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Investigation of the usability to nut shell ash as a mineral additive in concrete

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ABSTRACT

Experimental studies are being carried out to obtain puzzolan materials from agricultural wastes. The aim of this study was to minimize environmental damage of nut shells, which are discarded as waste material after the harvesting of crops. Puzzolanic activity test conducted in experimental study showed that nut shell ash provided compressive strength at 0.59 level. An analysis of compressive strength results revealed that compressive strength increases in 28-90 and 180 day values of the specimens containing nut ash additive. Reference compressive strength results showed that compressive strength increased by approximately 57% when water/cement ratio increases and that compressive strength decreased to 50% level with the increase of additive amount in both groups of concretes with nut shell additives. ASR test results showed that ash additive used in mortar types used in 5%-10%-15%-20%-25%-30% ratios had an effect and that it reduced ASR in mortar type containing 20% additive below 0.20 maximum value which is the standard value. Improvement of ash preparation conditions will enable the use of nut shell ash as a mineral additive.

1. Introduction

Increasing types of concrete structures requires the development and use of new technologies. Thus types of cements and concrete production continue to increase. Puzzolanic mineral materials have been used together with cement in production of concrete to improve the qualities of cement and concrete, to enhance their resistance and to save money. To this end, industrial by-products apart from puzzolans are used. Industrial puzzolanic materials used in concrete contain volatile ash, silica fume and ground granulated blast furnace slag.

Puzzolanic materials are natural materials consisting of silica, aluminum or the combination of these two. When mixed with water, puzzolanic materials do not naturally harden; however, when they are fine ground, they react to form calcium silicate and calcium silicate compounds that enhance resistance with dissolved calcium hydroxide ($CaOH_2$) at normal environmental temperature in the presence of water.

Puzzolans are in fact composed of reactive silicium dioxide (SiO_2) and aluminum oxide (Al_2O_2). The remaining part contains iron oxide (Fe_2O_2) and other oxides. Puzzolanic materials should be properly prepared, homogenized, dried, exposed to heat processing in production and should be fine ground [1].

Furthermore, experimental studies are being carried out to obtain puzzolan materials from agricultural wastes. Rice husk ash, wheat stem etc can are examples of these experimental studies.

Plants intake various minerals and silicates from the soil by their roots. Inorganic substances, especially silicates are known to be found in higher amounts in annual plants when compared to other types of trees. Annual agricultural productions such as rice, wheat, sunflower, tobacco, nut etc. are rich in silica and silicate due to their stem, leaves and protective layers. Inorganic compounds are found in plant in the form of free salts or particles or in the form of cations that are partially attached to anionic groups [2].

Burning of organic substances in agricultural wastes, formation of crystal phases or crystallization of amorphous substances are exothermic reactions. Weight

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decreases and ash is produced as a result of this reaction. Degradation of the structure of organic substances as a result of burning is called thermal decomposition [3].

When this ash, which is thinned by grinding into powder, is mixed with lime, material with a bonding property is obtained. The quality of this material varies largely depending on burning temperature, burning duration, sudden cooling and grinding conditions [4-6].

75% of the world's nut is produced in Turkey and approximately 85% of the world's nut export takes place in Turkey. Turkey is the most important determiner country in both production and exports of nut. According to 2004 data, Turkey produced 400.000 tons of nuts [7].

In a master's thesis, titled "Identification of Thermal Value of Organic Substances in Municipal Rubbish Composition", Halisdemir (2001) found that nut shell constitutes approximately 15% of the mass of nuts. In light of this information, it can be stated by a rough calculation that a total of 16.830 tons of shell is produced from the nuts that were exported in 2004.

Nut shell is an easily available and convenient potential source as it is produced in nut processing facilities. However, nut shell is usually used as a fuel, while it can be used as raw material in various industrial branches (plywood, chipboard, floor linoleum, plastic, dye, polishing oil etc.) [8].

Concrete elements are known to gain strength in the long term. Rheological behavior of concrete samples produced with nut ash additives remains unknown. In this respect, studies have concentrated on the usability of nut ash as a suitable additive when ash production conditions are improved.

In the present study, the coats on nut shell were subjected to pre-washing and the obtained ash was ground to 0-200µ. Puzzolanic activity test, compressive strength test and ASR test that affects strength were carried out using this ash.

