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THERMAL PROPERTIES OF CLAYS AND SHALES

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THERMAL PROPERTIES OF CLAYS AND SHALES

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ABSTRACT AND SUMMARY

Porosity, permeability and water content of clay-rich rocks are largely controlled by depth of burial, time and temperature. Grain densities for quartz and most of the clay minerals is between 2.6 and 2.7. Carbonate and iron minerals increase the bulk density of shales; expandable clay minerals (smectite and vermiculite) and organic matter decrease it.

Cenozoic shales characteristically have a high montmorillonite content and associated high water values. Only at depths deeper than 5,000 feet does the water content become less than 5%.

The near surface Cretaceous shales of the Black Hills and to the west are montmorillonitic and contain from 11 to 38% water and have an average density of 1.88. Where the shales do not contain montmorillonite (western Canada), bulk densities range from 2.4 to 2.7.

Most Paleozoic shales have bulk density values between 2.4 and 2.7 with water contents ranging less than 1% to 10%. Low density values are commonly due to organic matter. Bulk densities of some Devonian calcareous shales range from 2.4 - 2.6, with calculated water values of 0.8 to 5%.

In soils and marine muds thermal conductivity increases as the water content of the dried sample increases but reaches a maximum and decreases at high water values. For wet samples the thermal conductivity decreases as the water content increases. Shales and marls have conductivity values ranging from 3.3 to $7.3 \cdot 10^{-3}$ cal/cm^oC, rock salt values range from 12 to 17. Conductivity is greater parallel than perpendicular to bedding and decreases with increasing temperature. At 0°C the conductivity of halite is 3.2 times that of slate, at 400°C the difference is 1.2.

For any particular refractory product the conductivity is largely controlled by the porosity and decreases with increasing porosity. Glass has a lower conductivity than crystalline material but its conductivity increases with increasing temperature while that of the crystalline material decreases.

Unfired refractories (equivalent to natural clay or shale) develop a well-developed zoned structure when heated on one side. On the cool side the hydraulic bond is present and thermal conductivity is relatively high; in the middle, hydraulic and chemical bonds have been partially destroyed and conductivity is low; on the high temperature side a ceramic bond forms and conductivity is high. A similar zonation should develop in subsurface shales but will be less severe as the water content and the temperatures will probably be lower.

Specific heat and heat absorption values are given for some ceramic materials.

During the drying of ceramic products the continuous water film is first driven off; shrinkage is proportional to the water lost. Once the film is broken the pore water is converted to vapor which travels out through capillaries.

Bound and interlayer water is driven off clay minerals at temperatures below 100°C . At temperatures from 350 to 600°C the structural or hydroxyl water is lost with little deformation of the structure. Most clays heated to 600°C have the ability to readsorb hydroxyls when they are cooled and exposed to water. Above 900°C the clay structure is destroyed and a variety of new mineral and glasses formed. The presence of fluxes (Fe, K, Na, Ca, Mg) increases the proportion of glass developed. Organic matter starts to oxidize at 200 to 300°C and pyrite at 400 to 500°C . Carbonates lose carbon dioxide between 500° and 900°C .

Linear firing shrinkage of clay minerals ranges from 2 to 20% but is considerably reduced by the presence of quartz. Most of the shrinkage occurs above 800°C . When a rock is heated, at low temperatures, the grains with the largest thermal dilation expand, creating internal fractures and increasing the porosity.

Fusion (production of a fluid) for natural shales commonly starts at 1000 to 1500°C . The lower values are caused by the presence of fluxes. Fusion is preceded by vitrification which may extend over several hundred degrees

during which the amorphous component becomes increasingly abundant. Kaolinite has a long vitrification range; whereas it is short for the other clay minerals.

Rapid changes in temperature causes unequal rates of expansion or contraction in a brick (or shale) resulting in thermal spalling. Material with a low thermal conductivity is more likely to spall. Thus, a high glass content is conducive to spalling. When a brick is heated on one face the isothermals are parallel to the heated surface. The resultant normal stresses are nearly parallel and perpendicular to the surface of the brick and the shear stresses are at 45° to them. On sudden heating, spalling is due almost entirely to shear stresses and, on sudden cooling to tension stresses.

Almost any composition of clay or shale is satisfactory for the manufacture of common brick. The preferred quartz content is 25 to 50%, which is what most shales contain. Montmorillonite causes excessive shrinkage. Large amounts of iron, alkalies and alkaline earths also cause shrinkage and reduce the vitrification range.

Rapid heating of shales can cause bloating (formation of a cellular structure by gas bubbles). This is done deliberately to form lightweight aggregate. The most common sources of gas in shales are iron oxides, calcite, dolomite, pyrite, organic matter, and vermiculite. Only 1% of most of these minerals is necessary to produce bloating.

An impermeable layer must be formed on the surface of the particle or wall. Heating is rapid so that fusion starts just before the evolution of gas. Commercial firing is commonly done at 1100 to 1200°C. Paleozoic shales are extensively used for the preparation of lightweight aggregate.

The preceding described thermal response of clay and shales applies to rapid heating for short periods of time. When heat flow rates are low and heat is applied for long periods of time to buried shales the reaction is different and is termed diagenesis. Over a period of thousands of years at temperatures of 50 to 100°C most of the montmorillonite expanded layers will convert to illite with the release of interlayer water to the pores. Kaolinite is destroyed at approximately 150°C (compared to 450°C over periods of months) and chloritic material may form. A relatively pure illite-chlorite clay suite develops at 200°C and persists to 400°C (low grade metamorphism) where crystallinity and grain size increases. Shales which have been previously heated to 200°C or higher are less apt to undergo significant diagenetic changes when reheated.

At the same time the interstitial water interacts with the minerals and chemical changes occur. The ions in the porewaters, and the pore water migrate in the direction of high to low temperatures and at some temperature may precipitate calcite, silica, and chlorite, forming a seal impermeable to water. High pressure can develop below or in back of the seal. Similar diagenetic reactions would be expected to occur at some distance from a canister containing high-activity wastes.

In natural water saturated sediments heat is transported by conduction through grains and fluids, convective flow of fluids, and radiation. Conduction and convection heat flow are most important below 100°C. Ray transportation increases with increasing temperature. In a shale section when a seal is developed and the flow of water halted the geothermal flux above or on the "other" side the seal is reduced and overheating occurs below or on the other side.

In summary, near a hot canister a vitrious or brick-like phase should develop with possible bloating and fracturing. Thermal conductivity should be relatively high but will depend upon the porosity developed. At a farther distance from the canister dehydration and dehydroxylation will occur without much physical change and conductivity will be smaller. These changes will occur over a short period of time. Farther from the heat source water will be retained or migrate slowly and the conductivity will increase. With, increasing time diagenetic reactions will occur in the cooler zone farther removed from the canister; a seal may develop in some portion of the diagenesis zone and a pressure build-up develop. The pressure build-up could cause a heat sink to develop but in a low porosity shale porosity might be reduced by gradual precipitation in pores and by lithostatic pressure and thermal conductivity increased. With time the frontal boundaries of all three zones should move forward; however, this movement will be modified or stopped by the progressive decrease in the amount of heat generated in the canister.

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INTRODUCTION

This report contains a compilation of much of the data needed for evaluating the thermal properties of clays and shales. The data on shales are limited so much of the review is concerned with clays and ceramic products. The information presented should allow a preliminary evaluation of the problems that will arise when canisters containing high-activity wastes are buried in shales.

A computer library search was conducted and most of the data specific to the thermal properties of shales was probably found. Much more data is available on density, porosity, ceramic properties, diagenesis etc. but the main points have been summarized.

SHALE DENSITY, POROSITY, PERMEABILITY

General

The porosity, permeability, density and water content of clay-rich rocks are largely controlled by depth of burial, time and temperature. Clay mineral composition (particularly expandable clays), quartz and carbonate content are also important factors. Orientation, water salinity and grain size are factors of secondary importance.

The transition from clay to shale probably occurs at about 35% porosity, because of chemical changes and cementation between the grains which imparts a rigidity to the structure (Hamilton - 1959).

"Natural" density was defined by Hedberg (1936) as the density of the rock with all pore spaces filled with water. "Bulk" density is the density of the rock with the pore space free of liquids. "Grain" density is the density of the constituent particles of a rock.

Total porosity is calculated from the expression $\% \text{ porosity} = 100 (1 - \sigma_b / \sigma_g)$. Effective porosity is a function of permeability as well as porosity and is generally smaller than total porosity.

For clays and shales composed largely of nonexpanded clays, depth of burial and to a lesser extent time controls the release of interstitial water. Expanded clays (montmorillonite) can hold two to ten times more pore water than nonexpanded clays (illite and kaolinite) (Weaver - 1960 and Mead - 1966). The water associated with expanded clays is difficult to remove and temperature and time are relatively more important than depth of burial. Weaver (1960) has estimated the average density of shales containing expanded and non-expanded clays as a function of age (Table 1).

Table 1 Relation of Density (and Pore Water Content)
of Shales to Composition, Depth of Burial, and Age

Clay Composition	Depth of Burial	Age	Density
Non-Expanded	Deep	Old 45-50% <i>Young</i>	2.65
Non-Expanded	Deep	Young 40-50% <i>Old</i>	2.5
Expanded	Deep	Old	2.4
Non-Expanded	Shallow	Old	2.3
Expanded	Shallow	Old	2.2
Expanded	Deep	Young	2.2
Non Expanded	Shallow	Young	?
Expanded	Shallow	Young	2.0

Non-expanded = illite, kaolinite, chlorite.

Expanded = montmorillonite and mixed-layer illite-montmorillonite.

Deep = approximately 10,000 feet.

Shallow = approximately 2,000 feet.

Old = Paleozoic

Young = Tertiary.

Grain Density

In order to convert water weight to porosity and vice versa grain densities values are needed. Values for the most abundant clay minerals in shales are listed in Table 2 .

