ENGINEERING EXPERIMENT STATION

Georgia Institute of Technology

PROJECT INITIATION

Date 5-14-59

PROJECT TITLE: Deagglomeration of Kaolin by High Energy Ionizing Radiation

PROJECT NO: A-1446-5

PROJECT DIRECTOR: W. J. Corbett

SPONSOR: U.S.Atomic Energy Commission, Savannah River Operations

EFFECTIVE: 4-1-59 ESTIMATED TO RUN UNTIL: 3-31-60

TYPE AGREEMENT: Contract AT (38-1)-202

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Final Draft and Approved Copies

Contact: U.S.Atomic Energy Commission
Savannah River Operations Office
P.O.Box A, Aiken, South Carolina

Attn: Mr. Loren T. Palmer

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ENGINEERING EXPERIMENT STATION

Georgia Institute of Technology

PROJECT TERMINATION

Date 2-14-62

PROJECT TITLE: Deagglomerixation of Kaolin by High Energy Ionizing Radiation

PROJECT NO: A-446-5

PROJECT DIRECTOR: W. J. Corbett

SPONSOR: U. S. Atomic Energy Commission (Savannah River Operations Office)

TERMINATION EFFECTIVE: 1-31-62

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GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

May 31, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 1, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from April 1 to May 31, 1959

Gentlemen:

The objective of the research to be performed during the period of this project is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

Performance of experimental work cannot proceed until the multi-kilocurie cesium-137 source authorized under the contract establishing a Radioisotopes Development Center at Georgia Tech has been received. Since experimental work has not begun no technical personnel, other than the Project Director, have yet been assigned to the project.

During the period covered by this report a number of companies in the kaolin industry have been contacted. These companies have expressed great interest in the objective of this study and have cooperated by supplying samples of kaolin for use in the deagglomeration studies. Also, sections of the literature pertinent to this work have been reviewed.

During the next month the survey of the literature will be continued. Work will begin on design and construction of a suitable sample holder for containing the kaolin during irradiation as soon as the design of the cesium-137 source is completed.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

A-446-5

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

June 30, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 2, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from June 1 to June 30, 1959

Gentlemen:

The survey of pertinent sections of the literature has been continued through the period covered by this report. Sample holders for containing the samples of kaolin during irradiation have been designed. In the designs, consideration has been given to methods for measuring the temperature, cooling the sample, and measuring the effusion of water vapor and/or hydrogen during irradiation. The first sample holders constructed, however, will not incorporate all of these features, since it is not certain whether all will be of importance.

During the next month work will be started with control samples of kaolin. X-ray diffraction investigations, electron photomicrographs, grinding studies, etc., will be made for the kaolin which will be used in the irradiation studies.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and
Chief, Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

August 31, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 3, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from August 1 to August 31, 1959

Gentlemen:

During the period covered by this report, studies of the effect of X-radiation on kaolin have begun. A sample of kaolin having a reasonably good degree of crystallinity and containing about 90 per cent by weight of stacked agglomerates was subjected to X-radiation for 20 hours at 50 KVP and 45 MA. The total energy absorbed by the 30-gram sample of kaolin was found by ferrous ion dosimetry to be 4.6×10^{22} electron-volts. Samples of the kaolin, both irradiated and unirradiated, were examined by X-ray diffraction, electron micrography, low temperature nitrogen adsorption for surface area and gas sedimentation for particle size. The X-ray diffraction data indicated no change in crystallinity and lattice spacing of the two samples. However, both the electron photomicrographs and the surface area measurements indicate that some calcination occurred in the irradiated material. This apparent discrepancy in results will require careful investigation. The particle size distributions from gas sedimentation indicate a reduction of approximately 15 per cent in the median diameter for the irradiated sample. This reduction in size is open to question, however, until the distributions can be checked by a more accurate and reliable method such as the Coulter principle which was described in the Quarterly Technical Status Report No. 1.

During the next month the studies of the effect of X-radiation will

continue. The effect of amount of energy absorbed will be studied, and studies will be made with a kaolin from a different source.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

A-496-5

September 30, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 4, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from September 1 to September 30, 1959

Gentlemen:

During the period covered by this report, studies of the effect of X-radiation on kaolin have been continued. Another sample of the same kaolin used in the X-radiation experiment, discussed in Monthly Progress Letter No. 3, has been subjected to X-radiation. This sample weighed approximately 12 grams and was irradiated for 69.5 hours at 50 KVP and 45 MA. The total energy absorbed by this sample was found by ferrous ion dosimetry to be 12.23×10^{22} electron-volts. Further studies have also been conducted on the sample of kaolin which had been previously irradiated for 20 hours. This sample, which was discussed in Monthly Progress Letter No. 3, has been designated T-1-20. The sample which was irradiated for 69.5 hours has been designated T-1-70.

Carbon replicas were made for the unirradiated kaolin and samples T-1-20 and T-1-70. These carbon replicas are used with the electron microscope to obtain greater surface detail of the kaolin particles than is possible from normal observation of the particles in the electron microscope. The procedure for producing these replicas is to deposit a film of carbon on the particles, in a vacuum chamber, from a carbon arc. The particles are then removed from the carbon film by dissolution with hydrofluoric acid. The replicas prepared for the unirradiated kaolin and sample T-1-70 indicated that the kaolin agglomerates had not visibly changed. However, the replica for sample T-1-20 contained quite a number of kaolin agglomerates which had not been dissolved by the hydrofluoric acid, even though the replicas had been left in the acid two or three times longer than is usual. The reason for this abnormal behavior is not immediately apparent.

X-ray diffraction data for sample T-1-70 indicated no change in crystallinity and lattice spacing. Surface area measurements by low temperature nitrogen adsorption indicate a small increase in surface area for sample T-1-70, but not as large as found for sample T-1-20, which had not received as much energy during irradiation. These results do not seem to be in agreement.

Mr. John H. Burson III joined the project on September 1, 1959, as a Research Assistant. Mr. Burson has a Bachelor's Degree in Chemical Engineering from the Georgia Institute of Technology, and for the past four years he was Chief Chemist with Testworth Laboratories of Georgia, Inc., Carrollton, Georgia.

Difficulties have arisen at the Oak Ridge National Laboratory with the encapsulation of the cesium-137 for the cesium-137 source, authorized under Task VI of the Georgia Tech Radioisotopes Development Center contract, and the source will not become available for irradiation studies until January 1, 1960, at least. In view of this delay, and the fact that the use of the X-ray machine is too expensive for the limited amount of data which can be obtained with it, the rate of effort on this project will be considerably reduced until irradiation service from the cesium-137 source is available.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

November 30, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 5, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from November 1 to November 30, 1959

Gentlemen:

A 150-kv X-ray machine has been obtained, on loan, from Vanderbilt University, Nashville, Tennessee. Studies of the effect of X-radiation on kaolin will continue using this machine. A glass sample holder is being constructed for use with this X-ray machine, which has a rod anode tube. The sample holder consists of concentric, cylindrical compartments. The sample will be held around the X-ray tube in the inner compartment and the outer compartment will contain a ferrous ion solution for dosimetry studies.

During December, samples of the kaolin used in the previous X-ray studies will be investigated for various amounts of total energy absorbed.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

A-446-5

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

December 31, 1959

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 6, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-50-43
Covering the Period from December 1 to December 31, 1959

Gentlemen:

Studies of the effect of X-radiation on kaolin have been continued during this report period. A 20-gram sample of the same kaolin used in the previous studies was irradiated for 100 hours at 150 kv and 20 ma. The total energy absorbed by the sample was of the order of 10^{21} electron-volts per gram.

Particle size measurements of the irradiated material indicated no detectable change in particle size, and a surface area measurement indicated that the surface area had not changed significantly. However, studies with the electron microscope revealed some physical changes. Approximately 50 per cent of the agglomerates observed with the electron microscope could not be calcined with the electron beam. This behavior is similar to that observed with sample T-1-20, as reported in Technical Status Report No. 2. A much larger percentage of the agglomerates in this sample, T-1-100, exhibited this behavior than in sample T-1-20. Electron photomicrographs of carbon replicas of sample T-1-100 showed from 10 to 20 per cent of the kaolin stacks to be "collapsed." The kaolin plates seemed to be still held together, but in a very loose, disordered array. They appeared to be aggregated in a horizontal plane rather than the more normal vertical array. X-ray diffraction studies, though not yet complete, have shown a pronounced decrease in degree of crystallinity and indicate a decrease in crystalite size, for this sample.

During the month of January, studies of the effect of X-radiation of kaolin will continue with the 150 kv X-ray machine. A slurry of kaolin in water will be irradiated, and the kaolin examined for structural changes.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

February 29, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 7, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from February 1 to February 29, 1960

Gentlemen:

During the month of February, studies of the effect of gamma radiation on kaolin were begun. Approximately 200 grams of the kaolin, T-1, which has been used in all previous studies, were placed in the center well of the cesium-137 research irradiator. Samples, weighing 15 grams each, were removed from the irradiator every 50 hours up to a total irradiation time of 500 hours. The total doses for these samples ranged from 3.8×10^{21} electron-volts per gram for the sample removed at 50 hours to 3.8×10^{22} electron-volts per gram for the sample removed at 500 hours.

Electron microscope studies, X-ray diffraction studies, and surface area determinations are currently underway for these samples; however, results are available for only a few samples at this time. X-ray diffraction traces show a definite decrease in crystallinity and crystallite size with increasing irradiation time. A decrease in crystallinity was observed even with the first sample, which was taken at 50 hours. Electron photomicrographs of carbon replicas did not show a detectable change with the sample taken at 50 hours. However, changes were observed with the carbon replicas of the kaolin that had been irradiated 100 and 150 hours. The kaolin stacks appear to be collapsed in the same manner as in the sample irradiated with the 150-kv X-ray machine. Also, fewer stacks seem to be present in the samples irradiated for 100 and 150 hours. The surface area determinations for these same samples indicate a decrease in surface area with increasing irradiation time. This is not what would normally be expected. If the particle sizes in the sample are decreasing as the electron photomicrographs indicate, the surface area of the sample should be increasing. This apparent decrease in surface area may be due to some secondary effect of the radiation on the surface of the particles.

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During the coming month the above tests will be completed. Particle size distributions and differential thermal analyses will be obtained for these samples. A sample of approximately 200 grams of kaolin will be given a total dose of 10^{22} electron-volts per gram for mechanical shear and slurry viscosity tests. The annual report will be prepared.

Respectfully submitted,

William S. Gilbert
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

April 30, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 8, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from April 1 to April 30, 1960

Gentlemen:

The research performed on this project during the past month has been concerned with reflectance measurements, particle size determinations, and evaluation of electron diffraction patterns for samples of irradiated kaolin.

Reflectance measurements were made on samples of kaolin that had received various doses of high-energy, ionizing radiation and on a sample of unirradiated kaolin. The tests were made with a General Electric recording spectrophotometer using a magnesium oxide standard. The irradiated samples gave identical reflectance traces that were uniformly lower than the trace of the unirradiated kaolin by one reflectance point across the wavelength range of 380 to 700 millimicrons.

Particle size measurements on irradiated samples of kaolin with the Coulter Counter have been continued. Additional particle size measurements have been made using a liquid sedimentation technique. A definite decrease in particle sizes has been found for the irradiated kaolin samples, even on a weight per cent basis.

Further analyses of the electron diffraction patterns obtained during the last report period along with some additional ones obtained during this report period have indicated that even though changes are observed for the patterns of irradiated samples, no pertinent information can be obtained with this technique that cannot be obtained from X-ray diffraction. Therefore, no further electron diffraction measurements are contemplated.

Survey infrared spectra will be made for samples of unirradiated and irradiated kaolin during the next month. It is hoped that these spectra will reveal whether or not any lattice defects or strains are present in

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the individual kaolin layers of an irradiated sample. Some samples of unirradiated and irradiated kaolin have been ground with a ball mill during the past month. Work during the coming month will be concerned primarily with grinding more samples and obtaining results for the samples which have already been ground.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
May 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 9, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from May 1 to May 31, 1960

Gentlemen:

Research performed on this project during the past month has been concerned with infrared studies of kaolin before and after irradiation, X-ray diffraction and electron microscopy studies, particle size determinations and pH measurements of kaolin which had been irradiated and then ground in a ball mill.

Small wafers of finely divided potassium bromide containing 0.3 per cent kaolin by weight were prepared for a sample of unirradiated kaolin, and for samples of kaolin which had received 1×10^{20} and 1×10^{22} electron volts per gram gamma-radiation.

A complete infrared spectrum was obtained for these samples with a Perkin-Elmer Model 21 infrared spectrometer. The traces indicate that no significant differences exist in the positions of the atoms and radical groups in the kaolin after irradiation. Further infrared surveys will be made with samples which have received larger doses of gamma-radiation.

The X-ray diffraction and electron microscopy studies of irradiated, ball-milled kaolin have not yet been completed for the first samples.

Two samples of kaolin, one unirradiated and one that had received a dose of 1×10^{20} electron volts per gram gamma-radiation were ground in a ball mill for 50 hours each. A porcelain mill 9 inches in diameter with a charge of 100 grams of sample and 3 kilograms of 3/4-inch-diameter, 3/4-inch-length porcelain cylinders was used for these studies. Particle size determinations for these samples show a significantly greater amount of small particles for the kaolin which was irradiated before grinding.

The pH measurements of ground kaolin show a decrease in pH with an increase in the length of ball milling with no significant difference between irradiated and unirradiated samples ground for equal lengths of time.

Work during the coming month will be devoted to further studies of irradiated, ball-milled kaolin and preparation of Quarterly Technical Status Report No. 4.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
July 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 10, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from July 1 to July 31, 1960

Gentlemen:

Experimental work during the past month has been concerned with irradiation of samples for use in the studies of the effect of wet-grinding on kaolin and establishment of the grinding times to be used in these studies. Stockpiles of the Washington County, Georgia, kaolin that have received doses of 1×10^{20}, 1×10^{21} and 1×10^{22} electron-volts per gram have been established for use in the studies of the effects of wet-grinding on irradiated kaolin. These stockpiles contain approximately 300 grams of kaolin each. Small samples of each of these quantities of kaolin have been examined by X-ray diffraction and electron microscopy to assure that their characteristics are the same as those of previously examined samples that had received similar doses of high-energy, ionizing radiation.

Unirradiated samples of the Washington County, Georgia, kaolin have been wet-ground in a ball mill with various ratios of water and clay for various lengths of time to establish conditions that will produce a significant reduction in particle size. The effects of these variables are being evaluated from particle size distributions obtained with the Coulter Counter.

Work during the coming month will be concerned with the effects of wet-grinding on irradiated kaolin.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

August 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 11, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from August 1 to August 31, 1960

Gentlemen:

During this report period, samples of kaolin, before and after irradiation, have again been examined by infrared spectroscopy, using larger concentrations of kaolin in the potassium bromide pellets and with more attention given to certain adsorption bands. A careful re-examination of the infrared adsorption spectra that had been obtained previously, and reported in Quarterly Technical Status Report No. 4, revealed some doubt that the spectra were identical for samples of kaolin before and after irradiation. The spectra obtained during the present report period do not show any deviations which are immediately obvious; however, they are being analyzed in greater detail.

The cation-exchange capacity of unirradiated kaolin and kaolin which had received doses of 1×10^{20}, 1×10^{21}, and 1×10^{22} electron-volts per gram of gamma-radiation were redetermined during the past month since the cation-exchange curves reported in Quarterly Technical Status Report No. 4 appeared to contain anomalies. The same general technique was used as for the previous determinations, but the samples were dried more carefully and the sodium hydroxide was added in smaller increments. The results of these later determinations show a definite increase in the cation-exchange capacity with increasing doses of gamma-radiation.

Studies of the effects of wet-grinding on samples of irradiated kaolin have been continued during the past month. Consideration is also being given to techniques and apparatus for the irradiation of kaolin with the Cesium-137 Research Irradiator at liquid nitrogen temperatures. Data from such irradiations would aid in establishing the mechanism by which high-energy, ionizing radiation disorders the crystal structure of kaolinite.

Work during the coming month will be directed toward completing the studies of the effects of wet-grinding on irradiated kaolin and preparing Quarterly Technical Status Report No. 5.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA
October 31, 1960

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 12, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from October 1 to October 31, 1960

Gentlemen:

The research performed during this report period has been concerned with attempts to determine the effect of gamma-radiation upon the degree of crystallinity of kaolinite. Previous attempts using X-ray diffraction have been unsuccessful due to poor resolution of the $02\bar{1}$ diffraction maxima in the traces of the kaolin being used in these experiments. As pointed out in Quarterly Technical Status Report No. 5, it was first thought that this poor resolution was due to orientation of the kaolin particles in the preparation of the samples for diffraction studies. A procedure of mixing the kaolin with various amounts of finely divided silica was used to overcome the particle orientation. Contrary to expectations, the resulting reduction in particle orientation did not improve the resolution of the $02\bar{1}$ diffraction maxima significantly. Success has been obtained, however, by replacing the Gieger counter that is normally used with the diffractometer with a proportional counter and adding a pulse height analyser. This arrangement has suppressed the background noise considerably, improved the diffraction maxima to background ratio and reduced the effect of the beta ray reflection of the 002 diffraction maxima. This beta ray reflection creates a peak on the diffraction trace which is very close to the $02\bar{1}$ diffraction maximum, and interferes with the resolution of this maximum. It appears that these modifications improve the resolution of the $02\bar{1}$ diffraction maxima well enough to obtain consistent results, although these measurements are not yet complete.

Samples of kaolin have been irradiated with smaller doses of gamma-radiation than have been used previously in this work, in an attempt to obtain information about the variation of kaolinite crystallinity as a function of radiation dose over a wider range. These doses are 1×10^{18}, 5×10^{18}, 1×10^{19} and 5×10^{19} electron-volts per gram.

In Annual Technical Status Report No. 1 electron diffraction patterns were presented for both unirradiated and irradiated samples of kaolin. It was

subsequently pointed out in Monthly Progress Letter No. 8 that the electron diffraction technique which had been employed to obtain these patterns could supply no significant information that could not be obtained from X-ray diffraction, and that no more electron diffraction studies were contemplated. It now appears that any additional information on the structural changes in the kaolinite crystal as a result of high-energy, ionizing radiation will be helpful. Therefore, some very careful measurements of electron diffraction are being made to determine exactly what additional information can be obtained with this technique and whether or not it warrants further utilization.

During the coming month the surface area measurements, reflectance measurements and cation-exchange capacity measurements on the wet-ground, irradiated kaolin which had originally been scheduled for this past month will be carried out. These measurements were postponed, due to the greater importance of improving the technique of measuring the degree of crystallinity. The degree of crystallinity measurements will also be continued.

Respectfully submitted,

William J. Orbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

TABLE I

SPECIFIC SURFACE AREAS OF WET-GROUND KAOLIN
AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area (M^2/Gm)
Unirradiated	26.7
1×10^{20}	27.8
1×10^{21}	28.8
1×10^{22}	31.1

is the result that was anticipated when these experiments were undertaken, and this information will aid in establishing the deagglomerating mechanism.

The remainder of the research effort this month was concerned with X-ray and electron diffraction studies on samples of unirradiated and irradiated kaolin. A special status report was also prepared for the Office of Isotopes Development contractors meeting in Washington, D. C.

During the next month special effort will be exerted on the problem of particle size measurement in irradiated samples and irradiated, wet-ground samples. A series of irradiations will be performed on the kaolin from Twiggs County, Georgia, which has been introduced into this program, and the X-ray and electron diffraction studies will continue.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

January 31, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 14, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT(38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from January 1 to January 31, 1961

Gentlemen:

During this report period the research performed on this project has been concerned primarily with particle size measurements for samples of kaolin before and after irradiation. As has been pointed out in the last two reports, some doubt has arisen as to whether or not a true analysis of the change in size distributions due to the effects of radiation or the wet-grinding of irradiated kaolin has been obtained with the Coulter Counter. Data from specific surface area and cation-exchange measurements as well as electron micrographs have pointed to a greater change in particle size than has been observed with the Coulter Counter. Inspection of the electron micrographs for various samples of kaolin indicates that the kaolin stacks are broken down by the delamination of individual plates or thin layers of a very few plates, rather than the progressive division of stacks into smaller and smaller aggregates. Measurements taken from these micrographs indicate that the kaolin plates produced in this manner are predominately in the size range below 0.75 micron equivalent spherical diameter. Until recently, the lower limit of direct measurement of the Coulter Counter has been approximately 0.75 micron equivalent spherical diameter. However, the manufacturers of the Coulter Counter have just developed an aperture tube with a 10-micron orifice which extends the lower limit of direct measurement of the instrument to 0.25 micron. One of these aperture tubes has been obtained on loan from Coulter Industrial Sales and is being used to extend the lower range in the size distributions of the kaolin samples. This tube was not received until the last week of this report period, however, and this work has just begun.

A further problem with size measurement of the kaolin samples has been encountered. This is the loose agglomeration of the kaolin plates in suspension during the size measurements with the Coulter Counter. The presence of an electrolytic solution, which is necessary for operation of the Coulter Counter,

along with the natural Brownian movement associated with particles of this size has caused a considerable degree of flocculation in the smaller size ranges. Samples of irradiated and unirradiated kaolin have been subjected to high intensity ultrasonic vibrations immediately prior to examination with the Coulter Counter, and in every case the irradiated kaolins have shown a greater degree of fine particles than has the unirradiated kaolin, when both were examined immediately after removing from the ultrasonic generator. After a short length of time, usually 5 to 10 minutes, the flocculation process has reduced the apparent number of fine particles in the irradiated samples to approximately the same number as those present in the unirradiated samples.

Various techniques are now being investigated to overcome this difficulty. One possibility is to deflocculate with the ultrasonic generator prior to each size level measurement. Other methods such as the use of different electrolytes and various wetting agents are also being investigated.

During the next month, these problems associated with the particle size determinations will be investigated. A sample with a smaller particle size than any used to date will be irradiated and investigated for changes in surface area, cation exchange capacity and crystallinity.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

February 28, 1961

U. S. Atomic Energy Commission
1717 H. Street, N. W.
Washington 25, D. C.

Attention: Dr. Paul C. Aebersold, Director
Office of Isotopes Development

Subject: Monthly Progress Letter No. 15, Project No. A-446-5
"Deagglomeration of Kaolin by High-Energy, Ionizing Radiation"
Contract No. AT (38-1)-202
Task No. V, Contract Authorization No. 1A-59-43
Covering the Period from February 1 to February 28, 1961

Gentlemen:

The past month has been devoted primarily to X-ray diffraction studies and determination of cation-exchange capacities. A major problem with the X-ray diffraction studies has been the difficulty in resolving the $02\bar{1}$ diffraction maxima for the Washington County kaolin. This problem has been overcome. Since the last efforts at resolving this maxima for this particular kaolin a new high-intensity X-ray tube has been installed in the diffractometer used on this project. This tube can be operated at 40 kv and 40 ma as opposed to 40 kv at only 20 ma for the tube used previously. This higher intensity allows the use of a pulse-height analyzer in conjunction with a β-ray filter, and as a result the $02\bar{1}$ maxima, that previously was obscured by the β-ray reflection of the 002 diffraction maxima, can be resolved. From these data the degree of crystallinity has been calculated as a function of radiation dose. These results are presented in Table I.

TABLE I

VARIATION OF CRYSTALLINITY INDEX
WITH RADIATION DOSE FOR KAOLIN FROM WASHINGTON COUNTY, GEORGIA

Dose (EV/Gm)	Crystallinity Index
Unirradiated	0.160
1×10^{18}	0.152
5×10^{18}	0.166
1×10^{19}	0.152
5×10^{19}	0.162
1×10^{20}	0.162
1×10^{21}	0.157
1×10^{22}	0.147

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During the past month the cation-exchange capacities of samples of a raw kaolin from Twiggs County, Georgia, were determined as a function of radiation dose. The same technique of titrating the acidified clay with sodium hydroxide was used as has been used in the past. However, the raw kaolin used in these studies showed a definite decrease in cation-exchange capacity with increasing radiation dose, whereas the kaolin from Washington County, Georgia, which had been processed to remove the fine particles, showed a definite increase in cation-exchange capacity with increasing radiation dose (Quarterly Technical Status Report No. 5). The decrease was as much as 50 per cent, over the exchange capacity of the unirradiated kaolin, for the sample which had received 10^{22} ev/gm. An explanation of this behavior is not immediately obvious, and will probably require data for other kaolins from various sources before one can be reached.

As discussed in Monthly Progress Letter No. 14, it was planned that this month would be devoted primarily to particle size measurements with the aid of a recently obtained 10-micron Coulter Counter aperture tube. Unfortunately, however, this aperture tube developed a stress crack shortly after being placed in operation. Coulter Industrial Sales has agreed to make another 10-micron aperture tube, as well as a 19-micron aperture tube, available to the project on loan. These tubes are expected on or about March 1, 1961, and the coming month will be devoted to the measurement of particle size distributions of unirradiated and irradiated samples of kaolin.

Respectfully submitted,

William J. Corbett
Project Director

Approved:

Fred Sicilio
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN HIGH-ENERGY, IONIZING RADIATION

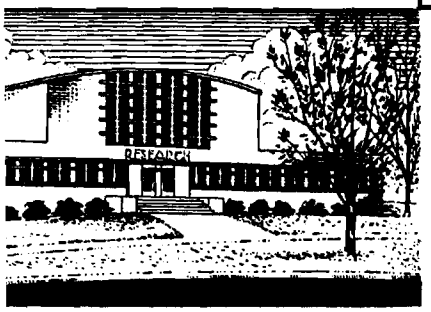
By

WILLIAM J. CORBETT

COVERING THE PERIOD
1 APRIL to 31 JULY 1959
Printed 10 August 1959

CONTRACT NO. AT(38-1)-202
TASK NO. V, CONTRACT AUTHORIZATION NO. 1A-59-43
Placed By
UNITED STATES ATOMIC ENERGY COMMISSION
SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT

COVERING THE PERIOD
1 APRIL to 31 JULY 1959
Printed 10 August 1959

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SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

Performed for
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OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

The objective of this research program is to investigate the possibilities of using high-energy ionizing radiation to reduce agglomerates of kaolin to discrete particles.

Kaolin, whose primary constituent is kalonite ($Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$), occurs in nature as flat, crystalline, hexagonal plates and aggregates of these plates. These aggregates of plates, known as stacks, are believed held together by hydrogen bonding between the plates. This research program will employ high-energy ionizing radiation in an attempt to degrade this hydrogen bonding so that these aggregates can be easily separated into discrete plates.

Companies in the kaolin industry have expressed great interest in the objective of this program.

Experimental work to date has been concerned with establishing and evaluating procedures for investigating the properties of kaolin before and after exposure to irradiation. Experiments to determine the effect of high-energy ionizing radiation on the amount of energy required to deagglomerate kaolin aggregates cannot proceed until the multi-kilocurie cesium - 137 source authorized under Task VI of the contract establishing a Radiosotopes Development Center at Georgia Tech has been received. Work in the immediate future will be concerned with irradiating small amounts of kaolin with an X-ray machine and evaluating the effects of this radiation by X-ray diffraction and electron photomicrography.

TABLE OF CONTENTS

I. INTRODUCTION

This report summarizes the work performed from April 1 to July 31, 1959. The objective of the research to be performed during the period of this project is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy ionizing radiation.

The primary constituent of kaolin is the mineral kalonite, a hydrated aluminum silicate ($Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$). The crystal structure of the kaolin group consists of one sheet of gibbsite ($Al_2O_3 \cdot 3\ H_2O$) condensed with one tetrahedral silica sheet, forming a stable non-expanding crystal lattice. The structure of kalonite is shown schematically in Figure 1. Discreet particles of kaolin appear as flat, crystalline, hexagonal plates. These plates are seldom found to have a diameter greater than 2 microns, equivalent spherical diameter. Frequently these plates are found aggregated into stacks. These stacks have an equivalent spherical diameter of from 2 microns to greater than 40 microns. Figure 2 is an electron photomicrograph of a typical kaolin sample. A stack of kaolin plates can be seen in the lower right hand corner of the figure.

According to Iler[1] the flat plate-like crystals of kaolin are held together in stacks by hydrogen bonding. The overall plate of kaolin is bounded on one side by siloxane atoms and on the other by a layer of hydroxyl groups attached to Al^{+++}. When these plates are stacked the hydroxyl groups of one plate fit directly above the holes in the hexangonal net of oxygen atoms of the next plate, and the layers are held together strongly by a multiplicity of

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[1] Iler, Ralph K., The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca, New York (1955) p. 203.

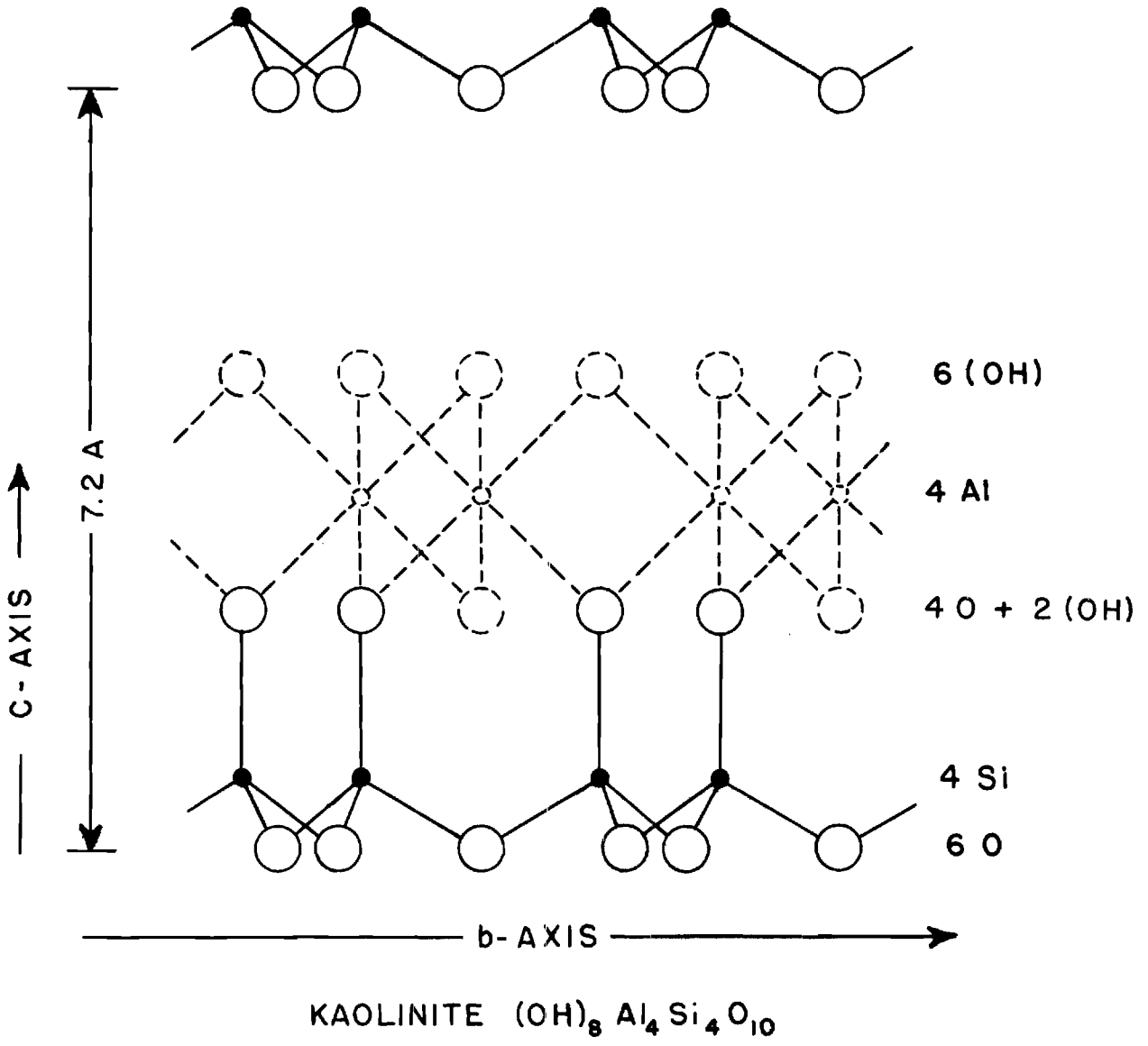

Figure 1. Schematic Presentation of the Crystal Structure of Kaolinite. [Grim, Ralph E., "Modern Concepts of Clay Materials", J. Geology Vol. L., 225-275 (1942)]

hydrogen bonds. There is clevage along this plane, but ordinary grinding procedures cannot reduce the thickness of the stacks of plates appreciably. Grim[2] cites the fact that the lattice structure does not expand with varying water content as being an indirect indication that the plates in a kaolin stack are held together by hydrogen bonding.

