

**AMENABILITY OF CERTAIN KANSAS CLAYS  
TO ALUMINA EXTRACTION BY THE  
LIME-SINTER PROCESS**

**By**

**E. D. KINNEY**

**State Geological Survey of Kansas, Bulletin 96, Part 7**

**UNIVERSITY OF KANSAS PUBLICATIONS**

**LAWRENCE, KANSAS**

**1952**



# STATE OF KANSAS

EDWARD F. ARN, Governor

## STATE BOARD OF REGENTS

OSCAR STAUFFER, Chairman

WALTER FEES  
MRS. LEO HAUGHEY  
A. W. HERSHBERGER  
WILLIS N. KELLY

DREW McLAUGHLIN  
LESTER McCoy  
GROVER POOLE  
LAVERNE B. SPAKE

## MINERAL INDUSTRIES COUNCIL

B. O. WEAVER ('53), Chairman  
LESTER McCoy ('52)  
J. E. MISSIMER ('52)  
CHARLES COOK ('52)  
K. A. SPENCER ('53)  
W. L. STRYKER ('53)

BRIAN O'BRIAN ('55), Vice-Chairman  
M. L. BREIDENTHAL ('54)  
HOWARD CAREY ('54)  
JOHN L. GARLOUGH ('54)  
O. W. BILHARZ ('55)  
GEORGE K. MACKIE, JR. ('55)

## STATE GEOLOGICAL SURVEY OF KANSAS

FRANKLIN D. MURPHY, M.D., Chancellor of the University of Kansas,  
and ex officio Director of the Survey

JOHN C. FRYE, Ph.D.  
Executive Director

### BASIC GEOLOGY

STRATIGRAPHY, AREAL GEOLOGY, AND PALEONTOLOGY

John M. Jewett, Ph.D., Geologist  
A. B. Leonard, Ph.D., Paleontologist\*  
Ruth L. Breazeal, Stenographer

### PUBLICATIONS AND RECORDS

Betty J. Hagerman, Secretary  
Grace Mullenburg, Journalist  
Alice M. White, B.F.A., Draftsman  
Joan Jaeger, B.F.A., Draftsman  
Regina Rodina, Draftsman  
Phyllis Miskimen, Clerk-Typist  
Phyllis Gibler, Clerk-Typist

### MINERAL RESOURCES

Robert O. Kulstad, M.S., Economic Geologist  
W. H. Schoewe, Ph.D., Coal Geologist  
Kenneth E. Rose, M.S., Met. Engineer  
Frank Bowdish, S.M., Met. Engineer  
H. E. Risser, E.M., Mining Engineer\*

### PETROGRAPHY

Ada Swineford, M.S., Petrographer  
Carrie B. Thurber, Laboratory Asst.

RAYMOND C. MOORE, Ph.D., Sc.D.  
State Geologist and Director of Research

### MINERAL RESOURCES

#### OIL AND GAS

Edwin D. Goebel, M.S., Geologist  
Walter A. Ver Wiebe, Ph.D., Geologist\*  
Charles F. Weinaug, Ph.D., Petroleum Engineer\*  
J. P. Everett, M.S., Petroleum Engineer\*

Ruby Marcellus, Well Sample Curator  
Lois Rissman, Clerk-Typist  
Vernon O. Cooper, Laboratory Asst.  
WICHITA WELL SAMPLE LIBRARY  
Ethelyn McDonald, M.A., Curator  
Della B. Cummings, Clerk

#### CERAMICS

Norman Plummer, A.B., Ceramist  
William B. Hladik, Asst. Ceramist  
J. Sheldon Carey, A.M., Ceramist\*  
Clarence Edmonds, Laboratory Asst.  
Ethel W. Owen, Laboratory Asst.

#### GEOCHEMISTRY

Russell T. Runnels, M.S., Chemist  
John Schleicher, B.S., Chemist  
H. S. Van Nortwick, B.S., Chemist

SOUTHEASTERN KANSAS FIELD OFFICE  
Allison Hornbaker, M.S., Geologist  
Christine Notari, Stenographer

### COOPERATIVE PROJECTS WITH UNITED STATES GEOLOGICAL SURVEY

#### GROUND-WATER RESOURCES

V. C. Fishel, B.S., Engineer in Charge  
Delmar W. Berry, A.B., Geologist  
Howard G. O'Connor, B.S., Geologist  
Glenn C. Prescott, M.S., Geologist  
Kenneth Walters, B.S., Geologist  
Charles K. Bayne, A.B., Geologist  
W. W. Wilson, Scientific Aide  
William Connor, Core Driller

Betty Henderson, A.B., Stenographer  
Betty J. Mason, Stenographer

#### MINERAL FUELS RESOURCES

Wallace Lee, E.M., Geologist in charge  
Holly C. Wagner, M.A., Geologist

#### TOPOGRAPHIC SURVEYS

D. L. Kennedy, Division Engineer  
Max J. Gleissner, Section Chief  
J. P. Rydeen, Topographer

SPECIAL CONSULTANTS: Ray Q. Brewster, Ph.D., Chemistry; Robert M. Dreyer, Ph.D., Geology and Geophysics; Eugene A. Stephenson, Ph.D., Petroleum Engineering; Robert W. Wilson, Ph.D., Vertebrate Paleontology.

COOPERATIVE STATE AGENCIES: State Board of Agriculture, Division of Water Resources. Robert Smrha, Chief Engineer; State Board of Health, Division of Sanitation, Dwight Metzler, Chief Engineer and Director, and Willard O. Hilton, Geologist.

\*Intermittent employment only.

# AMENABILITY OF CERTAIN KANSAS CLAYS TO ALUMINA EXTRACTION BY THE LIME-SINTER PROCESS

By  
E. D. KINNEY

## CONTENTS

ABSTRACT .....	303
INTRODUCTION .....	303
Acknowledgments .....	304
PREPARATION OF MATERIALS USED IN THE STUDY .....	305
Beneficiation of Kansas clays .....	307
THE LIME-SINTER PROCESS .....	308
Laboratory procedure .....	309
Purification of solutions .....	310
The sodalite seeding process .....	312
Sintering .....	313
Leaching the sinter with sodium carbonate solutions containing sodium chloride .....	313
Annealing of sinters .....	316
Discussion of purification processes .....	320
Loss of alumina in seeding .....	320
Synthetic sodalite .....	320
Other processes .....	322
Sinter residues .....	322
Alumina content of solutions .....	323
THE LIME-SINTER PROCESS VERSUS THE SODA-LIME-SINTER PROCESS .....	323
PREPARATION OF SUPER-DUTY FIRE-BRICK CLAYS BY ADDING CRUDE ALUMINA .....	324
FLOW SHEET OF LIME-SINTER PROCESS FOR EXTRACTING ALUMINA FROM KANSAS CLAY .....	325
CONCLUSIONS .....	325
REFERENCES .....	327

## ILLUSTRATIONS

FIGURE	PAGE
1. Percent alumina extracted versus mole ratio $\text{CaO}:\text{Al}_2\text{O}_3$ .	311
2. Percent alumina extracted versus sintering temperature	311
3. Flow sheet of lime-sinter process for extracting alumina from Kansas clay.	326

### TABLE

1. Kansas clays used in the investigation.	305
2. Chemical composition of samples used in the study.	306
3. Analyses of whittings used in the tests.	307
4. Results of beneficiation tests on three Kansas clays	308
5. Summary of best results after leaching sinter with 3 percent sodium carbonate solutions.	312
6. Sinter composition and extraction data after leaching with 3 percent sodium carbonate solutions.	314
7. Partial chemical analyses of sinters.	316
8. Partial analyses of annealed sinters.	317
9. Sinter extraction data after leaching with sodium carbonate solutions containing sodium chloride only.	317
10. Annealed sinter extraction data after leaching annealed sinters with sodium carbonate solutions containing sodium chloride only.	318
11. Effect of sodium chloride in sodium carbonate leaching solutions (average of all tests).	318
12. Summary of leaching sinters with sodium carbonate and sodium chloride solutions, showing highest and lowest individual recoveries of $\text{Al}_2\text{O}_3$ from sinter and conditions involved.	319
13. Desiliconization of sodium aluminate solutions.	321
14. Seed boiling time on successful desiliconizing experiments.	321
15. Analyses of sinter residues.	322
16. Melting points of clay EL-69-2 with and without added alumina.	324
17. A.S.T.M. standard classification of fire-clay refractories.	324

## ABSTRACT

The development of the lime-sinter process of extracting alumina from clay and the potential use of this method for beneficiation of Kansas refractory clays have prompted the Geological Survey to make further investigations of alumina extraction from Kansas clays. The Geological Survey's original studies of the soda-lime-sinter process were conducted under conditions of stress during World War II and were directed exclusively toward the ultimate production of aluminum metal. The present study tests the applicability of the lime-sinter process to Kansas clays and is directed primarily toward the development of high-alumina refractory materials with the possible utility of Kansas clay as a source of ore for aluminum metal as a secondary consideration. Laboratory tests indicate that Kansas clays are amenable to treatment by the lime-sinter process for both of these ultimate products, and that 80 to 84 percent of the alumina contained in the samples tested can be extracted as a high-grade product by this relatively simple process.

## INTRODUCTION

In 1943 the State Geological Survey of Kansas published a report on the results of studies directed toward the development of a method of extracting alumina from Kansas clay (Kinney, 1943). This early investigation was prompted by conditions existing during the war years, and although the experimental work was successful it did not lead to commercial development. During the subsequent years additional work has been carried on intermittently on this same problem.

The present investigation was undertaken to determine what extraction of alumina of metallurgical grade could be made from Kansas clay using the lime-sinter process (Archibald and Jackson, 1944) followed by purification of the resulting extract. An important new factor prompting further study of this problem was the desire to determine the utility of the process as an inexpensive method for the manufacture of high-alumina refractories. Such refractories may be produced by using alumina of lower grade obtained by this process, in raising the alumina content of ordinary fire clay to a suitable composition. There are extensive clay deposits in Kansas suitable for this method of treatment.

