

# **Bulletin of the Mineral Research and Exploration**

http://bulletin.mta.gov.tr

# The prediction of the expandability of clays using a ternary diagram

Ahmet ÖZGÜVEN<sup>a\*</sup>

<sup>a</sup> General Directorate of Mineral Research and Exploration, Ankara, Turkey orcid.org 0000-0002-3807-2267

Research Article

Keywords: Expanded clay, ternary diagram, prediction of expandibility.

# ABSTRACT

The aim of this study is to put forward a prediction scheme for the expandability of clays by use of inexpensive and rapid chemical analysis. Seventy clay ores from fourteen locations throughout central and west Turkey were characterized mineralogically, chemically, and for expansion testing. Using the ternary plotting scheme of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>2</sub>-fluxing samples exceeding 50% expansion plotted within and slightly beyond the region proposed by Riley (1951). This study newly extends the region in ternary space for samples suitable for expansion and use in light weight aggregate. Non-expanding samples are associated with mineral assemblages dominated by quartz. In this study, it was determined that the samples without the expandability property were lacking the required chemical aspect of SiO<sub>2</sub>-Al,O,-fluxing ratios, mineralogical clay structures, proportions and gas agents. In addition, the effect of having a too low or high position on the triangle diagram was found to have a negative impact on the expandability. When mineralogical analyses, mineral associations, chemical compositions and expandability results were evaluated together, it was observed that Mica GM-Chloride GM; Montmorillonite-Zeolite-Amorphous matter and Clay GM-Amorh Silica-Cristobalite are the samples showing expandability properties for the extent of this study. Also, it was noted that almost all samples with graphite content did expand. The extension of the suitability field on the ternary diagram for prediction of expansion properties, combined with low cost and rapid chemical analysis demonstrate benefits for the clay production industry in Turkey, particularly for saving energy and financial resources needed during exploration and early stages of production clay ores.

*Received Date: 18.02.2018 Accepted Date: 23.04.2018* 

## 1. Introduction

Since the discovery of the expansion of some clays approximately one hundred years ago, expanded clay aggregates have been used extensively in several sectors, especially in developed countries. In Turkey, production methods and other features have begun to be determined by studies performed in recent years. Expanded clay aggregate has better features than other light aggregates, and it is used in several industrial sectors, especially in the construction industry (Özgüven, 2009).

Expanded clay aggregates are used in many different industries for their high technical features and numerous advantages when compared to many other industrial raw materials. One of the materials with the greatest compressive strength among lightweight aggregates is expanded clay aggregates. This gives it a significant position in the construction industry. 20% may be saved in reinforcing steel while up to 50% may be saved in heating–cooling expenses in buildings containing expanded clay aggregate in Turkey (Doğan and Şener, 2004; Özgüven, 2009).

Expanded clay aggregates are a new topic for Turkey and detailed studies on their production have begun to be conducted recently. Considering that there is no factory manufacturing expanded clay aggregate in Turkey, this study is an original study, especially for Turkey. It is also very important to note that Turkish clays are spread over a large area and the reserves are high. Therefore, it is very important that studies on the use and production of expanded clay aggregate

\* Corresponding author: Ahmet ÖZGÜVEN, ahmet.ozguven@mta.gov.tr https://dx.doi.org/10.19111/bulletinofmre.417966. should be conducted rapidly and the use of it should be made more popular in Turkey considering its superior advantages to current alternatives (Özgüven and Gündüz, 2012).

The natural materials most used for the production of lightweight aggregates are sedimentary or very low-grade metamorphic rocks such as clays or shales (Purbrick, 1991). The main constituents of these rocks are: mica-illite, kaolinite, smectite, and chlorite with variable amount of quartz, feldspars, carbonates, iron oxi-hydroxides, and small amount of sulfides and organic matter. Since some of these components (e.g. iron or calcium compounds) contain the chemical elements considered to be in the so-called fluxing parameter [fluxing=CaO+MgO+Na<sub>2</sub>O+K<sub>2</sub>O+Fe<sub>2</sub>O<sub>3</sub>] (Riley, 1951), their presence may also influence the softening and melting temperatures as well as the bloating of the aggregates (de'Gennaro et al., 2004).

General statements regarding the chemical/mineral composition and other characteristics of materials with proven expandability are as follows (EIPPCB, 2005):

- relatively high plasticity, large fines content (less than 2 μm, 35 % min.); for lumpy shale, the primary grain size is the crucial factor
- relatively high content of layered silicates, particularly from the illite or mica group; more than 40 % is advantageous, and the kaolinite content is usually low
- calcite or dolomite content reduces expansion time; lumpy lime is harmful, because it may subsequently lead to spalling
- chemical composition:
- $Al_2O_3$ : 12 25 %
- SiO<sub>2</sub>: 50 78 %
- Flux (Na<sub>2</sub>O, K<sub>2</sub>O, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, FeO): 8 25 %
- $C_{\text{organic}}$ : 0.6 2.5 %
- FeS<sub>2</sub>: should be fine-grained (residue in the finished product ≤ 1.0 or 1.5 % SO<sub>3</sub>)
- expansion characteristics improve with higher Fe<sub>2</sub>O<sub>3</sub> content of the ceramic raw materials (usually 5 to 10 %, perhaps higher)
- the sinter and melting point temperatures should be relatively close to each other, preferably up to and less than about 1200 °C

 pyroplastic softening of the mass or the granules should occur during the most favourable stage of the gas formation process; this offers the most advantageous expansion range of at least 50 to 100 K

An expanded aggregate is formed by quick heating the materials which are able to bloat at high temperature. Three conditions are necessary to get a suitable expanded material (Riley, 1951):

- 1. It must contain substances that develop gases at high temperature (T1);
- 2. It must produce a highly viscous liquid phase at the temperature T1 that could entrap the gases;
- 3. It must develop an external glassy film during cooling, making the outer surface impervious to water, homogeneous, and mechanically resistant.

