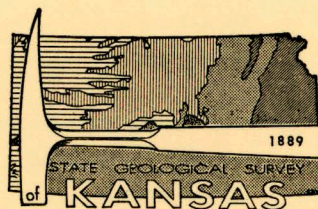


Preliminary Report on the Beneficiation of Some Kansas Clays and Shales

By Walter E. Hill, Jr., William B. Hladik,
and Wanda N. Waugh

**STATE
GEOLOGICAL
SURVEY
OF
KANSAS**

BULLETIN 165, PART 5



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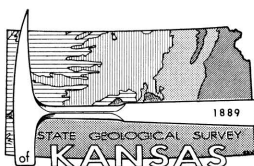
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Preliminary Report on the Beneficiation of Some Kansas Clays and Shales

ABSTRACT

Fifteen Kansas clays of differing physical properties were tested by sedimentation, acid, and Versene treatments. The amount and type of beneficiation was determined for various properties that would affect the clays' utilization for refractory, ceramic body, whiteware, stoneware, and other specialized applications. Some of the lighter colored clays were bleached almost white. Sedimentation and acid treatment significantly raised the firing temperatures of some kaolinitic clays from the Dakota Formation. However, the properties of the Pennsylvanian and Permian illitic shale samples were little affected by the treatments used.

Zusammenfassung

Fünfzehn Tone aus Kansas mit verschiedenen physikalischen Eigenschaften wurden durch Sedimentation, Säure und Behandlung mit Versene geprüft. Die Anzahl und Art der Aufbereitung war für verschiedene Eigenschaften, die die Verwendbarkeit der Tone für feuerfeste keramische Materialien, Porzellan, Steingut und andere Spezialanwendungen beeinflussten, festgelegt. Einige der heller gefärbten Tone wurden beinahe weiss gebleicht. Durch Sedimentation und Behandlung mit Säure wurden die Feuerungstemperaturen einiger Kaolinerden der Dakota Formation bedeutend erhöht. Die Eigenschaften pennsylvanischer und permischer illitischer Tonproben jedoch wurden durch die angewandten Verfahren nur wenig beeinflusst.

Resumen

Quince arcillas de Kansas con diferentes propiedades físicas fueron probadas con ácido, sedimentación y tratamientos de Verseno. La cantidad y el tipo de beneficiación fueron determinados para varias propiedades que afectarían la utilización de las arcillas en refractoría, cuerpo cerámico, porcelana, objetos de barro y otras aplicaciones especializadas. Algunas de las arcillas de color claro fueron blanqueadas. Sedimentación y tratamiento con ácido elevaron significativamente la temperatura de fogueo de algunas arcillas caoliniticas de la Dakota Formation; sin embargo, las propiedades de las muestras de lutitas illíticas del Pennsylvanian y del Permian fueron ligeramente afectadas por los tratamientos usados.

Résumé

On a essayé quinze argiles de variantes propriétés physiques par sédimentation, acide, et traitements de "Versene." On a déterminé la quantité et le type d'enrichissement pour les propriétés variées qui affecteraient l'utilisation de l'argile pour emplois réfractaires, emplois de corps céramique, de porcelaine, de poterie de grès, et d'autres emplois spécialisés. On a blanchi presque blanches quelques-unes des argiles d'une couleur plus claire. La sédimentation et le traitement acide a augmenté d'une manière significative les températures de la cuisson de quelques argiles kaolinitiques de la Dakota Formation. Cependant, les propriétés des échantillons de schistes illitiques des types Pennsylvaniens et Permians étaient peu affectées par les traitements employés.

INTRODUCTION

Kansas lacks a source of light- or white-firing clay in sufficient quantity to interest manufacturers of whiteware, dinnerware, tile, and pottery. At present almost all light-firing clay used in these products is shipped into the State from other areas. Present users of light-firing clay include one tile plant, a few small potteries, art and clay classes at colleges and universities, pottery classes in high schools, and hundreds of hobbyists. The total tonnage used might be greater if a source of suitable clay could be found in Kansas or one which could be up-graded by beneficiation at a cost comparable to or less than that of the imported material.

Potential sources of fireclays in Kansas have not been exploited; millions of tons of silicious fireclays, plastic fireclays, and impure plastic kaolinitic fireclays are available (Plummer and Romary, 1947; Plummer, Bauleke, and Hladik, 1960). Samples of some of these clays were included in this study.

The clays and shales selected for this preliminary study were not chosen entirely on the basis of possible commercial utilization, but also for their differences in properties.

