GAMMA-IRRADIATION OF KAOLINITE

by

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ABSTRACT

Studies have been made of the changes in physical and chemical properties of kaolinite produced by doses of 0.667 meV gamma-radiation ranging from 10^{18} to 10^{22} eV/g of ferrous ion dosimetry solution. Changes were observed in the degree of crystallinity, specific surface area, particle size, cation exchange capacity, and grinding properties. These changes are discussed in terms of the observed atomic displacements produced in the kaolinite structure by the radiation. Gamma-irradiation appears to provide a method for obtaining controlled variations in certain properties of kaolinite without the introduction of other complicating parameters.

INTRODUCTION

Frequently, kaolins whose primary constituent is the mineral kaolinite are found to contain large particles that appear to be laminates of individual platelike kaolinite particles. These large particles, often called stacks, range in size from 2 μ to greater than 40 μ equivalent spherical diameter. Since, theoretically, the kaolin layer has no unsatisfied valence bonds on the faces parallel to the a–b plane, interlayer bonding is believed to be accomplished by van der Waals' forces and long hydrogen bonds. An exploratory investigation was carried out to study the possibilities of reducing these large particles to small platelike particles with high-energy, ionizing radiation, and to investigate any changes in the physical and colloidal properties of kaolinite due to such radiation. This research was supported by the Division of Isotopes Development of the United States Atomic Energy Commission.

EXPERIMENTAL WORK

Two kaolins, whose primary constituent was kaolinite, were used in the studies. The kaolin from Washington County, Georgia, was fractionated after mining until 95 percent (by weight) of the particles were larger than 2 μ equivalent spherical diameter. The other kaolin, from Twiggs County, Georgia, received no treatment after mining and contained 85 percent of particles larger than 2 μ equivalent spherical diameter. Since kaolin particles with equivalent spherical diameters greater than approximately 2 μ are generally regarded to be stacks, both kaolins contained a large proportion of

stacks on a weight basis. The kaolins were dried for 4–6 hr at 110°C before irradiation.

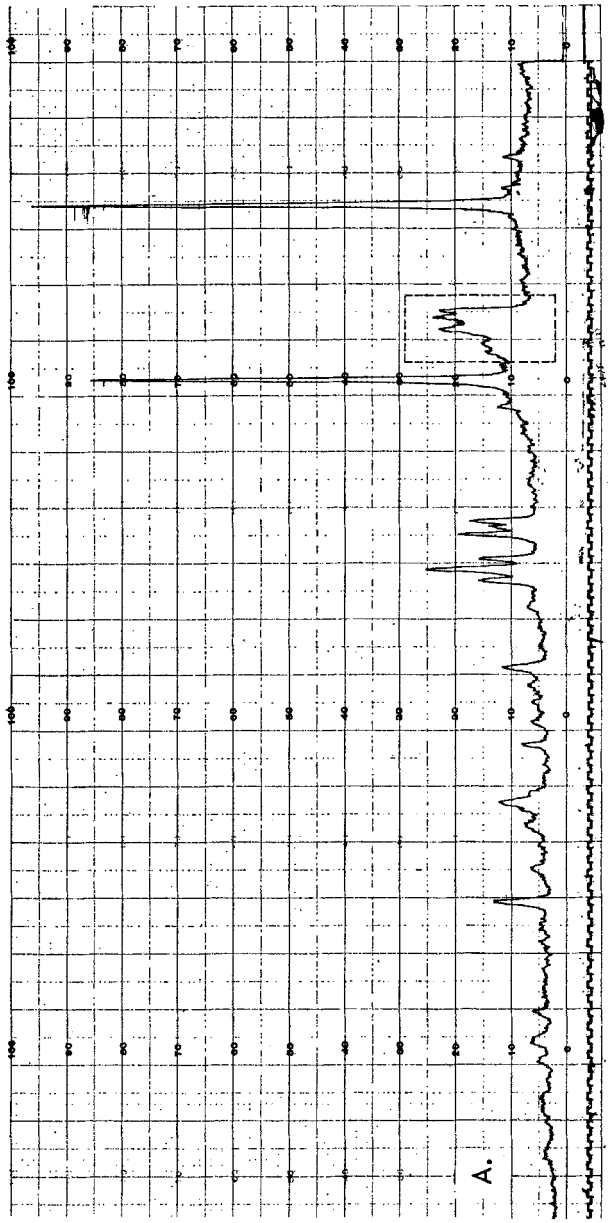
The samples were exposed to doses of 0.667 meV gamma-radiation ranging from 10^{18} to 10^{22} eV/g of ferrous ion dosimetry solution in the Georgia Tech 12,000-curie Cesium-137 Research Irradiator. An estimate of the temperature of the samples during irradiation was obtained with a copper constantan thermocouple placed in the center of a sample. The temperature appeared to rise uniformly from room temperature (approximately 70°F) to approximately 110°F in a period of 15 to 20 min, and to maintain this value during the remainder of the irradiation.