Table 2 Density of Clay Minerals (Grim - 1968)

Mineral	Dry Density	Density 100% Relative Humidity	% Moisture Oven-dry basis
Illite	2.65	2.13	19
Illite-smectite	2.64	1.48	76
Kaolinite	2.60-2.68	2.43	6.5
Chlorite	2.6 -2.96	-	-
Smectite	2.2 -2.7	1.77	46

The dry density values for all the clay minerals except smectite are very close to that of quartz, 2.65. Thus, 2.6 would be a good average grain density value to use for shales that do not contain appreciable smectite or Fe. Density values at 100% relative humidity are considerably lower. The water adsorbed at 100% humidity would be classed as adsorbed water. If a value of 2.6 is used to calculate water content or porosity both values would include adsorbed water as well as "true" pore water. The distinction is probably of little consequence in relating thermal conductivity to water content but may be of consequence in relating thermal conductivity to porosity (void space).

Average grain density values based on the study of soils and shales has been compiled by Hedberg (1936). (Table 3).

Table 3 Grain Density

Material	Region	Number of determinations	Average grain density
soil colloids		6	2.714
soil colloids		6	2.574
Pal. & Meso. shales	Kansas	25	2.72
clays and shales	Eastern U.S.	26	2.69
Tertiary shales	Venezuela	40	2.69
soils and clays	Germany	11	2.69
clay			2.68
shale			2.71
slate			2.7-2.85
Cretaceous shales	Black Hills	9	2.66
soils		2	2.618
same soils		2	2.545

Grain densities in most of the shales are raised by small amounts of heavy minerals such as pyrite, calcite, and siderite. However, organic matter which is also commonly present tends to lower grain density. These data suggest a value of 2.7 might be more typical than 2.6; however, because of the common presence of some expanded clay I have used the 2.6 value. Obviously no one value can be applied to all shales.

Permeability

Table 4 lists permeability values for shales ranging in age from Miocene to Paleozoic. Values are uniformly low but there is considerable variation. Data is from Rieke and Chilingarian - 1974 and Gondovin and Scala - 1958.

Table 4 Shale Permeabilities

Age and Location	Permeability (md)
Miocene (Calif.)	$4 \cdot 10^{-4}$
Paleozoic (?) (Okla.)	$8 \cdot 10^{-4}$
Paleozoic (?) (N. Mex.)	$2 \cdot 10^{-6}$
- (Texas)	$7 \cdot 10^{-6}$
Cenozoic (Gulf Coast)	$9 \cdot 10^{-8}$
Cenozoic (Gulf Coast)	$1.5 \cdot 10^{-8}$
Cretaceous (Pierre)	$1.1 \cdot 10^{-4}$
Cretaceous (Muddy)	$5 \cdot 10^{-2}$
Cenozoic (Gulf Coast)	$1 \cdot 10^{-8}$
Cenozoic (Gulf Coast)	$2.5 \cdot 10^{-9}$
Paleozoic (Ill.)	$2 \cdot 10^{-6}$
- (Texas)	$3 \cdot 10^{-4}$
- (Montana)	$6 \cdot 10^{-4}$
- (Utah)	$7 \cdot 10^{-6}$
Pennsylvanian (Ill.)	$9 \cdot 10^{-5}$
Cretaceous	$4 \cdot 10^{-3}$

Cenozoic

Studies by Weaver and Beck (1971) of Pliocene and Upper Miocene montmorillonitic muds from the Mississippi Delta region indicates that the pore water content is 20% 4,000 feet ($\sim$ 33% porosity) and decreases to only 15% ($\sim$ 28% porosity) at 16,000 feet. The calculated amount of interlayer water decreased from 5% to 2% over the same interval. Thus, total water decreased from 25% to 17%, a reversal increase in pore water, occurs in the 8,000 to 10,000 feet depth interval but it is not pertinent to the present discussion.

Kerr and Barrington (1961) found that the bulk densities of Miocene shales near a salt dome in the Mississippi Delta area increased from 2.1 (31% water) at 6,000 feet to 2.5 (4% water) at 16,000 feet.

Oligocene shale samples from the Gulf Coast area (Schmidt - 1973 and Myers and Van Siclen - 1964) have shale densities between 2.1 and 2.3 gm/cc. Porosity values range from 22% (10% water) at 2,000 feet to 12% (4% water) at 10,000 feet. Dickinson (1953) reported a shale density value of 2.58 (1.3% water) for a Gulf Coast Eocene shale sample from 8,600 feet.

A series of measurements on Cenozoic shales from Venezuela (Hedberg - 1936) indicated a gradual decrease in porosity from 35% (17% water) at the surface to 10% (4% water) at 6,000 feet. Measured bulk density values decreases from 1.9 to 2.4. These shales may contain less montmorillonite than the younger Gulf Coast shales.

McCulloch (1967) describes Pliocene age shales (5,000 to 6,000 feet deep) from California with density values of 2.5, (6% water), considerably higher than for the Gulf Coast. The California shales should have less montmorillonite and apparently have been subjected to more tectonic activity.

Table 5 list some bulk density values for the Eocene Green River oil shales. Even though the samples contains a significant content of calcite and dolomite the bulk densities are low due to the high content of organic matter. Estimated porosity values are in the range of 40 to 80%.

Table 5

Colorado Oil Shales (Green River Formation - Mahogany Zone)

<u>Name</u>	Bulk Density
Core A	2.37
Sample 1	1.87
Sample 15	1.72
Sample 11	1.506
Sample 12	1.854
Sample 2	2.115

Figure 1 shows the relation of dry density (bulk density) to wet density (natural density) as a function of depth (Johnson - 1950). Curves are based largely on analysis of Cenozoic shale sections. The two values converge as density increases. The assumption is made that composition is not a factor. Most of the data is from South America. The data for the montmorillonitic Gulf Coast shales show considerably lower densities for a given depth.

Figure 2 show the relation of density to porosity (Johnson - 1950).

Mesozoic

There is relatively little data on Mesozoic shales. One set of data on Russian shales was published by Maxwell (1964). The measured porosity was 30% (14% water) at the surface and 10% (4% water) at 4,000 feet. The porosity decrease from 7.5% (3% water) to 5% (2% water) at 9,000 feet and remains constant to 11,500 feet.

Cretaceous Muddy shale samples from a depth of 4,900 feet in Logan Co. Colorado have porosity values of 4.1 to 5.1%. Pore size is 0.1μ and the permeability is less than 0.05 millidarcy (Handin, et al. - 1963). The clay in the shale contains only a few expanded layers.

Abel and Gentry (1975) report the Cretaceous Pierre, Bearpaw and Claggett shales have natural moisture contents of 38% (61% porosity) to 12% (26% porosity). Values are highest at the surface and stabilize at 12% (26% porosity) to 18% (36% porosity) at depths of 200 to 300 feet. The permeability values are low, ranging from 1×10^{-6} to 1×10^{-10} cm/sec. The clays have a high content of montmorillonite.

Rubey (1930) studied outcrop samples of the montmorillonitic Upper Cretaceous shales (Graneros, Greenhorn, Niobrara and Pierre) from the Black Hills region. He noted that when shale chips were suddenly heated they exploded violently. Bulk densities ranged from 1.559 to 2.038, and averaged 1.88. Porosity values were based on weight loss at 200°C . Values ranged from 24% (11% water) to 38% (20% water), averaging 30% (14 % water). The average porosity at room temperature is 20% (9% water). The difference is presumably due to interlayer water. Rubey found that porosity decreased as the dip of the shale bed increased. This presumably showed the effects of Tectonic deformation. Samples from near faults also had low porosity values. Thus, horizontal beds have the maximum porosity (33 to 38%).

Table 6 contains bulk density values for Cretaceous age shales from western Canada (Kaarsberg - 1959). The mineralogy and depth below surface are also given, as well as calculated water content. Calculated water values are low except for the one sample containing montmorillonite.

Table 6 contains bulk density values for Cretaceous age shales from eastern Canada (Kaarsberg-1959). The mineralogy and depth below surface are also given; as well as calculated water content. Calculated water values are low except for the one sample containing montmorillonite.

Table 6
Cretaceous Shales

Canada Formation	Present Depth Below Surface (Feet)	Bulk Density	Calculated Water Content Grain Density = 2.6	Mineralogy
Blackstone	9,120	2.68	0	Illite, chlorite, quartz
Cardium	6,776	2.56	0	Illite, chlorite, quartz
Ostracod	7,849	2.53	4	Illite, chlorite, quartz calcite (17.9 percent)
Cardium	5,136	2.54	4	Illite, chlorite, quartz
Second specs	2,698	2.07	31	Illite, quartz, montmor- illonite, calcite (19%)
Dakota	4,340	2.42	11	Illite, chlorite, quartz

Muller (1967) described a study of the Triassic shales of Germany and reported the porosity decreased from 25% (11% water) at 400 feet to near zero at 4,000 feet. These shales values should be similar to those of the Triassic shales of the eastern United States.

Palcozoic

Athey's (1930) data on Permian and Pennsylvanian shales of Oklahoma indicates bulk densities start at 2.1 at 400 feet and increase to 2.62 at 5,000. He estimates 1400 feet of overlying sediments has been removed. Measured porosity values over the same depth interval decrease from 25% (11% water) to 2% (0.8% water). His density data indicates that for shallow sample from the same depth values could vary by as much as 0.3 (2.1 to 2.4). For the deepest samples the range of values was about half this value.

It should be pointed out that for most of the studies reported the various authors picked samples from areas where there was a minimum of tectonic deformation. Most studies were concerned with gravity compaction.

Gibson (1966) studied a series of Pennsylvanian shale cores from Union Co., Kentucky. Porosity values from 3% (1% water) to 15% (6% water) over a depth interval 31 to 1484 feet. Porosity is variable but decreases slightly with depth. Porosity decreased with an increase in preferred clay mineral orientation and an increase in illite content.

Kaarsberg (1959) reported bulk density values ranging from 2.40 (12% water) to 2.43 (11% water) for 3 samples of Pennsylvanian shale.