The gases causing expansion come from thermally instable materials, such as the following (Heller-Kallai et al., 1988; Kazantseva et al., 1996):

- 1. Water vapor from the volatilization of interlayer water molecules or crystallization water of clay minerals or other silicates,
- 2. CO and CO<sub>2</sub> from the combustion of organic matter,
- 3.  $CO_2$  from the dissociation of carbonates,
- 4. O<sub>2</sub> and CO<sub>2</sub> formed from the reduction of ferric iron,
- 5.  $SO_x$  from sulfide oxidation,
- 6. F and Cl from clay minerals,
- 7.  $O_2$  and  $CO_2$  generated by adding extra gasreleasing materials, such as coal, waxes, and hydrocarbons.

Some limits must exist in the proportions of silica, alumina, and total fluxing agents beyond which the mass of the clay either will not fuse at a low enough temperature or will fuse to a melt not viscous enough to trap gas. In order to establish these limits, the analyses made by Conley et al. (1948) plus those of the present author were plotted on a composition diagram with silica, alumina, and total fluxing constituents as the corners. Minor constituents and volatile material were excluded, and the analyses were then recalculated to 100% before being plotted on the diagram (Figure 1). A dashed line was drawn

around the points representing bloating clavs. and this is considered the approximate limit beyond which a clay will not bloat. It must be remembered, however, that this "area of bloating" defines only one of the two necessary conditions for a bloating clay, i.e., it indicates the correct chemical composition to produce a mass of the proper viscosity at the bloating temperature. If these approximated limits are correct, all bloating clays should fall in between them. It can be assumed, then, that any nonbloating clay which lies within this area satisfies the condition of viscosity but does not have a constituent which will produce a gas at the proper temperature and thus fails in terms of the other necessary conditions for bloating. Several such clays are plotted in figure 1. Other nonbloating clays, shown to the left of the area of bloating, are deficient in fluxing constituents and may lack a gas-producing agent as well (Riley, 1951).

There are important studies performed using the triangle diagram, which was proposed by Riley (1951). In their study on Italian zeolitic rocks light weight aggregates, de Gennaro et al. (2004) investigated whether the chemical composition of the samples take place in the areas shown in figure 1. According to the expansion results of the 15 samples, they came to the conclusion that chemical composition has a large impact on expansion. With results similar to those of this study, researchers like Salakhov et al. (2005), Tsai et al. (2006), Al-Bahar and Bogahawatta (2006), de Gennaro et al. (2008), Chen et al. (2010), and Kavas et al. (2011) conducted studies by performing expansion tests mainly using the Riley diagram (1951). All these researchers came to the conclusion that samples in the expansion area had expanded and, therefore, this



Figure 1- Riley's ternary diagram of bloating materials.

diagram would be important for prediction of the expandability of raw materials.

Therefore, in this study, It was aimed to put forward a prediction scheme for expandability by the use of a cheap, quick chemical analysis of samples from various regions of Turkey instead of time consuming and costly expansion tests.  $SiO_2$ ,  $Al_2O_3$  and Fluxing triangle diagrams which were proposed by Riley (1951) and used by the several researchers have been evaluated once more by considering the tests of the 70 samples used in this study.

#### 2. Materials and Methods

For this study, samples that might present expandability features were taken from 70 different clay fields in Turkey. Locations of the samples are given on the map in figure 2 and table 1. To determine the chemical composition of the samples, the XRF Spectrometric method was used. By evaluating the analysis results in the UQ program of the ARL XRF device, numerical values were obtained. Loss on ignition values were obtained at the temperature of 1050° C. Results of the chemical analysis are shown in table 2. To determine the basic mineralogical features of the samples, XRD analysis was performed at 2<sup>o</sup> and 70<sup>o</sup> ranges using the Bruker D8 with Cu X-ray Advance XRD analysis device. Results are given in table 3.

All samples taken from the study areas were crushed and then milled below 200 µm size. Ground clay was mixed with water only without any additives to produce clay dough. Dough preparations were left to mature for one day and shaped through an extruder. Pellets of 15 mm were prepared by using caps. The pellets were then dried in the ovens and then expanded in a furnace. When the sample preparation and shaping operations are well performed, greater expansion of the clay can be obtained. Only optimum furnace conditions produce the desired expanded clay aggregate. In this study, a high volume stationary furnace, which is resistant to sudden thermal shocks, allowing the temperature to be raised rapidly, was employed. Studies were conducted at different furnace temperatures to determine at which temperature expansion was effective, at which temperature raw pellets began to expand, and which temperature yielded optimum expansion. The firing processes took place at different temperatures ranging between 1000 °C and 1300 °C. Raw pellets were kept inside



Figure 2- Locations of the samples used in this study.

the furnace for various durations (i.e. 5, 10, 15 and 20 minutes) at the same temperature in order to determine optimum time. Then the fired pellets were removed from the furnace and cooled rapidly.