Some of the Kansas clays as mined fall into the range of low- and medium-duty fireclays, but there is insufficient demand for them to warrant their continuous production. Deleterious compounds of sodium, potassium, magnesium, and calcium that occur naturally in fireclays function as active fluxes and reduce the vitrification or softening temperature of products fabricated from the clays, thus making them unsuitable for many high-temperature applications. Removal, at low cost, of part or all of these elements and compounds should result in a more salable product adapted to a greater variety of temperature applications.

Ferric iron, manganese, titanium, and vanadium compounds are the chief coloring materials in light-firing clays which make them unsuitable for use in whiteware, dinnerware, and other products demanding a white or light-colored ceramic body.

Chemical analyses of the raw clay samples were made. Differential thermal analyses (DTA) were made in order to determine the effect of the different treatments on gross mineralogic character and the lattice structure of the clays. For comparison with the untreated

samples, $R_2O_3^*$ and total iron determinations were made on the clay fractions after each of the various beneficiating treatments. Pyrometric cone equivalent (PCE) analyses were performed on the raw clay and clay fractions at the different stages of beneficiation. Fired-color data were collected and small test bricks were made.

ACKNOWLEDGMENTS

We wish to thank Norman Plummer for his advice on many phases of this study and Maynard Bauleke for the differential thermal analyses.

ECONOMIC CONSIDERATIONS

The upgrading of Kansas clays by physical or chemical treatment, or both, presumes the need for and salability of beneficiated clays. It would be necessary to mine and beneficiate a Kansas clay at a price competitive with the cost of similar clays from other states (including delivery to Kansas). Owing to increases in the price of clay and the trend toward increased shipping costs, the practicability of local production of specialized clays for a given market area or direct consumption into a manufactured product is increasing and can be expected to continue to increase. The total cost of chemicals involved in such beneficiation should be held to a minimum in actual production.

SAMPLES

The physical properties of clays are linked very closely to the chemical contaminants. Sodium, potassium, calcium, and magnesium compounds act as fluxes that lower the softening or melting temperature of the clay during firing. In addition, free CaO after firing may hydrate in air, causing spalling and cracking of the fired surface. These contaminants render many clays completely unsuitable for some applications. It was of interest to include in this investigation even the poorest clays available, in order to ascertain the effects of various methods of beneficiation.

The fifteen clay and shale samples listed (Table 1) are representative of the various types available for exploitation within the State. Two

* The total R_2O_3 value includes primarily Fe_2O_3 , and Al_2O_3 , but the RO_2 group consisting of Ti, Mn, and Zr oxides and P_2O_5 , where present, are included in this summation.

TABLE 1.—Kansas clays and shales used in beneficiation tests.

| KGS clay no. | County | Location | Stratigraphic position | Thickness, feet | Remarks | % of clay greater than 10 microns in size removed in sedimentation |
|----------------------|-----------|-----------|--------------------------------------|--------------------|--|--|
| <i>Pennsylvanian</i> | | | | | | |
| AL-2 | Allen | 33-25-18E | Lane-Bonner Springs Shale | 28.0 | Shale, light-gray, calcareous | 34.4 |
| CK-8 | Cherokee | 32-31-25E | Underclay under Neutral Coal | 6.0 | Clay, gray | 39.9 |
| FR-3 | Franklin | 23-17-19E | Weston Shale | 15.0 | Shale, yellow, weathered | 73.6 |
| <i>Permian</i> | | | | | | |
| M-5 | Marion | 34-21-1E | Wellington Shale | 14.5 | Shale, light-gray, calcareous, plastic | 58.6 |
| MP-20 | McPherson | 35-17-5W | Ninnescah Shale | 12.0 | Shale, light-gray and red, plastic | 43.2 |
| <i>Cretaceous</i> | | | | | | |
| C-27-13 | Cloud | 32-8-2W | Dakota Formation, Terra Cotta Member | 12.3 | Fireclay, gray, plastic (ball clay) | 4.8 |
| C-30-5 | do | 31-8-1W | do | 6.0 | Fireclay, high-duty, impure, kaolinitic | 15.0 |
| C-52 | do | 7,8-8-1W | do | 6.0 | Fireclay, light-gray, siliceous | 29.3 |
| C-53 | do | 5-8-2W | Dakota Formation, Janssen Member | 18.0 | Fireclay, light-gray, siliceous | 37.4 |
| C-77-C | do | 13-6-3W | do | 20.0 | Fireclay, yellow, siliceous | 33.3 |
| C-77-LB | do | 13-6-3W | do | 20.0 | Fireclay, light-gray, siliceous | 25.8 |
| EL-60-6 | Ellsworth | 19-15-9W | do | 4.1 | Fireclay, light-gray, some yellow, kaolinitic | 15.4 |
| O-5-6 | Ottawa | 18-11-4W | do | 4.2 | Fireclay, medium-duty, dark-gray, some red and yellow, plastic | 4.2 |
| O-40-3 | do | 5-9-2W | Dakota Formation, Terra Cotta Member | 6.3 | Fireclay, plastic (ball clay), gray to light-gray | 15.0 |
| OS-2 | Osborn | 12-7-15W | Blue Hill Shale | 58.3 | Shale, gray, montmorillonitic | 55.1 |