Table 7 gives bulk density values of some subsurface Devonian shales from western Canada (Kaarsberg-1959). The clay minerals are illite and chlorite. All samples contain some calcite and dolomite which would cause the average grain density to be more than 2.6. If the grain density is assumed to be 2.7 (measured bulk density for deepest sample) then samples with a bulk density of 2.6 should contain 6% water.

Table 7

Devonian Shales

Canada Formation	Present Depth Below Surface (Feet)	Bulk Density	Minimum Calc. Water; Grain Density =	
			2.6	2.7
Mid-Ireton	5,231	2.585	0	6
Mid-Ireton	5,248	2.60	0	6
Mid-Ireton	5,297	2.61	0	6
Lower Ireton	3,778-3,796	2.585	0	6
Mid-Ireton	2,770-2,780	2.43	11	16
Upper Ireton	6,544-6,565	2.71	0	0
.....	5,165	...	...	...
Ireton	3,148	2.49	7	12

In 1950 (Hammer - 1950) reported on a study of in situ density measurements (gravimeter) of shales from a vertical shaft, 2,247 feet deep. He found that density values determined in the laboratory were significantly lower (5%) than those obtained by gravimeter measurements in the shaft.

Incidentally Hammer (1950) made his study in a limestone at Barberton, Ohio owned by the Pittsburgh Plate Glass Company. The shaft penetrates Mississippian and Devonian shales from approximately 200 to 2200 feet, where limestone is encountered. This might be a good test site. Similar mines occur in New York (U.S. Army Corps of Engineers - 1956, 26-27).

More recently (McCulloh (1965) duplicated the study of Hammer's with considerably more care and found Hammer had made a number of mistakes. He found that the laboratory measurements of dry bulk densities afforded an

average natural density value 0.013 gm/cm^3 or less than that obtained from in situ values calculated from gravity variations. He concluded that accurate laboratory measurements of bulk and grain density of cores could be used to calculate values of natural density that closely approximated in situ densities of rocks of low porosity.

McCulloh (1965) suggested changes in rock volume due to elastic expansion upon unloading should be less than 0.1% for shale from 2,000 feet. This amounts to a density decrease of less than 0.002 gm/cm^3 .

Figure 3 shows the lithologic section and the laboratory determined density values of the Mississippian-Devonian shales. These values are reasonably typical of Paleozoic shales. Natural density values range from 2.43 to 2.65. The lower values are for carbonaceous and anthracite containing shales. Most of the "normal" gray shales have a narrow range of values - 2.62 to 2.65. Porosity values ranges from 0.4 to 7.2% with most samples having values between 2 and (0.8% water) and 4% (2% water).

There is a slight increase in average density with depth. The upper 100 feet of the section has appreciably lower density values than the deeper samples.

Figure 4 and 5 show the effects of calcite in shales on density and porosity as a function of depth (McCrossan - 1961). For any given depth density increases and porosity decreases as the calcite content increases. These data are obtained from Devonian age, illite-chlorite containing shales and the values and trends are probably characteristic of most Paleozoic calcareous shales.

Ricke and Chilingarian (1974) have compiled much of the available data showing the variations of density and porosity with depth. Much of the data is not particularly pertinent. Both increase with depth and age.?

THERMAL PROPERTIES

Soils

Smith and Byers (1938) found that, for soils in the dry state, the thermal conductivity of the actual soil material is practically constant (3 to 5 $k \times 10^4$) and varies little from one soil to the other; perhaps to less degree than do the densities. The thermal conductivity of a given soil packing is determined by the porosity to which it is packed; those of greatest porosity permit the transfer of least heat, those of least pore space, most heat. To less exact degree of approximation, it can be said that soils of least volume-weight transmit least heat, and those of greatest volume-weight, most heat.

When the same soil samples were wetted (Smith - 1939), the moisture content increases, the thermal conductivity increases, and the ability of the soil to transmit heat may in the case of a soil wetted to moisture equivalent be almost treble that of the oven-dried soil. The horizons highest in organic matter, show the lowest conductivities. The horizons higher in clay content have an intermediate ability to transmit heat while those of sandy texture show greatest ability to transmit heat. Noticeable increase in the thermal conductivity occurs, in most cases, for moisture contents between 50% moisture equivalent and 100% moisture equivalent. Thermal conductivity values commonly increase from 3 to 4 for over dry samples to 8 to 12 $k \times 10^4$ for 100% moisture equivalent.

Carter (1951) studied a series of soils from the Tennessee Valley Area and reported that although water is a poorer conductor of heat than the soil materials, the first additions of water to a dry soil materially increase the soil conductivity. This is because water is a better conductor than air, and being initially adsorbed on the surface of the grains, provides a connecting film from grain to grain. As the pore spaces become filled, the soil conductivity tends to approach a maximum value since in the additional volume provided for heat flow the ratio of water to soil material approaches a limit. For a given volume of grains, the connecting film will be formed in coarse-grained soils from less water than would be required for finer-grained soils. Thus, the rate of increase in conductivity with

increased moisture content should be greater for coarser-grained soils. i.e., those having smaller liquid limits. Also, a flake-like particle should provide better contact for heat transfer than a spherical particle, so that for soils with equal liquid limits, the one containing the most clay (lowest plastic limit) should be the best conductor. Thus, for a given moisture content the thermal conductivity of soils should be inversely proportional to both the liquid and plastic limits. This trend is shown in Table 8.

Table 8

Relationship Between Liquid and Plastic Limits and Thermal Conductivity

Soil Location	Product of Liquid Limit and Plastic Limit	Thermal Conductivity, Btu per hr sq ft (deg F/ft)						
		Moisture Content, per cent (dry basis)						
		0	5	10	15	20	25	30
Columbus, Miss.	0	0.28	0.66	1.06	1.43	1.74	2.00	2.28
Cleveland, Tenn.	669	0.15	0.33	0.52	0.68	0.80	0.89	0.94
Murfreesboro, Tenn.	1210	0.21	0.30	0.42	0.59	0.70	0.79	0.84
Bristol, Va.	2180	0.14	0.19	0.27	0.34	0.43	0.52	0.60

The thermal diffusivity of a soil is related to the thermal conductivity as follows:

$$a = \frac{k}{\rho C}$$

where

a = thermal diffusivity, sq ft per hr

k = thermal conductivity, Btu per hr sq ft (deg F per ft)

ρ = density, lb per cu ft

C = specific heat, Btu per lb deg F

The specific heat of water is approximately five times that of soil material, and as more and more water is added to a soil the increase in density and specific heat becomes greater than the increase in conductivity. Therefore, the curves of thermal diffusivity versus moisture generally go through a maximum to a subsequent decrease. Since the increase in conductivity with added moisture is slower for the fine-grained soils, the increase in diffusivity should also be slower, and the rate of increase of diffusivity with moisture should also be inversely proportional to both the liquid and plastic limits. This trend is shown in Table 9.

Table 9

Relationship Between Liquid and Plastic Limits and Thermal Divvusivity

Soil Location	Product of Liquid Limit and Plastic Limit	Thermal Diffusivity, sq ft per hr Moisture Content, per cent (dry basis)						
		0	5	10	15	20	25	30
Columbus, Miss.	0	0.016	0.029	0.038	0.0425	0.045	0.0455	0.046
Cleveland, Tenn.	669	0.0115	0.018	0.022	0.024	0.024	0.024	0.022
Murfreesboro, Tenn.	1210	0.0145	0.016	0.0195	0.0225	0.024	0.024	0.0235
Bristol, Va.	2180	0.0090	0.0105	0.012	0.0135	0.0145	0.0155	0.016

Marine Mud

In a study of ocean bottom muds Ratcliffe (1960) found that thermal conductivity decreased as the water content increased (Fig. 6). He constructed a graph (Fig. 7) showing the relation between conductivity, bulk density, water volume and water weight.

In order to obtain a wider range of values Ratcliffe (1960) made some measurements on artificial mixtures and plotted conductivity data versus water content (Fig. 8).

As the water content is increased from zero, the air between the powder grains is gradually replaced by the higher-conductivity liquid, and the conductivity of the wet powder increases, at first rapidly and then more slowly. Saturation occurs at 30 to 37 percent content by volume, when all voids are filled. Further additions of water will lead to diminution in solid material per unit volume as this is replaced by liquid, and, if the conductivity of the water is less than that of the grain material, the conductivity of the mix will decrease after saturation point has been reached, to a lower limit, which is the thermal conductivity of water. Loss of contact between the grains may also aid this decrease. The ratio of the conductivity of a water/copper powder mix to that of a water/sand mix for a water content of 50 per cent by volume is about 2:1 whereas the ratio of the conductivities of the solid grains is probably of the order 50:1. It is clear that the relatively small differences in the conductivities of ocean sediment grains can be neglected and that the diagram of Fig. 7 may be used to obtain conductivity values for diverse sediments.

Sandstones

Studies of sandstones and unconsolidated sand by Woodside and Messmer (1961) showed that in dry sandstones conductivity increased as the porosity decreased (from 15.5 for 3% porosity to 3.69 for 29% porosity). When the pores were filled with water all six samples had higher conductivity values and the percentage increased with increasing porosity; however, as for the dry samples, conductivity increased with decreasing porosity. Though water is more conductive than air it is considerably less conductive than most minerals.

Zierfuss (1969) measured the heat conductivity of clayey sandstones (natural condition) to determine the effects of clay. He found no clear trend but confirmed that clay decreases the heat conductivity of sands as does pore space. He obtained heat conductivity values of 2.5 milli cal/cm sec^{°C} for sands containing 40 to 57% clay by bulk volume. Clean sand had a value of 6.5. Both had 15 to 20% porosity. A plot of heat conductivity values against porosity plus clay content shows a fairly linear relation. He also made measurements on carbonate rocks.

Shales and Slates

The Geological Society of America's Handbook of Physical Constants (Special Paper 97, 196) contains the most complete compilation of thermal conductivity data for rocks.

