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Permeability features of concretes produced with aggregates coated with colemanite

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Abstract. In the world total boron reserve rating, Turkey is taken place on the first rank, meeting the demand of refined mineral and main boron chemicals. Development of the new boron products and production technologies, spreading the using area of the boron are the study topics which must be finically discussed. In this study, with the help of colemanite taken in ratio as (0%, 7.5%, 12.5%, and 17.5%) by being mixed by the cement, surfaces of the pumice aggregates have been covered. Permeability of the samples has been investigated by producing lightweight concrete with 400 dose with the help of aggregates covered with colemanite. For this, the experiments of water absorption, capillary water absorption, depth of penetration of water under pressure and rapid chloride permeability have been performed. In addition, analyses of the thin section of covered and uncovered pumice aggregates and SEM (Scanning Electron Microscope) have been investigated. When the control samples produced with the covered aggregates and concretes produced with colemanite covered aggregates are compared each other, it has been determined that special lightweight concretes whose values of capillary water absorption experiment, depth of penetration of water under pressure experiment and rapid chloride permeability are low can be produced.

Keywords: aggregates; lightweight aggregate concrete (LWA); durability; concrete products; construction materials

1. Introduction

Boron minerals are important mines known and used since very old times and they contain boric oxide (B_2O_3) in different ratios. In nature, approximately more than 230 boron mineral exist (Yenmez 2009 and www.enerji.gov.tr 2011). Boron (colemanite) deposits in high concentrations and economic dimensions, components of the boron bonded to oxygen are found rather arid,

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volcanic areas and the area having hydrothermal activity in Turkey and USA (DPT 2008). Sodium based tincal, calcium based colemanite and sodium-calcium based ulexite constitutes 90% of the boron used by the sector all across the world (www.minerals.usgs.gov 2012). These minerals are enriched by being subjected to the physical process, then, turned into various boron chemicals by being refined (www.enerji.gov.tr 2011). Volkman and Bussolini (1992) have studied on usability of the boron in construction materials and on impact of the products with thin particle boron on the concrete and Gencel *et al*. (2009) have studied on the features of the concrete including colemanite.

Pumice aggregate used common in production of the lightweight concrete is generally described as rhyolite component, with overly pore, glassy lava and light enough to float on the water (TS 10088 EN 932-3, 1997). Pumice aggregates having low intensity due to their cellular structure and high porosity (Kogel *et al*. 2006, Artuso and Wargo 1998) have intensity as between 480 and 880 kg/m^3 and are the most used ones among the aggregates with natural low intensity (Artuso and Wargo 1998). Lightweight concrete is a multi-directional material for the structures offering technical, economical and environment improving protection advantages (Haque *et al*. 2004). Due to its cellular inner structure, it has lower unit weight and resistance and high heat insulation features (Neville 1994). It can be used for the same aim with normal concrete. Lightweight concrete characteristics depend on the aggregate water content prior to mixing. Excessive water content causes lack of adherence between the aggregate and mortar, while low aggregate water content causes the aggregate to soak up part of the mortar water, thus causing a cement sub-hydration and consequent reduction of the concrete shape alteration capacity. Both cases result in lower resistance characteristics than when the aggregates are moderately soaked just prior to concrete preparation (Gündüz 2008). In order to improving the performance in respect of reducing water absorption and enhance the workability, Müller and Linsel (2005) have applied a special covering technology which will allow interesting application of the lightweight concrete with high resistance in construction sector by covering the mineral lightweight aggregates with a concrete layer whose Blaine fineness is high and intense. In concrete application under the water pressure, it has been detected that covering on the aggregate has prevented absorption of the mixture water and has increased pumpability of the concrete by providing a sufficient workability for fresh concrete mixture and Sallı Bideci *et al*. (2013) has detected that water absorption ratios in lightweight concretes produced with the pumices covered with polymer have respectively decreased according to the control samples.

