COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 29 ANNÉE : 1983

Effect Of Mold Gases On The Cation Exchange Capacity Of Sodium Bentonite

by

O. ŞANLI - E. TİRYAKİOĞLU*

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les diciplines scientifique représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III etait composé de trois séries

Série A : Mathématiques, Physique et Astronomie,
Série B : Chimie,
Série C : Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1: Mathématiques,
Série A_2: Physique,
Série A_3: Astronomie,
Série B : Chimie,
Série C_1 : Géologie,
Série C_2 : Botanique,
Série C_3 : Zoologie.

A partir de 1983 les séries de C_2 Botanique et C_3 Zoologie ont été réunies sous la seule série Biologie C et les numéros de Tome commencerons par le numéro 1.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université d'Ankara. Elle accepte cependant, dans la mesure de la place disponible les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagnés d'un resume.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, les dessins et figures portes sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler-Ankara
TURQUIE

Effect Of Mold Gases On The Cation Exchange Capacity Of Sodium Bentonite

by

O. ŞANLI - E. TİRYAKİOĞLU

Engineering and Architecture Faculty of Gazi University

*Middle East Technical University.

(Received 14 March, 1983, and accepted 27 April, 1983)

SUMMARY

In this study the effect of sulfurdioxide, carbondioxide, and ammonia gases, on the cation exchange capacity of ÇANKIRI sodium bentonite used as a binder for foundry molding sand has been investigated.

Cation exchange capacity of sodium bentonite samples have been determined in a temperature range of 50°C-350°C being exposed for definite periods to continious gas streams, sodium acetate method has been used to determine cation exchange capacities.

It was found that cation exchange capacity decreases from 3.44 % - 14.4 % for carbondioxide, from 6.28 % - 15.6 % for sulfurdioxide and 6.27 % - 8.7 % for ammonia at the end of 100 minutes exposure of gas stream in the temperature range of 50°C - 350°C.

It was found that with longer times of exposure and higher temperatures, the sodium bentonite would gradually loose its bonding ability and reactivation process would be valuable in order to restore its properties.

INTRODUCTION

In making molds clays most commonly used are bentonites in the foundry industry all the world. They are mainly of two types namely sodium and calcium bentonites of these sodium bentonite is preferred. The high price of sodium bentonite has enforced the foundryman to the use of calcium bentonites as activated with sodium carbonate. However the use of activated bentonite in the United Kingdom and West Germany has resulted in many complaints from the fondymen. The bonding properties were drastically decreased after one cycle in the process and the clay had to be reactivated. This was shown to be the effect of mold gases which formed by the heat introduced the cooling of the liguid metal poured into the mold in an extensive study of Hoffman (1). However in that work natural sodium bentonite was not studied. The present investigation was planned to fill this gap. to draw comparasion and possible variations in the foundary characteristics of sodium bentonite with regards to temperature in contact with various kinds of gas streams. The cation exchange capacity which controls mainly the bonding characteristics was measured as the main variable since its determination needed only very small samples, yielding higher accuracy.

EXPERIMENTAL WORK

A. The Selection of Experimental Condition

In addition to clay and water mixed with sand to make molds other materials of small amounts are also added for special purposes. Buffer materials such as wood flour, fine saw dust, cereals are added to the sand to minimize sand expansion defects, Additions are also made to sand molds to improve the surface smoothness of castings,

When molten metal has been poured, either decomposition or burning of the materials generate carbon dioxide, sulfur dioxide, ammonia gases, to evaluate the effect of these gases, each gas had to passed through heated bentonite, the heating temperature ranged from 50°C to 350°C.

Hoffman and Endell (2) showed that the property of sodium bentonite regain interlayer water rapidly and its expansion was lost after heating to 390°C to 490°C For this reason, maximum temperature limit was selected as 350°C at which bentonite does not lose its ability to recapture water.

After the gas passed through heated bentonite cation exchange capacity was determined by chemical method.

There are commonly two basic methods for determining the cation exchange capacity (3).

a) The soil is electrodialyzed or leached with a dilute acid, and the hydrogen and alumina saturated exchange material is titrated to PH 7 with barium hydroxide or to about PH 8,5 with sodium hydroxide.

b) Exchangeable cations are replaced by acetate of ammonium barium, calcium or sodium and amounts of the cation adsorbed are determined by appropriate means

Numerous investigators have indicated that electrodialysis of the clay minerals may cause their decomposition. Kelley (4) showed that as the cations are replaced by H, aliminum moves from octahedral positions to exchange positions and Giese (5) showed that in general unexchangeable cations are lost within the lattice before all the exchangeable cations are replaced by H, for these reasons electrodialyzed method was not selected.