Two cgs units of heat are in common use, and thermal conductivity is commonly given in either of two units: units of $\text{cal/cm sec}^{\circ}\text{C}$; to convert to $\text{watts/cm}^{\circ}\text{C}$, these values are multiplied by 4.184. A unit sometimes encountered in engineering work is the British thermal unit per square foot per hour for a temperature gradient of 1°F per inch; this unit equals $3.446 \times 10^{-4} \text{ cal/cm sec}^{\circ}\text{C}$.

Rocks are not homogeneous, and their constituent crystals predominantly are of low symmetry. If no large-scale departures from isotropy exist, however, a single conductivity, determined from a sufficiently large sample, suffices to give the relationship between average heat flow and average thermal gradient. Such factors as bedding, schistosity, and fracturing may introduce marked differences in the conductivity in different directions.

Table 10 contains conductivity values for clay and mica-rich rocks. Measurements were made at a temperature of about 20°C .

Values for gneiss and schist range from 6.2 to 8.9. Shale values are slightly less, ranging from 3.3 to 5.7. Marls and argillaceous limestone values range from 3.5 to 7.3. The range for all rock types is 3.5 to 16. 67% of the values for all rocks fall in the narrow range of 5.0 to 8.0. Quartzites have the highest average values and shales the lowest. Rock salt has values ranging from 12 to 17.

The data for soils and muds suggest differences in the type of clay minerals comprising the bulk of the rock has relatively little effect on thermal conductivity. Thus, the porosity or water content of a shale would have more of an effect than variations in the clay mineral suite. Montmorillonitic shales have a higher water content than shales containing other types of clay minerals and should have lower conductivity values. When the water is expelled, the pore space (filled with air) of a montmorillonitic shale would be higher than other shales and the conductivity would show a greater decrease. Quartz and carbonate minerals in shales should increase the conductivity values.

Table 10
Conductivity of Rocks

Rock type and locality	Number of determinations	Conductivity (10^{-3} cal/cm sec $^{\circ}$ C)		Ref.
		Mean	Range	
Gneiss				
Gotthard Tunnel, Switzerland	15	6.68	5.1-8.0	1
Gneiss				
Simplon Tunnel, Switzerland				
Perpendicular	22	6.34	4.6-7.7	1
Parallel	8	8.90	6.0-11.4	1
Schists Lustrees				
Simplon Tunnel, Switzerland				
Perpendicular	8	5.74	4.1-6.8	1
Parallel	7	7.50	6.8-8.9	1
Gneiss				
Chester, Vt.				
Perpendicular	9	6.24	4.9-8.7	2
Parallel	9	8.33	6.1-10.4	2
Karoo Shale				
Kestell Bore, Orange Free State (35 $^{\circ}$ C)	6	5.7	4.7-6.9	3
Argillaceous Limestone				
Resolute Bay, N.W.T.	5	7.3	6.6-8.0	4
Fars Marl, Shale, etc.				
Masjid-i-Sulaiman, Iran	5	4.9	=.3	5
Shale				
Berry No. 1 Well, Kern Co., Calif.				
1000-5290 feet	14	3.55	2.8-4.2	6
5290-8780 feet	17	4.20	3.2-5.6	6
Permian Marl				
Yorkshire, England	5	5.22	4.2-6.6	7
Carboniferous Shale				
England	11	3.26	3.0-4.3	7
Triassic Marl				
Yorkshire	5	3.52	2.2-5.3	7

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2. Clark, S. P., unpublished
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5. Coster, Mon. Not. Roy. Astr. Soc., Geophys. Suppl. 5, 131, 1947
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At relatively low temperatures ($<400^{\circ}\text{C}$), conductivity of slates and most other rocks decreases with increasing temperature. The conductivity of quartz and most minerals show this same trend. Table 11 lists some values for slate, pyrophyllite and quartz. The slate values should be similar to those that would be obtained from well consolidated Paleozoic shales. The data also indicates that for pyrophyllite the conductivity parallel to the bedding is about twice as high as perpendicular to the bedding. A similar relation should hold for shales.

Table 11
Effect of Temperature on the Conductivity of Rocks

Rock type and locality	Temperature $^{\circ}\text{C}$	Conductivity ($10^{-3}\text{cal/cm sec}^{\circ}\text{C}$)	Density (gm/cm^3)	Ref.
Slate				
	0	5.2		1
	100	4.7		
Pa.	0	4.6		2
Perpendicular to bedding	100	4.2		
	200	4.1		
Pyrophyllite				
Transvaal				
Parallel to bedding	0	11.9		3
(Values read from curve; 100		10.0		
Conductivity perpen-	200	8.5		
dicular to the bedding	300	7.5		
is about half as large	400	6.7		
as parallel to the bedding.)				
Quartzitic Sandstone				
Parallel to bedding	0	13.6		
	100	10.6		
	200	9.0		
Perpendicular to bedding	0	13.1		
	100	10.3		
	200	4.1		

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1. Ensor, Proc.Phys.Soc. (London) 43,590,1931
2. Birch and Clark, Am. Jour.Sci. 238,529 and 613, 1940
3. Carte, Brit.Jour.Appl.Phys.6,326,1955

It is of interest to note that for most kaolin and silica based fireclay brick and refractory brick the conductivity increases with increasing temperature (see Tables 14 and 15). This is due to the presence of glass. The thermal conductivity of glass always increases with increasing temperature (Norton - 1949). Conceivably temperatures could get high enough in the immediate vicinity of the canister to produce a glass phase.

Figure 9, from Birch and Clark (1940), shows the thermal conductivity of a number of sediments as a function of temperature. At 0°C the conductivity of halite is 3.2 times that of slate; at 200°C the factor is reduced to 1.8. By extrapolation the factor should be approximately 1.2 at 400°C.

The limited data in Table 12 indicates the conductivity of shales and slates increases from 5 to 10% when they are compressed (decreased pore space) or wetted. These samples should have low porosities (< 5%) and thus water has little effect on conductivity. Perhaps it is possible to calculate the porosity from the increase in conductivity when the pores are filled with water.

Table 12

Effect of Wetting and Simple Compression on the Thermal Conductivity

K_o conductivity of dry, uncompressed rock at 45°C, in 10^{-3} cal/cm sec °C.

ΔK_p increase of conductivity of dry rock on compressing to 10,000 lbs/in².

K_m maximum observed conductivity for compressed wetted rock.

Rock	Bulk density (gm/cm ³)	K_o	$\frac{\Delta K_p}{K_o}$	K_m
Shale Sunderland, Mass.*	2.67	3.87	10	4.25
Slate Penna.*	2.76	4.32	4	4.50

*Clark, Trans. Am. Geophys. Union, 543, 1941

Experiments and theoretical calculations (Yong-1967) for montmorillonite containing interlayer water show that an increase in temperature, from 25°C to 45°C, produces an increase in swelling pressure or, if unconfined, an increase in volume. It is not clear to what temperature this relation holds but the effect can presumably be calculated (Yong and Warrentin - 1966). The ability of the water to escape from the clay would be the controlling factor. If high temperatures cause an impermeable seal to form in the vicinity of the canisters considerable volume increase would occur in a vertical direction.

WATER

Table 13 list the conductivity values for water as a function of temperature and pressure. Increases in both temperature and pressure cause an increase in conductivity.

Table 13

Conductivity of Water as Function of Pressure and Temperature
Units of 10^{-3} cal/cm sec $^{\circ}\text{C}$

T ^o C	P kg/cm ²					
	1	1000	2500	4000	8000	
0	1.34*					
10	1.39*					
20	1.43*					
30	1.47*	1.46	1.55	1.69	1.80	2.04
40	1.50*					
50	1.53*	1.52	1.62	1.76	1.88	2.12
60	1.56*					
70	1.58*	1.56	1.67	1.82	1.94	2.20
80	1.60*					
90		1.59	1.72	1.87	1.99	2.26
110		1.62	1.75	1.91	2.05	2.31
130			1.78	1.95	2.10	2.36

* From Powell, Adv. in Physics 7, 276, 1958 (All other values from Lawson, Lowell, and Jain, Jour.Chem.Phys.30,1959).

Refractories

Thermal Conductivity

The coefficient of thermal conductivity (K) is defined as "the quantity of heat that will flow across unit area in unit time, if the temperature gradient across this area is unity." In standard engineering units, as applied to refractories, the "thermal conductivity" K represents the amount of heat, in British thermal units, which will flow through the refractory per hour, per square foot of surface, per degree F. temperature difference between the hotter and the colder faces, and for 1-inch thickness.

The approximate thermal conductivities of various refractories are given in Tables 14 to 16 (Harbison - Walker Refractories Co - 1961 and Norton - 1949). The main factors which affect the thermal conductivity of refractory materials are the chemical and mineral composition of the refractory, the amount of amorphous material (glass or liquid) which it contains, its porosity, and its temperature.

For any particular type of refractory, the proportion of pore space is unquestionably the most important factor affecting the amount of heat which will flow through it at a given temperature. Within the temperature range covered by this study, the thermal conductivity decreases with increasing porosity.

At atmospheric temperatures, the thermal conductivity of a glass is considerably lower than that of crystalline material of the same composition. With rising temperatures, the conductivity of glasses tends to increase, while that of crystalline material tends to decrease. However, in refractory bodies consisting of crystal aggregates with a limited amount of glass, this effect is often obscured by other factors. The conductivity of a refractory in service at high temperature is changed somewhat either by an increase in the amount of glass or liquid it contains, or by devitrification of the glass.

The conductivity of some refractories appears to increase more rapidly at temperatures above approximately 1100°C , although only limited data are available for temperatures this high. This effect may be due, at least partly,

to increased radiation across the pores of the refractory at these temperatures. There would be greater transmission of heat across large pores than across small ones.

The conductivity curve of a refractory material may be obtained by plotting the results of a series of laboratory tests taken at different temperature intervals. In each test, the conductivity reported is the mean value between temperatures recorded for thermocouple points situated near the hot and the cold faces of the refractory. The line connecting the various points representing a series of tests gives the conductivity curve, and represents the mean conductivities. Only if the conductivity "curve" is a straight line does it represent true conductivities also. However, even if the conductivity is represented by a cruved line, the deviations from true conductivity values are usually less than the errors of observation.