Strength of the concrete is depended on, pore structure, pore ratio and whether the pore are bonded each other. Interactions of the substances which can be hazardous for the concrete affect the deterioration process. For this reason, permeability of the concrete appears to be the most important parameter affecting the resistance. In some studies made on this issue, Chia and Zhang (2002) correlate concrete with lightweight aggregates having lower permeability than the ones with normal aggregates with interfacial transition boundaries surrounding the surfaces of the lightweight aggregates being intense by investigation the impact of the aggregate type on the water permeability of the concrete. Parhizkar *et al*. (2012) state that concrete content have an important role on the capillary water absorption, then, lightweight aggregates show lower capillary permeability feature than the normal ones. Hossain *et al*. (2011) have found the coefficient of 12 weeks capillary water absorption as 2.5-4.2x10-5 cm/s$^{1/2}$ for lightweight concretes and as 3.0-3.5x10-5 cm/s$^{1/2}$ for semi-lightweight concretes in the lightweight concretes with cement in different mixture ratios which includes pumice. Sağlık *et al*. (2009) have detected that permeability of the concretes produced with the boron modified active bellite cement with boron stays relatively lower that the ones produced with the Portland cement and their chloride penetration is better than the concretes produced with normal Portland cement. Özkul *et al*. (2006) have investigated impermeability as depended on the component in concretes including two different puzzolans (fly ash and silica fume) in their study. As a result of the study, it has been seen that the most effective component on the experiment results related to rapid chloride permeability of the concretes kept in the air is water/concrete ratio. It is emphasized that fly ash/cement ratio is important in equivalent concretes cured in the water. This case has been explained with the requirement of sufficient cure conditions for rising the puzzolanic impact. Mirza (2009) has produced concrete with lightweight aggregate by using normal sand in 0%, 25%, 50% and 75% ratios instead of silica fume in 10% ratio by weight of cement addition and fine lightweight aggregate in his study. He has obtained that chloride permeability of the lightweight concretes decreases with the help of using the sand and chloride permeability of the concretes with 28 days has dropped even a little according to the concretes with 306 days in all concrete types. Assas (2012) produced lightweight aggregate concrete by adding 0%, 25%, 50%, and 75% ratios sand and cement added silica fume 10% ratio by weight in his study. As a result of the study, he states that the intensity of the mixtures has increased in 30% and concrete compressive strength has increased in 27% with the help of increasing of the sand content. In addition, he has detected that chloride permeability is low (< 2000 C) in concretes with all lightweight aggregates containing silica fume.

In this study, surface of the pumice aggregate having cellular structure has been covered with the cement and cement-colemanite mixture (0%, 7.5%, 12.5% and 17.5%). In order to investigate the positive and negative impacts of the covering on the aggregate and concrete, lightweight concrete control samples with 400 doses have been produced with the help of covered pumice aggregates. Permeability features of produced concrete samplings have been analyzed by performing water absorption, capillary water absorption, depth of penetration of water under pressure and rapid chloride permeability experiments. Moreover, thin section and SEM (Scanning Electron Microscope) analyses of the pumice aggregates covered with colemanite and uncovered have been performed.

2. Materials and method

2.1 Material

Table 1 Chemical analysis of the pumice aggregate and colemanite

Chemical Composition	**B_2O_3**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**SO_4**	**As (ppm)**	**Loss on Ignition**
Pumice	-	74.10	13.45	1.40	1.17	0.35	4.10	3.70	-	-	1.54
Colemanite	40.09	4.98	0.15	0.029	26.95	2.37	-	0.09	0.31	11.36	0.27

Table 2 The chemical and physical analysis of CEM I 42.5R cement

Component (%)	CEM I 42.5R	TS EN 197-1	Physical Analysis			TS EN 197-1
CaO	63.92	$C+S \geq 50\%$	Setting Time (Min.)	Start	145	min. 60
SiO_2	19.55			Finish	195	-
Al_2O_3	5.12	-	Density (g/cm^3)		3.11	-
Fe_2O_3	2.52	-	Specific Surface (cm^2/g)		3912	-
MgO	1.02	Lim.≤5%	Total Volume Expansion (mm)		1	max.10
SO_3	2.96	Lim.≤4%	Over 40µ Sieve Residue		23.1	-
Na_2O	0.27	-	Over 90µ Sieve Residue		2.4	-
K_2O	0.67	-	Compressive Strength (N/mm^2)	2 days	25.9	min. 20
Cl-	0.0089	Lim.≤0.10%		7 days	45.1	-
Loss on Ignition	4.08	Lim.≤5%		28 days	-	min. 42.5 max. 62.5
Result Solution	0.36	Lim.≤5%				

Pumice: It has been taken from the mine belonging to the Metaş Mining Ltd in Nevsehir – Cardak. Chemical analyze of the pumice has been given in Table 1 (Report No 001, 2012).

