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PREVIEW

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PREVIEW

THE CLAYS OF NEBRASKA

A THESIS

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BY

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PREVIEW

PREFACE

The data recorded in the following pages, constitute the results of an effort to provide a more or less comprehensive description of Nebraska's chief mineral wealth, her clays, and the status of her clay industry. At present practically nothing is available in this field but brief and scattered publications.

However, the present treatise does not pretend to be exhaustive. To sample and study all of the clay deposits in the state is obviously too inclusive a task for one investigator, especially when such research is supplementary to teaching. Mention of some deposits, a few of importance, perhaps, will be found missing. Nevertheless, the varieties within the commonwealth are, it is believed, well represented.

It is to be pointed out also that a searching historical and stratigraphical study was not the aim of the work, though some attention, of course, has been paid to such phases of the subject. Greater emphasis has been placed on the physical and chemical characteristics of the clays studied, i.e. those qualities that govern the utility of the materials and concern scientific interest in clay technology. All of the results were obtained by small scale laboratory tests.

The investigations were carried on under the auspices of the Nebraska Geological Survey. My especial gratitude is therefore due to Dr. E. H. Barbour, State Geologist and Professor of Geology at the University of Nebraska, whose official assistance, personal enthusiasm and cooperation have been fundamental to the work. I desire to extend thanks to Dr. G. E. Condra and Dr. Benton Dales, respectively Professors of Geography and Chemistry at the University of Nebraska, for their interest and helpful suggestions; to Messrs. J. E. Burnett, H. R. Grumann and P. B. Wright who aided in collecting samples and field data and preparing the former for testing; to Miss Anna Hintz-long who molded and glazed the pieces for the pottery and floor tile tests; to Mr. E. C. Abbott for cooperation in chemical research; and to the many owners of clay pits and plants who assisted us in the field.

February 7th, 1916
Lincoln, Nebraska.

G. B.

CHAPTER I

Definitions, Origins, Classifications and Clay Distribution in Nebraska.

The term clay does not signify a substance of definite composition or qualities. It covers a large class of materials varying considerably in mineral contents and physical conditions. All have the property, however, in greater or less degree, of becoming plastic when wet, permitting molding into permanent shapes and becoming hard when baked. It is customary to attribute these properties chiefly to a certain constituent in these mineral mixtures, i.e. hydrated silicate of alumina of the composition of kaolinite or similar compound. Such silicates are always present but clay characteristics are also due to a number of other minerals, the chemical nature of which is less important than the physical quality, i.e. the colloidal condition.

This physical state is the result of disintegration and chemical alteration of crystalline rocks, containing siliceous minerals such as feldspar, muscovite, biotite, hornblend, etc. The disintegration is brought about by mechanical and chemical agencies. The mechanical forces are mainly those of temperature changes, glacial action or moving water. The solvent effects of water are also potent influences in rock disintegration and owing to dissolved oxygen and acids, such as carbonic acid, this action may be largely of chemical nature. Some constituents such as soluble alkali compounds are leached out and carried away; others are converted to relatively insoluble products such as oxide of iron and calcium carbonate which remain in the residue. Besides its solvent action water with or without carbonic acid also hydrates or combines chemically with some rock particles. Thus the alteration of orthoclase feldspar KAISi_3O_8 results in the hydrous silicate of aluminum known as kaolinite $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ as represented by the following equation:



Other silicates yield similar compounds such as nontronite, halloysite, pyrophyllite, etc. In addition to hydrous silicates other minerals are also hydrated, e.g. oxides of iron and alumina.

The foregoing operations constitute what is known as weathering and doubtless account for the formation of most clays from silicate rocks. In some cases unusual circumstances appear to be operative, such as pneumatolysis—action of thermal waters and gases.

Mechanical disintegration and chemical alteration of rocks probably proceed simultaneously in general, though sometimes extreme disintegration appears to precede chemical changes. An instance.

of this is the "rock flour" from glacial action. Another case is the formation of rock dust by volcanic disintegration of silicate rocks. It is now thought that the highly colloidal clay known as bentonite results from wind-born volcanic dust depositing in water and then undergoing the usual aqueous alteration.