Since the bonding of kaolin stacks along their cleavage planes is apparently due to hydrogen bonding, it is believed that the force required for cleavage can be reduced by exposing the kaolin stacks to high-energy ionizing radiation. It has been established that high-energy ionizing radiation can bring about the degradation of chemical bonds in both inorganic and organic solids[3]. The hydrogen bond is a relatively weak chemical bond and it is reasonable to assume that it can be degraded by ionizing radiation from a high-energy source.

Even though the hydrogen bonding between plates may be degraded, some mechanical shear will probably still be required to separate the plates. Mechanical shear devices such as a ball mill, or small orifices through which a slurry of the material is passed at high pressures, can be employed.

Several companies in the kaolin industry have been informed of this project and its purpose. These companies have expressed great interest in the objective of this study.

Since irradiation experiments have not begun, no technical personnel, other than the project director, have yet been assigned to the project.

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[2]Grim, Ralph E., "Modern Concepts of Clay Materials", J. Geology Vol. L, 225-275 (1942).

[3]Heal, H. G., "The Chemical Effects of Ionizing Radiation in Solids I, II", Atomics (British) 6, 205-208, 241-246 (1955).

II. EXPERIMENTAL WORK

Two samples of kaolin have been obtained from different kaolin companies for use in the deagglomeration studies. One of the samples, designated H-1, contains approximately 50% by weight of stacked aggregates. The other sample, designated T-1, contains approximately 90% by weight of stacked aggregates.

On the basis of tests run with a typical kaolin sample, the Coulter Counter, Coulter Industrial Sales Co., Elmhurst, Illinois has been selected for determining the particle size analyses for this study. This device determines the number and size of particles suspended in an electrically conductive liquid. The suspension flows through a small aperture having an immersed electrode on either side, with particle concentration such that the particles traverse the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperature, momentarily changing the resistance between the electrodes and producing a voltage pulse of magnitude proportional to particle volume. The resultant series of pulses is electronically amplified, scaled and counted. The data from this instrument are easily converted to the typical per cent by weight versus diameter type of distribution curve.

A standard technique has been adopted for determining the viscosity of a slurry of the kaolin samples before and after irradiation. Into a tared cup, 400 grams of dried clay are weighed along with 171 grams of a 0.20% solution of tetrasodium pyrophosphate. This slurry is stirred for 10 minutes in a Hamilton Beach Mixer No. 30 at high speed, stopping occasionally to remove clay mixture from the wall of the mixer cup. After stirring the mixture is screened through a 100-mesh screen and the temperature is adjusted to 25° C. The viscosity of the mixture is then determined in a Stormer Viscometer using a driving weight of 150 grams and a hollow cylinder type rotor.

Experience has been gained with the Brunauer, Emmett and Teller[4] method of low-temperature, nitrogen-gas adsorption for determining the surface areas of kaolin samples.

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[4] Brunauer, S., Emmett, P. H. and Teller, E., "The Adsorption of Gases in Multimolecular Layers", J. Am. Chem. Soc. 60, 309-19 (1938).

III. DISCUSSION AND CONCLUSIONS

Performance of actual irradiation experiments cannot proceed until the cesium - 137 source authorized under Task VI of the contract establishing a Radiosotopes Development Center at Georgia Tech has been received.

The technique of determining particle size by the Coulter Counter is as accurate, if not more accurate, than by sedimentation, or optical microscopy in addition to being less tedious and time consuming. The colloidal and surface properties of kaolin are of importance in connection with its industrial uses. Therefore, viscosity and surface area measurements are necessary to determine what effect irradiation has on these properties.

IV. FUTURE PROGRAM

At least a few hundred grams of kaolin are required to perform actual deagglomeration studies. A ball mill will be employed as the device to produce mechanical shear on the irradiated material, and this device requires a fair quanitity of material. Therefore, this phase of the work cannot proceed until the cesium - 137 source has been received. However, an X-ray machine can be used to study some of the effects of X-rays on kaolin. Only a small quantity of kaolin can be handled in this manner, but large quantities are not required for x-ray diffraction and electron photomicrography investigations. The work during the immediate future will be concerned with obtaining and comparing data from those techniques for unirradiated kaolin and kaolin irradiated with an x-ray machine.

Respectfully submitted:

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON III

COVERING THE PERIOD
1 AUGUST to 31 OCTOBER 1959
Printed 10 November 1959

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TASK NO. V, CONTRACT AUTHORIZATION NO. 1A-59-43
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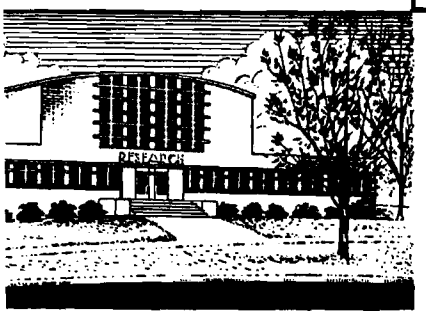
GERMANTOWN, MARYLAND



Engineering Experiment Station
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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 2

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON III

COVERING THE PERIOD
1 AUGUST to 31 OCTOBER 1959
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Performed for
UNITED STATES ATOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

ABSTRACT

Experimental work during this report period was concerned with the effect of X-radiation on kaolin.

Samples of kaolin were irradiated with an X-ray machine at 50 kvp and 45 ma for 20 hours and 69.5 hours. The samples absorbed 1.6×10^{21} and 9.8×10^{21} electron-volts per gram respectively.

In general no significant changes were observed for the irradiated kaolin. The changes which were observed seem to be anomalous and inconclusive.

The cesium-137 source to be used on this project will not become available until January 1, 1960, at least. Experimental studies of the effect of X-radiation will continue using a 150-kv X-ray machine, if it becomes available as expected. Otherwise the rate of effort on this project will be considerably reduced until the cesium-137 source becomes available.

TABLE OF CONTENTS

This report contains 7 pages.

I. INTRODUCTION

This report summarizes the work performed from August 1, 1959, to October 31, 1959. The purpose of work under this contract is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

Mr. John H. Burson III joined the project on September 1, 1959, as a Research Assistant. Mr. Burson has a Bachelor's Degree in Chemical Engineering from the Georgia Institute of Technology and for 4 years was Chief Chemist with Testworth Laboratories of Georgia, Inc., Carrollton, Georgia.

II. EXPERIMENTAL WORK

A. Apparatus

The effect of X-radiation on kaolin has been studied during this report period. Samples of a reasonably well crystallized kaolin which contains about 90 per cent by weight of stacked agglomerates were subjected to X-radiation at 50 kvp and 45 ma.

Irradiation of the kaolin was accomplished by placing the sample in a hollow steel cylinder, approximately 7 cm in diameter and 3 cm long, which had a thin mica window in one end. This window served to support the sample. Mica was chosen because this material gives less back-scatter and beam attenuation than glass or plastic. The cylinder with its contents was fitted over the end of the X-ray tube. This arrangement is shown schematically in Figure 1.

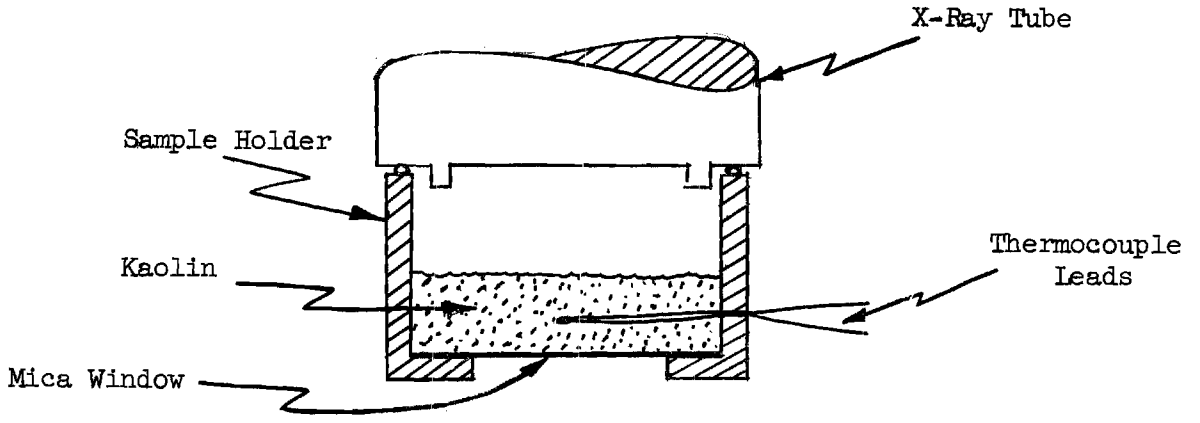

Figure 1. Schematic Diagram of Irradiation Apparatus.

B. Dosimetry

Dosimetry measurements were made by the ferrous ion technique. One hundred milliliters of 0.01015 N Fe^{++}, as ferrous ammonium sulfate, were diluted, in a crystallization dish, to 2 liters by 0.8 N H_2SO_4. This solution was then placed under the X-ray tube, which had the sample holder and mica window in place, and irradiated for 30 minutes. During irradiation, oxygen was bubbled into the solution at the rate of approximately 60 bubbles per minute, and the solution was agitated by means of a glass-covered stirring bar and a magnetic stirrer. This same procedure was then repeated with a fresh solution and with the kaolin sample in the sample holder. It was necessary, however, to increase the exposure time of the solution to 2 hours in order to obtain a significant conversion of Fe^{++}. The two solutions were then titrated with 0.01025 N $K_2Cr_2O_7$ to obtain the degree of conversion in the two solutions. From the fact that 15.5 molecules of Fe^{++} are converted per 100 electron-volts of energy, the energy absorbed by the kaolin sample was calculated.

One kaolin sample, designated T-1-20, was irradiated for 20 hours. This sample, which weighed 29.5 grams, absorbed 1.6×10^{21} electron-volts per gram. Another sample of the same kaolin, designated T-1-70, was irradiated for 69.5 hours. This sample weighed 12.4 grams and absorbed 9.8×10^{21} electron-volts per gram.

C. Physical Measurements

Small quantities of samples T-1-20, T-1-70 and the unirradiated kaolin were examined by X-ray diffraction for possible changes in the crystal structure. Direct comparison of the X-ray diffraction patterns of the three samples indicated no observable increase in the crystal lattice spacings or change in the degree of crystallinity. Electron photomicrographs were made, with the electron microscope, to determine any visible changes which the kaolin might have undergone during irradiation. These photomicrographs did not show any detectable differences between the irradiated and unirradiated material. Typical photomicrographs of both irradiated and unirradiated kaolin are shown in Figure 2. These photomicrographs, unfortunately, are not suitable for making size distributions because of the small ratio between the field of view and the size of the

agglomerates which are known to be present in large quantities. Carbon replicas of particles of samples T-1-20, T-1-70 and the unirradiated kaolin were also photographed by means of the electron microscope. These replicas were produced by depositing a thin film of carbon on the kaolin particles, in a vacuum chamber, from a carbon arc. The particles were then removed from the carbon film by dissolution with hydrofluoric acid. Replicas of the surface prepared in this manner and observed with the electron microscope show much greater surface detail than can be obtained by direct observation of the particles. Figure 3 presents electron photomicrographs of replicas of both irradiated and unirradiated material. Figure 3, C, shows an undissolved kaolin agglomerate which was left on the replica after treatment with hydrofluoric acid.

Surface areas of the unirradiated kaolin, sample T-1-20 and sample T-1-70 were determined by low-temperature, nitrogen-gas adsorption. The surface areas were found to be 6.0, 6.6 and 6.2 m^2/gm respectively.

Particle size measurements were made on the irradiated samples by air sedimentation with a Sharples Micromerograph, Sharples Research Corporation, Bridgeport, Pa. This method indicated that there was a slight decrease in particle size for the irradiated samples.

III. DISCUSSION AND CONCLUSIONS

In general, there seems to be little effect on kaolin from X-radiation. The changes which are observed do not seem to be consistent. Sample T-1-20 contained some agglomerates which would not dissolve in hydrofluoric acid, as shown in Figure 3. This same sample, when observed in the electron microscope, contained some agglomerates which could not be calcined by the electron beam. In a normal kaolin sample an agglomerate exposed to the electron beam, at high intensity, will first become calcined, as evidenced by expansion of the agglomerate, and then melt completely. This would seem to be significant since the sample had been irradiated; however, no evidence was found of any agglomerates of this type in sample T-1-70 which had received a higher energy dose. Also, sample T-1-70 contained no agglomerates which resisted dissolution by hydrofluoric acid. Whether or not the agglomerates that could not be dissolved and the agglomerates

that could not be calcined are the same is not known. The temperature of the kaolin was measured during the irradiation of sample T-1-70 and was found to be approximately 100° F. This is not even close to the bulk temperature required for calcination, which is approximately 650° C. Also, if the agglomerates had in fact been calcined, some change should have been noted in the degree of crystallinity in the X-ray diffraction measurements.

The slight increases of the surface areas of the irradiated samples indicate that some changes occurred in the samples. However, here again the results are not consistent since sample T-1-70, which received a larger energy dose, exhibits a smaller increase than sample T-1-20.

The slight decrease in particle size which was observed with the micromerograph was no greater than the limit of accuracy of the instrument and therefore cannot be considered significant. Also, the lower limit of this instrument is only one micron and individual kaolin particles are all smaller than about 2 microns. The Coulter Counter, Coulter Industrial Sales, Chicago, Illinois, is to be used for the size measurements on this project, but difficulties in calibration have prevented the use of this instrument to date.

IV. FUTURE PROGRAM

Difficulties in purification of the cesium-137 have arisen at Oak Ridge National Laboratories, and the cesium source will not become available for use on this project until January 1, 1960, at the earliest.

In view of the nature of the data obtained from the relatively low energy X-radiation on kaolin along with the high cost of using the machine, no more work will be carried out with the machine presently available. However, the prospects look very good for obtaining the use of a 150-kv X-ray machine during the next month. If this machine does become available, studies of the effect of X-radiation of kaolin will continue. Otherwise

the rate of effort on this project will be reduced considerably until the cesium-137 source becomes available.

Respectfully submitted:

William J. Corbett
Project Director

Approved:

Earl W. McDaniel
Co-Technical Director

Richard C. Palmer
Co-Technical Director

Wyatt C. Whitley
Co-Technical Director and Chief,
Chemical Sciences Division

QUARTERLY TECHNICAL STATUS REPORT NO. 3

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON III

COVERING THE PERIOD
1 NOVEMBER 1959 to 31 JANUARY 1960
Printed 10 February 1960

CONTRACT NO. AT (38-1)-202
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SAVANNAH RIVER OPERATIONS OFFICE
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UNITED STATES STOMIC ENERGY COMMISSION
OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
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ENGINEERING EXPERIMENT STATION
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Atlanta, Georgia

QUARTERLY TECHNICAL STATUS REPORT NO. 3

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON III

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ABSTRACT

Experimental work during this report period was concerned with the effect of X-radiation on kaolin.

Samples of kaolin were irradiated both dry and in a water slurry for 100 hours at 150 kv and 18 ma. The sample irradiated as a slurry did not undergo any observable physical changes. The sample of kaolin irradiated in the dry state underwent a significant decrease in the degree of crystallinity and crystallite size. Electron photomicrographs of this same sample showed 10 to 20 per cent of the stacks to be broken down.

Differential thermal analysis has been adopted as another method of determining what physical changes have taken place in the irradiated kaolin.

During the next report period irradiation experiments will be conducted using the 12-kilocurie cesium-137 source.

TABLE OF CONTENTS

This Report Contains 7 Pages.

I. INTRODUCTION

This report summarizes the work performed from November 1, 1959, to January 31, 1960. The objective of the research under this contract is to determine the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

II. EXPERIMENTAL WORK

A. Apparatus

The cesium-137 source which has been intended as the primary source of high-energy, ionizing radiation still had not become available to this project during this report period. However, a 150-kv X-ray machine was obtained, on loan, from Vanderbilt University, Nashville, Tennessee.

This machine has an X-ray tube of the rod anode type. The radiation from this tube is emitted from the side in a horizontal plane, rather than vertically from the end as is the radiation from the tube in the 50-kv X-ray machine used in previous work on this project. Therefore, a different type of sample holder was needed. It was constructed of Pyrex, and can hold up to 100 grams of kaolin. The sample holder and irradiation setup is shown schematically in Figure 1.

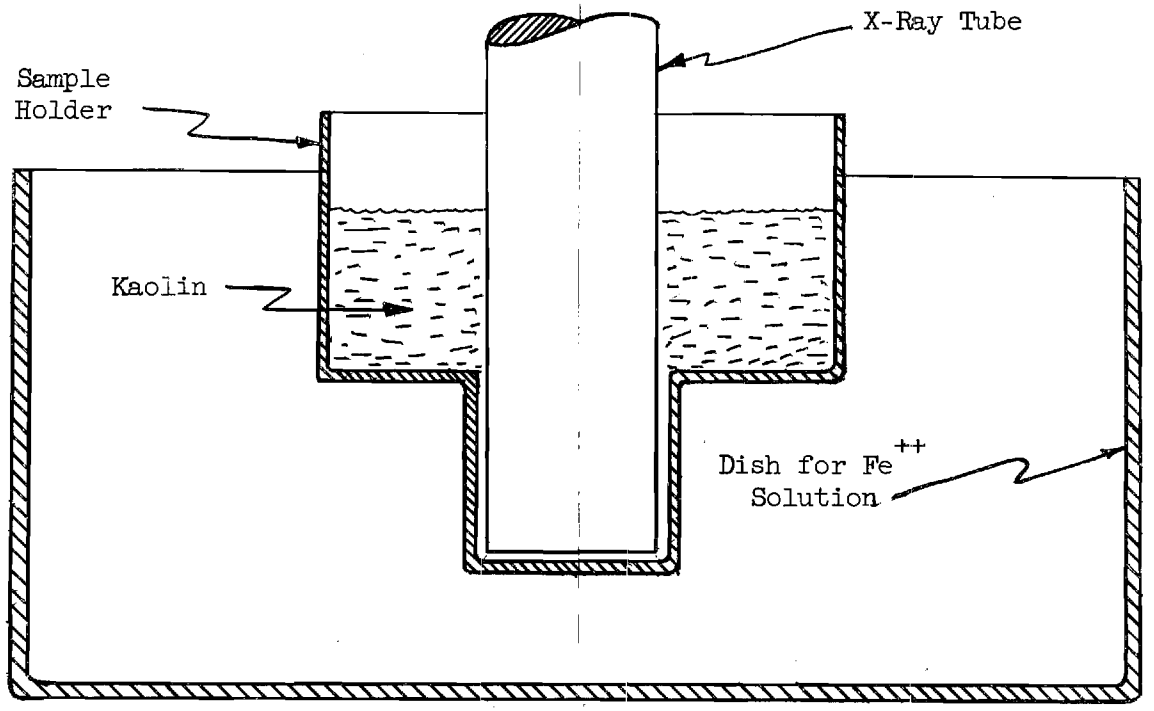

Figure 1. Schematic Illustration of Irradiation Assembly.

B. Kaolin Irradiation

Two samples of kaolin were irradiated for 100 hours each at 150 kv and 18 ma. The kaolin used was the same as that used in previous investigations. One sample, designated T-1-100, weighing 20 grams was dried in an oven and irradiated in the dry state. The other sample, designated T-1-100S, weighed 75 grams and was mixed with water to form a slurry which was approximately 60 per cent by weight. No attempt was made to keep the water content of this slurry constant during irradiation.

Dosimetry measurements were made by the ferrous ion technique that was presented in detail in Technical Status Report No. 2. The total energy absorbed by each sample was of the order of 10^{21} electron-volts per gram.

C. Physical Measurements

Surface area and particle size measurements on Sample T-1-100 showed no change from the values obtained for the unirradiated kaolin.

X-ray diffraction studies of sample T-1-100S (slurry) showed no difference between it and the unirradiated kaolin. X-ray diffraction studies of sample T-1-100, however, indicated that the kaolin had been changed significantly. A pronounced decrease in crystallinity and crystallite size was noted. The lattice spacings were not changed.

Studies with the electron microscope indicated no noticeable changes for the sample T-1-100S. However, sample T-1-100 showed considerable change from the unirradiated kaolin. In the transmission observations of the kaolin particles it was found that approximately 50 per cent of the agglomerates could not be calcined with the electron beam. Electron photomicrographs of carbon replicas of the sample showed 10 to 20 per cent of the kaolin stacks to be collapsed. The kaolin plates seem to be still held together, but in a very loose disordered array. They appear to be aggregated in a horizontal plane rather than in the more normal vertical array. Some of these collapsed stacks are shown in Figure 2.

Another method of analysis has been adopted for obtaining information about the physical characteristics of kaolin before and after irradiation. Known as differential thermal analysis, the technique involves comparsion of the changes which occur in a clay sample with those of a reference material, as a function of temperature. A few grams (2 or 3) of the kaolin being

tested are compressed into a pellet. This pellet, along with a pellet of the reference material, is heated at a constant rate in a suitable furnace to some arbitrary temperature and the difference in temperature between the two pellets is recorded. The temperature differences observed are indications of endothermic and exothermic processes which are taking place in the kaolin. The magnitude of these differences and the range at which they occur are determined by the chemical composition and the physical condition of the kaolin. The reference material is usually calcined alumina. However, in this work a calcined pellet of unirradiated kaolin is used as the standard. Figure 3 shows a typical plot of the data obtained from a differential thermal analysis. The abscissa is the temperature to which the pellets have been heated, with 1000° C being the maximum for this work, and the ordinate is the millivolt difference between the Pt - Pt10Rh thermocouples placed beneath each pellet. The first deviation along the abscissa, which is negative--indicating an endothermic process, extending from a temperature of approximately 60° C to a temperature of approximately 375° C, is caused by the driving off of absorbed water. The next deviation, also an endothermic process, from a temperature of about 475° to 850° C, is the result of driving off chemically bound water from the crystal lattice. This process, which is actually calcination of the kaolin, has a maximum at 625° C. The final deviation, which is an exothermic process, is the result of a phase change which takes place at about 965° C. No difference was found in the data from differential thermal analysis of samples T-1-100, T-1-100S or the unirradiated kaolin T-1.

III. DISCUSSION AND CONCLUSIONS

The fact that the particle size determinations and surface area measurements showed no change for sample T-1-100 even though the electron microscope showed some of the stacks to be broken down, can probably be attributed to the intensity gradient which existed in the sample during irradiation. The X-ray beam was probably greatly attenuated in a very short distance through the sample so that only a very small quantity of the stacks received enough energy to break them down. This would account for the fact that only 10 or 20 per cent of the stacks seemed to be collapsed. Also, a change of no more

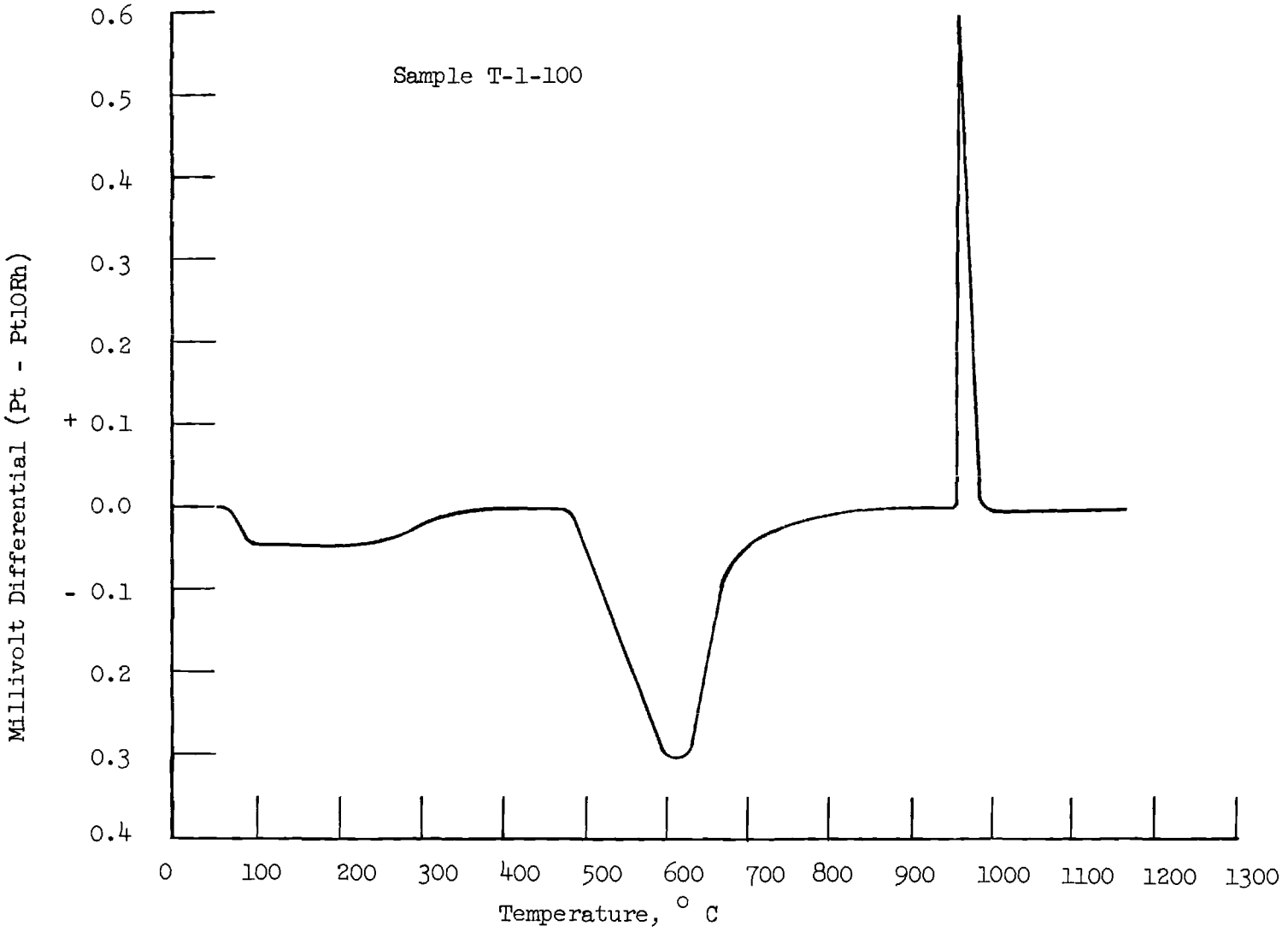

Figure 3. Typical Plot of Differential Thermal Analysis Data.

than 10 per cent in the surface area or size distribution would be very difficult to detect since the limits of precision of these measurements are probably no better than that.

The results of the X-ray diffraction measurements on sample T-1-100 indicate that either the aluminum atoms are being moved from one available site to another within the kaolinite crystal, or that the layers within a crystallite are being displaced with respect to one another along planes perpendicular to the c-axis. It is very improbable that the aluminum atoms are being moved about in the crystal lattice by X-radiation. The shifting of one crystal layer with respect to another does not seem very likely either since this involves the apparent movement of masses. However, this apparent movement could be taking place along the interface between two adjacent kaolinite units where hydrogen bonding occurs as described in Technical Status Report No. 1. Therefore, this apparent movement could be due to the breaking of this hydrogen bonding at one site and the remaking at another site.

The possibility existed that the kaolin had been calcined to some degree during irradiation. Checks on the bulk temperature of the kaolin showed that the temperature during irradiation, approximately 40° C, was not anywhere close to that required to calcine the kaolin (650° C), and examination of the stacks with the electron microscope did not show the expanded structure which calcined stacks exhibit. However, approximately 50 per cent of the stacks could not be calcined by the electron beam of the electron microscope, which seemed to indicate that some of the kaolin had been calcined. It was for this reason that differential thermal analysis was added to the various methods of testing the physical properties of the kaolin before and after irradiation. This method of analysis can show whether or not a sample of kaolin has been calcined. As pointed out in Chapter II, EXPERIMENTAL WORK, the identical results obtained for the thermal analysis of the kaolin before and after irradiation mean that the kaolin was not calcined by the X-radiation.

After the encouraging physical changes obtained with sample T-1-100, it was decided to irradiate sample T-1-100S in a water slurry. This was an attempt to accomplish two things; if the lattice spacings were expanding

during irradiation the water molecules might enter these interstitial spaces and prevent the crystal structure from contracting to its original spacings and the ions formed from the water during irradiation might combine with any ions formed in the kaolinite crystals. This latter effect would tend to stabilize these ionized atoms in the crystal structure and prevent them from recombining. However, as the results of the physical measurements show, the kaolin irradiated in the slurry was not changed. Therefore, it appears that the presence of the water contributed to the stability of the kaolin stacks rather than aid in breaking them down as expected. This will be investigated further in future experiments.

IV. FUTURE PROGRAM

During the next month samples of kaolin will be subjected to various amounts of gamma radiation from the 12-kilocurie cesium-137 source. The energy of incident radiation from this source will be at least four times greater than that obtained with the 150-kv X-ray machine. In view of the improvement in results with the 150-kv X-ray machine over the 50-kv machine, even greater degrees of physical change are expected with this source of higher energy radiation.

It is expected that large enough quantities of material can be irradiated with this source to perform some mechanical shear and slurry viscosity measurements on the irradiated kaolin. The irradiated kaolin will also be subjected to the other techniques established for measuring physical properties.

Respectfully submitted:

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QUARTERLY TECHNICAL STATUS REPORT NO. 4

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON, III

COVERING THE PERIOD
1 APRIL 1960 to 30 JUNE 1960
Printed 10 July 1960

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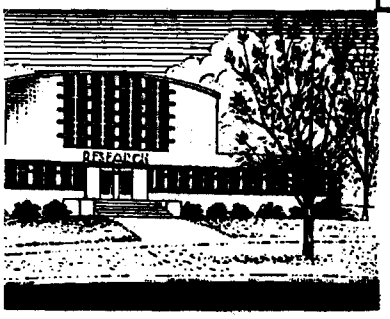

Engineering Experiment Station
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ABSTRACT

Research performed on this project during the period covered by this report has been concerned with particle size distributions, reflectance measurements, infrared absorption studies, and cation-exchange measurements of kaolin before and after irradiation. Grinding studies have been conducted with both irradiated and unirradiated kaolin and the results evaluated by particle size determinations, X-ray diffraction measurements, and electron microscopy.

The particle size distributions obtained give further evidence that the size of kaolinite stacks can be reduced by gamma-radiation. The light reflectance of kaolin is slightly reduced by irradiation. The results of infrared absorption measurements show no significant changes in the basic lattice structure of kaolinite by gamma-radiation. The cation-exchange capacity of the kaolin used in these studies appears to be significantly affected by gamma-radiation although no conclusive trend can be observed at present. Dry grinding of an unirradiated and an irradiated kaolin shows the irradiated kaolin to grind more easily.

Work during the coming month will be concerned with the effect of wet grinding on kaolin before and after irradiation. Wet grinding will be used because this produces a greater proportion of shearing forces than dry grinding; crushing forces lead to a less desirable product.

TABLE OF CONTENTS

This Report Contains 12 Pages.

LIST OF FIGURES

I. INTRODUCTION

This report summarizes the work performed from April 1, 1960, to June 30, 1960. The objective of the research under this contract is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

II. EXPERIMENTAL WORK

A. Particle Size Measurements

Further particle size distributions have been made for samples of irradiated kaolin using both the Coulter Counter and liquid sedimentation. The technique of obtaining size distributions with the Coulter Counter was presented in Annual Technical Status Report No. 1. The liquid sedimentation measurements are based on Stokes' law that deals with the settling rate of small particles suspended in a fluid medium.

The liquid sedimentation procedure used in this work was the Casagrande hydrometer-centrifuge method. Ten grams of clay with 0.05 gram tetrasodium pyrophosphate and one liter of water were blended with a Waring Blendor for 5 minutes. The resulting suspension was placed in a one-liter glass cylinder and the particles allowed to settle. The particle density of the suspension was measured with a Casagrande hydrometer at various time intervals up to an hour and then the suspension was centrifuged at high speed for various intervals of time and hydrometer readings made after every centrifugation. The use of a centrifuge serves both to speed up the sedimentation of the particles and to reduce the effect of thermal gradients on the smaller particles. The temperature of the room in which the sedimentation measurements were made was carefully controlled to reduce the effect of thermal gradients on the suspension. With the hydrometer data and appropriate equations[1] the equivalent diameter of the clay particles can be calculated.

Figure 1 presents comparative size distributions of kaolin samples that had received various doses of gamma-radiation. These distributions

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[1] Clyde Orr, Jr. and J. M. DallaValle, Fine Particle Measurement. (New York: The Macmillan Co., 1959), p. 60-66.