Colemanite: In the study, ground colemanite provided from the Eti Mining Bigadic Boron Exploitation Directorate has been used. Chemical analyze of the Colemanite has been given in Table 1.

Cement: In the study CEM I 42.5R cement produced in compliance with has been used TS EN 197-1 in Kırklareli Limak Trakya Cement Factory has been used. Chemical analyze of the Cement has been given in Table 1.

2.2 Method

2.2.1 Cover process

Pumice aggregates have been used in 0%, 7.5%, 12.5% and 17.5% ratios with addition of the colemanite to the cement besides the using as covered. Aggregates have been separated to range of grades with 4-8 mm and 8-16 mm for covering. Special for the covering process, covering machine with roller volume has been used. Surface is provided to be covered completely by spilling the cement and cement-colemanite grout on the aggregates put into the machines as two layer. In order to separate each layer, ground colemanite powder has been spilled on the aggregates. Aggregates has been tried to be covered with material with the same layer. The ones covered with the cement with B_2O_3 in 0% have been coded as 0-CLM, the ones covered with B_2O_3 in 7.5% as 7.5-CLM, the ones covered with B_2O_3 in 12.5% as 12.5-CLM and the ones covered with B_2O_3 in 17.5% as 17.5-CLM among the aggregate experiment samplings.

Table 3 Concrete mixture design

Components		Unit	Mixing Amount (400 Dosage)				
			Control	0-CLM	7.5-CLM	12.5-CLM	17.5-CLM
Aggregate Sieve Range (mm)	8 - 16	kg	118.88	169.67	163.99	175.10	167.16
	4 - 8	kg	173.93	278.56	275.75	281.69	268.63
	0 - 4	kg	914.25	914.25	914.25	914.25	914.25
Water		kg	254.53	207.00	205.00	204.00	208.00
Cement		kg	400.00	400.00	400.00	400.00	400.00

2.2.2 Concrete mixture design

In the study, concrete mixture calculation has been performed considering the principles in TS 2511 structural lightweight concrete standards. Accordingly, sand ratio in total aggregate volume has been defined as 50% by weight, aggregate ratio in 4/8 mm screen opening has been defined as 30% and aggregate ratio in 8/16 mm screen opening has been defined as 20%. Concrete mixture design has been given in Table 3.

2.2.3 Water absorption and permeability

Water absorption experiment has been performed in compliance with TS EN 480-11 standard on hardened concrete. For the experiment, 100 mm cubic samples have been used.

2.2.4 Capillary water absorption

In TS EN 772-11 experiment, 100x100 mm cylindrical samples have been turned into the oven dry. After the dry weights of the samples have been determined, they have been placed on water logged plate with grid in a way that their surface which has been not covered gets into touch with water. In the experiment, except from the sections of the samples which are in contact with the water, they have been covered with paraffin in order to prevent them to absorb water from other surfaces. Water absorption process of the samples whose cure times are 28 and 90 days has continued 60, 240, 540, 960, 1500, 2160, 2940, 3840 seconds and their capillary water absorption coefficients have been determined in the end.

2.2.5 Depth of penetration of water under pressure

Depth of penetration of water under pressure on concrete gives an idea about permeability features of the concrete. The experiment related with that trait has been performed in compliance with the TS EN 12390-8 standards. The samples taken out of the 28 and 90 days cure are dried with towel, then they are replaced to the machine for 24 hours with the use of 3 MPa (instead 5 MPa) and the samples are divided into two pieces in a vertical way to the surface that would be applied water pressure.

2.2.6 Rapid chloride permeability

Rapid chloride permeability experiment has been performed in compliance with the ASTM C 1202 standard. In the experiment, cylindrical samples with 50 mm thickness and 100 mm diameter were used.

