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HALLOYSITE INTERCALATION OF NORTHWEST ANATOLIA

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Intercalation, Halloysite, Kaolinite, Dimethyl Sulfoxide, Formamide.

ABSTRACT

In this study, the representative samples were taken from the halloysite deposits located in Çanakkale-Balıkesir regions, in NW Anatolia. At first, the dehydration temperatures of the samples were determined after sample preparation and characterization studies. It was found that halloysite samples began to lose their interlayer waters at 50°C and continued up to 70°C. The intercalation studies were carried out on dehydrated samples by using ethylene glycol, potassium acetate, dimethyl sulfoxide and formamide. Although there were negative results by ethylene glycol and potassium acetate, the satisfactory results were obtained by dimethyl sulfoxide and formamide. It was understood that the most effective reagent in terms of intercalation was formamide.

1. Introduction

Double layered (1:1) halloysite mineral, which is formed by the disintegration of aluminum silicate minerals, is generally associated with kaolinite. The chemical formula of its dehydrated structure is the same with that of kaolinite ($Al_2Si_2O_5(OH)_4$) and consists of nanometer sized tubes, in different prismatic shapes mainly the cylindrical type (Kirkman, 1981).

The halloysite mineral shows similar mineralogical and chemical characteristics with kaolinite, and it can absorb water molecules between its layers. This halloysite mineral is called as "halloysite (10 Å)" or "hydrated halloysite", and the layer distances are 10 Å as it contains water (Churchman and Carr, 1973). The ion exchange and reactivity etc. of the interlayer water in halloysite (10 Å) have important effects on the physical characteristics of the mineral (Jousssein et al., 2005). The distance between layers in halloysites, which lost their interlayer waters, is 7 Å and this value is the same as kaolinite. Actually; it is reported that this distance is 7.2 Å and the thickness of water molecules is 2.8 Å (Hiller and Ryan, 2002). Halloysites, which lost their interlayer waters, are named as "dehydrated" or "halloysite (7 Å)". In figure 1, the atomic structure for halloysite (7 Å) and (10Å) is given (Murray, 2007).

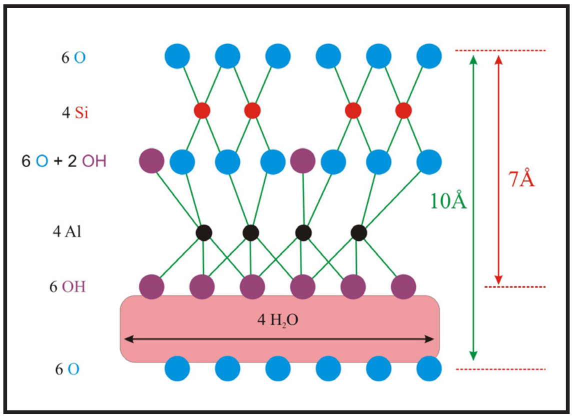

Figure 1- The atomic structure of halloysite (Murray, 2007).

When halloysite (10Å) structures are heated above low temperatures such as 35-40°C, they irreversibly lose their interlayer waters. It is also stated that the dehydration temperature depends on factors such as; the relative humidity (air) of the environment and the ore mineralogy-geology (Churchman et al.,

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1972). It was also pointed out that, samples in high relative humid environments could preserve their interlayer waters at higher temperatures. In other words; the relative humidity of the environment in which samples are preserved is important rather than the temperature in dehydration process (Harrison and Greenberg, 1962; Joussein et al., 2006). Such that, the dehydration begins under relative humidity conditions below 70%; therefore, the halloysite should carefully be stored.

The intercalation means, "intervene" or "forming a complex", and it is used as the intake of other atoms into crystal structure (cage) in mineralogy. Active guest molecules, during halloysite intercalation, destruct hydrogen bonds and enter layers of which waters have extruded. Thus, the interlayer distance again increases from 7Å to 10 Å (Horvarth et al., 2011). So, it is easily separated from kaolinite in XRD analysis.

The XRD patern of a halloysite mineral, between 5-15°, for 10 Å and 7 Å forms, which was taken from a halloysite mine in Balıkesir-Gönen region, is given in figure 2 (Başara et al., 2013). Dehydrated halloysites have the same basal peak with that of kaolinite in XRD analysis. Therefore, the intercalation method is necessary in order to distinguish them.

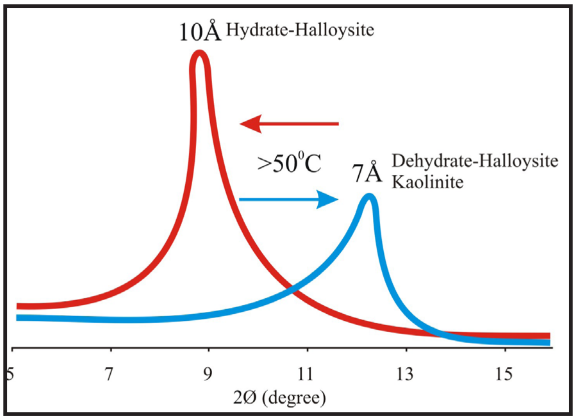

Figure 2- Basal XRD patern of both hydrated and dehydrated halloysite (Başara et al., 2013).