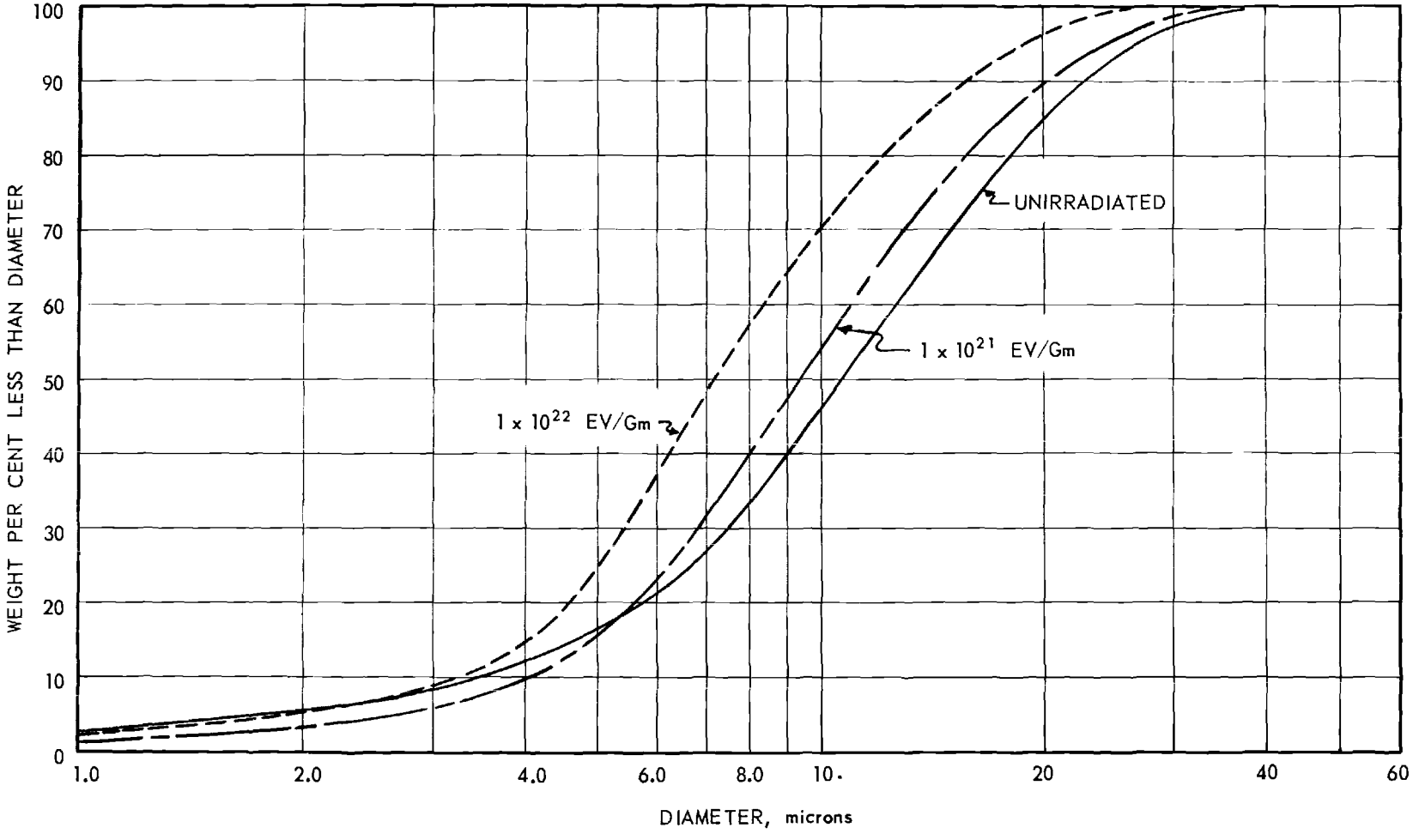

Figure 1. Size Distributions for Irradiated and Unirradiated Kaolin Determined with the Coulter Counter.

were made with the Coulter Counter and the size is given as the diameter of a sphere of equivalent volume. Figure 2 presents liquid sedimentation size distributions for kaolin samples that had received various doses of gamma-radiation. The diameter presented in this figure is the diameter of a sphere with equivalent cross-section.

B. Reflectance Measurements

Light reflectance measurements were made on samples of kaolin that had received various doses of gamma-radiation. The tests were made with a General Electric recording spectrophotometer. Approximately 10 grams of kaolin were pressed into a pellet 1-1/4 inches in diameter under a pressure of 60 pounds per square inch. The amount of incident light reflected from the surface between wave lengths of 380 and 700 millimicrons was measured relative to a similar size pellet of magnesium oxide. The results of these measurements are presented in Table I.

C. Infrared Absorption Measurements

Small wafers 0.5 inch in diameter were prepared by pressing a 0.01-gram sample of potassium bromide containing 0.3 per cent kaolin with a pressure of 12.5 tons per square inch in an appropriate press. These wafers were prepared with samples of unirradiated kaolin and kaolin which had received 1×10^{20} and 1×10^{22} electron-volts per gram of gamma-radiation. A Perkin-Elmer Model 21 infrared spectrometer, Perkin-Elmer Corporation, Norwalk, Connecticut, was used to obtain an infrared absorption spectrum for these wafers. The samples showed no significant difference in absorption over the range of 1.5 to 15 microns wave length.

D. Surface Area Measurements

The surface areas have been determined for two kaolins of different particle size distributions and sources than the kaolin from Washington County, Georgia, that has been used as the control material in all studies to date. One of these clays has been water-washed and dried, but has not been treated with a dispersing agent. This sample contains approximately 60 per cent by weight of stacks. The other kaolin has received no treatment whatever; its condition is exactly as mined. The particle size distribution for this clay has not been determined. These clays are from Twiggs County, Georgia. The surface areas of both kaolins were found by low-temperature nitrogen adsorption to be 7.2 square meters per gram.

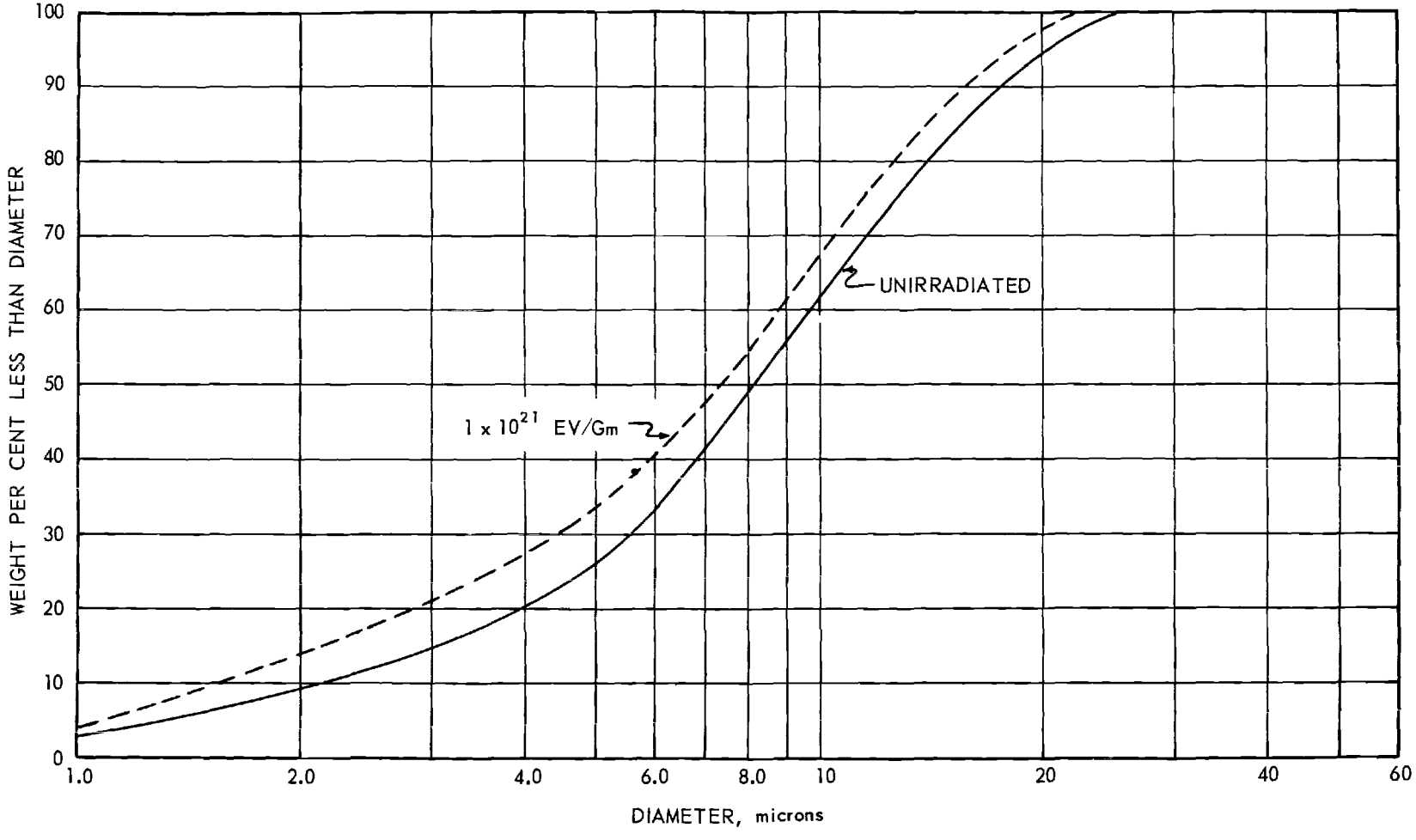

Figure 2. Size Distributions for Irradiated and Unirradiated Kaolin Determined by Sedimentation.

TABLE I

REFLECTANCE MEASUREMENTS FOR KAOLIN SAMPLES
WITH VARIOUS TOTAL ENERGY DOSES

Wave Length (Millimicrons)	Per Cent Reflectance		
	Unirradiated	1 x 10^{21} EV/Gm	1 x 10^{22} EV/Gm
380	66.0	65.0	65.0
400	69.7	68.7	68.5
450	77.0	76.0	76.0
500	80.5	79.8	80.0
550	84.0	83.0	83.2
600	86.2	85.2	85.3
650	88.0	86.8	86.8
700	89.5	88.5	88.2

E. Grinding Studies

Two samples of kaolin, one unirradiated and one that had received a dose of 1 x 10^{20} electron-volts per gram of gamma-radiation were ground in a ball mill for 50 hours each. A porcelain mill 9 inches in diameter was used for these studies. The mill was charged with 100 grams of sample and 3 kilograms of 3/4-inch-diameter, 3/4-inch-length porcelain cylinders. Electron micrographs, X-ray diffraction traces, and particle size distributions were made for these samples. The electron micrographs of these kaolin samples and the unirradiated unground material are presented in Figure 3. The X-ray diffraction traces showed the samples to be very poorly crystallized, in fact, almost amorphous material, after grinding. The traces did not show any significant difference in the crystallinity of the samples after grinding. The particle size analyses of the ground samples and an unirradiated, unground sample are presented in Figure 4.

F. Cation-Exchange Measurements

Samples selected for cation-exchange measurements were dried for 3 hours at 110° C, treated with dilute hydrochloric acid solution for 2 hours, and then filtered and washed with distilled water. These "acid" clays were then

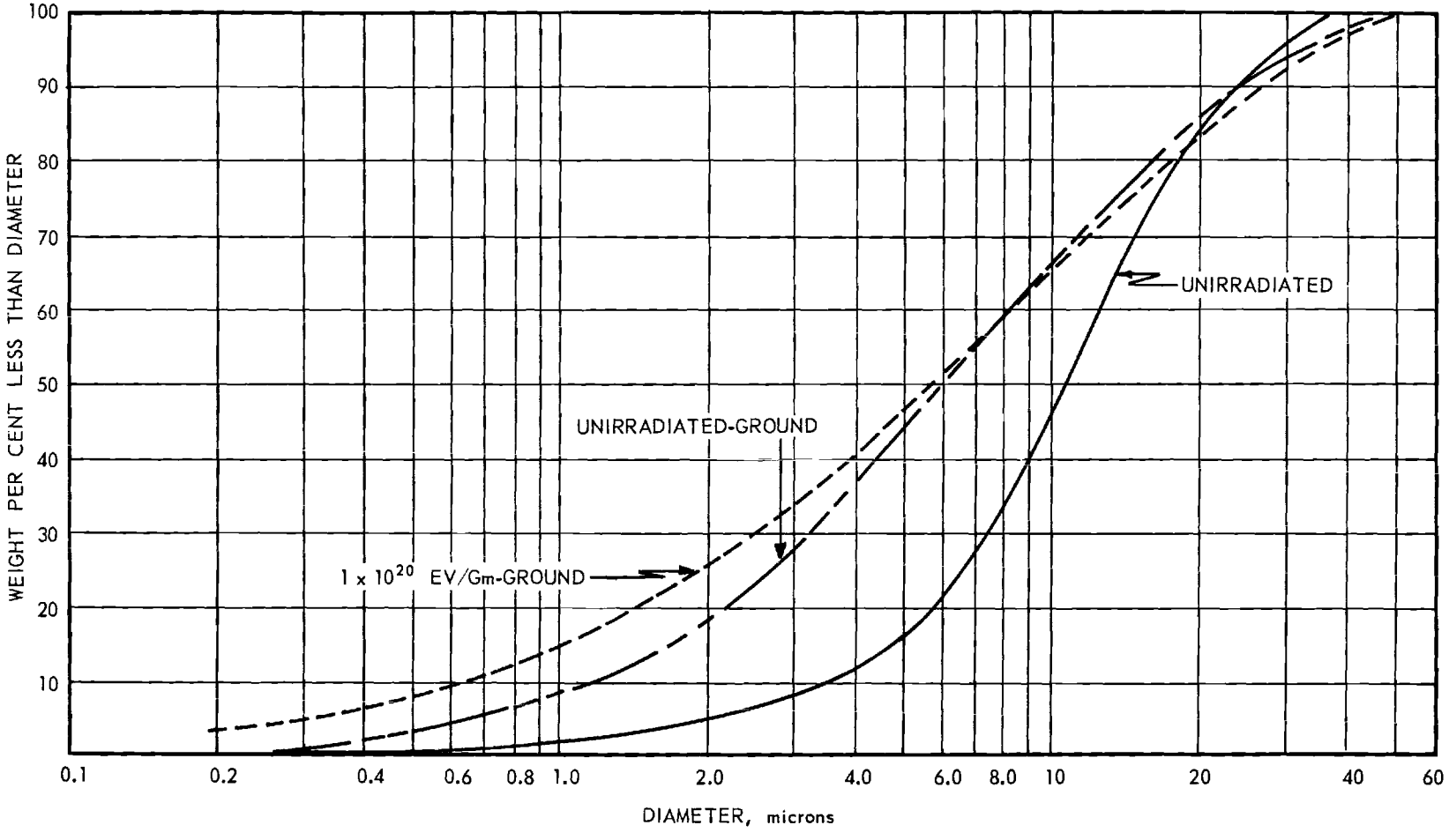

Figure 4. Size Distributions for Ground and Unground, Irradiated and Unirradiated Kaolin.

dried to constant weight at 110° C, and a 20 per-cent-by-weight suspension in distilled water was prepared. The clay suspensions were then titrated with 0.1N sodium hydroxide solution and pH determinations were made after the addition of each 0.5 ml of sodium hydroxide until a pH of 7.0 was reached.

The results for an unirradiated sample and for irradiated samples of three different dosages are presented in Figure 5.

III. DISCUSSION AND CONCLUSIONS

In Annual Technical Status Report No. 1, a great deal of scatter was noted in the comparison of data on such factors as degree of crystallinity, particle size distribution, surface area, etc. with various dose rates. It now appears that the difficulty was due to uncertainty in the total dose absorbed by samples. These uncertainties arose from the fact that the variation of the dose rate with change in vertical height in the irradiator extended further from each end than had originally been assumed and from errors in the method of taking samples from the tube in which they were irradiated. These difficulties have been overcome by irradiating a test tube containing approximately 100 grams of kaolin at a time, instead of removing smaller samples from the tube as was done previously. The total dose absorbed is now calculated by integrating the area under the dose-rate-versus-vertical-movement curve that was presented in Annual Technical Status Report No. 1 for Project A-446-6 to obtain an average dose rate for the entire sample. The average dose rate in the center hole of the research irradiator was found to be 1.11 megarads per hour. All total doses reported here have been calculated by multiplying this average dose rate by the exposure time.

The particle size distributions versus total dose reported here show the same results as those reported in Annual Technical Status Report No. 1; that is the kaolin is deagglomerated by the effects of gamma-radiation. The particle size distributions obtained by liquid sedimentation, while not directly comparable to the distribution obtained with the Coulter Counter due to the difference in basis for expressing the particle diameter, were obtained as an independent check on the results obtained with the Coulter

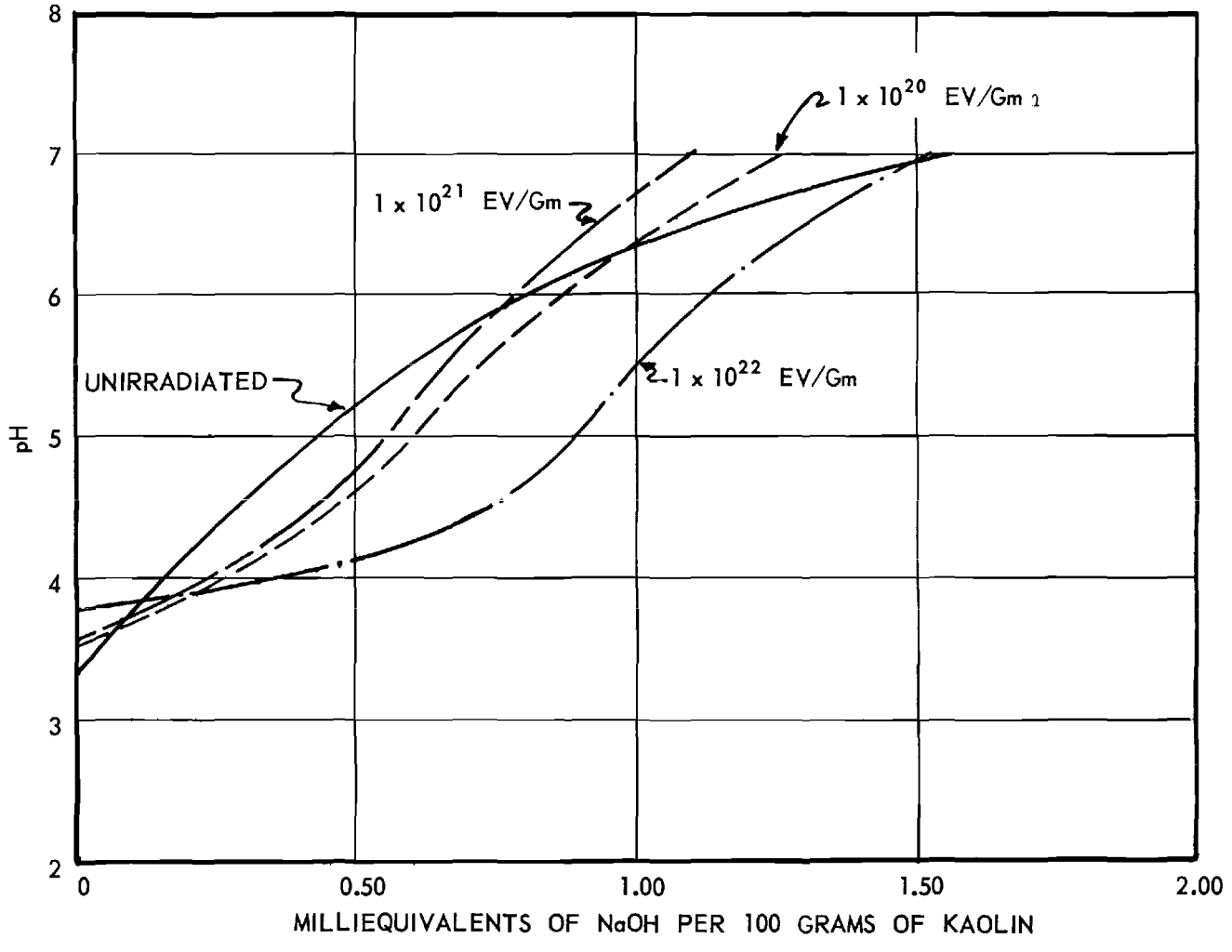

Figure 5. Titration Curves for Hydrogen-Kaolinite.

Counter. It can be seen from the data contained in Figure 2 that this method also shows the particle size of kaolin to be reduced after irradiation.

A change in the light reflection of the irradiated kaolin was found. However, a reduction in the particle size of a kaolin normally produces an increase in the reflectance of the sample. The data of Table I show an almost uniform decrease for the reflectance of the kaolin after irradiation with the irradiated samples having practically identical reflectance regardless of total energy dose. The only explanation that can be offered at the present time is that the effects of gamma-radiation on the impurities which are present in kaolin, such as iron and titanium oxides, reduced the reflectance more than the reduction in particle size raised it.

The infrared adsorption of kaolin samples before and after irradiation was studied to determine whether or not any significant changes were present in the crystal lattice. No significant changes were found. The surface areas of two new control samples of kaolin that are to be used in future tests were determined for future reference.

As pointed out in Annual Technical Status Report No. 1, the data collected to date point to some type of recrystallization mechanism in the disordering of the kaolinite structure which probably produces many weak areas in a kaolinite stack. If such weak areas are produced, an irradiated sample of kaolin should grind more easily than an unirradiated one. The resulting particle size distributions contained in Figure 4 show a significantly smaller particle size for the material which was irradiated and then ground, indicating that the irradiated material is indeed easier to grind. These findings are in agreement with the results of Takahashi,[2] who found that a kaolin which was naturally poorly crystalline was easier to grind than one which had a high degree of crystallinity. Unfortunately the product obtained from the dry grinding of kaolinite is an amorphous material that has lost the hexagonal, plate-like structure, one of its most desirable characteristics. Therefore, all further grinding tests will probably be made with the addition of a liquid since the wet grinding action is more of a shearing

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[2] Hiroshi Takahashi, "Effects of Dry Grinding on Kaolin Minerals. I. Kaolinite," Bull. Chem. Soc. Japan 32, 235-45 (1959).

process than the crushing action of dry grinding. Some tests may also be conducted with a device which exerts only a shearing action, such as the Kady Mill, Kinetic Dispersion Corporation, Buffalo, N. Y.

The cation-exchange capacity of kaolin before irradiation and after various doses of gamma-radiation was measured to determine what effect irradiation has on this property. The data presented in Figure 5 show that the effects of gamma-radiation reduced the cation-exchange capacity of this particular kaolin for doses of 1×10^{20} and 1×10^{21} electron-volts per gram. However, it can be seen that the data for the sample that received 1×10^{22} electron-volts per gram of gamma-radiation produced a curve radically different from those of the two samples which received lower energy doses. These results appear to be anomalous and must be regarded as tenative pending further experimental work.

IV. FUTURE WORK

Research during the next month will be concerned with grinding tests that produce a greater amount of shearing forces than crushing forces. These tests will be conducted with samples of kaolin which have received various doses of gamma-radiation and the results will be evaluated by X-ray diffraction, electron microscopy, particle size analysis, cation-exchange measurements, surface area measurements, reflectance measurements and possibly viscosity determinations.

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QUARTERLY TECHNICAL STATUS REPORT NO. 5

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT and JOHN H. BURSON, III

COVERING THE PERIOD
1 JULY 1960 to 30 SEPTEMBER 1960
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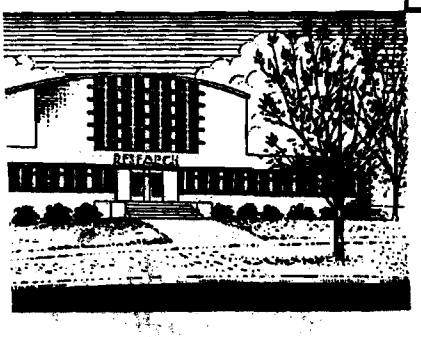

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ABSTRACT

Research performed on this project during the period covered by this report has been concerned with the re-determination of the variation of crystallinity index, the variation of infrared adsorption spectrum, and the variation of cation-exchange capacity of kaolin with varying doses of gamma-radiation. The research performed has also been concerned with the effects of wet grinding on samples of kaolin that have received various doses of gamma-radiation. The particle size distributions of these wet-ground samples were determined with the Coulter Counter.

The index of crystallinity of kaolin does not show a definite trend with increasing doses of gamma-radiation, but instead appears to fluctuate from higher to lower and back to higher degrees of crystallinity. This fluctuation is the result of difficulties in resolving one of the necessary relections used for computing the crystallinity index. The infrared adsorption spectra of kaolin do not appear to change with exposure to gamma-radiation. The cation-exchange capacities of samples of kaolin increases with increasing doses of gamma-radiation. Samples of kaolin that have been subjected to shearing along the kaolinite cleavage plane through wet grinding show no significant difference in particle size reduction for increased doses of gamma-radiation.

Future work on this project will be concerned with determining the change in cation-exchange capacity, surface area and reflectance measurements for the wet-ground samples of kaolin, and the effect of gamma-radiation on the crystallinity of kaolin.

TABLE OF CONTENTS

This report contains 7 pages.

I. INTRODUCTION

This report summarizes the work performed from July 1, 1960, to September 30, 1960. The objective of the research under this contract is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

II. EXPERIMENTAL WORK

A. Crystallinity Measurements

X-ray diffraction patterns were obtained for samples of kaolin which had received doses of 1×10^{20}, 1×10^{21} and 1×10^{22} electron-volts per gram of gamma-radiation, and the relative intensity ratios of two diffraction maxima $(02\bar{1}):(060)$ were computed from these patterns. The ratio of these two diffraction maxima, one affected by the random displacement of adjacent kaolinite layers relative to each other $(02\bar{1})$, and the other unaffected by these displacements (060), serves as a measure of the degree of crystallinity of the kaolin. The value of this ratio should be 1.0 for the best crystallized kaolins and 0 for the poorest. The $02\bar{1}$ diffraction maxima is normally of medium intensity with respect to the other diffraction maxima that occur for kaolinite. However, the $02\bar{1}$ diffraction maxima for the kaolin being used in these studies has been very poorly resolved and the uncertainty of its intensity has been too great to allow an accurate determination of the crystallinity index.

B. Infrared Adsorption Measurements

Infrared adsorption spectra were obtained for samples of kaolin which had received doses of 1×10^{20}, 1×10^{21} and 1×10^{22} electron-volts per gram of gamma-radiation. These spectra were obtained by the procedure outlined in Quarterly Technical Status Report No. 4, except that the concentration of kaolin

in the KBr was increased to 1 per cent. The adsorption spectra was determined over the wavelength range 2 to 15 microns. The regions from 2.5 to 3.5 microns and 10.25 to 11.25 microns were carefully examined by using a very slow scanning speed. These are the region of OH^- adsorption and Al-O-OH adsorption respectively.

C. Cation Exchange Measurements

The cation exchange capacities of samples of kaolin which had received doses of 1×10^{20}, 1×10^{21} and 1×10^{22} electron-volts per gram of gamma-radiation, and a sample which had not been irradiated, were determined by the procedure outlined in Quarterly Technical Status Report No. 4. However, greater care was taken to dry the samples all at the same time for exactly the same length of time, and to insure that the samples were treated with exactly the same amount of dilute hydrochloric acid for the same length of time. The results of these measurements are shown in Figure 1.

D. Grinding Studies

Samples of kaolin that had received 1×10^{20}, 1×10^{21} and 1×10^{22} electron-volts per gram of gamma-radiation and a sample of unirradiated kaolin were subjected to 50 hours of wet-grinding. A porcelain mill 9 inches in diameter was used for these studies. The mill was charged with 100 grams of sample, 3 kilograms of 3/4-inch-diameter, 3/4-inch-length porcelain cylinders and 400 grams of water. The milling speed was 120 revolutions per minute. The particle size distributions obtained for these samples with the Coulter Counter showed no significant difference in particle size. Samples of unirradiated kaolin and kaolin that had received a dose of 1×10^{22} electron-volts per gram gamma-radiation were wet-ground under the conditions given previously for 10

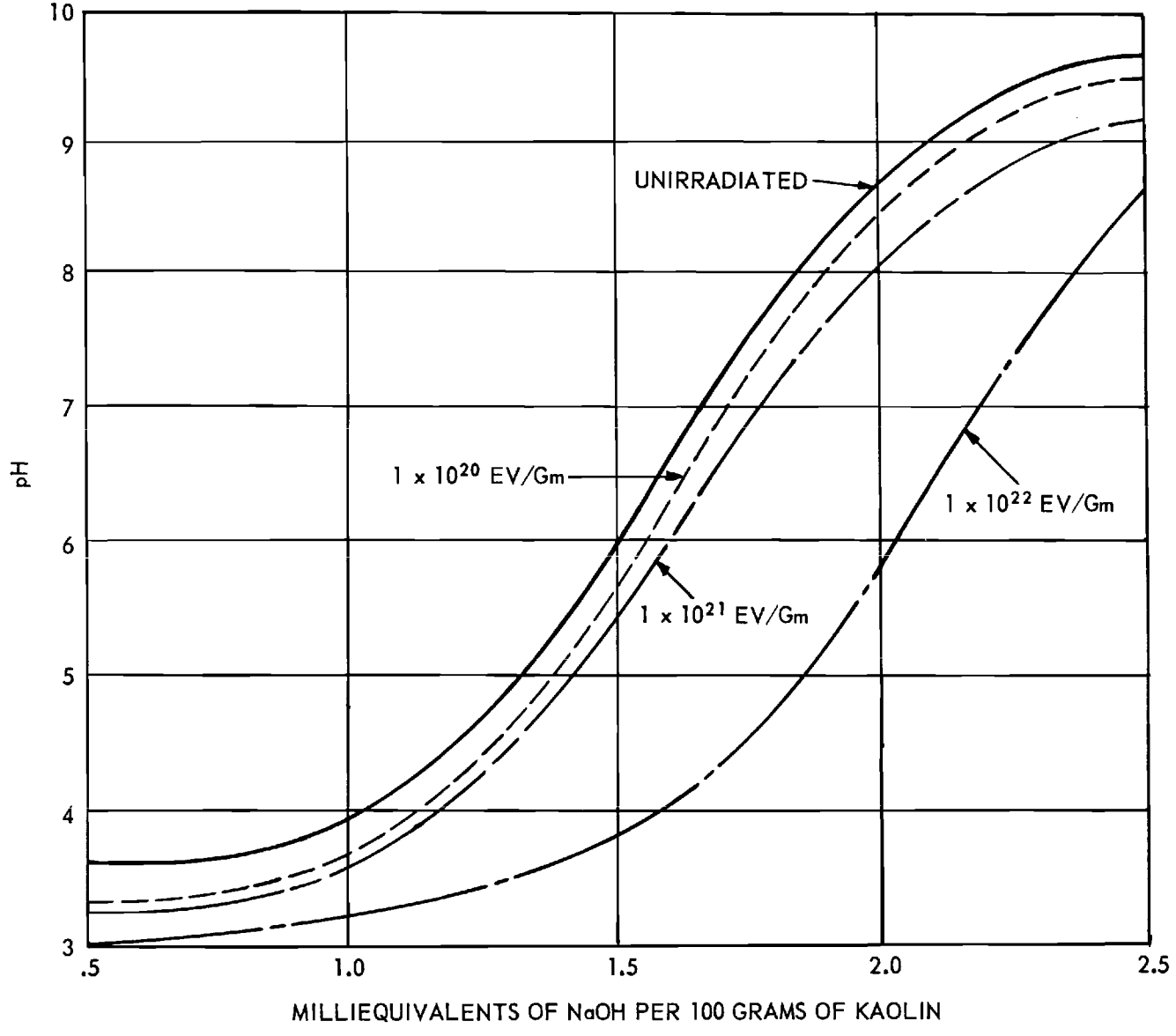

Figure 1. Titration Curves for Hydrogen-Kaolinite.

and 20 hours. Particle size distributions were obtained for these samples with the Coulter Counter. These distributions did not show any significant difference in particle size reduction either.