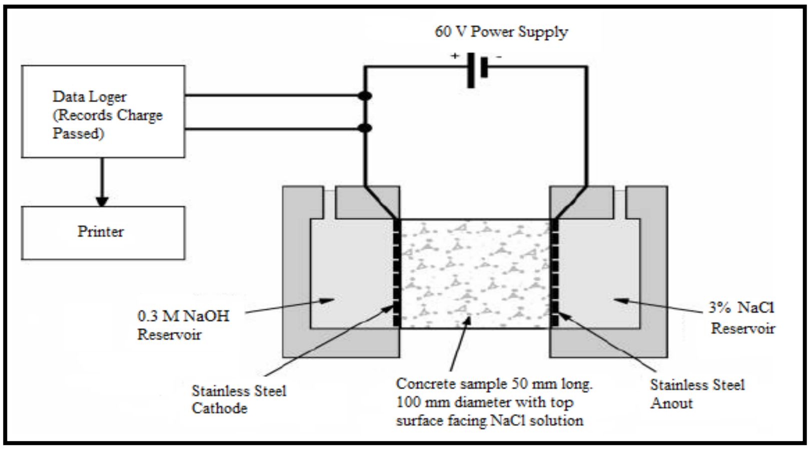


Fig. 1 Experiment schemata of rapid chloride permeability

The curvilinear surfaces of 28 and 90 days cylindrical samples acquired from the cure has been covered with an isolated material Air pores of mentioned samples under vacuum (priorly in 3 hours) have been removed and then, saturated surface is dried by absorbing the pure water in one hour period. Then, the samples have been set to the experiment container in which NaOH and NaCI were situated (Fig.1) (Özkul and Doğan 2003). The current intensity (ampere) with 30 minutes intervals have been measured while the cylindrical samples are exposed to 60 volts electrical field.

The transmitted electrical load amount (coulomb) at defined time has been calculated with the help of the area from intensity-time diagram obtained from the 6 hours long experiment. Electrical load amount is assessed by assuming proportional with ion amount (Erdoğan 2007).

2.2.7 Microstructure analysis

For basis to the experiment, 100 g parts have been taken per the concrete samples taken out of the 7, 28 and 90 days cures. These parts have been kept in pure acetone for 12 hours in order to stop hydration (Oymael 1995). The parts have been sent to the analysis by putting them into the glass bottles. The surfaces of the samples are covered with gold (200 A°) and micro structures of the samples have been investigated in different magnification ratios with the method of secondary electron display in LEO 435 VP device with Scanning Electron Microscope in Turkey Cement Producer Association labs (Report No 1854, 2012).

3. Results and discussions

3.1 Water absorption and permeability

At the end of the 28 days-water cure, data related to the water absorption has been given in Table 4. The water absorption ratios of 28 days concrete samples are investigated at 24, 48 and 72 hours duration. It has been detected that samples produced with covered aggregates have absorbed average 5% water while the control samples have absorbed 6% water.

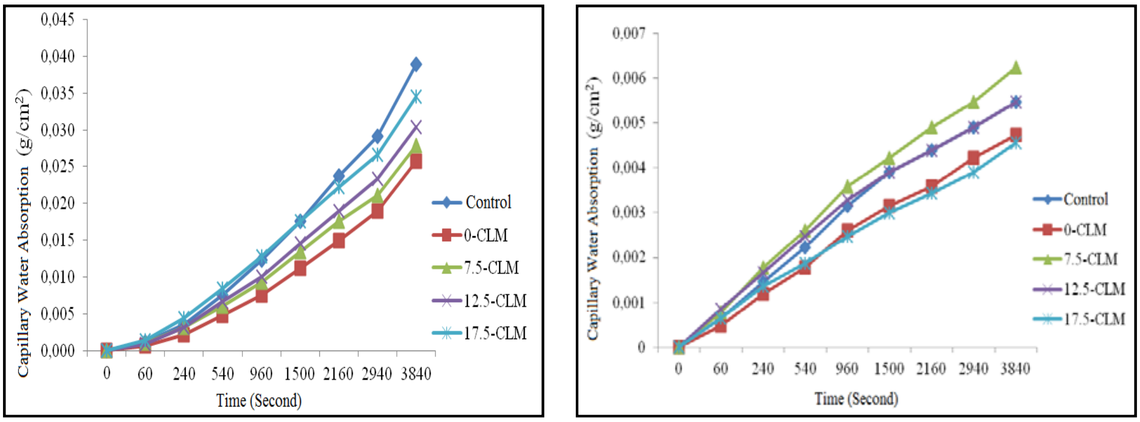
Table 4 Water absorption ratios in concrete samples (%)

Samples	Water Absorption Rates (%)		
	24 Hours	48 Hours	72 Hours
Control	5.5	5.8	6.1
0-CLM	5.1	5.3	5.4
7.5-CLM	5.4	5.6	5.6
12.5-CLM	5.3	5.5	5.5
17.5-CLM	5.3	5.3	5.5

It means that covering the aggregate does not change relatively water absorption ratio of the concrete.