2. Some Studies Conducted on Nut Shell

The literature contains studies on the use of nut shell ash as biogas and on nut cultivars that are grown in terms of the diversity geographical origin.

In a previous study on the removal of cadmium ions from aqueous solutions, it was found that obtaining nut shell and nut shell ash is more advantageous using absorption method [9] In another study which aimed to determine the effect of different carbonization conditions on solid crop yield nut shell (Corylus Avellana) was carbonized and the effect of temperature, heating rate and particle size on carbonization solid crop yield was analyzed. In conclusion, it was found that the solid product that was obtained as a result of carbonization can be used as an environmentally friendly, solid fuel with high energy content [10].

Another study studied the effects of particle size and mini reactor internal pressure and liquefaction yield in conversion of nut shell, which is a potential waste, under high pressure and high temperature (HP/HT). The study reached the following results:

Potential benefits can be achieved by converting nut shell which has a great potential especially for Turkey using liquid products.

- CO_2 production is zero,
- Prevention of climate change and conservation of the environment
- Conservation of resources,
- Conservation of energy,
- Reduced need for petroleum by the use of the obtained oil.
- Product composition can be used as a source of chemical substance instead of petroleum [11].

3. Materials Used in the Experimental Process

3.1 CEN Standard Sand

Rilem-Cembureau standard sand compatible with TS EN 196-1was used to prepare cement mortar specimens. Granulometric properties of the sand are presented in Table 1. Unit weight of the sand was found to be 2.01 gr/cm^3 [12].

Table 1.Granulometry values of rilem sand

Sieve Mesh Size (mm)	Material retained on the sieve (%)
0.08	98 ±2
0.16	87 ±2
0.50	67 ±2
1.00	33 ±2
1.60	9 ±2
2.00	0

3.2 Aggregate

The aggregate we used in experimental study was supplied from a sand gravel quarry near Sakarya River–Geyve town. The aggregate had a thickness of 0-7 mm. Firstly, amount of active silica on the aggregate was determined using chemical analysis method in accordance with ASTM C289, TS 2517 standard. It is presented in Table 2 that it is on harmful zone [16, 17].

Table 2. Chemical ASR report conducted in accordance with TS 2517

NaOH (Consumed)	350 (mmol/L)
SiO_2 (Solved)	700 (mmol/L)
Result	III. Zone (Hazardousaggregate)

Analysis values of cement and nut shell ash used in ASR test are presented in Table 3.

3.3 Cement and Nut Shell Ash

In this study CEM I 42.5 R cement was used. Chemical properties of this cement are presented in Table 2 [13].

Ash was obtained by burning the nutshells that were collected after harvesting season in heating boiler. The ash was ground in mill. Chemical analysis of the ash presented in Table 2 was conducted in laboratory of Oyak Bolu Cement Factory.

Nut shell, which is an organic waste, was converted to ash by burning. The ash was ground to power form. When this ash is mixed with lime, a material with bonding quality is obtained. The quality of this material largely varies depends on burning duration, shock cooling and grinding conditions. Chemical analysis results of the ash revealed excessive potassium oxide (K_2O) CaO_2 calcium oxide amount was found to be very low.

According to ACI 221, cement equivalent alkali amount ($Na_2O+0.658K_2O$) should be maximum 0.6%and it is recommended that this limit be 0.4%. Ratio of alkali amount of cement used in the test was ($Na_2O+0.658(K_2O)$) = 0.22*0.658*0.46=0.52 (Na_2O), which is below the value of 0.6%.[14] Chemical analyses of nut shell ash and cement are presented in table 3. SEM and microscope images are presented in Figure 1.

Table 3. Chemical analysis values of cement and nut shell ash

	CEM I 42.5 R	Nut Shell Ash
SiO_2	19.95	17.36
Al_2O_3	5.12	2.38
Fe_2O_3	3.75	3. 34
CaO	63.82	12.73
MgO	1.64	5.56
SO_3	3.36	2.77
Na_2O	0.22	0.33
K_2O	0.46	45.04
Na_2O Equivalent	0.52	-----
Loss on ignition	1.11	-----
sCaO	1.23	-----
45 Micron	1.90	57. 2
90 Micron	---	---
Specific Weight	3.13	2.62
Blaine	3971	2837

4. Experimental study

4.1 Puzzolanic Activity Test

The activity of pozzolansis determined by mechanical and chemical tests [15]. Mixture ratios of mortar specimens produced for puzzolan activity test is presented in table 4. The ash that was used as puzzolan was prepared by replacing 20% cement. In this mixture ratio, 6 pieces were prepared from each group of size 40 * 40 * 160 mm.

