

The Effects of Exchangeable Cations and Salts on the Gel Structure of Swelling and Non-swelling Bentonite Clays

Nurfer Güngör

*College of Science, Physics Department
Istanbul Technical University, 80626, Maslak, Istanbul, Turkey*

ABSTRACT. The effect of the exchangeable cations upon the gel structure of slurries obtained from two different types of bentonites found in Turkey and identified as swelling and non-swelling were determined. NaCl, KCl and CaCl₂ of varying concentrations were added to these slurries and their effects on the rheological properties were determined. The results of this investigation highly suggests that the resulted swelling thixotropic gels depends mainly on the exchangeable cations added.

Montmorillonite belongs to the 2:1 layer minerals derived from pyrophyllite (Van Olphen 1977, Worrall 1986, Searle and Grimshaw 1986, Reed 1988). The general name given to clays which contain appreciable quantities of montmorillonite minerals is bentonite. It is very common to refer to these bentonites by the name of the exchangeable cation present in their structure; such as Na⁺-bentonite, Ca⁺⁺-bentonite, *etc.* The exchangeable cations that exist between the bentonite layers are the effective parameters determining all characteristic properties of bentonite clays.

There are many studies concerning the effects of exchangeable cations upon different characteristic properties of the bentonite clays (Heath and Tadros 1983, Larsson and Siffert 1983, Schrann and Kwak 1982, Khandal and Tadros 1988). There are also various studies on the distinct effects, upon these properties, of different electrolytes, polymers and organic materials added to the bentonite slurries (Delgado *et al.* 1984, Güngör and Tulun 1994, Erzan and Güngör 1995, Güngör and Dilmaç 1995, Güngör 1995).

Key Words: Bentonite, Montmorillonite, Exchangeable Cations, Rheological Properties.

When dispersed in water, bentonitic clays are known to gel under certain conditions (Healh and Tadros 1983). This behaviour could be utilized in different industrial drilling fluids, pharmaceuticals and cement.

There are, generally, two mechanisms for gel formation in bentonite-water systems: a) The gel formation is attributed to the long-range repulsion between interacting double layers. This was originally suggested by Norrish (Norrish 1954, Norrish and Russel-Colom 1961). b) The gel formation is ascribed to an electrostatic attraction between the positively charged edges and negatively charged faces of plate-like particles, which results in a linked structure similar to a house of cards. This was suggested by Van Olphen (Van Olphen 1951, 1956 and 1962).

In this study, one swelling bentonite and one non-swelling bentonite from different regions have been studied. Their properties, and electrokinetic and rheological behaviour were first determined on bentonite slurries prepared from natural samples. Gel strength measurements were obtained as a function of time. Afterwards, different percentages of KCl, NaCl and CaCl_2 were added to these systems as electrolytes and changes in the gel structure were determined by taking into the concentration of electrolyte in the interpretation of the results.

Experimental Study

Samples of sodium and calcium bentonites were provided from two different regions of in Turkey, bentonite from Kursunlu, which is used in casting and concrete, sample from Unye, which finds application in ceramic and dye industries. Minerological and chemical identification of the samples have been carried out previously (Güngör and Tulun 1994, Erzan and Güngör 1995, Güngör and Dilmaç 1995, Güngör 1995). The chemical compositions of the investigated samples are given in Table 1, and some of their characteristic properties are included in Table 2.

In addition, a trace elemental analysis on the samples was performed using the neutron activation technique. For irradiations the Triga Mark II reactor at ITU Nuclear Energy Institute was used. The reactor had a constant 250 kW power and approximately 15 mg of the sample was subject to a neutron flow of 1.66×10^{12} neutrons/cm² for a period of 5 minutes. The irradiated sample was then removed unto a Canberra Nuclear Inc. model G x 2018 Hp-Ge detector cooled by liquid nitrogen. The spectra were obtained with a Sampo 90 (a γ -spectrum analysis program). Mn, Cl, V, Dy trace elements were identified.

