International Journal of Scientific Research in Chemical Sciences
Vol.9, Issue.4, pp.12-16, August (2022)
Research Paper
E-ISSN: 2455-3174

Determination of Major and Minor Oxides in Bentonite Samples From Quarries in Turkey

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Available online at: www.isroset.org

Received: 21/Jun/2022, Accepted: 20/Jul/2022, Online: 31/Aug/2022

Abstract— Bentonite mineral is widely used as additive raw or filling material in various sectors (ceramics, cosmetics, paint, textile, casting, construction, etc.). The effective and efficient use of bentonites in these sectors depends on their chemical components. In this study, a total of ninety-eight bentonite samples collected from twenty-three quarries located in different geographical regions of Turkey were analyzed by EDXRF to determine the major and minor element distributions of bentonite quarries. The mean concentrations of K_2O, Na_2O, MgO, Fe_2O_3, CaO, Al_2O_3, SiO_2, MnO, P_2O_5, SO_3 and TiO_2 analyzed in all bentonite samples were found as 1.40%, 2.78%, 3.25%, 4.36%, 4.65%, 15.24%, 54.12%, 0.10%, 0.20%, 0.35% and 0.58%, respectively. The highest concentrations of SiO_2, Fe_2O_3, K_2O and SO_3, and TiO_2 were analyzed in samples collected from bentonite quarries located in Ordu, Çorum, Trabzon, and Çankırı provinces, respectively. The bentonite quarries in Konya province have the highest concentrations of Al_2O_3, MgO, P_2O_5, and MnO, while the bentonite quarry in Trabzon province has the highest concentrations of Na_2O and CaO.

Keywords— Bentonite, Major oxides, Minor oxides, EDXRF, Turkey.

I. INTRODUCTION

Bentonite formed by the chemical decomposition of volcanic ash in aqueous environments is a clay rock mainly composed of montmorillonite from the smectite group [1-2]. Bentonite is a soft, malleable, fine-grained, porous, light-colored soft clay rock [1]. The geological properties of bentonite vary from region to region, depending on whether it is composed of calcium (Ca), sodium (Na), and Ca-Na montmorillonite. Bentonites generally occur in two main varieties: the most widely available calcium (Ca) or non-swelling bentonite and the more industrially important sodium (Na) bentonite or swelling bentonite [3]. The world's most important bentonite reserves are located in China, the United States, India, Turkey, Russia, Greece, Germany, Japan, Italy, Spain, and England. Turkey has approximately 20% of the world's bentonite reserves of 370 million metric tons (Mt) [1]. Turkey was the fourth largest producer with 1.5 Mt of bentonite after China, America, and India as of 2019 [4]. Bentonites are utilized in a variety of applications in different industries (petroleum, paint, cat litter, rubber, food, ceramics, paper, plastics, pharmaceuticals, etc.) such as foundry processes, drilling, iron ore pelletization, filtering, adsorbents, civil engineering, clarifying and decolorizing due to their important chemical and physical properties, small crystal size, chemical composition, swelling behavior and hydration [5].

II. RELATED WORK

In the last decade, many studies were performed on the geological, mineralogical, and geochemical properties of some bentonite samples collected from quarries in Turkey and other countries for different industrial applications [6-24]. However, with respect to our literature survey, there is no detailed research related to determining the chemical compositions of Turkish bentonites or bentonite quarries. Yıldız and Çalımlı [6] determined the concentrations major and minor oxides of 3 bentonite samples from Çankırı and Kütahya provinces. Karakaya et al. [7] determined the concentrations of elements in 14 sodium and calcium bentonite samples from Ordu province. Çoban [11] determined the mineralogical and chemical properties of 15 bentonite samples from Balıkesir (Bigadiç) province. The objective of this study is to complete this lack of information in the literature by determining the major and minor element distributions of Turkish bentonites used in the construction, drilling, packaging, and foundry industry in Turkey and exported to European countries. In this study, the concentrations of major (K_2O, Na_2O, MgO, Fe_2O_3, CaO, Al_2O_3, and SiO_2) and minor (MnO, P_2O_5, SO_3, and TiO_2) in 98 bentonite samples collected from 23 quarries located in different geographical regions of Turkey were determined by using an energy dispersive X-ray fluorescence (EDXRF) spectroscopy.

III. METHODOLOGY

A total of 98 bentonite samples were obtained from 23 bentonite quarries (BQs) located in Ankara, Çankırı, Çorum, Edirne, Konya, Ordu, Trabzon, and Tokat provinces of Turkey (Table 1). The bentonite samples were carried to the laboratory of sample preparation and dried in a temperature–controlled furnace at 110 °C for 10 h to remove moisture. Then, the samples were crushed and pulverized to get the calibrated powder geometry and five grams of each bentonite sample were analyzed [25].