3.2 Capillary water absorption

According to the data obtained, capillary water absorption coefficients have been found as 0.67-1.01x10^{-5} cm/$s^{1/2}$ for 28 day-samples and as 0.12-0.16x10^{-5} cm/$s^{1/2}$ for the 90 day-samples (Fig. 2). The 28 days-samples are investigated according to the control samples, so it has been detected that decrease of 34% for 0-CLM, in 29% for 7.5%-CLM, in 22% for 12.5-CLM and in 11 % for 17.5-CLM. The 90 days-samples are examined according to the control samples again; decrease of 14% for 0-CLM and 17.5-CLM, increase of 14% for 7.5-CLM and no change for 12.5-CLM have been detected.



(a) 28 days (b) 90 days

Fig. 2 Capillary water absorption amounts of the samples

3.3 Depth of penetration of water under pressure

The maximum depth in samples that water penetrates is measured as ‘mm’ (Fig. 3). When the depth of penetration of water under pressure values obtained from the uncovered aggregates and aggregates covered with cements containing colemanite, in 28 day-samples the highest value has been obtained from 12.5-CLM (76.82 mm) and lowest value has been obtained from 0-CLM (41.34 mm) sample; in 90 days-samples the highest value has been acquired from control sample (18.3 mm) and the lowest value has been acquired 17.5-CLM (5.3 mm), as well. The 28 day-samples are investigated according to the 90 day-samples, it is seen that a decrease 69% in control samples; 56% in 0-CLM; 76% in 7.5-CLM; 89% in 12.5-CLM and also 93% in 17.5-CLM.

3.4 Rapid chloride permeability

Experiment results have been given in Table 5 and Fig. 4. When examining the fast chloride permeability values of 90 days concrete samples obtained from the uncovered (control) and coated aggregates with colemanite added cements; the max value 0-CLM (1127 coloumb) and min value 17.5-CLM (337 coloumb) has been taken.

Table 5 Permeability limit values of the concrete and the samples with 90 days in rapid chloride permeability results

Limit Values		Samples		
Charge Passing, C (coulomb)	Chloride Permeabilite	Codes	Charge Passing, C (coulomb)	Chloride Permeabilite
>4000	High	Control	1115	Low
2000-4000	Moderate	0-CLM	1127	Low
1000-2000	Low	7.5-CLM	655	Very Low
100-1000	Very Low	12.5-CLM	497	Very Low
< 100	Negligible	17.5-CLM	337	Very Low