The mass of a unit volume of the produced aggregates was measured by using the ASTM C493-98 standard to determine which manufacturing conditions yielded reasonable results. Because the unit volume of the aggregates is very small and it is impossible to weigh them in water, the mass of a unit volume was found by using the mercury method. Submerges the test object in a pool of mercury and measures the displaced mercury volume. Mercury is a non-wetting fluid that bridges the pore entrances and does not penetrate small cracks, holes, or pores. The volume of the medium displaced by the sample is measured. If the sample material is porous, fine particles will not penetrate into the smaller pores that liquids or gases can enter. Mercury, being a non-wetting liquid to most solids, also will not penetrate pores under ambient pressure. The unit volume masses of the expanded clay aggregates were compared with the Unit Volume Masses (UW) of the raw pellets to calculate the expansion ratio. The expansion ratio was calculated as (UVMorj/UVMexp) x 100. The results are given in table 2 and 3 with chemical and mineralogical analysis results.

Table 1- Region where the sample taken.

No	Samples	Region
1	1-3	Kırşehir
2	4	Kayseri
3	5-19	Adana
4	20-27	Mersin
5	28-30	Niğde
6	31-33	Edirne
7	34-41	Kırklareli
8	42-45	İstanbul
9	46-49	Kocaeli
10	50	Sakarya
11	51	Bolu
12	52-57	Tokat
13	58	Ordu
14	59-63	Çorum
15	64-70	Kastamonu

Table 2- Chemical	compositions	of the samples	
-------------------	--------------	----------------	--

No	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	<b>P</b> <sub>2</sub> <b>O</b> <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	Fluxing	LOI	UW (g/ cm <sup>3</sup> )	ER (%)
1	1,18	2,94	16,94	58,76	0,13	5,01	4,22	0,54	0,06	5,63	18,98	4,35	1,32	124
2	1,45	2,38	15,04	57,94	0,14	2,79	7,16	0,68	0,08	5,03	18,81	7,15	-	-
3	0,62	1,73	16,08	67,83	0,12	2,80	1,21	0,73	0,06	5,33	11,69	3,35	-	-
4	0,87	2,78	10,36	38,93	0,12	1,36	33,40	0,59	0,19	7,39	45,8	22,75	-	-
5	1,15	2,39	20,55	57,18	0,13	2,47	1,21	0,75	0,09	7,79	15,01	5,55	0,96	197
6	1,25	2,37	21,46	55,95	0,14	2,36	1,02	0,75	0,06	8,55	15,55	5,20	0,81	235
7	1,51	2,35	24,02	53,15	0,11	2,52	0,32	0,83	0,02	9,40	16,1	5,10	0,92	207
8	1,11	2,56	22,21	56,06	0,13	3,07	0,83	0,80	0,05	7,41	14,98	5,25	0,78	248
9	0,77	1,67	14,74	35,24	0,48	2,68	12,00	0,73	0,05	6,11	23,23	20,95	-	-
10	0,61	2,02	12,84	53,67	0,16	2,00	8,88	0,56	0,20	4,72	18,23	12,75	1,14	166
11	0,51	0,20	5,14	84,53	0,02	0,95	0,07	0,18	0,01	1,36	3,09	4,80	-	-
12	1,73	2,68	21,50	56,64	0,20	3,27	0,37	0,93	0,04	8,02	16,07	4,10	0,64	293
13	0,93	0,35	5,47	82,56	0,03	0,96	0,10	0,20	0,02	2,08	4,42	5,70	-	-
14	1,11	2,32	22,54	56,56	0,14	3,54	0,49	0,80	0,03	7,06	14,52	4,45	1,00	191
15	1,31	2,91	22,56	53,31	0,22	3,32	0,75	0,92	0,07	8,79	17,08	5,20	0,69	288
16	0,54	2,02	16,55	39,85	0,52	2,60	10,70	0,91	0,08	10,30	26,16	13,90	1,18	167
17	0,77	11,90	11,93	43,18	0,05	0,26	10,50	0,35	0,13	8,93	32,36	11,80	-	-
18	0,26	7,18	6,39	23,88	0,04	0,21	28,10	0,18	0,13	5,55	41,3	27,35	-	-
19	0,42	14,90	10,00	42,74	0,03	0,24	9,20	0,34	0,12	8,85	33,61	12,90	-	-
20	1,59	2,04	21,24	57,57	0,12	2,63	1,24	0,76	0,08	6,94	14,44	5,00	1,30	144
21	0,36	1,84	16,63	45,91	0,16	3,86	11,30	0,6/	0,28	6,24	23,6	11,85	0,95	198
22	0,86	3,8/	/,62	27,28	0,13	1,49	29,40	0,37	0,22	4,15	39,77	24,30	-	-
23	0,13	2,93	0,17	54.20	0,00	2.10	2 21	0,50	0,08	2,04	39,71	20,73	-	-
24	1,40	2,10	20,40	52 19	0,20	3,10	0.41	0,85	0,09	0,38	10,39	7,13	1.02	190
25	0,82	2,32	24,39	54.71	0,09	2.88	0,41	0,82	0,02	0,42	13,30	5,00	0.86	225
20	1.47	1.24	22,82	51.85	0,14	2,00	0,71	0,85	0,03	6.68	13.46	635	0,00	101
28	1,47	8 22	15.02	47.94	0.12	2.24	5 75	0.85	0.16	8 70	26.41	9.10	0.77	241
29	1,40	5 24	14 55	43.95	0.05	2,20	10.70	0.58	0.22	7 55	26,79	13.00	1 21	163
30	1 40	2 10	20.04	54 29	0.20	3.10	3 21	0.85	0.09	6.58	16.39	8 10	1,21	186
31	1 1 3	2,10	18.52	60.34	0.35	1 71	2.62	0.58	0.10	5.16	13.02	6.85	0.56	341
32	0.54	2.31	18.84	62.11	0.22	1,84	2.28	0.54	0.04	3.92	10.89	7.10	0.82	215
33	0.75	4.99	14.35	43.99	0.15	1.83	11.60	0.58	0.09	6.47	25.64	14.90	-	-
34	0,68	2,53	20,37	55,27	0,35	2,61	0,54	0,76	0,57	10,80	17,16	5,30	1,04	159
35	0,98	1,51	26,47	50,80	0,21	3,97	0,59	0,99	0,18	6,86	13,91	7,25	1,26	129
36	1,73	1,92	21,80	58,48	0,19	2,28	0,25	0,76	0,25	7,58	13,76	4,40	0,78	241
37	1,72	1,23	21,82	60,10	0,13	2,57	0,05	0,78	0,05	6,36	11,93	4,80	0,99	183
38	1,08	1,94	22,30	58,71	0,11	2,93	0,12	0,81	0,11	7,26	13,33	4,45	0,84	212
39	0,85	1,55	23,08	56,66	0,20	3,06	0,21	0,79	0,15	7,66	13,33	5,60	0,76	240
40	0,48	0,79	21,30	58,97	0,22	3,60	0,10	0,78	0,02	8,01	12,98	5,40	1,15	159
41	1,36	1,60	20,43	61,72	0,13	2,58	0,14	0,71	0,07	6,78	12,46	4,30	1,16	150
42	2,39	3,98	18,43	56,30	0,15	2,25	1,82	0,87	0,10	8,06	18,5	4,95	0,68	274
43	2,11	4,04	19,53	55,19	0,16	2,56	1,76	0,86	0,13	8,78	19,25	4,55	0,55	346
44	0,42	1,77	21,91	50,66	0,09	3,65	3,62	0,69	0,11	6,31	15,77	10,35	0,88	194
45	0,79	3,53	16,98	59,12	0,16	2,09	1,58	0,70	0,22	7,62	15,61	7,00	0,91	216
46	1,52	1,58	20,89	62,49	0,17	3,46	0,11	0,58	0,03	4,90	11,57	4,15	1,00	175
47	1,18	1,63	22,17	59,28	0,11	4,31	0,10	0,69	0,02	4,83	12,05	5,50	1,23	131
48	1,75	2,26	19,34	62,81	0,11	3,15	0,56	0,55	0,07	5,40	13,12	3,85	0,89	167
49	1,28	1,78	20,85	61,70	0,13	3,66	0,22	0,59	0,06	5,43	12,37	4,15	0,86	192
50	1,37	4,30	13,12	43,59	0,16	1,78	12,60	1,00	0,09	7,51	27,56	13,50	-	-
51	0,80	3,07	9,22	28,31	0,09	1,50	27,10	0,69	0,14	5,74	38,21	22,85	-	-
52	0,66	2,18	16,62	56,04	0,14	3,42	1,14	0,79	0,26	8,40	15,8	10,10	0,85	223
53	0,37	2,36	15,34	63,90	0,12	0,87	3,29	0,34	0,06	3,92	10,81	9,10	-	-
54	2,81	2,41	15,05	62,28	0,13	0,65	3,62	0,32	0,12	3,87	13,36	8,50	0,52	302
35	2,71	2,19	14,13	58,60	0,15	1,10	0,15	0,31	0,16	4,06	16,21	10,15	0,65	218

