

ON THE STRUCTURAL STABILITY OF MONTMORILLONITE SUBMITTED TO HEAVY γ -IRRADIATION

ALICIA NEGRON¹, SERGIO RAMOS¹, ALEXANDER L. BLUMENFELD², GRACIELA PACHECO² AND JOSE J. FRIPIAT^{2,*†}

¹Instituto de Ciencias Nucleares, UNAM, A.P.70-543 C.U. México 04510 D.F., Mexico

²Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, Wisconsin, USA

Abstract—The effect of heavy doses (up to 200 Mrad) of γ -radiation on the short-range structural organization in montmorillonite was studied using infrared (IR) spectroscopy and solid-state high-resolution ²⁷Al and ²⁹Si nuclear magnetic resonance (NMR). No change attributable to irradiation was observed. A small variation in the water content was noted but it is not systematic. The results show that the montmorillonite structure can accumulate high doses of radiation without damage and therefore this clay is a suitable material for use in the safe disposal of radioactive waste.

Key Words— γ -radiation, Smectite.

INTRODUCTION

Although the use of clay minerals as backfill materials in radioactive waste isolation systems is well documented, our understanding of the effect of high-level radiation on the relevant properties of the clays is not. By ‘relevant properties’, we mean the cation exchange capacity (CEC), the cation mobility in the interlayer, the internal surface, the swelling of the material, *etc.* See Dayal and Wilke (1982) and Bonne and Heremans (1982), and references therein.

The modest goal of this short paper is to show that short-range structural organization in montmorillonite is not modified by heavy doses of γ -radiation. Montmorillonite is a typical clay used for radioactive waste disposal (Tamura, 1966).

In the course of studies intended to modify the reactivity of organic molecules adsorbed on montmorillonite by exposure to γ -radiation, the structure of the clay was unexpectedly resistant.

A Pyrex glass container turns black after being exposed to an accumulated dose of 200 Mrad, *i.e.* 200×10^6 rad. This is due to the formation of a large number of color centers. However, the clay exposed to the same dose became a weak brownish color. As far as we know, such resistance has not been reported previously. Therefore we considered it worthwhile to investigate the effect of radiation on the short-range structural features. As far as the long-range order is concerned, it was expected that the X-ray diffraction (XRD) patterns would not show any modification. On

powdered smectite samples, the *hk0* reflections are the most easily observed and the least likely to be modified. The swelling caused by atmospheric moisture did not change as the amount of adsorbed water was not significantly affected. The modifications most likely to be generated by the radiation were expected to be within the silicate layers.

EXPERIMENTAL

The clay used in this work was the SWy-1 bentonite (Na-montmorillonite) obtained from the Source Clays Repository of the Clay Minerals Society. No purification was carried since clay barriers are made from raw materials. A full description of SWy-1 bentonite was given by Van Olphen and Fripiat (1979). The main impurities were quartz and carbonates.

The physical techniques used to estimate the short-range structural perturbations were IR spectroscopy, and the solid-state high-resolution nuclear magnetic resonance (NMR) of ²⁷Al and ²⁹Si. Over the last 20 years, ²⁹Si NMR has become an important tool for structural studies of silicates as illustrated by Engelhardt and Michel (1987).

Four different clay samples were packed in a closed Pyrex glass container. They were irradiated for various periods of time in a γ source of ⁶⁰Co, with a dose rate of 1.1 Mrad/h at room temperature. The difference between samples was the loading in fatty acids and the pH (between 4 and 9) of the solution from which the organic material was adsorbed. The integrated doses were up to 200 Mrad in all cases.

RESULTS

As the experimental results obtained for the four samples were similar, only one set is presented.

* E-mail address of corresponding author:

fripiat@aleph.cinstrum.unam.mx

† Present address: 95 Montserrat, casa 12, Col. Los Reyes, 04330, México D.F., México

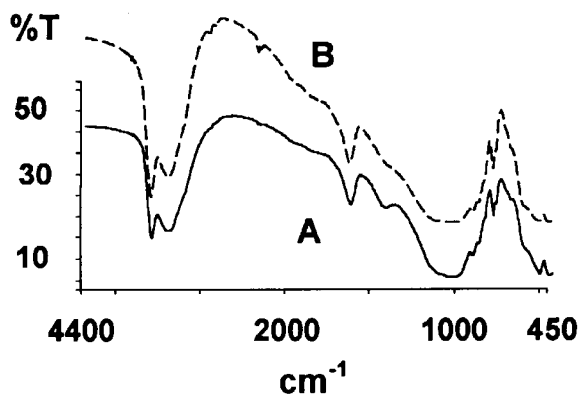


Figure 1. IR spectra of the SWy-1 bentonite studied. (A) Not irradiated; (B) irradiated in water (2% suspensions) with a dose of 200 Mrad.

