic wastewater.

It is concluded that the major chemical composition and flexural and compressive strengths of the Sandıklı natural pozzolanas are higher than the values given in the ASTM and the Turkish Standards; therefore, they can be used as pozzolanas.

Tuffs with high contents of chabazite and phillipsite have the pozzolanic properties and the reactive ability necessary to compose cement components; therefore, they can be mixed in the OPC and used as blended cement. According to TS EN 197-1 (TS 26) standard requirement, it has been understood that as 30 % of maximum additive amount can be mixed in the OPC. When the ion exchange behaviours, the channel configuration, the channel dimensions, the ion dimensions, and the electrolyte concentration of the solution are assessed, it is observed that phillipsite possesses superior reactive abilities is comparable to those of the chabazite.

These results show that zeolitic tuffs are used as blend materials and building stone, and to remove heavy metal ions from domestic wastewater because cation exchange properties provide economical and environmental advantages. In case of using at appropriate technology of zeolites or high content zeolite-bearing tuffs, their importance increase from the viewpoint of redusing problems the heavy metals concentrations of the soils, removing heavy metal ions from domestic wastewater, because of cement manufacturing industry has crucial a place for CO_2 emissions, and also for sustainable development.

ACKNOWLEDGEMENTS

The authors want to thank TUBITAK (The Scientific and Technical Research Council of Turkey) for support of this study (Project No. TÜBİTAK - YDABÇAĞ-198Y102).

REFERENCES

Englert, A.H. & Rubio, J., 2005. *Characterization and environmental application of a Chilean natural zeolite*, Int. J. Miner. Process. 75, 21– 29.

Caputo, D., Liguori, B., & Colella, C., 2008. *Some advances in understanding the pozzolanic activity of zeolites:* The effect of zeolite structure, Cement & Concrete Composites, 30, 455–462

Christidisa, G.E., Moraetisa, D., Keheyanb, E., Akhalbedashvilic, L., Kekelidzec, N., Gevorkyand,R., Yeritsyane, H., & Sargsyan; H., *2003. Chemical and thermal modification of natural HEU-type zeolitic materials from Armenia, Georgia and Greece,* Applied Clay Science 24, 79 – 91, doi:10.1016/S0169-1317(03)00150-9

Colella, C., *1996. Ion exchange equilibria in zeolite minerals,* Deposita, 31, 6, 554-562, DOI: 10.1007/BF00196136.

Colella, C., De' Gennaro, M., Langella, A., & Pansini,M., 1998. Evaluation of Natural Phillipsite and Chabaziteas Cation Exchangers for Copper and Zinc, Separatıon Scıence and Technology, 33, 4, 467-481.

Coppola E.; Battaglia G.; Bucci M.; Ceglie D.; Colella A.; Langella A.; BuondonnoA. & Colella C., 2003. *Remediation of Cd polluted soil by Treatment with Orhanazeolite Conditionery,* Clays and Clay Minerals, 51, 6/1,609-615.

Çobanoğlu, I., Özpınar, Y., & Özbek, A., 2003. *Engineering properties of tuffs in the Sandikli region (Afyon-Turkey) and their possible use as concrete aggregates,* Bull Eng Geol Env, 62, 369-378.

Englert, A.H., & Rubio, J., 2005. *Characterization and environmental application of a Chilean natural zeolite,* Int. J. Miner. Process. 75, 21– 29.

Ercan, T., 1986. *Orta Anadolu'daki Senozoyik Volkanizması,* MTA Dergisi (Bülletion of Mineral Research and Exploration), 107, 119-141.

Erdem, E., Karapinar, N., & Donat, R., 2004. T*he removal of heavy metal cations by natural zeolites,* Journal of Colloid and Interface Science 280, 309–314

Gomonaj, V.I., Golub, N.P., Szekeresh, K.Yu., Gomonaj, P.V., Charmas, B., & Leboda, R., 2001. *Adsorption of Lead(II) Ions on Transcarpathian Clinoptilolite,* Adsorption Science & Technology, 19, 465-473, DOI: 10.1260/0263617011494321.

Ibrahim, K.M., NasserEd-deen, T., & Khoury, H., *2002. Use of natural chabazite-phillipsite tuff in wastewater treatment from electrolating factories in Jordan,* Environmental Geology, 41, 547-551, DOI.10.1007/S00254100430.