Unfired Refractories

The estimation of heat flow through refractories which have not been fired in the manufacturing process presents serious difficulties. Chemically-bonded brick and monolith-forming refractories, which fall in this category, begin to undergo physical and chemical changes almost as soon as they are heated in service. These changes have a pronounced and complicating effect on the thermal conductivity of the refractories.

Consider the case of a wall built of castable material, to be heated on one side in service, while exposed to the air on the other. Before heat is applied, the completed wall has a strong hydraulic bond throughout its entire thickness. When the furnace is fired, a temprature difference develops between the interior and exterior surfaces. In any part of the wall heated above 450°C , the chemically combined water is gradually driven off. In any part above 1000°C to 1100°C , a second change, the development of a ceramic bond, thakes place also. Consequently by the time the wall has essentially reached thermal equilibrium, and no further appreciable changes are occurring, the wall has a well-developed zoned structure.

In the first or coolest zone, where the maximum temperature is below 450°C , the refractory retains its hydraulic bond, and the thermal conductivity is relatively high.

In the second or middle zone, the hydraulic and chemical bonds have been partly destroyed, but the temperature is not high enough for the development

of a ceramic bond. The strength is moderate, and the conductivity is low.

In the third or highest temperature zone, where the minimum temperature is above 1000°C ., pyrochemical reactions have taken place which form a strong permanent bond - the so-called ceramic bond. The thermal conductivity is much higher than that of the middle zone.

The conditions described above are illustrated schematically in Figure 10 which shows that each zone has its own thermal conductivity characteristics.

Depending on the particular construction and the operating temperature, a monolithic component of a refractory structure could consist of (1) all three zones, (2) the unaffected portion alone (Zone 1), (3) the portion with a ceramic bond alone (Zone 3), or (4) a combination of any two adjacent zones.

Considerable data are available from the thermal conductivity of castables which have been preheated to 1000°C to 1100°C . This corresponds roughly to the minimum temperature at which the ceramic bond is developed. Relatively little other information is available in the literature regarding the conductivities of castable and other unfired refractory materials.

A similar type of zonation will be produced, with the added complication of confining pressure, when a shale mass is heated from a cylindrical source. However, the zonation will be less severe as the water content of shale will be less than that of the cast clay.

Table 14

Approximate Thermal Conductivities of Fireclay Brick

Btu per Hour, per Square Foot, per Degree F. Temperature Difference,
for One-Inch Thickness

Kind of Brick	Den- sity*	Mean Conductivity at T°F.													
		200	400	600	800	1000	1200	1400	1600	1800	2000	2200	2400	2600	2800
Superduty Fireclay High-Fired (cone 18)	147	9.7	9.7	9.7	9.8	9.9	10.0	10.2	10.3	10.5	10.7	10.9	11.1	11.3	...
Conventional Firing (Alamo)	146	8.7	8.8	9.0	9.1	9.3	9.4	9.6	9.7	9.9	10.0	10.2	10.4	10.5	...
High-Duty Fireclay Aluminous	136	8.4	8.5	8.7	8.8	9.0	9.2	9.3	9.5	9.6	9.8	9.9	10.1	...	...
Glaucous (Woodland X)	127	7.1	7.3	7.4	7.6	7.8	8.0	8.1	8.3	8.5	8.7	8.8	9.0	...	...
Semi-Silica Fireclay (Kaasil)	125	5.8	6.2	6.5	6.9	7.3	7.6	8.0	8.3	8.7	9.0	9.4	9.8	...	...

*Pounds per Cubic Foot

Note: For brick of the same type, class, composition, and burn, the conductivities are approximately proportional to the bulk densities (weights in pounds per cubic foot).

Table 15

Heavy Refractory Brick

Mean Thermal Conductivity* at a Mean Temperature, °F

Type of Brick	Apparent porosity per cent	400	800	1200	1600	2000	2400
Alumina, fused	21.3	18.5	21.7	24.2	26.7	28.4	30.0
Carbon					18.5	22.0	
Chrome	30.5	10.0	10.8	11.3	11.6	11.8	12.0
	15.2	8.1	8.4	10.1	10.8	11.4	12.0
Fireclay	18.4	7.3	8.7	9.8	10.6	11.6	11.8
	26.7	7.0	7.8	8.7	9.3	10.2	10.5
Super-duty Fireclay		7.5	8.4	9.0	9.5	9.8	
Graphite		730	500	400	310	220	
	10.8	13.5	15.0	16.3	18.0	18.8	19.7
Kaolin	23.2	10.0	10.9	11.9	12.8	13.4	13.8
	49.1	3.0	4.4	5.2	6.1	6.7	7.1

* k expressed as Btu per hr per sq ft per in. per °F.

Table 16

Thermal Conductivity of Insulating Materials (High Porosity)

Type of Insulation	Linear shrinkage- 5-hr.reheat, percent at °F	Density, lb. per cu.ft.	Mean thermal conductivity* at a mean temperature of						
			200°F.	400°F	800°F	1200°F	1500°F	2000°F	2400°F
Insulating firebrick:									
Kaolin base	1.00 at 2900	55			2.9	3.3	3.9	4.5	5.2
Kaolin base	1.00 at 2800	44			2.1	2.8	3.3	3.8	4.4
Fireclay base	3.10 at 2600	48		2.5	2.8	3.2	3.7		
Kaolin base	0.10 at 2300	26		0.8	1.0	1.3	1.5		
Insulating brick:									
Raw diatomaceous earth base	1.00 at 1400	33	0.7	0.8	0.9	1.0			
Calcined diatomaceous earth base	2.80 at 2300	43			1.4	1.6	2.0		
High-temperature block insulation:									
Diatomaceous earth base	3.10 at 1900	23	0.58	0.62	0.70	0.80			
Vermiculite base . . .	0.75 at 1600	18.5	0.55	0.67	0.80	0.95			
Mineral wool base . .	1.69 at 1600	22	0.42	0.56	0.84				
Kaolin base		19	0.58	0.67	0.91	1.21			

* expressed as Btu per hr per ft per in per °F.

Specific Heat

The term "specific heat" has been used in the ceramic literature rather loosely and, in many cases, has been applied not only to specific heat values but to values of latent heat of association, inversion, or crystallization. Specific heat may be defined as a number expressing the ratio of the heat quantity required to raise, respectively, 1 g of the given material 1°C at a definite temperature and 1 g of water from 19.5 to 20.5°C. Specific heat can correctly refer only to the heat required for raising the temperature of a thermally stable material that is free from any changes through the measured interval. We can, therefore, correctly speak of specific heat as applying to stable refractory materials that have been previously fired to complete all irreversible reactions and that have no reversible changes in the temperature range being measured. For example, the specific heat of quartz is continuous up to 573°C, where a crystal change takes place giving off a small amount of latent heat of inversion that must be added to the specific heat to give the total heat content. The use of the term specific heat for raw clays, as is often done, is very unfortunate.

In Table 17 are given some values of specific heat for a number of ceramic materials that are somewhat similar to heated shales.

Table 17

Values of Mean Specific Heat (Norton - 1949)

Material	Temperature range °C	Mean specific heat
Fireclay brick - 35 per cent Al_2O_3	25-600	0.228
	25-1000	0.265
	25-1200	0.284
	25-1400	0.297
Fireclay brick	200	0.204
	400	0.222
	600	0.236
	800	0.248
	1000	0.256
	1200	0.263
Lime, fused	375-400	0.181
	590-680	0.193
Magnesia, pure	30-100	0.234
	30-300	0.247
	30-500	0.259
	30-700	0.269
	30-900	0.277
	30-1100	0.283
	30-1300	0.288
	30-1500	0.291
	30-1700	0.294
	30-1800	0.295
Mullite, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	20-200	0.161
	20-400	0.167
	20-600	0.173
	20-800	0.175
Quartz glass SiO_2	0-200	0.201
	0-400	0.223
	0-600	0.239
	0-800	0.251
	0-1000	0.258
	0-1200	0.262
	0-1400	0.269
	0-1600	0.278
	0-200	0.203
	0-400	0.223
	0-800	0.259
	0-1000	0.271
	25-600	0.226
	25-1000	0.263
	25-1200	0.282
	25-1400	0.293

Heat Absorption

The determination of the heat required to raise a clay to a certain temperature is a very difficult measurement because the calorimeter method, which can be used for stable materials, is not applicable here. The heat given up on cooling is quite different from the heat absorption in raising the temperature. It is therefore, necessary to find some way of actually measuring the heat going into a given specimen as it is raised through definite temperature intervals. A number of methods have been used to make these measurements; but because of the inherent difficulties of measuring the heat directly absorbed by the specimen, the results are not highly precise.

In Table 18 are values for the heat required to raise various types of clays (Al-rich) to definite temperature levels.

Table 18 The Heat Required to Burn Unfired Bodies

Material	Temperature °C.	cal. to heat 1 g. from 20° to t°C.
Ball clay (Kentucky) . .	0-200	68
	0-400	159
	0-600	285
	0-800	366
	0-1000	465
Diaspore clay	0-200	70
	0-400	150
	0-600	274
	0-800	350
	0-1000	450
Firebrick body . . .	0-200	68
	0-400	145
	0-600	268
	0-800	337
	0-1000	415
	0-1200	507
Fire clay, raw Chamotte	200	35
	400	80
	600	201
	800	243
	1000	326
	1200	452
	1400	572

Table 18 continued

	0-200	79
	0-400	183
Kaolin, Georgia	0-600	332
	0-800	402
	0-1000	496
	200	37
	400	86
	600	241
Kaolin, Zettlitz	800	333
	1000	420
	1200	489
	1400	560

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A completely dry piece of clay is apt to be brittle.

The water lost from the clay in drying between its original condition and the critical point is referred to as "shrinkage water" and the remainder as "pore water". In well compacted shales containing no expanded clay the only water present, by the above definition, is probably pore water.