Table 1. Chemical analysis of the samples

	Swelling bentonite (% weight)	Non-swelling (% weight)
SiO ₂	70.30	60.60
Al ₂ O ₃	15.00	13.75
Fe ₂ O ₃	1.10	3.00
TiO ₂	0.30	0.32
CaO	1.60	4.20
MgO	2.30	1.85
Na ₂ O	3.30	1.41
K ₂ O	1.20	1.66
% loss on ignition	4.90	13.21

Table 2. Some characteristic properties of the investigated samples

Sample	Density (g/cm ³)	Swelling capacity in water (ml)	Average particle size (μ m)	Mean zeta potential (mV)	Plastic Limit	Liquid Limit	Plasticity Index
Swelling bentonite	2.5	12	0.56	-33.14	88.16	210	121.84
Non-swelling bentonite	2.0	5.5	0.80	-26.60	121.4	215	93.6

Table 3. The rheological properties of the samples

Sample	Apparent viscosity, 600 rpm mPa.sec	Gel strength mPa	Yield point mPa
Swelling-bentonite	600	2150	3360
Non-swelling	350	1600	1920

Table 4. The change of the rheological properties of the samples when salts are added at 7 wt %

Sample	Apparent viscosity mPa.sec			Gel strength mPa			Yield point mPa		
	KCl	NaCl	CaCl ₂	KCl	NaCl	CaCl ₂	KCl	NaCl	CaCl ₂
Swelling bentonite	4850	1800	1400	10200	5700	46550	9950	6200	4850
Non-swelling bentonite	460	430	425	3250	2500	2000	2850	2300	2050

The particle size distribution and the zeta potential values for the sample were determined using Malver Zetasizer-3, based on the technique of reflection of the laser by the particles 0.05% wt (Calgon solution was again used as dispersive medium). The instrument used was 5 mV He-Ne laser gas lamp, which gives the percent of particle size in a given interval. The results obtained are shown in Table 2.

The specific surface areas of the samples were determined by dye adsorption technique (Davis and Worrall 1971), the data obtained were 96 and 120 m²/g for Kursunlu and Unye respectively.

Liquid Limit (LL), of bentonite/water mixture was determined according to BS1377 and ASTM D4318 Standard methods using a Casagrande (Ele, G-B) instrument. Plasti Limit (PL) is also determined according to the ASTM standard procedure. The difference between LL and PL is given as range plasticity Index (PI), which is due the of water content of the plastic system (Table 2).

Viscosity, gel strength, and yield point (Table 2) of bentonite slurries, obtained by dispersion, were determined with a Fann type (model 35 SA) viscometer. The weighed amount of sample in distilled water (22.5 g/350 ml water) was stirred mechanically at 1800 rpm for 5 minutes, then, the left to stand for a 24 hours. Gel strength of bentonite slurries were measured by Fann viscometer giving rotational movement as 3 cycle min⁻¹. Between each subsequent measurement, the slurry was left to stand for 10 minutes in order to regain the gel structure.

Results and Discussion

The stability of the gel structure formed is related to the nature of the exchangeable cations; the adjoining particles of swelling bentonite (Na⁺-bentonite)

slurry exhibit a net-like appearance, whereas, non swelling (Ca^{++} -bentonite) sample displays a water image.

The variation in gel strength with time has been determined by periodical recesses of the slurry (Fig. 1). As is observed in the swelling sample, there is a stepwise increase; whereas, there is a progressive deterioration in the non-swelling bentonite. Swelling-bentonite system tends to be dispersed, while non-swelling bentonite system become aggregated. Furthermore, it is difficult to recover the gel strength of a swelling-bentonite slurry after a certain time compared to the non-swelling bentonite slurry.

