Applied Clay Science 42 (2009) 422–426

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Rheological properties of sepiolite ground in acid and alkaline media

M. Çınar [a,*], M.F. Can [b], E. Sabah [c], C. Karagüzel [a], M.S. Çelik [b]

[a] Dumlupinar University, Engineering Faculty, Mining Engineering Department, 43100 Kutahya, Turkey
[b] Mineral & Coal Processing Section, Istanbul Technical University, Maslak 80626, Istanbul, Turkey
[c] Afyon Kocatepe University, Engineering Faculty, Mining Engineering Department, 03200 Afyonkarahisar, Turkey

ARTICLE INFO

Article history:
Received 21 August 2007
Received in revised form 20 March 2008
Accepted 24 April 2008
Available online 3 May 2008

Keywords:
Sepiolite
Rheology
Viscosity
Acid-base treatment
Grinding

ABSTRACT

Effects of different acids (HCl, H_2SO_4 and citric acid) on rheological properties of brown sepiolite from the Eskisehir region of Turkey have been determined. The optimum apparent viscosity value was obtained at the natural pH of the suspension. Below the natural pH, partial collapse of the structure due to the release of Mg ions causes a significant decrease in viscosity values. However, below pH 1, there is a substantial increase in viscosity values owing to gel formation. On the other hand, above the natural pH of suspension, increased amounts of OH ions lead to a decrease in viscosity values and inhibit gel formation. The reversible nature of sepiolite was tested by changing the pH of acid and alkaline treated sepiolite suspensions back to its natural pH by washing with water and acid, respectively. In summary, from a practical point of view, there is no favorable effect of acid treatment of sepiolite on its rheological properties. On the contrary, reducing the pH to natural pH after grinding in a basic environment led to an improvement in rheological properties.

1. Introduction

Layer structured smectite, needle structured sepiolite, and palygorskite type clays are utilized in a variety of rheological applications (Santaren, 1993). The mechanism of gel formation for each clay mineral differs because of their unique structures. The layer composition and high ion exchange capacity are the main factors dictating the extent of gel formation in montmorillonite. Activation is usually done to change the clay without deforming its structure through chemical or physical processes. As has been previously proposed by Gonzales et al. (1988), the main objective of acid activation in sepiolite is to loosen fiber bundles in order to increase the mesoporosity. Acid activation leads to the dissolution of octahedral sheets with a resultant increase in micro porosity built up within the tetrahedral silicate sheets, but the mineral skeleton consisting of silanol groups is maintained (Inukai et al., 1994; Lazarević et al., 2007).

Silanol groups are developed by the acidic hydrolysis reactions leading to an increase in both surface area and pore volume and a concomitant increase in adsorption capacity (Jimenez-López et al., 1978; Aznar et al., 1996). However, increases in acid concentrations and treatment periods cause modifications of the silanol groups resulting in a decrease in adsorption capacity (Valentin et al., 2007; Valentin et al., 2006). Corma et al. (1987) applied acid activation using HCl on sepiolite and palygorskite and stated that acid activation affected mineral outer surfaces but acid could not penetrate into the channel structure. Different types of clays responded differently indicating that the amount of inaccessible pores has a greater effect on activation than the chemical composition of each mineral. Gonzales et al. (1988) focused on the two structurally different types in palygorskites; one rich in aluminum and the other rich in magnesium. Acid activation with different acid (HCl) concentrations revealed that the highest activation occurred with the magnesium rich palygorskites. Differences in the behavior of magnesium-rich sepiolite were ascribed to the concentration of Mg in the octahedral layer, viz. the smaller size of fibers and higher outer surface area (Corma et al., 1990). Acid activation at high acid concentrations typically resulted in amorphous silicate formation and the destruction of fiber structure (Barrios et al., 1995).

Sepiolite with its unique structure has a variety of applications in which rheological properties play a significant role (Sabah, 1998; Alvarez, 1984; Galan, 1996). The needle like fibers holding the bundles of sepiolite control not only the surface characteristics but also the rheological properties (Santaren, 1993; Simonton et al., 1988). The ability of sepiolite to give high viscosity values at low solid concentrations provides a major advantage over other clays (Mart et al., 2003).