The production of aluminum in the United States has increased from 175,000 tons in 1939 to an output of about 1,200,000 tons in 1951. Bauxite, the common ore, contains 40 to 60 percent alumina ( $\text{Al}_2\text{O}_3$ ). To extract aluminum from bauxite or from

clay (which has only half the alumina content of bauxite) it is first necessary to separate alumina, which is then subjected to electrolysis in an electric furnace for reduction to metal. Conventional smelting cannot be employed. After calcination the ore is treated by wet methods to obtain alumina. Bauxite is leached directly, but clay commonly must be sintered with fluxes to form a soluble aluminate before leaching.

Because of its higher alumina content and cheaper processing, bauxite is the ore for practically all aluminum production at the present time. However, on account of the rapid depletion of bauxite deposits in this country, attention in recent years has been directed to the possible utilization of clay to augment production. Bauxite deposits in the United States are estimated at only 60 million tons, of which 4 million tons are high grade (Reynolds, 1951). Yearly consumption is 7 million tons, more than half of which is imported from the Guianas, South America. The condition of bauxite reserves has been changed recently with the discovery in Haiti of what is claimed to be the world's largest deposits of high-grade ore, reported as 350,000,000 tons (Reynolds, 1951). While cheap water transportation is available from Dutch Guiana to Mobile, Alabama, a distance of 2,500 miles, cargoes must be transshipped from shallow river boats to deep-water vessels at Trinidad. From Haiti the distance is only 1,000 miles and no transshipment is required. Increased supplies of bauxite may be expected from Haiti for many years.

Although the easing of the bauxite ore situation may temporarily delay any program for the use of clay as an ore of alumina, there is little doubt as to its eventual use. Furthermore, if during an emergency foreign sources of bauxite are closed to us, it will certainly become necessary to utilize clay as a substitute source. It is judged that the most eminent value of the present study will be in its application to the production of refractories.

*Acknowledgments.*—Thanks are expressed to Norman Plummer and William Hladik, who supplied clay samples and information on the beneficiation of clay, and to Russell Runnels and staff of the geochemistry laboratory who made all chemical analyses.

## PREPARATION OF MATERIALS USED IN STUDY

Clays typical of known Kansas high-alumina deposits were selected for study (Plummer and Romary, 1947). Samples of clay from four localities in Ellsworth, Ottawa, and Wilson Counties, Kansas, were used. The location and laboratory number of these clay samples are given in Table 1. For comparison purposes samples of commercial-grade Georgia kaolin were included in all tests.

Clay from locality O-38-4 was tested in both the natural state and after beneficiation by sedimentation. Clay samples from Ellsworth County (EL-69-2 and EL-60-6) were beneficiated. Wilson County clay (WL-1) was tested both in the natural state and after leaching with hydrochloric acid to remove some iron. The Georgia kaolin was used in the natural condition. All samples were calcined at 800° C. as a preliminary operation.

Chemical analyses of clay samples are shown in Table 2. Certain impurities present in the clay or flux used in the lime-sinter process may seriously affect extraction of alumina (Grim, Machin, and Bradley, 1945). Quantities of magnesium oxide (MgO) in the sinter in amounts greater than 2 percent and of phosphorous pentoxide ( $P_2O_5$ ) greater than 0.3 percent are particularly damaging. Ferric oxide ( $Fe_2O_3$ ) can be tolerated to about 3 percent. Except for the illite type, Kansas clays are relatively free from excessive amounts of impurities.

The lime necessary for the chemical reactions in the sinter is added in the form of calcium carbonate. For this study commercial grades of ceramic whiting were used. However, deposits of high-purity limestone suitable for this purpose are available in Kansas (Runnels, 1951).

The amount of silica present as an impurity in the calcium carbonate must be known so that suitable corrections for it can

TABLE 1.—*Kansas clays used in the investigation*

Clay no.	Location	County	Type of clay
O-38-4	NW¼ NW¼ 8-9-2W	Ottawa	Kaolinitic
EL-69-2	W½ NW¼ 30-15-6W	Ellsworth	Kaolinitic
EL-60-6	SW¼ 19-15-9W	Ellsworth	Kaolinitic
WL-1	Excelsior Brick Co., Fredonia, Kansas	Wilson	Illite

TABLE 2.—*Chemical composition of samples used in the study*  
(Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Rannels)

Clay	Treatment	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SO <sub>3</sub>	MgO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O* + Na <sub>2</sub> O	Loss on ignition, 1000° C.
O-38-4	Dried 140° C.	64.78	22.24	0.27	1.58	1.32	0.05	0.66	Nil	1.66	7.49
O-38-4	Calcined 880° C.	70.02	24.04	0.29	1.71	1.43	0.05	0.71	Nil	1.79	
O-38-4	Concentrated	50.20	32.26	0.43	2.34	1.23		0.79		2.11	10.64
O-38-4	Conc. & calcined	56.17	36.11	0.48	2.62	1.37		0.88			
EL-69-2	Dried 140° C.	66.08	23.70	2.03	0.46	***					6.62
EL-69-2	Concentrated	49.29	33.03	0.37	2.14	1.13		0.97		2.13	10.91
EL-69-2	Concentrated**	47.75	32.23	0.30	2.12	1.20	0.05	0.71	0.05	2.82	12.82
EL-69-2	Conc. & calcined	55.33	37.07	0.41	2.41	1.27		1.08			
EL-69-2	Conc. & calcined**	54.73	36.94	0.34	2.43	1.38	0.06	0.81	0.06	3.23	0.07
EL-60-6	Dried 140° C.	71.80	19.12	0.18	0.88	1.30		0.16		0.82	6.05
EL-60-6	Concentrated	46.92	36.53	0.19	1.42	1.57		0.12			13.58
EL-60-6	Concentrated**	46.22	35.58	0.12	1.30	1.79	0.05	0.07	0.03	0.31	14.59
EL-60-6	Conc. & calcined	54.30	42.27	0.22	1.64	1.81		0.14			
EL-60-6	Conc. & calcined**	53.56	41.23	0.14	1.51	2.07	0.06	0.07	0.03	0.36	0.88
WL-1	Dried 140° C.	55.94	22.42	0.49	7.47	1.76		1.93	0.20	2.44	7.40
WL-1	Calcined	60.41	24.21	0.53	8.07	1.90		2.08	0.20		
WL-1	Leached & calcined	63.97	25.67	0.56	2.64	2.01		2.21			
Georgia kaolin	Dried 140° C.	44.67	38.40	0.19	1.97						14.75
Georgia kaolin	Calcined	52.40	45.04	0.22	2.31						

\* Undetermined difference

\*\* 1951 samples

\*\*\* Reported with Al<sub>2</sub>O<sub>3</sub>.



be made in the process. Chemical analyses of the two batches of whiting used are given in Table 3. Whiting no. 1 was used in sinters 1 to 21 (Table 6), whereas whiting no. 2 was used in all other tests.

#### BENEFICIATION OF RAW CLAY

The beneficiation of raw clay raises the amount of alumina in the product to be treated by eliminating some of the silica and concentrating the alumina in a mass weighing less than the original clay. It reduces the amount of material to be processed for a given amount of alumina, saves on freight and fluxes, and the beneficiated clay yields a higher percentage of its alumina on extraction than does untreated clay. This is shown by a comparison of extraction results for clay O-38-4 in both the beneficiated and unbeneficiated condition (Table 6). The extraction of 80 to 84 percent alumina mentioned in this bulletin is from beneficiated clay.

The main constituents of the clay studied are quartz ( $\text{SiO}_2$ ) and kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) with specific gravities of approximately 2.65 and 2.61 respectively. Quartz occurs in granular form, kaolinite more or less in thin flakes. Beneficiation is possible by reason of the slower settling rate of kaolinite compared to quartz when the clay is ground, agitated in water, and allowed to settle. Quartz tends to concentrate at the bottom of the settler, kaolinite in the supernatant emulsion. The latter is drawn off and the clay, now enriched in alumina, is recovered by prolonged settling. Clay can also be concentrated in classifiers or centrifuges. Results are influenced by the ratio of quartz to kaolinite and by the grain size of the clay treated. The greater the amount of quartz and the finer its size, the poorer the concentration. Usually the alumina in the concentrate is increased 30 to 40 percent.

Beneficiation of clay in its present state of development is by no means a perfect process. The ratio of concentration is in the

TABLE 3.—Analyses of whittings used in the tests

Constituent	No. 1	No. 2
Percent $\text{CaCO}_3$	98.40	98.00
Percent $\text{SiO}_2$	0.63	1.83

order of 2 to 2.5 of clay to 1 of concentrate; not in itself a great handicap, as clay at the mine is cheap, but costs rise with increase in amount of raw material processed for a given amount of product. A redeeming feature is that the residues, or tailings, still contain enough clay to be plastic and can be used in the manufacture of face brick or siliceous fire clay brick.

Concentrated clays mentioned in this report were prepared in the Geological Survey laboratory using agitation in water followed by settling in glass cylinders. A very small amount of ammonium hydroxide was added to help deflocculate the clay. Some results are shown in Table 4.

### THE LIME-SINTER PROCESS

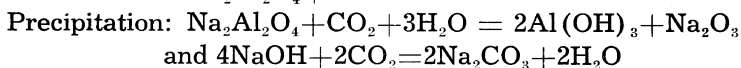
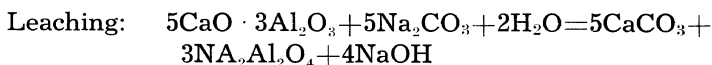
The lime-sinter process consists of heating a mixture of lime and calcined clay to a sintering temperature, removing the soluble calcium aluminate by leaching with sodium carbonate solution, and precipitating the alumina with carbon dioxide gas.