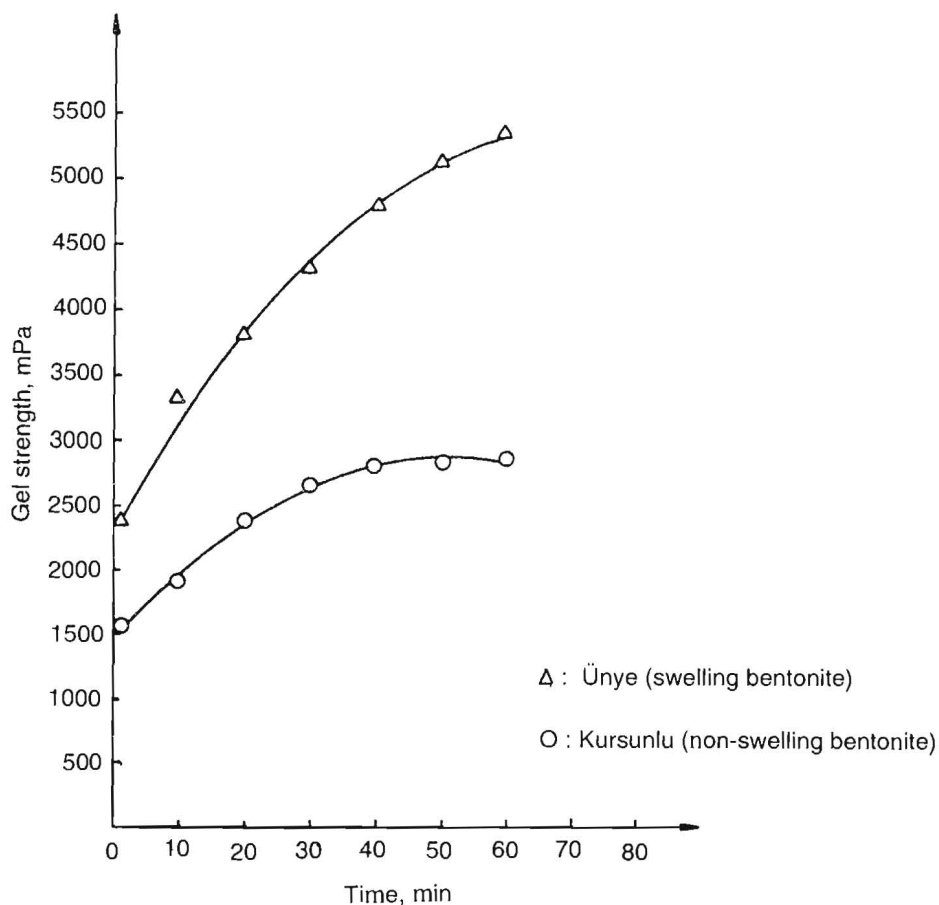


Fig. 1. Variation of the time with gel strength.

Sodium-bentonite has the ability to enhance the gel formation because of its high swelling property. The swelled particles become disintegrated after time giving numerous small particles that having a large surface area. If the Na-bentonite water system is prepared as slurry which provides a large interaction of particles, viscosity and binding water increase and a physical, reversible gel can be formed as a cluster. In addition, the repulsive electrostatic and Van der Waals forces that bring the particles to equilibrium state contribute to gel formation.

The $\tau=f(\dot{\gamma})$ curves (Fig. 2) for the samples, which are consistent with the Bingham plastic-flow model, exhibit different values for slope and yield point