of the samples are of Permian age and three are of Pennsylvanian age; the other ten samples are Cretaceous in age.

LABORATORY PROCEDURES

Coarse sediment and silt consisting primarily of pyrite, calcite, quartz, and iron oxides and hydroxides were removed from samples of the clays by sedimentation. A 5-pound sample of clay was added slowly to 14 liters of distilled water and stirred vigorously for 30 minutes. After 3 minutes of settling the clay-water slurry was carefully decanted and the coarse residue dried and weighed. Much of the coarse fraction (greater than 10 micron) was removed in this step and a saving in the amount of chemicals needed in subsequent treatments was effected.

At this point the samples were divided into two groups (Fig. 1). Each group contained both good and poor quality clays. The eight clay samples of group I (Table 2) received a minimal chemical treatment of approximately the amount of chemicals that could be expended economically in beneficiation. The seven clays of group II received larger amounts of the same chemicals to determine whether the use of these increased amounts could be justified by improvement of the clays' properties.

All clay samples were first freed of carbonates by small additions of muriatic acid (HCl). Clays AL-2 and M-5 contained excessive amounts of carbonate of clay size and fine silt size but were retained for further testing.

To group I, muriatic acid was added in an amount proportional to 20 lbs. HCl/ton of clay remaining after sedimentation. To group II, muriatic acid was added to be proportional to 200 lbs. HCl/ton of clay. Both groups were leached in the acid solution for 48 hours.

The acid treatment removes varying amounts of sodium, potassium, calcium, magnesium, iron, and other metals. Some aluminum also may be removed; this is not desirable, but the loss of small quantities of it does not greatly affect the clays' properties. Acid treatment results in a hydrogen clay, and iron or aluminum from the clay lattice is substituted into the exchange positions of the clay (Grim, 1962). Fifty-gram samples were extracted after washing and were dried for analysis.

Tetra sodium ethylenediaminetetraacetate (tetra sodium EDTA, or Versene*), a chelat-

ing or sequestering agent for di- and trivalent metals, was used to remove some of the residual contaminants after the acid treatment. EDTA is expensive (\$0.50/lb. in 1962) compared with muriatic acid (about \$0.04/lb.) and only small quantities could be used economically. Use on a large scale, however, would permit economic recovery and reuse of the EDTA reagent (Martell and Calvin, 1952; Hill and Runnels, 1960). After the acid-soluble di- and trivalent metals had been removed, EDTA was used in the tests in the hope that there would be some preferential removal of iron. The use of the tetra sodium salt probably results in the reversion of the clay lattice to the sodium-substituted form; this addition of a flux consequently lowers the firing temperature of the clay. This change would be acceptable within limits if a white- or very light-gray-firing clay were obtained. Both group I and group II were treated with 6 lbs. EDTA/ton of clay. The samples were allowed to stand for one week in the EDTA reagent, with occasional agitation. The group I clays were allowed to settle and were then decanted, washed, and dried. Some clays completely deflocculated and would not settle. These were centrifuged and dried and then remixed with a distilled water wash; this process was repeated twice, and the clays were dried for analysis. The equivalent of 20 lbs. NaOH/ton of clay was added to group II clays in a slurry with the Versene reagent to determine if the addition of a base would reactivate and prolong the action of the Versene reagent. After one week of standing, with occasional stirring, the clays were adjusted to pH 7 with muriatic acid. They were then centrifuged and washed in the same manner as group I.

ANALYSES

Chemical analyses (Table 2) were performed on the raw clay samples as outlined by Hill, *et al.* (1961). For tests of the beneficiated clays a simple R_2O_3 - Fe_2O_3 determination (Table 3), excerpted from the scheme of analysis presented by Hill, *et al.* (1961), was considered sufficient for this preliminary study. The Fe_2O_3 and R_2O_3 values gave a good approximation of the effect of treatments on the removal of the primary coloring material.