III. DISCUSSION AND CONCLUSIONS

It was pointed out in Quarterly Technical Status Report No. 4 that much of the scatter observed for the data presented in Annual Technical Status Report No. 1 was probably due to poor sampling technique in some of the early experiments, and that this technique had been improved. As a result the determinations of crystallinity index for irradiated kaolin were performed again. It was expected that the crystallinity would decrease continuously with increased doses of gamma-radiation rather than fluctuate as the results in Annual Technical Status Report No. 1 indicated. However, the crystallinity index measurements made during this report period show that the fluctuations observed are due primarily to poor resolution of the $02\bar{1}$ diffraction maxima in the X-ray diffraction trace for kaolinite. This poor resolution leads to a large uncertainty in the value of the intensity of the maxima, and therefore a large uncertainty in the calculated index of crystallinity. The cause of the poor resolution appears to be a high degree of orientation of the kaolin particles when a sample is packed for use in the X-ray diffractometer. This orientation problem is not usually encountered for kaolin. However, the sample of kaolin being used in these studies is larger than is normally found in kaolin and the unusually high degree of orientation seems to be a result of the large size fraction being used. Experiments are presently being conducted with mixtures of the kaolin and silica in an attempt to overcome this orientation problem. It is expected that the addition of finely divided silica to

the kaolin before it is packed for use in the X-ray diffractometer will allow a more random arrangement of the kaolin particles and improve the resolution of the $02\bar{1}$ diffraction maxima. This area certainly warrants further investigation, since an explanation of the manner in which high-energy, ionizing radiation interacts with kaolin must be based on an understanding of the disordering mechanism.

A careful re-examination of the infrared adsorption spectra that had been obtained previously, and reported in Quarterly Technical Status Report No. 4, revealed some doubt that the spectra were identical for samples of kaolin before and after irradiation. Therefore, samples of kaolin before and after irradiation were again examined using larger concentrations of kaolin in the KBr pellets and with more attention given to certain adsorption bands. These new spectra do not show any significant deviations which are immediately obvious; however, the detailed analyses are not yet complete.

It was pointed out in Quarterly Technical Status Report No. 4 that the cation-exchange capacity measurements reported there appeared to be inconsistent. These measurements were repeated with more attention to technique and more consistent results were obtained. As can be seen from Figure 1 the cation-exchange capacity of kaolin increases with increasing doses of gamma-radiation. An increase in the cation-exchange capacity indicates a greater number of broken chemical bonds in a sample, which would be expected to accompany a reduction in particle size. Therefore, the results showing an increased reduction of particle size (Annual Technical Status Report No. 1) with increasing doses of gamma-radiation are consistent with the results of cation-exchange capacity.

Shaw[1] and Takahashi[2] have demonstrated that wet grinding produces primary shearing along the cleavage plane of kaolinite. Since the interlayer forces which bind kaolin layers together act perpendicular to this cleavage plane, any reduction in these binding forces should reduce the shearing force required to separate these layers. If these interlayer binding forces are reduced, a greater reduction in particle size from the shearing action of wet grinding should be observed. Since no difference in particle size reduction was found between the wet-ground samples of kaolin before and after irradiation these interlayer forces must not have been affected by gamma-radiation.

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[1]B. T. Shaw, "Nature of Colloidal Clay," J. Phys. Chem. 46, 1032-43 (1942).

[2]Hiroshi Takahashi, "Wet Grinding on Kaolin Minerals," Bull. Chem. Soc. Japan 32, 381-87 (1959).

IV. FUTURE WORK

Cation-exchange capacities, specific surface areas, and reflectance measurements remain to be determined for the samples of wet-ground kaolin. These will be obtained during the next month. Further experiments will be conducted during the next month in an effort to obtain an accurate index of crystallinity for the kaolin before and after various doses of gamma-radiation. The design of a cell for the irradiation of kaolin at liquid-nitrogen temperature is under consideration. During the next quarterly report period a cell will be constructed, and some determinations made of the effect of gamma-radiation on kaolin at liquid-nitrogen temperatures.

Respectfully submitted,

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QUARTERLY TECHNICAL STATUS REPORT NO. 6

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT and JOHN H. BURSON, III

COVERING THE PERIOD
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GERMANTOWN, MARYLAND

ABSTRACT

During this report period the technique for irradiation of kaolin has been modified to minimize any nonuniformity of gamma ray flux received. A raw, untreated kaolin from Twiggs County, Georgia, has been introduced into these studies. The range of radiation dosages has been increased. The variation of specific surface area and index of crystallinity has been measured as a function of radiation dose, the latter only for the kaolin from Twiggs County, Georgia, but the change in specific surface area was also determined for the kaolin from Washington County, Georgia. The variation in specific surface area and cation-exchange capacity has been determined for the wet-ground samples of unirradiated and irradiated kaolin. Both of these properties were found to increase with increasing radiation dose, which is not in agreement with the particle size distributions previously determined for these samples. Some tentative measurements taken from the infrared absorption spectra of unirradiated and irradiated kaolin indicate an increase in the ratio of unbonded to bonded OH in these samples.

Future work on this project will be concerned with problems of anomalous data which have been encountered in the measurement of particle size distribution, specific surface area and crystallinity index. Further infrared absorption measurements will be made with more attention to sample preparation, and electron diffraction studies will be conducted on both unirradiated and irradiated kaolin. At least one more kaolin from a different source will be introduced into these studies.

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I. INTRODUCTION

This report summarizes the work performed from October 1, 1960, to December 31, 1960. The objective of the research under this contract is to investigate the possibilities of reducing agglomerates of kaolin to discrete particles by high-energy, ionizing radiation.

II. EXPERIMENTAL WORK

A. Irradiation of Kaolin

During this report period a series of irradiations were performed with samples of a crude kaolin from Twiggs County, Georgia. This kaolin was just as mined with no processing treatment. A new series of irradiations was performed with samples of the fractionated kaolin from Washington County, Georgia. The dosages obtained in this last series of irradiations ranged from 1×10^{18} to 1×10^{22} electron-volts per gram, which covers a wider range than used previously. A different type sample holder was used. The holder consisted of an aluminum cylinder, with a wall thickness of approximately 1/8 inch, divided into two compartments by a partition perpendicular to its cylindrical axis, and closed at either end by threaded aluminum plugs. These compartments will hold between 10 and 15 grams of kaolin each. The cylinder is 5-1/4 inches long and is placed on a spacer within the sample carrier of the Cesium-137 Research Irradiator. This spacer locates the sample holder in the region of most uniform radiation flux.

B. Specific Surface Area Measurements

The specific surface areas of both unirradiated and irradiated samples of Washington County and Twiggs County kaolins were determined by low-temperature nitrogen adsorption. As was found previously for the Washington County kaolin

the specific surface areas of both kaolins decreased with increasing doses of gamma-radiation. These data are given in Table I.

TABLE I

SPECIFIC SURFACE AREA OF KAOLIN AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area: Washington County Kaolin (M^2/Gm)	Specific Surface Area: Twiggs County Kaolin (M^2/Gm)
Unirradiated	6.1	7.2
1×10^{18}	5.4	6.6
5×10^{18}	5.2	6.6
1×10^{19}	4.7	6.0
5×10^{19}	5.0	6.7
1×10^{20}	5.2	5.8
1×10^{21}	4.1	6.1
1×10^{22}	4.5	5.5

The specific surface areas of the wet-ground samples of unirradiated and irradiated kaolin that were discussed in Quarterly Technical Status Report No. 5 were also determined by low-temperature nitrogen adsorption. These samples show a definite increase in specific surface area with increasing doses of gamma-radiation. These data are contained in Table II.

C. Cation-Exchange Measurements

Cation-exchange capacities were determined for the wet-ground samples of irradiated and unirradiated kaolin that were discussed in Quarterly Technical Status Report No. 5. These measurements were obtained by the procedure outlined in Quarterly Technical Status Report No. 4. The cation-exchange capacities

of the wet-ground kaolin samples were found to increase with increasing radiation doses. These data are presented in Figure 1.

TABLE II

SPECIFIC SURFACE AREA OF WET-GROUND KAOLIN
AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area (M^2/Gm)
Unirradiated	26.7
1×10^{20}	27.8
1×10^{21}	28.8
1×10^{22}	31.1

D. Index of Crystallinity Measurements

Previous attempts to establish a quantitative measurement of the decrease in crystallinity with increase in radiation dose for the Washington County kaolin by a comparison of the intensity of the $02\bar{1}$ X-ray diffraction maxima with the 060 X-ray diffraction maxima have met with very little success. The difficulty encountered was that the $02\bar{1}$ diffraction maxima could not be resolved well enough to obtain reproducible measurements. It was first thought that this poor resolution was due to orientation of the kaolin particles, as a result of their unusually large size, in the preparation of the samples for diffraction studies. A procedure of mixing the kaolin with various amounts of finely divided silica was used to overcome the particle orientation. Contrary to expectations, the resulting reduction in particle orientation did not improve the resolution of the $02\bar{1}$ diffraction maxima significantly. Limited success

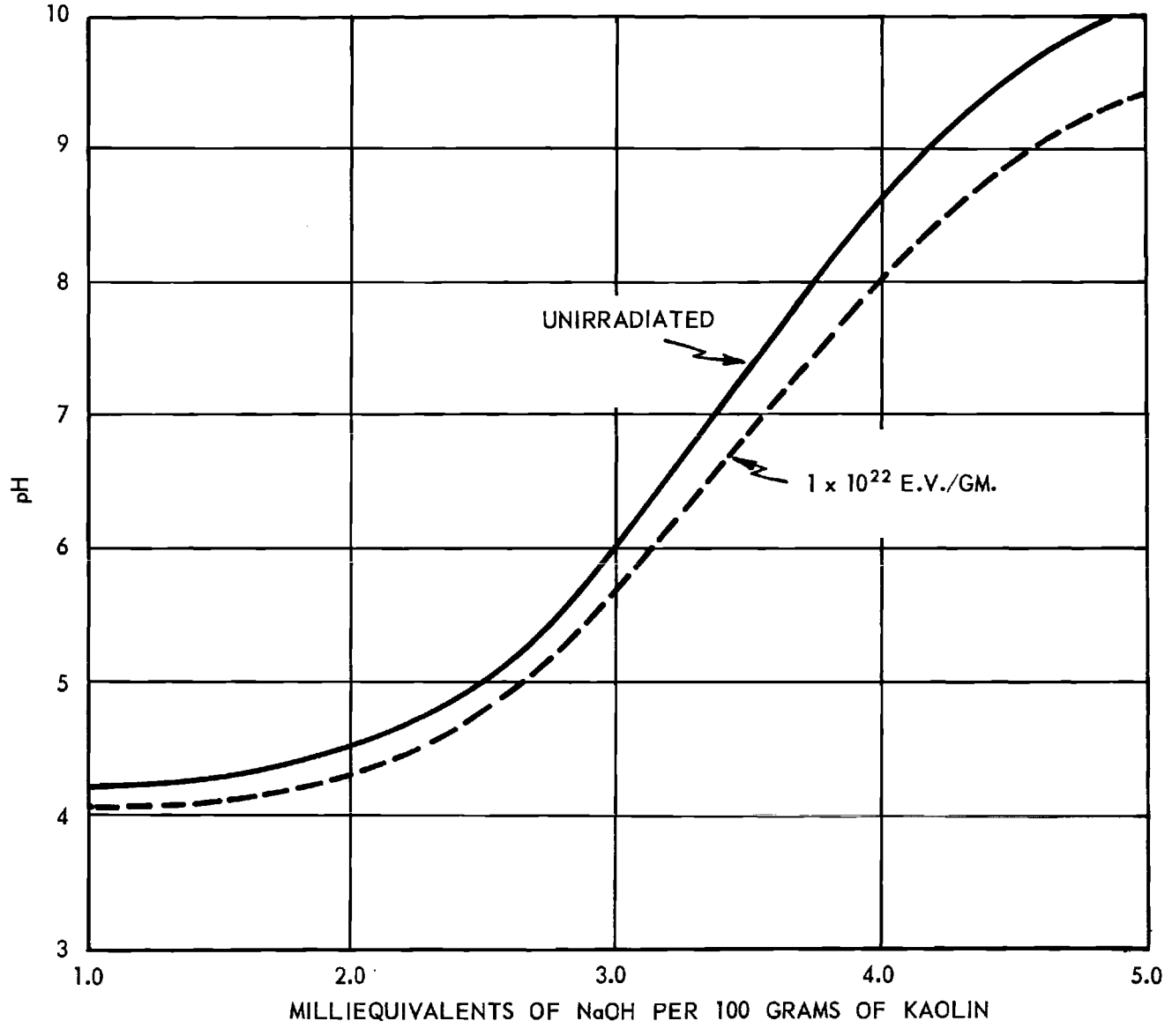

Figure 1. Titration Curves for Hydrogen-Kaolinite from a Washington County, Georgia Kaolin. Wet-Ground for 50 Hours.

was obtained by replacing the Gieger counter that is normally used with the diffractometer with a proportional counter and adding a pulse height analyser. This arrangement suppressed the background noise considerably, improved the diffraction maxima to background ratio and reduced the effect of the beta ray reflection of the 002 diffraction maxima. However, the beta ray reflection could not be suppressed well enough to allow reproducible measurements of the $02\bar{1}$ diffraction maxima.

The Twiggs County kaolin does not exhibit the difficulty of beta ray interference that was encountered with the larger particle sized Washington County kaolin. The crystallinity index of samples of this kaolin that had received various doses of gamma-radiation were obtained and these data are presented in Table III. The crystallinity index varies ideally from 0 to 1, with 1 being the best-crystallized material and 0 the poorest.

TABLE III

VARIATION OF CRYSTALLINITY INDEX WITH RADIATION DOSE
FOR KAOLIN FROM TWIGGS COUNTY, GEORGIA

Dose (EV/Gm)	Crystallinity Index
Unirradiated	0.90
1×10^{18}	0.90
5×10^{18}	0.96
1×10^{19}	0.91
5×10^{19}	0.97
1×10^{20}	0.86
1×10^{21}	0.86
1×10^{22}	0.84

E. Infrared Absorption Measurements

A careful re-examination of the infrared absorption spectra that were obtained previously, as reported in Quarterly Technical Status Report No. 4, revealed some doubt that the spectra were identical for kaolin before and after irradiation. In these studies 0.5 inch diameter wafers of potassium bromide containing 0.3 per cent kaolin were prepared by pressing 0.01 gram of the mixture at 12.5 tons per square inch in an appropriate press, and these wafers were examined with a Perkin-Elmer Model 21 infrared spectrometer. These studies have been repeated using 1.0 per cent by weight of kaolin in the potassium bromide pellets. From the absorption spectra of these latter studies the ratio of the intensity absorption maxima of unbonded OH to the intensity of the absorption maxima of the bonded OH was determined. The absorption maxima of the unbonded OH in kaolinite appears at 2.75 microns. The bonded OH produces a broad, poorly defined absorption band from 2.7 to 3.2 microns, a fairly sharp absorption maxima at 6.15 microns, and a weaker band at 7.55 microns. Since the absorption maxima for the bonded OH at 6.15 microns is the most sharply defined, it was chosen for calculating the relative intensity ratios. These intensity ratios, which are presented in Table IV, should represent a quantitative measure of the relative ratios of unbonded OH to bonded OH in the various samples studied.

TABLE IV

VARIATION OF THE RATIO OF UNBONDED OH TO BONDED OH
WITH RADIATION DOSE FOR KAOLIN FROM WASHINGTON COUNTY, GEORGIA

Dose (EV/Gm)	Ratio of Unbonded to Bonded OH
Unirradiated	6.3
1×10^{20}	9.2
1×10^{21}	8.9
1×10^{22}	11.4

III. DISCUSSION AND CONCLUSIONS

Even though previous modifications had been made in the technique of irradiating samples (Quarterly Technical Status Report No. 4) a great deal of

deviation was still observed for data on surface area, crystallinity index, etc. with variation in radiation dose. For this reason it was decided to irradiate the samples in the manner outlined in EXPERIMENTAL WORK to minimize as much as possible the nonuniformity of gamma ray flux received by the sample.

The decrease in specific surface area observed for the Twiggs County kaolin with increasing radiation dose is apparently the same phenomenon encountered with the Washington County kaolin discussed in Annual Technical Status Report No. 1. That is, the decrease in the number of capillary crevices in the stacks reduces the apparent specific surface area by a greater amount than the increase in number of smaller particles raises it. The most unexpected result of the surface area studies has been the increase in surface area with increasing doses for the wet-ground samples of kaolin. As was reported in Quarterly Technical Status Report No. 5, no difference in particle size was found with the Coulter Counter for these wet-ground kaolin samples. For this reason no difference in specific surface area was expected. This indication of a difference in particle size reduction provided by the surface area measurements is supported by the difference in cation-exchange capacity that also was observed. This raises a very serious question as to the suitability of the Coulter Counter for analysing the particle size distributions of the samples used in this work, or the suitability of the method of reducing the data obtained from the Coulter Counter. The latter appears to be the most probable, and this problem is presently under investigation.

In spite of the improved method of irradiating the kaolin samples, abnormal deviations appear to exist in the data for change in specific surface area and crystallinity index. The only solution appears to be repetitive measurements to determine whether or not these apparent deviations are real and significant or merely due to sample inhomogeneities.

The data obtained from infrared absorption measurements concerning the relative amounts of unbonded and bonded OH present in the samples appears quite interesting. However, these data must be considered as very tentative. While reasonable care was taken to dry the samples of kaolin before preparing the pellets for infrared absorption measurements, extreme care was not taken since quantitative measurements were not anticipated. These measurements will be repeated with careful attention to drying all samples under identical conditions and guarding against subsequent exposure to the atmosphere in order to eliminate any variations due to adsorbed moisture.

IV. FUTURE WORK

During the next three months the problems which will receive the most attention are (1) a careful analysis of the technique for measuring and expressing the particle size distributions, (2) further measurements of the specific surface area and crystallinity index to determine whether or not the apparent deviations in data are significant or merely due to sample inhomogeneities, (3) a determination of the absorption spectra under more carefully controlled conditions and for a wider range of radiation doses, and (4) continuation of the electron diffraction studies of unirradiated and irradiated kaolin for which the preliminary work has already been accomplished. The foregoing investigations will be performed with the two kaolins already under investigation and at least one more kaolin of a different type.

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ANNUAL TECHNICAL STATUS REPORT NO. 1

PROJECT NO. A-446-5

DEAGGLOMERATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

By

WILLIAM J. CORBETT AND JOHN H. BURSON, III

COVERING THE PERIOD
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Printed 20 April 1960

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OFFICE OF ISOTOPES DEVELOPMENT
GERMANTOWN, MARYLAND

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

ENGINEERING EXPERIMENT STATION
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ABSTRACT

The objective of this research program is to investigate the possibilities of using high-energy, ionizing radiation to reduce agglomerates of kaolin plates to discrete particles.

Samples of a well-crystallized kaolin from Washington County, Georgia, were subjected to both X-radiation and gamma-radiation. The results of physical tests made on the samples irradiated with the gamma research irradiator and a sample given a total energy dose of 1×10^{21} electron-volts per gram with a 150-kv X-ray machine indicate that kaolin stacks can be deagglomerated with high-energy, ionizing radiation. The data from X-ray diffraction studies show a definite decrease in the degree of crystallinity for kaolin subjected to high-energy, ionizing radiation.

Research in the immediate future will be concerned with further evaluation of the samples irradiated to date, particularly with respect to particle size, reflectance and electron-diffraction studies. In view of some of the results contained in this report, grinding studies of kaolin before and after irradiation have become of prime importance. These studies will begin early in the next year. Future experiments will be designed to obtain more information as to the processes that take place when kaolin is subjected to high-energy, ionizing radiation.

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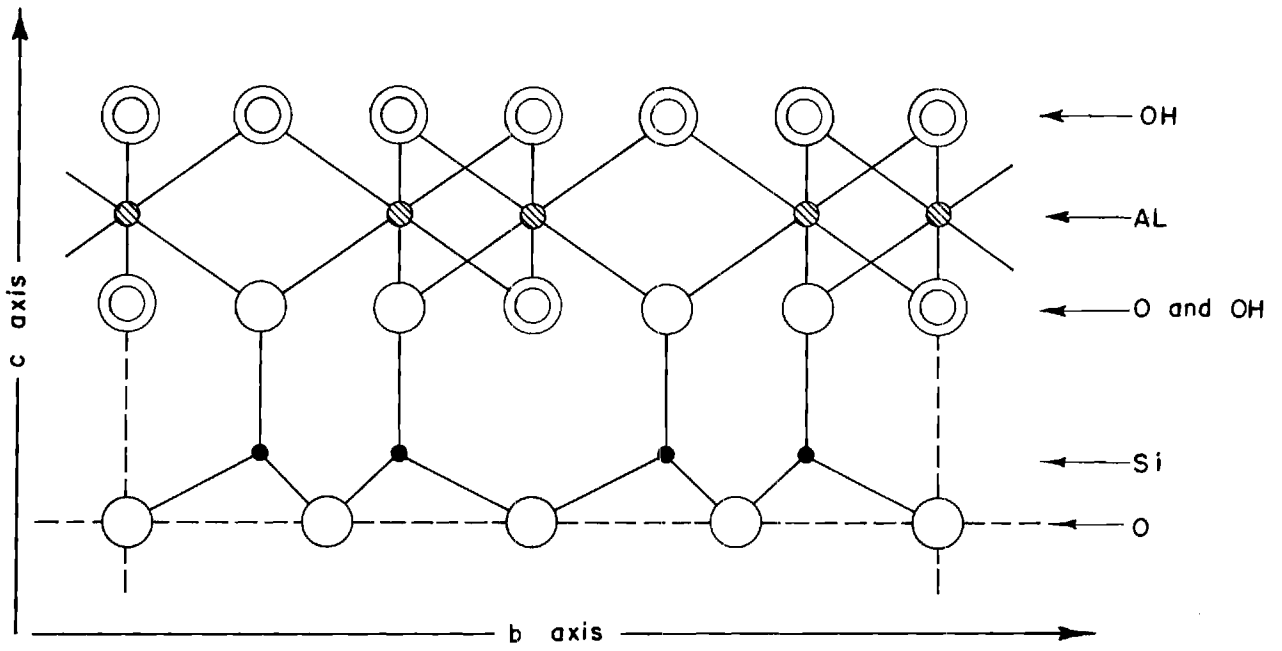
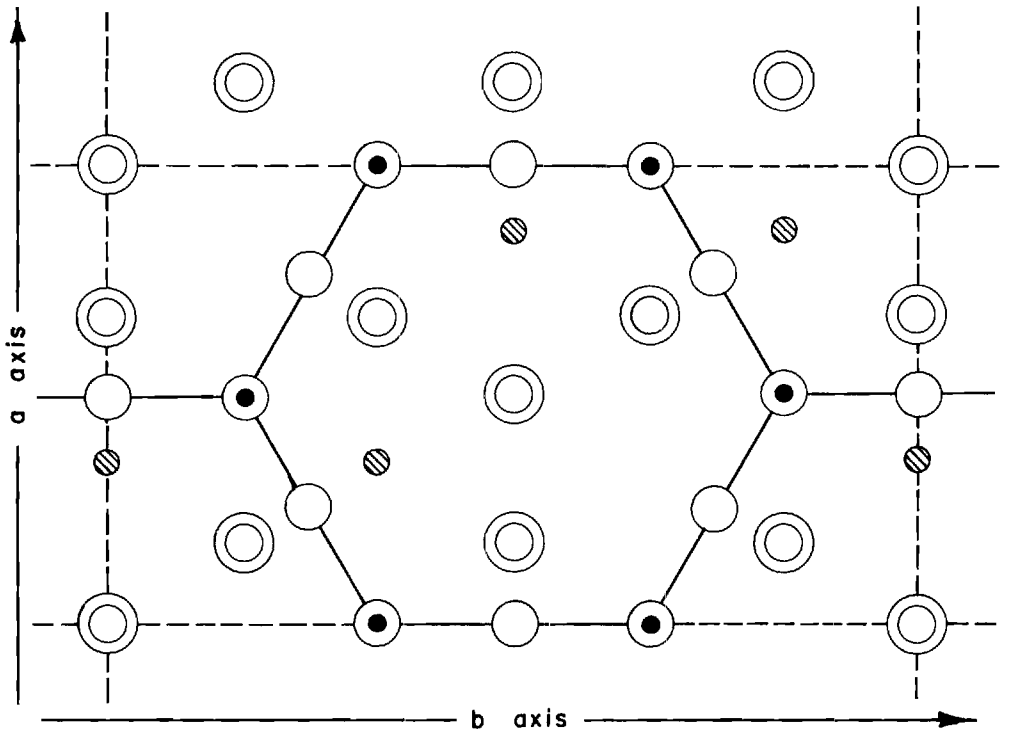


A. SIDE VIEW



B. TOP VIEW (001 PLANE)

Figure 1. The Kaolin Layer.

water molecules per unit cell.[2] Other minerals, livisite, anauxite and allophane, have been suggested as belonging to the kaolin group. However, little is known about the constitutents or the structure of these minerals, and this study will not be concerned with them.

Since the unit layer is common to all the kaolin minerals, their a_o and b_o dimensions are all very similar. The dimension of a unit cell along the c axis is determined by the relative positions of the aluminum atoms in successive kaolin layers. For example, if two layers are placed directly above another, the oxygen atoms of the lowest sheet in one layer will lie on a vertical line with the similar atoms in the next layer. The same holds true for the silicon atoms in the adjacent layers and for the hydroxyl atoms. This does not necessarily hold true for the aluminum atoms. There are six possible locations for the four aluminum atoms in a layer, which means for a given arrangement of aluminum atoms in one layer there are three alternate arrangements of these atoms in the next layer. Addition of successive layers introduces additional complications.

The relative position and arrangement of successive layers depends on the orientation of the oxygen atoms and hydroxyl layers of adjacent layers. One stable configuration is achieved when the layers are placed directly above each other. Then the angles α and β, which represent the angle between the c axis and the b and a axis respectively, are 90°. This arrangement is closely obtained in the rare mineral nacrite. Certain displacements of one layer relative to another can also result in a stable arrangement of O - HO linking. These displacements are distances of $na_o/6$ of $mb_o/6$, along the a and b axis respectively, where n and m are integers and a_o and b_o are the cell dimensions. The values of these shifts and the resulting angles have been determined and are well documented.[3, 4]

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[2] S. B. Hendricks and M. E. Jefferson, "Structures of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays," Am. Mineral 23, 863-875 (1938).

[3] G. W. Brindley, X-Ray Identification and Crystal Structures of Clay Minerals, (London: The Mineralogical Society, 1951).

[4] Alfred B. Searle and Rex W. Grimshaw, The Chemistry and Physics of Clays, (Third Edition; London: Ernest Benn Ltd., 1959).

The general structural characteristics of the kaolin minerals are in accord with these principles. The a_o and b_o dimensions of the unit cells are all very similar since the kaolin layer is common to all. The c_o dimension is determined by the type of stacking and the arrangement of aluminum atoms in successive layers. The angular relationship of the c axis to the a and b axes is governed by the relative displacement of the layers.

Kaolinite, the primary constituent of kaolin, forms plate-like, hexagonal crystals whose thickness is very small in comparison with their length and breadth. Individual crystals of kaolinite usually occur in the colloidal size range, and they vary from a few thousandths to a few tenths of a micron in thickness. It is obvious, therefore, that an individual crystal must be several unit cells thick. The exact nature of the forces that hold these layers together is not known with certainty. Most authorities agree that the force is probably hydrogen bonding between the hydroxyl sheet and the oxygen sheet of adjacent unit cells.

Frequently kaolin is found to contain very large crystallites that appear to be aggregates of individual crystal plates stacked one on another. Such a stack is shown in Figure 2. A stack is actually a single crystallite that contains many stacking faults along the a and b axis. At the crystallite faces, parallel to the c axis, these stacking faults produce the appearance that many individual kaolinite crystals have been "cemented" together in some manner. The distance between two of these faults is approximately the same as the thickness of individual kaolinite plates. The planes along which these faults occur are planes of cleavage as are the same planes between any adjacent unit cells of kaolinite. However, the very fact that stacking faults are present would mean that adjacent unit cells are not bound together as strongly at these interfaces as they would be at other interfaces in the crystallite. As a result the crystallite would be expected to break at these points when subjected to shearing forces. Experiments performed with devices that develop very high shearing forces have produced some individual plates from these stacks. These plates are of the size as those that occur naturally in kaolin.

Stacks of kaolinite plates range in size from 2 to greater than 40 microns equivalent spherical diameter. Ordinary size reduction techniques cannot reduce the thickness of a stack of plates appreciably. Since the bonding of kaolin layers along their cleavage planes is apparently due to hydrogen bonding, these researchers felt that high-energy, ionizing radiation could be used to aid in reducing these stacks. It has been established that high-energy, ionizing radiation can bring about the degradation of chemical bonds in both inorganic and organic solids.[5]

Many of the companies in the kaolin industry have been informed of this project and its purpose. These companies have expressed great interest in the objective of this study.

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[5] H. G. Heal, "The Chemical Effects of Ionizing Radiation in Solids I, II," Atomics (British) 6, 205-208, 241-246 (1955).

II. EXPERIMENTAL WORK

All experimental work during this report period was performed with a kaolin from Washington County, Georgia. This kaolin was well crystallized and had been fractionated with respect to particle size until 90 per cent of the material, by weight, had a particle size above 2 microns equivalent spherical diameter. The kaolin received no further treatment before irradiation except a drying period of 4 to 6 hours at a temperature of 110° C.

A. Irradiation with X-Rays

The initial experiments for this project were performed with X-radiation. Two samples of kaolin were irradiated with X-rays at 50 kvp and 45 ma. These samples weighed 29.5 and 12.4 grams and received total doses of 2×10^{21} and 1×10^{22} electron-volts per gram respectively. The absorption thicknesses were 0.76 and 0.32 gram per square centimeter respectively. Two other samples of kaolin were subjected to X-radiation at 150 kv and 18 ma. One of these samples weighed 20 grams and absorbed approximately 1×10^{21} electron-volts per gram; the absorption thickness was 0.40 gram per square centimeter. The other kaolin sample weighed 75 grams and was irradiated as a 60-per-cent-by-weight water slurry. The total energy dose absorbed by this sample was approximately 1×10^{21} electron-volts per gram. The total absorption thickness of this sample was 0.85 gram per square centimeter.

The dosimetry measurements for these experiments were made with the standard ferrous ion technique.

B. Irradiation with Gamma Rays

The gamma irradiation of kaolin was accomplished using a 12,000-curie, cesium-137 research irradiator. This irradiator is of the Notre Dame type with a dose rate of 7.5×10^{19} electron-volts per gram per hour in the center well. All irradiations performed with the research irradiator during this report period were made in the center well.

The first experiment with gamma radiation was designed to determine the effect of various total energy doses. A large pyrex test tube containing approximately 200 grams of kaolin was placed in the research irradiator. The absorption thickness of the sample was 0.80 gram per square centimeter. Every 50 hours a 15-gram sample was removed up to a total of 500 hours.

The total absorbed doses of the samples ranged from 3.8×10^{21} to 3.8×10^{22} electron-volts per gram. Two other samples of 150 grams each were irradiated with the research irradiator. These samples, which were intended primarily for viscosity measurements, absorbed total doses of 1×10^{21} and 1×10^{22} electron-volts per gram. The absorption thickness was 1.0 gram per square centimeter for both of these samples.

C. X-Ray Diffraction Measurements

X-ray diffraction measurements were made on all samples subjected to either X-radiation or gamma-radiation as well as the unirradiated material. These measurements were made to determine if any changes in lattice spacing, crystallite size or degree of crystallinity had occurred. The samples of kaolin irradiated with the 50-kvp X-ray machine showed no changes in any of these properties. The sample of kaolin irradiated as a water slurry with the 150-kv X-ray machine exhibited no changes either. However, the dry sample of kaolin irradiated with the 150-kv machine did show significant changes. The lattice spacings did not appear to be changed, but the crystallite size was smaller and the material appeared to be very poorly crystallized. All of the samples subjected to gamma-radiation exhibited no apparent change in the lattice spacings, but significant changes in crystallite size and degree of crystallinity. Figure 3 contains typical X-ray diffractometer traces of an unirradiated and an irradiated kaolin.