The hydrated rock particles are softer, less compact and finer grained than the original minerals and are easily carried away by water and wind and deposited elsewhere. Separation is thus effected from unaltered silicates and sand and the redeposited material is frequently richer in clay qualities than the original beds. This sorting power of water is of great importance in clay bed formation. The character of transported and deposited material depends on the velocity of the moving water at different times. At various points along a river, for instance, we may have all gradations in deposits from sand free from clay to clay free from sand. Clays occupying the position of the parent rock are residual, such as the kaolins, characterized by the mineral kaolinite. We have thus a broad classification into residual and transported clays. In the latter division further distinctions are made in the terms marine, alluvial and glacial clays signifying those that have been deposited in the sea, along rivers, or by glaciers respectively. Glacial clays differ also in their genesis from other transported clays in that the disintegration of the parent rock by weathering has been aided by the grinding action of the ice. Sometimes finely divided "rock flour" from this glacial abrasion has not suffered further alteration from weathering, yet from its fine state of division possesses clay properties and is used for brick making. Another variety of transported clay of special interest in Nebraska is the loess. This material is characterized by extremely fine particles, frequently with much calcium carbonate, loose formations lacking stratification, yellowish color and the presence of fossils of land animals. The history of the loess is a matter of uncertainty but it is probably of glacial origin altered and transported by intermittent contacts with water. Some deposits are believed to have been carried by wind.

Both residual and transported clays are subject to further alterations. Water may slowly leach out certain constituents or add new ones by base exchange chemical action and absorption. That is, clay and other hydrated rock particles have power to extract bases from percolating waters by double decomposition and certain colloidal gels such as those of oxides or iron and aluminum may take up molecules of dissolved salts by absorption.

Certain properties of the clay may therefore be considerably modified, such as plasticity and fusibility. Physical changes may also take place such as subjection of clay beds to great pressure, resulting in the hard compact variety known as shale.

Clays may be classified from standpoints other than the geologic discussed above, e.g., according to physical properties. In this grouping Grout¹ selects the more important properties for main division and the less important for subdivisions, stating that plasticity, strength and firing behavior are most noteworthy, particularly fusion phenomena. Additions of other clays may correct deficiency in plasticity or strength, whereas brief vitrification period is difficult to correct. He suggests the following tabulation:

		<u>Main Uses</u>
I. Refractory	Earthy, usually residual, non-plastic	China Clay
	Plastic	Ball Clay
	Flint-like, non-plastic	Fire Clay
	red burning	Sewer pipe Paving brick
	Safely vitrifying buff or cream burning	Stoneware
II. Semi-refractory	Rapidly fusing	Low grade fire clay
	Red burning	Drain tile Foundation brick
	Safely vitrifying buff or cream burning	Vitrified brick Foundation & Sewer brick
III. Non-refractory		
	Rapidly fusing	Common brick.

Finally, clays may be classified according to uses and this method of naming them is useful commercially. Reis² lists the following types according to important uses:

1. Preliminary Report on Clays and Shales of Minn., by F. F. Grout and E. K. Soper.
2. Clays, Occurrence, Properties and Uses.

Fire clay	Brick clay	Paper clay
Slip clay	Glasspot clay	Tile clay
Stoneware clay	Paving brick clay	Sewer pipe clay
Sagger clay	Paint clay	Pottery clay
Terra cotta clay	Adobe clay	China clay.

It must not be supposed that the various types of clays mentioned in many of the classifications are always distinct and clear-cut. Geologic distinctions are sometimes difficult to make, owing to conflicting evidences; and in the last classification according to uses we find the same term applied to widely different specimens. The only classification indicating the utility of a clay is that based on physical properties.

Distribution in Nebraska

The essential geological structure of Nebraska is shown in figure 1. As indicated, the rock beds of the state are of sedimentary nature, no original formations such as granite being observable; hence no residual clays are found in Nebraska.