No	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	Fluxing	LOI	UW (g/ cm <sup>3</sup> )	ER (%)
56	0,31	1,73	17,04	55,97	0,16	2,08	1,50	0,78	0,07	7,35	12,97	12,75	0,43	455
57	1,47	3,21	18,10	52,17	0,23	3,74	1,77	2,07	0,12	11,69	21,88	4,95	1,04	177
58	0,46	3,35	13,83	66,48	0,02	1,59	1,98	0,16	0,02	2,28	9,66	9,60	1,17	150
59	1,02	2,20	16,62	61,73	0,19	3,12	1,07	0,74	0,09	7,67	15,08	5,25	0,89	201
60	1,44	2,51	17,51	59,51	0,20	3,82	1,00	0,79	0,12	7,69	16,46	5,15	0,55	333
61	1,16	3,26	15,38	58,21	0,16	3,24	3,97	0,75	0,13	7,11	18,74	6,15	0,74	235
62	1,66	2,82	16,85	60,63	0,18	3,42	0,58	0,87	0,09	8,32	16,8	4,30	0,60	323
63	1,75	3,90	13,85	51,23	0,19	1,98	7,75	0,97	0,15	8,73	24,11	9,10	0,91	204
64	1,28	2,65	13,77	60,11	0,14	2,51	4,03	0,68	0,12	6,63	17,1	7,40	0,89	204
65	1,45	1,50	16,62	59,07	0,17	3,48	3,15	0,78	0,10	7,50	17,08	5,90	1,35	121
66	1,13	1,66	19,56	59,67	0,17	3,47	0,23	0,88	0,11	7,66	14,15	5,15	1,29	145
67	1,21	1,83	19,13	59,82	0,20	3,34	0,22	0,88	0,13	8,21	14,81	4,75	0,93	205
68	1,06	1,81	19,14	60,39	0,16	3,25	0,23	0,88	0,09	7,69	14,04	5,05	1,16	161
69	1,01	1,53	17,67	62,60	0,20	2,84	0,69	0,80	0,09	7,48	13,55	4,75	1,10	174
70	1,19	2,04	18,98	59,74	0,15	3,00	0,22	0,87	0,25	8,82	15,27	4,45	0,95	187
Fluxi	ng: CaO+	MgO+Na	$O+K_0O+$	Fe,O,; LO	DI: Loss o	n Ignition	; UW: Ur	nit weight	of expand	led clay a	gregate; El	R: Expans	sion ratio;	

Table 2- continued.