No attempts were made to determine the reduction in crystallite size quantitatively since this could be more easily determined by particle size measurements and electron microscopy. The customary method of evaluating differences in the degree of kaolinite crystallinity is to make qualitative rankings by inspection of diffractometer traces. However, Johns and Murray[6] have recently developed a method of expressing the degree of kaolinite crystallinity quantitatively. This method employs a ratio of the intensities of two reflections, one which is affected by $nb_o/3$ shifts of crystal layers ($02\bar{1}$ reflection), and one which is not (060 reflection). This ratio varies

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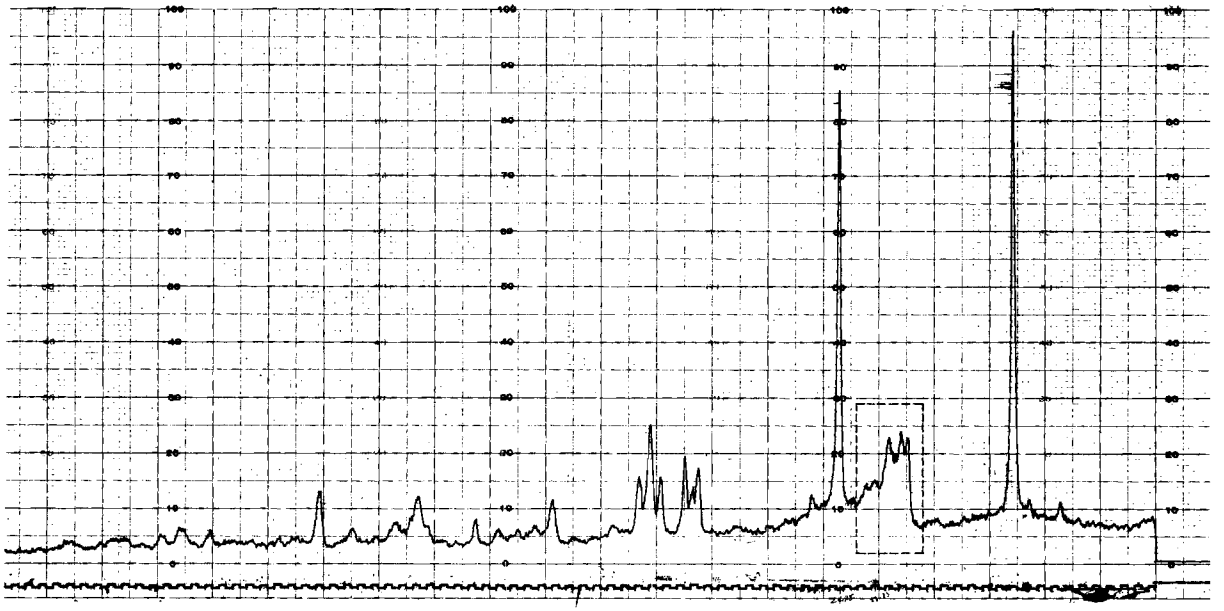
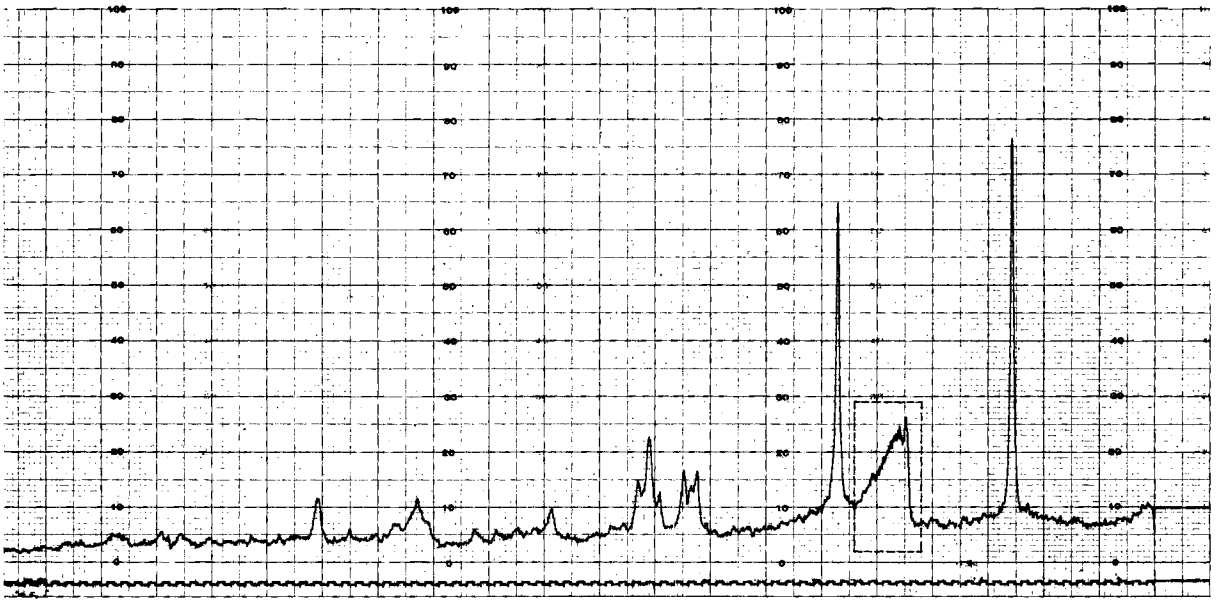
[6] W. D. Johns and H. H. Murray, "An Empirical Index for Kaolinite Crystallinity," Paper presented at the 1959 meeting of the Mineralogical Society of America.



A. UNIRRADIATED KAOLIN



B. IRRADIATED KAOLIN
7.5×10^{21} e.v./gm

Figure 3. Typical X-Ray Diffractometer Traces.

ideally from 0 to 1, with 1 being the best-crystallized material and 0 the poorest. All of the samples that were subjected to high-energy, ionizing radiation and that exhibited a change in crystallinity were assigned a degree of crystallinity in this manner. These results and the results for the unirradiated material are presented in Table I.

D. Electron Microscopy

Electron micrographs of carbon replicas of the kaolin samples were obtained with the electron microscope, to determine any visible changes the kaolin might have undergone during irradiation. These replicas are produced by depositing a thin film of carbon on the kaolin particles, in a vacuum chamber, from a carbon arc. The particles are then removed from the carbon film by dissolution with hydrofluoric acid. These replicas show much greater surface detail when observed with the electron microscope than when the particles are observed directly.

Visible changes in the kaolin samples were observed for the one 20-gram sample of dry kaolin irradiated with the 150-kv X-ray machine and all the samples irradiated with gamma rays. Some of these electron micrographs are presented in Figures 4, 5 and 6.

E. Specific Surface Area Measurements

Specific surface areas were determined, for the unirradiated material and all irradiated samples, with the Brunauer, Emmett, and Teller[7] method of low-temperature, nitrogen-gas adsorption. Complete adsorption isotherms were also determined for the unirradiated material and a gamma-irradiated sample that had absorbed a total dose of 3.8×10^{22} electron-volts per gram. These results are presented in Table II and Figure 7.

F. Particle Size Determinations

The Coulter Counter, Coulter Industrial Sales Co., Elmhurst, Illinois, has been selected for determining particle size distributions for this study. This device determines the number and size of particles suspended in an electrically conductive liquid. The suspension flows through a small aperture having an immersed electrode on either side, with a particle

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[7] S. Brunauer, P. H. Emmett, and E. Teller, "The Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc. 60, 309-19 (1938).

TABLE I

DEGREE OF CRYSTALLINITY OF KAOLINITE FOR VARIOUS TOTAL ENERGY DOSES

Dose (EV/Gm)	Degree of Crystallinity
Unirradiated kaolin	0.46
1.0×10^{21}[a]	0.40
1.0×10^{21}[b]	0.23
3.8×10^{21}[a]	0.29
7.5×10^{21}[a]	0.18
1.0×10^{22}[a]	0.30
1.1×10^{22}[a]	0.27
1.5×10^{22}[a]	0.33
1.9×10^{22}[a]	0.26
2.3×10^{22}[a]	0.32
2.6×10^{22}[a]	0.30
3.0×10^{22}[a]	0.40
3.4×10^{22}[a]	0.23
3.8×10^{22}[a]	0.25

[a] Irradiated with 0.665-Mev gamma rays.

[b] Irradiated with X-rays at 150 kv and 18 ma.

TABLE II

SPECIFIC SURFACE AREAS OF KAOLIN SAMPLES
FOR VARIOUS TOTAL ENERGY DOSES

Dose (EV/Gm)	Surface Area (M^2/Gm)
Unirradiated Kaolin	6.3, 5.9, 6.0
1×10^{21}[a]	6.2
1×10^{21}[b]	5.9
2×10^{21}[a]	6.3
3.8×10^{21}[c]	5.2
7.5×10^{21}[c]	5.9
1.1×10^{22}[c]	5.6
1.5×10^{22}[c]	5.6
1.9×10^{22}[c]	5.4
2.3×10^{22}[c]	5.2
2.6×10^{22}[c]	5.4
3.0×10^{22}[c]	5.0
3.4×10^{22}[c]	5.6
3.8×10^{22}[c]	5.7

[a] Irradiated with X-rays at 50 kvp and 45 ma.

[b] Irradiated with X-rays at 150 kv and 18 ma.

[c] Irradiated with 0.665-Mev gamma rays.

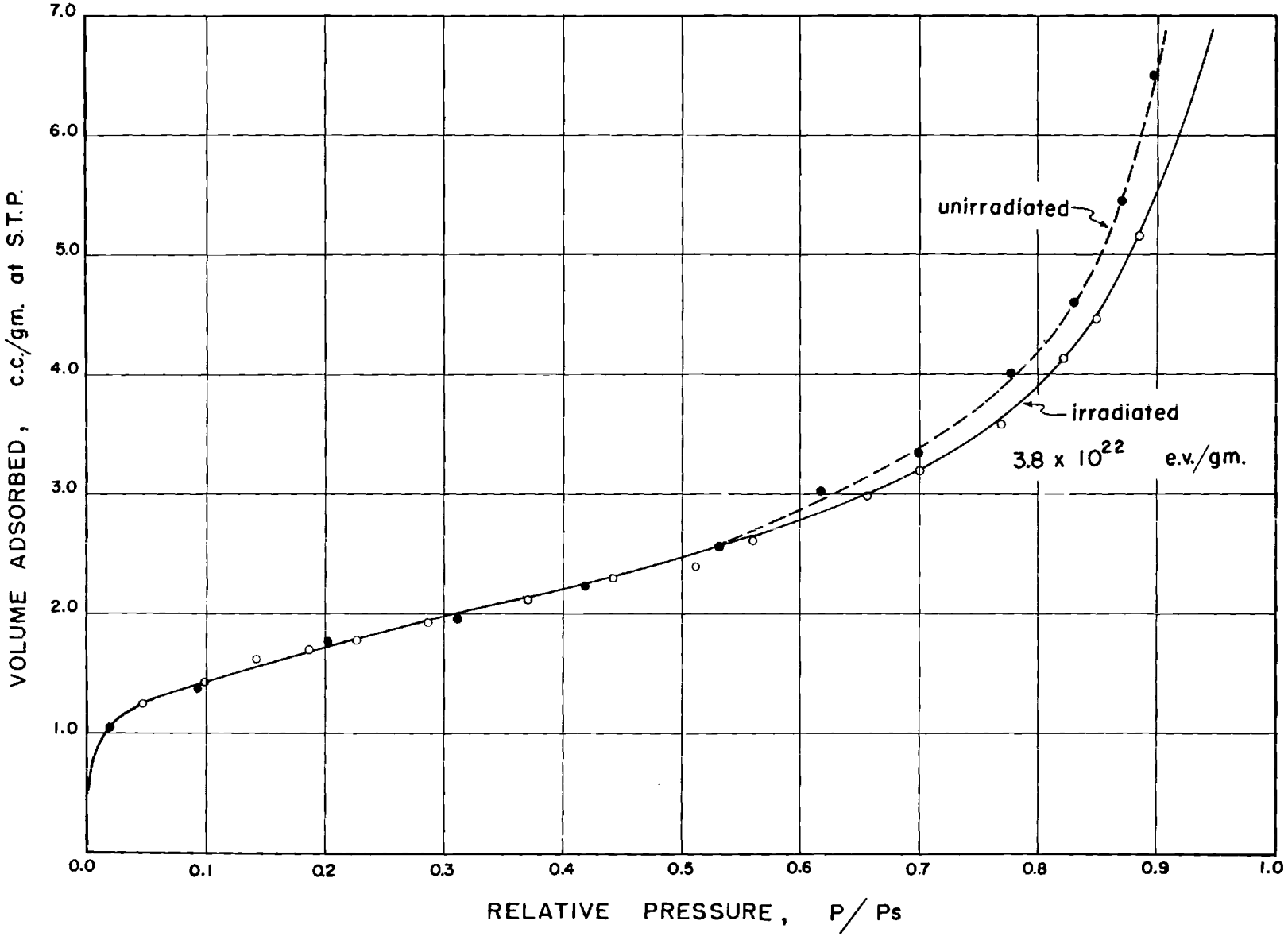

Figure 7. Adsorption Isotherms for an Unirradiated and an Irradiated Kaolin.

concentration such that the particles pass through the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperture, momentarily changing the resistance 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.

Samples of the unirradiated material and a sample that had received a total dose of 3.8×10^{22} electron-volts per gram with gamma-radiation were made up to the same weight per cent concentration in an electrolyte solution. Equal volumes of these dispersions were analysed with the Coulter Counter to determine the number of particles, of a given size and larger, present in the sample. These data are presented in Table III.

TABLE III

COMPARATIVE SIZE DISTRIBUTIONS OF KAOLIN
BEFORE AND AFTER IRRADIATION

Equivalent Spherical Diameter (Microns)	Number of Particles of Stated Size And Larger, in Unit Volume	
	Unirradiated	Irradiated
17.13	400	420
10.05	3,200	3,100
7.96	6,500	6,200
4.65	22,000	20,500
3.69	29,500	29,000
2.16	58,000	71,000
1.71	80,000	125,000
1.01	200,000	560,000
0.80	310,000	950,000
0.47	960,000	5,800,000

G. Viscosity Determinations

Viscosity determinations were made on an unirradiated kaolin sample and two 150-gram irradiated samples that had received doses of 1×10^{21} and 1×10^{22} electron-volts per gram respectively.

A slurry containing 55 per cent by weight of kaolin was prepared with a 0.75 per cent solution of tetrasodium pyrophosphate. The kaolin and tetrasodium pyrophosphate solution were blended together in a Waring Blendor and agitated for 5 minutes. The temperature of the slurry was adjusted to 81° F and the apparent viscosity determined with a Brookfield viscometer, model LVF, at varying rates of shear. The data obtained are presented in Table IV.

TABLE IV

APPARENT VISCOSITIES OF KAOLIN SLURRIES FOR VARIOUS TOTAL ENERGY DOSES

Dose (EV/Gm)	Spindle (Number)	Rate of Rotation (RPM)	Apparent Viscosity (Cps)
Unirradiated kaolin	2	12	40.0
	2	30	68.0
	2	60	89.5
1×10^{21}	2	12	80.0
	2	30	85.0
	2	60	100
1×10^{22}	2	12	113
	2	30	100
	2	60	104

H. pH Determinations

The pH of an unirradiated and two irradiated samples that had received doses of 1×10^{22} and 3.8×10^{22} electron-volts per gram with gamma-radiation were determined with a Beckman pH meter, model 96, using calomel and glass electrodes.

A 10 per cent by weight solution of kaolin was made up with freshly distilled water. The temperature of the slurry was adjusted to 80° F and the pH measurements were made. The data obtained are presented in Table V.

TABLE V

CHANGE OF pH OF KAOLIN DISPERSIONS WITH VARIOUS TOTAL ENERGY DOSES

Dose (EV/Gm)	pH
Unirradiated kaolin	6.78
1×10^{22}	5.85
3.8×10^{22}	5.23

I. Electron Diffraction Measurements

Electron diffraction patterns were obtained for the unirradiated kaolin and for a sample that had received a total dose of 3.4×10^{22} electron-volts per gram of gamma-radiation. Both selected area and powder diffraction patterns were made. These patterns are presented in Figures 8 and 9.

J. Differential Thermal Analysis

All the samples of kaolin that had been subjected to 150-kv X-rays, those irradiated with the research irradiator, and the unirradiated kaolin were subjected to differential thermal analysis. This technique involves comparison of the changes that occur in a clay sample with those of a reference material, as a function of temperature. A few grams (2 or 3) of the kaolin being tested are compressed into a pellet. This pellet, along with a pellet of the reference material, is heated at a constant rate in a suitable furnace to some arbitrary temperature and the difference in temperature between the two pellets is recorded. The temperature differences observed are indications of endothermic and exothermic processes that are taking place in the kaolin. The magnitude of these differences and the range at which they occur are determined by the chemical composition and the physical condition of the kaolin. The reference material is usually calcined alumina. However, in this work a calcined pellet of unirradiated kaolin is used as the standard. Figure 10 shows a typical plot of the data obtained from a differential thermal analysis. The abscissa is the temperature to which the pellets have been heated, with 1000° C being the maximum for this

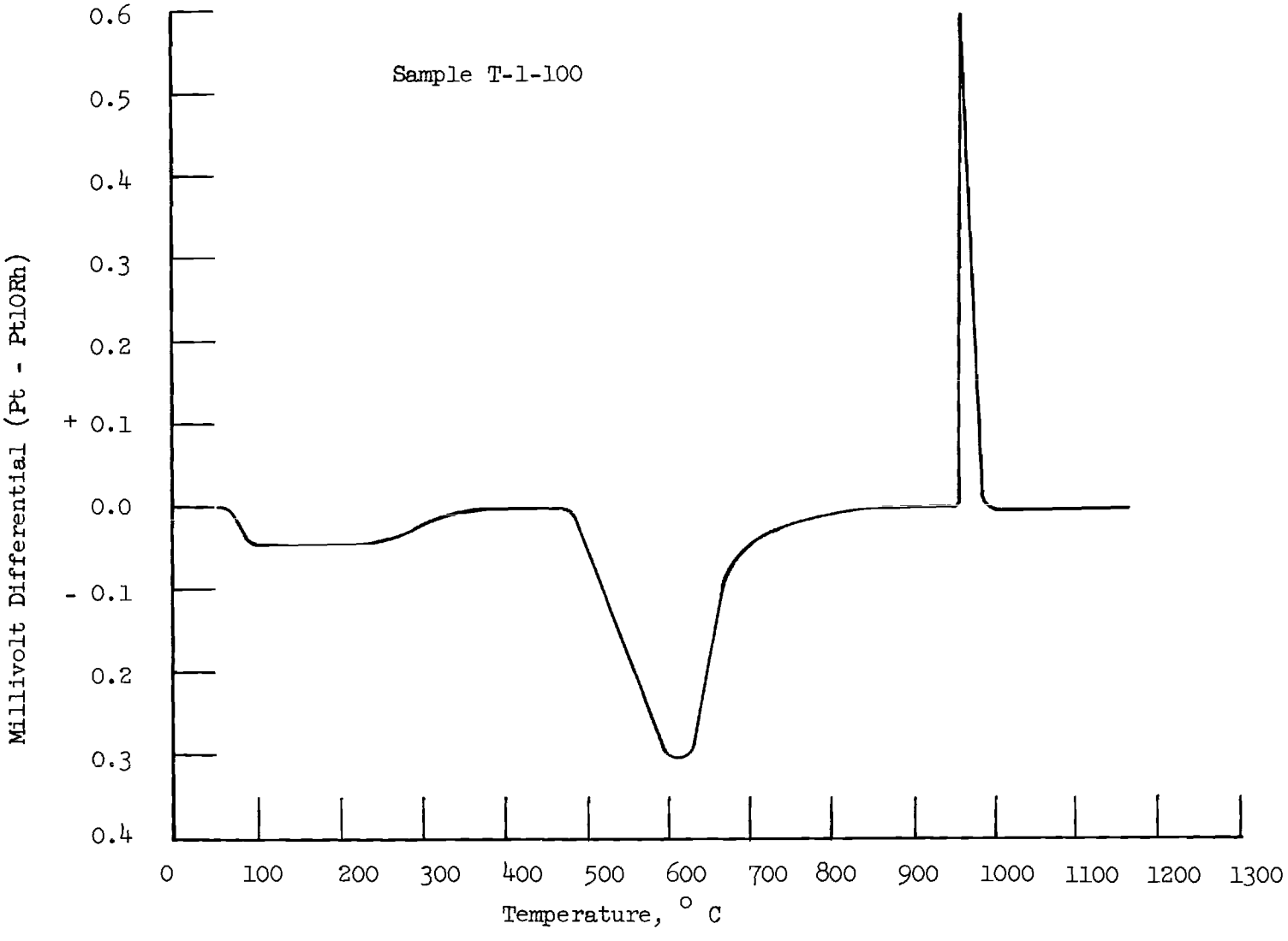

Figure 10. Typical Plot of Differential Thermal Analysis Data.

work, and the ordinate is the millivolt difference between the Pt - Pt10Rh thermocouples placed beneath each pellet. The first deviation along the abscissa, which is negative--indicating an endothermic process, extending from a temperature of approximately 60° C to a temperature of approximately 375° C, is caused by the driving off of absorbed water. The next deviation, also an endothermic process, from a temperature of about 475° to 850° C, is the result of driving off chemically bound water from the crystal lattice. This process, which is actually calcination of the kaolin, has a maximum at 625° C. The final deviation, which is an exothermic process, is the result of a phase change that takes place at about 965° C. No difference was found between the data obtained from the irradiated kaolin and that obtained with unirradiated kaolin.

III. DISCUSSION AND CONCLUSIONS

All the results obtained for kaolin samples irradiated with the gamma research irradiator and the sample that was given a total energy dose of 1×10^{21} electron-volts per gram with the 150-kv X-ray machine indicate that kaolin stacks can be deagglomerated with high-energy, ionizing radiation.

Broadening of some of the reflections of the X-ray diffractometer traces gave a qualitative indication that the crystallite size had been reduced. Likewise, the broadening of the lines of the electron diffraction powder patterns (see Figure 8) for the irradiated material shows that the crystallite size has been reduced. The most direct evidence, of course, is obtained from the electron micrographs and the size distributions. A comparison of the electron micrographs, Figure 4, 5, and 6 shows many more individual kaolinite plates in the irradiated material than in the original. These are only a very few of the many micrographs that were made of both the irradiated and the unirradiated kaolin. They are, however, quite representative of the results found in every case. The size distributions show a tremendous increase in the number of particles in the size range of individual plates. Unfortunately, the lower limit of the Coulter Counter extends only into the upper portion of the colloidal size range, which is the range in which individual kaolinite plates occur. Therefore, the number of individual kaolinite plates in the irradiated material is probably even greater than these data show. The electron micrographs certainly seem to bear this out, since many of the particles shown in them are smaller than a half micron. A technique is presently being developed to extend the lower limit of the data from the Coulter Counter.

Viscosity and pH determinations both give indirect evidence that deagglomeration has taken place. The increase in viscosity of an irradiated kaolin slurry over the viscosity of a slurry of the unirradiated material is undoubtedly due to the presence of smaller particles in the irradiated material. Kaolins that contain smaller plates have more individual edges and corners to cause friction and their slurry viscosities are therefore

higher.[8] The increase in pH observed with dispersions of irradiated kaolin is most likely due to the exposure of new surfaces (which would result from the breaking off of smaller kaolinite particles from the stacks) containing sites for chemical activity. The exact nature of the chemical activity that produces this change in pH is not understood; it is an empirical relationship established by experiment.[9] The initial pH of almost 7 exhibited by the unirradiated clay was due to the fact that the kaolin used in these studies was treated with an alkaline deflocculating agent during processing to remove the finer material. Normally kaolin clays have a pH of about 4.3 to 5.5.

The differential thermal analyses were performed to determine whether or not any chemically bound water had been removed and if any phase changes had taken place during irradiation. The fact that all of the traces were unchanged for the irradiated material indicates that neither of these processes occurred. However, in the future the differential thermal analyses will be conducted in such a manner as to obtain the best resolution of the exothermic peak associated with the phase change from kaolinite to mullite. Special emphasis was not placed on this point during the analyses reported here.

Surface area results for the irradiated kaolin samples seem to be very scattered and inconclusive, probably due to either one of two causes, or possibly a combination of both. First of all, the limits of accuracy in a specific surface area range of 5.0 m^2/gm are probably not better than ± 0.2 m^2/gm, which means the error between two different measurements could be as much as 0.4 m^2/gm. An inspection of the range of differences found for the surface areas of the samples shows that this much error would be very significant. The other cause may be due to variations in absorption thickness. The bulk density of the clay probably exhibits local variations and the method of sampling was not carried out in a manner that would

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[8] H. H. Murray and S. C. Lyons, "Correlation of Paper-Coating Quality with Degree of Crystal Perfection of Kaolinite," Proc. of Fourth Nat'l. Conf. on Clays and Clay Minerals, National Research Council Publication 456, 31-40 (1956).

[9] G. C. Harman and F. Fraulini, "Properties of Kaolinite as a Function of Its Particle Size," J. Am. Ceramic Soc. 23, 252-58 (1940).

minimize such an error. The scatter observed in the measured degrees of crystallinity could also be accounted for with this latter explanation. In the only tests conducted to date where changes in physical properties with increasing total energy doses were observed with no apparent anomalies, the sampling was conducted in such a manner as to minimize any errors due to variations in absorber thickness. These were the tests for changes in pH and viscosity. In these cases the 150-gram samples were removed from the research irradiator and each was thoroughly mixed. A small portion of each sample was removed for the pH tests and almost all of the remaining material was used for the viscosity tests. Of course, it must be taken into account that these data do not contain as many determinations as the specific surface area or crystallinity tests.

The surface area data, in spite of their scatter, indicate a decrease in specific surface area with increasing total energy doses. This relationship is not what would normally be expected for samples of material when particle size was decreasing. If the sizes of the kaolinite crystallites were decreasing, and all the data from other physical tests indicated that they were, specific surface area would be expected to increase. However, in the case of the kaolin stacks where a large number of cracks and crevices are present for capillary condensation, the surface area of the material may appear to be larger than it actually is. Multilayer adsorption takes place in these capillaries while monolayers adsorption is taking place on the surface, and when the surface area is evaluated on the basis of monolayer absorption the capillaries make a disproportionate contribution. As a result, when the kaolinite stacks are broken into discrete plates containing very few if any of these capillaries, the surface area appears to decrease up to a point. This can be visualized as two separate effects, one a decrease in the amount of nitrogen adsorbed with the decrease in the number of capillaries and the other an increase in the amount adsorbed with an increase in surface area due to the smaller particles. The total adsorption process will appear as the summation of these effects with the first controlling in the early stage of deagglomeration and the second effect controlling as deagglomeration becomes more complete. If more deagglomeration had been achieved in this work, the surface area would

have been expected to reach a minimum value and then rise again. Since the theory could not be checked in this manner, complete adsorption isotherms were determined for the unirradiated kaolin and a sample that had received a total dose of 3.8×10^{22} electron-volts per gram. These isotherms, presented in Figure 7, are plots of the volume of nitrogen adsorbed versus the relative adsorption pressure. If adsorption is taking place in a limited space such as a capillary crack rather than a free surface, then only a finite number of layers can be absorbed at saturation. Therefore, the adsorption isotherm of a sample containing capillary cracks would rise more sharply than an isotherm for a sample with more free surface. It can be seen from Figure 7 that this was the case with the unirradiated sample and supports the theory of more capillary cracks being present in the unirradiated material.[10]

As an aid to determining eventually the exact mechanism by which high-energy, ionizing radiation deagglomerates kaolinite stacks, the X-ray diffraction data are probably the most important. This may also be true for the electron diffraction data, but the patterns obtained in the work reported here have not been fully analysed yet. The X-ray diffraction data show definite evidence of $nb_o/3$ shifting of adjacent kaolin layers. This shifting is observed by certain reflections in the diffraction patterns becoming poorly resolved or disappearing altogether, particularly in the areas contained in the rectangular outlines in Figure 3. The loss in resolution of the reflections in this area for the irradiated material is due to a more random arrangement of the aluminum atoms in the crystal lattice. As pointed out in the INTRODUCTION, there are four possible arrangements of the aluminum atoms in a kaolin layer. In a well-crystallized kaolin the arrangements of aluminum atoms in many of the successive unit cells along the c axis of a kaolinite crystal are similar, whereas, in a poorly crystallized kaolinite the arrangements are very random. Therefore, the kaolin layers are said to have been moved by some integral number of $b_o/3$ shifts so that the aluminum

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[10] If the reader desires a more complete discussion of capillary condensation or adsorption isotherms see: Clyde Orr, Jr. and J. M. DallaValle, Fine Particle Measurement, (New York: Macmillan Co., 1959).

atoms are no longer located one above another in adjacent layers. The X-ray diffraction data for the irradiated kaolin show then that the kaolin layers in the kaolinite crystals have a more random arrangement than the unirradiated material.

The randomness of arrangement of these aluminum atoms is somehow associated with the presence of stacks in kaolin. Murray and Lyons[11] found that kaolins that contained a large number of thick kaolinite crystallites usually had a high degree of geometric crystallinity. Kaolins that had a more random arrangement of layers as shown by X-ray diffraction contained thinner plates.

The determination of the mechanism by which these layers undergo shifting, or random rearrangement, requires a great deal more experimental work. However, the most probable explanation at present seems to involve a displacement of the aluminum atom with a subsequent recrystallization of the surrounding atoms. The displacement of these aluminum atoms by knock-on collisions seems highly improbable. Even if this could be accomplished with gamma rays of 0.665-Mev, which are below the accepted energy for knock-on displacements, the fact remains that this same disorder was achieved with X-rays of 150 kv energy, which is far below the accepted energy. The observed effect could possibly be caused by thermal diffusion of ionized aluminum atoms. An inspection of Figure 3 shows that an aluminum atom ionized by a gamma ray or X-ray would not have far to travel, by thermal diffusion, before arriving at a vacancy. If on arriving at this vacancy the ionized atom should capture an electron from one of the many ionizations that must be occurring in the crystal, it would become trapped at this site, which , since it was a vacant site previously, is a nonequilibrium site with respect to the surrounding atoms. The portion of the crystal surrounding this site has a tendency, therefore, to undergo recrystallization. Since the unit cell extends only in the a and b directions, the recrystallization would take place only in these directions and produce a displacement with respect to adjacent layers.

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[11] H. H. Murray and S. C. Lyons, loc. cit.

IV. FUTURE PROGRAM

The anticipated rate of effort could not be expended on this project during its first year due to the lack of a source of high-energy, ionizing radiation. The Cesium-137 Research Irradiator was expected to become available during the early months of the project; however, it did not become available until the last 2 months of the period covered by this report. The 150-kv X-ray machine, with which some of this work was done, did not become available until the eighth month of the first year. All of the significant experimental work to date was accomplished in the last 4 months of the project, with most of that being done in the last 2 months. As a result, the first few weeks of the next year will be spent in further analysis of the samples of irradiated kaolin discussed in this report. Particle size analyses are needed for all of the samples and these determinations need to be extended further into the colloidal size range. Reflectance measurements will be made for these samples and the electron diffraction studies must be completed.

With the data collected so far pointing to some type of recrystallization mechanism, grinding studies have become of prime importance. If recrystallization is taking place, it is possible that many weak areas are being created within the kaolinite stacks. That is, positions where the alignment between adjacent layers is so poor that the force with which they are held together is greatly reduced. Samples of irradiated and unirradiated kaolin will be ground under identical conditions and analysed to determine if the unirradiated material can be broken down more easily.

Samples of kaolin from other sources and with a wider size range will be irradiated and examined.

Experiments will be devised to aid in establishing the exact nature of the changes that take place when the kaolin is subjected to high-energy, ionizing radiation. If for example, the irradiation could be carried out at liquid nitrogen temperature and analysed with X-ray diffraction techniques without allowing the sample to come to room temperature in the meantime, information could be obtained as to whether or not the observed disorder is due to thermal diffusion and subsequent recrystallization, or to some other process.

During the next year irradiation experiments will also be performed with other minerals of the kaolin group, such as nacrite and dickite. Since these exhibit a stacking order different to that found in kaolinite, further information could be obtained about the effect of high-energy, ionizing radiation on the crystalline order of the kaolin minerals. Montmorillonite, a layer-lattice aluminum silicate of another mineral group may also be included.

Respectfully submitted:

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Proj. A-446-5
Final Report

DELAMINATION OF KAOLIN BY HIGH-ENERGY, IONIZING RADIATION

by

William J. Corbett and John H. Burson, III

Prepared for

THE DIVISION OF ISOTOPES DEVELOPMENT
UNITED STATES ATOMIC ENERGY COMMISSION

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ABSTRACT

The objective of the research performed under this project was to investigate the possibilities of reducing large particles of kaolin to small plate-like particles with high-energy, ionizing radiation, and to investigate the changes in the physical and colloidal properties of kaolin due to the effects of high-energy, ionizing radiation.

Two different kaolins from the Cretaceous Tuscaloosa formation in Georgia were used in these studies. The kaolins differed in degree of crystallinity, particle size, and extent of processing before irradiation. Samples of these kaolins were exposed to doses of 0.667 Mev gamma-radiation ranging from 10^{18} to 10^{22} electron-volts per gram. Significant changes were observed in the degree of crystallinity, specific surface area, cation exchange capacity and slurry viscosity. Delamination of the larger particles into smaller platelike particles was detected for one of the samples, but not the other. Some unusual alterations in the appearance of the surface were found for a significant portion of the particles examined. Indications of a decrease in the ratio of hydrogen bonded to unbonded hydroxyl groups were detected by infrared absorption. Samples of irradiated kaolin appeared to grind more readily than did the unirradiated.

The changes in physical and chemical properties are discussed in terms of the observed atomic displacements produced in the kaolinite structure by the gamma-radiation. Recommendations for future research are presented.