Figures 1, 2 and 3 show the IR spectra and the ^{29}Si and ^{27}Al NMR spectra before and after irradiation, respectively.

In Figure 1, no change attributable to irradiation is observed in the structural OH^- -stretching region ($\sim 3600\text{ cm}^{-1}$) or in the Si-O -stretching domain

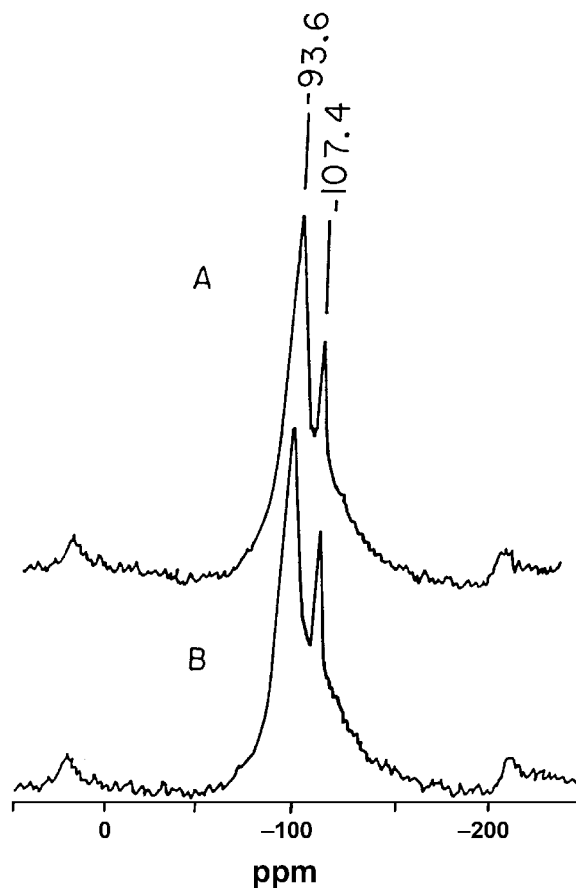


Figure 2. ^{29}Si NMR spectrum (resonance frequency: 99.4 MHz). (A) Blank; (B) irradiated with 200 Mrad. Chemical shift in ppm.

($<1100\text{ cm}^{-1}$). A small change in the water content (H_2O bending vibration near 1600 cm^{-1}) is noted but it is not systematic. This also applies to the carbonate band near 1400 cm^{-1} .

Figure 2 shows a characteristic, $^3\text{Q}_4(\text{Si},\text{OAl})$ cluster line in bidimensional silicates at -93.6 ppm (for line assignment see Engelhardt and Michel (1987) and Fripiat (1988)). The line at -107.4 ppm is due to the $^4\text{Q}_4(\text{Si},\text{OAl})$ resonance in quartz impurities. No other intensity which would be assigned to a $^3\text{Q}_4(\text{Si}-1\text{Al})$ cluster was detected near -88 ppm . We observed no modification that could be related to irradiation.

The same applies also to the ^{27}Al NMR spectra shown in Figure 3. The line at 62.4 ppm is attributable to four-fold coordinated, Al^{IV} , and the line at 4 ppm is due to octahedral aluminum, Al^{VI} . The spinning side bands at -94.4 and $+102.6\text{ ppm}$ are strong because of the relatively high Fe_2O_3 content. The tetrahedral Al may be contained in the clay structure but is probably in the feldspar impurities.

Proton NMR relaxation measurements were carried out on the same samples to detect the eventual formation of new paramagnetic centers other than those associated with Fe_2O_3 . Again there was no observable effect, in accord with the very weak color change.