X-Ray Diffraction Observations

Typical X-ray diffractometer traces are presented in Fig. 1 for (A) a sample of unirradiated kaolin, and (B) a sample that had received a gamma-radiation dose of 1.0×10^{22} eV/g. It is immediately evident that, in current terminology, trace 1B indicates the less "well-crystallized" material. For 1B as compared to 1A there is a loss of resolution by such diffraction maxima as the 020, $1\bar{1}0$, and $11\bar{1}$ (area enclosed by dotted lines); the intensities and relative intensities of the 001 and 002 maxima are changed; and such maxima as the 111, 004, and 203 and three minor maxima beyond 060 have disappeared almost completely. Since qualitative rankings based on observations such as these were not adequate for establishing the degree of crystallinity as a function of radiation dose, the method of Johns and Murray (1959) was used to obtain an empirical index of "nb/3-crystallinity".[1] The method employs a ratio of the integrated intensities of two reflections, one of which is affected by nb/3 translations, $02\bar{1}$, and one which is not, 060. According to Johns and Murray, this ratio should vary ideally from 0 for the poorest to 1 for the best crystallized kaolins. This index is related to the extent to which aluminum atoms are displaced by units of nb/3. The effect on the index is similar whether the displacements occur by translations of whole kaolinite layers or, as in the probable case here, by translations of individual aluminum atoms.

The nb/3-crystallinity indices obtained are shown in Fig. 2. The significance of the observed maxima is not readily apparent. Taken at face value, they imply that the arrangement of the aluminum atoms in the lattice became more ordered up to a dose of about 5×10^{18} eV/g and then became progressively disordered by further irradiation. However, from a thermodynamic viewpoint, the probability of a random disordering process resulting in a more orderly crystal structure is very remote and such a phenomenon would be most unlikely. One factor which must be considered is that not only was the intensity of the $02\bar{1}$ reflection changing owing to the displacement of aluminum atoms, but disorder was also being produced in the remainder of the lattice by displacements of other atoms. Since nothing is known concerning the rates of displacement production or recombination, except that the intensity of the $02\bar{1}$ reflection underwent a much greater reduction with

[1] See the paper by Head *et al.*, this volume, for further discussion of this term.