#### 3. Results

The chemical data of the ground mixtures (recalculated to 100%) were plotted on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>2</sub>-Fluxing elements (CaO+MgO+K<sub>2</sub>O+Na<sub>2</sub>O+FeO+Fe<sub>2</sub>O<sub>2</sub>) diagram (Riley, 1951). The raw materials with a chemical composition located within the "bloating area" are shown on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>2</sub>-Fluxing Triangle diagram which is drawn according to the results of the chemical analysis, and the expansion tests of the samples is shown in figure 3. In figure 3, it can be seen that 60 of the 70 total samples presented within the expansion area, which had been proposed by Riley (1951) and it is determined that this constituted 85.7 % of the total test samples.



Figure 3- Expansion results in a ternary diagram.

Seven samples of the total 55 that exhibited expandability features were out of the expansion area. Only approximately 12.7 % of the total expanded samples were out of the area, which was proposed by Riley (1951). Samples having the expandability features but out of the area were the samples numbered 16, 21, 27, 28, 29, 35, and 63. These seven samples circumscribed the expansion area.

Three of the total 15 and 20 % of the total unexpanded samples that did not exhibit expandability features did not expand although they were in the expansion area with respect to their chemical compositions. Samples that did not expand in spite of being in the expansion area were the samples 2, 3 and 53.

The samples no 2 and no 3 were observed not to expand although they were in the expandability area. The reasons behind these conditions are thought to be not having enough clay in its mineralogical content for the sample no 2, and not having enough content to form gaseous structure for the sample no 3. It is considered possible for the sample no 3 to gain expandability properties with additive materials. In addition, the sample no 53 is thought to have low clay and melting contents, therefore it was not able to expand.

In figure 3, a new expansion area was proposed with the samples that expanded outside of the expandability area although expansion area proposed by the Riley (1951) represents the majority of the expanded samples. This area is in figure 3. By extending the expansion area, all the expanded

Table 3. XRD analysis results.

V																																				
Mont.																																				
z																															х		х			
Ь																															ХХ	х				
•																							х				x									
Gy																					х						x									
Am																	XXX		XX						Х			Х			Х					
s																	XXX	×	ХХ			_						х		х						
F																	XXX	х	ХХ																	
Clay GM																	ххх	хх	ххх						х		ХХ				ххх	ххх				[
Cris.													x				XX	х										х	х		XXX	XXX				
AS									хх																		х				XXX	XXX				
Apa.						x																												х	x	
Hem.							×		ХХ							х	Х	x	х					х						Х						
Graphite					х	х				XXX	XXX	х	ххх		ххх	хх					ххх	XXX	XXX	х	х									хх	ХХ	х
Cal.		xx		хх			x		XXX	XX						хх	XXX	XXX	ХХ		XX	XXX	XXX	х			х	XX	xx	XX	XX		XX			
Dol.	Х			хх		x		х	ххх	хх						х			х	х		х	х	х		×		х			х	х	х			
Quartz	XX	ххх	XXX	ххх	XXX	XXX	ххх	XXX	XXX	XXX	XXX	XXX	ххх	XXX	ххх	XXX	XXX	хх	XX	XXX	XXX	XXX	XXX	XXX	XXX	ххх	XXX	XXX	ххх	XXX	XX	XX	XXX	xx	XXX	XXX
Feld.	х	x	х	хх	х	×	×	х	xx	x	х	xx	×	х	xx	х	xx	x	х	х	x	х	х	х	х	×	х	xx	x	хх	ххх	XXX	х	x	хх	x
Chloride GM		x	XXX	x	XX	XXX	ххх	XX	XX	х		XX		XXX	ххх	XX	XXX	х	XX	XXX	XX	XX	XXX	x	XX	XXX	х	XX	xx	XX	х		XX	XXX	XX	XX
Mica GM	XXX	х	XXX	х	xx	хх	ххх	x	XX	x	х	XX		XX	хх	xx	XX	х	XX	х	XX	XX	XXX	x	х	хх	XX	х	хх	х		х	XX	XXX	XXX	x
ER (%)	124				197	235	207	248	ı	166	,	293	,	191	288	167	ı		,	144	198	'	ı	196	185	225	191	241	163	186	341	215	ı	159	129	241
UW (g/ cm <sup>3</sup> )	1,32				0,96	0,81	0,92	0,78	ı	1,14		0,64	ı	1,00	0,69	1,18	ı		1	1,30	0,95	,		0,94	1,03	0,86	0,97	0,77	1,21	1,03	0,56	0,82	ı	1,04	1,26	0,78
No	-	2	3	4	5	9	7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36