Table 1. Information on bentonite quarries

Quarry Code	Quarry Number	Location (Province/Region)	Bentonite type
BQ-1	5	Çankırı/Central Anatolia	Na-bentonite
BQ-2	1	Ankara/Central Anatolia	Na-bentonite
BQ-3	3	Konya/Central Anatolia	Ca-bentonite
BQ-4	2	Trabzon/Black Sea	Ca-bentonite
BQ-5	4	Ordu/Black sea	Ca-bentonite
BQ-6	3	Tokat/Black Sea	Na-bentonite
BQ-7	3	Edirne/Marmara	Ca-bentonite
BQ-8	2	Çorum/Black Sea	Na-bentonite

Analysis of concentrations of the oxides in the bentonite samples was conducted by EDXRF spectroscopy (Spectro Xepos) supplied with an X-ray tube (50 kV, 60 W). Detailed information on the EDXRF spectroscopy was presented in the research conducted by Turhan et al. [26]..

IV. RESULTS AND DISCUSSION

Some descriptive statistical data such as mean, standard error (SE), standard deviation (SD), median, etc. on the concentrations of major and minor oxides analyzed in all bentonite samples are presented in Tables 2 and 3. The mean and range (min-max) values of major and minor oxides analyzed in bentonite quarries are given in Tables 4 and 5, respectively. A comparison of mean concentrations of major and minor oxides analyzed in Turkish bentonites with Earth's continental crust is shown in Figure 1. The oxides analyzed in bentonite samples are as follows according to their mean concentrations: $MnO < P_2O_5 < SO_3 < TiO_2 < K_2O < Na_2O < MgO < Fe_2O_3 < CaO < Al_2O_3 < SiO_2$.

Table 2. Some descriptive statistical data on the concentrations of major oxides in Turkish bentonites

	Concentration (%)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O
Mean	54.12	15.24	4.65	4.36	3.25	2.78	1.40
SE	1.00	0.44	0.44	0.23	0.17	0.19	0.07
Median	52.97	14.03	3.12	4.53	2.99	2.60	1.33
SD	9.91	4.33	4.31	2.26	1.67	1.87	0.73
Kurtosis	0.35	-0.17	11.63	-0.71	8.08	-0.47	-0.52
Skewness	0.55	0.62	2.85	0.13	2.20	0.62	0.49
Min	32.05	6.86	0.61	0.51	0.99	0.32	0.30
Max	80.63	28.87	29.23	10.03	12.00	7.80	3.47
N	98	98	98	98	98	98	98

SE: standard error, SD: standard deviation

Table 3. Some descriptive statistical data on the concentrations of minor oxides in Turkish bentonites

	Concentration (%)			
	TiO_2	SO_3	P_2O_5	MnO
Mean	0.58	0.35	0.20	0.10
SE	0.03	0.09	0.02	0.01
Median	0.59	0.05	0.15	0.08
SD	0.34	0.93	0.24	0.13
Kurtosis	-0.33	27.45	45.46	51.92
Skewness	0.38	4.89	5.84	6.37
Min	0.07	0.001	0.02	0.01
Max	1.60	6.67	2.18	1.22
N	98	98	98	98

Table 4. The distributions of major oxides analyzed in bentonite quarries

		The concentration of major oxides (%)						
		SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O
BQ-1	Mean	54.4	16.3	3.5	3.4	5.9	1.6	4.2
	Range	41.0-72.2	11.5-21.4	1.3-7.4	1.4-6.2	2.2-10.0	0.3-2.7	0.7-7.8
BQ-2	Mean	49.8	14.5	5.3	4.1	5.6	0.9	4.0
	Range	32.1-66.9	9.1-21.0	1.3-10.9	2.8-5.5	3.8-7.3	0.6-1.4	2.1-6.2
BQ-3	Mean	50.4	20.2	7.2	4.3	5.3	1.7	1.5
	Range	40.5-63.1	10.6-23.2	1.4-20.7	1.0-12.0	4.3-6.5	1.2-2.6	0.6-3.0
BQ-4	Mean	55.4	19.8	1.8	3.9	3.5	2.0	1.5
	Range	46.6-68.1	14.2-28.9	1.4-2.1	2.8-5.6	2.1-5.9	1.2-2.5	0.7-2.0
BQ-5	Mean	61.1	12.1	2.8	2.2	1.2	1.0	1.3
	Range	44.3-79.3	8.2-17.8	0.6-11.6	1.4-3.2	0.5-1.8	0.3-2.9	0.3-4.1
BQ-6	Mean	51.4	15.8	8.5	2.6	3.6	1.4	4.2
	Range	41.4-64.4	8.20.-23.8	2.3-29.2	1.4-4.4	2.7-5.0	0.8-3.5	1.9-6.1
BQ-7	Mean	54.2	16.6	3.7	3.6	4.4	1.7	1.4
	Range	45.3-65.7	11.8-23.5	0.7-8.1	1.8-8.8	1.8-6.2	0.4-3.1	0.4-3.2
BQ-8	Mean	48.3	13.0	7.1	3.6	6.1	1.3	3.3
	Range	35.9-80.6	6.9-21.5	3.0-15.7	1.2-8.4	3.0-9.4	0.5-2.3	1.2-6.3