The ground siliceous alumina-bearing ore and ground calcium carbonate are mixed in calculated amount (ignoring volatile constituents) to give a mixture corresponding in percentage composition to dicalcium silicate ( $2 \text{ CaO} \cdot \text{SiO}_2$ ) and pentacalcium trialuminate ( $5 \text{ CaO} \cdot 3 \text{ Al}_2\text{O}_3$ ), or other calcium aluminates approaching it in composition. The dicalcium silicate gram mole ratio ( $\text{CaO} : \text{SiO}_2 :: 2 : 1$ ) is essential for the success of the process. The calcium aluminate, depending on the ore, may be pentacalcium trialuminate, with a mole ratio ( $\text{CaO} : \text{Al}_2\text{O}_3 :: 1.66 : 1$ ), or in any event the ratio in the case of clays will be somewhere between 1.5 and 2.0. The mixture is then heated to suitable sintering temperature and for such a time as may be necessary to develop the compounds. The ground sinter is then leached with

TABLE 4.—*Results of beneficiation tests on three Kansas clays*

No.	Original composition, percent		Weights of agitation mixture, percent			Concentrate Percent of original		Tailings Percent of original		Settling time, hours
	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	Clay	Water	$\text{NH}_4\text{OH}$	clay	$\text{Al}_2\text{O}_3$ , percent	clay	$\text{Al}_2\text{O}_3$ , percent	
O-38-4	22.24	68.74	13.00	86.9	0.01	52	36	48	19	
EL-69-2	23.70	66.08	13.00	86.7	0.03	40		60		22
EL-60-6	19.12	71.80	16.70	83.2	0.01	35		65		23

dilute sodium carbonate to dissolve alumina as sodium aluminate, which is removed by filtering, leaving the silica and lime in the sinter residue as calcium silicate and calcium carbonate. The dicalcium silicate has two functions: (1) it holds nearly all the silica in insoluble form, and (2) it undergoes crystallographic transformation, on cooling below about 675° C., with an increase in volume which results in a disintegration of the sinter to a fine powder easily attacked by the leaching agent without further grinding. This phenomenon is called "dusting." Carbon dioxide gas is added to the aluminate solution to precipitate aluminum as aluminum hydroxide. Reactions are as follows:



The sodium carbonate is regenerated and the solution used for further leaching.

#### LABORATORY METHODS

The following sequence of operations represents the procedure followed in the original tests:

(1) A 300-gram clay sample was ground to pass a 60-mesh screen, calcined at 800° C. for 1 hour, ground to pass a 100-mesh screen, mixed thoroughly, and a sample analyzed chemically.

(2) The chemical analysis was used to calculate the amount of whiting to add to the clay to give a calcium oxide to silica ratio of 2:1 and a calcium oxide to alumina ratio as desired. Only the "available" calcium carbonate in the whiting was used in calculations. The clay and whiting were mixed in a jar mill for 5 hours, then mixed briefly on a cloth.

(3) The clay-whiting mixture was prepared for briquetting by adding 5 percent water. Briquettes weighing 20 grams were made by using a pressure of 5,000 psi. After drying at 120° F., the briquettes were sintered by heating slowly in an electric furnace and holding at the desired temperature, between 1340° C. and 1400° C., for 1 hour. The power was then shut off and the furnace made to cool to 1100° C. in 30 minutes. At 690° C. to 800° C. the briquettes were removed and the dusting character-

istics observed as they cooled to near room temperature. It was necessary to set the briquettes on a  $\frac{1}{2}$ -inch thick disc of carbon placed in a fire-clay dish to prevent their sticking to the container. The dusted sample was passed through a 100-mesh screen. Any oversize was recorded and reduced to size. The material was mixed and sampled for chemical analysis. The balance was placed in closed jars.

(4) A 10-gram sample of the sinter was leached with 3 percent sodium carbonate solution for 15 minutes at 65° C., using high-speed agitation. Enough solution was employed to insure 1.66 moles of sodium carbonate for each mole of alumina in the 10-gram sample. The leach was filtered and washed four times with fresh carbonate solution. The extract was analyzed for total alumina and silica, and the percentage of alumina extracted was calculated from the known amounts in the sinter and extract. The percent silica associated with the alumina extracted was calculated from the amounts of each in the extract.

Preliminary work on the process was done in the laboratories of the Geological Survey in 1950 to determine the amount of lime to use, the sintering temperature, and the time of leaching to give optimum results. At that time sodium carbonate solutions used for leaching gave satisfactory extraction results, but the silica content of the aluminate solutions was as much as 3.5 percent. Most of the silica is precipitated with alumina when carbon dioxide is added and 3.5 percent is far too much to enable alumina of high grade to be made, although sufficiently pure to produce a product satisfactory for the ceramic industry. The results of leaching the sinters with simple sodium carbonate solutions are shown in Table 6 and in Figures 1 and 2. A summary of Table 6 showing factors involved in giving best extraction results for each clay tested is shown in Table 5.

In 1951, it was found that seeding with sodalite, in the presence of sodium chloride added to the sodium carbonate leaching solution, was effective in removing silica from the leached solutions, and from then on this method was adopted in our work.

#### PURIFICATION OF SOLUTIONS

The sodium aluminate solutions obtained by leaching the sinter of the lime-sinter process with sodium carbonate solutions

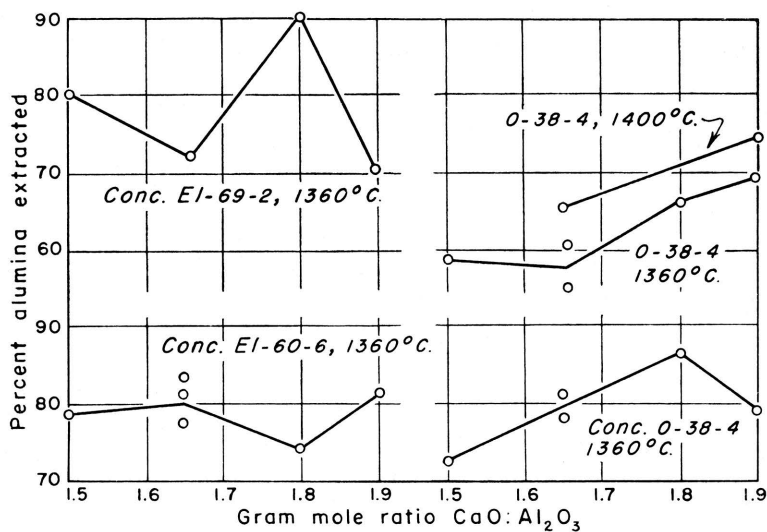


FIG. 1.—Percent alumina extracted versus mole ratio CaO:Al<sub>2</sub>O<sub>3</sub>.

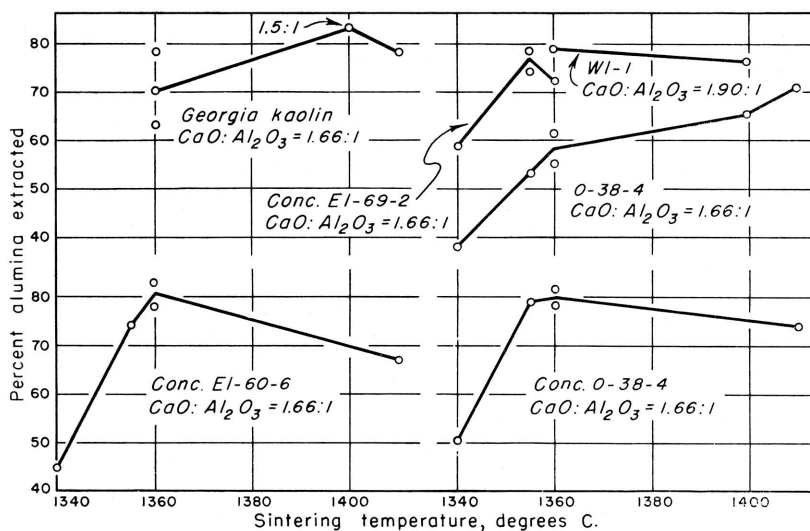


FIG. 2.—Percent alumina extracted versus sintering temperature.

TABLE 5.—*Summary of best results after leaching sinter with 3 percent sodium carbonate solutions*

Clay	Alumina extraction, percent	Ratio CaO : Al <sub>2</sub> O <sub>3</sub> in sinter	Sintering temperature, degrees C.
EL-69-2 beneficiated	90.4	1.80	1360
EL-60-6 beneficiated	83.3	1.66	1360
O-38-4 beneficiated	86.1	1.80	1360
O-38-4	74.2	1.90	1400
Georgia kaolin	84.5	1.50	1400
WL-1-illite	79.1	1.90	1360

will contain appreciable silica as sodium silicate. Unless this is removed first it will seriously contaminate the aluminum hydroxide, when the latter is precipitated, and the alumina and aluminum made will carry prohibitive amounts of silica. This is especially true of dilute aluminate solutions such as considered in this report. The upper limit for silica in high-grade alumina is 0.06 percent. This degree of purity cannot be obtained without a preliminary purification of the aluminate solutions.

Many processes have been suggested for the removal of silica from aluminate solutions. With the exception of the sodalite seeding process, developed by the National Bureau of Standards (Flint and others, 1946), none have been entirely successful.

#### THE SODALITE SEEDING PROCESS

The composition of the mineral sodalite is  $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{NaCl}$ . When sodalite powder is added to an aluminate solution containing sodium chloride, under proper conditions it will start to grow without change of composition due to assimilation of alumina, silica, and sodium chloride from the surrounding liquid. Removal of the sodalite seed by filtration reduces the silica content of the solution, but at the expense of a small amount of alumina and sodium chloride. This loss is not particularly important as seed can be used repeatedly or recycled with the ore.