Many studies have been carried out on halloysite intercalation, and the fastest and effective intercalation reactive has been searched. The formamide is the first reactive which transform dehydrated halloysites into hydrated halloysites (Churchman and Theng, 1984; Churchman et al., 1984; Churchman, 1990). The usability of other reactives such as; dimethyl sulfoxide, potassium acetate, hydrazine, urea have also been investigated (Wada, 1961, Churchman and Carr, 1973; Mellouk, et al., 2009; Nicolini, et al., 2009; Horvath, et al., 2011).

It was effectively observed that, the use of formamide in intercalation is effective for naturally dehydrated halloysites which show different mineralogy and formation. However, successful results could not be taken by formamide in halloysites which were dried in ovens above 110°C. Moreover; it was stated that formamide had not been effective at all in some cases (Joussein et al., 2007).

In this study, the intercalation experiments were performed on representative samples taken from halloysite deposits which are traded and form in NW Anatolia in the country. Relative humid loss temperatures of samples, reactive of intercalation and the method were established. The results obtained by the intercalation method were used in the investigation of halloysite/kaolinite association in samples, and the sample description was carried out by XRF analysis.

2. Northwest Anatolian Halloysite Deposits

The economical halloysite deposits of Turkey are located in northwest, especially in Balıkesir – Çanakkale region (Saklar et al., 2011). The northwest Anatolian halloysite deposits are observed in the form of NE-SW extending tectonic zones (Duru et al., 2007; Duru et al., 2012). It is pointed out that, Halloysite formations are occur in Tertiary volcanic units (Ilgar et al., 2012). However, Uygun (2012) suggested that, halloysite deposits in the region had occasionally been emplaced into partly faulty contacts between Jurassic dolomitic limestones and andesitic volcanics. He also stated that, these deposits had been formed due to the effect of acidic volcanics such as; latite and rhyodasite or hypogenic hydrothermal melts. It is also emphasized that, halloysites were formed as a result of hydrothermal effects related with fault zones in low pH environments (2-3) due to dissolution-precipitation mechanism of andesitic tuffs (Akçay, et al., 2008; Dönmez et al., 2008; Erdoğan et al., 2012). Similar suggestions were also stated by other investigators saying that, NW Anatolian halloysite deposits were hydrothermally formed by low pH, silica and aluminum rich solutions (Laçin and Yeniyol, 2006; Ece and Schroeder, 2007).

New Zealand is the leader country in the production of halloysite, and the source of its deposits are hydrothermal which is similar to that of Turkey (Christie, et al., 2000; Murray, 2007; Christie, et al., 2011).

3. Material and Method

Halloysite deposits, in which representative samples were used, are respectively Balıkesir-Gönen-Alacaoluk limonitized halloysite deposit (BGL), Balıkesir-Gönen-Alacaoluk pyritized halloysite deposit (BGP), Çanakkale-Yenice-Soğucak halloysite deposit (HAL) and Çanakkale-Yenice-Kırıklar (ALCL) halloysite deposit.

The chemical analyses were performed by Philips Axios XRF Spectrometer by making fire loss under 1050°C. XRD analyses were performed by Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation, between 2-70° 2θ intervals, 40kV voltage and 40 mA current. In order to make more detailed reading in studies for intercalation, the XRD analysis was carried out between 1°/d, 5-30° goniometer velocity.

In order to perform XRD analyses of clay contents of pulverized samples more sensitive, the parts of raw materials thinner than 2 μm were obtained by decantation method using Stokes equation, and the oriented clay fraction samples were prepared (Wills and Napier-Munn, 2006).

In order to detect the dehydration temperature, samples were kept 1 hour under temperatures of 40°C, 50°C, 60°C, 70°C, 80°C and 100°C. Later on, samples dried under 100°C were used in intercalation experiments.

Merck brand glycol ($C_2H_6O_2$), potassium acetate (CH_3COOK), dimethyl sulfoxide ($(CH_3)_2SO$) and formamide (CH_3NO) were used in intercalation experiments. Ethylene-glycol samples were prepared by keeping them 2 hours under 70°C temperature in a desiccator in which there is lethylene-glycol in it. Potassium acetate, which is available in powder form, were heated and dissolved in pure water, then applied on samples nearly 10 seconds from a 20 cm distance by using a spray gun. However, formamide and dimethyl sulfoxide were directly sprayed on samples, because they were in liquid phase. As formamide is more poisonous compared to other agents, the experiments were carried out under fume cupboard. The XRD analyses for dimethyl sulfoxide and others were carried out resting them 3 and 1 hour, respectively after spraying.