Table 5. The distributions of minor oxides analyzed in bentonite quarries

		The concentration of minor oxides (%)			
		P_2O_5	SO_3	TiO_2	MnO
BQ-1	Mean	0.23	0.12	0.85	0.10
	Range	0.08-0.58	0.01-0.75	0.32-1.28	0.01-0.26
BQ-2	Mean	0.11	0.66	0.78	0.15
	Range	0.07-0.18	0.29-1.04	0.43-0.97	0.02-0.37
BQ-3	Mean	0.62	1.30	0.63	0.26
	Range	0.15-2.18	0.07-5.03	0.44-0.86	0.03-1.22
BQ-4	Mean	0.10	2.23	0.46	0.06
	Range	0.04-0.13	0.01-6.67	0.26-0.75	0.02-0.09
BQ-5	Mean	0.04	0.04	0.15	0.07
	Range	0.02-0.19	0.001-0.570	0.07-0.23	0.02-0.25
BQ-6	Mean	0.20	0.16	0.34	0.11
	Range	0.15-0.26	0.03-0.89	0.27-0.44	0.03-0.15
BQ-7	Mean	0.20	0.06	0.61	0.10
	Range	0.04-0.43	0.002-0.330	0.21-0.99	0.02-0.19
BQ-8	Mean	0.27	0.77	0.81	0.09
	Range	0.07-0.68	0.01-2.73	0.46-1.60	0.03-0.22

From Table 2, the SiO_2 concentrations in Turkish bentonites ranged from 32.05 to 80.63% with a mean of 54.12%. As shown in Figure 1, the mean SiO_2 concentration is very close to the Earth's continental crust (ECC) mean of 54.55% [27]. This mean SiO_2 concentration is smaller than the mean values of 68%, 65% and 58% measured in Kütahya, Ordu and Balıkesir bentonites respectively [6-7,11], while it is bigger than the mean of 53% measured in Çankırı bentonite [6]. From Table 4, the highest SiO_2 concentration was analyzed in the BQ-8. The mean SiO_2 concentrations in bentonite quarries are summarized in descending order as follows: BQ-5 (61.13%) > BQ-4 (55.41%) > BQ-1 (54.35%) > BQ-7 (54.18%) > BQ-6 (51.39%) > BQ-3 (50.39%) > BQ-2 (49.84%) > BQ-8 (48.27%).

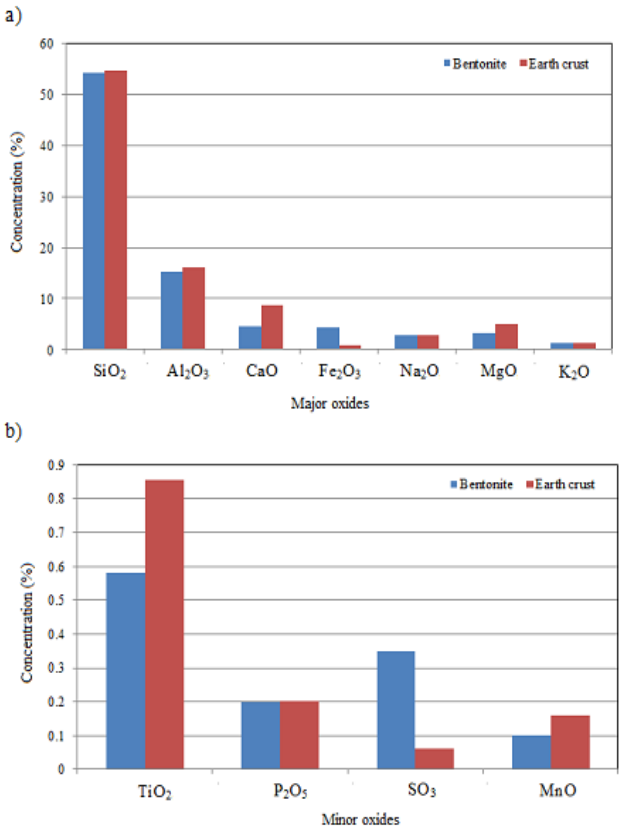

Figure 1. Comparison of mean concentrations of major (a) and minor (b) in Turkish bentonites with Earth's continental crust