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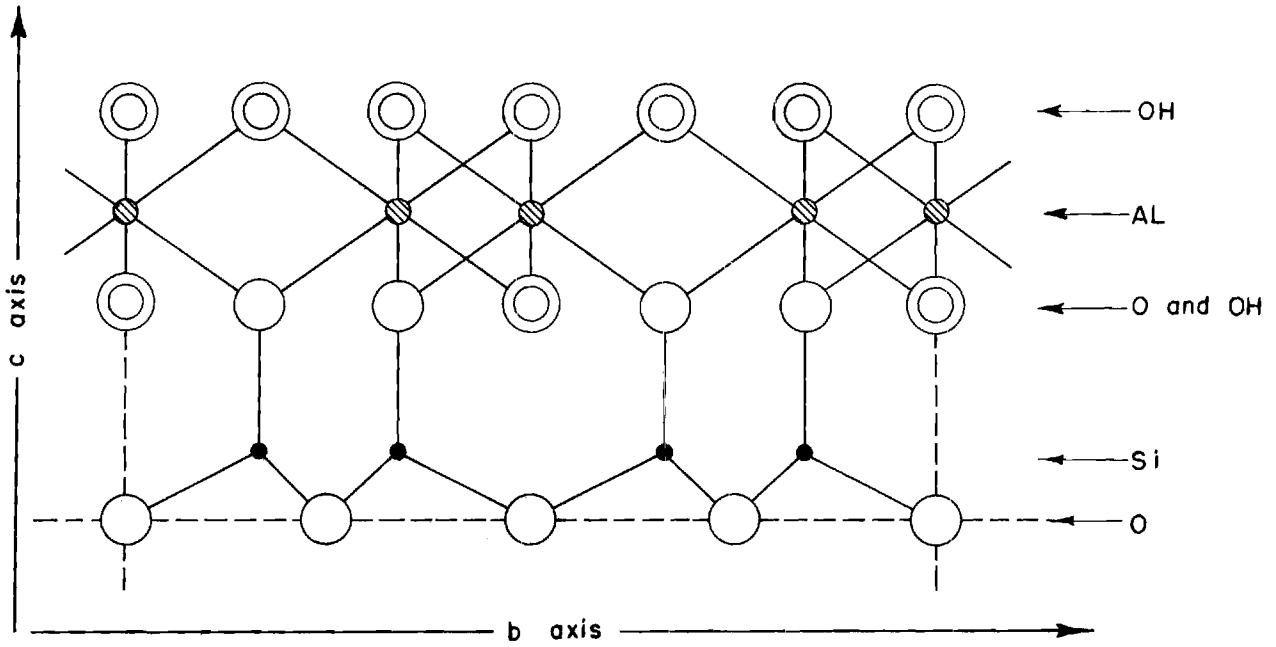
I. INTRODUCTION

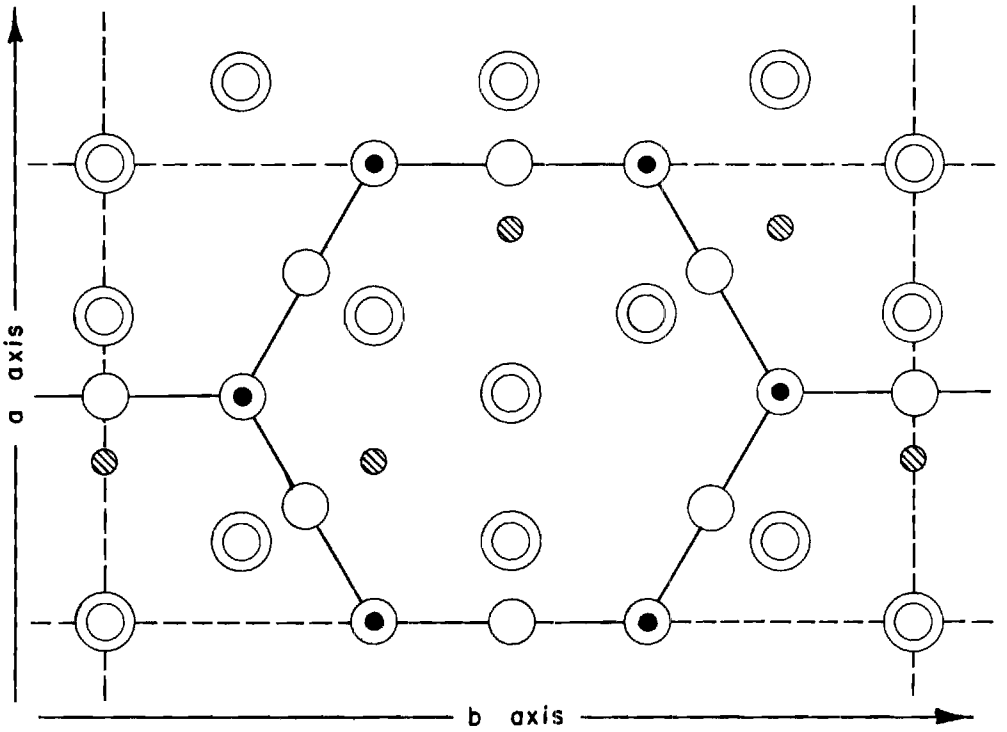
This report summarizes the work performed from April 1, 1959, to March 31, 1961. The objective of the research performed under this project was to investigate the possibilities of reducing large particles of kaolin to small plate-like particles with high-energy, ionizing radiation, and to investigate the changes in the physical and colloidal properties of kaolin due to the effect of high-energy, ionizing radiation.

The structure of the kaolin layer is shown in Figure 1. Figure 1a is a diagrammatic representation of the layer viewed from the side. The base plane is a sheet of oxygen atoms linked to silicon atoms in the sheet immediately above. The third sheet contains both oxygen atoms, which are connected to the silicon atoms of the second sheet, and hydroxyl groups, linked to the aluminum atoms of the sheet above. The aluminum atoms are also linked to a sheet of closely packed hydroxyl groups which comprise the fifth, and final, sheet of the layer. Each silicon atom is bound to three oxygen atoms of the base sheet and one oxygen atom of the third sheet in a tetrahedral coordination. The aluminum atoms form an octahedral coordination with two oxygens and a hydroxyl group of the third sheet and three hydroxyl groups of the fifth sheet. It can be seen from the diagrammatic representation of the view down into the layer (Figure 1b) that only two-thirds of the available sites are occupied by aluminum atoms. This is necessary for the structure to be electrically neutral.

The thickness of the layer is 4.31 angstroms; the layer has no unsatisfied bonds in the top and bottom sheets of atoms. The unit layer extends 8.93 angstroms along the b axis and 5.14 angstroms along the a axis. However, the unit can extend itself indefinitely along the a and b axes since



A. SIDE VIEW



B. TOP VIEW (001 PLANE)

Figure 1. The Kaolin Layer.

it has unsatisfied valence bonds at the edges.

The above structure is known as the kaolin layer because it is the basic structure of minerals belonging to the kaolin group. Some of these minerals are kaolinite, nacrite, dickite, endellite, and halloysite. These minerals differ primarily in the number of kaolin layers per unit cell. Kaolinite contains one layer per unit cell, nacrite six layers per unit cell, dickite two layers per unit cell, endellite one layer plus four layers of water molecules per unit cell,[1] and halloysite one layer plus one layer of water molecules per unit cell.[2] The term kaolin is usually used to describe a clay which contains one or more of the above minerals as a primary constituent.

Since the unit layer is common to all the kaolin minerals, their $\underline{a}_o$ and $\underline{b}_o$ dimensions are all very similar. The dimension of a unit cell along the $\underline{c}$ axis is determined by the relative positions of the aluminum atoms in successive kaolin layers. For example, if two layers are placed directly above one another, the oxygen atoms of the lowest sheet in one layer will lie on a vertical line with the similar atoms in the next layer. The same holds true for the silicon atoms in the adjacent layers and for the hydroxyl atoms. This does not necessarily hold true for the aluminum atoms. There are six possible locations for the four aluminum atoms in a layer, which means for a given arrangement of aluminum atoms in one

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[1] S. B. Hendricks, "On the Crystal Structure of Clay Minerals: Dickite Halloysite and Hydrated Halloysite," Am. Mineral. 23, 295-301 (1938).

[2] S. B. Hendricks and M. E. Jefferson, "Structures of Kaolin and Talc-Pyrophyllite Hydrates and their Bearing on Water Sorption of Clays," Am. Mineral. 23, 863-875 (1938).

layer there are three alternate arrangements of these atoms in the next layer. Addition of successive layers introduces additional complications. The relative position and arrangement of succesive layers depends on the orientation of the oxygen atoms and hydroxyl layers of adjacent layers. One stable configuration is achieved when the layers are placed directly above each other. The angles α and β, which represent the angle between the $\underline{c}$ axis and the $\underline{b}$ and $\underline{a}$ axes are 90°, respectively. This arrangement is closely obtained in the rare mineral nacrite. Certain displacements of one layer relative to another can also result in a stable arrangement of O-HO linking. These displacements are distances of $ma_o/6$ of $nb_o/6$, along the $\underline{a}$ and $\underline{b}$ axis, respectively, where $\underline{m}$ and $\underline{n}$ are integers and $\underline{a}_o$ and $\underline{b}_o$ are the cell dimensions. The values of these shifts and the resulting angles have been determined and are well documented.[3,4]

The general structural characteristics of the kaolin minerals are in accord with these principles. The $\underline{a}_o$ and $\underline{b}_o$ dimensions of the unit cells are all very similar since the kaolin layer is common to all. The $\underline{c}_o$ dimension is determined by the type of stacking and the arrangement of aluminum atoms in successive layers. The angular relationship of the $\underline{c}$ axis to the $\underline{a}$ and $\underline{b}$ is governed by the relative displacements of the layers.

Kaolinite, the most common form of kaolin, forms plate-like, pseudo-hexagonal crystals whose thickness is very small in comparison with their length and breadth. Individual crystals of kaolinite usually occur in

[3] G. W. Brindley, X-ray Identification and Crystal Structures of Clay Minerals, (London: The Mineralogical Society, 1951).

[4] A. B. Searle and R. W. Grimshaw, The Chemistry and Physics of Clays, (Third Edition; London: Ernest Benn Ltd., 1959).

the colloidal size range, and they vary from a few thousandths to a few tenths of a micron in thickness. It is obvious, therefore, that an individual crystal must be several unit cells thick. Since the kaolin layer has no unsatisfied valence bonds on the faces parallel to the a and b axes, interlayer bonding is accomplished by van der Waals forces and long hydrogen bonds.

Frequently, kaolin is found to contain very large particles that appear to be laminates of individual kaolinite crystals. Such a particle, or stack, is shown in Figure 2. These large particles range in size from 2 microns to greater than 40 microns equivalent spherical diameter. The terms "stack" or "booklets," which are often used to describe these particles because of the resemblance in appearance to a stack of cards or the edges of the pages in a closed book, are very apt from the standpoint of appearance, but misleading in terms of structure. Rather than aggregates of individual plate-like kaolinite crystals, these particles are actually homogeneous, crystalline solids that contain a number of kaolinite crystallites. Due to their crystal habit, these crystallites are preferentially oriented in a laminar manner, and the etch pits that occur at the interfaces between these crystallites give rise to the serrated surfaces which produce the effect of an aggregate of individual plates. This effect is further enchanced by the fact that the crystallites have a thickness equivalent to that of the individually occurring kaolinite crystals. In fact, experiments with devices capable of exerting very high shearing forces parallel to the crystallite interfaces have produced individual plates of sizes comparable to naturally occurring plates. This is not surprising, since any plane perpendicular to the c crystallographic

axis represents a plane of cleavage and the interfaces are no doubt the areas of greatest weakness within the large particles.

The presence of stacks in kaolin is very undesirable from an economic viewpoint. The presence of individual colloidal-sized plates is the very characteristic which endows kaolin with some of its most valuable commercial properties. Ordinary size reduction techniques are unable to produce colloidal-sized plates from stacks.

II. EXPERIMENTAL WORK

All the experimental work on this project was performed with kaolins whose primary constituent was the mineral kaolinite. One of these kaolins came from a deposit in Washington County, Georgia. This kaolin was fractionated after mining until 95 per cent of the material, by weight, had a particle size above 2 microns equivalent spherical diameter. The other sample of kaolin used in these studies came from a kaolin deposit in Twiggs County, Georgia. This kaolin received no treatment after mining, and the material contained 85 per cent, by weight, of particles above 2 microns equivalent spherical diameter. Since kaolin particles with equivalent spherical diameters greater than 2 microns represent stacks,[5] these kaolins both contained a large proportion of stacks on a weight basis. The kaolins received no further treatment before irradiation except a short drying period of 4 to 6 hours at 110°C.

A. Irradiation of Samples

The gamma irradiation of kaolin was accomplished using the Georgia Tech 12,000-curie Cesium-137 Research Irradiator. This irradiator is of the Notre Dame type, and an average dose rate of 7.5×10^{19} electron-volts per gram per hour is obtainable in the center well. The maximum dose rate obtainable in the center well is 8.75×10^{19} electron-volts per gram per hour, and this maximum uniform dose is available over a vertical height of 3 inches. All irradiations performed with the Research Irradiator were made in the center well.

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[5] J. H. Koenig and S. C. Lyons, "Correlation of Kaolinite Crystal Shape With Particle Size and Some Effects on Ceramic Behavior," Ceramic Age 66, No. 1, 8-14 (1955).

Radiation doses ranging from 10^{18} to 10^{22} electron-volts per gram were employed in this work. Two different procedures, utilizing two different sample holders, were employed for sample irradiation. In one of these two procedures a large pyrex test tube was used as a sample holder. Approximately 100 grams of kaolin were placed in this test tube and irradiated in the center well of the irradiator. The samples were therefore located in the entire region of radiation flux and the dose received by the sample was calculated from the average dose rate of the center well. This dose was determined by integration of the area under a dose-rate-versus-vertical-height curve which had been obtained for the Research Irradiator by other investigators.[6] When the samples were removed from the irradiator they were thoroughly mixed to compensate for the nonuniformity of dose rate over the vertical length of the sample holder. Irradiations were also performed using a sample holder consisting of an aluminum cylinder, with a wall thickness of approximately 1/8 inch, divided into two compartments by a partition perpendicular to its cylindrical axis, and closed at either end by threaded aluminum plugs. These compartments held between 10 and 15 grams each. The cylinder, which was 5-1/4 inches long, was placed on a spacer within the sample carrier of the Cesium-137 Research Irradiator. This spacer located the sample holder only in the region of uniform radiation flux. In addition to providing a more uniform dose rate, this procedure allowed samples of two different kaolins to be irradiated simultaneously.

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[6] R. C. Palmer and R. W. Carter, "A High Intensity Cesium-137 Research Irradiator," International Journal of Applied Radiation and Isotopes 9, 123-24 (1960).

The temperature of the samples during irradiation was determined by placing a copper-constantan thermocouple in the center of a sample contained in the pyrex tube and automatically recording the temperature as a function of time. The temperature was found to rise uniformly from room temperature (approximately 70° F) to 100° F in a period of 15 to 20 minutes. The temperature remained constant at 100° F during the remainder of the irradiation.

B. Electron Microscopy

Unirradiated and irradiated samples of both kaolins were examined qualitatively by electron microscopy. The particles were replicated by depositing a thin film of platinum and carbon on them, in a vacuum chamber, from an arc. The particles were removed from the film by dissolution with hydrofluoric acid, and micrographs were obtained from these replicas with an electron microscope. These replicas show much greater surface detail when observed with the electron microscope than when the particles are observed directly. The field of view of the electron microscope was not large enough to contain a sufficient number of particles, the size of those found in the kaolin samples, to provide a very representative estimate of the particle-size distribution. The Washington County kaolin did appear to contain more small, plate-like particles after irradiation although a large number of stacks remained. The appearance of the micrographs of the Twiggs County kaolin was quite similar before and after irradiation. Typical micrographs of these two kaolins are shown in Figures 3 and 4.

Some unusual physical surface appearance was observed in a number of the micrographs. In Figures 5 and 6, for example, an unusual etched appearance can be seen on the edges of the kaolinite crystallites composing

the large stacks. A close examination of these micrographs reveals ridges and pits--some of which appear to be almost hemispherical--on the crystallite edges. Figures 7, 8, and 9 are micrographs of what appear to be kaolinite stacks with areas of vitrified material on their surfaces. The stack shown in Figure 9 contains areas suggestive of the early stages of mullite formation; a phase transition that normally occurs at about 960° C.

C. Particle Size Measurement

Size analysis methods have characteristically relied upon some measure of particle "diameter" as a criterion of particle size. Many methods have been developed and devised based on a variety of principles and depending upon different properties of the particle for their operation. Consequently, there is much confusion when one speaks of particle "diameters" as measured by different sizing methods. For instance, a "diameter" measured by a sedimentation technique depends upon the drag coefficient of the particle as it falls through a fluid; whereas the same "diameter," as measured microscopically, depends upon the judgment of the observer as to what its characteristic dimension is. The Coulter counter is one of a new series of "sensing zone" devices that have recently become available for particle size measurements. This device determines the number and size of particles suspended in an electrically conductive liquid. The suspension flows through a small aperture having an immersed electrode on either side, with a particle concentration such that the particles pass through the aperture substantially one at a time. Each particle passage displaces electrolyte within the aperture, momentarily changing the resistance 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 of a particle as it passes through an electric sensing zone. In the case of kaolin plates, which are flat and thin, a volume measure is much more meaningful than some fictitious diameter; therefore, the Coulter counter was selected as the best measuring device for this application.

The task of evaluating the effect of irradiation by particle-size-measuring techniques led to a number of difficult problems. During the first months of this project the lower limit of the Coulter counter was fixed at approximately 0.8-micron equivalent spherical diameter. However, a very few months before termination of the project the lower limit of the Coulter counter was lowered to approximately 0.2-micron equivalent spherical diameter by the production of smaller diameter aperture tubes. Two of the newer aperture tubes with orifice diameters of 20 and 10 microns were obtained on loan from Coulter Industrial Sales, Chicago, Illionis, and it was possible to investigate more completely the small end of the size distribution.

Attendant with the lowering of the limit of measurement of the Coulter counter, came the further problem of accurately measuring small particles in the presence of much larger particles. Large particles produce large voltage pulses in the amplifier portion of the instrument which tend to obscure the presence of very small particles. This ability of large particles to obscure changes in the smaller size ranges resulted in negligible observable differences in the respective overall size distributions of the two kaolins after exposure to high-energy radiation.

The small end of the overall size distribution was investigated by removing the large particles 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. Fractionated samples of the Twiggs County kaolin, scaled to a common weight basis, exhibited a progressive increase in concentration of very small particles with increasing radiation dosage.

It was further observed during the analysis of the very small particles that there was a pronounced tendency for the particles to flocculate and cause a net change during the course of a size determination. This tendency indicated the presence of fewer small particles as time elapsed. This difficulty was alleviated by the use of tetrasodium pyrophosphate in the electrolyte medium to act as a suitable electrolyte for conduction of current between the electrodes of the Coulter counter and to provide a further synergistic benefit by being an effective dispersant for kaolin. An ultrasonic generator was used to assure proper initial dispersion of all samples whose size distributions were measured with the Coulter counter.

The overall size distributions of the two samples of kaolin used to date are presented in Figure 10. Figure 11 is a series of distributions of the smaller particles present in samples of kaolin from Twiggs County, Georgia, which had received varying doses of radiation. As can be seen from Figure 11, an increase of approximately 300 per cent was observed for the number of particles with volumes less than 10 cubic microns after a dose of 1×10^{22} electron-volts per gram of gamma-radiation. No reduction in particle-size was observed for the Washington County kaolin even after

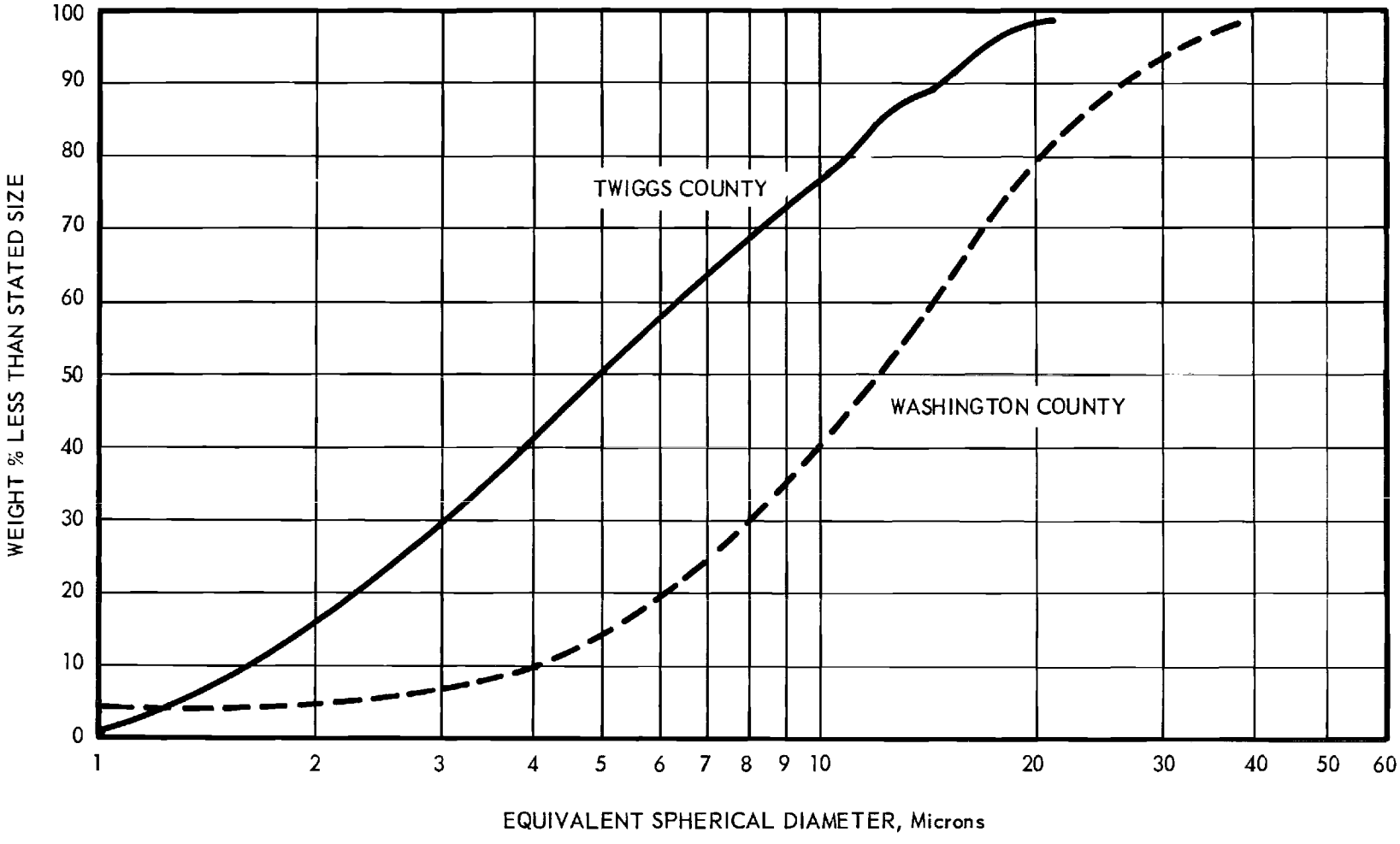

Figure 10. Particle Size Distributions of the Washington County Twiggs County Kaolins.

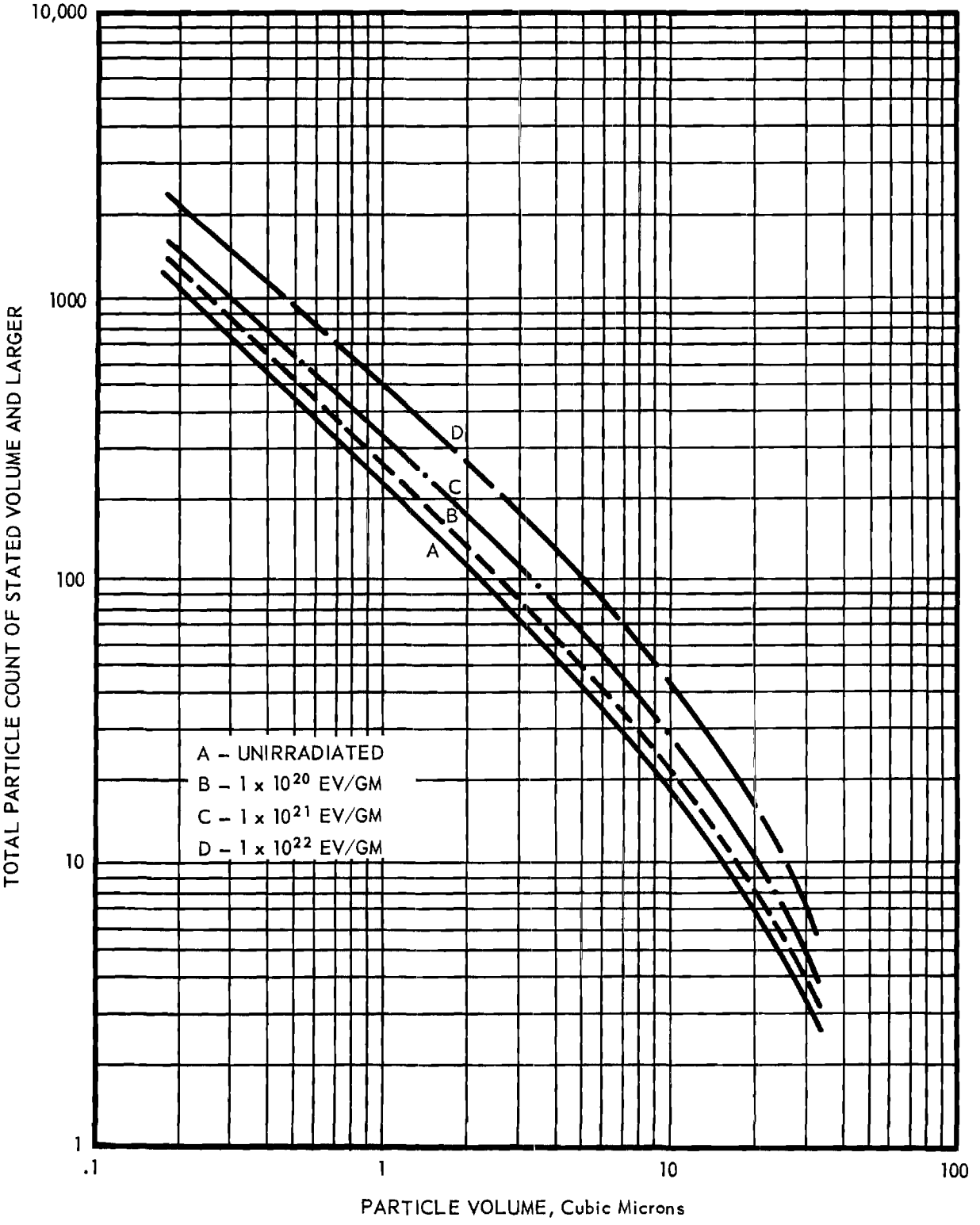

Figure 11. Distribution of Particles with Volumes of $10\mu^3$ or Less for Samples of Twiggs County Kaolin Before and After Irradiation.

1×10^{22} electron-volts per gram of gamma-radiation, and fractionation to isolate the smaller particles.

D. Surface Area Measurements

Specific surface areas were measured for samples of both kaolins used in these studies as a function of radiation dose. The Brunauer, Emmett and Teller[7] method of low-temperature, nitrogen-gas adsorption was used in the determinations. The cross-sectional area of the nitrogen molecule was taken as 15.8 square angstroms.[8] These results are presented in Table I.

TABLE I

SPECIFIC SURFACE AREA OF KAOLIN AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area: Washington County Kaolin (M^2/Gm)	Specific Surface Area: Twiggs County Kaolin (M^2/Gm)
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

[7] S. Brunauer, P. H. Emmett, and E. Teller, "The Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc. 60, 209-19 (1938).

[8] A. S. Joy, "The Determination of Specific Surface by Gas Adsorption," Vacuum 3, 254-78 (1953).

The data contained in Table I have been plotted in Figure 12 to illustrate the trend of specific surface area with increasing radiation dose.

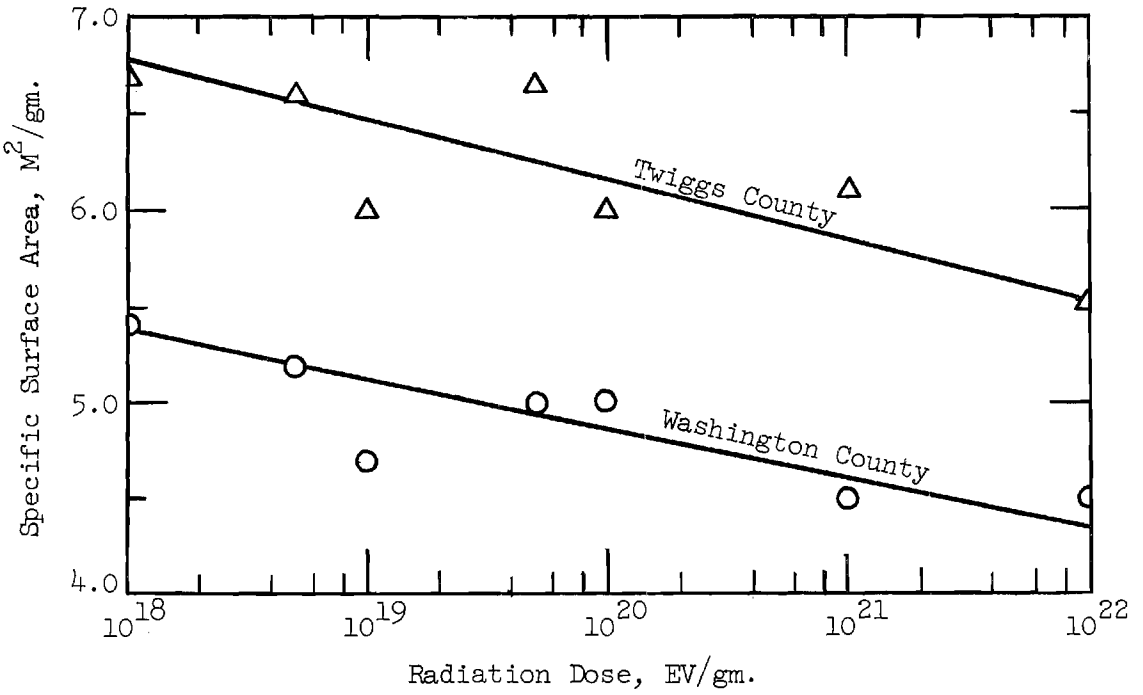

Figure 12. Specific Surface Area of Kaolin as a Function of Radiation Dose.

The trend is unquestionably a decreasing one in spite of the observed scatter in the data. A decrease of approximately 25 per cent between the unirradiated material and the samples that had received 1×10^{22} electron-volts per gram was found for both kaolins. From repeated measurements on several samples the reproducibility of the specific surface area measurements was found to be ± 3 per cent. Since the specific surface area of the kaolins decreased with increasing radiation dose, complete adsorption isotherms were obtained for several samples to determine

if the number of pores and capillary cracks were changing also. When a significant number of cracks and crevices are present, as they undoubtedly are in the kaolin stacks, the surface area of the material will appear to be larger than it actually is. Multilayer adsorption takes place in these capillaries while monolayer adsorption is taking place on the surface, and when the surface area is evaluated on the basis of monolayer adsorption, the capillaries make a disproportionate contribution. If these sites for capillary condensation are then destroyed and the surface area redetermined, a lower value will be obtained for the specific surface area. The difference in the number of cracks and crevices for two samples can be evaluated by determining total adsorption isotherms for the samples. If adsorption is taking place in a limited space such as a capillary crack rather than a free surface, only a finite number of layers can be adsorbed at saturation. The results of these measurements, however, were inconclusive. The deviations in experimental results were of the same order of magnitude as any differences that were observed. This technique is actually better suited to highly porous materials such as porous silicas and carbon blacks. Very careful determinations of pore volume by the adsorption and subsequent desorption of nitrogen could possibly measure any change in the number or size of the capillary cracks, but time limitations would not permit measurements of this type.