4. Findings

The chemical compositions of samples (Table 1) indicate that, SiO_2, Al_2O_3 and fire loss ratios are close to each other and are in high quality when compared with exported products (Saklar et al., 2012). Iron amounts are few in BGL and BGS samples; however, there is SO_3 amount higher than 1% in BGP, and these originate from limonite, pyrite and alunite (Saklar et al., 2011). Although; XRF analyses were performed in the same region with the study of Saklar (2011) in some samples (BGP, ALCL), there are small differences between the previous study and the results of the analysis since samples used were collected from different locations of deposits.

Table 1- Chemical compositions of halloysite samples (%).

Sample	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	P_2O_5	CaO	TiO_2	MnO	Fe_2O_3	SO_3	*F.L.
ALCL	47.8	35.5	<0.1	<0.1	0.1	0.3	0.1	<0.1	<0.1	0.6	0.11	15.35
BGL	46.7	35.0	<0.1	0.3	0.2	<0.1	<0.1	0.1	<0.1	1.6	0.14	14.75
HAL	47.3	35.9	<0.1	<0.1	0.1	0.6	<0.1	0.1	<0.1	0.2	0.31	15.20
BGP	45.1	34.7	<0.1	0.1	1.0	0.4	0.2	0.1	<0.1	1.0	1.17	15.95

*F.L: Fire Loss

XRD basal peak values of hydrated halloysite samples were published by Anthony et al. (1995). These are, respectively, 10,0 Å (100), 4,36 Å (70), 3,35 Å (40), 2,54 Å (35), 1,480 Å (30), 1,672 Å (14) and 1,281 Å (8). In figure 3, XRD results of unprocessed samples were given. In all samples, the halloysite peak is observed, and this peak in samples of BGP and ALCL is wider than samples HAL and BGL. Besides; 7 Å and 4.46 Å peaks showing the halloysite (7 Å) except for ALCL and 7 Å and 3.58 Å peak showing the kaolinite are observed in low intensities. Therefore; it can be considered that there is a few amount of kaolinite in samples except for ALCL.

In figures 4, 5, 6, 7, 8 and 9; XRD diffractograms of raw samples heated under 40°C, 50°C, 60°C, 70°C, 80°C and 100°C are given. When studying these graphics, there was not observed any change in samples at 40°C. However; it was seen that, hydrated halloysites lost most of their interlayer waters in samples BGL and HAL at 50°C, but there was not any change in other samples. At 60°C, it was observed that halloysites in samples ALCL and BGP began to lose their interlayer water; however, the halloysites in samples BGL and HAL had completely lost their interlayer water. It was detected that, halloysites in samples ALCL and BGP completely had lost their interlayer water at 70°C.

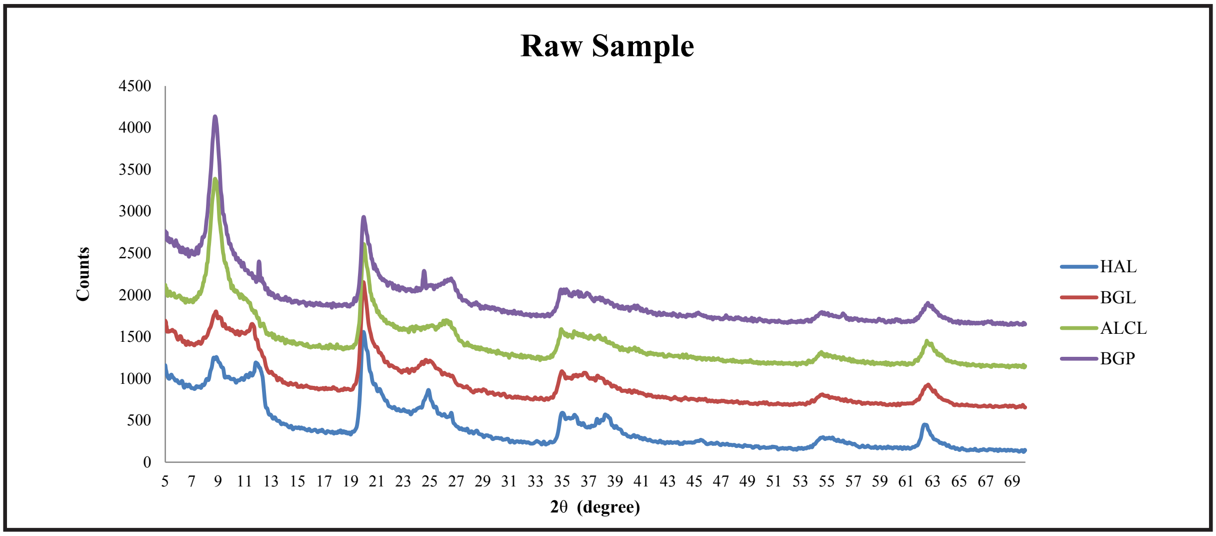

Figure 3- XRD diffractograms of raw samples.