It should be recalled that in precipitating aluminum hydroxide with carbon dioxide, sodium carbonate is regenerated and the solutions are recycled for further leaching. If seeding is practiced there will also be sodium chloride in the aluminate solutions so that sodalite will develop spontaneously in small



amount in the solutions during leaching. To limit the development of this insoluble compound which would otherwise be discarded with the leached ore, causing a loss of alumina, the time of leaching is made as short as possible.

Using sodium chloride solutions the extraction of alumina will be slightly lower than where straight sodium carbonate is employed, but the advantage of having a sound process for the removal of silica far outweighs this disadvantage.

Desiliconization of sodium aluminate solutions is favored by the following factors: (1) the presence of a high concentration of sodium chloride in the solution; (2) the presence or formation of a seed charge of sodalite; (3) a boiling temperature; and (4) sufficient time for precipitation of sodalite to approach completion.

In our work of evaluating the lime-sinter process, using sodium carbonate-sodium chloride leaching solutions and seeding, the effect of the added salt on extraction of alumina was first determined followed by tests to determine the efficiency of sodalite seed in removing silica from the extract.

*Sintering.*—In making the sinter mixture of calcined clay and limestone the following gram mole ratios were employed: for sample EL-60-6,  $\text{CaO} : \text{Al}_2\text{O}_3 : : 1.66 : 1$ ,  $\text{CaO} : \text{SiO}_2 = 2 : 1$ ; and for sample EL-69-2,  $\text{CaO} : \text{Al}_2\text{O}_3 : : 1.75 : 1$ ,  $\text{CaO} : \text{SiO}_2 = 2 : 1$ . No allowance was made in the fluxing calculations for compounds in the calcined clay other than silica, alumina, and lime.

The sinter mixture briquettes were heated slowly and kept at  $1360^\circ \text{C}$ . for 1 hour. They were then cooled to  $1100^\circ \text{C}$ . in 30 minutes. On further cooling sample EL-60-6 dusted completely in 20 minutes. Sample EL-69-2 dusted completely in 30 minutes. Partial analyses of the sinters are given in Table 7.

*Leaching the sinter with sodium carbonate solutions containing sodium chloride.*—In all leaching tests, except those noted, 20 gram samples of sinter were leached for 15 minutes with 6 percent sodium carbonate solutions containing salt at  $65^\circ \text{C}$ ., using high-speed agitation. The residue was washed four times by decantation using sodium chloride solutions of the same concentration, and approximately the same volume, as used in leaching. For purposes of comparison a few sinters were leached with sodium carbonate solution without salt and washed with

TABLE 6.—*Sinter composition and extraction data after leaching with 3 percent sodium carbonate solutions*  
(Final solutions not purified) (Analyses in State Geological Survey geochemistry laboratory under supervision of  
Russell Runnels)

Sample designation	Percent					Al <sub>2</sub> O <sub>3</sub> weight from 10 gms.	Alumina extraction, percent	Weight SiO <sub>2</sub> from 10 gms.	$100 \times \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{SiO}_2}$ in extract	Mole ratio CaO : Al <sub>2</sub> O <sub>3</sub> in sinter	Sinter temp., degrees C.	Remarks
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>							
<b>EL-69-2</b>												
Enriched and calcined	55.33	37.07	0.41	2.41	1.27	1.08						
Sinter 10	23.07	15.10	57.66	1.71		0.99	79.38	0.031	2.60	1.66	1,355	{ 2 : 1 Na <sub>2</sub> CO <sub>3</sub> : Al <sub>2</sub> O <sub>3</sub> in leach }
Sinter 14	23.07	15.10	57.66	1.71			72.20	0.036	3.02	1.66	1,360	
Sinter 18	22.89	14.77	58.30	1.85			58.80	0.031	3.45	1.66	1,340	
Sinter 10 B	23.07	15.10	57.66	1.71		0.99	75.95	0.070	5.60	1.66	1,355	
Sinter 23	23.96	15.37	57.27	1.07	0.82		80.20	0.035	2.70	1.50	1,360	
Sinter 28	23.89	13.93	59.10	2.72			90.40	0.031	2.42	1.80	1,360	
Sinter 34	22.94	14.64	58.53	1.57			70.56	0.018	1.70	1.90	1,360	
<b>EL-60-6</b>												
Enriched and calcined	54.30	42.27	0.22	1.64	1.81	0.14						
Sinter 9	22.53	16.74	57.96	1.98		0.74	73.60	0.043	3.42	1.66	1,355	{ 25 min. leach }
Sinter 15	22.53	16.74	57.96	1.98			77.50	0.041	3.08	1.66	1,360	
Sinter 15A	22.53	16.74	57.96	1.98			83.30	0.061	4.20	1.66	1,360	
Sinter 5	22.53	16.74	57.96	1.98			67.44	0.028	2.48	1.66	1,410	
Sinter 15B	22.53	16.74	57.96	1.98			80.64	0.058	4.10	1.66	1,360	
Sinter 19	22.53	16.74	57.96	1.98			43.96	0.042	5.40	1.66	1,340	{ 2 : 1 Na <sub>2</sub> CO <sub>3</sub> : Al <sub>2</sub> O <sub>3</sub> in leach }
Sinter 24	23.20	17.21	57.37	0.66	0.79		78.90	0.042	3.00	1.66	1,360	
Sinter 29	22.88	16.81	58.41	1.44			74.65	0.060	4.56	1.80	1,360	
Sinter 33	21.87	16.24	58.63	1.38			81.93	0.052	3.80	1.90	1,360	

	O-38-4 (test 1)		O-38-4 (test 2)		Enriched and calcined		Georgia kaolin		WL-1 (Illite)		Sample leached with HCl	
	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined	Calcined
Sinter 16	70.02	24.04	0.29	1.71	1.43	0.71	0.37	38.30	0.045	10.80	1.66	1.340
Sinter 11	27.30	9.64	59.54	1.60		1.04	0.53	54.50	0.025	4.50	1.66	1.355
Sinter 21	27.57	9.68	59.35	1.60	0.67		0.54	55.07	0.045	7.70	1.66	1.360
Sinter 12	27.57	9.68	59.46	0.76			0.60	61.80	0.040	6.20	1.66	1.360
Sinter 2	27.30	9.64	59.84	1.60			0.67	70.01	0.016	2.35	1.66	1.410
Sinter 35	27.31	9.99	60.09	1.49			0.65	65.31	0.043	6.30	1.66	1.400
Sinter 25	28.22	9.81	59.07	1.39			0.58	58.99	0.020	3.30	1.50	1.360
Sinter 26	28.44	9.79	59.86	1.56			0.65	66.26	0.022	3.35	1.80	1.360
Sinter 31	27.75	9.74	59.73	1.38			0.68	69.71	0.061	8.20	1.90	1.360
Sinter 36	27.20	9.95	60.56	1.33			0.74	74.25	0.051	6.50	1.90	1.400
O-38-4 (test 2)												
Enriched and calcined	56.17	36.11	0.48	2.62	1.37	0.88						
Sinter 8	23.21	14.85	57.21	1.13	0.64		1.17	78.80	0.032	2.70	1.66	1.355
Sinter 13	23.26	14.85	57.21	1.13	0.64		1.18	79.40	0.041	3.30	1.66	1.360
Sinter 13A	23.26	14.85	57.21	1.13	0.64		1.19	80.00	0.065	5.20	1.66	1.360
Sinter 4	23.26	14.85	57.21	1.13	0.64		1.11	74.95	0.017	1.55	1.66	1.410
Sinter 13B	23.26	14.85	57.21	1.13	0.64		1.20	80.80	0.058	4.60	1.66	1.360
Sinter 17	23.26	14.85	57.21	1.13	0.64		0.75	50.50	0.046	5.80	1.66	1.340
Sinter 22	24.38	15.02	57.01	1.70			1.09	72.30	0.035	3.10	1.50	1.360
Sinter 27	24.24	14.75	59.09	1.77			1.27	86.10	0.038	2.95	1.80	1.360
Sinter 32	23.43	14.53	58.41	1.57			1.16	79.56	0.046	3.80	1.90	1.360
Georgia kaolin												
Calcined	52.40	45.04	0.22	2.31								
Sinter 7	21.90	17.73	58.43	1.48			1.13	63.73	0.023	2.10	1.66	1.360
Sinter 20	21.90	17.73	58.43	1.48			1.40	78.30	0.043	3.04	1.66	1.360
Sinter 37	22.70	18.56	56.64	1.27			1.56	84.46	0.070	4.20	1.50	1.400
Sinter 3	21.90	17.73	58.43	1.48			1.39	78.40	0.038	2.71	1.66	1.410
WL-1 (Illite)												
Calcined	60.41	24.21	0.53	8.07	1.90	2.08						
Sample leached with HCl												
Sinter 30	26.07	9.82	57.95	4.03			0.78	79.13	0.041	5.00	1.90	1.360
Sinter 38	26.94	9.60	59.63	1.67			0.74	77.34	0.026	3.40	1.90	1.400

{ K<sub>2</sub>O Na<sub>2</sub>O  
1.79 percent }

{ 25 min.  
leach  
{ 2 : 1 ::  
Na<sub>2</sub>CO<sub>3</sub> :  
Al<sub>2</sub>O<sub>3</sub>  
in leach }

TABLE 7.—*Partial chemical analyses of sinters*

Sinter	SiO <sub>2</sub> , percent	Al <sub>2</sub> O <sub>3</sub> , percent
EL-60-6	22.47	17.11
EL-69-2	23.34	15.22

water. Also some were leached with 15 percent sodium carbonate solutions and salt (Table 9).