	V																		ххх	ХХХ																Cris:
	Mont.																		ххх	ххх																us Silica;
	z																	x	xxx	XXX			х													vmorpho
	Р						×	×		×													х													AS: A
	0																		ххх	XXX																patite;
	Gy																																			pa: A ter
	Am																	×																		natite, A ous Matt
	$\mathbf{N}$																											_			_					n: Hen norphe
	Т																																			e, Hen ; A: Ar
	Clay GM															ххх		xxx			ххх		ххх													l: Calcit orillonite
	Cris.						×	×					х										XXX					х								mite; Ca Montme
	AS																						XXX													ool: Dolc te; Mont
	Apa.			х	х	x					х	х	х	х																						ldspar; D ; Z: Zeoli
	Hem.															×						х						х				х				Feld:Fe xen GM
	Graphite	×	×	x	x	×			×		хх	хх	ХХХ	хх							х			хх	хх	ХХ	ХХ		XX	ХХ	XXX		XXX	XX	XX	Minerals; F; P: Pyro
	Cal.														хх	ххх		x	ххх	XXX		xx						XX	XX	х	х					Groups : Opal-C
	Dol.								×	x								xx			х		х													tio; GM: psium; O
	Quartz	XXX	XXX	XXX	ххх	XXX	XXX	XXX	XXX	XXX	ххх	XXX	ххх	XXX	XXX	хх	XXX				XXX	XXX		ххх	XXX	Gy: Gy										
	Feld.	×	×	×	x	×	xx	xx	×	×	x	x	xx	x	×	×	×	×	XXX	xxx	x	x	x	x	x	x	x	x	х	XX	х	х	х	X	x	ER: Expa
	Chloride GM	×	xxx	XXX	x	XXX	xx	XXX		x	хх	ХХ	х		x	×	xx	x				xx	Х	ххх	XXX	XXX	XXX	XX	XX	XX	XX	XX	Х	ХХ	XXX	agregate; ] .m: Amphib
	Mica GM	×	xx	XXX	ххх	xx	×	хх	хх	x	ххх	XXX	х	XXX	x	×	XXX				Х	xx	х	хх	XX	ХХ	xx	х	XX	XXX	XX	х	х	x	xx	anded clay rpentine; A
	ER (%)	183	212	240	159	150	274	346	194	216	175	131	167	192			223		302	218	455	177	150	201	333	235	323	204	204	121	145	205	161	174	187	t of exp lc; S: Se
continue.	UW (g/ cm <sup>3</sup> )	0,99	0,84	0,76	1,15	1,16	0,68	0,55	0,88	0,91	1,00	1,23	0,89	0,86			0,85		0,52	0,65	0,43	1,04	1,17	0,89	0,55	0,74	0,60	0,91	0,89	1,35	1,29	0,93	1,16	1,10	0,95	nit weigh ulite; T:Ta
Table 3-	No	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	UW: U <sub>1</sub> Cristobe

# Bull. Min. Res. Exp. (2019) 158: 299-310

samples were included in this area. Despite the three unexpanded samples that were in the area proposed by Riley (1951), there were five unexpanded samples in the new area. However, the location of the additional two unexpanded samples was at the edge of the newly proposed area, and this should not be neglected. It was observed that the expansion area will be very useful for prediction beforehand of the expandability of the clays because, excluding a few exceptional ones, this area was applicable for all the investigated samples. Besides the location of the samples within this area, another feature was their appropriate SiO<sub>2</sub>-Al<sub>2</sub>O<sub>2</sub>-Fluxing content. De Gennaro et al. (2004 and 2008) has stated that the quantity of the silica and the dissolver elements were factors in the expansion mechanism, and they played an important part in the determination of the liquid phase viscosity.

When the chemical analyses results (Table 2) are examined, the chemical content intervals for the samples that were able to expand are noted as 39.85 - 66.48 % SiO<sub>2</sub> (samples no 16 - 58), 12.84 - 27.07 % Al<sub>2</sub>O<sub>3</sub> (samples no 10 - 27) 9.66 - 26.79 % Fluxing (samples no 58 - 29).

It is not surprising to observe that the samples (no 2, 4, 9, 11, 13, 22, 23, 33, 50 and 51) with low clay content were not able expand when the mineralogical analyses results (Table 3) are examined. From the results, it can be deducted that the fundamental condition for the expandability is to have an expandable structure like clay, along with other supporting conditions.

High  $SiO_2$  content is expected to affect the expansion negatively. This event requires more dissolver quantity that would be adequate for softening the  $SiO_2$  which would form the cage structure. For content that provides sufficient viscosity for expansion, one of the components that constitute the structure should be extremely high. This factor is very important for prediction. It can also be understood from the fact that the samples no 11 and 13 with very high SiO<sub>2</sub> proportions did not expand.

When table 2 is examined, the sample with the lowest  $Al_2O_3$  proportion to expand is found to be the sample no 10 (12.84%), and the 9 samples with lower  $Al_2O_3$  content (samples no 4, 11, 13, 17, 18, 19, 22, 23 and 51) were noted as not expanding. Only 6 samples (2, 3, 9, 33, 50 ve 53) with slightly higher  $Al_2O_3$  contents were found not to be expanding due to their low clay content or high melting proportions.

It was observed that the samples with more than 25% melting content were also not able to expand. Additionally, the samples no 11 and 13 were not able to expand, with melting contents 3% and 4%, respectively. Very high flux content also negatively affects expansion. The important thing is to sustain the minimum level of dissolvers to maintain a viscosity adequate to form a pyroclastic structure along with a gas exit within the cage structure. If there is too much flux, viscosity will decrease, and gas will not stay in the system. With the help of additions that decrease the dissolver level, expandability can be increased. Having low melting content also would not be helpful for expandability, as it would not create any significant melting effect. Optimal proportion should be provided for this condition.

When figure 3 is examined, it is understood that expanded samples are gathered inside an "expandability area", and clay samples should have a chemical equilibrium in order to expand, also having too high contents of  $SiO_2$  and Fluxing or too low  $Al_2O_3$  content would affect the expandability adversely. In the light of these results, expandability area is considered to be promising.

Mineralogical contents in reference to fields were investigated and the results below were obtained;

- Samples 1-3 (Kırşehir Region) contain both Mica GM-Chloride GM with Quartz.
- Sample 4 (Kayseri Region) contains calcitedolomite and mica GM-Chloride GM alongside its main content of Quartz.
- Samples 5-19 (Adana Region) contains mostly Quartz, alongside Mica GM-Chloride GM, calcite-dolomite, feldspar and graphite. Nonexpanding samples were noted to have low levels of these associations or none at all.
- Samples 20-27 (Mersin Region) contain mostly Quartz, also Mica GM-Chloride GM, calcite-dolomite associations with graphite and feldspar content. Clay samples with this structure have a high expandability property. The reason for samples no 22 and 23 not having the same property is thought to be related to their high melting proportions (38.77-39.71%).
- Samples 28-30 (Niğde Region) also contain mostly Quartz, and Mica GM-Chloride GM associations with minor abundance of calcite

and feldspar. High expandability features were observed with all of these samples.