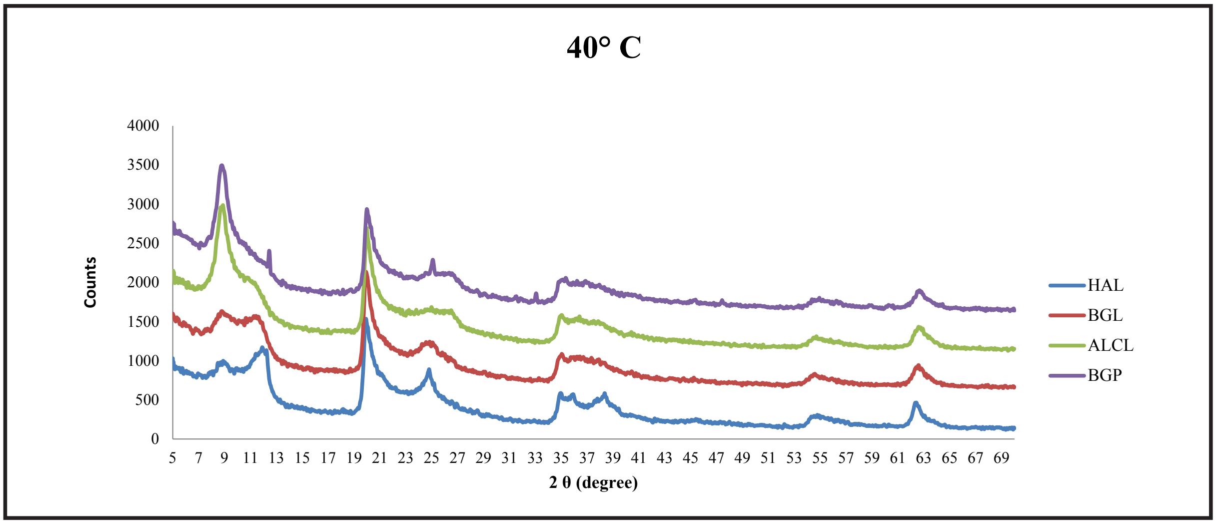

Figure 4- XRD diffractograms of raw halloysite samples heated up to 40°C.

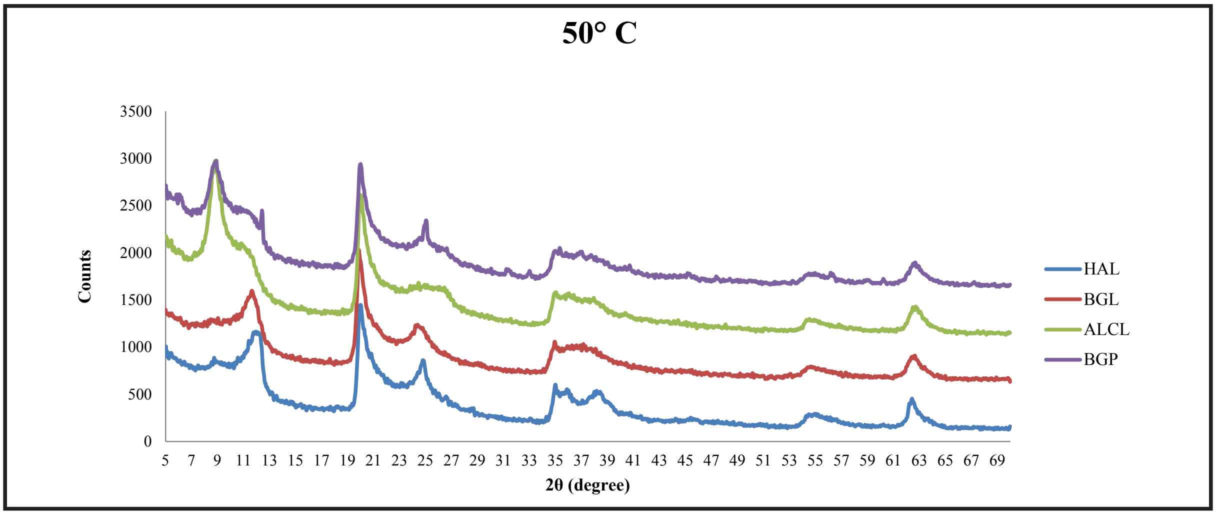

Figure 5- XRD diffractograms of raw halloysite samples heated up to 50°C.