The critical point of montmorillonitic clays is poorly defined because of the presence of interlayer water. The last interlayer water leaves and the final shrinking occurs just before dryness. Some other clays have a slight expansion at the end of the drying process.

Drying shrinkage is measured either by a length change or a volume change. A near linear relation exists between the two types of measurement. From 0 to 5% linear shrinkage (dry basis), the volume shrinkage is 3 times the linear value. The conversion factor gradually decreases to 2.5 at 18% linear shrinkage.

Linear shrinkage for molded kaolin and fire clays is on the order of 5.5%. The initial water content ranges from 25 to 40%. Most of the shrinkage is completed where approximately half the water is driven off.

Drying is generally done at temperature of 50 to 90°C and is completed in 24 to 48 hours.

Effects of Heat on Individual Minerals

When clays are exposed to higher temperatures the process is called firing. If the temperature is high enough ($\sim 900^{\circ}\text{C}$) the clay is altered into a strong and partly vitreous mass.

There is considerable data on the thermal properties of clay-rich materials (bricks) heated to temperatures of $\sim 900^{\circ}\text{C}$ and higher and at temperatures of 25 to 100°C . What happens between 100° and 900°C is of relatively little interest to the ceramist and there are few available on the properties of clays in this temperature range. As this is the temperature range that is most pertinent to subsurface storage of radioactive waste the effects of temperature on the various minerals in shales will be reviewed.

The structure or hydroxyl water of kaolinite is driven off between approximately 550 to 700°C. The peak temperature of the endothermic dehydration process commonly ranges from 550°C to 700°C. The peak temperature of the endothermic dehydration process commonly ranges from 550°C to 625°C (Richardson - 1961 and Grim - 1968). Static heating for 24 hr periods indicate dehydroxlation occurs at approximately 450°C. The dehydrated material is called metakaolin. The weight loss produced by the loss of the hydroxyls is 14% but the density decrease is only 1.5%. The a and b dimensions of the kaolinite layer remains unchanged but calculations indicate the C dimension (perpendicular to the kaolin sheet) decreases by 12.4% (Brindley and Nakahara - 1959). The hexagonal shape of the flakes remain unchanged.

Little happens to the metakaolin until 900°C (heated for 20 hrs.) at which temperature the SiO_2 starts to leave the metakaolin layers and a spinel-type phase is formed ($2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$). The following crystalline phases are formed over varying temperature ranges:

900-1150°C	γ -alumina
1100-1350°C	cristobalite
950-1400°C	mullite.

The presence of illite (K) lowers the temperature at which mullite begins to form to 900°C (Slaughter and Keller - 1959).

Dehydration curves for illite (Grim - 1968) indicates a gradual loss of water ($\sim 1\%$) between 100 and 350°C. This is mostly adsorbed water and trapped interlayer water. There is a relatively abrupt loss of hydroxyl structural water between 350 to about 600°C. This is accompanied by a slight expansion in the C dimension. The structure of illite is destroyed at about 850°C and spinel formed. Total weight loss at this temperature is about 7% for pure illite. The spinel increases in amount and particle size up to about 1200°C. The Al, Mg and Fe in the octahedral layer is thought to form the spinel and the alkalis and Si forms an amorphous glass. Mullite become apparent at 1100°C and persists to at least 1400°C.

After heating illite to 600°C and 800°C and cooling there is a rapid pickup of both adsorbed and hydroxyl lattice water. Additional amounts are regained slowly for a period of many months.

Smectites (montmorillonites) loose their interlayer water ($\sim 15\%$ by weight) from 100 to 200°C. The layers contract from 15 to 12Å (depending on the type of interlayer cation) to 9.4 to 10Å. The OH lattice water is lost at a wide range of temperatures depending on the composition of the smectite. For most, loss of OH water starts at about 500°C and is complete at 800°C. These values are for continuous heating (usually 10°C per minute). During static heating most of the OH water (7 to 8% by weight) should be lost at 500°C or slightly lower. The loss of OH is accompanied by an increase of 0.1 to 0.3Å in the c direction. An endothermic reaction at 800 to 900°C is believed due to the destruction of the lattice.

Following this third endothermic reaction there are a wide variety of thermal reactions for various smectites indicating considerable variation in the phases formed. The most common new phases at 1000°C are spinel and quartz, others are enstatite, cristobalite and mullite. By 1300°C cristobalite, cordierite and mullite are the most common phases.

Montmorillonites heated to 600°C and cooled remains about one-fourth of their OH lattice water in 268 days; however, these samples were only heated for 1 hr.

Chlorites loose their hydroxyl lattice water in two stages. The first is lost between 500 and 700°C and the second between 600 and 800°C. An exothermic reaction between 800 and 950°C is due to the formation of olivine. Total water lost ranges from 10 to 14%.

Gibbsite, $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, starts to loose its water at 110°C and loses most of it by 200°C (Rooksby - 1961). The water content decreases from $3\text{H}_2\text{O}$ (34.6% by weight) to $0.5\text{H}_2\text{O}$. At 425°C completely anhydrous alumina (Chi alumina) is obtained. The anhydrous form goes through a number of various structural modification $\text{Chi} \rightarrow \text{Kappa} \rightarrow \text{Alpha}$ (corundum) or $\text{Gamma} \rightarrow \text{Delta} \rightarrow \text{Theta} \rightarrow \text{Alpha}$ depending on the starting material and grain size. The surface area decreases and crystal size increases with increased heat. Corundum is not obtained till 1000°C.

The specific gravity increases from 2.3-2.4 for gibbsite to 3.95-4.10 for corundum. Most of this change should occur by 200°C and probably lower.

Goethite, $\text{FeO} \cdot \text{OH}$, contains approximately 10% water. It begins to decompose at 250°C and at 300°C is converted to α -ferric oxide (hematite) (Rooksby - 1961). The initial grain size is small but grows as the temperature increases to $600\text{--}700^{\circ}\text{C}$.

The volume change would appear to be relatively small. Ten percent by weight of water is lost (14.5% for limonite, a poorly crystallized goethite). The specific gravity increases from 3.6-4.0 to 4.9-5.3.

At approximately 573°C quartz inverts from the low to high form (alpha-beta inversion). This is a minor structural change and causes an 0.86% increase in volume. The change is reversible (Fronde11-1962).

In addition, thermal expansion increases the volume of quartz approximately 3% between 100°C and 573°C .

Firing Properties of Clay Bodies

General

Much of the review on the firing properties of clays is taken from (Grim-1962). It should be noted that the components of clay minerals other than the clay minerals may play a dominant role in determining the characteristics developed on firing. Indeed, small amounts of certain elements, such as the alkalis, may largely determine what high-temperature phases may develop and the temperature of fusion.

As the temperature is raised to about 100 to 150°C , the shrinkage and pore waters are lost with attendant dimensional changes as indicated in the discussion of drying shrinkage. In the case of the expanding clay minerals, temperatures of the order of 100 to 300°C cause the loss of the ability to swell again. The loss of swelling potential is related to the complete loss of interlayer water; hence, heating must be continued at the indicated temperature for a considerable time. The precise temperature for the permanent loss of swelling is dependent on the nature of the adsorbed cation with the loss taking place in montmorillonites at 105 to 225°C , 300 to 390°C , and 390 to 490°C when lithium, calcium, and sodium, respectively, are the adsorbed cations. The very low temperature required by lithium for the loss of swelling potential is explained by the ease of penetration of this small ion into vacant octahedral positions in the dioctahedral lattice and the consequent reduction of charge on the lattice.

At temperatures of the order of 200 to 300°C, the oxidation of any organic material begins. The rate of oxidation depends on the nature of the organic material, the amount of oxygen available, the ease of its access through the mass of clay to the organic material, and the temperature. The nature of the organic material depends on its composition, its particle size if in discrete particles, and whether or not it is adsorbed on the clay mineral surfaces. The second factor is concerned with the texture of the clay, whether it permits the oxygen to enter and the reaction products to leave the clay body. In general, the rate of oxidation increases as the temperature increases. Actually, the vital factor in firing many clays is the elimination of any gas-forming components before vitrification. The objective is to raise the temperature as high as possible short of vitrification in order to get the most rapid and safe rate of oxidation of the organic material and other oxidizable components.

The oxidation of sulfides, which are present in many clays, frequently in the form of pyrite, begins between 400 and 500°C. Fine-grained pyrite in the presence of abundant oxygen loses its sulfur and oxidizes with an abrupt exothermic reaction in this temperature range. In the actual firing process, the lack of sufficient oxygen may greatly retard the oxidation of the sulfides. Further, the sulfur liberated from the sulfides may react with aluminum and/or iron, made available by the partial disruption of the lattice structures of some of the clay minerals at about the same temperature, to form compounds which are resistant to oxidation; the lattice disruption is that accompanying the loss of hydroxyls from the structure of the clay minerals. The nature of these compounds is not well understood, but their presence is often indicated by a black core showing up in the center of fired bricks.

Beginning somewhat below 500°C and in some cases continuing to 900°C, the hydroxyl water is driven from the clay minerals. The exact temperature, rate, and abruptness of loss of hydroxyls depends on the nature of the clay minerals and their particle size.

Carbonates lose carbon dioxide in the temperature interval from about 500 to 900°C with the exact temperature varying with the nature of the carbonate and its composition. These reactions are abrupt and endothermic and would take place, therefore, when the material reaches the proper temperature. Slight increases in pressure because of the difficulty in the escape of the carbon dioxide would probably slightly increase the

abruptness of the reaction.

The structure of the dehydrated form of the dioctahedral micas is lost by about 900°C, and all of the clay minerals are completely dehydrated by this temperature. In the presence of a large quantity (more than about 5 per cent) of iron, alkalies, and alkaline earths (fluxes) as components of the clay minerals, as adsorbed ions, or as nonclay mineral material, there may be little development of distinct high-temperature crystalline phases with the consequence that the clay mineral begins to fuse into a glassy mass at about this temperature.