In using second method since normal acetate salts of monovalent ions usually dissolve only traces of organic material in the clay in addition having PH values in the range from 7 to 8.3 either sodium acetate or ammonium acetate method was thought to use.

Between ammonium acetate and sodium acetate method sodium acetate method is preferred. Because sodium bentonite clays are somewhat alkaline (PH = 8) in water saturation determining the cation exchange capacity at PH = 8.2 with sodium acetate method is more reliable and capacity found at PH = 7 is found smaller than capacity found at PH = 8 for montmorillonite type of clay minerals.

B. Experimental Apparatus

The apparatus used in this investigation consisted of, An electrically heated oven, a sample tube (made up of 13% chromium steel) with screws at both ends, gas supply tank, connecting lines, a gas flowmeter, potentiometer and chromel-alumel thermocouple.

C. Experimental Procedure

Sample tube was filled with bentonite and placed in the oven when the desired temperature was reached and remained constant. The gas stream was passed for the reguired length of time, The periods of passing were selected as 1, 3, 5, 10, 35, 100 minutes. The study was carried over for a range of temperatures namely 50°C, 100°C, 200°C, 250°C, 350°C, for each gas.

Cation exchange capacity of samples were determined by treating sample with sodium acetate of PH = 8.2 first then the excess of the acetate is washed with 95 % ethanol. The adsorbed sodium is replaced from the sample with 1 N ammonium acetate the sodium concentrations of the extract after proper dilutions is determined by flame photometric method. (6)

RESULTS and DISCUSSION

The maximum cation exchange capacity was found to be 87,4 meq / 100 g at 50°C and minimum 86,5 meq /100 g at 350°C that may be considered to be constant (Table 1) This is in agreement with the results found in Literature (7)

Table 1

Effect of Heating on the Cation Exchange Capacity of Sodium Bentonite

Temperature	Cation Exchange Capacity meq /100 g
50	87.4
100	86.3
150	86.9
200	86.25
250	86.6
350	86.5

Despite the practically constant cation exchange capacity of the samples heated 50-350°C temperature range, exposure of sodium bentonite to each of mold gases, ammonia, sulfur dioxide, carbon dioxide effected to decrease the cation exchange capacity (Table II)

The decrease is the most significant with sulfur dioxide gas and least with carbon dioxide gas in the 50° to 250°C temperature range (Figure 1)

Ammonia is between the other two. However cation exchange capacity sharply decrease at 350°C with the carbon dioxide gas exposure that is being more than ammonia

From the experimental results, the temperature and cation exchange capacity relationship can be expressed as in the following in the 50°C-250°C temperature range

Table II

Effect of Mold Gases on the Cation Exchange Capacity

	Time (Minutes)	Temperature (°C)					
		50	100	150	200	250	350
For SO_2 gas	1	85.6	82.5	81.9	81.0	79.9	79.4
	3.5	84.4	81.9	80.6	79.4	78.75	78.5
	10.0	83.8	81.4	78.8	79.4	77.5	77.0
	35.0	82.5	81.4	78.8	78.8	76.6	77.0
	100.0	82.0	80.5	78.8	78.5	74.4	73.8
For CO_2 gas	1	87.5	87.0	86.25	86.26	84.4	81.4
	3.5	87.0	86.25	85.2	84.4	83.1	81.1
	10.0	86.0	86.25	85.2	83.2	82.9	78.8
	35.0	86.7	85.2	84.5	82.9	82.9	76.9
	100.0	85.0	85.0	84.5	82.9	82.9	76.9
For NH_3 gas	1	82.5	82.5	81.25	81.2	81.22	80.6
	3.5	81.9	91.9	81.22	81.25	81.25	80.00
	10.0	81.25	81.25	81.20	81.9	81.22	80.00
	35.0	81.9	82.5	80.00	80.00	81.22	79.5
	100.0	81.25	81.25	80.00	80.00	80.05	79.5

$$C = a_1 \,.\, T^{n1}$$

Where C, is the cation exchange capacity, T is the temperature, a, is a constant, n_1 is a constant

For the case of 100 minutes exposure time the values of the constant a, for sulfur dioxide, carbon dioxide and ammonia gases are 82.6, 86.5, 81.5, respectively, Similarly the power n, are 0.05, 0.0247, 0.0468 in the above order.