The oldest outcropping beds are the carboniferous, about 1200 feet thick. These appear in the southeastern counties, dipping towards the west and not showing again until the mountains are reached. The formation consists chiefly of limestone, shales and sandstone. The carboniferous is very important from an economic point of view, furnishing much of our building stone, clay and lime. A little coal has been found but of no commercial importance. The carboniferous, like the other formations, is subdivided into five or six beds, the principal one being the topmost known as the cottonwood and the underlying Atchison shales. The clays and shales are an important source of our ceramic products, valuable outcrops appearing at Wymore and Beatrice, Gage County; Humboldt, Richardson County; Table Rock, Pawnee County and Nebraska City, Otoe County.

The Cretaceous is also of economic prominence particularly the Dakota division. The latter resting upon the carboniferous is from 300 to 400 feet in thickness, consisting mostly of a ferruginous sandstone and clay. It outcrops in several localities in northeastern and southeastern Nebraska and provides many of our best clays. Important deposits have been studied at Steel City and Endicott, Jefferson County; Burnham, Lancaster County; Louisville, Cass County; and Tekamah, Burt County. The Graneros division of the Cretaceous lying upon the Dakota ranging from 0 to 300 or 400 feet, in thickness, also furnishes some excellent clay, notably at Reynolds, Jefferson County.

The bulk of our clay products, however, comes from more recent formations--the drift, loess and alluvium. The drift is the thin reddish layer of glacial origin observable in the eastern part of the state, lying under the yellow loess usually. It is characterized by boulders and pebbles aside from its

color. York County is about the extreme western limit. The drift is less important for its clay than for sand and gravel. The loess is the chief source of common brick as well as constituting the clutivable soil of the eastern half of the state. It covers the greater part of the latter roughly bounded on the west by a line running diagonally from northeast to southwest. It is a soft, very fine grained material of yellowish color frequently sandy and limy, the latter often occurring as limestone or concretions. The origin of the loess is unknown. It appears probable, however, that it is a well weathered glacial debris. For common brick it serves as a very valuable resource, simple treatment frequently producing a very satisfactory product. In some places drying difficulties are encountered but are usually overcome by admixture of sand or other clay. The alluvium or valley wash is found to some extent in all river valleys in the state. The material in it available for brick making, is the result of the sorting power of water, the light, fine, highly disintegrated rock being deposited in various localities and serving for common brick.

Among the other less important formations providing clay for economic use, may be mentioned the Oligocene or Bad Lands in the extreme western part of the state. These beds are from 200 to 600 feet deep and lie on the Pierre shale. They furnish a little clay for brick, notably at Gering. The material, known as brule, is a lean sandy substance of pinkish color.

CHAPTER II.

Chemical and Physical Characteristics of Clays and Laboratory Methods

As previously stated, clays are mineral mixtures, chiefly hydrated silicates of alumina. Small amounts of other minerals such as quartz, carbonate and sulphate of lime and oxide of iron occur in the purer types but abundantly in the common clays. The working properties and utility of a clay depend mainly on the relative amounts of these minerals and their physical nature, i.e., size of particles and whether they are crystalline or colloidal.

The most useful chemical examination of a clay would be one that would indicate the relative amounts of minerals present--that is, the chemical combinations. Such a procedure is available, known as the rational analysis, introduced by Forchhammer, but it is of very limited application. It is valuable only with the simpler types such as kaolin. The procedure consists in dissolving the hydrous silicates with sulphuric acid. The insoluble residue then consists of alkali soluble silica resulting from the hydrous silicate, quartz and acid insoluble silicate such as feldspar. The soluble silica is dissolved with sodium carbonate and hydroxide and the

insoluble residue dried and weighed. The percentages of clay substances and impurities are then easily calculated.

In examining common clays the centesimal or ultimate analysis is frequently employed. This throws no light on the chemical combinations present but is useful in indicating the amounts of the various basic and acidic oxides, such as silica, sulphur trioxide, carbon dioxide, iron oxide, lime, magnesium and the alkalies. The determination of the amount of organic and other matters volatile at red heat is usually included. A complete centesimal analysis is not ordinarily made, the determination of the principal constituents being sufficient in most cases to characterize a specimen.

Nearly all clays contain all of the above mentioned constituents, the relative percentages having some bearing on the physical behaviour of the clay, though the relation is not definite owing to the influence of two factors, viz., state of combination and physical condition.