The highest single extraction of alumina, 85.3 percent, was made on a sinter of clay EL-69-2 using a solution without salt. Next highest, 84.3 percent, was on a sinter of clay EL-60-6, with salt. The insoluble compound sodalite ( $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{NaCl}$ ) is believed to form more or less during the leach, when salt is used in the leaching solution, thus reducing alumina extraction. For the same reason the percentage of silica to alumina  $\left[ \frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \right]$  in the aluminate extract is lower where salt is employed. Compare results shown in Table 6, where no salt was used, with those of Table 9. Results also indicate that for best extraction the mole ratio of Na<sub>2</sub>O in the leaching solution to Al<sub>2</sub>O<sub>3</sub> in the sinter should be from 2 : 1 to 2 : 4. Sinters leached with 15 percent sodium carbonate and salt solutions showed rather poor extraction due to the low volume of leaching agent compared to the mass of sinter. A thick pulp formed making filtering difficult. It is believed trouble from this source would be less in a plant of commercial size.

The effect of various amounts of sodium chloride on alumina extraction and the silica content of the extract, when added to sodium carbonate leaching solutions, is shown in Tables 9, 10, and 11. Sodium chloride in excess of 150 grams per liter is believed to reduce greatly alumina extraction by forming insoluble sodalite which remains in the solid residue, and such excess was not used.

#### ANNEALING OF SINTERS

On heating a mixture to sintering temperature a certain amount of viscous or molten material is formed which is probably a solution of calcium aluminate in beta dicalcium silicate. On slow cooling through the solidus line and below, the beta silicate inverts to the gamma allotropic form at 675° C. with an ex-

TABLE 8.—Partial analyses of annealed sinters\*

Sample	SiO <sub>2</sub> , percent	Al <sub>2</sub> O <sub>3</sub> , percent
EL-60-6a	23.14	17.48
EL-60-6a'		16.48
EL-69-2a	23.20	16.20
EL-69-2a'		16.20

\* Extraction data of annealed sinters are given in Table 10.

pansion of volume. This causes dusting and the liberation of calcium aluminate. If the cooling is rapid, inversion is retarded and aluminate may be held in glassy beta silicate. In annealing, the sinter is reheated to 1300° C. for 1 hour and then the temperature is slowly dropped to 1200° C. over a period of 1½ hours. The treatment is supposed to promote the change of beta silicate from glassy to granular form, give more complete dusting, and provide more efficient leaching because of better separation of the aluminate.

TABLE 9.—Sinter extraction data after leaching with sodium carbonate solutions containing sodium chloride only (Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Runnels)

Sample	Sinter	Solvent	Salt in solvent g/l	Mole ratio Na <sub>2</sub> CO <sub>3</sub> in solvent to Al <sub>2</sub> O <sub>3</sub> in sinter	Volume, cc	Unpurified filtrate			
						Al <sub>2</sub> O <sub>3</sub> , g/l	SiO <sub>2</sub> , g/l	SiO <sub>2</sub> × 100 SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	Recovery of Al <sub>2</sub> O <sub>3</sub> , percent
1	EL-60-6	6%Na <sub>2</sub> CO <sub>3</sub>		1.8:1	184	15.06	0.2	1.31	81.3
2	do	do	75	1.66:1	140	18.49	0.156	0.82	75.6
3	do	do	75	2:1	185	15.5	0.16	1.02	83.8
4	do	do	150	1.66:1	164	15.89	0.096	0.60	76.2
5	do	do	150	2:1	201	14.33	0.104	0.72	84.3
37	EL-69-2	do		2:1	201	12.67	0.172	1.34	83.6
28	do	do	75	2:1	217	11.30	0.132	1.15	80.4
23	do	do	75	2:1	192	12.35	0.144	1.15	77.8
27	do	do	150	2:1	171	12.50	0.124	0.99	70.1
24	do	do	150	2:1	191	11.39	0.132	1.15	71.2
25	do	do		2.4:1	206	12.60	0.048	0.38	85.3
26	do	do	75	2.4:1	229.5	11.10	0.112	0.99	83.6
33	do	do	75	2.4:1	230	10.58	0.132	1.22	80.9
34	do	do	150	2.4:1	212.5	10.61	0.108	1.01	74.2
6	EL-60-6	15%Na <sub>2</sub> CO <sub>3</sub>		1.66:1	184	13.06	0.144	1.09	70.3
7	do	do		2:1	196	13.9	0.20	1.42	79.8
9	do	do	75	2:1	175	15.06	0.184	1.21	76.8
8	do	do	150	2:1	170	12.33	0.04	0.32	68.0
11	do	do	150	1.66:1	178	13.24	0.108	0.73	68.7

**TABLE 10.**—*Annealed sinter extraction data after leaching annealed sinters with sodium carbonate solutions containing sodium chloride only (Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Runnels)*

Sample	Sinter	Solvent	Salt in solvent g/l	Mole ratio Na <sub>2</sub> CO <sub>3</sub> in solvent to Al <sub>2</sub> O <sub>3</sub> in sinter	Volume, cc	Unpurified filtrate			Recovery of Al <sub>2</sub> O <sub>3</sub> , percent
						Al <sub>2</sub> O <sub>3</sub> , g/l	SiO <sub>2</sub> , g/l	$\frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	
12	EL-60-6a*	6%Na <sub>2</sub> CO <sub>3</sub>		2:1	216	13.16	0.032	0.24	81.3
13	do	do	75	1.66:1	223	12.02	0.064	0.53	76.9
14	do	do	75	2:1	203	13.64	0.12	0.87	79.3
15	do	do	150	1.66:1	194	13.52	0.096	0.70	75.1
16	do	do	150	2:1	210	13.53	0.064	0.40	81.3
35	do	do	75	2.4:1	217	12.57	0.112	0.87	78.0
36	do	do	150	2.4:1	207	13.47	0.10	0.74	79.7
53	EL-60-6a'***								
	14.2 gms.	do	150	2:1	209	8.3			74.1
54	do	do	150	2.4:1	218	8.02			74.8
17	EL-60-6a'	15%Na <sub>2</sub> CO <sub>3</sub>		2:1	220	12.2	0.08	0.65	76.9
18	do	do	75	1.66:1	202	9.73	0.024	0.24	56.3
19	do	do	75	2:1	234	12.27	0.08	0.65	82.2
20	do	do	150	1.66:1	188	11.90	0.012	0.10	63.9
21	do	do	150	2:1	200	11.46	0.04	0.35	65.6
30	EL-69-2a	6%Na <sub>2</sub> CO <sub>3</sub>		2:1	231	10.77	0.172	1.58	76.6
31	do	do	75	2:1	185	12.36	0.108	0.86	70.6
32	do	do	150	2:1	228	9.84	0.088	0.88	70.0
55	EL-69-2a'	do		2:1	232	9.99			71.5
56	do	do	75	2:1	217	10.52	0.116	1.05	70.4
57	do	do	75	2.4:1	208	10.70			68.9

\*a Indicates annealed, cooled to 1200° C. in one-half hour.

\*\*a' Indicates annealed, cooled to 1200° C. in 1½ hours.

**TABLE 11.**—*Effect of sodium chloride in sodium carbonate leaching solutions (average of all tests) (Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Runnels)*

Sintered clay	Sodium carbonate solution, percent	No NaCl		NaCl, 75 g/l		NaCl, 150 g/l	
		Al <sub>2</sub> O <sub>3</sub> , percent	$\frac{\text{SiO}_2 \times 100^*}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$ in extract	Al <sub>2</sub> O <sub>3</sub> , percent extraction	$\frac{\text{SiO}_2 \times 100^*}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$ in extract	Al <sub>2</sub> O <sub>3</sub> , percent extraction	$\frac{\text{SiO}_2 \times 100^*}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$ in extract
EL-60-6	6	81.3	1.33	79.7	0.93	80.2	0.66
do	15	75.0	1.27	76.8	1.22	68.4	0.53
EL-60-6a	6	81.3	0.24	78.1	0.79	79.0	0.65
do	15	76.9	0.65	69.2	0.44	64.8	0.23
EL-69-2	6	84.5	0.68	80.7	1.14	71.8	1.01
EL-69-2a	6	76.6	1.58	70.6	0.87	70.0	0.89
Averages		79.3	0.96	75.4	0.90	72.4	0.66

\* Extract not purified.



TABLE 12.—Summary of leaching sinters with sodium carbonate and sodium chloride solutions, showing highest and lowest individual recoveries of  $\text{Al}_2\text{O}_3$  from sinter and conditions involved (Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Runnels)

Sample	Sinter	$\text{Na}_2\text{CO}_3$ , percent	High extraction		Low extraction		$\text{Al}_2\text{O}_3$ recovery, percent
			Salt, g/l	Mole ratio $\text{Na}_2\text{O}$ in solvent to $\text{Al}_2\text{O}_3$ in sinter	Salt, g/l	Mole ratio $\text{Na}_2\text{O}$ in solvent to $\text{Al}_2\text{O}_3$ in sinter	
5	EL-60-6	6	150	2:1			84.3, highest
2	EL-60-6	6			75	1.66:1	75.6, lowest
16	EL-60-6a*	6	150	2:1			81.3, highest
15	EL-60-6a	6			150	1.66:1	75.1, lowest
53	EL-60-6a'**	6	150	2.4:1			74.8, highest
54	EL-60-6a'	6			150	2:1	74.1, lowest
19	EL-60-6	15	75	2:1			82.2, highest
18	EL-60-6	15			75	1.66:1	56.3, lowest
26	EL-69-2	6	75	2.4:1			83.6, highest
29	EL-69-2	6			150	2:1	70.1, lowest
31	EL-69-2a	6	75	2:1			70.6, highest
32	EL-69-2a	6			150	2:1	70.0, lowest
56	EL-69-2a'	6	75	2:1			70.4, highest
57	EL-69-2a'	6			75	2.4:1	68.9, lowest

\*a Indicates annealed, cooled at 1200° C. in one-half hour.