- Out of Samples 31-33 (Edirne Region), samples no 31 and 32 were noted to show similar expandability properties. It was possible to produce a clay aggregate with specific weights of 0,56-0,82 g/cm<sup>3</sup> with Clay GM-Amorh Silica-Feldspar-Cristobalite associations. Sample no 33 was obserbed to have a low level of clay content with a high amount melting content of 25.64%, and these are the reasons thought to be the main factors in its failing to expand.
- Almost all of the Samples 34-41 (Kırklareli Region) show the same mineral association and all of them were observed to expand. In addition to Quartz, Mica GM-Chloride GM combination and graphite, apatite and feldspar contents provide good expansion results (0.76-1.26 g/cm<sup>3</sup>).
- Samples 42-45 (Istanbul Region) have Mica GM-Chloride GM association and Feldspar contents besides Quartz. Apart from these, very few pyroxene, dolomite and cristobalite are contained. It is observed that all the samples in this region were able to expand.
- Samples 46-49 (Kocaeli Region) are similar in mineral content. In addition to Quartz, Mica GM-Chloride GM association and graphite are the main components. Feldspar and Apatite are also found in all samples. Good expansion results were obtained with the samples from this region.
- Sample 50 (Sakarya Region) did not demonstrate any expansion characteristics. The reason behind this is thought to be the lacking content (clays and fluxing). Quartz and calcite are observed in the results of mineralogical analyses.
- Sample 51 (Bolu Region) sample also did not demonstrate any expansion characteristics. Despite the fact that main structure is formed by Clay GM, due to its Calcite content and its high melting proportion of 38.21% the sample was not able to expand.
- Among the Samples 52-57 (Tokat Region), three different groups of samples were investigated and all of them were able to expand. Only the sample no 53 was not able to show any expandability characteristics due

to lacking content (fluxing). The associations observed in the expanding samples can be listed as; a) Mica GM-Chloride GM-Quartz; b) Montmorillonite-Zeolite-Amorph Matter; c) Clay GM-Quartz. All samples contain feldspar.

- Sample 58 (Ordu Region) shows mainly Clay GM-Amorph Silica-Cristobalite association. With this expandable sample, expanded clay aggregates weighing 1.17 g/cm<sup>3</sup> were able to be produced.
- Samples 59-63 (Çorum Region) contain Mica GM-Chloride GM association, Graphite and Feldspar besides their Quartz content. All samples were able to produce expanded clay aggregates with low unit weights such as 0.55-0.91 g/cm<sup>3</sup>.
- Samples 64-70 (Kastamonu Region) have similar mineral associations with Çorum Region and high expansion rates. Graphite, Mica GM-Chloride GM association, feldspar and calcite contents are observed beside Quartz in the examined samples.

Considering the mineralogical analyses, mineral associations, chemical contents and expandability results according to regions stated above, the mineral groups with expandability characteristics are noted as; a) Mica GM-Chloride GM; b) Montmorillonite-Zeolite-Amorph Madde; c) Clay GM-Amorh Silica-Cristobalite. It was also noted that almost all the samples with graphite content demonstrated expandability features. Out of 37 samples with graphite content, 33 were able to observed to be expanding. Samples no 11 and 13 were not able expand due to their high content of SiO<sub>2</sub> contents, 84.53 and 82.5% respectively. As for the samples no 22 and 23, it was found to be the high melting contents preventing the expansion, 38.77 and 39.71% respectively.

Unit weights of the expanded and investigated samples range between 0.43 and 1.35 g/cm<sup>3</sup>. Expansion rates range between 121 % and 455 %. The location of the samples with the best expanding features on the triangle diagram were investigated, and results are shown in figure 4(a). As can be seen here, the unit weights of the best expanded samples range between the 0.43 and 0.69 g/cm<sup>3</sup>. Since they located at almost the same places in the triangle area, this event shows the importance of the chemical composition. 10 samples that had minimum expandability features were investigated, the locations of the samples with

unit weights between 1.16 and 1.35 g/cm<sup>3</sup> are shown in the triangle diagram in figure 4(b). Here, it can be seen that the chemical compositions of the samples that have low expandability features are quite different from each other. All three of these samples were out of the expansion area which was proposed by the Riley (1951). Prediction of the expansion shows the importance of results that can be obtained from chemical analysis as shown in figure 4.

## 4. Conclusions

Following results were obtained when the results received from the chemical analysis and expansion tests were evaluated by the  $SiO_2-Al_2O_3$  – Fluxing triangle diagram:

- Expansion area in the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> Fluxing triangle diagram which was proposed by Riley (1951) gives an idea of the expansion before the expansion tests. However, chemical analysis or the mineralogical structure alone is not sufficient. Expansion can be sustained by the combination of an optimal temperature and the duration with adequate content and mineralogical structure.
- Although most of the expansion results are within the expansion area, the samples of chemical compositions which are outside the area can be expanded.
- Although most of the samples not having expandability features lie outside the area, it

was understood that, among the samples within the expansion area, not all the samples could exhibit expandability features.