The aim of this study is to determine the rheological properties of sepiolite, to identify its flow characteristics and to understand the mechanisms for its viscosity development in the absence and presence of acid and alkaline media.

2. Materials and methods

Run of mine brown sepiolite crushed to <5 mm produced by MAYAS Company in Eskisehir, Turkey, was used for the experiments. The chemical and mineralogical

* Corresponding author. Tel.: +90 274 2652031; fax: +90 2742652066.
E-mail address: mcinar@dumlupinar.edu.tr (M. Çınar).

0169-1317/$ – see front matter
doi:10.1016/j.clay.2008.04.010

Table 1
Chemical analysis of sepiolite sample

Sample	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	LOI %	Tot./ C %	Tot./ S %
Sepiolite	51.29	1.37	0.58	22.57	0.26	0.09	0.21	0.08	23.6	0.38	0.03

analyses of sepiolite used in this study are presented in Table 1 and Fig. 1 respectively. The chemical analysis was made by Inductively Coupled Plazma (ICP) in ACME laboratory of Canada. The mineralogical analysis was made by Shimadzu XRD-6000 equipped with Cu Ka X-rays. The X-ray Diffraction (XRD) analysis reveals that the sepiolite sample is composed of 90% sepiolite and 10% other minerals, basically of feldspar and quartz. The sepiolite sample was prepared at 3% by weight with distilled water at the desired pH value and then ground in a ceramic mill for 30 minutes. Gel formation in sepiolite suspensions was induced before the viscosity measurements. The viscosity measurement was performed by a Brookfield, RVDV-II model spinning disc programmable viscometer operated at constant speed. Two different methods were utilized. In the first method, suspensions of 3% by weight were prepared in 500 ml volume and then transferred to a 600 ml beaker in which viscosity measurements were conducted using RV1-2-3 spindles; these measurements are considered to be only apparent viscosity values. Mixing at high speed of 17,500 rpm for 10 minutes was observed to absorb heat and raise the temperature of the suspension to 35-40 °C. Thus all suspensions were cooled down at room temperature for 10 minutes until the temperature of the suspension was brought to 25±1 °C at which viscosity measurements were performed.

The second method involves the use of a small sample cell equipped with a SC-21 cylindero-conical shaped mill. The temperature of suspension was maintained at the desired temperature (25±1 °C) by a jacket which allows circulation of water around the cell. A volume of 8 ml suspension is sufficient to perform each test. In addition to apparent viscosities, in this set of measurements shear stress [Pa] and shear rate [s^{-1}] values are also recorded and thus each datum is analyzed in more detail. Since sepiolite suspensions exhibit a time dependent flow pattern of thixotropy, the viscosity measurements were recorded versus time for 30 minutes. For interpretation, the value at the 15th minute was selected according to the method presented elsewhere (Mart et al., 2003; Çınar et al., 2004).

In both methods, the ground material taken out of the mill was subjected to blending at 17,500 rpm for 10 minutes (Çınar et al., 2004) for viscosity measurements. Electrokinetic measurements were carried out using a Zeta Meter 3.0 equipped with microprocessor unit. This automatically calculates the electrophoretic mobility of particles and converts it to the zeta potential by a built-in microprocessor unit which uses the Smoluchowski equation (Hunter, 1988). Since the blended material was rather viscous, a centrifugation technique which has been described in detail for such relatively concentrated solutions (Sabah et al., 2007) was applied.