Differential thermal analysis curves were produced by heating the clay samples in an alumina ceramic holder (inert alumina and calcined clay reference) at a programmed heat-

* Trademark Dow Chemical Company.

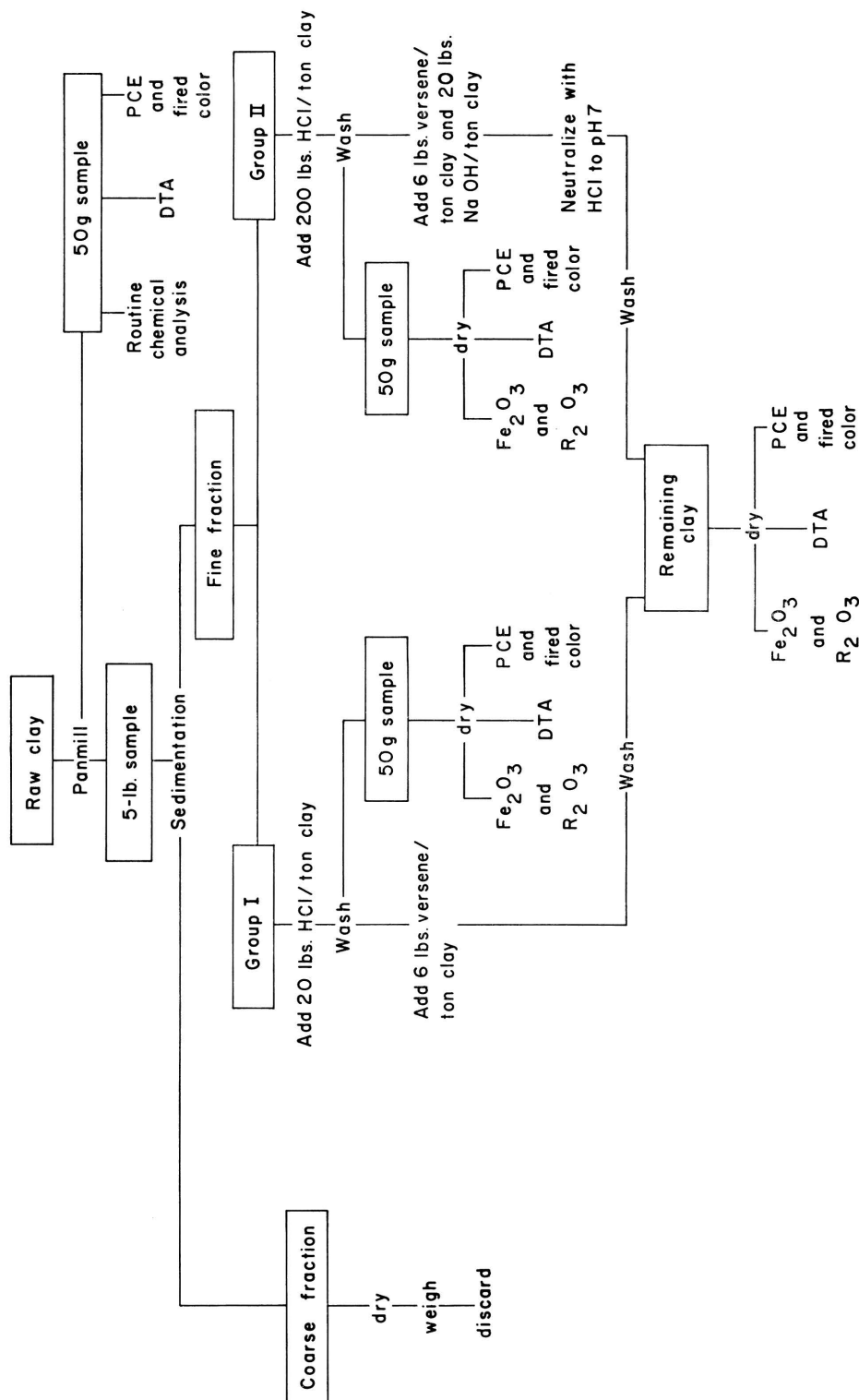


FIGURE 1.—Flow chart of clay and shale samples through beneficiation treatments. (For description, see "Laboratory Procedures.")