Following the loss of hydroxyls from their structures, the clay minerals may, under some conditions, regain these hydroxyls and substantially develop their initial structures again. There is little structural change accompanying the loss of hydroxyls, the rehydration and regain of structure is relatively easy and may take place under ordinary conditions of temperature and pressure. In cases where the loss of hydroxyls is accompanied by substantial structural changes, the rehydration and regain of structure is slow and may not take place to any substantial extent unless the dehydrated material is subjected to moderately elevated temperatures and pressures in the presence of water vapor.

In the absence of considerable quantities of fluxes, new crystalline phases develop from the clay minerals immediately, or after only a brief temperature interval, following the loss of the clay mineral structure and/or complete dehydration. New crystalline phases develop from all of the clay minerals except those containing large amounts of iron, alkalies, and/or alkaline earths in which case fusion may result after dehydration without any intervening crystalline phase. Frequently, there is a series of new high temperature phases developing in an overlapping sequence as the mineral is heated to successively higher temperatures. This is followed by eventual complete fusion of the mineral.

Dimensional Changes on Firing

Values for the linear firing shrinkage of the clay minerals are given in Table 19.

Table 19

Linear Firing Shrinkage of Clay Minerals
(in Per Cent)

Kaolinite	2-17
Illite	9-15
Montmorillonite	.20

The values indicate that the total shrinkages on firing of kaolinites and illites are small and substantially equal. The range in the percent of shrinkage is due to variations in the size and shape of the clay mineral particles and in the case of the illites also to variations in composition. In the case of illite increases in the amount of fluxing material would be expected to provide a relative increase in the amount of total firing shrinkage. Values for chlorites are probably similar to those for illites. Firing shrinkage of montmorillonite would be expected to be variable depending on composition but in general rather large, perhaps about twice that of kaolinite, illite, or chlorite.

Firing shrinkage varies with the particle-size distribution tending to increase as the amount of small-particle-size material increases and as the sorting increases. The firing shrinkage also varies with composition and tends to increase as the fluxing components increase with the production of relatively more glassy material and less high-temperature crystalline phases during the firing. It is interesting that there is no correlation between the content of hydroxyls in the clay mineral structure and the firing shrinkage, indicating that this is not a significant factor in the amount of such shrinkage.

It must be remembered that constituents other than the clay minerals in a clay or shale may exert a controlling influence on firing shrinkage. Thus, the presence of a considerable amount of quartz may be important in reducing the shrinkage. The clay minerals do, however, largely control the rate of shrinkage and the temperature intervals during which shrinkage takes place.

Figures 11 through 14 illustrate the dimensional changes taking place in specific clay minerals as they are heated. Starting between 500 and 600°C there is modest shrinkage accompanying the loss of hydroxyl water from kaolinite. Starting about 900°C there is a rapid and considerable shrinkage accompanying the formation of high-temperature crystalline phases.

The data for illite (Fig. 11) show a slight expansion from about 450 to 800°C followed by a rapid continuous shrinkage. The expansion accompanied the development of the anhydrite structure and the shrinkage accompanied the loss of the structure. The relative rate of this high temperature shrinkage would be expected to be greater in samples of illite which showed the least development of high-temperature crystalline phases. Kiefer (1957) has presented data (Fig. 12) for muscovite showing the increase in shrinkage as the particle size is reduced by grinding. Note the large amount of expansion perpendicular to the muscovite cleavage surface.

No data are at hand for clay mineral chlorites, but they would probably show about the same characteristics as the illites.

The aluminous montmorillonites (Fig. 13) show no dimensional changes from about 200 to 800°C except for a slight expansion in some cases between about 600 and 800°C. Above about 800°C, there is a relatively rapid shrinkage to about 1000°C after which there is no change in dimension, except in some cases where there is a slight expansion, until fusion temperatures are reached, about 1200°C; at this temperature very rapid shrinkage again takes place. The dimensional changes above 1000°C vary greatly from one montmorillonite to another as would be expected by variations in composition with the consequent variations in the high temperature phases formed and the temperature of fusion.

In general, it may be stated that the loss of hydroxyl water is accompanied by slight shrinkage if there is some loss of crystalline structure accompanying the loss of hydroxyls. If the structure is not substantially altered, as in the case of the dioctahedral micas and montmorillonites, the loss of hydroxyls may be accompanied by a slight expansion. This expansion accompanying the formation of an anhydride phase may not cause an over-all expansion in the fired piece as there may be adequate pore space to take care of the increase in dimension of the clay minerals. Also,

it must be remembered that textural variations or the formation of gaseous material may cause expansion on heating which is not related to a volume change in the clay mineral structure. The major shrinkage begins at the temperatures corresponding to the formation of high-temperature crystalline phases and, in general, becomes most rapid as vitrification begins with the development of glassy material. Again, the development of glassy material during the vitrification interval maybe accompanied by bloating.

Thermal Expansion of Rocks

The following discussion of rock expansions, by E.B. Dane, Jr., is quoted from the first Handbook of Physical Constants.

"Thermal expansion data for rocks are given here only to 100°C as tests at high temperature and at one atmosphere pressure on such aggregates of many different anisotropic crystals have little relation to the expansions of rocks buried even to moderate depths. When a rock specimen is measured in the laboratory, it is found that the coefficients of expansion are very different on heating and cooling, with a still different result on each subsequent run. This is due to the unlike expansions of adjacent grains because of differences both of composition and of orientation. As a result, when a rock is heated the grains with the largest thermal dilation tend to determine the apparent change of length of the whole specimen, creating internal fractures and "pores." Thus what is actually measured is rather the increase in porosity than the true thermal expansion. In the earth, several factors tend to minimize these effects, The directions of maximum compressibility usually lie close to those of maximum thermal expansion, so that, when temperature and pressure tend to vary in the same direction at the same time, the effects partly cancel each other. Most changes of conditions within the earth proceed slowly so that there is ample time for recrystallization to relieve the points of greatest stress and thus close the pores. However, the fact that all rocks have some porosity, which can be largely eliminated by about 1000 atmospheres of pressure, indicates that such readjustments and compensations are not complete. Considering these facts, it is believed that a better figure for the mean expansion of any rock under the conditions found deep in the earth will be obtained by averaging the weighted volumetric expansions of its constituent minerals. For the mean linear dilatation,

this figure must be divided by three."

The limited data on the thermal expansion of rocks is listed in Table 20 . There appears to be relatively little difference between the thermal expansion of slates (similar to shales) and other rocks.

Table 20 Thermal Expansion of Rocks
Temperature interval, 20-100°C

Rock type	Number of determinations	Average linear expansion coefficient
		$\frac{1}{L} \frac{\Delta L}{\Delta T}$
Granites and rhyolites	21	$8 \pm 3 \times 10^{-6}$
Andesites and diorites	4	7 ± 2
Basalts, gabbros, and diabases	10	5.4 ± 1
Sandstones	10	10 ± 2
Quartzites	2	11
Limestones	20	8 ± 4
Marbles	9	7 ± 2
Slates	3	9 ± 1

The limits include nearly all the determined values. Data from the following sources were used in making these averages:

Wheeler, Trans. Roy. Soc. Canada 3, 1910

Souder and Hidnert, U.S. Bur. Stands. Sci. Paper 352, 1919

Griffith, Iowa Eng. Exp. Sta. Bull. 131, 1937

Specific Gravity

The specific gravity of kaolinite drops abruptly at about 450°C when the mineral is dehydrated and a poorly ordered structure develops. The specific gravity gradually increases as the kaolinite is heated to higher temperatures, probably indicating some development of order; at 950 to 1000°C there is an abrupt increase in specific gravity to a value higher than that of the original. This sudden increase in specific gravity can be correlated with the high-

temperature crystalline phase developing at this temperature interval. A sample of the illite showed a decrease in specific gravity accompanying the loss of hydroxyl water above about 400°C . The decrease continued to 800°C after which there was no further change until about 1000°C when there was a slight increase in specific gravity accompanying the formation of a high-temperature crystalline phase. A sample of montmorillonite from Wyoming showed a decrease in specific gravity beginning about 700°C , which perhaps accompanied the formation of an anhydride phase. There was a slight increase in specific gravity at 950°C , which could be correlated with the development of a new high-temperature crystalline phase, with an unexplained decrease again at 1000°C .

Fusion Temperature

According to Norton (1949), kaolinite fuses at 1650 to 1775°C . The fusion point is preceded by a vitrification interval which may extend over several hundred degrees during which an amorphous component is an increasingly abundant phase. The fusion temperature of halloysite is about equal to that of the kaolinites.

In general, all the other clay minerals have a much lower fusion point than kaolinite, because they contain iron, alkalies, and/or alkaline earths as essential constituents. Also, there is no definite fusion temperature for these clay minerals as the values vary within each clay mineral group with variations in the composition. In general, the fusion point ranges from about 1000 to 1500°C with the lower values being found in materials relatively rich in iron, alkalies, and the alkaline earths.

It must be emphasized again here that components other than the clay minerals may largely control the fusion temperature and, further, that the particle size of any nonclay mineral may exert a very significant influence.

Weld or union between particles may occur during firing at temperatures below the melting point. This is called sintering and it is accompanied by shrinkage and a decrease in void space and surface area. This may be either a dry solid-state process or may involve a fluid phase. Material is transferred from point contacts to form a connecting neck or bridge between particles (Gillot - 1968).

Vitrification Range

By vitrification range is meant the temperature interval between the beginning of the development of a vitric bond in a ceramic body and the fusion of so much of the body that the shape of the ware is lost and the shrinkage is excessive. A long vitrification range is necessary practically so that the firing process can be safely controlled. In general, a mixture of mineral components in a clay will extend the vitrification range, since a likely consequence is an extended interval for the development of crystalline and glassy phases. The presence of some relatively large particles and a wide particle-size distribution will also tend to widen the vitrification range since the rate of fusion varies with particle size.