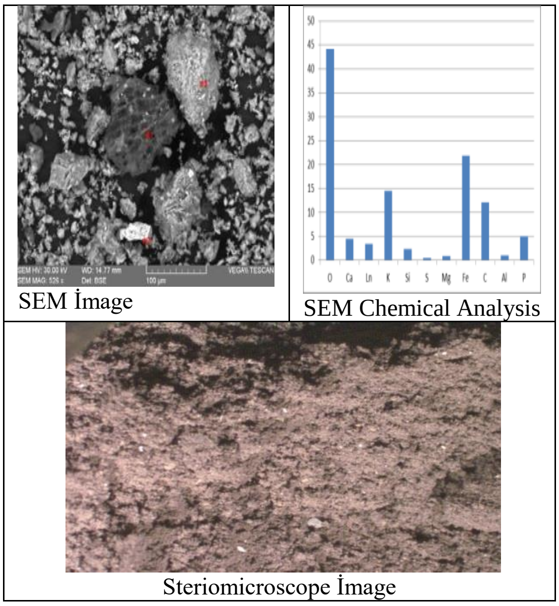

Figure 1. Sterio Microscope and SEM İmages of Nut Shell Ash

Table 4. Puzzolanic activity mortar mixture amount

	Pozzolan Additive (20%) (g)	Cement (g)	Standard Sand (g)	S/C=0.5 Water (g)
Reference Specimen	---	500	1320	250
Nut Shell Ash	100	400	1320	250

7 day and 28 day compression strength tests were carried out with these specimens. Test results are presented in table 5 and Figure 2.

Table 5. Puzzolanic activity compressive strength results of nut shell ash

	7-day results		28-day results	
	Compressive Strength (N/mm^2)	Percentage of Compressive Strength	Compressive Strength (N/mm^2)	Percentage of Compressive Strength
Reference Specimen	26.7	1.00	46.8	1.00
Concrete with nut shell ash additive	18.5	0.69	27.4	0.59

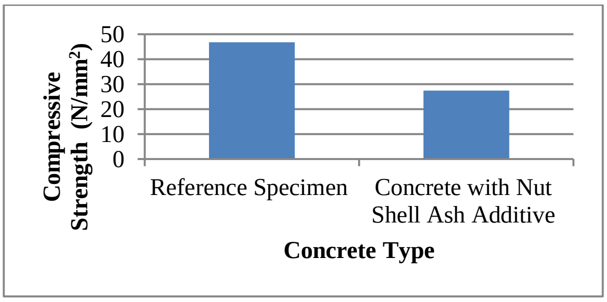

Figure 2. Nut Shell Ash Puzzolanic Activity Test 28-day Compressive Strength

As a standard, ash should have a value of 70% (0.70) in order to be used as puzzolan. Results of puzzolan activity test revealed a compressive strength of 59% (0.59) in 28-day test. This was believed to stem from the fact that nut shells were not burned in appropriate furnace and temperature in laboratory conditions. It was observed that puzzolanic property would be better if ash preparation conditions are improved.

4.2 Test Method for Potential Alkali Reactivity Aggregates (Accelerated Mortar Bar Test)

4.2.1 Preparation of Specimen Groups

Appropriate aggregate was prepared by sieving the aggregate according to mixture ratios in ASTM-C 227. In our tests, while preparing 5%-10%-15%-20%-25%-30%mortar bars in accordance with ASTM-C 227 standard using nut shell ash replacing cement, mortar mixture was prepared in such a way to have an aggregate/cement ratio of 2.25; a spread value of 120-150 mm and W/C ratio of 0.47. Minimum four mortar specimens were prepared from each group in 25×25×285 mm prismatic molds [18]. Material mixture ratios of the control mixture and of the specimens produced by 5%-10%-15%-20%-25%-30% nut shell ash replacing cement are presented in table 6.