\*\*a' Indicates annealed, cooled to 1200° C. in 1½ hours.

Two sets of sinters were annealed but gave lower extraction results, especially sample EL-69-2a (Table 8), than the unannealed samples. The time in cooling from 1300° C. to 1200° C. for the first group, designated "a", was 30 minutes and for the second group, designated "a'," was 1½ hours. The dusting characteristics differed. The first group dusted completely; sample EL-60-6a in 3 hours, sample EL-69-2a in 15 hours. The second group dusted poorly—sample EL-69-2a' required 2 days. Sample EL-60-6a' dusted rapidly to the extent of 84 percent and the balance, which failed to dust, was removed before leaching. The second group briquettes, where in contact with the carbon discs on which they rested, were of a much lighter color than the first group, indicating reduction. The material which failed to dust, or dusted poorly, came from this section. These sinters contain small amounts of iron, titanium, and magnesium as oxides. At the prolonged annealing temperature they probably reacted to form slag which tended to inhibit dusting.

The average silica content of the extract from annealed sinters is lower than that from the unannealed sinters, owing prob-

ably to the formation of more insoluble calcium silicate in the sinter with the prolonged time of sintering. The poorest extraction was obtained when the ratio of  $\text{Na}_2\text{O}$  in the solvent to  $\text{Al}_2\text{O}_3$  in the sinter was lowest.

#### DISCUSSION OF PURIFICATION PROCESSES

The desiliconization experiments indicate the high efficiency of sodalite in removing silica. Of 32 tests made, 18, or 56 percent, yielded solutions with silica to alumina ratios of 0.06 percent or lower, the amount allowable in high-grade alumina. Considering the factors involved—the use of different amounts of seed and salt and the time of boiling, all of which were varied—the results appear satisfactory and indicate desiliconization can be accomplished by observing proper precautions. A factor not conducive to good results was the use of pyrex beakers from which silica could have dissolved on boiling the alkaline solutions. Some special corrosion resistant beakers were also used and should have been used entirely. Glass would not be used as a container if this operation were conducted on a commercial scale. Complete desiliconization tests are shown in Table 13.

Definite conclusions were not reached as to the length of time the solution with seed should be boiled. It depends somewhat on the quantity of silica to be removed and the amount of seed used. Best results were obtained by boiling from 1 to 1½ hours (Table 14).

*Loss of alumina in seeding.*—The approximate loss of alumina in seeding calculated from the 32 tests completed is 5 percent of the alumina content of the solution at the start of seeding. This alumina contributes to the formation of more seed. It is really not a total loss as it can be used for further seeding operations or, because it contains about 35 percent alumina, after calcination to remove water it can be recycled as ore.

*Synthetic sodalite.*—The sodalite used in these experiments was made as follows. Kaolin was first activated by heating at 700° C. for 1 hour. A batch of 200 grams of this dehydrated kaolin, 150 grams of  $\text{NaCl}$ , 100 grams of  $\text{NaOH}$ , and 400 cc of water, was kept at 150° C. in an autoclave for 4 days. The product was then removed, washed with hot water, and dried at 110° C.

TABLE 13.—*Desiliconization of sodium aluminate solutions* (Analyses in State Geological Survey geochemistry laboratory under supervision of Russell Runnels)

Sample no.	Original solution			Desiliconized solution				Boiling time, hours	Seed g/l	SiO <sub>2</sub> removed, percent
	Al <sub>2</sub> O <sub>3</sub> , g/l	SiO <sub>2</sub> , g/l	$\frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	Al <sub>2</sub> O <sub>3</sub> , g/l	SiO <sub>2</sub> , g/l	$\frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	NaCl g/l			
2	18.47	0.156	0.82	18.00	0.012	0.06	75	1	10	92
3	15.50	0.16	1.02	15.19	0.009	0.06	75	1	7	94
9	15.01	0.184	1.21	15.02	0.008	0.053	75	1	7	95
14	13.64	0.12	0.87	12.78	0.017	0.13	75	1	6	86
15	13.52	0.096	0.70	13.20	0.022	0.16	150	1	7	77
19	12.27	0.08	0.65	12.70	0.001	0.008	75	1	5	98
21	11.46	0.04	0.35	11.19	0.001	0.008	150	1	6	97
4	15.89	0.096	0.60	14.41	0.007	0.048	150	1	4	92
11	13.24	0.108	0.73	12.94	0.003	0.023	150	1	4	97
16	13.52	0.064	0.40	13.13	0.018	0.13	150	1	3	72
31	12.36	0.108	0.86	10.19	0.028	0.27	75	1	3	74
32	9.84	0.088	0.88	9.01	0.025	0.27	150	1	3	72
50	13.46	0.134	0.99	13.46	0.003	0.022	75	1	26	98*
58	12.38	0.163	1.30	10.03	0.001	0.010	150	1	10	99*
59	12.38	0.163	1.30	10.03	0.004	0.039	150	1	16	97*
23	12.35	0.144	1.15	10.92	0.002	0.019	75	1.5	7	98
24	13.85	0.132	1.15	10.91	0.001	0.009	150	1.5	7	99
35	12.57	0.112	0.87	12.00	0.032	0.260	75	1.5	6	71
36	13.47	0.10	0.74	12.41	0.014	0.11	150	1.5	6	86
33	10.58	0.132	1.22	8.81	0.045	0.51	75	1.5	6	66**
34	10.61	0.108	1.01	10.34	0.023	0.22	150	1.5	6	79**
26	11.10	0.112	0.99	9.98	0.026	0.26	75	1.5	3	77
28	11.30	0.132	1.15	11.37	0.033	0.29	75	1.5	3	75**
29	12.50	0.124	0.99	12.71	0.009	0.07	150	1.5	4	93
51	13.49	0.134	0.99	13.47	0.008	0.059	75	1.5	26	94*
60	12.38	0.163	1.31	10.03	0.001	0.01	150	1.5	15	99*
43	13.76	0.144	1.04	13.76	0.008	0.058	150	2.0	10	94**
44	13.76	0.144	1.04	13.76	0.006	0.043	150	2.0	10	96
45	13.76	0.144	1.04	13.76	0.006	0.043	150	2.0	10	96
52	13.46	0.134	0.99	13.47	0.022	0.163	75	2.0	26	83*
61	12.38	0.163	1.31	10.03	0.003	0.029	150	2.0	15	98*
49	13.46	0.134	0.99	13.47	0.012	0.089	75	0.5	26	91

\* Indicates chemically resistant beaker used.

\*\* Indicates seed had been used before.

TABLE 14.—*Seed boiling time on successful desiliconizing experiments*

Number of tests	Weight of seed added g/l	Hours of boiling	Average $\frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$
10	9.5	1	.033
4	12.0	1.5	.024
4	11.0	2.0	.043

*Other processes.*—Many unsuccessful attempts were made to purify aluminate solutions from the lime sinter process by other methods. These include the use of lime, both solid and as milk of lime, and carbon dioxide gas. A considerable portion of the silica could be removed but never enough to give the desired purity. Carbon dioxide will effectively remove silica from solutions of the soda-lime process by fractional precipitation as silicic acid (Kinney, 1943), but not from those of the lime-sinter process, because although both contain sodium aluminate, the lime-sinter filtrate also has considerable sodium hydroxide. Since using sodalite seeding other methods of purification have been abandoned.

#### SINTER RESIDUES

About 7 tons of residue are produced in extracting 1 ton of alumina; therefore the possibilities for profitable disposal of the residue are of interest. Its suitability for the manufacture of Portland cement is well known. Other uses are for fertilizer, plastics, industrial fillers, and as a clarifying filter for certain solutions. Analyses of residual sinters after leaching are shown in Table 15.

Based on the amounts of alumina in sinter and residue, the losses of alumina in the lime-sinter process are 17.6 percent and 15.2 percent in sinters from clays EL-60-6 and EL-69-2 respectively. The amounts of soda ash and salt lost are largely dependent on the efficiency of washing. Such losses are low but could not be accurately determined as the sodium oxide shown in the analyses comes from both the sodium chloride and car-

TABLE 15.—*Analyses of sinter residues*

Constituent	EL-60-6	EL-69-2
SiO <sub>2</sub>	18.45	20.76
Al <sub>2</sub> O <sub>3</sub>	3.02	2.32
Fe <sub>2</sub> O <sub>3</sub>	0.54	0.93
TiO <sub>2</sub>	0.55	0.42
CaO	48.46	52.97
MgO	0.50	0.82
K <sub>2</sub> O (total)	0.18	0.28
Na <sub>2</sub> O (total)	2.75	1.43
Cl (chloride)	3.14	1.64
Remainder by difference (mostly CO <sub>2</sub> and H <sub>2</sub> O)	22.41	18.43

bonate used as reagents as well as from the small amount present in the original ore.

#### ALUMINA CONTENT OF SOLUTIONS

The concentration of alumina in solutions should preferably be from 40 to 80 grams per liter. Obviously the greater the concentration the less volume required for the same output. Another important reason is that alumina precipitated from concentrated solutions contains less silica. In practice, only three-fourths of the alumina contained is precipitated in any one cycle. The solution is then recycled for further leaching. Under these conditions high-grade alumina can be precipitated even though the solution contains as much as 0.13 gram per liter silica (Archibald, 1948).

In the experimental work covered by this report the alumina averaged 15 grams per liter. In the laboratory there are difficulties in obtaining concentrated solutions which are less prevalent in plant operation. Extraction results, however, even though working with dilute solutions, are an accurate measure of what can be accomplished on a larger scale, and with richer solutions.