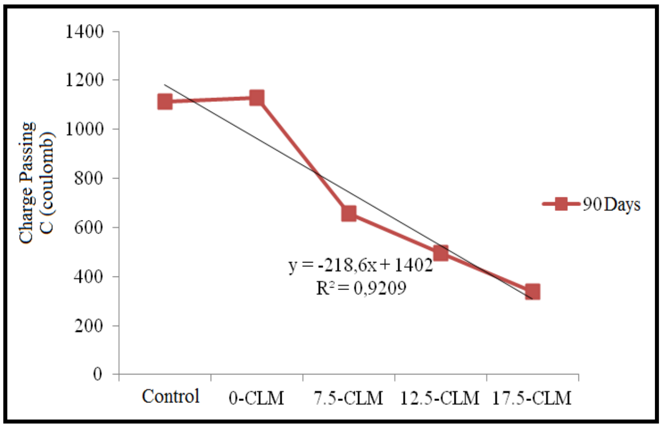


Fig. 4 Rapid chloride permeability in 90 day-samples

3.5 Microstructure analysis

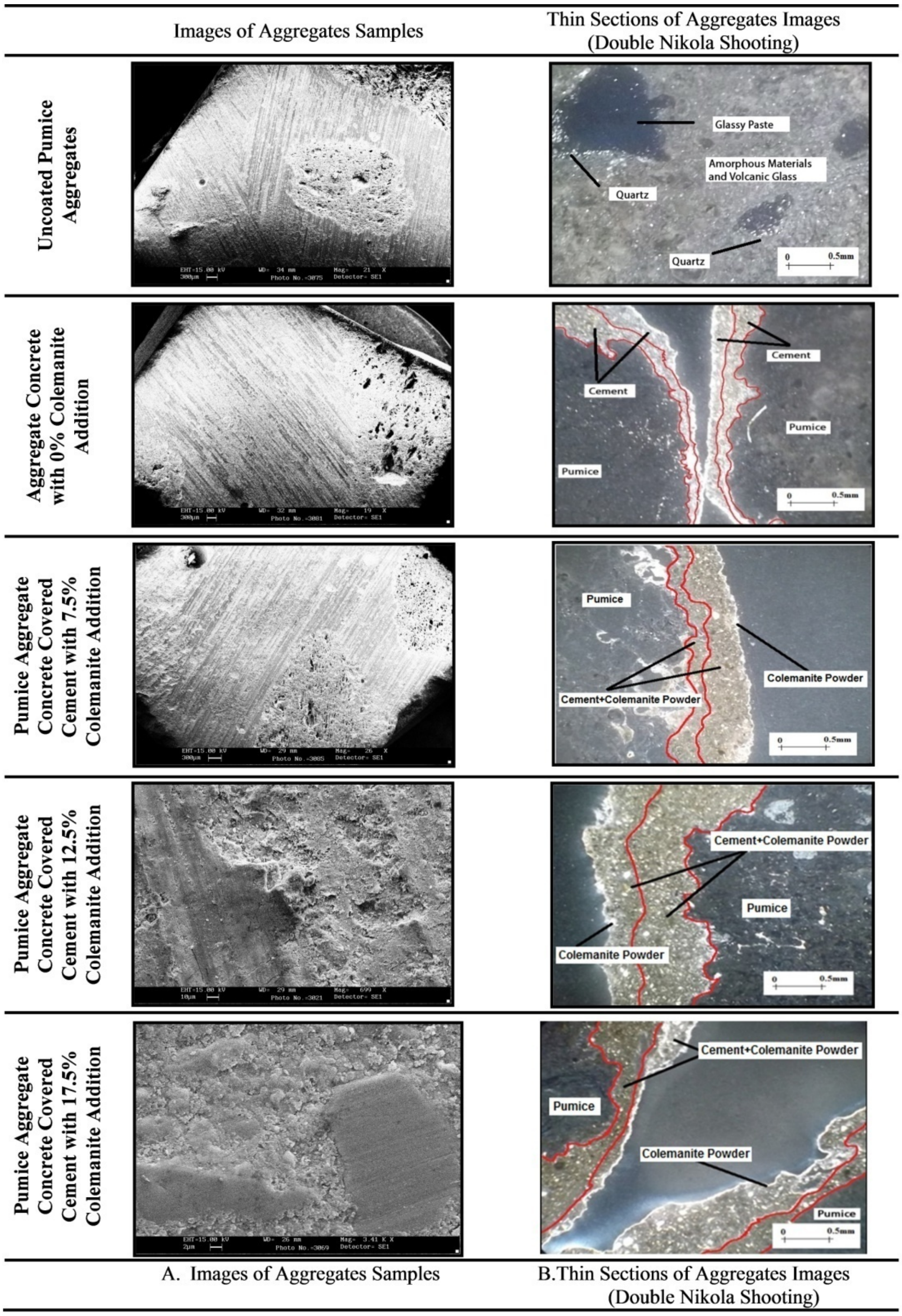


Fig. 5 SEM and thin section displays of the aggregates

SEM images belonging to the samples with 400 doses obtained from the uncovered pumice aggregates and aggregates covered with cements containing colemanite have been given in Fig. 5.

The thin section views of the pumice aggregate samples under the microscope are attained. It is observed that the volcanic glass in amorphous structure constitutes the great majority of the rock. This volcanic glass which forms the paste contains a lot of opaque minerals (ferric-oxide and hydroxide). SiO_2 components in opal chalcedony type have been also observed in the rock. Pore amount in the rock is approximately in 2-3% and there is small amount of the crypto crystal quartz sides of the cellular. Thin section which has been prepared for the petrographic analysis of the rocks can be described by defining the features of the light passing through the polarizing microscope (Erdoğan 2007).