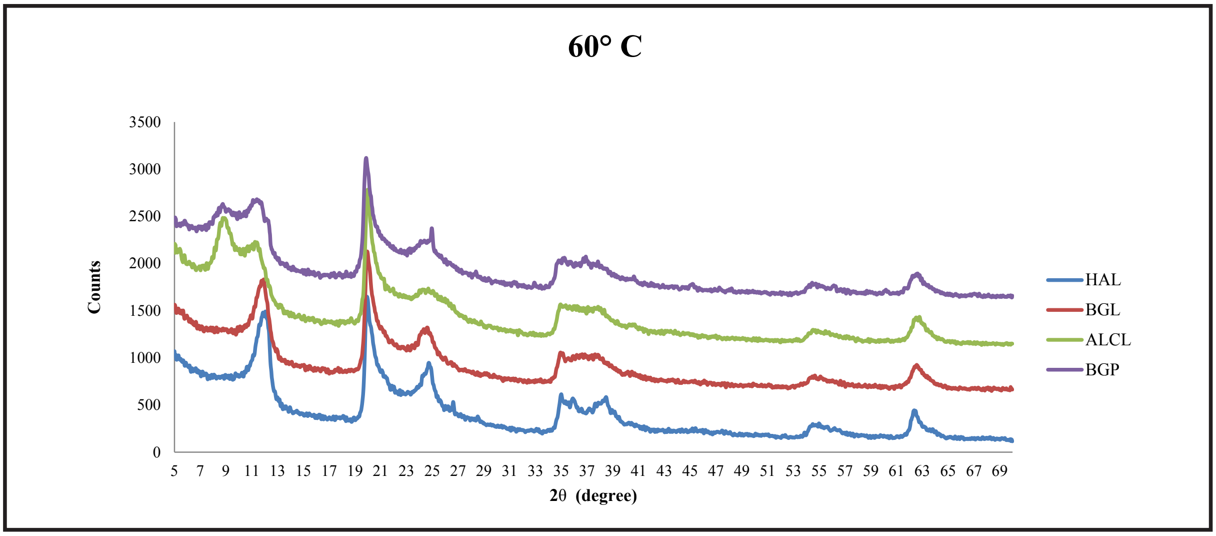

Figure 6- XRD diffractograms of raw halloysite samples heated up to 60°C.

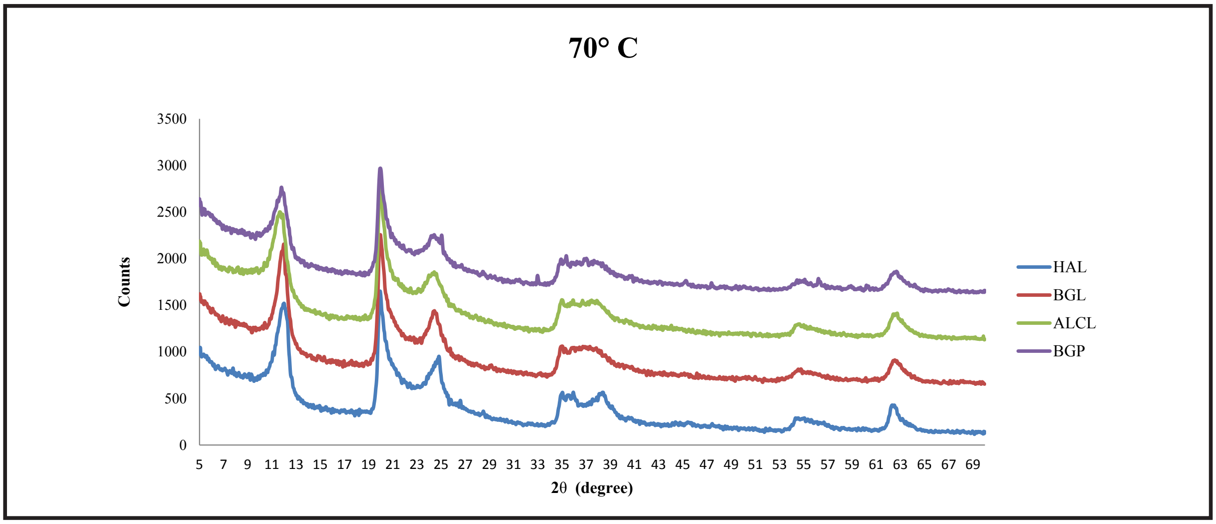

Figure 7- XRD diffractograms of raw halloysite samples heated up to 70°C.