E. Crystallinity Studies

All samples of both the Washington County and Twiggs County kaolin that had been subjected to gamma-radiation were examined by X-ray diffraction. These studies were made to determine what structural disorder had been produced in the kaolinite by the gamma-radiation. The customary

method of evaluating differences in the degree of crystal perfection of kaolinite is to make qualitative rankings by inspection of diffractometer traces; the bases for rankings being loss of resolution for certain diffraction maxima and the absence of certain diffraction maxima. From this qualitative point of view, the samples of kaolin that had been irradiated were less well crystallized than the unirradiated kaolin. Two typical X-ray diffractometer traces are presented in Figure 13 for a sample of unirradiated kaolin and a sample that had received 1.0×10^{22} electron-volts per gram of gamma-radiation. From these traces the loss of resolution of such diffraction maxima as the (020), $(1\bar{1}0)$ and $(11\bar{1})$(areas enclosed by the dotted lines) can readily be seen; the intensities and relative intensities of the (001) and (002) maxima are changed; and such maxima as the (111), (004), (203), and three minor maxima beyond (060) have disappeared almost completely for the irradiated material. These particular traces were made with CuK_{α} radiation, at one degree (2θ) per minute, a chart speed of 15 inches per hour, a time constant of 4 seconds, a scale factor of 8, at 40 kv and 20 ma using a slit width of 6 mils with a Geiger counter.

The above method of qualitative rankings was not adequate for establishing degree of change in crystallinity as a function of radiation dose. Therefore, the recently developed method of Johns and Murray[9] was used to obtain an empirical "index of crystallinity." This method employs a ratio of the intensities of two reflections, one which is affected by $nb_o/3$ translations of kaolinite layers (021), and one which

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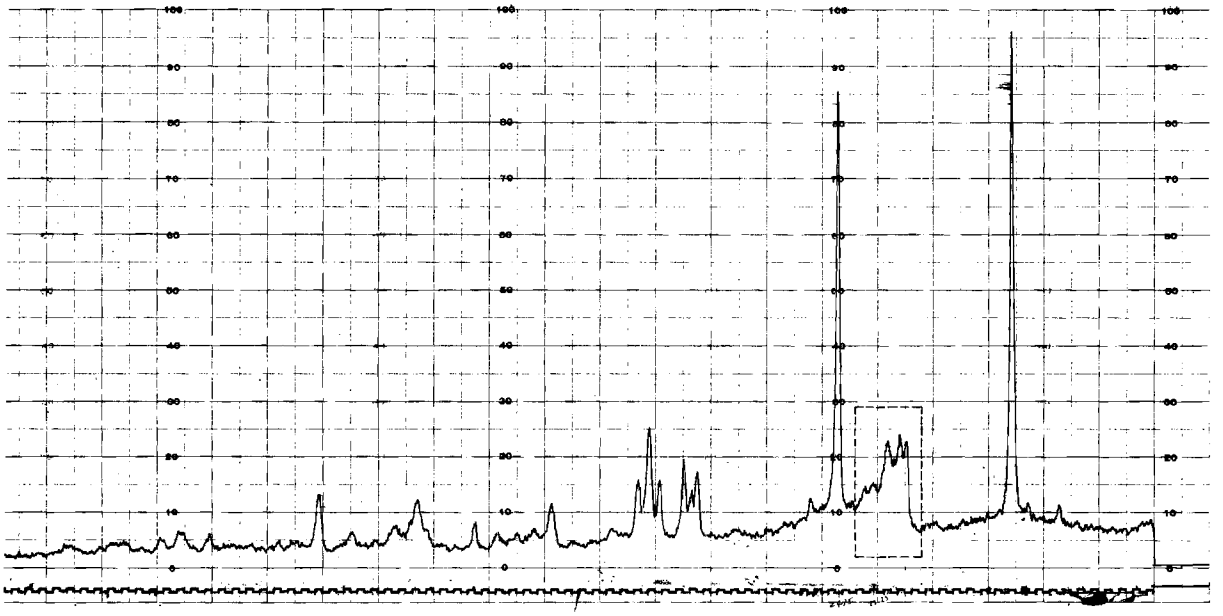
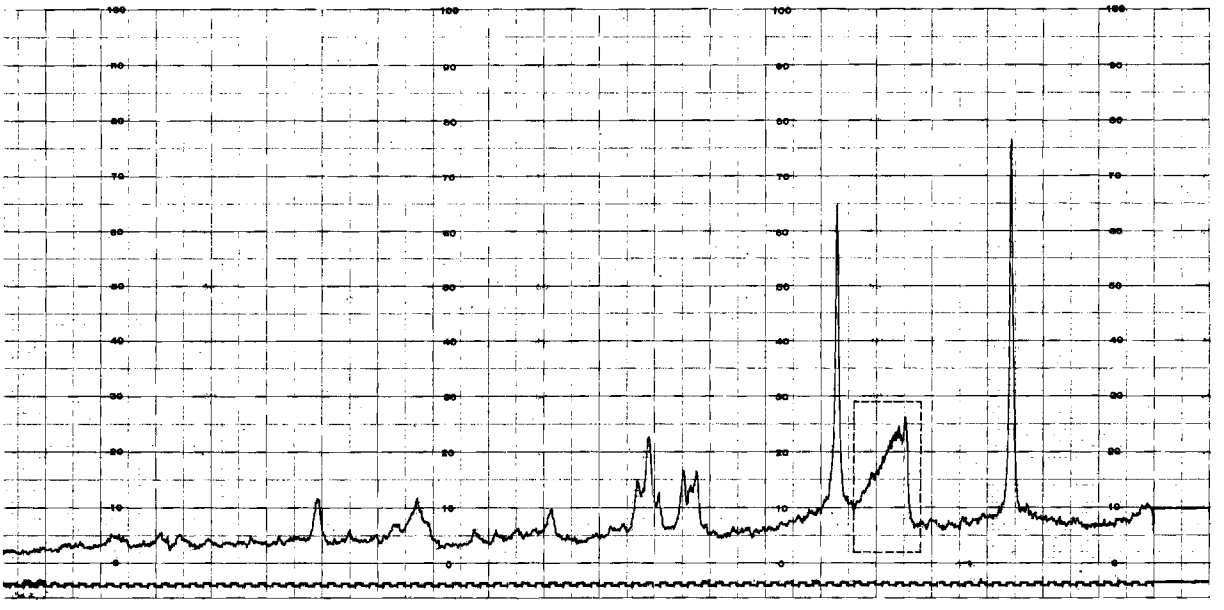
[9] W. D. Johns and H. H. Murray, "An Empirical Index for Kaolinite Crystallinity," Paper presented at the 1959 meeting of the Mineralogical Society of America. To be published in Am. Mineral.



A. UNIRRADIATED KAOLIN



B. IRRADIATED KAOLIN
1×10^{22} EV/GM

Figure 13. Typical X-Ray Diffractometer Traces for Washington County Kaolin.

is not (060). For this reason a more descriptive term for this ratio would seem to be an "index of $nb_o/3$ crystallinity." The ratio has been found to vary from 0 to approximately 1, with 1 being the best crystallized material and 0 the poorest. The first attempts at obtaining traces of these maxima met with very limited success. The Washington County kaolin had a relatively low crystallinity and a large particle size that promoted some sample orientation. As a result, the $(02\bar{1})$ maximum had a very low intensity and a very strong CuK_β reflection from the (002) crystallographic plane appeared very near the $(02\bar{1})$ maximum. After trying a number of techniques, this difficulty was finally overcome by the use of a high intensity X-ray tube. This tube, operated at 40 kv and 40 ma, produced reflections of sufficient intensity that a beta filter could be used to significantly reduce the intensity of the CuK_β reflection. The use of a proportional counter and a pulse height analyzer in conjunction with the beta filler permitted very good resolution of the $(02\bar{1})$ maximum. The samples of Twiggs County kaolin, while not subject to these difficulties, were also analyzed with this same arrangement.

The integrated intensity of the (060) reflection could be readily evaluated since no other reflections are located immediately adjacent to it. This, however, was not the case for the $(02\bar{1})$ reflection since portions of this reflection probably overlap into the region in which the (002) reflection occurs on one side and into the region in which the beta-reflection of the (002) reflection occurs on the other side. Therefore, only the area over a fixed angular region was measured (2θ equal to 22.75° - 23.50°), and the relative change in this area taken as being proportional

to the change in the total area. The crystallinity indices calculated from these data are presented in Figures 14 and 15. The indices of $nb_o/3$ crystallinity are primarily a measure of the amount of disorder produced in the arrangement of aluminum atoms in successive layers ($nb_o/3$ translations). The significance of the maxima observed in the curves of Figures 14 and 15 is not readily apparent. Strictly in terms of the index of $nb_o/3$ crystallinity as devised, these maxima imply that the arrangement of aluminum atoms in the kaolinite lattice becomes more ordered with radiation up to a dose of about 5×10^{18} and then becomes progressively less ordered with increasing radiation dose. However, from the standpoint of what is known concerning radiation-damage processes in general, and an intuitive feeling for the entropy changes demanded by such an event, the possibility of a more orderly arrangement of the aluminum atom seems most unlikely. One factor which must be considered is that not only was the intensity of the $(02\bar{1})$ reflection changing, but the intensity of the (060) was also changing. That is to say, not only were the aluminum atoms being displaced, giving rise to apparent $nb_o/3$ translations, 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 the recombination rates, except that the intensity of the $(02\bar{1})$ reflection underwent a much greater reduction with 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 impossible at the present time. The fact that an overall decrease in the index of $nb_o/3$ crystallinity with radiation dose was observed, coupled with the fact that the $(02\bar{1})$ maximum always exhibited an intensity decrease as the

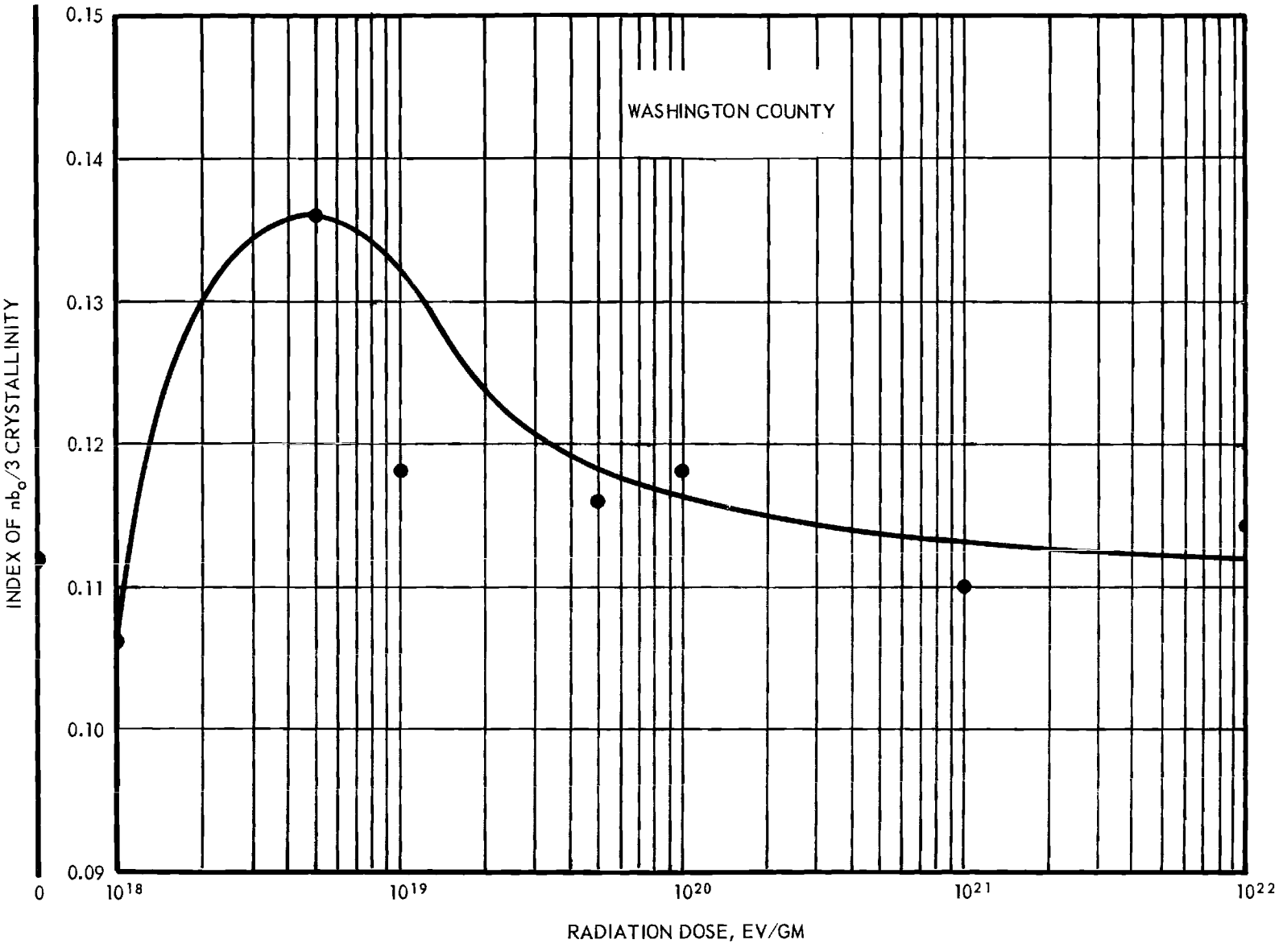


Figure 14. Index of $nb_o/3$ Crystallinity as a Function of Radiation Dose for Washington County Kaolin.

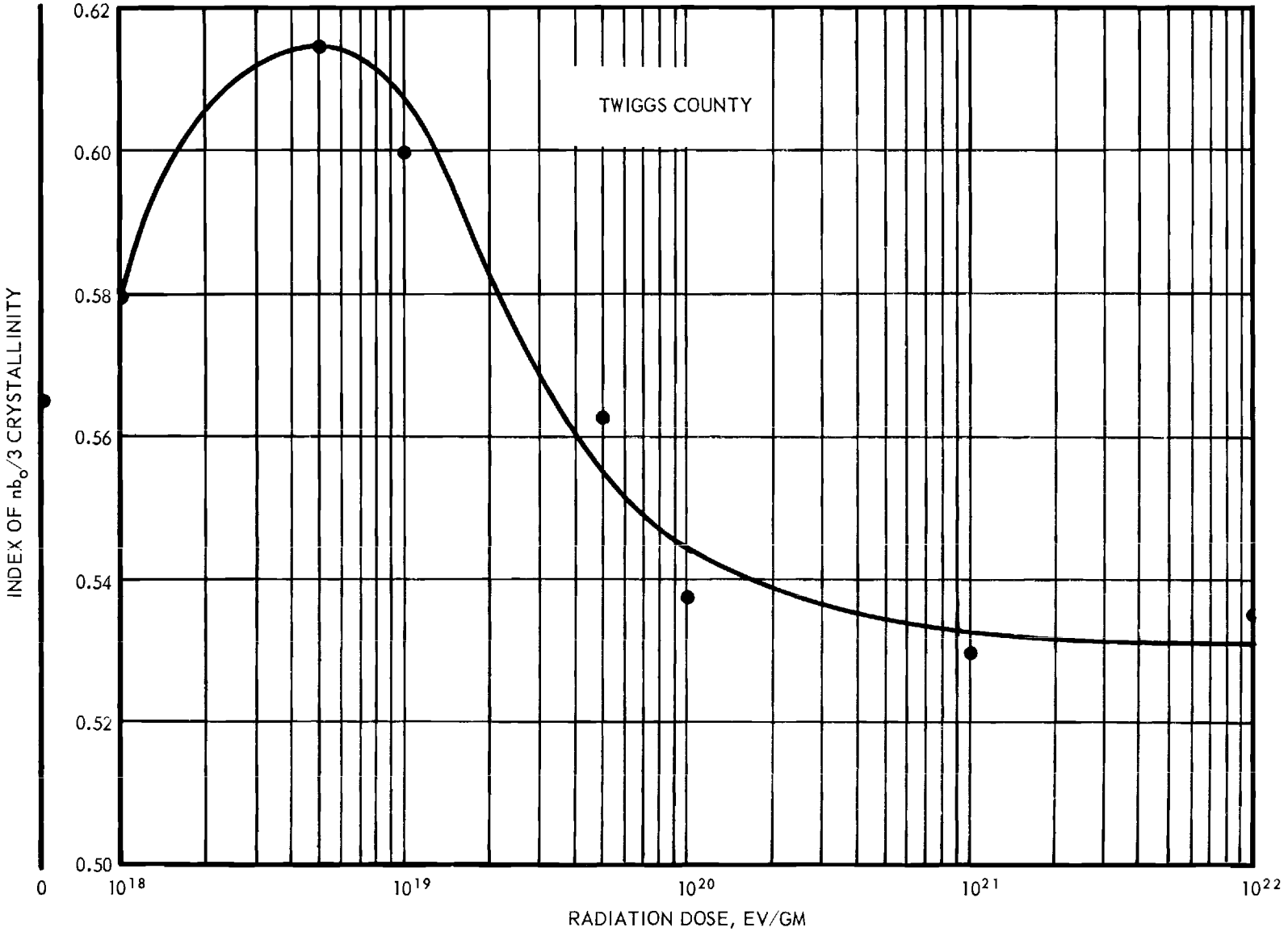


Figure 15. Index of $nb_o/3$ Crystallinity as a Function of Radiation Dose for Twiggs County Kaolin.

radiation dose was increased, does, however, indicate that disordering of the aluminum atom was obtained.

In a radiation-damaged material, localized, static, lattice defects are produced which are usually considered to be isolated interstitial lattice 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. Zachriasen,[10] Huang,[11] and Borie[12] have been significant contributors to a general theory of the X-ray effects to be expected from localized static lattice defects in crystals. These treatments postulate that displacement of atoms from their normal lattice sites leads to a reduction in the integrated intensities of Bragg maxima by a factor $\exp[-2M']$ and to diffuse scattering. It can be shown in a manner exactly analogous to that for the well known temperature factor of X-ray scattering for crystals that

$$\exp[-2M'] = \exp[16\pi^2 \bar{u}_d^2 \operatorname{Sin}^2 \theta/\lambda^2] \qquad (1)$$

where $\bar{u}_d^2$ is the mean square of the average atomic displacement in one dimension, θ is the Bragg angle, and λ is the wave length of the X-radiation. Therefore, the ratio of the peak area of a radiation-damaged sample to peak area of an undamaged sample for the same reflection should give

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[10] W. H. Zachriasen, Theory of X-Ray Diffraction in Crystals, (New York: John Wiley and Sons, 1947).

[11] K. Huang, "X-Ray Reflections from Dilute Solutions," Proc. Royal Soc. London A 190, 102-17 (1947).

[12] B. Borie, "X-Ray Diffraction Effects of Atomic Size in Alloys," Acta. Cryst. 10, 89-96 (1957).

$$I_o/I_d = \exp\left[(-2\Delta M) - 16\pi^2 \bar{u}_d^2 \Delta(\mathrm{Sin}^2\theta/\lambda^2)\right] \quad (2)$$

where the term $(-2\Delta M)$ represents the difference in the Debye factors for ordered and disordered samples. This particular analysis, however, requires the use of absolute intensities. A more convenient analysis is to compare the ratios of intensities for different orders of the same reflection for the undamaged material and the irradiated material. The integrated intensities of different orders of the same reflection are reduced in the same manner as outlined in the above analysis

$$\left[\frac{I_{hkl}}{I_{n(hkl)}}\right]_d = \left[\frac{I_{hkl}}{I_{n(hkl)}}\right]_o \cdot \exp\left[-16\pi^2 \bar{u}_d^2 \Delta(\mathrm{Sin}\,\theta/\lambda^2)\right] \quad (3)$$

where the subscripts d and o refer to the irradiated and unirradiated material respectively, and n is some integer.

Equation 3 was used with the integrated intensities of the (001) and (002) reflections from the X-ray diffraction traces to obtain a root mean square of the average atomic displacement along the c axis for the samples of irradiated kaolin. These data are presented in Figure 16. Since the root mean square of the average atomic displacement is dependent upon the number of displacements, these values are a measure of the number of defects present in the lattice as a function of the absorbed radiation-dose. In this analysis the difference in the Debye factors was assumed negligible. This is not exactly true since the elastic constants were no doubt altered by the radiation damage. However, this should amount to only a very few per cent at most. It should be noted that the above theory predicts that there should be no broadening of the

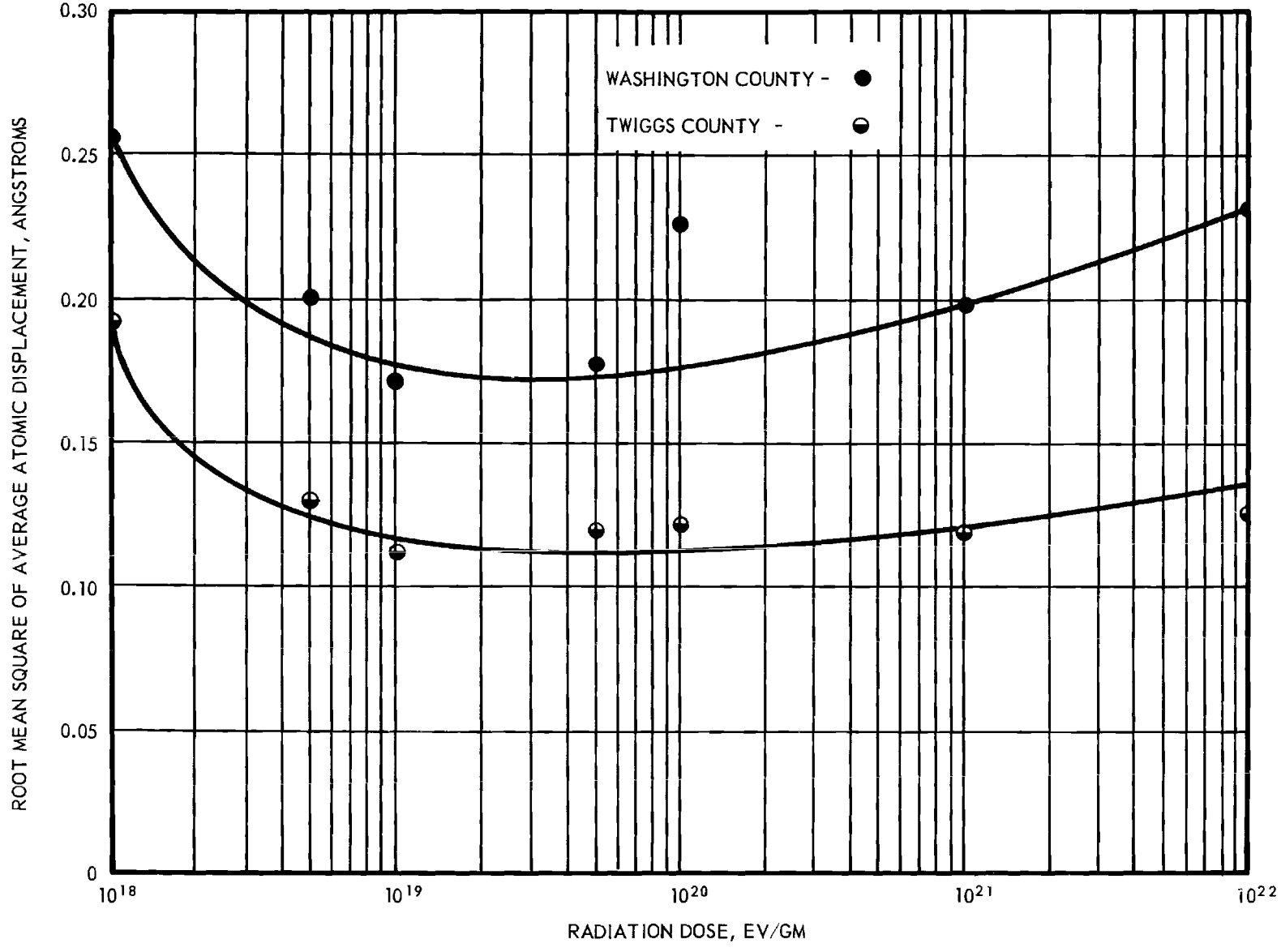

Figure 16. Root Mean Square of the Average Atomic Displacement as a Function of Radiation Dose.

diffraction peaks, and none was observed.

F. Differential Thermal Analysis

Irradiated and unirradiated samples of both the Washington County and Twiggs County kaolin were subjected to differential thermal analysis. This technique involves comparison of the changes that occur in a clay sample with those of a reference material, as a function of temperature. A few grams (2 or 3) of the kaolin being tested are compressed into a pellet. This pellet, along with a pellet of the reference material, is heated at a constant rate in a suitable furnace to some arbitrary temperature, and the difference in temperature between the two pellets is recorded. The temperature differences observed are indications of endothermic and exothermic processes that are taking place in the kaolin. The magnitude of these differences and the range at which they occur are determined by the chemical composition and the physical condition of the kaolin. The reference material is usually calcined alumina. However, in this work a calcined pellet of the unirradiated kaolin was used as the standard. Figure 17 shows a typical plot of the data obtained from a differential thermal analysis. The abscissa is the temperature to which the pellets have been heated, with 1000° C being the maximum for this work, and the ordinate is the millivolt difference between the Pt - Pt10Rh thermocouples placed beneath each pellet. The first deviation along the abscissa, which is negative--indicating an endothermic process, extending from a temperature of approximately 60° C to a temperature of approximately 375° C--is caused by the driving off of absorbed water. The next deviation, also an endothermic process, extending from a temperature of about 475° to 850° C, is the result of driving off chemically bound water from the

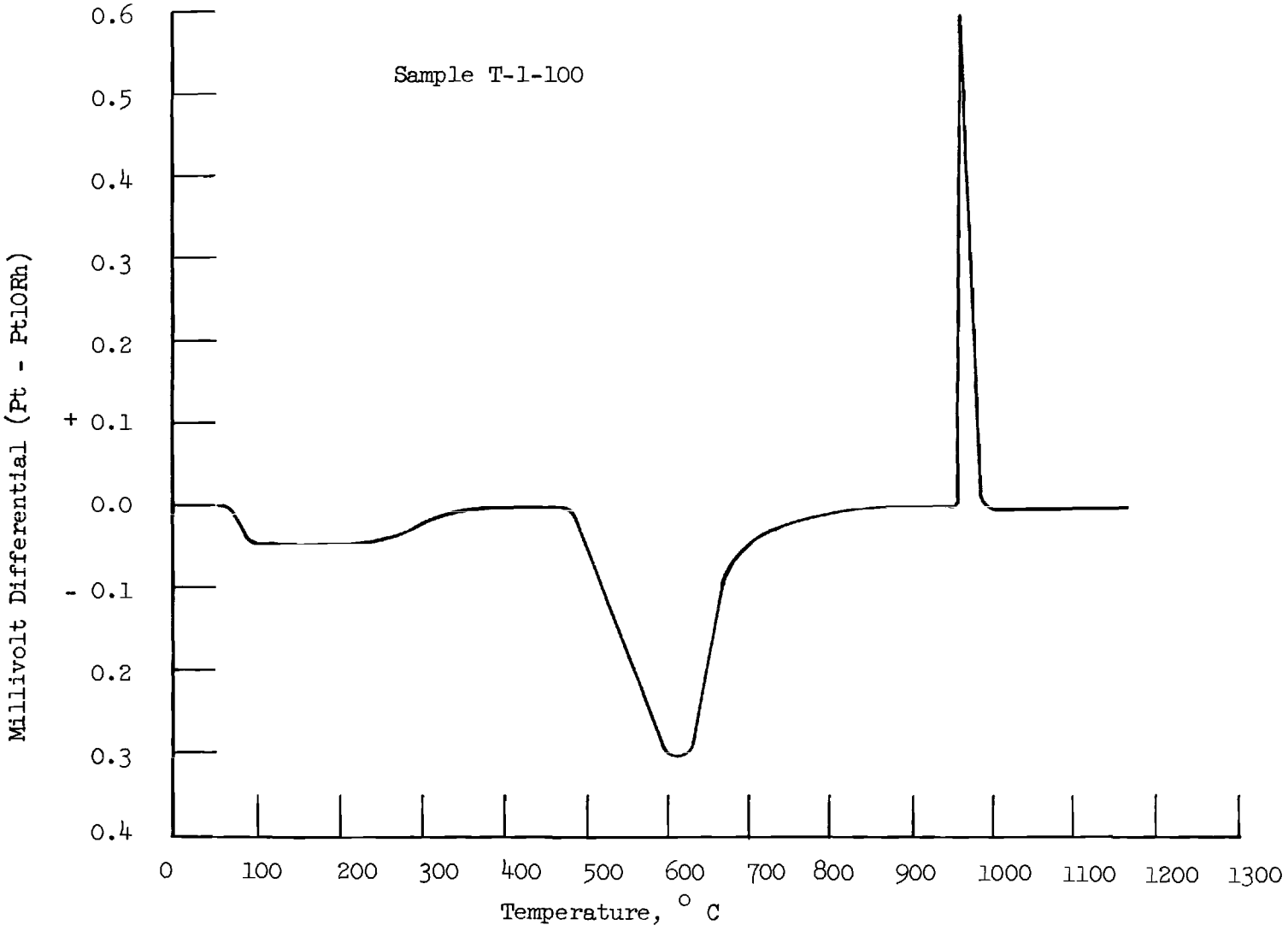

Figure 17. Typical Plot of Differential Thermal Analysis Data.

crystal lattice. This process, which is actually calcination of the kaolin, has a maximum at 625° C. The final deviation, which is an exothermic process, is the result of a phase change that takes place at about 965° C. These analyses were performed in an attempt to measure the amount of stored energy due to dislocations in the crystal lattices, and as a corollary method of determining the amount of structural disorder. No difference was found between the data obtained from the irradiated kaolin and that obtained with unirradiated kaolin. This was probably due to the fact that the apparatus used was not sensitive enough to detect the difference in the temperature of the exothermic phase transition which should have resulted from the crystalline disorder detected in the X-ray diffraction work. Also, the integrated area of the exothermic phase transition peak should have varied with radiation dose due to the extra energy stored in the lattice by the atomic displacements. However, when these analyses were performed, the fact that this effect should have been present was not recognized, and no particular attempt was made to keep the upper portion of this peak on the recorder scale. Unfortunately, time limitations would not permit these analyses to be repeated. Other investigators have shown, however, that the temperature at which this transition phase occurs is altered by the effects of gamma-radiation on kaolinite.[13]

G. Infrared Absorption Measurements

The infrared absorption spectra for samples of the Washington County kaolin that had received various doses of gamma-radiation were carefully examined for any changes in hydroxyl absorption. In these studies

[13] C. A. Head, "Effect of Radiation on Formation of Mullite in Kaolinite," Masters Thesis, School of Ceramic Engineering, Georgia Institute of Technology (1961).

0.5-inch-diameter wafers or potassium bromide containing 1.0 per cent by weight of kaolin were prepared by pressing 0.01 gram of the mixture at 12.5 tons per square inch in an appropriate press. These wafers were examined with a Perkin-Elmer Model 21 spectrophotometer, Perkin-Elmer Corporation, Norwalk, Connecticut, using a rock salt optical system. The unbonded OH in kaolinite produces a strong absorption maximum at 2.70 microns. Other OH absorption maxima appearing in the kaolinite spectrum are: at 2.75 microns, a moderate shoulder from 2.87 to 2.92 microns, and a fairly strong maximum at 6.15 microns.[14,15,16] The adsorption maximum at 2.75 microns is apparently associated with long hydrogen bonds. The absorption maximum at 6.15 microns appears to be a result of water adsorbed on the surface of the kaolin. Although this maximum is always found in the spectrum when the kaolin samples are handled in a normal manner, it is not observed when rigorous techniques are employed for drying and excluding the readsorption of water. The shoulder observed from 2.87 to 2.92 microns appears also to be associated with adsorbed water. As semi-quantitative measures of the relative amounts of bonded and unbonded hydroxyl groups associated with the kaolinite, a ratio, R_1, of the relative intensities of the maximum at 2.70 microns to the maximum at 2.75 microns and a ratio, R_2, of the relative intensitites of the maximum at 2.70 microns to the maximum at 6.15 microns to the maximum at 6.15 microns, were calculated. The ratio, R_1,

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[14] J. M. Hunt, M. P. Wishero, and L. C. Bonham, "Infrared Absorption Spectra of Minerals and Other Inorganic Compounds," Analytical Chemistry 22, 1478-97 (1950).

[15] J. P. Lyon and W. M. Tuddenham, "Infrared Determination of the Kaolin Group Minerals," Nature 185, 835-36 (1960).