#### THE LIME-SINTER PROCESS VERSUS THE SODA-LIME-SINTER PROCESS

Considering results obtained in testing Kansas clays by both the lime-sinter and the soda-lime-sinter processes (Kinney, 1943) the former appears definitely the better for the following reasons. (1) The extraction of alumina is about 15 percent greater. (2) Consumption of soda ash is less. Also, in the lime-sinter process soda ash is regenerated in solution and can be recycled at once, while in the soda-lime-sinter method evaporation of solutions is necessary because the ash is used in solid form. (3) Desilicization is probably cheaper. Both processes have effective means of removing silica, but sodalite seeding requires less control and would probably be less expensive than fractional precipitation by carbon dioxide as required in the soda-lime process.

TABLE 16.—*Melting points of clay EL-69-2 with and without added alumina*

Clay		Alumina added, percent	Total Al <sub>2</sub> O <sub>3</sub> , percent	Conditions under which sample failed to melt	
				Seeger cone	Temp. °F.
EL-69-2		none	23.70	27	2921
do	beneficiated	none	32.23	31	3056
do	do	5	35.45	32½	3137
do	do	10	38.39	33	3173
do	do	15	41.07	34	Insufficient heat to test at cone 34.
do	do	20	43.50	34	do

### PREPARATION OF SUPER-DUTY FIRE-BRICK CLAYS BY ADDING CRUDE ALUMINA

Melting point cones were prepared by adding ground alumina to clay using polyvinyl alcohol as a binder. Melting points were determined by comparing with Seger cones. The alumina was obtained as described by precipitation from impure solutions with carbon dioxide and probably contained as much as 3.5 percent silica. Results of these tests are shown in Table 16.

The melting point of the raw clay EL-69-2, containing 23.70 percent alumina, used in the preceding test is not particularly high, being a little more than 2921° F. Other Kansas clays which might have been used have melting points of 3000° F. or more before beneficiation. Table 17 shows a classification of fire-clay refractories. Comparing it with Table 16 it is evident that any type of fire-clay brick, including super-duty fire-clay brick, can be made from ordinary Kansas fire clay by first beneficiating the clay and then adding as much as 10 percent crude alumina as produced by the lime-sinter process without desiliconization. These tests also suggest that sillimanite or other high-alumina

TABLE 17.—*A.S.T.M. standard classification of fire-clay refractories*  
(A.S.T.M., 1949, Designation: C 27-41)

Classification	Description
Super-duty fireclay brick:	A fireclay brick having a pyrometric cone equivalent not lower than cone 33.
High-duty fireclay brick:	Pyrometric cone equivalent (P.C.E.) not lower than cone 31-32.
Intermediate-duty fireclay brick:	Pyrometric cone equivalent not lower than cone 29.
Low-duty fireclay brick:	Pyrometric cone equivalent not lower than cone 19.



refractories could also be made from beneficiated Kansas clay enriched with alumina produced by the lime-sinter process. Pure sillimanite contains 62.85 percent alumina and 37.15 percent silica and melts at 3280° F.

### FLOW SHEET OF THE LIME-SINTER PROCESS FOR EXTRACTING ALUMINA FROM CLAY

A tentative flow sheet of the lime-sinter process for the extraction of alumina from clay is suggested in Figure 3. It should be tried for defects in a pilot plant before considering larger scale operation.

One apparent problem is that of limiting the volume of sodium carbonate leaching solution, which is regenerated in the process and must be recycled, despite additions of wash water in every cycle. Some wash water is of course discarded with the sinter residue. The use of sensible heat in the discharged kiln gases to eliminate the excess by evaporation may be the answer. Some pure water condensed in this operation could be used to wash the precipitated aluminum hydroxide.

The flow sheet shows conventional filtering being used to separate the leached sinter from aluminate solution. It is possible the use of counter current decantation washing of the residue, after it leaves the settling tank, would be more satisfactory. Aside from those mentioned, there seem to be no problems of consequence associated with the flow sheet.

### CONCLUSIONS

In appraising the lime-sinter process, tests have been conducted under varying conditions to determine the best method of operation. Probably no one set of conditions is suitable for every Kansas clay, but in general, by following procedures giving the best results, as shown in this report, net recoveries of 80 to 84 percent of the alumina, in the purest commercial form, can be obtained from beneficiated Kansas clays. Further tests with annealed sinters might show greater recoveries on certain clays.

For the lime-sinter process, clay, limestone, water, fuel, and soda ash are required. Kansas has the first four in abundance

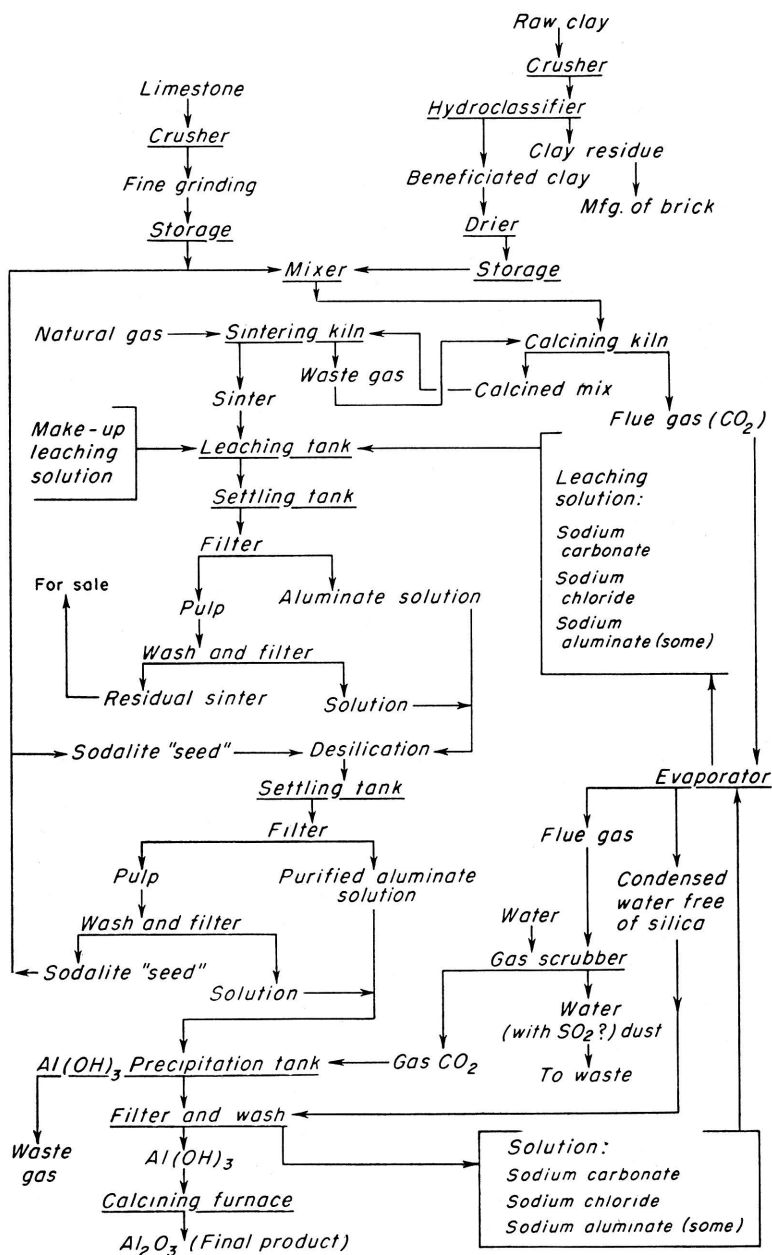


FIG. 3.—Flow sheet of lime-sinter process for extracting alumina from Kansas clay.

and the manufacture of soda ash may soon start in the State. Compared with other states Kansas is in a favorable position to produce alumina when and if clay can compete with bauxite as an ore.

The advantages of the lime-sinter process, besides giving good extraction, are (1) small loss of alkali, (2) all steps can be carried out at atmospheric pressure, and (3) the process is simple and no unusual equipment is required. A disadvantage is the limestone needed—about 2.5 tons per ton of clay.

The competitive production of metallic aluminum under existing economic conditions has never been seriously considered as a possibility in Kansas, partly because of a lack of abundant cheap power in the State. Even this view may need revision in the face of recent developments where, in two new aluminum plants in Texas, Diesel engines to supply power for the aluminum reduction cells are operated with natural gas—a mineral resource with which Kansas is abundantly endowed. The production of alumina of metallurgical grade to be shipped elsewhere for conversion to metallic aluminum or production of alumina of a lower grade to be used locally as an addition to existing clay in the manufacture of high-alumina refractories are potentialities that may be worthy of serious consideration by Kansas industry in the not too distant future.

## REFERENCES

- American Society for Testing Materials (1949) A.S.T.M. Standards, part 3, cement, concrete, ceramics, thermal insulation, road materials, water-proofing, soils: Am. Soc. Testing Materials, Baltimore, Md., pp. 1-1344.
- ARCHIBALD, F. R. AND JACKSON, C. F. (1944) Alumina from clay by the lime-sinter method: Am. Inst. Mining and Metal. Engineers Trans., vol. 159, pp. 227-238, figs. 1-4.
- ARCHIBALD, F. R. AND NICHOLSON, C. M. (1948) Alumina from clay by the lime-sinter method II: Am. Inst. Mining and Metal. Engineers, Metals Technology, Tech. Paper 2390, pp. 1-25, figs. 1-13.
- EDWARDS, J. D., FRARY, F. C., AND JEFFRIES, ZAY (1930) The aluminum in dustry, aluminum and its production: McGraw-Hill Book Co., New York, vol. 1, pp. 1-358, figs. 1-63.
- FLINT, E. P., and others, (1946) Extraction of alumina from clays and high-silica bauxites: Natl. Bur. Standards, Jour. Research, vol. 36, pp. 63-106, figs. 1-18.
- GRIM, R. E., MACHIN, J. S., AND BRADLEY, W. F. (1945) Amenability of various types of clay minerals to alumina extraction by the lime-sinter and lime-soda sinter process: Illinois Geol. Survey, Bull. 69, pp. 1-77, figs. 1-24.
- KINNEY, E. D. (1943) A process for extracting alumina from Kansas clay: Kansas Geol. Survey, Bull. 47, pt. 4, pp. 113-136.