The more nearly a clay corresponds to the formula for kaolinite, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, the more refractory it is. The presence of fluxes, acidic or basic, lowers the melting temperature, in accordance with Richter's law. Lime fluxes rapidly, it being impracticable to vitrify clay high in this constituent, for the vitrification and fusion temperatures are too close together. Magnesia acts like lime but to a less extent. Ferric oxide in the absence of reducing agents is not an active flux. In the presence of carbon or other reducer and also at high temperatures it becomes ferrous oxide, a stronger base capable of readily fluxing acidic matter such as silica. Oxides of sodium and potassium are powerful fluxes but are present ordinarily in small amounts.

Color also is governed largely by composition. Seger states that the color of burned ware depends on:¹

1. Quantity of iron oxide in the clay.
2. The other constituents accompanying the iron.
3. The composition of the fire gases during the burning.
4. The degree of vitrification.
5. The temperature at which the clay is burned.

He also proposes the following classification of clays according to their color burning qualities:²

1. Seger's Collected Writings. Vol. 1, Page 109.
2. Ibid.

<u>Group</u>	<u>Character of Clay</u>	<u>Color After Burning</u>
1.	High in alumina and low in iron	White or nearly so.
2.	High in alumina and moderate iron content	Pale yellow-pale
3.	Low in alumina and high in iron	Red
4.	Low in alumina and high in iron and lime	Cream or yellow

Segar implies oxidizing conditions in the foregoing. With reducing atmosphere, the color may be brown, green or blue-black, due to the formation of ferrous iron compounds. Figure 3 illustrates the coloring effects of iron under oxidizing conditions in several Nebraska clays. Series No. 1 is a highly calcareous clay from Blue Springs, carrying 3.38% ferric oxide. The bleaching effect of the lime is very evident. At cone 09 the color is decidedly red and at cone 1 is buff. The bleaching is apparently due to the formation of light colored ferrites or silicates of lime and iron. Series No. 2 illustrates the effect of practically the same amount of iron in a clay of moderate lime content, a specimen of loess from Kearney. The color of the ware deepens from cone 09 to cone 1, being dark red at the latter. Series No. 3 illustrates the effect of a very small amount of iron in a clay very low in lime, a cretaceous specimen from Tekamah. At cone 018 the color is pink; at 09 yellowish pink; at 04 pale yellow, almost white; at cone 1 deeper yellow and at cone 5 still darker. It is evident in this series that what small amount of iron is present enters into light colored combinations with the progressive rise in temperature, the optimum of whiteness occurring at cone 04.

Iron is usually present in clay in the oxidized form but occasionally as sulphide of iron or pyrites. The latter is troublesome since it is not readily oxidized in the firing process. It may be converted to soluble iron sulphate either in the firing or in subsequent weathering. Soluble salts, especially sulphates, are undesirable, since they frequently leach out and form an efflorescence or discoloration on the fired ware. This effect of sulphates is commonly overcome by adding to the clay before firing, barium carbonate in proportion to the amount of sulphate found by analysis. The sulphuric acid radicle of the soluble sulphate is thereby converted to insoluble barium sulphate.

However, as stated above, it is not safe to predict the behavior of a clay from the chemical analysis alone. Two clays of practically identical composition by centesimal analysis may act in widely different manners on firing, due to different mineralogical compositions and textures.

There are several physical properties of clays that are exceedingly important in their relations to the utility of the material. Among the more significant are plasticity, air shrinkage, tensile strength of dry clay, behavior when heated (shrinkage, temperature of vitrification, temperature of fusion, color, hardness and absorption of the fired ware.) Among the less important may be mentioned slaking, fineness, specific gravity and homogeneity.