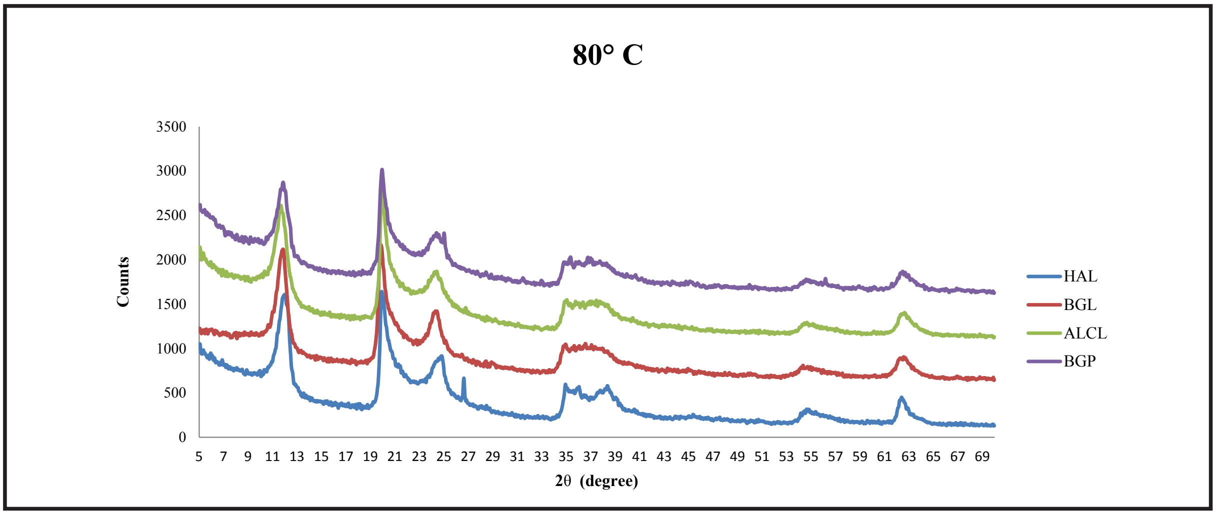

Figure 8- XRD diffractograms of raw halloysite samples heated up to 80°C.

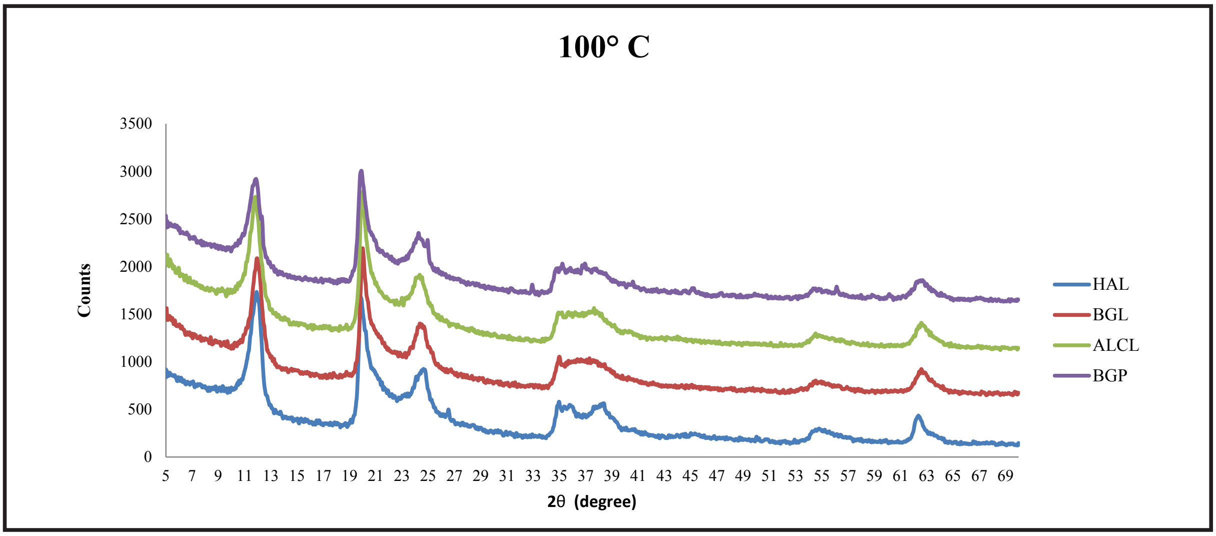

Figure 9- XRD diffractograms of raw halloysite samples heated up to 100°C.

In order to observe any change that might occur, the experiments were performed at 80°C and 100°C too, but there were not observed any change in XRD diffractograms. As a result of these analyses, halloysites in samples HAL and BGP, which had been collected from the study area, transformed into 7 Å (dehydrated) halloysite completely losing their water between 50-60°C. However; the halloysites in samples BGP and ALCL turned into 7Å (dehydrated) halloysites losing their water at 60-70°C. Results show that, halloysite minerals will not lose their interlayer water as long as they will be kept under normal room conditions. It is considered that, this is due to relative humidity ratios of the environment in which samples are present.

Halloysite (7Å) samples were used for intercalation experiments, and the result of analyses by ethylene-glycol treatment is given in figure 10. The vapor of ethylene-glycol, which can widen the interatomic distance by entering into bodies of smectite group clay minerals, were not successful in (7Å) halloysite samples, and there was not observed any change in XRD diffractograms. The similar result was also obtained for potassium acetate, and it was seen that this reactive was not effective for intercalation neither (Figure 11).