TABLE 2.—Chemical analyses of untreated clays (in weight percent).

| KGS clay no. | Laboratory sample no. | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | TiO ₂ | CaO | MgO | P ₂ O ₅ | SO ₃ | K ₂ O | Na ₂ O | S | LOI* at 1000°C | Total |
|-----------------|--------------------------|------------------|--------------------------------|--------------------------------|------------------|------|------|-------------------------------|-----------------|------------------|-------------------|-------|-------------------|--------|
| <i>Group I</i> | | | | | | | | | | | | | | |
| C-77-LB | 62285 | 71.36 | 16.54 | 3.63 | 1.15 | 0.22 | 0.15 | 0.01 | 0.11 | 0.61 | 0.04 | 0.08 | 6.25 | 100.07 |
| C-53 | 62286 | 69.05 | 20.09 | 1.67 | 1.00 | 0.30 | 0.16 | trace | 0.03 | 0.92 | 0.07 | 0.04 | 6.68 | 99.97 |
| C-77-C | 62287 | 72.48 | 15.11 | 4.52 | 1.24 | 0.21 | 0.15 | trace | 0.07 | 0.80 | 0.06 | nil | 5.10 | 99.74 |
| C-52 | 62288 | 68.99 | 19.96 | 1.47 | 1.20 | 0.19 | 0.32 | trace | 0.01 | 0.75 | 0.09 | nil | 6.61 | 99.59 |
| C-27-13 | 62289 | 59.25 | 26.27 | 2.81 | 0.41 | 0.34 | 0.67 | 0.04 | trace | 1.84 | 0.08 | nil | 8.12 | 99.83 |
| AL-2 | 62290 | 54.51 | 17.37 | 6.49 | 1.20 | 5.74 | 1.20 | 0.10 | trace | 3.06 | 0.87 | 0.09 | 9.16 | 99.70 |
| FR-3 | 62291 | 67.64 | 15.88 | 7.19 | 0.55 | 0.38 | 0.51 | 0.08 | trace | 2.45 | 0.73 | nil | 4.64 | 100.05 |
| CK-8 | 62292 | 62.87 | 20.54 | 3.57 | 2.31 | 0.08 | 0.34 | trace | trace | 2.31 | 0.21 | 0.09 | 7.31 | 99.54 |
| <i>Group II</i> | | | | | | | | | | | | | | |
| C-30-5 | 62318 | 59.93 | 24.53 | 3.59 | 1.42 | 0.61 | 0.08 | trace | 0.05 | 0.10 | 0.04 | nil | 9.30 | 99.65 |
| EL-60-6 | 62319 | 72.97 | 16.87 | 2.10 | 0.99 | 0.12 | 0.03 | 0.01 | 0.25 | 0.66 | 0.10 | trace | 5.76 | 99.86 |
| O-5-6 | 62315 | 61.54 | 23.78 | 3.80 | 1.03 | 0.27 | 0.11 | trace | 0.15 | 0.92 | 0.11 | nil | 7.94 | 99.65 |
| O-40-3 | 62317 | 74.81 | 15.09 | 1.54 | 1.16 | 0.51 | 0.33 | 0.01 | trace | 0.58 | 0.14 | nil | 5.37 | 99.54 |
| OS-2 | 62321 | 60.86 | 20.71 | 4.37 | 0.67 | 0.32 | 0.40 | 0.09 | 0.80 | 2.74 | 0.43 | 0.06 | 8.71 | 100.10 |
| M-5 | 62316 | 45.40 | 17.02 | 5.12 | 0.89 | 7.23 | 7.00 | 0.12 | 0.07 | 3.46 | 0.38 | trace | 13.35 | 100.04 |
| MP-20 | 62320 | 60.46 | 16.56 | 5.28 | 1.02 | 2.00 | 3.74 | 0.13 | trace | 2.99 | 1.13 | nil | 6.10 | 99.41 |

* Loss on ignition.

ing rate of 10°C per minute. Curves were recorded by electronic equipment described by Plummer, *et al.* (1954).

The PCE or pyrometric cone equivalent of a clay was derived by comparison of the softening or fusion point of test cones with standard pyrometric cones. For each sample a number of clay test cones were mounted alternately with standard cones in a circular fireclay plaque and heated at a specified rate until the clay cones and one of the standard cones bent over and touched the fireclay plaque simultaneously.

For each set of test cones 20 grams of clay was ground to pass through a 60-mesh Tyler standard series screen and then was put in small roasting dishes and calcined to 1750°F. A solution of 3 percent polyvinyl alcohol in water was added to the calcined clay until a stiff mud was formed. The mud was then pressed into a metal mold in the shape of a standard cone. After drying, these cones were mounted with standard cones in a test plaque. A Denver Fireclay Com-

pany gas-fired furnace designed for the purpose by the American Refractories Institute according to A.S.T.M.* Standard C-24-56 (1962, p. 417-420) was used.