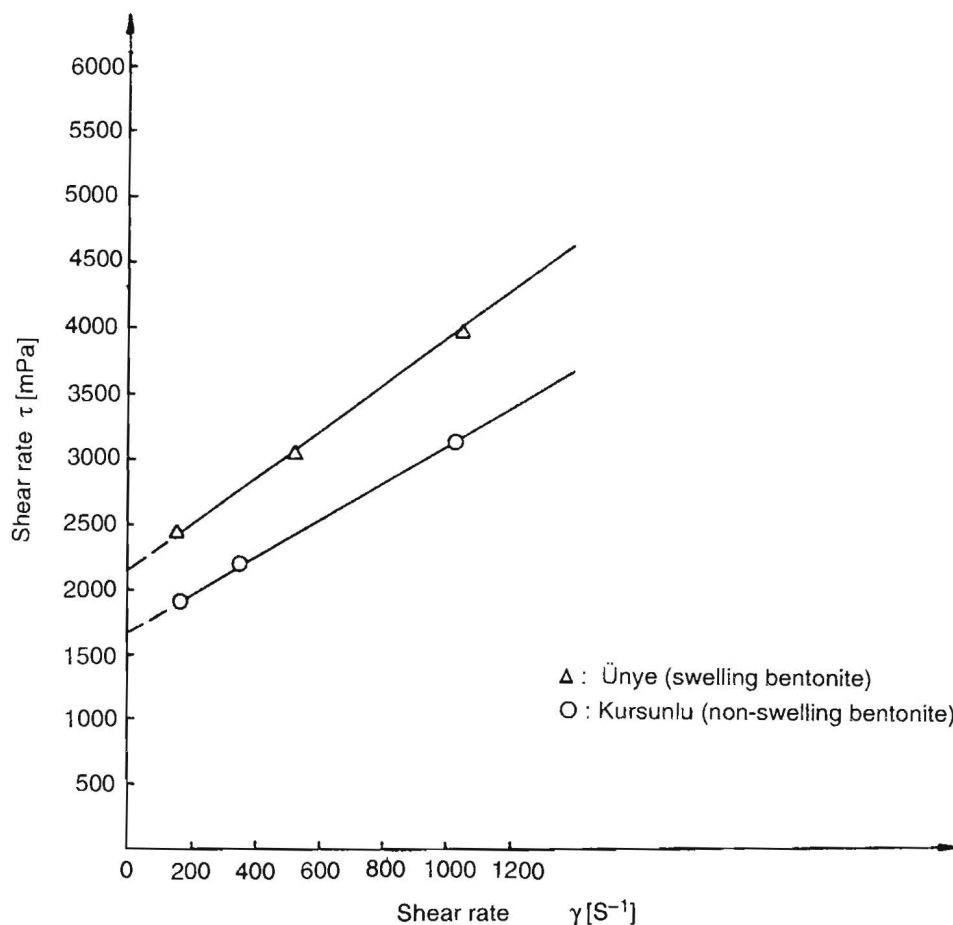


Fig. 2. Variation of the shear stress with shear rate.

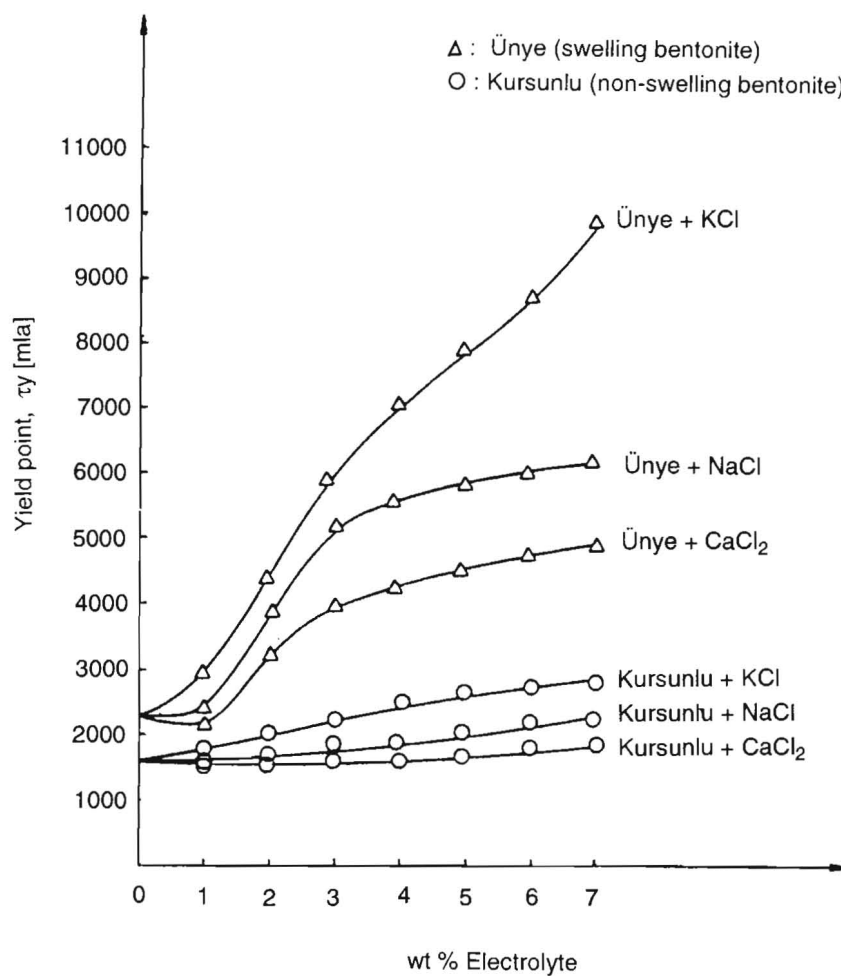


Fig. 3. The change of the yield points of the samples, when KCl, NaCl and CaCl_2 electrolytes are added at different amounts.