The effect of an exposure time of 1,3,5,10,35,100 minutes at various temperatures for each of three mold gases at a constant flow rate, was investigated and from those, a relationship between cation exchange capacity and exposure time, were found as in the following equation

$$C = a_2\, \theta^{n2}$$

where C, is the cation exchange capacity, θ is the exposure time, a_2 is a constant, and n_2, is a constant. The values of the constants a_2 and n_2 are tabulated for various mold gases in Table III

The effect of the mold gases on the cation exchange capacity may be explainable with the formation of certain salts in the bentonite st-

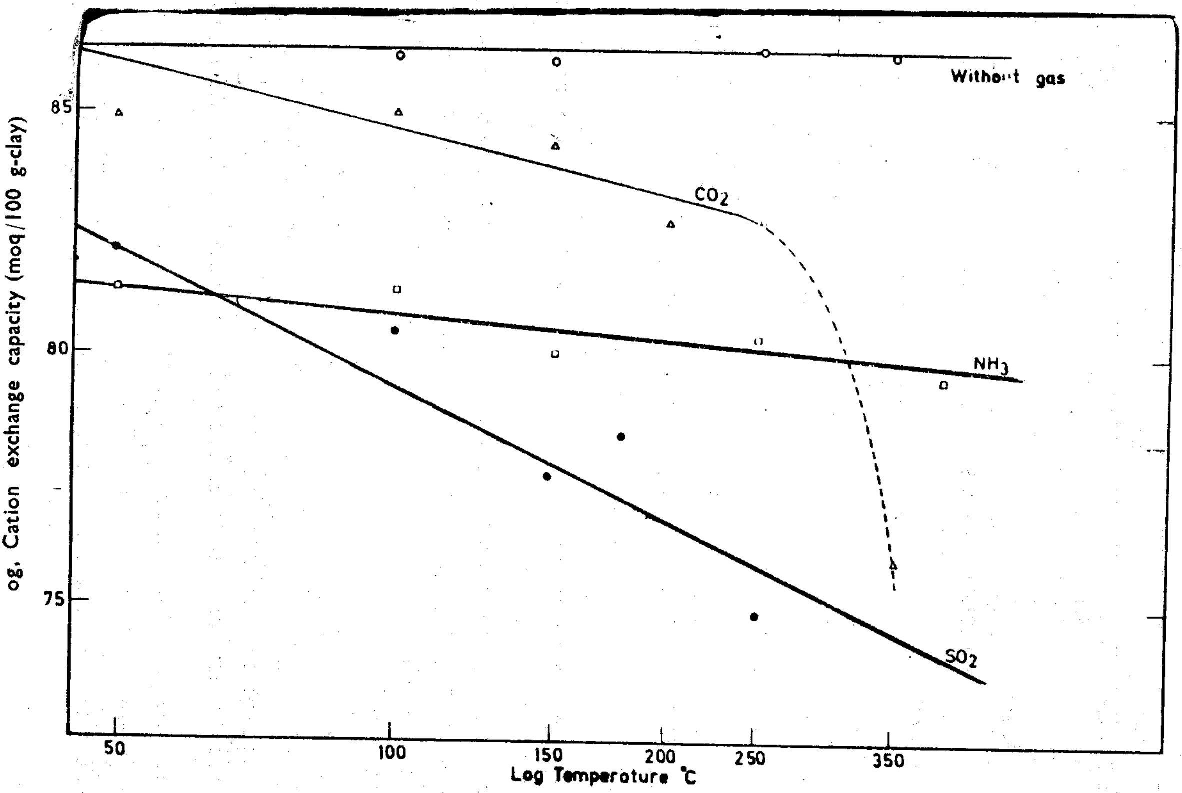

Figure 1: Effect of Mold Gases and Temperature on Cation Exchange Capacity of Sodium Bentonite. (Exposure time, Θ = 100 min.)