- Being out of the expansion area but exhibiting expandability features and being within the expansion area but not having expandability features shows us that mineralogical structure is very important.
- Clays, shales, slates, etc., which are appropriate for the production of the expanded clay aggregate, will be useful for predicting the expansion if the chemical analysis and mineralogical analysis are performed before the expansion tests.
- It was seen that the raw material should exhibit adequate chemical content for the occurrence of the expansion. It was also seen that all the elements that constitute the triangle diagram have importance separately. Any deficiency in one of the elements, negatively affects the expansion. In this study, it was observed that clays with high SiO<sub>2</sub> and fluxing contents were not able to expand. It is obvious that there is a certain balance when considering the place in the triangular diagram.
- In this study, if the clays in Turkey, mineralogical analyses, mineral associations, chemical contents and expansion results are evaluated together, the mineral groups with expandability characteristics were noted as; a) Mica GM-Chloride GM; b) Montmorillonite-



Figure 4- The best (a) and the worst (b) expansion samples in a ternary diagram.

Zeolite-Amorph Madde; c) Clay GM-Amorh Silica-Cristobalite. Different associations can be identified by increasing the number of samples.

- This study shows the prominence of graphite content in the production of expanded clay aggregate. Almost all of the samples with graphite content were found to exhibit expansion.
- The expansion area proposed previously was tested once more by investigating the various samples. After considering the test results, a new expansion area was proposed. It was also determined that this area is appropriate for the clays of Turkey.

As a result,  $SiO_2-Al_2O_3$ -Fluxing triangle diagram is very important for the raw materials that exhibit expandability features. It was determined that most of the raw materials exhibiting expandability features are within this area. Using this diagram before the expansion tests will be useful in predicting of the expansion.

## Acknowledgements

Author is thankful to Dr. Mustafa Albayrak and Dr. Sezin Özaksoy for XRD analyses of the samples and to Yasemin Güneş Dulkadir for XRF analyses of the samples.

## References

- Al-Bahar, S., Bogahawatta, V.T.I. 2006. Development of lightweight aggregates in Kuwait. Arab J Sci Eng:31:231-239.
- ASTM C493–98. 1998. Standard test method for bulk density and porosity of granular refractory materials by mercury displacement.
- Chen, H.J., Wang S.Y., Tang, C.W. 2010. Reuse of incineration fly ashes and reaction ashes for manufacturing lightweight aggregate. Constr Build Mater. 24,46-55.
- Conley, J.R., Wilson, H., Klinefelter, T.A. 1948. Production of lightweight concrete aggregates from clays, shales, slates, and other materials, US Bur Mines Repts Invest, 4401, 121 pp.
- de'Gennaro, R., Cappelletti, P., Cerri, G., de'Gennaro, M., Dondi, M., Langella, A. 2004. Zeolitic tuffs as raw materials for lightweight aggregates, Appl Clay Sci, 25, 71-81.
- de'Gennaro, R., Langella, A., D'Amore, M., Dondi, M., Colella, A., Cappelletti, P., de'Gennaro, M. 2008.

Use of zeolite-rich rocks and waste materials for the production of structural lightweight concretes, Appl Clay Sci, 41, 61-72.

- Doğan, H., Şener, F. 2004. Hafif yapı malzemeleri (pomza-perlit-ytong-gazbeton) kullanımının yaygınlaştırılmasına yönelik sonuç ve öneriler. TMMOB. The Newsletter of the Chamber of Geology Engineers, vol. 1, p. 51–3 (in Turkish).
- EIPPCB, 2005. Best Available Techniques in the Ceramic Manufacturing Industry, European Comission Directorate General Joint Research Center, Draft Reference Document, 253 p.
- Heller-Kallai, L., Miloslavski, I., Aizenshtat, Z., Halicz, L. 1988. Chemical and mass spectrometric analysis of volatiles derived from clays. Am Miner.73:376–82.
- Kavas, T., Christogerou, A., Pontikes, Y., Angelopoulos, G.N. 2011. Valorisation of different types of boron-containing wastes for the production of lightweight aggregates. J Hazard Mater. 185:1381-1389.
- Kazantseva, L.K., Belitsky, I.A., Fursenko, B.A. 1995.
  Zeolite containing rocks as raw material for siberfoam production. In: Kirov G, Filizova L, Petrov O, editors. Natural Zeolites, Sofia'95., Sofia, Bulgaria: Pensoft Publishers. p. 33–42.
- Kazantseva, L.K., Belitsky, I.A., Fursenko, B.A, Dement'ev, S. N. 1996. Physicomechanical properties of sibirfom, a porous building material zeolitecontaining rock. Glass Ceram52:257–60.
- Özgüven, A. 2009. Genleşen kil agrega üretimi ve endüstriyel olarak değerlendirilmesi. PhD thesis. Isparta: University Süleyman Demirel; (in Turkish).
- Özgüven, A, Gündüz, L., 2012. Examination of effective parameters for the production of expanded clay aggregate, Cement & Concrete Composites, v. 34 pp. 781-787.
- Purbrick, J. 1991. Lightweight aggregates-manufacture and applications. Exploration, Mining and Uses of Ceramic Raw Materials, Proc. 23rd Ann. Symp. African Ceram. Soc., pp.45-49.
- Riley, C.M., 1951. Relation of chemical properties to the bloating of clays, J Am Ceramic Soc, 34(4), 121-128.
- Salakhov, A.M., Morozov, V.P., Tuktarova, G.R. 2005. Upgrade of production technology of building ceramics and expansion of product range. Glass Ceram. 62:80-83.
- Tsai, C.C., Wang, K.S., Chiou, I.J. 2006. Effect of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-flux ratio change on the bloating characteristics of lightweight aggregate material produced from recycled sewage sludge. J Hazard Mater. B134:87-93.