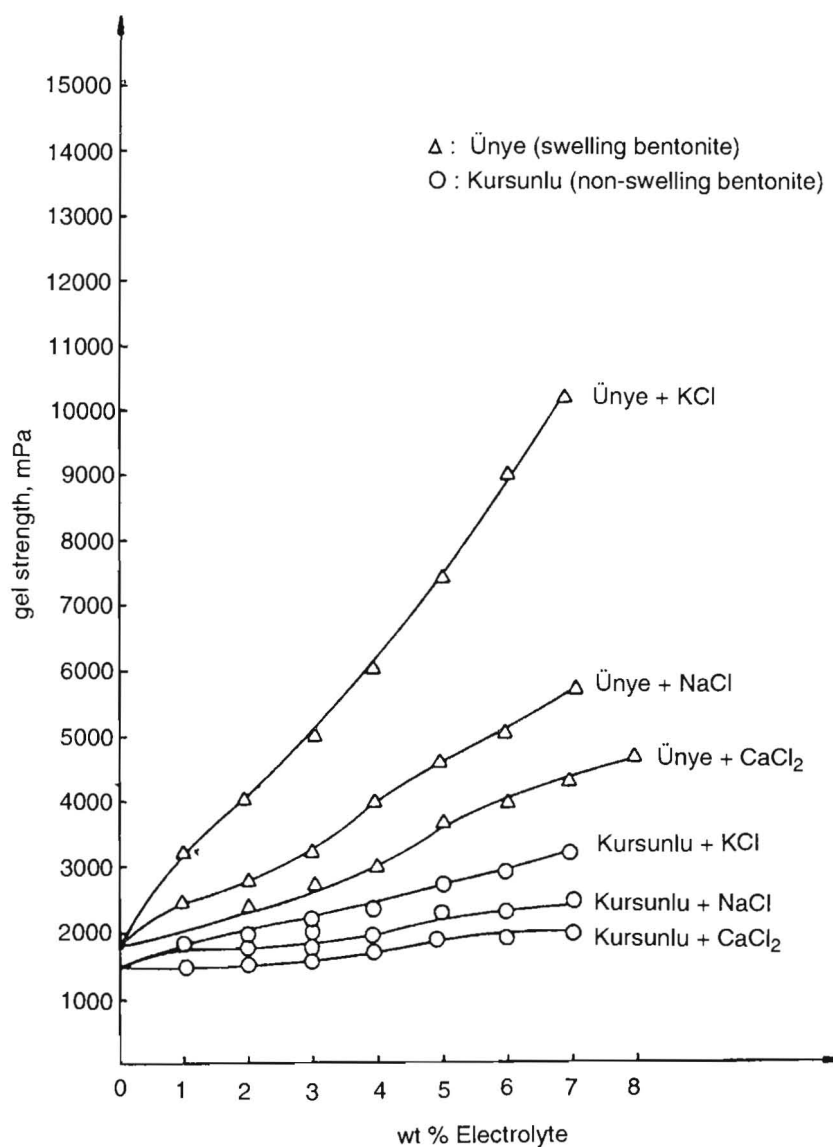


Fig. 4. The change of the gel strength of the samples, when KCl, NaCl and CaCl₂ electrolytes are added at different amounts.