- PLUMMER, NORMAN, AND ROMARY, J. F. (1947) Kansas clay, Dakota formation: Kansas Geol. Survey, Bull. 67, pp. 1-241, figs. 1-17, pls. 1-7.
- REYNOLDS, R. J. JR. (1951) Reynolds Metal Company, Annual Report for 1950, pp. 1-22.
- RUNNELS, R. T. (1951) Some high-calcium limestones in Kansas: Kansas Geol. Survey, Bull. 90, pt. 5, pp. 77-104, figs. 1-3, pls. 1-2.

# STATE GEOLOGICAL SURVEY OF KANSAS

## *Recent Publications*

- BULLETIN 71.** Ground-Water Resources of the Kansas City, Kansas, Area, by V. C. Fishel, 109 pages, 1948. Mailing charge, 25 cents.
- BULLETIN 72.** Upper Cambrian and Lower Ordovician Rocks in Kansas, by Raymond P. Keroher and Jewell J. Kirby, 140 pages, 1948. Mailing charge, 25 cents.
- BULLETIN 73.** Ground-Water Resources of Republic County and Northern Cloud County, Kansas, by V. C. Fishel, 194 pages, 1948. Mailing charge, 25 cents.
- BULLETIN 74.** The Stratigraphy and Structural Development of the Salina Basin of Kansas, by Wallace Lee, Constance Leatherock, and Theodore Botinelly, 155 pages, 1948. Mailing charge, 25 cents.
- BULLETIN 75.** Oil and Gas Developments in Kansas During 1947, by W. A. Ver Wiebe, G. E. Abernathy, J. M. Jewett, and Earl K. Nixon, 230 pages, 1948. Mailing charge, 25 cents.
- BULLETIN 76.** 1948 Reports of Studies (Six parts issued separately). Mailing charge, 10 cents each part.
- BULLETIN 77.** Oil and Gas in Eastern Kansas, with special reference to developments for 1944 through 1948, by J. M. Jewett, 308 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 78.** Oil and Gas Developments in Kansas During 1948, by W. A. Ver Wiebe, J. M. Jewett, and Earl K. Nixon, 186 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 79.** Geology and Ground-Water Resources of a Part of South-Central Kansas with special reference to the Wichita municipal water supply, by Charles C. Williams and Stanley W. Lohman, 455 pages, 1949. Mailing charge, 40 cents.
- BULLETIN 80.** Geology and Ground-Water Resources of Pawnee and Edwards Counties, Kansas, by Thad G. McLaughlin, 189 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 81.** Geology and Ground-Water Resources of Norton County and Northwestern Phillips County, Kansas, by John C. Frye and Alvin R. Leonard, 144 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 82.** 1949 Reports of Studies (Three parts issued separately). Mailing charge, 10 cents each part.
- BULLETIN 83.** Divisions of the Pennsylvanian System in Kansas, by Raymond C. Moore, 203 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 84.** Ground-Water Conditions in the Smoky Hill Valley in Saline, Dickinson, and Geary Counties, Kansas, by Bruce F. Latta, 152 pages, 1949. Mailing charge, 25 cents.
- BULLETIN 85.** Geology and Ground-Water Resources of Rice County, Kansas, by O. S. Fent, 142 pages, 1950. Mailing charge, 25 cents.
- BULLETIN 86.** 1950 Reports of Studies (Six parts issued separately). Mailing charge, 10 cents each part.
- BULLETIN 88.** Geology and Ground-Water Resources of Barton and Stafford Counties, Kansas, by Bruce F. Latta, 228 pages, 1950. Mailing charge, 25 cents.
- BULLETIN 89.** The Kansas Rock Column, by Raymond C. Moore, John C. Frye, J. M. Jewett, Wallace Lee, and Howard G. O'Connor, 132 pages, 1951. Mailing charge, 25 cents.
- BULLETIN 91.** The Manufacture of Lightweight Concrete Aggregate from Kansas Clays and Shales, by Norman Plummer and William B. Hladik, 100 pages, 1951. Mailing charge, 25 cents.
- BULLETIN 92.** Oil and Gas Developments in Kansas During 1950, by W. A. Ver Wiebe, J. M. Jewett, E. K. Nixon, R. K. Smith, and A.L.Hornbaker, 187 pages, 1951. Mailing charge, 25 cents.
- BULLETIN 93.** Geology and Ground-Water Resources of Lane County, Kansas, by Glenn C. Prescott, Jr., 126 pages, 1951. Mailing charge, 25 cents.
- BULLETIN 94.** Ground-Water Resources of Pawnee Valley, Kansas, by V. C. Fishel, 144 pages, 1952. Mailing charge, 25 cents.
- BULLETIN 95.** Geology and Ground-Water Resources of Lincoln County, Kansas, by Delmar W. Berry, 96 pages, 1952. Mailing charge, 25 cents.
- BULLETIN 97.** Oil and Gas Developments in Kansas During 1951, by W. A. Ver Wiebe, J. M. Jewett, E. D. Goebel, and A. L. Hornbaker, 188 pages, 1952. Mailing charge, 25 cents.
- VOLUME 11.** Geology, Mineral Resources, and Ground-Water Resources of Chase County, Kansas, by Raymond C. Moore, John Mark Jewett, Howard G. O'Connor, and R. Kenneth Smith, 49 pages, 1951. Mailing charge, 40 cents.
- KANSAS ROCKS AND MINERALS,** by Laura Lu Tolsted and Ada Swineford, 56 pages, 1948. Mailing charge, 5 cents.
- GROUND WATER IN SOUTHWESTERN KANSAS,** by John C. Frye and V. C. Fishel, 24 pages, 1949. Mailing charge, 5 cents.
- SCENIC KANSAS,** by Kenneth K. Landes, 16 pages, 1949. Mailing charge, 5 cents.



# STATE GEOLOGICAL SURVEY OF KANSAS

## BULLETIN 90

### 1951 REPORTS OF STUDIES

- PART 1. KANSAS PITTS AND QUARRIES**, by Robert O. Kulstad and Earl K. Nixon, pp. 1-12, pl. 1, March 15, 1951.
- PART 2. THE GEOLOGY OF THE DAVIS RANCH OIL POOL**, Wabaunsee County, Kansas, by R. Kenneth Smith and Ellis L. Anders, Jr., pp. 13-52, figs. 1-6, pls. 1-2, April 15, 1951.
- PART 3. COAL RESOURCES OF THE PERMIAN SYSTEM IN KANSAS**, by Walter H. Schoewe, pp. 53-68, figs. 1-4, pl. 1, April 15, 1951.
- PART 4. PHYSICAL PROPERTIES OF EASTERN KANSAS CRUDE OILS**, by Charles F. Weinaug, pp. 69-76, fig. 1, May 15, 1951.
- PART 5. SOME HIGH-CALCIUM LIMESTONES IN KANSAS**, by Russell T. Runnels, pp. 77-104, figs. 1-3, pls. 1-2, June 30, 1951.
- PART 6. GEOLOGIC STRUCTURES IN KANSAS**, by John Mark Jewett, pp. 105-172, figs. 1-2, August 15, 1951.
- PART 7. STUDIES OF PLEISTOCENE GRAVEL LITHOLOGIES IN NORTHEASTERN KANSAS**, by Stanley N. Davis, pp. 173-192, figs. 1-4, September 30, 1951.
- PART 8. BENEFICIATION OF KANSAS NUMBER FOUR SALT**, by Frank W. Bowdish, pp. 193-218, figs. 1-2, pl. 1, December 15, 1951.

## BULLETIN 96

### 1952 REPORTS OF STUDIES

- PART 1. KANSAS VOLCANIC ASH RESOURCES**, by J. Sheldon Carey, John C. Frye, Norman Plummer, and Ada Swineford, pp. 1-68, figs. 1-4, pls. 1-7, February 15, 1952.
- PART 2. COAL RESOURCES OF THE CRETACEOUS SYSTEM (DAKOTA FORMATION) IN KANSAS**, by Walter H. Schoewe, pp. 69-156, figs. 1-23, pls. 1-6, February 29, 1952.
- PART 3. OIL SHALE IN KANSAS**, by Russell T. Runnels, Robert O. Kulstad, Clinton McDuffee, and John A. Schleicher, pp. 157-184, figs. 1-2, pls. 1-3, March 15, 1952.
- PART 4. MINOR ELEMENTS IN KANSAS SALT**, by Russell T. Runnels, Albert C. Reed, and John A. Schleicher, pp. 185-200, pl. 1, April 15, 1952.
- PART 5. GEOLOGY AND GROUND-WATER RESOURCES OF THE KANSAS RIVER VALLEY BETWEEN LAWRENCE AND TOPEKA, KANSAS**, by Stanley N. Davis and William A. Carlson, pp. 201-276, figs. 1-8, pls. 1-7, June 1, 1952.
- PART 6. EXPERIMENTAL PRODUCTION OF FELDSPAR AND SILICA FROM SEVERAL RIVER SANDS IN KANSAS**, by Frank W. Bowdish and Russell T. Runnels, pp. 277-300, figs. 1-3, June 1, 1952.
- PART 7. AMENABILITY OF CERTAIN KANSAS CLAYS TO ALUMINA EXTRACTION BY THE LIME-SINTER PROCESS**, by E. D. Kinney, pp. 301-328, figs. 1-3, October 15, 1952.