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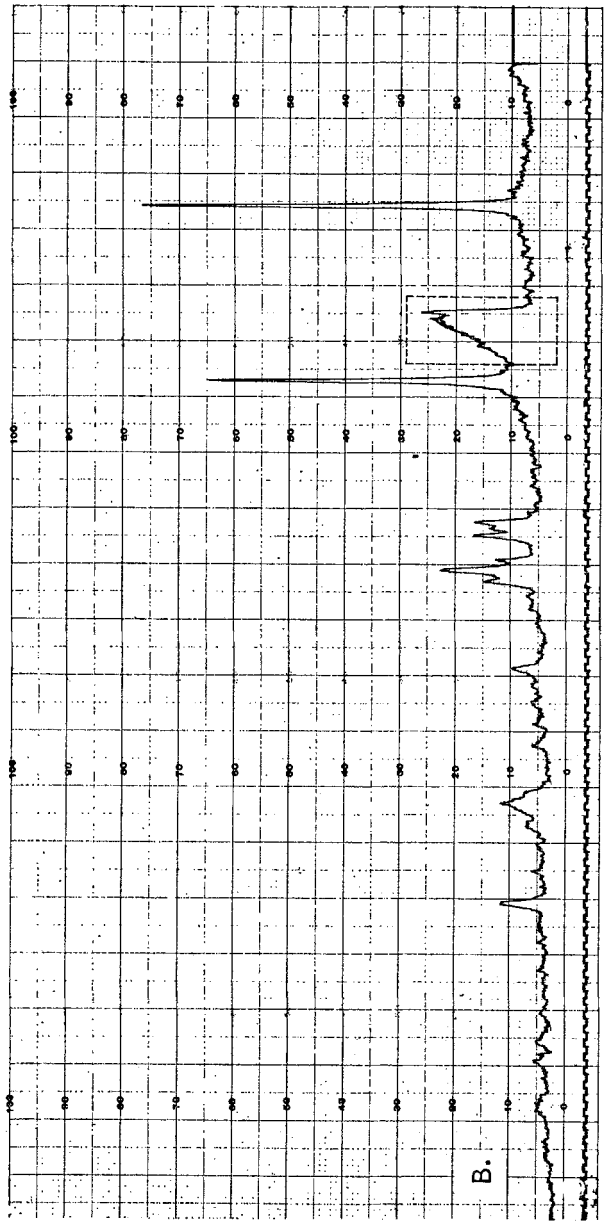

FIGURE 1.—Typical X-ray diffractometer traces for Washington County kaolin. A, unirradiated kaolin; B, irradiated kaolin (1×10^{22} eV/g).

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increased radiation dose than did the intensity of the 060 reflection, it can be seen that any firm interpretation of a maximum in the ratios is presently impossible. Despite the lack of any quantitative explanation of the maxima exhibited by the $nb/3$ crystallinity indices, the gross effects noted of an overall decrease in the $nb/3$ crystallinity index with radiation dose along with the consistent decrease of the 02$\bar{1}$ reflection with increasing radiation dose both indicate that disordering of the aluminum atom arrangement was obtained.

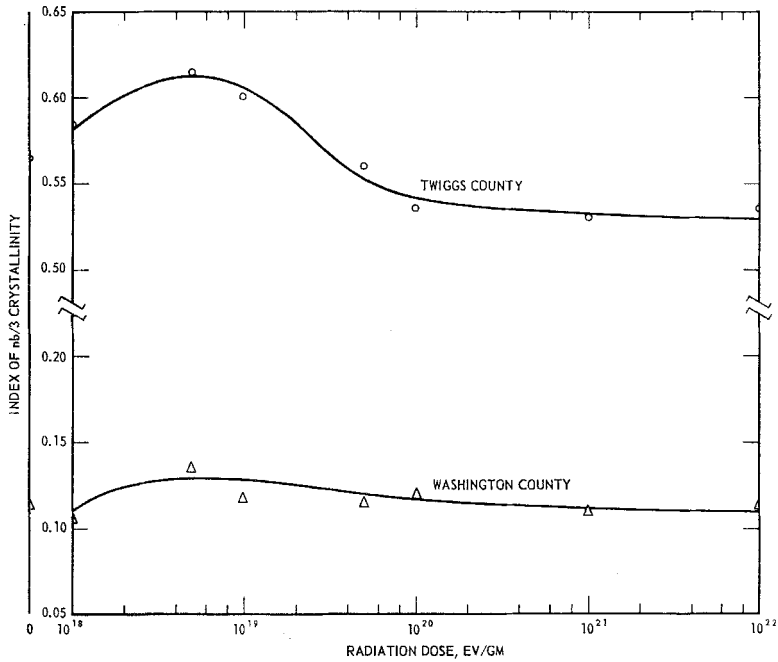

FIGURE 2.—Index of $nb/3$ crystallinity as a function of radiation dose.