Table III

Experimentally determined values of the constants in equation $C = a_2 \Theta^{n_2}$

	Temperature (°C)					
For SO_2 gas	50	100	150	200	250	350
a_2	85.5	83	81,6	81	79,25	79,5
n_2	-0.008675	-0.007375	-0.001102	0.0009175	-0.0135	-0.01540
For NH_3 gas						
a_2	82,25	82,2	81,4	81,1	81	80,4
n_2	-0,003225	-0.00278	-0.00301	-0.002985	-0.002	-0.0023
For CO_2 gas						
a_2	87,5	87	86,2	84,7	84,2	—
n_2	-0.00568	-0.00572	-0.00517	-0.00629	-0.00715	—

ructure that are not exchangeable. In the case of sulfur dioxide gas, formation of sodium sulfate, and sodium carbonate with the carbon dioxide exposure are possible. However validity of a possible chemical reaction on the pores of the bentonite requires further investigation.

Effect of ammonia can be explained based on the Zettlemayer (7) explanations, so that although the initial decrease from 87,5 meq/100 g, capacity is great when gas sorbed at low temperature and small exposure time. Decrease in the slope of the curves as the temperature increases is not great. This can be explained on the basis of the work done by Kelley (4) such that as the temperature is increased adsorbed ammonia releases and the formed NH^+_4 ions decomposes and cation exchange capacity do not fall further.

CONCLUSIONS

Sodium bentonite does not exhibit a pronounced deactivation when exposed to carbon dioxide, sulfur dioxide and ammonia gases compared to activated sodium bentonites reported in the literature.

Decrease in cation exchange capacity is noticeable especially at higher temperatures and longer exposure durations.

Effect of mold gases on cation exchange capacity are in order of

$$SO_2 > NH_3 > CO_2$$

in the temperature range of 50°C – 250°C However this order change to at 350°C

$$SO_2 > CO_3 > NH_2$$

The temperature and cation exchange capacity can be related by the equation

$$C = a_i\ T^{n1}$$

Further the cation exchange capacity and exposure time can be related.

$$B = a_2\ \theta^{n2}$$

Interaction mechanisms are thought to be sorption or complex formation in the case ammonia, sodium sulfate formation in the case of sulfur dioxide, sodium carbonate formation in the case of carbon dioxide.

ÖZET

Bu çalışmada karbon dioksit, kükürt dioksit ve amonyak gazlarının döküm kumunda bağlayıcı olarak kullanılan Çankırı Sodyum bentonitinin katyon değişim kapasitesine etkisi araştırılmıştır.

Sodyum bentonit örneklerinin katyon değişim kapasiteleri 50-350°C aralığında, belirli bir süre sürekli gaz akımına maruz bırakıldıktan sonra tayin edilmiştir.

50-350°C aralığında 100 dakika gaza maruz bırakılma sonucunda katyon değişim kapasitesinin karbon dioksit için 3,44 %,-14,4 %, kükürt dioksit için 6,28 %,-15 % ve amonyak için 6,27 % - 8,7 % düştüğü bulunmuştur.

Sıcaklığın yükseltilmesi ve gaza maruz bırakılma süresinin uzatılması sonucu sodyum bentonitin, bağlanma kabiliyetinin tedrici olarak azaldığı ve bu özelliğini tekrar kazanabilmesi için aktifleştirme proseslerinin gerekli olacağı sonucuna varılmıştır.

REFERENCES

(1) **Hoffman F.** Clay Minerals for foundry Molding Sands, British Foundryman, V. 58,pp 305-307, 1959.

(2) **Hoffman,** Endell and Wilm, Crystal Structure and the Swelling of Montmorillonite, Zeitschrift fur Kristallographie V. 86, pp 340-348, 1933.

(3) **Blach C.A.** Evans, D.D., White, J.L., Ensminger, L.E.Clark, F.E., Methods of Soil Analysis.

(4) **Kelley, W.P.,** The Agronomic Importance of Calcium, Soil V. 40 pp. 103-109, 1935.

(5) **Giese, K.** Hofmann, U. Ueberden Katiunenaustausch an Tonmineralier, Kolloid -2 V. 87, pp. 21-36, 1959.

(6) Diagnosis and İmprovements of Saline and Alkaline Soils, Agriculture Hand book No. 60 United States Salinity Laboratory Staff.

() **Zettlemayer, A.C.,** Young, G.J. and Chessiek, J.J., Studies of the Surface Chemistry of Silicate Minerals, J. Physical Chemistry, V. 59, pp. 962-966.

Ankara Üniversitesi Basımevi. Ankara – 1984