Table 6. Material mixture values of test specimens

Additive Ratios	Aggregate (g)	Cement (g)	Mineral Additive (g)	Water (g)
Reference Specimen	1320	587	---	276
5% Nut Shell Ash	1320	557.65	29.35	276
%10 Nut Shell Ash	1320	528.3	29.35	276
%15 Nut Shell Ash	1320	498.95	58.7	276
%20 Nut Shell Ash	1320	469.6	88.05	276
%25 Nut Shell Ash	1320	440.25	117.4	276
%30 Nut Shell Ash	1320	410.9	146.75	276

Standard values of this method which is known as ASTM-C 1260 accelerated mortar bar test are presented below [19]. Expansion percentages at the end of 16-day test are evaluated as follows:

* If the expansions at the end of 16 days are below 0.10%, the aggregates show harmless behavior.

* If the expansions at the end of 16 days are above 0.20%, the aggregates show potentially harmful expansion.

* If the expansions at the end of 16 days are between 0.10%, and 0.20%, the aggregates can show both harmful and harmless behavior at construction site conditions. If the expansions at the end of 16 days are between the values of 0.10% and 0.20%, test duration for the aggregates had better be continued for 28 days [19]. Expansion results of control mixture and specimens with nut shell ash are presented in table 7. ASR formation graph is presented in Figure 3.

Table 7. Expansion values of accelerated mortar bar test

	Reference Specimen	Nut shell ash additive ratios					
		5%	10 %	15 %	20 %	25 %	30 %
9 Day	0.60	0.24	0.20	0.17	0.15	0. 21	0. 17
16 Day	0.83	0.31	0.25	0.19	0.16	0. 22	0. 18
28 Day	0.92	0.37	0.37	0.29	0.23	0. 19	0. 22

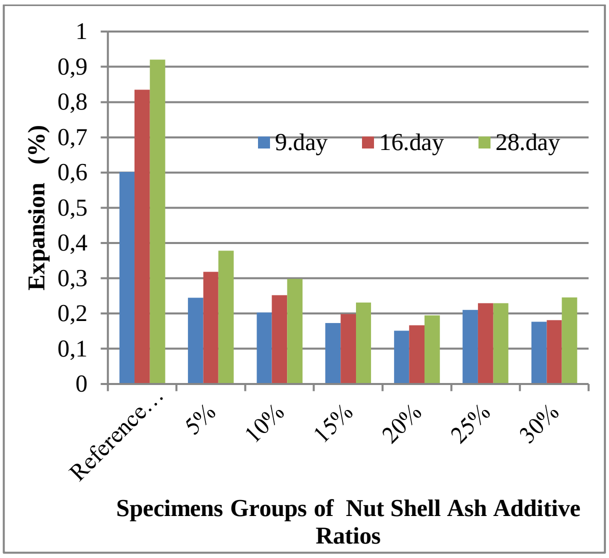

Figure 3. ASR Formation in Mortar Groups with Nut Shell Ash Additive

Results of ASTM-C 1260 accelerated mortar bar test revealed that when maximum standard value was taken as 0.20, it reduced below the standard value in the product with 20% additives. In other groups it was observed that;

* It reduced expansion at a ratio of approximately 0.59 in mortar type with 5% additive, when compared to the control mixture,

* It reduced expansion at a ratio of approximately 0.68 and 0.75 in mortar types with 10% and 15% additive respectively,

* It reduced expansion at a ratio of 0.79 and 0.75 in mortar types with 20% and 25% additive respectively,

* It reduced expansion at a ratio of 0.73 in mortar type with 30% additives.

It can be stated that this fluctuation in determination of ASR results from excessive amount of potassium oxide in the ash.

4.3 Determination of Compressive Strength of Test Specimens

Concrete compressive strength is expressed as $f_{c\ cube}$ if cube shaped specimens in compliance with the standard are produced for compressive strength. Compressive strength is determined in specimens of 7 and 28 days [20]. Fine aggregates exposed to 60% ASR, 40% fine chips and cement and nut ash, whose analysis values are explained above, were used in compressive strength tests. Concrete mixture groups were prepared in 10×10×10 cm test cubes. Six groups of concrete with a W/C ratio of 0.45 and 0.60; nut ash additive ratio of 10% and 20% were prepared for compressive strength test.

Material ratios of concrete mixture are presented in table 8 in unit of m^3. Compressive strength values are presented in table 9 and figure 4.