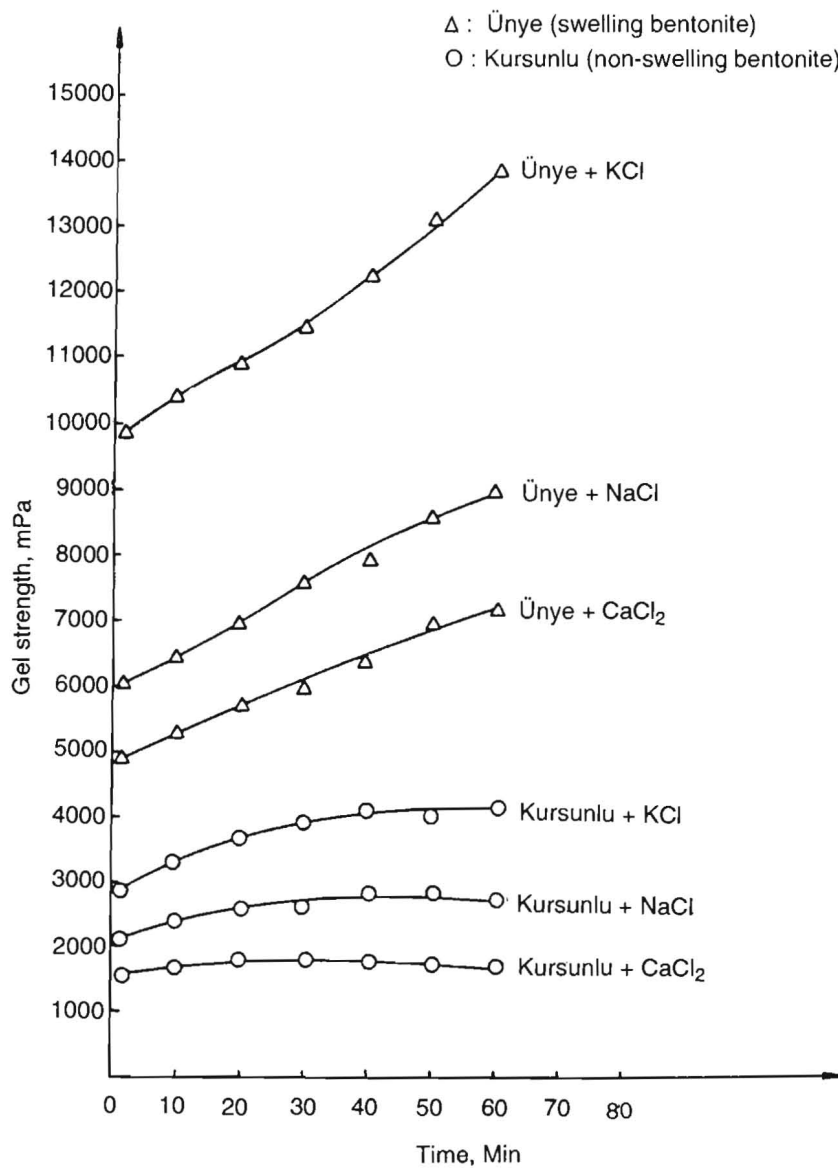


Fig. 5. Variation of the time with gel strength of the samples when salts are added at 7 wt %.

depending on the content of the samples. The linear relationship between shear rate and shear stress show that the yield value of swelling bentonite is higher than non-swelling bentonite system. This phenomenon can be explained by the nature of colloidal micelles of the both systems. Since the water molecules, which are held by the particles, are influenced in their amount and the rigidity of their binding associated cations, swelling bentonite systems flow more easily than non-swelling bentonite systems, which have a rigid nature.

The variations in the yield point and gel strength values, as a function of added electrolytes, are given in Figs. 3 and 4. As shown, the sample which is most sensitive to the addition of electrolytes is the sample of swelling bentonite. The smaller ionic radius and the greater mobility of the sodium ion are the major effective factors in this study. Therefore, the sample with a greater cation-exchange capacity is expected to be more sensitive towards interactions with electrolytes.

Particularly, KCl added to swelling-type bentonite-water system increased its stability.

It is deduced that a more rigid gel structures can be obtained by adding electrolyte.

The curves shown for the gel strengths as a function of time, after the addition of electrolytes, are approximately parallel to the curves given in Figs. 3 and 4.

In summary, our results conclude the following: a) The rheological properties of bentonites and the formation of gel structures with water are altered by the addition of electrolytes. The type of bentonite, the type of the electrolyte and the concentration are influential factors, in the order given. b) The structures of the samples in sludge form should be further clarified by an effective enlargement of particle size using an electron microscope, in order to understand whether or not the mechanism other than the electrostatic and Van der Waals interactions exist in the modelling of particles.