Plasticity is that property of clay that permits it to be molded when mixed with water. This quality is all important, yet, notwithstanding many attempts,¹ no satisfactory method has been devised for its accurate measurement. The simple marking of a small mass of moistened clay between the fingers is a useful way of testing plasticity and no one experienced in clays has any difficulty in thus distinguishing between a "fat" or very plastic material and a "lean" one, deficient in this property. The plastic state is developed by mixing with water. By maximum plasticity is meant that condition when the clay carries all the water it can without becoming sticky. Usually the amount of water required to bring about this condition is a measure of plasticity. There are exceptions to this rule however; moreover, the method is not very precise since the results are somewhat dependent on the judgment of the operator. Many theories are to be found in the clay literature concerning the cause of plasticity. The true explanation seems to be evident from the genesis of these substances. As previously explained, clay is a product of the weathering of crystalline rocks such as feldspars and similar silicates. They are thus changed from a hard, compact crystalline structure to a soft, loose, amorphous or colloidal condition. Colloidal matter mixes intimately with water to form adherent, pasty or sticky substances. The more thorough the weathering process, the looser, more flocculent will be the clay product with consequent greater capacity for water and plasticity. Clays are frequently improved in working qualities by exposing them to weathering influences after they are dug from the pit.

shrinkage is the contraction suffered by clay in drying from the plastic state at ordinary temperature. It may be expressed as linear or volume shrinkage. The more water required in making up the plastic mass the greater will be this contraction. Hence the more plastic clays show the greater shrinkage. The property is of practical importance since in making fired ware of certain dimensions it is of course necessary to know how much to allow for this loss of volume. Sometimes it is excessive and unless carefully regulated by slow and uniform drying, cracked or warped ware results. This tendency is frequently remedied by the addition of nonplastic materials such as sand or grog (burned clay reground). The work of Bleininger³ shows that the preheating of such clays at about three hundred degrees centigrade (572° F) in many cases eliminates this irregularity. Sometimes the defect may be remedied by mixing lean clay with the excessively plastic specimen.

1. Bischof. Die Feuerfesten Thone, p. 84.
2. K. C. Stover, Trans. Amer. Cer. Soc. VII. p. 397, 1905.
3. Ladd, Geol. Surv., Bull. 62, p. 51, 1898.
4. Ries, Clays, Occurrence, Properties and Uses, p. 96-104.
A. V. Bleininger, The Effect of Preliminary Heating Treatment upon the drying of clays, Technologic Papers of the Bureau of Standards, No. 1.

The tensile strength of a clay is a measure of the strength of air dried material. A test of the crushing strength would give more direct evidence. However, the former is more easily applied and since it bears a direct relation to the latter, it is usually made. The data obtained are useful in indicating the load the bricks or other ware will be able to carry in the kiln; also the care required in handling. There seems to be some relation between the plasticity and the tensile strength though it is not a constant one. Usually the one property increases with the other. One hundred pounds per square inch for tensile strength is considered sufficient for raw ware in most cases. This property varies considerably among different types of clay, kaolin for example being deficient in it, while impure clays such as loess are frequently much stronger.

The study of the behavior of a clay in burning involves a number of observations, such as additional shrinkage, changes in color, hardness and absorption or capacity for water, these being noted after firing to various temperatures. The temperatures of vitrification and of fusion are also observed. By vitrification is meant the stage at which a clay shows first evidence of melting. The ware still retains its shape but the pores are filled with glass. It will absorb very little water. If the temperature is raised above this point more clay particles fuse and eventually the mass flows. This is known as the temperature of fusion or viscosity. The chief factors involved in vitrification and fusion are chemical composition and texture. The process of fusion in a clay is a very gradual one; the finer and more fusible combinations melt first, this glass dissolving more material until finally the coarse undissolved particles are no longer supported and the mass loses its shape or flows. The range of temperature between vitrification and viscosity is important; likewise between incipient fusion and vitrification. If the range in the first instance is short, the ware is likely to be overburned; on the other hand a short range in the second pair of temperatures results often in an underburned product. Clays vary much in heat behavior. Other circumstances being the same, the material having the higher percentage of fluxes (oxides of lime, magnesium, sodium and potassium) will melt at the lower temperature. Clays with high content of lime fuse suddenly with a very short range between vitrification and viscosity.

When clay is thrown into water it disintegrates more or less readily, or slakes. The time required for this process is important since thorough slaking is essential in the tempering of clay preparatory to molding or forming. The period is very short with the softer varieties and longer with shales.

The fineness of grain in a clay is a factor in its behavior. It influences the plasticity, the latter increasing with fineness of texture; it influences the fusibility, other conditions