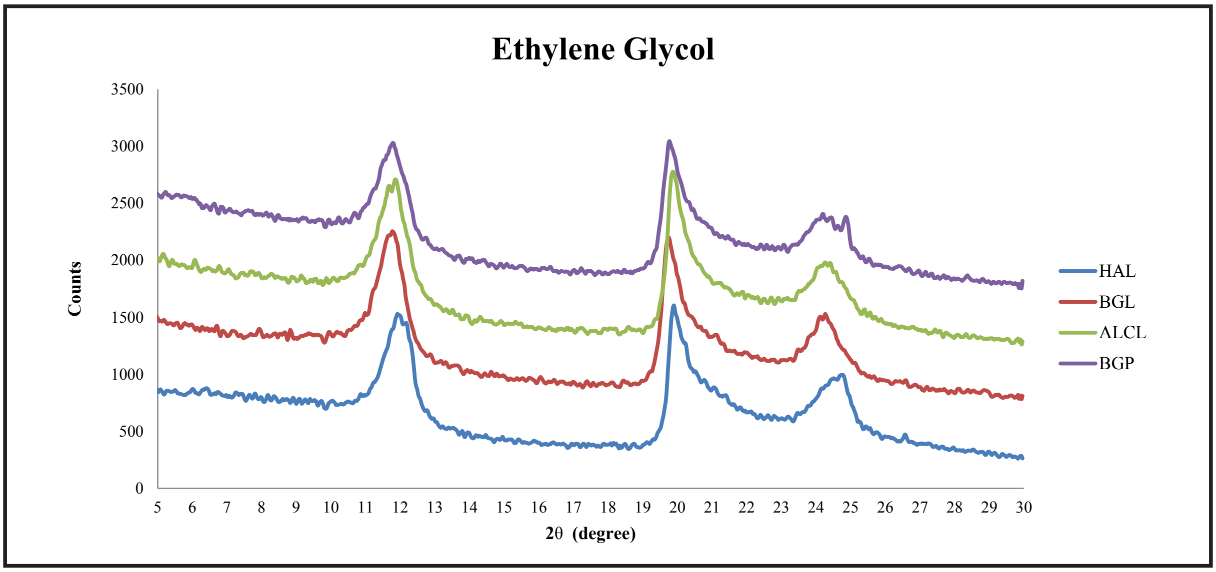

Figure 10- XRD diffractograms of halloysite samples (7Å) performed by ethylene-glycol.

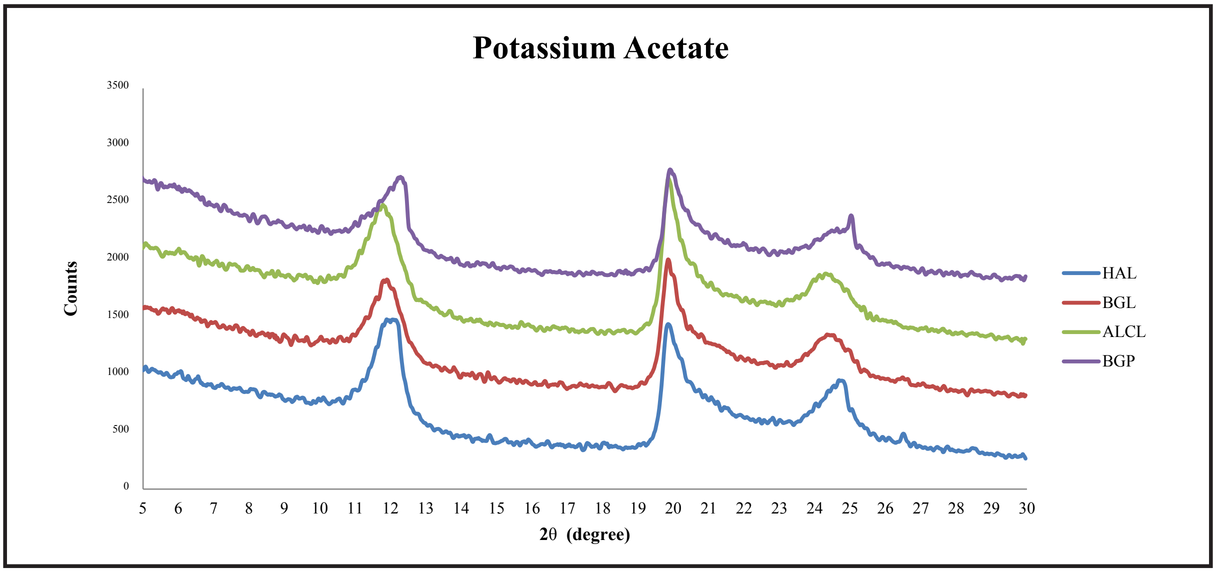

Figure 11- XRD diffractograms of halloysite samples (7Å) performed by potassium acetate.