[16] W. D. Keller and E. E. Pickett, "The Adsorption of Infra-red Radiation by Clay Minerals," Amer. J. Sci. 248, 264-73 (1950).

is therefore a measure of the relative amounts of unbonded OH groups in the kaolinite to the bonded OH groups. The ratio R_2 is a measure of the relative amounts of adsorbed water on the kaolinite. The fact that the intensity of the absorption maximum at 6.15 microns (apparently representing adsorbed water) was referred to the intensity of the absorption maximum at 2.70 microns has no significance other than serving to eliminate any effect of concentration differences between pellets. The values obtained for R_1 and R_2 are presented in Table II. The ratio R_1 shows a slight increase with irradiation dose indicating the possibility of an increase of the amounts of unbonded to bonded OH groups in the kaolinite. However, the change is relatively small and may not be significant. This could be established only with further investigation with a complete error analysis. The ratio R_2 shows a very significant increase with irradiation dose that strongly indicates exposure to gamma-radiation decreases the affinity of the kaolinite for adsorbing water vapor. A significant change was noted for the shoulder of the adsorption spectra extending from 2.82 to 2.92 microns. The width of this shoulder decreased significantly with increasing radiation dose, disappearing almost entirely for the higher radiation doses.

TABLE II

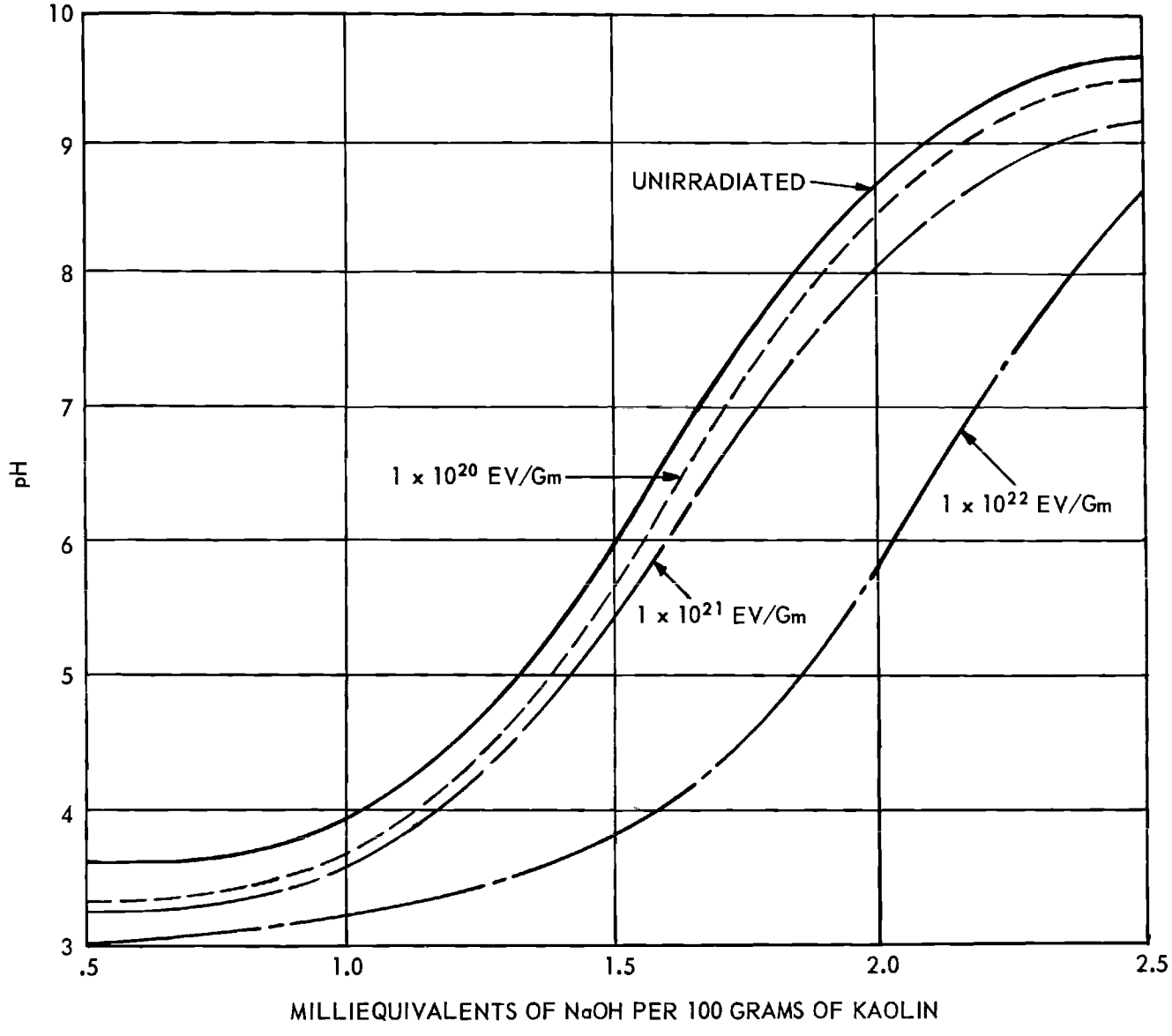
VARIATION OF RATIOS OF OH ABSORPTION INTENSITIES WITH RADIATION DOSE FOR WASHINGTON COUNTY KAOLIN

Dose	R_1	R_2
Unirradiated	1.150	6.3
1.0×10^{20}	1.17_7	9.2
1.0×10^{21}	1.18_2	8.9
1.0×10^{22}	1.18_2	11.4

H. Cation-Exchange Measurements

The cation-exchange capacities of the clays used in these studies have been measured as a function of radiation dose. This measurement, while not difficult in technique is quite sensitive, and particular care must be exercised to insure that the various samples for a series of determinations receive identical treatment. Five-gram quantities of each sample from a series of irradiations of kaolin were dried simultaneously for 3 hours in an oven at 110° C, treated with 50 ml of dilute hydrochloric acid for 2 hours, and then filtered and washed with distilled water. These "acid" clays were then dried to constant weight in an oven at 110° C, and a 20-per-cent-by-weight suspension in distilled water was prepared. These clay suspensions were then titrated with a 0.1023N 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 pH determinations was made with a Beckman Model 96 Zeromatic pH meter, Beckman Instruments, Inc., Fullerton, California. These data are presented in Figures 18 and 19.

The behavior of these kaolins appears to be completely anomalous. The cation-exchange capacity of the Washington County kaolin increases with increasing radiation dose while that of the Twiggs County kaolin decreases. However, an explanation may lie in the treatment the two kaolins received before irradiation. The Washington County kaolin was fractionated according to particle size and had been treated with a deflocculating agent such as tetrasodium pyrophosphate. Some cation-exchange with sodium no doubt occurred at this time. This view is supported by the fact that the cation-exchange capacities of the two kaolins before irradiation were almost identical while the X-ray diffraction results showed a significant difference in the crystallinity



18. Titration Curves for Hydrogen-Kaolinite Prepared from Washington County Kaolin.

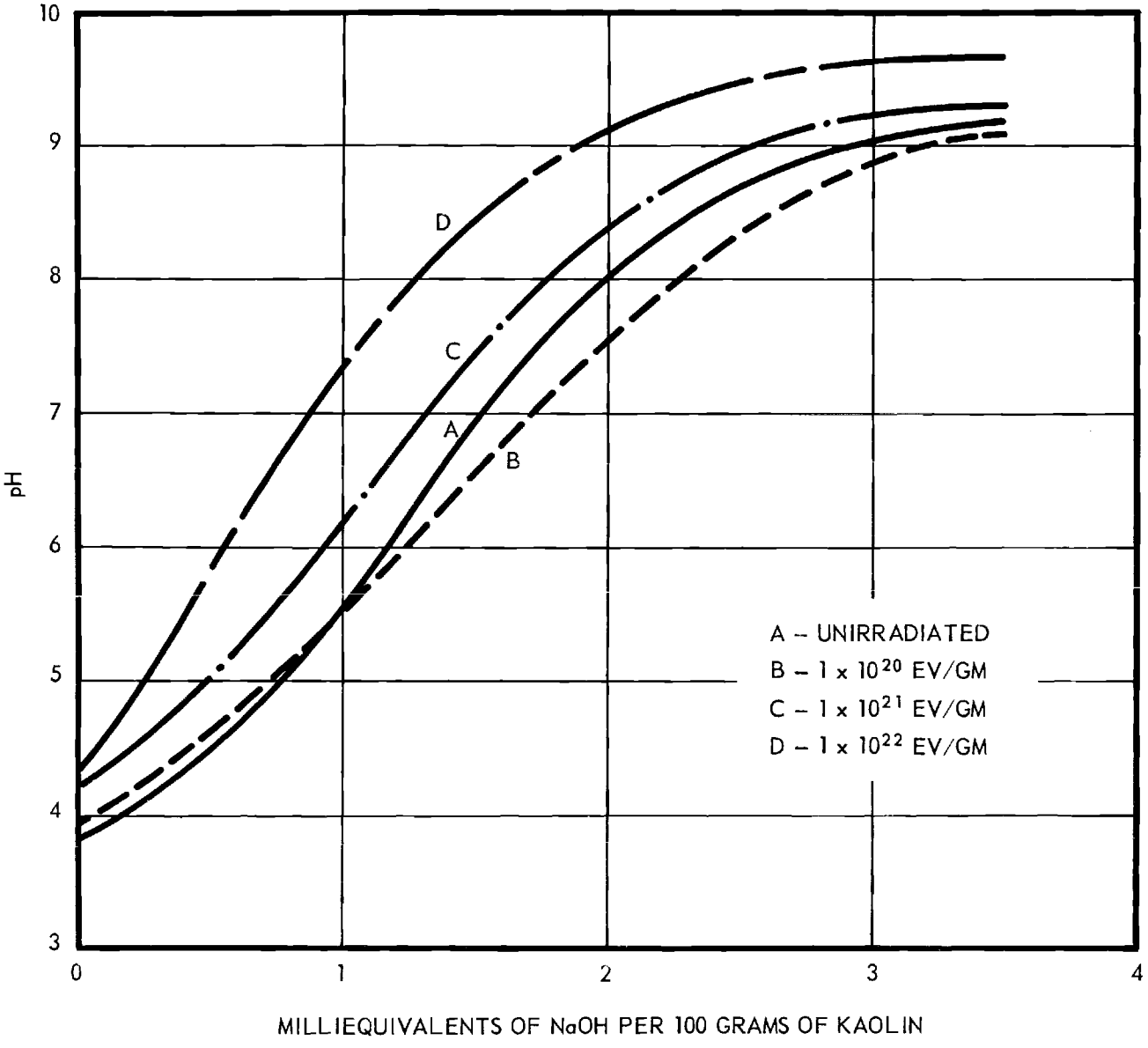


Figure 19. Titration Curves for Hydrogen-Kaolinite Prepared from Twiggs County Kaolin.

of the two unirradiated clays. Murray and Lyons[17] have shown that the cation-exchange capacity of a poorly crystallized kaolin is as much as four times that of a well crystallized kaolin. Therefore, the cation-exchange capacity of the Washington County kaolin which was very poorly crystallized should have been much greater than the Twiggs County kaolin. The fact that it was not is strong evidence that cation-exchange had taken place with the deflocculating agent.

I. Viscosity Determinations

Viscosity determinations were made on an unirradiated sample and two irradiated samples of Washington County kaolin. A slurry containing 55 per cent by weight of kaolin was prepared with 0.75 per cent solution of tetrasodium pyrophospate. The kaolin and tetrasodium pyrophosphate solution were blended in a Waring Blendor and agitated for 5 minutes. The temperature of the slurry was adjusted to 81° F and the apparent viscosity determined with a Brookfield viscometer, model LVF, at varying rates of shear. The data obtained are presented in Table III. These data show an increase in slurry viscosity with increasing radiation dose.

J. Reflectance Measurements

Light reflectance measurements were made on samples of the Washington County kaolin that had received various doses of gamma-radiation. The results of these measurements are presented in Table IV. The tests were made with a General Electric recording spectrophotometer. Approximately 10 grams of kaolin were pressed into a pellet 1-1/4 inches in diameter under a pressure of 60 pounds per square inch. The amount of incident light

[17] H. H. Murray and S. C. Lyons, "Further Correlations of Kaolinite Crystallinity with Chemical and Physical Properties," Eighth National Conference on Clays and Clay Minerals - Pergamon Press, 11-17 (1960).

TABLE III

APPARENT VISCOSITIES OF SLURRIES OF WASHINGTON COUNTY KAOLIN AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Spindle (Number)	Rate of Rotation (RPM)	Apparent Viscosity (Cps)
Unirradiated kaolin	2	12	40.0
	2	30	68.0
	2	60	89.5
1.0×10^{20}	2	12	80.0
	2	30	85.0
	2	60	100
1.0×10^{22}	2	12	113
	2	30	100
	2	60	104

TABLE IV

REFLECTANCE MEASUREMENTS FOR KAOLIN SAMPLES WITH VARIOUS TOTAL ENERGY DOSES

Wave Length (Millimicrons)	Per Cent Reflectance		
	Unirradiated	1×10^{21} EV/Gm	1×10^{22} EV/Gm
380	66.0	65.0	65.0
400	69.7	68.7	68.5
450	77.0	76.0	76.0
500	80.5	79.8	80.0
550	84.0	83.0	83.2
600	86.2	85.2	85.3
650	88.0	86.8	86.8
700	89.5	88.5	88.2

reflected from the surface between wave lengths of 380 and 700 millimicrons was measured relative to a similar size pellet of magnesium oxide. No detectable difference was observed in the reflectance as a function of radiation dose.

K. Grinding Studies

Samples of the Washington County kaolin, both unirradiated and irradiated, were subjected to 50 hours of wet-grinding. A porcelain mill 9 inches in diameter was used for this study. The mill was charged with 100 grams of sample, 3 kilograms of 3/4-inch diameter, 3/4 inch-length porcelain cylinders, and 400 grams of water. The milling speed was 120 revolutions per minute. Specific surface areas were determined for these samples after they had been ground. The technique used for these measurements was the same as outlined earlier in this report, and the results are contained in Table V.

A significant increase in specific surface areas was obtained for the irradiated kaolins. Since the grinding conditions were identical for these samples, the increase in specific surface area is a good indication that the kaolin is more easily ground with increasing radiation dose. Wet grinding, as opposed to dry grinding, produces more shearing forces than crushing forces. Therefore, the fine particles produced by wet grinding are predominantly plate-like as a result of shearing forces exerted along the cleavage planes of the crystallites comprising a stack.

TABLE V

SPECIFIC SURFACE AREAS OF WET-GROUND KAOLIN
AS A FUNCTION OF RADIATION DOSE

Dose (EV/Gm)	Specific Surface Area (M^2/Gm)
Unirradiated	26.7
1.0×10^{20}	27.8
1.0×10^{21}	28.8
1.0×10^{22}	31.1

III. DISCUSSION AND CONCLUSIONS

There are three possible mechanisms for the interaction of gamma-rays with matter: the photoelectric effect, the Compton effect and pair production. Of these three mechanisms the atomic cross-section for the Compton process is at least four times greater than the sum of the other two (that for pair production is zero at this energy) for the interaction of 0.667-Mev gamma-rays with the principal atoms comprising kaolinite. In the Compton process, electrons are ejected with an energy spectrum in which the maximum energy is comparable to the original gamma-ray energy, and thus the substance being irradiated is subjected to an internal bombardment of energetic electrons. Most of the energy of the beta-radiation (primary electrons) is dissipated in producing further ionization, but some atomic displacements are produced. The defects produced by this internal electron bombardment are of the simplest type: isolated interstitial vacancy pairs, which are called "close-Frenkel-pairs."[18] For a certain minimum separaration there is evidence that such defects are quite stable, and highly resistant to recombination, in covalent lattices. A covalent bond is formed from the hybridization of atomic wave functions in such a manner that two-electron links between atoms have a low energy for certain directions only. This more-or-less rigid directional property is the dominant factor which governs the behavior of covalent solids (i.e., hardness, resistance to cleavage, etc.). A vacancy or interstitial in such systems is therefore subject to an environment which behaves quite differently from that of a metal or ionic crystal. The neighboring atoms are more

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[18] D. S. Billington and J. H. Crawford, Jr., Radiation Damage in Solids (Princeton, New Jersey: Princeton University Press, 1961) p. 47.

rigidly fixed in position such that diffusion of the interstitial is somewhat unlikely, and bond rupture and reformation is necessary when an adjacent atom exchanges place with a vacancy. Therefore, the activation energy for motion of either defect is expected to be higher for a covalent crystal than that for a metal or ionic crystal with an equal cohesive energy.

The layer lattice of the kaolin minerals presents an unusual situation in that for the aluminum atoms only two-thirds of the available lattice sites are filled. As pointed out in the Introduction, this condition is necessary from the standpoint of valency. However, an aluminum atom that had been displaced from its normal lattice site could occupy one of these vacant sites even though its energy state in this new location might be considerably higher than that in its initial location. As has also been pointed out previously, one of the criteria for crystal perfection in kaolinite is the degree to which the arrangement of aluminum atoms in successive layers is duplicated. The X-ray diffraction results definitely indicate that this order is decreased by gamma-radiation. The aluminum atoms in the layer lattices are apparently being displaced from their original sites in a random fashion and thus producing the effect that the various layers had been displaced by $nb_o/3$ shifts with respect to one another. Since any aluminum atom is surrounded by three immediately adjacent vacant sites, these displaced atoms may not necessarily remain as interstitials. They may instead fall into one of the vacancies. In either case, the effect is one of producing randomness in the aluminum positions which will appear in the X-ray diffraction pattern. The situation with the remaining atoms comprising the kaolin layer is the

same as that for any common crystal lattice with all available lattice sites being filled except for vacancies arising from growth defects. In the remainder of the lattice the atoms most likely to be displaced are the silicon atoms and the oxygen atoms. In the silica tetrahedra each silicon atom is surrounded by four oxygen atoms, and each oxygen, in turn, is shared by adjoining tetrahedra, thereby forming a complex network array. Hence, only two bonds need to be broken to displace any oxygen while four bond ruptures are needed to displace a silicon atom. In addition, many of the oxygens need be displaced only short distances ($\approx$1 angstrom) to find a relatively large interstitial void.

From the foregoing discussion it can be seen that the decrease in the crystallinity of kaolinite can be evaluated in terms of two separate mechanisms: the increase in the apparent $nb_o/3$ shifting and the production of interstitial-vacancy pairs in the lattice. The index of $nb_o/3$ crystallinity is presented in Figures 14 and 15, while the data of Figure 16 are a measure of the total number of interstitial-vacancy pairs that are formed. It is interesting to note that in both these plots the crystallinity of the samples appears to become better from the lowest irradiation dose up to a point and then decreases. That is, the index of $nb_o/3$ crystallinity in Figures 14 and 15 appears to become higher and the total number of interstitial-vacancy pairs, as indicated in Figure 16, becomes less. For doses greater than 10^{19} electron-volts per gram the crystalline order becomes progressively worse, as would normally be expected from radiation damage.

Since nothing is known concerning the rates of displacement or recombination for either of these systems, any firm interpretation of the critical points in these curves is not possible. One interesting point is

that the residence time for a dose of approximately 1 x 10^{19} electron-volts per gram corresponds very closely to the time required for the sample temperature to reach a constant value.

Some of the changes in physical properties that have been observed in this work can be explained on the basis of the interstitial atoms produced by the gamma-radiation. The lattice vacancies within the layers cause a marked alteration in vibrational frequencies in their vicinity and the interstitial atoms will cause a buckling of the adjacent lattice layers which will change the vibration frequencies in this region. The effects should produce an increase in the interlayer or c_o lattice spacing. Unfortunately, time and funds would not permit additional X-ray diffraction studies necessary to measure this increase in lattice spacing. However, the delamination of stacks, the decrease in specific surface area and the apparent reduction in the amount of hydrogen bonding are probably all a direct result of the production of interlattice atoms and vacancies. The layer lattices of kaolinite are known to be held together by long hydrogen bonds and van der Waal's forces. The latter decrease in strength with the square of separation distance and Hendricks[19] has pointed out that the key feature of the interlayer coordination is the manner in which oxygens and hydroxyls approach one another in pairs to form long hydrogen bonds. Therefore, any interlayer distortion produced by interlattice atoms would tend to reduce both of these interlayer binding forces. Indeed, the results of the infrared adsorption studies with the Washington County

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[19] S. B. Hendricks, "The Crystal Structure of Nacrite and the Polymorphism of the Kaolin Minerals," Zeit Krist 100, 509-18 (1938).

kaolins indicate a possible reduction in the degree of interlattice hydrogen bonding. Within the normal kaolin layer, the silicon tetrahedral layers show considerable distortion from their idealized geometry, indicative of the strong interlayer forces between them.[20,21] The nature of these distortions are tension in the octahedral layer and compression of the silica sheet. It is very likely that a reduction in the interlayer binding forces between lattice layers by the presence of interlayer atoms would promote a relaxation of these stresses in adjacent faces. This would lead to a complete misfit between the layers and a severe reduction in the interlayer binding forces. This effect is probably responsible for the production of small particles observed for the Twiggs County kaolin. Significant increases in particle concentration of the irradiated and fractionated Twiggs County kaolin begin to appear at approximately 10 cubic microns particle volume. Koenig and Lyons[22] have reported that individual kaolin plates begin to appear at approximately 2 microns, equivalent spherical diameter. Although a direct correlation of these two observations is not possible, it is obvious that the first manifestation of change in the irradiated Twiggs County kaolin is in the same size range as the first appearance of individual kaolins plates. This is a very significant result. It indicates that these small particles are being produced by a delamination process. Any comminution process

[20] L. C. Pauling, "The Structure of Micas and Related Minerals," Natl. Acad. Sci. Proc. 16, 123-129 (1930).

[21] R. E. Newnham, "A Refinement of the Dickite Structure and Some Remarks on Polymorphism in Kaolin Minerals," Mineral. Mag. 32, 683-704 (1961).

[22] Koenig and Lyons, Loc. cit.

graually reduces all the particles in a sample to smaller and smaller sizes until the desired size distribution is reached. However, the reduction of particle size occurring by the effect of high-energy, ionizing radiation seems to produce particles by the delamination or "flaking off" of plates of a size below 2 microns equivalent spherical diameter rather than continuously reducing the size of all the particles by a proportional amount. This could account for the fact that no difference can be detected in the size distributions for the larger particles which are stacks of plates. Many small plates of the size represented in the range below 2 microns would have to be removed from a large stack of plates before any change in the apparent volume of the stack would be detectable. If all the stacks in a sample of one of the clays studied were to have one plate delaminated from each stack, an increase in the number of very small particles such as found for Twiggs County kaolin would be possible without any detectable changes in the size of the stacks. Even if the delamination process is not this uniform, quite a few plates would have to be removed from a large number of stacks before a detectable change in the upper portion of the size distribution would occur. A size reduction of the stacks will become noticeable only when a greater degree of delamination is obtained than has been accomplished in this work, or by using a sample of clay in which the sizes of the stacks are smaller so that the removal of one or two plates from a significant percentage of these stacks will produce a detectable change in the overall size distribution.

Both the Washington County kaolin and the Twiggs County kaolin contained a great number of stacks. However, delamination was found for

the Twiggs County kaolin and none for the Washington County kaolin. A careful examination of the nature of the stacks present in the Washington County kaolin and Twiggs County kaolin (Figures 3 and 4, respectively) reveals a significant difference. The stacks of the Washington County kaolin are composed of many very small crystallites whose length and breadth are much smaller than the dimensions of the stacks perpendicular to the axis of preferred orientation, and the stacks have a very tightly packed appearance. There appears to be considerable overlapping of the crystallites within a single layer of the stack, which indicates some bonding between the edges of adjacent crystallites, and certainly points to physical interference to the removal of any one crystallite even if its interlayer forces were reduced. The situation with the Twiggs County kaolin, however, is quite different. The individual crystallites comprising the stacks in this kaolin appear to have a length and breadth equal to the dimensions of a stack perpendicular to the axis of preferred orientation. Therefore, a layer or laminate of one of these stacks is a single crystallite rather than a number of small crystallites. Also, the individual stacks appear to be smaller with a more loosely pack and flaky appearance. This difference in structure is also reflected in the observed difference in the crystallinity of the two unirradiated kaolins. This difference in crystalline arrangement probably accounts for the fact that delamination was observed for the Twiggs County kaolin, and not for the Washington County kaolin. A crystallite on the surface of one of the stacks in the Twiggs County kaolin would meet no further resistance to flaking off once the interlayer binding forces were reduced, while a crystallite in a surface layer of a stack in the Washington County kaolin

would receive hindrance from overlapping adjacent crystallites and edge bonding with adjacent crystallites. The relatively low crystallinity of the Washington County kaolin may also be an indication that the tensile and compressive forces between adjacent alumina and silica sheets may not be so pronounced due to the poor order present initially and further disorder produced by irradiation causes very little relaxation for promoting delamination.

A clear explanation for the observed reduction in the specific surface areas of the two kaolins is not possible on the basis of the information available. At least two explanations are possible, and further experimental work would be necessary to arrive at any definite conclusions. The most probable explanation is that the buckling and distortion of the lattice layers caused expansion into the cracks and crevices between the crystallites at the surface of the stacks. This effect was found to be responsible for the reduction in specific surface area of artificial graphites, a layer lattice material, upon exposure to neutron irradiation.[23] Another explanation could be that the gamma-radiation alters the surface properties of the kaolin. The electron micrographs presented in Figures 5, 6, 7, 8, and 9 suggest that the surfaces of the stacks are altered quite significantly by the gamma-radiation, particularly in the case of Figures 7, 8, and 9 where the surfaces have developed a vitrified appearance. However, less than about 20 per cent of the stacks examined exhibited such radical surface alteration, and the effect was observed less frequently for the irradiated samples of Twiggs County kaolin where a more significant

[23] C. N. Spalaris, L. P. Bupp, and E. C. Gilbert, "Surface Properties of Irradiated Graphite, J. Phys. Chem. 61, 350-54 (1957).

amount of alteration would actually be needed to overcome the increase in specific surface area due to the small plates produced by delamination.

An explanation for the surface change noted in some of the kaolin stacks after irradiation is not available. As already mentioned, some surfaces exhibit a vitreous appearance that is not observed, at least to the knowledge of these investigators, in a normal, unirradiated kaolin. It is expected that the production of such a condition would require local temperatures far in excess of the bulk temperature observed during irradiation. The surfaces seem to have been etched by some means as ridges and pits of considerable size are visible on the edges of the stacks. Surface irregularities of this size arising from the diffusion of interstitials and vacancies to the surface seems quite unlikely. An interesting factor is that this etching was observed only for the Washington County kaolin. It is quite conceivable that this surface behavior is responsible for the increase in cation-exchange capacity observed for the Washington County kaolin. Since cation-exchange in kaolinite is due primarily to broken bonds[24] and to negative charges on the lattice due to vacancies of aluminum or silica positions, the etching may have exposed more sites for cation-exchange. The Washington County kaolin, as has been pointed out previously, was treated with a sodium pyrophosphate deflocculating agent before the material was selected for irradiation studies. This probably accounts for the subsequently measured, low cation-exchange capacity of the unirradiated material for sodium, and it is possible that the etching is a result of the initial sodium-exchange. In

[24] S. Spiel, "Affect of Adsorbed Electrolytes on Properties of Monodispersed Clay-Water Systems," J. Am. Cer. Soc. 23, 33-38 (1940).

the presence of the radiation field this sodium may have combined with oxygen from the lattice to form an oxide of sodium which then dissolved when the kaolin was dispersed in water prior to being deposited on the electron microscope grids. The etch effect would then be a result of the removal of oxygen atoms from the kaolinite lattices. This in turn would make more sites available for cation-exchange for the irradiated material. The above hypothesis could account for the difference in surface etching and cation exchange capacity noted for the two kaolins used in this study. The lowering of the cation-exchange capacity for the irradiated Twiggs County kaolin is probably due entirely to the observed decrease in surface area which blocked off some of the sites normally available for cation-exchange.

The measurements of slurry viscosity for the Washington County kaolin produced some very interesting results. It has been demonstrated that a significant correlation exists between the kaolinite crystallinity and the viscosity of a slurry of the material.[25,26] This correlation was thought to exist principally because poorly crystallized kaolins usually contain smaller particles than well-crystallized ones, and the higher viscosity was a result of the friction of the many more edges and corners available; although the possibility of the presence of a greater concentration of valence forces to provide a higher electrokinetic component of viscosity was recognized. Since no significant reduction in particle

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[25] H. H. Murray and S. C. Lyons, "Correlation of Paper-Coating Quality with Degree of Crystal Perfection of Kaolinite," Proc. Fourth Natl. Conf. on Clays and Clay Minerals - National Research Council Pub. 456, 31-40 (1956).

[26] Murray and Lyons, Loc. cit.

size was detected for the Washington County kaolin while a significant increase in the viscosity with increasing radiation-dose was observed, it appears that the observed viscosity increase was due to an electrokinetic effect arising from a greater number of valence forces in the irradiated material.

The data from the wet-grinding of the Washington County kaolin after irradiation provide further support for the discussion of weakening interlayer forces presented earlier. Since wet-grinding provides primarily shearing forces, any reduction in the strength of the interlayer binding forces would be expected to result in a greater degree of size reduction for equal energy input. Using the specific surface area of the ground material as a measure of the degree of size reduction, this is exactly what was observed. Unfortunately, time limitations did not permit the direct measurement of particle sizes resulting from the wet-grinding experiments.

Since the nature of this research program has been primarily exploratory, and the experiments have of necessity been limited to two kaolins, some of the conclusions drawn from this work are necessarily quite tentative. The conclusions that can be drawn are:

(1) Lattice defects of isolated interstitial-vacancy pairs, which are stable at room temperature, are produced in the kaolinite lattice by the effect of 0.667-Mev gamma-rays.

(2) Some physical surface alteration is produced on the kaolinite crystallites by the gamma-radiation used in this work. A portion of the alteration observed may be due to a chemical process--with adsorbed cations--initiated by the gamma-radiation.

(3) The interlattice bonding forces of the kaolinite appear to have been reduced due to interlattice atoms produced by the gamma-radiation.

(4) Delamination of kaolinite crystallites may occur from the stacks as a result of this weakening of interlayer bonding. Whether or not delamination does occur appears to depend on the presence of other hindrances, i.e., overlapping crystallites, edge bonding between crystallites in the same layer, etc. The initial degree of crystallinity may also be an important factor.

(5) The specific surface area of kaolin is reduced by the effect of gamma-radiation.

(6) The cation-exchange capacity of a raw, untreated, kaolin is reduced by the effect of high-energy, ionizing radiation. This is probably due to the blocking off of available exchange sites by whatever mechanism is reducing the specific surface layer.

(7) The slurry viscosity of an irradiated kaolin is greater than for the unirradiated kaolin and the viscosity increases with increasing radiation dose. This effect is apparently an electrokinetic one arising from a greater number of valence forces in the irradiated material.

(8) The ease with which kaolin can be wet-ground is enhanced by exposure to gamma-radiation.

IV. RECOMMENDATIONS

The exploratory nature of this research project has uncovered a number of points that justify further investigation and has suggested other areas that warrant research. In general, the investigations performed during the course of this research should be extended to include at least five or six more kaolins from various sources and possessing diverse physical properties (i.e. particle size, specific surface area, degree of crystallinity) to provide a more firm foundation for acceptance or rejection of the conclusions drawn from this work. In addition, some of the more specific points that appear to warrant extensive investigation are:

(1) The examination of individual stacks of kaolin exposed to varying doses of gamma-radiation. This could be accomplished by depositing single stacks on electron microscope grids, and irradiating the stacks without removing them from the grids. This would allow examination, by electron microscopy and electron diffraction, of individual stacks and thereby eliminate some of the statistical fluctuations due to sampling that were undoubtedly encountered here.

(2) The examination of the effect of crystal orientation within a unidirectional radiation field on the amount and type of damage produced by high-energy, ionizing radiation may be dependent upon crystal orientation.

(3) Examination of the increase in c_o spacing produced by the presence of interlattice atoms. This could be accomplished with X-ray diffraction traces using a scale with sufficient

expansion to detect small changes in the Bragg angle of the 001, 002, or 003 diffraction maximum.

(4) Preheating of the samples to 100° F before introducing them into the Research Irradiator to ascertain whether or not the apparent reduction in radiation damage observed for the lower radiation doses is actually due to the rise in sample temperature during irradiation.

(5) Careful examination of the pore volumes of kaolin samples before and after exposure to gamma-radiation. This work would help to establish exactly the nature of the mechanism that reduces the specific surface area during irradiation. For this work kaolins with a wide range of initial surface area should be employed.

(6) Irradiation and subsequent examination by electron microscopy of kaolins with and without exchanged cations to determine whether or not the surface etching observed in this work is a chemical effect.

(7) Examination of the extent of delamination produced by neutron irradiation. Due to the more extensive damage of the displacement type produced by neutron irradiation, the degree of delamination of kaolin stacks might be much greater.

(8) More precise and extensive investigations of the infrared adsorption spectra of kaolins as a function of radiation dose. Information of this type would be very valuable in establishing the exact nature of the structural disorder produced by the gamma-radiation.

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