In a radiation-damaged material, lattice defects are produced which usually are considered to be isolated interstitial atoms, vacancies, and perhaps rather small agglomerates of these defects. If a sufficiently large number of these defects are built up, they can be detected by X-ray diffraction. Zachariasen (1945), Huang (1947), and Borie (1957) have contributed significantly to the general theory of the X-ray effects to be expected from lattice defects in crystals. These treatments show that displacements, u_d, of atoms from their normal lattice sites lead to diffuse scattering. In a manner similar to that used for derivation of the well-known Debye–Waller temperature factor for X-ray scattering, it can be shown that the ratio of integrated intensities, I,

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of different orders of the same reflection for unirradiated material is related to the same ratio for irradiated material by the following equation:

$$\left(\frac{I_{(hkl)}}{I_{n(hkl)}}\right)_d = \left(\frac{I_{(hkl)}}{I_{n(hkl)}}\right)_0 \cdot \left\{-\frac{16\pi^2 \overline{u_d^2}}{\lambda^2}[\mathrm{Sin}^2\theta_{(hkl)} - \mathrm{Sin}^2\theta_{n(hkl)}]\right\}$$

where the subscripts d and 0 refer to the irradiated and unirradiated material respectively, n is some integer, $\overline{u_d^2}$ is the mean square average of the static atomic displacements perpendicular to the planes (hkl), θ is the Bragg angle, and λ is the wavelength of the X-radiation. The preceding equation was used with the integrated intensities of the 001 and 002 reflections to obtain a mean square average of the atomic displacements parallel to the c-axis for the samples of irradiated kaolin. These data are presented in Table 1. Since the

TABLE 1.—MEAN SQUARE AVERAGE OF THE STATIC ATOMIC DISPLACEMENT PARALLEL TO c-AXIS AS A FUNCTION OF RADIATION DOSE

Nominal dose (eV/g)	$\overline{u_d^2}$	
	Washington County Kaolin ($Å^2 \times 10^2$)	Twiggs County Kaolin ($Å^2 \times 10^2$)
1×10^{18}	6.6	3.7
5×10^{18}	4.0	1.7
1×10^{19}	2.9	1.2
5×10^{19}	3.1	1.4
1×10^{20}	5.1	1.5
1×10^{21}	3.9	1.4
1×10^{22}	5.4	1.6

mean square average of the atomic displacements is dependent upon the fraction of atoms displaced, these values are related to the number of defects present in the lattice as a function of the absorbed radiation dose. In this analysis the difference in the Debye–Waller factors between the unirradiated and irradiated material was assumed negligible.

Particle Size

Particle size distributions were measured with a Coulter counter, Coulter Electronics, Inc., Chicago, Illinois. This instrument determines the number and sizes of particles suspended in an electrically conductive liquid. The suspension flows through a small aperture having an immersed electrode on either side. The particle concentration is such that the particles pass through the aperture substantially one at a time. Each particle's passage displaces some electrolyte within the aperture, momentarily changing the resistance

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between the electrodes and producing a voltage pulse of a magnitude proportional to particle volume. The resultant series of pulses is electronically amplified, scaled, and counted. This instrument measures, directly, the volume