The Munsell Book of Color (1929-1942) was used to determine the color of the fired bricks of the original, the acid treated, and the Versene treated samples. Generally any reduction in the amount of ferric iron in the sample is accompanied by a lighter color in the fired sample. Where a significant amount of calcium was removed from an iron-bearing clay the fired color tended to be darker, because calcium compounds partially mask the red color in fired clays.

RESULTS

The fifteen clays and shales tested exhibited significant differences in response to treatment.

* American Society for Testing and Materials.

TABLE 3.—Comparison of iron and R_2O_3 * values of raw clays and sedimented clays after acid and Versene treatments (in weight percent).

| KGS clay no. | Raw clay | | Clay after sedimentation and HCl treatment | | Clay after sedimentation, HCl, and Versene treatment | |
|-----------------|-----------|----------|---|----------|---|----------|
| | Fe_2O_3 | R_2O_3 | Fe_2O_3 | R_2O_3 | Fe_2O_3 | R_2O_3 |
| <i>Group I</i> | | | | | | |
| C-77-LB | 3.63 | 21.33 | 2.20 | 26.21 | 1.84 | 21.11 |
| C-53 | 1.67 | 22.76 | 1.94 | 32.94 | 1.47 | 22.54 |
| C-77-C | 4.52 | 20.87 | 4.67 | 33.05 | 3.28 | 22.82 |
| C-52 | 1.47 | 22.63 | 1.88 | 29.03 | 1.63 | 22.99 |
| C-27-13 | 2.81 | 29.49 | 2.27 | 30.20 | 2.15 | 28.32 |
| AL-2 | 6.49 | 25.16 | 7.33 | 27.91 | 7.01 | 27.08 |
| FR-3 | 7.19 | 23.62 | 7.70 | 30.31 | 7.26 | 30.38 |
| CK-8 | 3.57 | 26.42 | 1.84 | 27.37 | 1.67 | 26.50 |
| <i>Group II</i> | | | | | | |
| C-30-5 | 3.59 | 29.54 | 3.19 | 33.49 | 3.06 | 33.16 |
| EL-60 | 2.10 | 19.97 | 2.28 | 23.62 | 1.92 | 22.36 |
| O-5-6 | 3.80 | 28.61 | 2.93 | 28.38 | 2.71 | 26.93 |
| O-40-3 | 1.54 | 17.80 | 1.66 | 20.40 | 1.68 | 20.34 |
| OS-2 | 4.37 | 25.84 | 4.29 | 25.43 | 4.09 | 24.69 |
| M-5 | 5.12 | 23.03 | 6.26 | 26.83 | 6.30 | 26.97 |
| MP-20 | 5.28 | 22.99 | 5.71 | 23.99 | 5.30 | 22.24 |

* R_2O_3 value includes all ammonium hydroxide precipitated trivalent metals plus P_2O_5 , TiO_2 , MnO_2 , and ZrO_2 where present. The last four are normally present only in small quantities; therefore, a rough approximation of the percentage of Al_2O_3 is obtained by subtracting the Fe_2O_3 from the R_2O_3 .

The Pennsylvanian and Permian shales in general contained too much ferric iron for removal by the methods used. They also contained varying amounts of finely divided carbonates which reduced the effects of the acid and Versene treatments. The greatest beneficiation was effected in the marginal-quality Dakota fire-clays. Sedimentation and acid treatment significantly raised the PCE in several of the clays, and the combination of acid and Versene treatment lightened light-yellow clays to an off-white color, which would make the clays usable for a number of ceramic products.

Sedimentation of the clays and shales was performed to remove the silt, sand, and any coarser material, and varying amounts of these components were removed (Table 1). Comparison of the Fe_2O_3 and the R_2O_3 values of the raw clay and the clay after sedimentation and treatment with muriatic acid (Table 3) showed that significant changes in composition were brought about. The Fe_2O_3 and R_2O_3 values were increased in most of the clays, indicating removal of a large amount of siliceous silt and sand in the sedimentation treatment; in other clays these values decreased, showing removal of coarse particles of iron sulfides or oxides or both. The acid treatment was used to remove residual carbonates and acid-soluble compounds of the various fluxes and coloring elements. The much stronger acid treatment used on the group II samples induced little change in the amount of Fe_2O_3 or R_2O_3 removed. The treatment with the equivalent of 200 lbs. HCl/ton of clay in group II raised the PCE values only slightly for some of the Dakota clays and showed no advantage over the weaker acid treatment. Both treatments were relatively ineffective on the Pennsylvanian and Permian shales.