The Al_2O_3 concentrations in Turkish bentonites ranged from 6.86 to 28.87% with a mean of 15.24%. The mean Al_2O_3 concentration is smaller than the ECC mean of 16.17% [27]. This mean Al_2O_3 concentration is bigger than the mean values of 12%, 14% and 14% measured in Çankırı, Kütahya and Ordu bentonites respectively [6-7], while it is smaller than the mean value of 16% measured in Balıkesir bentonite [11]. From Table 4, the highest Al_2O_3 concentration was analyzed in the BQ-4. The mean Al_2O_3 concentrations in bentonite quarries are summarized in descending order as follows: BQ-3 (20.19%) > BQ-4 (19.77%) > BQ-7 (16.55%) > BQ-1 (16.26%) > BQ-6 (15.82%) > BQ-2 (14.45%) > BQ-8 (13.00%) > BQ-5 (12.09%).

The CaO concentrations in Turkish bentonites ranged from 0.61 to 29.23% with a mean of 4.65%. The mean CaO concentration is approximately 2 times smaller than the ECC mean of 8.72% [27]. This mean CaO concentration is bigger than the mean values of 3%, 2% and 2% measured in Kütahya, Ordu and Balıkesir bentonites respectively [6-7,11], while it is smaller than the mean value of 7% measured in Çankırı bentonite [6]. From Table 4, the highest CaO concentration was analyzed in the BQ-6. The mean CaO concentrations in bentonite quarries are summarized in descending order as follows: BQ-6 (8.47%) > BQ-3 (7.11%) > BQ-8 (7.07%) > BQ-2 (5.26%) > BQ-7 (3.73%) > BQ-1 (3.49%) > BQ-5 (2.76%) > BQ-4 (1.81%).

The Fe_2O_3 concentrations in Turkish bentonites ranged from 0.51 to 10.03% with a mean of 4.36%. The mean Fe_2O_3 concentration is significantly bigger than the ECC mean of 0.92% [27]. This mean Fe_2O_3 concentration is bigger than the mean values of 3%, 1%, 2% and 1% measured in Çankırı, Kütahya, Ordu and Balıkesir bentonites respectively [6-7,11]. From Table 4, the highest Fe_2O_3 concentration was analyzed in the BQ-1. The mean Fe_2O_3 concentrations in bentonite quarries are summarized in descending order as follows: BQ-8 (6.05%) > BQ-1 (5.94%) > BQ-2 (5.63%) > BQ-3 (5.33%) > BQ-7 (4.43%) > BQ-6 (3.60%) > BQ-4 (3.54%) > BQ-5 (1.22%).

The MgO concentrations in Turkish bentonites ranged from 0.99 to 12.00% with a mean of 3.25%. The mean MgO concentration is smaller than the ECC mean of 4.91% [27]. This mean MgO concentration is bigger than the mean values of 4%, 1% and 3% measured in Çankırı, Kütahya, and Ordu bentonites respectively [6-7], while it is very close to the mean concentration of 4.7% measured in Balıkesir bentonite [11]. From Table 4, the highest MgO concentration was analyzed in the BQ-3. The mean MgO concentrations in bentonite quarries are summarized in descending order as follows: BQ-3 (4.27%) > BQ-2 (4.05%) > BQ-4 (3.88%) > BQ-8 (3.61%) > BQ-7 (3.58%) > BQ-1 (3.42%) > BQ-6 (2.64%) > BQ-5 (2.23%).

The Na_2O concentrations in Turkish bentonites ranged from 0.32 to 7.80% with a mean of 2.78%. The mean concentration of Na_2O is the same as the ECC mean value of 2.74% [27]. This mean Na_2O concentration is bigger than the mean values of 2%, 1%, 1% and 0.2% measured in Çankırı, Kütahya, Ordu and Balıkesir bentonites respectively [6-7,11]. From Table 4, the highest Na_2O concentration was analyzed in the BQ-1. The mean Na_2O concentrations in bentonite quarries are summarized in descending order as follows: BQ-6 (4.17%) > BQ-1 (4.15%) > BQ-2 (3.95%) > BQ-8 (3.26%) > BQ-4 (1.50%) > BQ-3 (1.48%) > BQ-7 (1.44%) > BQ-5 (1.25%).