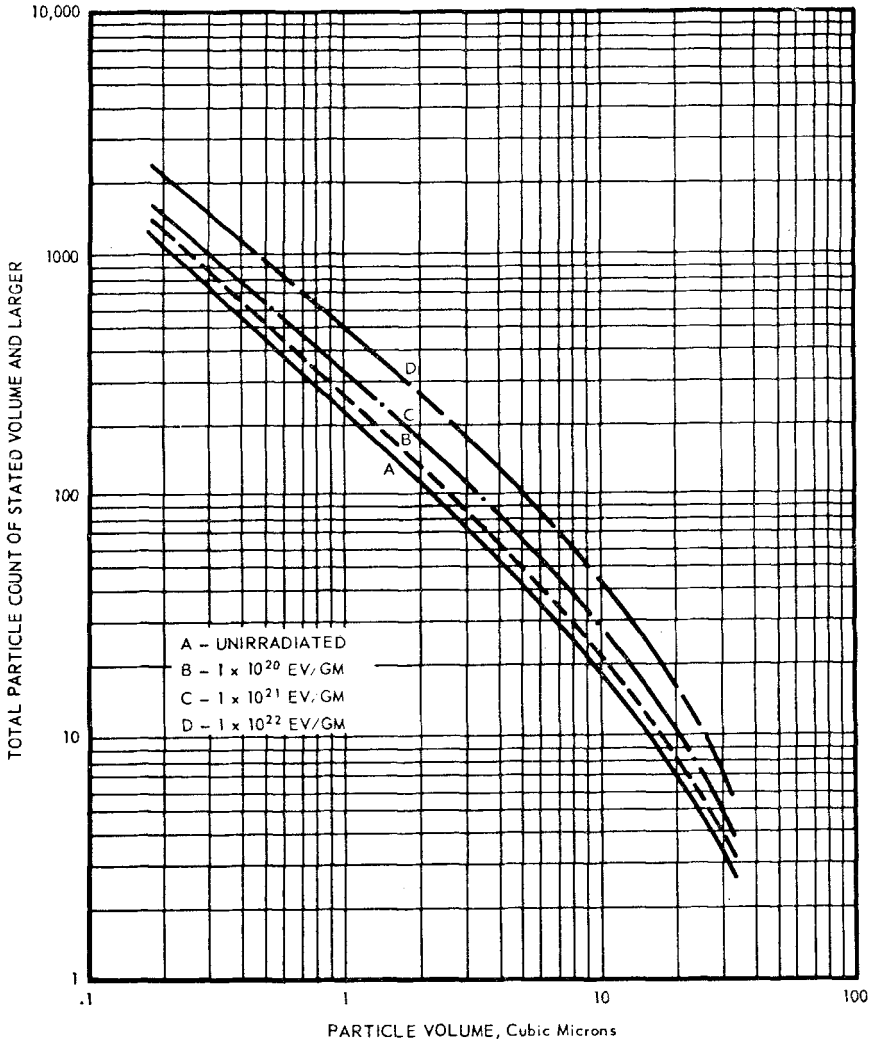

FIGURE 3.—Distribution of particles with volumes of $10\mu^3$ or less for samples of Twiggs County kaolin before and after irradiation.

of a particle. In the case of kaolinite plates, which are flat and thin, a volume measurement is much more meaningful than is a fictitious diameter based on the particle drag coefficient in some fluid or the measurement of a single

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dimension. Through the use of a number of aperture sizes (e.g. 400, 200, 100, 50, 20 and 10 μ diameter) it is possible to measure particle sizes from 200 μ to approximately 0.2 μ equivalent spherical diameter with the Coulter counter. The principal difficulty encountered in measuring particle size distributions of typical kaolin samples is that a single aperture size cannot be utilized to measure the entire distribution. This is due to the fact that the ratio of measurable sizes in a kaolin sample is often as great as 200 to 1, while the ratio of sizes that can be measured with any one aperture diameter is at most 50 to 1. Therefore, to measure the size distributions of kaolin samples such as those used in this work at least two different aperture diameters (e.g. 100 and 10 μ) must be employed. Such a technique, however, requires that the sample be divided into at least two size fractions so that the smaller diameter aperture is not blocked or plugged by the larger particles in a sample. The kaolins investigated in this work were fractionated, after irradiation, by a sedimentation technique. In this technique, a suspension of known concentration was prepared and allowed to settle for a sufficient length of time such that all particles larger than a given size had settled below a sampling point in the sedimentation tube. Two size fractions, one containing the smaller particle sizes and the other the larger, were obtained for each sample and intercomparisons were made by scaling to a common weight basis. Tetrasodium pyrophosphate was found to serve satisfactorily both as a dispersing agent and an electrolyte medium. An ultrasonic generator was used to assure proper initial dispersion of all samples just prior to analysis with the Coulter counter.