Results obtained for dimethyl sulfoxide are given in figure 12. As seen, dimethyl sulfoxide intervene halloysite layers though partly and increases interlayer distance. In order to get the best result from the intercalation experiment using this reactive, it is necessary to wait more than 1 hour. When waited 3 hours after spraying, it was seen that halloysites (7Å) formed halloysite/dimethyl sulfoxide intercalate complex. (7Å) structure completely disappears in BGL and ALCL samples; however, it partly stops in samples BGP and HAL. So, more standby duration should be made after dimethyl sulfoxide treatment.

Results of the intercalation experiment for formamide is seen in Figure 13. In all of the dehydrated halloysites available in samples, the halloysite/formamide intercalation occurred. In other words, it was detected that, 7Å peaks had disappeared and 10 Å peaks had been formed again. This result indicates that the most effective reactive used for intercalation among the others is formamide.

The other result is that all reflections around 7 Å increase to around 10 Å. Samples (HAL, BGL, ALCL and BGP) used in tests fully contained 7 Å and 10 Å halloysites.

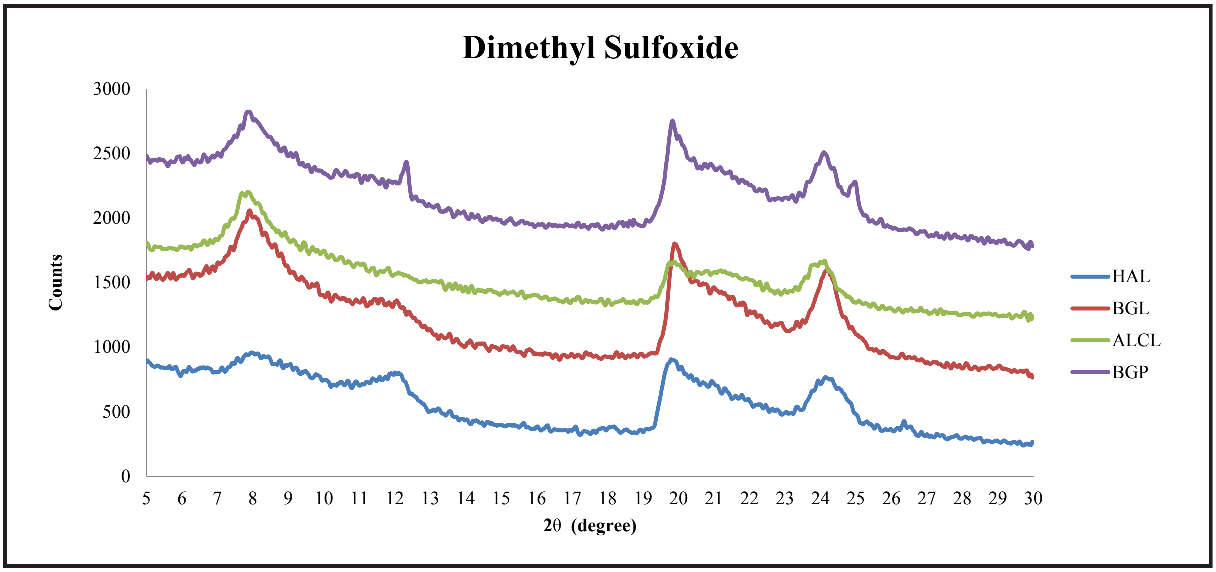

Figure 12- XRD diffractograms of 7Å halloysite samples treated by dimethyl sulfoxide.

5. Discussion and Results

Fire assay tests performed on samples taken in NW Anatolia region showed that these should be subjected to temperatures of 50°C or more for halloysite 10 Å structures to transform into 7 Å. This transformation is fully completed at 70°C. In conditions when halloysite minerals, which will be quarried from deposits in the region and stored, would be kept in room conditions (at temperatures below 50°C) and in less relative humidity ratios, hydrate halloysites might preserve their interlayer waters.

The transformation process from hydrate structure to dehydrate structure is irreversible under natural conditions. That is; halloysite minerals, which lose their waters at temperatures of 50°C or more, cannot retake this atomic water into their bodies which they lost from humidity and other water sources.

The ethylene-glycol, which is used to distinguish clay minerals, was tested in halloysite minerals in intercalation, but there was not achieved any success. Similar results were also taken for potassium-acetate, but there was not detected any effect of intercalation. There was achieved a successful result by spraying dimethyl-sulfoxide and formamide chemicals. A full transformation from 7 Å to 10 Å was determined especially in all samples studied with formamide. Therefore; it was understood that, the formamide was an effective reactive also for NW Anatolian halloysite as being compatible with literature.

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