Inglezakis, V. J., Papadeas, C. D., Loizidou, M. D., & Grigoropoulou, H. P., 2001. *Effects of Pretreatment on Physical and Ion Exchange Properties of Natural Clinoptilolite,* Environmental Technology, 22,75-82.

Kallo, D., *1988. Catalysts from Hungarian natural clinoptilolite and mordenite. In: Kallo, D., Sherry, H.S. (Eds.), Occurrence, Properties and Utilization of Natural Zeolites.* Akademiai Kiado, Budapest, pp. 601– 624.

Kesraoui-Quki, S.,Cheeseman,C. & Perry, R., 1993. *Effect of conditionning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal,* Environ. Csi.Technol., 27, 1108-1116.

Khan, S.A., Rehman, U.R., & Khan, M.A., 1995. *Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite Waste Manage. 15, 4, 271-283*

Kılınçarslan, Ş., 2007. *Thermo-Mechanical Properties of Concrete Containing Zeolite,* Süleyman Demirel Üniversitesi, Fen Bilimleri Enstitüsü Dergisi, 11,3, 262-267.

Langella, A., Pansini, M., Guido Cerri, G., Cappelletti, P., & de'Gennaro,M., 2003. *Thermal Behavıor Of Natural And Catıon-Exchanged Clınoptılolıte From Sardınıa (Italy),* Clays and Clay Minerals**,** 51, 6; 625-633; DOI: 10.1346/CCMN.2003.0510605.

Mehta, P.K., 2002. *Greening of the concrete industry for sustainable development*, Concrete International 24, 3, 23-28.

Mertens, G., Snellings, R., Van Balen, K., Bicer-Simsir, B., Verlooy, P., & Elsen, J., 2009, *Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity,* Cement and Concrete Research, 39, 233–240

Mumpton, F.A., 1999. *La roca magica: Uses of natural zeolites in agriculture and industry, Proc. Natl. Acad. Sci. USA, 96, pp. 3463–3470*

Özkahraman, E.T., & Işık, E.C., 2003. *Isparta Kaynaklanmış Tüflerinin Kaplama Taşı Olarak Kullanılmasının Önemi Ve Uygun Yapıştırma Harcı Üretimi*, Türkiye IV. Mermer Sempozyumu (Mersem'2003) Bildiriler Kitabı ((in Turkish), pp 201-211.

Özpınar, Y., 2008. *Mineralogic, Petrograhic And Ion Exchange Capacity Features Of Tuffs Contain Of Chabazite And Phillipsite Minerals In Sandikli (Afyon) Region And Their Evaluation For Healthing (Southwesthern Anatolia, Turkey),* Bülletion of Mineral Research and Exploration, ISSN:0026-4563, 38, 29-48.

Pansini, M., 1996. *Natural zeolites as cation exchangers for environmental protection,* Mineralium Deposita, Volume 31, Number 6, 563-575, DOI: 10.1007/BF00196137.

Rubio, J., & Tessele, F., 1997. *Removal of heavy metal ions by adsorptive particulate flotation*, Minerals Engineering, 10, 7, 671-679.

Sersale, G.P., 1987. *Portland-zeolite-cement for minimizing alkali-aggregate expansion,* Cement and Concrete Research 17, 404-410.

Shibue, Y., 1981. *Cation-Exchange Reactions Of Siliceous And Aluminous Phillipsites*, Clays and Clay Minerals, 29, 5, 397-402.

Tarhan,T.,1996. *Mühendislik Jeolojisi Prensipleri*, K.T.Ü. Mimarlık–Mühendislik Fakültesi (in Turkish), Trabzon, 384p.

Tsitsishvili, G.V., Andronikashvili, T.G., Kırov, G.N., Filizova, L.G., Potashnikov, I.B., & Williams, P.A., 1992. *Natural Zeolite,* Ellis Horwood, Singapore, 293 p.

Yılmaz, B., Uçar,A., Öteyaka,B. & Uz, B., 2007. *Properties of zeolitic tuff (clinoptilolite) blended portland cement,* Building and Environment 42, 3,808–3815.

Received at:17. 05. 2010
Revised at: 12. 10. 2010
Accepted for publication at: 25.10.2010
Published online at: 01. 11. 2010