The greatest effect of the sedimentation and acid treatments was shown by C-77-C (one of the Dakota test clays) with 20 lbs. HCl/ton of clay, raising the PCE by 218°F. The PCE values for the other Dakota clays were raised at least 100°F, except for C-27-13 which was raised only 72°F (Table 4). Again, PCE values of the Pennsylvanian shales either were not greatly affected or were adversely affected by the HCl treatment except for CK-8 (the underclay) which exhibited an increase in fusion temperature of about 100°F.

The Versene treatment was used primarily to lighten the fired color by sequestration and removal of iron and other di- and trivalent ele-

TABLE 4.—Pyrometric cone equivalents of test clays before and after treatment.

| KGS clay no. | Original sample | HCl treated | Versene treated |
|-----------------|-----------------|-------------|-----------------|
| <i>Group I</i> | | | |
| C-77-LB | 20* | 26-27 | 23 |
| C-53 | 23 | 30 | 23 |
| C-77-C | 18 | 27 | 18-19 |
| C-52 | 26 | 31 | 26 |
| C-27-13 | 26+ | 29 | 29 |
| AL-2 | 6 | 6 | 7 |
| FR-3 | 13 | 11 | 14 |
| CK-8 | 20-23 | 28 | 23-26 |
| <i>Group II</i> | | | |
| C-30-5 | 31+ | 32 | 32 |
| EL-60-6 | 26-27 | 28 | 28 |
| O-5-6 | 29-30 | 31 | 30 |
| O-40-3 | 20 | 26 | 23 |
| OS-2 | 10 | 11 | 12 |
| M-5 | 5 | 5 | 6 |
| MP-20 | 3 | 5 | 6 |

* Temperature equivalents of the pyrometric cones used, in degrees Fahrenheit:

| | | | |
|----------|----------|----------|----------|
| 18—2743° | 23—2894° | 28—2971° | 31—3054° |
| 19—2782 | 26—2921 | 29—2993 | 32—3121 |
| 20—2820 | 27—2961 | 30—3009 | 33—3166 |

ments from the clay. Table 5 shows the Munsell color descriptions of the clays after various treatments. In general the fired colors of the Dakota clays were lightened slightly with succeeding beneficiation treatments. The red-firing Pennsylvanian and Permian shales tended to darken with acid treatment owing to removal of calcium carbonate, and they either remained dark or lightened only slightly with Versene treatment.

Dakota clay C-53 was beneficiated from ivory (2.5 Y 9/3) to off-white (2.5 Y 9/2)—sufficient decolorization for use as a white ceramic body. Clays C-52 and CK-8 were lightened to a cream color (2.5 Y 8/3-4), and clay O-40-3 was lightened to an ivory color (10 YR 9/3), but none were acceptable for white body ceramics unless slightly underfired.

The Versene treatment used on group I removed iron and aluminum from the Dakota clays in greater quantity than would have been expected, considering the extremely low concentration of EDTA used. The R_2O_3 was

lowered as much as 11.5 percent by EDTA solutions calculated to remove 0.1 percent or less as the stable chelate. However, iron or aluminum is moved to the exchange positions of the clay by laboratory conversion to the acid clay, and dilute Versene solutions remove iron and aluminum from the clay lattice of acid clays. The iron and aluminum are hydrolyzed from the Versene complex (Welcher, 1958, p. 9). Seemingly the Versene is liberated by this hydrolysis to react again with the clay, chelating more

iron and aluminum, which are then hydrolyzed, and the cycle is repeated until the Versene is completely spent in the formation of stable chelates not susceptible to hydrolysis (Welcher 1958, p. 6). The Pennsylvanian shales were little affected by the Versene treatment, probably because of their relatively high calcium content and the stability of the calcium versenate complex. However, the predominant clay mineral present and the way in which the iron is bound into its lattice may affect the removal of iron and aluminum by the Versene treatment. In general the kaolinitic Dakota clays were affected most, and the illitic Pennsylvanian and Permian shales altered the least.

In group II additions of excess NaOH to the Versene solutions had relatively little effect. Instead of increasing the hydrolysis reaction, the Versene removed relatively little iron or aluminum.

The PCE values of both groups of Versene-treated samples were lowered to approximately the values exhibited by the raw clay before treatment (Table 4). None were lowered below the original values. The excess sodium ion in the Versene solution probably substituted into the exchange positions of the clay lattice and converted the clay from acid to sodium clay, and thus lowered the softening temperature.