The K_2O concentrations in Turkish bentonites ranged from 0.30 to 3.47% with a mean of 1.40%. The mean K_2O concentration is slightly bigger than the ECC mean of 1.32% [27]. This mean K_2O concentration is bigger than the mean values of 0.2%, 1% and 1% measured in Çankırı, Ordu and Balıkesir bentonites respectively [6-7,11], while it is smaller than the mean value of 2% measured in Kütahya bentonite [6]. From Table 4, the highest K_2O concentration was analyzed in the BQ-6. The mean K_2O concentrations in bentonite quarries are summarized in descending order as follows: BQ-4 (1.99%) > BQ-7 (1.74%) > BQ-3 (1.72%) > BQ-1 (1.60%) > BQ-6 (1.35%) > BQ-8 (1.26%) > BQ-5 (1.00%) > BQ-2 (0.88%).

From Table 3, the TiO_2 concentrations in Turkish bentonites ranged from 0.07 to 1.60% with a mean of 0.58%. The mean TiO_2 concentration is smaller than the ECC mean of 0.86% [27]. This mean TiO_2 concentration is bigger than the mean values of 0.1%, 0.1%, 0.2% and 0.1% measured in Çankırı, Kütahya, Ordu and Balıkesir

bentonites respectively [6-7,11]. From Table 5, the highest TiO_2 concentration was analyzed in the BQ-8. The mean TiO_2 concentrations in bentonite quarries are summarized in descending order as follows: BQ-1 (0.85%) > BQ-8 (0.81%) > BQ-2 (0.78%) > BQ-3 (0.63%) > BQ-7 (0.61%) > BQ-4 (0.46%) > BQ-6 (0.34%) > BQ-5 (0.15%).

The SO_3 concentrations in Turkish bentonites ranged from 0.001 to 6.67% with a mean of 0.35%. The mean SO_3concentration is bigger than the ECC mean of 0.06% [27]. From Table 5, the highest SO_3 concentration was analyzed in the BQ-3. The mean SO_3 concentrations in bentonite quarries are summarized in descending order as follows: BQ-4 (2.23%) > BQ-3 (1.30%) > BQ-8 (0.77%) > BQ-2 (0.66%) > BQ-6 (0.16%) > BQ-1 (0.12%) > BQ-7 (0.06%) > BQ-5 (0.04%).

The P_2O_5 concentrations in Turkish bentonites ranged from 0.02 to 2.18% with a mean of 0.20%. The mean P_2O_5 concentration is the same as the ECC mean of 0.20% [27]. From Table 5, the highest P_2O_5 concentration was analyzed in the BQ-3. The mean P_2O_5 concentrations in bentonite quarries are summarized in descending order as follows: BQ-3 (0.62%) > BQ-8 (0.27%) > BQ-1 (0.23%) > BQ-6 (0.21%) > BQ-7 (0.20%) > BQ-2 (0.11%) > BQ-4 (0.10%) > BQ-5 (0.04%).

The MnO concentrations in Turkish bentonites ranged from 0.01 to 1.22% with a mean of 0.10%. The mean MnO concentration is below the ECC mean of 0.16% [27]. From Table 5, the highest MnO concentration was analyzed in the BQ-3. The mean MnO concentrations in bentonite quarries are summarized in descending order as follows: BQ-3 (0.26%) > BQ-2 (0.15%) > BQ-6 (0.11%) > BQ-7 (0.10%) > BQ-1 (0.09%) > BQ-8 (0.08%) > BQ-5 (0.07%) > BQ-4 (0.06%).

V. CONCLUSION AND FUTURE SCOPE

This study is the first detailed research on the distributions of major and minor oxides of bentonite quarries in Turkey. Seven major oxides major (K_2O, Na_2O, MgO, Fe_2O_3, CaO, Al_2O_3, and SiO_2) and four minor (MnO, P_2O_5, SO_3, and TiO_2) oxides in a total of ninety-eight bentonite samples collected from twenty-three quarries located in different geographical regions of Turkey were analyzed using the EDXRF spectrometer. The lowest mean concentrations of Al_2O_3, Fe_2O_3, MgO, Na_2O, TiO_2, SO_3, and P_2O_5 were analyzed in BQ-5 located in Ordu province.

The data obtained as a result of this study can be used in the efficient evaluation of Turkish bentonites in different areas both in Turkey and in European countries where bentonite is exported.

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