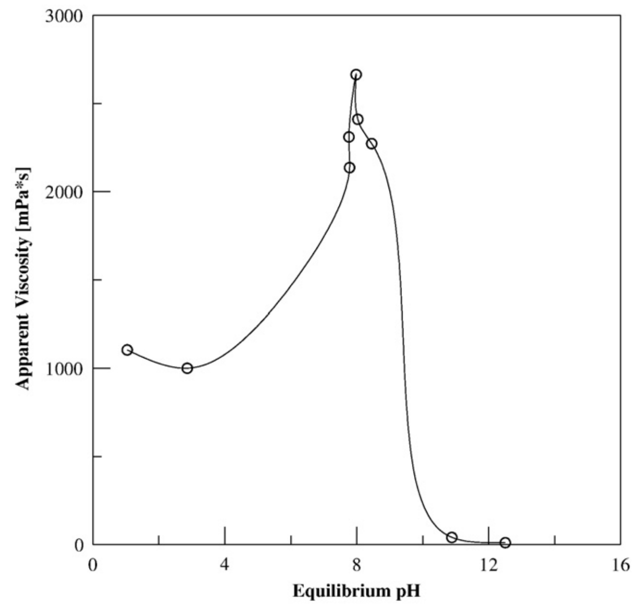

Fig. 2. Apparent viscosity of sepiolite as a function of pH.

For acid activation, HCl (38% purity Merck), H_2SO_4 and citric acid from Merck company were used. For pH adjustments, an Orion brand digital pH meter was used.

The viscosity of sepiolite was investigated upon washing the acidic suspension that causes the release of acid from the media. The experiment was performed with 3% solids concentration of sepiolite ground at pH 0.9 and the solution pH was adjusted with HCl. During the experiment, the solution was first filtered, equal amount of fresh

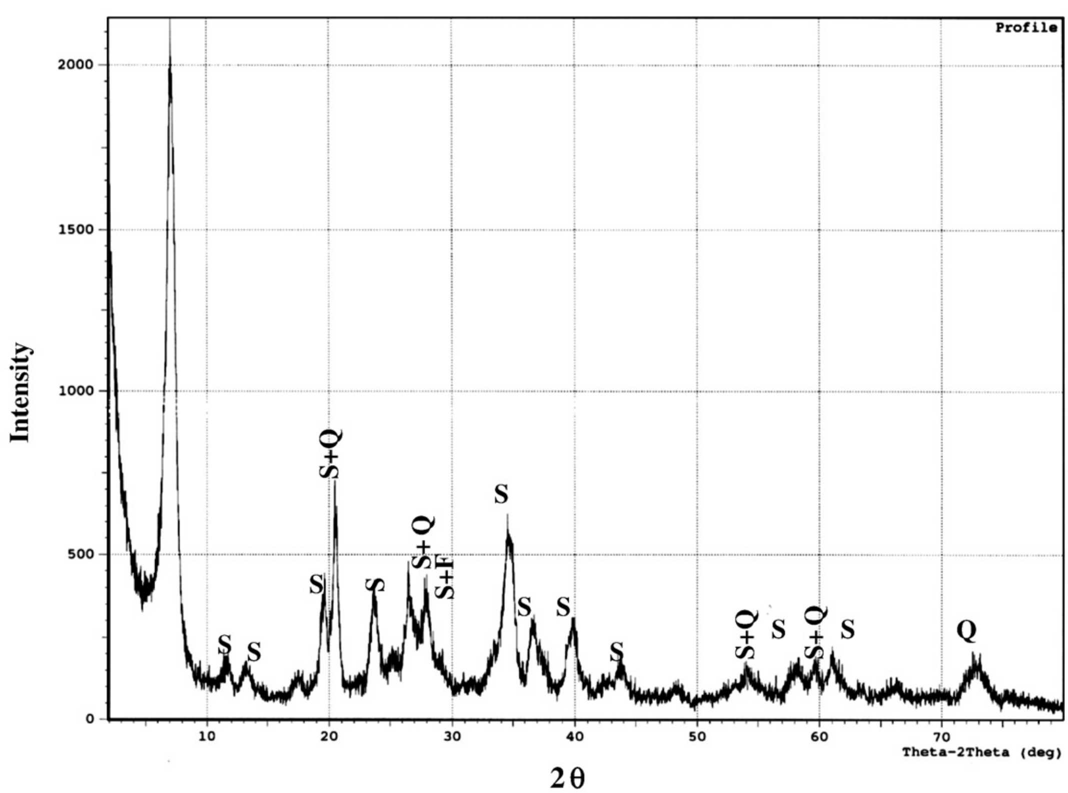

Fig. 1. XRD pattern of sepiolite sample (S: sepiolite, Q: quartz, F: feldspar).