Beneficiation by weak acid or Versene solutions produced no significant change in the differential thermal analysis pattern of the clay mineral. One sample (M-5) showed an incomplete removal of calcium carbonate. As expected, the sedimentation process removed the coarse-particle impurities such as pyrite and sand. Very little organic matter was removed by any process used. Any iron compounds removed by chemical treatment were present in such small amounts that their removal was not detected on the DTA curves.

Samples C-30-5 and C-53 produced DTA patterns typical of well-crystallized kaolinite, similar to those of the Kentucky "ball clays." Whether or not these two clays could be used as direct substitutes for ball clays in slip cast bodies would depend upon the nature and amount of nonkaolinitic clay minerals present. Kansas kaolinitic clays normally contain small percentages of swelling clay minerals (Plummer, *et al.*, 1960) that influence the viscous properties of slips.

TABLE 5.—Color descriptions* of fired raw clays and clays after sedimentation and treatment.

| KGS clay no. | Raw clay | Clay after sedimentation and HCl | Clay after sedimentation, HCl, and Versene |
|-----------------|------------------------------|--|--|
| Group I | | | |
| C-77-LB | cream 10 YR 8/4* | cream buff 10 YR 8/6 | dark cream 10 YR 8/4 |
| C-53 | ivory 2.5 Y 9/3 | off white 2.5 Y 9/2 | off white 2.5 Y 9/1 |
| C-77-C | red 10 R 4/6 | pink 10 R 5/6 | pink 10 R 5/6 |
| C-52 | cream 10 YR 9/3 | ivory 5 Y 9/2 | cream 2.5 Y 9/4 |
| C-27-13 | dk. yellow buff 2.5 Y 7/4 | cream buff 10 YR 8/5 | dk. yellow buff 2.5 Y 8/5 |
| AL-2 | red 10 R 5/6 | red 10 R 5/7 | pink 2.5 YR 5/7 |
| FR-3 | light red 10 R 5/6 | dark red 10 R 4/6 | light red 10 R 5/8 |
| CK-8 | yellow buff 10 YR 8/3 | cream 2.5 Y 9/3 | cream 2.5 Y 9/3 |
| Group II | | | |
| C-30-5 | pink buff 7.5 YR 8/4 | pink buff 7.5 YR 8/4 | pink buff 5 YR 8/3 |
| EL-60-6 | cream buff 10 YR 8/5 | cream buff 10 YR 8/4 | cream buff 10 YR 8/4 |
| O-5-6 | cream buff 10 YR 8/5 | buff 7.5 YR 8/5 | buff 7.5 YR 8/5 |
| O-40-3 | cream 2.5 Y 8/3 | cream 10 YR 9/4 | ivory 10 YR 9/3 |
| OS-2 | red buff 2.5 YR 6/8 | orange 2.5 YR 6/7 | orange 5.0 YR 7/8 |
| M-5 | pink buff 5 YR 7/7 | light red 10 R 5/6 | light red 10 R 5/6 |
| MP-20 | light red 10 R 5/8 | red 10 R 5/6 | light red 10 R 5/6 |

* The color names assigned to the table as a guide are those commonly used by brick manufacturers. Wherever any question of exact color arises please refer to the Munsell designations.

SUMMARY

The preliminary results of beneficiation treatments on Kansas clays are encouraging. The processing or beneficiation of clays in a clay-water slurry gives an extremely uniform clay. Sedimentation and a mild muriatic acid treatment can effectively change a medium-duty fireclay to a high-duty fireclay useful for more applications and commanding a higher price. The color of some fired clays can be lightened by sedimentation, acid, and Versene treatment. The properties of the Dakota kaolinitic clays were altered the most by these treatments. The illitic Pennsylvanian and Permian shales were generally little affected. The results offer sufficient encouragement for further bleaching studies with EDTA and other chelating agents.

The removal of significant quantities of iron and aluminum from the clay shows promise and may prove more economical than other methods developed to date for the recovery of alumina from Kansas clays. In conjunction with the production and sale of beneficiated clays the alumina recovered could be added to the refractory clays or sold separately.

The increased use of special ceramics and the freight costs from point of origin to plants producing the finished ceramic products should encourage the production of special ceramic bodies and refractories from Kansas clays. Production of special clays and manufacture of clay products can be handled within the state of Kansas by utilizing the abundant raw material and fuel reserves of the State.

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- Part 2. Sources of Error in Thermoluminescence Studies, by Jesse M. McNellis, p. 1-23, fig. 1-26, December, 1963.
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- Part 4. Kansas Basement Rocks Committee Report for 1962 and Additional Precambrian Wells, by Virgil B. Cole, Daniel F. Merriam, and William W. Hambleton, p. 1-10, December, 1963.
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