For the Twiggs County kaolin an increase in the number of particles in the fractions containing the smaller particles was found with increasing radiation dose (Fig. 3). For the samples that had received the highest radiation dose, the portion of the size distribution below 10 μ^3 (approximately 2 μ equivalent spherical diameter) was found to contain 300 percent more particles per unit weight than did the unirradiated material. This increase, while representing a very small change on a basis of weight percent, does indicate that new particles, of the size of naturally occurring kaolinite plates, are appearing in the irradiated material. These small particles are thought to be the result of delamination from the large kaolinite particles present in the samples. No such change in particle size was observed for the Washington County kaolin.

Specific Surface Area

Specific surface areas were determined by the Brunauer, Emmett and Teller (1938) method of low-temperature, nitrogen adsorption. These results are presented in Table 2. There is a definite trend toward reduced specific surface with increasing radiation dose. For both kaolins the most heavily irradiated samples were found to have specific surface areas approximately 25 percent lower than the corresponding unirradiated samples. (From repeated measurements on several samples, the reproducibility of the specific surface area measurements was found to be ± 3 percent.)

TABLE 2.—SPECIFIC SURFACE AREA OF KAOLIN AS A FUNCTION OF RADIATION DOSE

Nominal dose (eV/g)	Specific surface area	
	Washington County Kaolin (m^2/g)	Twiggs County Kaolin (m^2/g)
Unirradiated	6.1	7.2
1×10^{18}	5.4	6.7
5×10^{18}	5.4	6.6
1×10^{19}	4.7	6.0
5×10^{19}	5.0	6.7
1×10^{20}	5.0	6.0
1×10^{21}	4.5	6.1
1×10^{22}	4.5	5.5

Cation-Exchange Capacity

Cation-exchange capacities were measured as a function of radiation dose. Five-gram quantities of each sample from a series of irradiations of a kaolin were dried simultaneously for 3 hr in an oven at 110° C, treated with 50 ml of dilute hydrochloric acid for 2 hr, then filtered and washed with distilled water. These "acid" clays were then dried to constant weight at 110° C, and 20-percent by weight suspensions in distilled water were prepared. These clay suspensions were titrated with a 0.1023 N sodium hydroxide solution, with pH determinations after the addition of each 0.1 ml of sodium hydroxide until a pH of 7.0 was reached.

The two kaolins gave radically different results. The Washington County kaolin exhibited an increase in cation-exchange capacity with increasing radiation dose while the Twiggs County kaolin exhibited a decrease. For the most heavily irradiated samples, an increase of approximately 40 percent was found for the Washington County kaolin and a decrease of approximately 30 percent was found for the Twiggs County kaolin compared with the respective unirradiated clays. The explanation of this behavior may lie in the treatment that these two clays had received prior to irradiation. As was pointed out, the Washington County kaolin had been fractionated after mining. This fractionation was carried out in water suspension, and the clay was treated with a sodium phosphate deflocculating agent. Some cation-exchange undoubtedly occurred at this time. This supposition is further supported by the fact that the cation-exchange capacity of the unirradiated clay was lower than would be expected from observed correlations with initial degrees of crystallinity (Murray and Lyons, 1960). Exposure to gamma-radiation may have made some of these exchange sites re-available and the number of such sites was a function of radiation dose.

Grinding Studies

Samples of the Washington County kaolin, both unirradiated and irradiated, were subjected to 50 hr of wet-grinding. Nine-inch diameter, porcelain ball mills were used. The mills were each charged with 100 g of sample, 3 kg of $\frac{3}{4}$-in. diameter, $\frac{3}{4}$-in. length porcelain cylinders, and 400 g of water. The milling speed was 120 rpm. After grinding and drying, specific surface areas were determined for these samples by low-temperature nitrogen adsorption. These results are presented in Table 3. Owing to the maintenance

TABLE 3.—SPECIFIC SURFACE AREA OF WET-GROUND KAOLIN AS A FUNCTION OF RADIATION DOSE

Nominal dose (eV/g)	Specific surface area (m^2/g)
Unirradiated	26.7
1×10^{21}	27.8
1×10^{21}	38.8
1×10^{22}	31.1

of identical grinding conditions and grinding times the energy input during grinding was assumed to be essentially the same for each sample. Therefore, the increase in specific surface area with increasing radiation dose can only be attributed to a reduction in the amount of energy necessary to produce a given amount of specific surface.