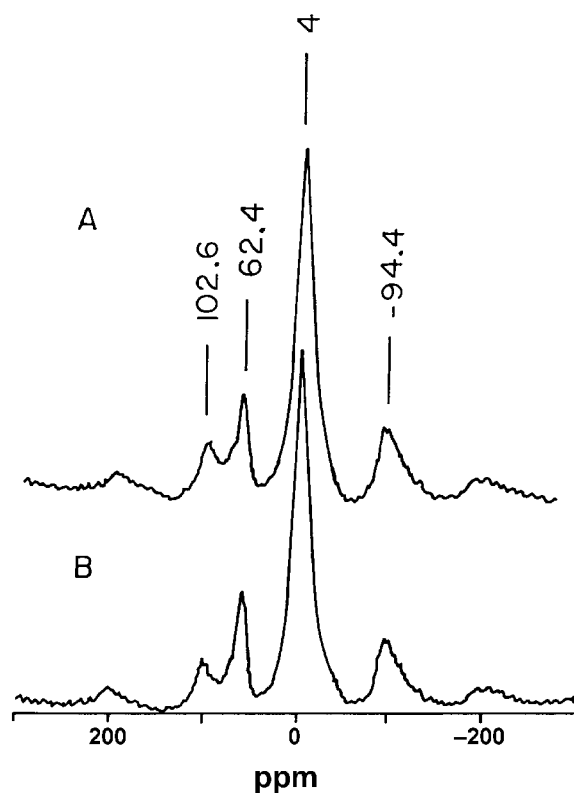


Figure 3. ^{27}Al NMR spectra of the same samples (resonance frequency: 130 MHz). (A) Blank; (B) irradiated with 200 Mrad. Chemical shift in ppm.

DISCUSSION

Bonne and Heremans (1982) used a γ -irradiated clay as a barrier in the disposal of radioactive waste. The clay was a mixture of 20–30% illite, 20% smectite, plus an interstratified illite-vermiculite-chlorite material. For an integrated dose of 100 Mrad, the release of H₂ and CO₂ was detected; CO₂ must have originated from carbonates and the H₂ from the radiolysis of water. None of these products indicates alteration of the clay structure.

Clozel *et al.* (1994) studied the effect of γ -irradiation (48 h exposure to a MoK α , 35 mA, 50 kV source) on kaolinite. They detected, by electron paramagnetic resonance, the formation of three kinds of defects: two different Si–O centers in the tetrahedral sheet and one Al^{VI}–O–Al^{VI} defect in the octahedral sheet. Only the relative concentrations of these defects were measurable, but they were of the same order of magnitude as those of the natural defects accumulated over the ages in these kaolinites. Such concentrations cannot influence the NMR or IR spectra and they are not expected to affect the performances of the clay as a barrier.

Thus, the scarce information obtained from this brief survey seems to support the surprising results reported here: the montmorillonite structure resists a cumulated dose of 200 Mrad of γ rays.

REFERENCES

- Bonne, A.A. and Heremans, R.H. (1982) Investigation on the Boom Clay, a candidate host rock for final disposal of high level solid waste. *Proceedings of the International Clay Conference 1981* (H. Van Olphen and F. Veniale, editors). *Developments in Sedimentology*, **35**, 799–818. Elsevier, Amsterdam.
- Clozel, B., Allard Th. and Muller, J.-P. (1994) Nature and stabilization of radiation-induced defects in natural kaolinites: new results and a reappraisal of published works. *Clays and Clay Minerals*, **42**, 657–666.
- Dayal, R. and Wilke, R.J. (1982) Role of clay minerals as backfill in radioactive waste disposal. *Proceedings of the International Clay Conference 1981* (H. Van Olphen and F. Veniale, editors). *Developments in Sedimentology*, **35**, 771–788. Elsevier, Amsterdam.
- Engelhardt, G. and Michel, D. (1987) *High-resolution Solid-state NMR of Silicates and Zeolites*. Wiley, New York.
- Fripiat, J.J. (1988) High resolution solid-state NMR study of pillared clays. *Catalysis Today*, **2**, 281–295.
- Tamura, T. (1966) Development and applications of minerals in radioactive waste disposal. *Proceedings of the International Clay Conference 1966, Jerusalem* (L. Heller and A. Weiss, editors). Israel Program for Scientific Translation.
- Van Olphen, H. and Fripiat, J.J. (1979) *Data Handbook for Clay Materials and Other Non-Metallic Minerals*. Pergamon Press, Oxford, UK.
- (Received 14 November 2000; revised 25 May 2001; Ms. 499; A.E. W. Crawford Elliott)