Table 8. Material mixture ratios of concrete prepared for compressive strength

Additive Ratios	0-8 mm Sand (kg) %60	8-13 mm Gravel (kg) %40	Cement (kg)	Mineral Additive (Nut Shell Ash)	Water (kg)
Reference Specimen 1	1040	714	420	----	189
FK 1 % 10	1040	714	378	42	189
FK 2 % 20	1040	714	336	84	189
Reference Specimen 2	1040	714	250	----	150
FK 3 % 10	1040	714	225	25	150
FK4 % 20	1040	714	200	50	150

Setting time of concrete specimens was approximately 10 hours in witness sample, while setting occurred in approximately 44-48 hours in specimens no FK3 and FK4 containing nut shell ash.

Table 9. Compressive strength values of the prepared concrete groups

	28 day (MPa)	90 day (MPa)	180 day (MPa)
ReferenceSpecimen 1	56.62	58.3	59.9
FK 1 %10	31.64	33.3	36
FK 2 %20	27.88	30.37	32.6
Reference Specimen 2	32.28	36.22	37.6
FK3 %10	20.54	25.2	27.8
FK4 %20	20.92	22.89	24

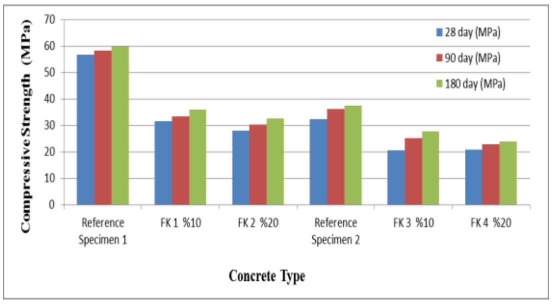

Figure 4. Compressive Strength Results of Concrete Groups with Nut Ash Additive

According to compressive strength test results,

* In reference specimen 1, in concrete group with a water/cement ratio of 0.45, compressive strength decreased by 56% in specimen with 10% nut ash additive and by 49% in specimen with 20% nut ash additive when compared to the reference specimen.

* In reference specimen 2, compressive strength decreased by 63% in concrete group with a water/cement ratio of 0.6 in specimens with 10%nut ash additive and by 65% in the group with 20% additives.

* In reference specimen 1 and reference specimen 2, strength decreased by 57% when water/cement ratio increased.

*According to the results of 90 and 180 day compressive strength test it was observed that strength increased, however it decreased by increasing at the same ratios.

Figure 5. Image of Concrete Specimen containing 10% Nut Shell Ash Additive

In specimen groups with a water/cement ratio of 0.45, setting occurred normally.

It was understood from Figure 5 that hardening of the concrete groups with a water/cement ratio of 0.60 was delayed. This delay in setting time is believed to be caused by excessive amount of potassium oxide in the ash.

5. Results and Discussion

Nut ash puzzolanic activity test, concrete compressive strength test and alkali silica reaction test affecting strength were carried out in this study, which analyzed the usability of nut shell ash in concrete products.

Results of puzzolanic activity test showed that the specimens showed a strength ratio of 0.59 when compared to the control specimen. According to test result, although it has lost the property of being a puzzolan at the level of 0.11, it was observed that it will give a better result when it is produced in a better environment.

ASR test was carried out to determine reduction level of alkali silica reaction, which affects concrete strength. An analysis of ASR test results revealed that ash additive used in mortar types containing additives at the ratios of 5%-10%-15%-20%-25%-30% had an effect and that it reduced ASR below the standard level of maximum 0.20 in mortar type containing 20% additive.

High potassium oxide (K_2O) observed in nut culture analysis was thought to cause fluctuation of expansion values.

According to compressive strength test results;

* In Reference specimen 1, in concrete group with a water/cement ratio of 0.45, compressive strength decreased by 56% in specimen with 10% nut ash additive and by 49% in specimen with 20% nut ash additive when compared to the reference specimen.

* In Reference specimen 2, in concrete group with a water/cement ratio of 0.60, compressive strength decreased by 63% in specimens with 10% nut ash additive and by 65% in specimens with 20% nut ash additive when compared to the control specimen.

* In Reference specimen 1 and References specimen 2, strength decreased by 57% when water/cement ratio increased.

* According to 90 and 180-day compressive test results, it was observed that strength increased however strength decreased by increasing at the same ratios.

Based on these results, this material can be used in filling works on roads. Diversification of the content of studies will enable the use of nut shell ash in economy instead of a waste material.

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