DISCUSSION

Of the three possible mechanisms for the interaction of gamma-rays with matter, the atomic cross-section of the Compton process is at least 400 times greater than the sum of the other two (that for pair production is zero at this energy) for the interaction of gamma-rays with the principal atoms in kaolinite. In the Compton process, electrons are ejected with an energy comparable to the original gamma-ray energy and thus the substance being irradiated is subjected to an internal bombardment of energetic electrons. The lattice defects produced by this internal electron bombardment are isolated interstitial-vacancy pairs (Billington and Crawford, 1961, p. 47). It is probably this mechanism which produces the disordering of the atoms in kaolinite.

The apparent delamination of stacks, and the decrease in specific surface, are probably both direct results of the production of interstitial atoms and vacancies. Kaolinite layers are believed held together by long hydrogen bonds and van der Waals' forces. The latter decrease in strength with the seventh power of separation distance, and Hendricks (1939) has pointed out that the

key feature of the interlayer coordination of the kaolin minerals is the manner in which oxygens and hydroxyls approach each other in pairs to form long hydrogen bonds. Therefore, any interlayer buckling produced by interstitial atoms would tend to reduce both of these interlayer binding forces. Within the normal kaolin layer, the silica tetrahedra layers show considerable distortion from their idealized geometry, indicative of the strong interlayer forces between them (Pauling, 1930; Newnham, 1961). The nature of these distortions is tension in the octahedral layer and compression of the silica sheet. It seems likely that a reduction in the binding forces due to the presence of interlayer atoms would promote a relaxation of these stresses in adjacent faces. Such a relaxation would lead to a complete misfit between the layers and a severe reduction in the interlayer binding forces. Such an effect might be responsible for the production of small particles observed for the Twiggs County kaolin.

The concept of reduced interlayer binding forces is in agreement with the results of the wet grinding of the Washington County kaolin. Shaw (1942) and Takahashi (1959) have shown that the wet grinding of kaolinite causes shearing along the cleavage plane. Therefore, any weakening of the interlayer forces in the irradiated kaolin would be expected to result in a greater specific surface area for this material than the unirradiated kaolin for equal energy inputs. Buckling and distortion of the lattice layers, causing expansion into the cracks and crevices between the crystallites at the surface of the stacks, is a plausible explanation for the observed reduction in specific surface area. This effect was found to be responsible for the reduction in specific surface area of artificial graphite, a layer-lattice material, upon exposure to neutron irradiation (Billington and Crawford, 1961, p. 408). The lowering of the cation-exchange capacity of the Twiggs County kaolin by gamma-radiation is probably a result of the blocking of exchange sites by whatever mechanism is reducing the specific surface area.

Other investigators (Murray and Lyons, 1960) have found that the specific surface area and cation-exchange capacity increase with decreasing kaolinite crystallinity where the variations in crystallinity occur naturally. It is interesting to note that for the raw, untreated kaolin used in these studies, decreases in specific surface area and cation-exchange capacity were observed to accompany radiation-induced reductions in crystalline perfection.

CONCLUSIONS

The conclusions that can be drawn from this work are:

1. Measurable changes were produced in several of the physical and colloidal properties of kaolinite as a result of exposure to large doses of gamma-radiation.

2. Structural defects which are stable at room temperature are produced in kaolinite by the effect of 0.667 meV gamma-rays.

3. $nb/3$-crystallinity changes are produced by gamma-irradiation as a result of $nb/3$-translations of individual aluminum atoms, rather than of entire

layers (*nb*/3-translations of layers are presumed to be the principal cause of naturally occurring variations in *nb*/3-crystallinity).

4. For one of the kaolins studied, the number of particles of the size of naturally occurring kaolinite plates increased as a result of exposure to gamma-radiation.

5. Exposure of kaolin to gamma-radiation reduces the specific surface area available for low-temperature, nitrogen adsorption, and affects the cation-exchange capacity.

6. For one of the kaolins used in this study, the rate of specific surface area production by wet-grinding was increased by prior exposure to gamma-radiation.

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