- *Microstructure analysis of the covered pumice aggregate (Control)*

The thin section views of the pumice aggregate samples under the microscope are taken. It is found that the volcanic glass in amorphous structure constitutes the great majority of the rock. This volcanic glass which forms the paste contains a lot of opaque minerals (ferric-oxide and hydroxide). Amorphous material amount is about 4-5%. SiO_2 components in opal chalcedony type have been also observed in the rock. Pore amount in the rock is approximately in 2-3% and there is small amount of the crypto crystal quartz sides of the cellular. Flow textures have also been found on the rock. Possible rock passes to lava flows. It has been determined that the rock is a product of the dacidic magma.

- *Microstructure analysis of the pumice aggregate covered with cement (0-CLM)*

It has been observed that first layer covering is with granular and second layer is thinner in pumice aggregate. Depended on the section preparation of the covering thicknesses, not being homogenous case is possible and the thickness changes between 0.3 and 1.8 mm.

- *Microstructure analysis of pumice aggregates covered with cement-colemanite (7.5-CLM, 12.5-CLM, 17.5-CLM)*

Covering thicknesses of the pumice aggregatess covered with cement-colemanite change in 0.6-1.0 mm for 7.5-CLM samples, in 0.8-1.2 mm for 12.5-CLM samples and in 0.3-1.0 mm for 17.5-CLM samples. Thin section displays belonging to the aggregates have been given in Fig. 5.

4. Conclusions

In the study, 400 doses lightweight aggregate concrete has been produced with uncovered pumice aggregates (control sample) and CEM I 42.5R cements containing colemanite in 0%, 7.5%, 12.5%, 17.5% by weight. Permeability features of the concretes mentioned have been investigated. For this, water absorption, capillary water absorption, depth of penetration of water under pressure and rapid chloride permeability experiments has been performed. In addition, thin section and SEM analysis of the uncovered and covered pumice aggregates have been performed.

- When the water absorption ratios of the concrete samples are investigated, it has been determined that the ratio of the control samples is 6% and the ratio of the concrete samples covered with the cements containing colemanite is 5%. It has been observed that covering in concretes produced with the aggregates covered with cements containing colemanite does not relatively change the water absorption in concrete samples. In this case, internal stress difference between the layers with cement covered on the pumice aggregate can cause crack on the covering and increase the water absorption ratio.

- Capillary water absorption coefficient has been found as 0.67-1.01x10^{-5} cm/$s^{1/2}$ for control samples with 28 day-samples and 0.12-0.16x10^{-5} cm/$s^{1/2}$ for 90 day-samples. While 28 day-samples are not found as meaningful, it has been detected that the water absorption ratios of 90 day-samples have been decreased 5-6 times in concrete series produced with the whole cements covered with colemanite. This decrease depends on the increase of the hydration products such as C_3S, C_2S, C_3A and C_4AF in concrete structure in time.
- It has been determined that the values of the depth of penetration of the water under pressure are 41.3-76.8 mm for 28 day-samples and does not provide the standard values and changes between 5.3-18.3 mm for 90 day-samples and are relevant for the standard values. In addition, increase of cure time of 90 day-samples decrease depth of penetration of the water under pressure.
- When values of rapid chloride permeability of control samples with uncovered aggregates are compared with the covered aggregates, it has not observed a relative change for 0-CLM, it has been detected that there is 40-70% decline for 7.5-CLM, 12.5-CLM and 17.5-CLM samples. It has been found that chloride permeability of control and 0-CLM samples is "low" and of 7.5-CLM, 12.5-CLM and 17.5-CLM is "very low". It means that chloride permeability of CEM I 42.5R cements containing colemanite is low.
- The SEM images of the lightweight concrete samples were examined. It has been observed that there are lightweight aggregates having cellular glassy structure including minerals and in the structure, there are minerals such as quartz, alkaline feldispat, and calcite and hydrate phases such as C-S-H, portlandite and ettringite and cement particles which are not hydrated. There is no negative impact of the ettringite excessiveness because of the fact that SO_3 amount which is the source of the ettringite is under the standards both in concrete and in pumice aggregates. It is seen that the microstructure of 90 day-samples is more intense than the 7 and 28 day-samples.

As a result, it has been determined that concretes produced with aggregates covered with the CEM I 42.5R cement containing 12.5% colemanite are available producing special lightweight concrete whose capillary water absorption, rapid chloride permeability and depth of penetration of water under pressure values are low. Performance enhancing of these type concretes is directly proportional with the age of the concrete. If the colemanite is being used in recommended ratios, it should be considered the chemical structure of the colemanite which will be used.

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