References

- Davis, G.A. and Worrall, W.E. (1971) The Adsorption of Water by Clays, *Trans. J. Br. Ceram. Soc.*, **70**: 2.
- Delgado, A., Gonzalez-Cabellero, F. and Bruque, J.M. (1986) On the Zeta Potential and Surface Charge Density of Montmorillonite in Aqueous Electrolyte Solutions, *J. Colloid Interface Science*, 203-211 pp.
- Erzan, A. and Güngör, N. (1995) Fractal of Gemoetry and Size Distribution of Clay Particles, *J. of Colloid and Interface Science*, **176**: 301-307.
- Güngör, N. (1955) The Effects of Electrolytes and Polymers on the Rheological Properties of Swelling and Non-Swelling Bentonite Clay Powder Handling and Processing, **70**(4): 317-320.
- Güngör, N. and Dilmaç, S. (1995) Influence of Some Electrolytes on Rheological Properties of Turkish Bentonite Slips, *Interceram.*, (in press).
- Güngör, N. and Tulun, T. (1994) Studies on the Zeta Potential of Bentonite Clay in Aqueous Solution *Revue Roumaine de Chimie*, **39**(z): 177-182.
- Heath, D. and Tadros, Th.F. (1983) Influence of pH, Electrolyte and Poly (Vinyl Alcohol) Addition on the Rheological Characteristics of Aqueous Dispersions of Sodium Montmorillonite, *J. of Colloid and Interface Sci.*, **93**(2): 307-319.
- Khandal, R.K. and Tadros, Th.F. (1988) Application of Viscoelastic Measurements to the Investigation of the Swelling of Sodium Montmorillonite Suspensions, *J. of Colloid and Interface Sci.*, **125**(1): 122-128.
- Larsson, N. and Siffert, B. (1983) Formation of Lysozyme-Containing Crystals of Montmorillonite, *J. of Colloid Interface Sci.* **93**(2).
- Norrish, K. (1954) Discuss. *Faraday Soc.*, **18**: 120.
- Norrish, K. and Russel-Colom, J.A. (1961) Proceedings, 10th National Conference Clays and Clay Minerals, Pergamon, New York, 123 p.
- Reeds, J.S. (1988) *Introduction to the Principles of Ceramic Processing*. John Wiley and Sons, New York.
- Schrann, L.L. and Kwak, J.C.T. (1982) Influence of Exchangeable Cation Composition on the size and shape of Montmorillonite Particles in Dilute Suspension; *Clays and Clay Minerals*, **30**(1): 40-48.
- Searle, A.B. and Grimshaw, R.W. (1986) *The Chemistry and Physics of Clays*, Ernest Benn Limited, London.
- Van Olphen, H. (1951) Discuss. *Faraday Soc.*, **11**: 82.
- Van Olphen, H. (1956) Proceedings, 4th National Conference Clays and Clay Minerals, Nat. Res. Council, Nat. Acad. Sci. (U.S.) Washington, D.C., 204 p.
- Van Olphen, H. (1962), *J. Colloid Sci.*, **17**: 660.
- Van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*, Interscience, London.
- Worrall, W.E. (1986) *Clays on Ceramic Raw Materials*, Elsevier Applied Sci. Publishers Ltd., London.

(Received 21/01/1996;
in revised form 22/07/1996)

تأثير الأملاح والأيونات الموجبة القابلة للتبادل على تركيب الجل المستحصل عليه من طين البيتونيت (الأسمت الخاص) القابل للانتفاخ والبيتونيت غير قابل للانتفاخ

جرجور نورفر

قسم الفيزياء - كلية العلوم - جامعة اسطنبول التقنية

مسلك - ٨٠٦٢٦ - اسطنبول - تركيا

تم البحث عن تأثير الايونات (المواد المضافة) المتغيرة على طبيعة الطين من حيث الكثافة (جيل) والمحصل من بيتونيت (الأسمت الخاص) قابل للانتفاخ وبيتونيت غير قابل للانتفاخ . وتم تعيين تأثيرات الاملاح NaCl ، CaCl_2 و KCl_3 على الخصائص الريولوجية (توازن طبيعة الأرض بالمواد المضافة) . وقد ثبت أن كثافة الطين (تيكسوتروبيك جيل) مرتبطة بالأيونات (المواد المضافة) المتغيرة المضافة .