Vitrification can be expected to begin at temperatures somewhat above the formation of the initial high temperature phases. At the first high-temperature-phase development, a change in bonding and the nucleation of a new order takes place, probably without freeing much material that would be unorganized, i.e., glassy material that would act as a bond. Only at a higher temperature where there is substantial unorganized material left over from the high-temperature-phase requirements and when the high temperature phases have developed to a considerable extent and themselves caused bonding by the intergrowth of new crystalline forms would there be substantial development of hardness and strength in the clay body.

In Fig. 17, the shrinkage and adsorption characteristics of a kaolinite clay are shown in relation to firing temperature. It is seen that the shrinkage curve levels off at 2100°F and continues at a slower rate up to at least 2350°F. The adsorption curve also levels off. The contour of these curves suggests that at some temperature above 2350°F the shrinkage curve again rises sharply and the adsorption curve drops sharply. The interval from 2050 to 2350°F represents the temperature interval in which the commercial product should be fired. Steel hardness is developed at 2200°F in this temperature range. The clay shows an interval of about 300°F following major shrinkage and the development of low adsorption before final rapid shrinkage accompanies complete fusion. There is, therefore, a long temperature interval for the satisfactory firing of this clay.

Also in Fig.15 the firing characteristics of an illite shale are shown. At 1800°F after the shrinkage begins to rise into a long sloping curve to a temperature of approximately 2050°F, there are no shoulders or breaks as are characteristic of the kaolinitic materials. The temperature of steel hardness, which corresponds very closely with that necessary to produce 10 per cent adsorption, is relatively low, in this case 1900°F. This particular shale has a very good firing range because of the relatively gentle slope of the shrinkage curve. The data indicate a firing range of about 200°F, between 1850 and 2000°F, which should make firing this material relatively easy.

Kaolinite has a long vitrification range; whereas it is short for the illite and chlorite clay minerals. Stone's data are in accord with this conclusion but indicate that the range for illite may not be too short to cause difficult firing problems. In the case of the clay minerals other than kaolinite and halloysite, the vitrification range would be expected to decrease as the content of iron, alkalies, and alkaline earths increases. In other words, for these clay minerals no general correlation would be expected between vitrification range and the identity of the clay mineral, as the range would be expected to vary from relatively long to very short depending on the composition of the mineral including that of the adsorbed ions.

In refractory bodies of simple mineral composition, the presence of small amounts of fluxes may actually extend the vitrification range by causing some vitrification at lower temperatures and yet not significantly reducing the fusion point. The fluxes serve essentially to block the formation of high-temperature crystallizing phases; that is, they cause the development of amorphous glassy materials at relatively low temperatures. Fluxes are much more effective when they are present as part of the clay mineral or as adsorbed ions than when they are present in other crystalline compounds. For example, potassium when present as a constituent of the clay minerals is a much more effective flux than when it is added to the body in a feldspar. Muscovite lowered the vitrification temperature in a ceramic body more than feldspar for a given alkali content. These data emphasize that in considering the firing properties of a clay, particularly prior to complete fusion, the manner of the occurrence of the chemical components is likely to be extremely important.

Calcium is well known by ceramists to have a potent tendency to reduce the vitrification range. It should be emphasized that the effect of fluxes depends somewhat on the particle size of the fluxing components. There are, for example, refractory clays of appreciable iron content in which the iron is present in sizable particles of pyrite, so that the effect of the iron is restricted to small areas, and the over-all refractories of a brick is not materially affected. Expansion curves for refractory Fire Clay bricks (Norton - 1949) show that they expand linearly from 0 to 1200°C up to a maximum of 0.8%.

Strength

Raw clay, in many cases, has considerable mechanical strength. As of the strength usually decreases slightly because of the lessened attraction between particles. When the structural OH's are driven off there is often a further decrease in strength. At about 1000°C in pure clay the strength begins to increase because of the formation of glass and recrystallization of the remaining components. The strength increases rapidly up to the softening point (melting point or fusion point). The fusion point of clays range from 1600 to 1800°C (Norton - 1949).

Rehydrated and Refired Kaolin

Hill (1953, 1956) has shown that when a test specimen of well-crystallized kaolinite is dehydrated at 600°C, rehydrated in saturated steam at 200°C, and then fired again at 600°C the compressive strength is increased manyfold from about 3,000 to 20,000 psi. This is explained by a breaking up of the kaolinite particles into smaller and more irregular units giving a great bond between particles. The dehydration causing disorder and the subsequent rehydration must be continued long enough to regenerate the kaolinite; otherwise, the increase in strength is not developed. If the process is repeated through several cycles and/or the dehydration is continued for very long intervals, the gain in strength is much reduced, apparently because the dehydration causes so much disorder that rehydration develops little or no kaolinite. Hill (1956) found that the increase in strength also was not developed when he started with poorly ordered kaolinite.

Data are not at hand to show the possible influence of dehydration and rehydration of the other clay minerals on their fired properties.

Spalling

Thermal spalling is caused by stresses resulting from unequal rates of expansion or contraction in different parts of a brick (or shale) and usually is associated with rapid changes in temperature. Bricks with low thermal expansion and highest thermal conductivity have less spalling (Harbison - Walker Refractories Co. - 1961). The spalling characteristics of fireclay brick are largely dependent upon the proportion of free silica in the clays, upon the size and fit of the particles and upon the amount and composition of the glassy bond. A high glass content is conducive to spalling.

Shales spall much more readily than brick. The slight relief of pressure caused by the removal of a few tens of feet of overburden will cause appreciable spalling. In part this is due to preferred orientation and the anisotropic nature of shales. Massive mudstones and siltstones which have little orientation of the dry flakes have less tendency to spall.

It is important to consider the distribution of stress in an elastic solid when its surface is heated or cooled (Norton - 1949). There has been little recognition of the difference in stresses resulting from heating as differentiated from cooling. The stresses as well as the fracture are quite different in the two cases. Investigation have been carried out by the photoelastic method to determine the stresses occurring in various objects when suddenly heated and cooled at the surface.

The method of studying stresses in various structures by photoelasticity has been used to a considerable extent in determining the distribution of stress in objects where a direct computation is impossible.

Photoelastic models must be made from a transparent isotropic medium. In this case, clear bakelite was selected because of its high stress-optical coefficient.

Polarized light is passed through a plane specimen, which becomes double refracting under stress and retards the two wave systems according to the values of the principal stresses p and q . The two wave systems interfere when passed through an analyzer and give isochromatic bands proportional to the difference $p-q$. The isochromatic lines are also lines

of principal shear, for the principal shear stress at any point is equal to one-half the difference of the two principal stresses. The separate values of p and q can be determined by repeating the observations with circularly polarized light, which shows the isoclinic lines, or lines of equal direction of principal stresses. The values of p and q can be calculated from the isoclinic and isochromatic lines, the boundary conditions, and the constants of the material. It should be emphasized that this method applies only to a plane object.

The model tested was a brick heated on the end. The stresses are shown in Fig. 16. On heating, a compression maximum occurred at the center of the end; but on cooling, this was changed to a tension. It will be noted that the directions of the shear stresses are approximately 45 deg to the surface everywhere and are a maximum at the center of the end.

In the case shown in Fig. 17, the model brick was heated at the end and about one-third of the way up the side. A somewhat different type of stress distribution resulted, for the increase in stresses at the sides causes the stresses at the end to decrease. It will be noted that at the corners, the shear lines are curved and follow the isothermals closely.

Figure 18 shows a model representing a brick in a wall when this wall is heated and cooled at the surface. The isothermals will then be parallel to the heated surface. It will be noted that the resultant normal stresses are nearly parallel and perpendicular to the surface of the wall and that the shear stresses are at 45 deg to them.

In order to correlate the types of cracks formed in the material when heated and cooled, with the stress distribution previously determined, a number of spheres and bricks were made up with a fine-grained, porecelin-like structure in order to make spalling occur readily. These objects were gradually heated to 900°C for the first condition and were placed in still air to cool. Under the second condition, the objects were heated by placing suddenly in a furnace that had a temperature of 900°C.

In the sphere that was suddenly cooled, in general, the fractures follow great circles. When the portions of the sphere were separated, it was noted that the cracks entered the surface in every case at approximately 90 deg. On the other hand, when the sphere is suddenly heated, a quite different type of fracture is obtained, as shown in Fig 19. In this case,

the fractures entered the surface at 45 deg and tended to split off circular segments of the sphere having a height of approximately one-quarter the diameter.

Standard-size bricks were made up of the same material as the spheres. They were also heated and cooled in the same way. In Fig. 19 are shown the fractures resulting from rapid cooling. It will be noted that the fractures enter, in nearly every case, at right angles to the surface and tend to break the brick into cubes. Figure 19 shows the same brick when heated suddenly. The typical spalling failure is shown at the edges and corners; and in every case, cracks enter the surface at approximately 45 deg.

We may conclude from the preceding studies that spalling is due to both shear and tension failures. On sudden heating, spalling is due almost entirely to shear stresses and, on sudden cooling, to tension stresses except at the corners and edges, where shear stresses may still cause failure. The shear values are about equal on heating and cooling, but there are no large tension stresses on rapid heating.

Shear failure occurs suddenly; i.e., complete pieces are split off at each cycle of heating, and they begin to split at the edges and corners, so that a brick tends to approach a spherical shape on the end. The shear cracks follow in the lines of shear determined by the photoelastic method very closely, as is indicated by the slight curvature of the shear fractures at the corners.

Tension cracks seldom occur near the corners but usually first appear halfway up the brick where the tensile stresses are a maximum. The tension cracks enter the surface at 90 deg. They do not occur as suddenly as do shear fractures but penetrate deeper and deeper at each cycle until finally the cracks meet at the center. In every case, the tension failures follow approximately the lines of principal stress, although the deviation was considerably more than for the shear stress, owing undoubtedly to the length of the cracks and the greater influence of discontinuities.

It should be noted that the stress distribution is much altered after a crack starts. Generally, however, the tension cracks enter and leave at 90 deg and shear cracks at 45 deg to the surface. The fracture need not follow the direction of stress everywhere but will travel in such a way as to release the maximum strain energy. A great deal of confusion has been caused in the past by failure to differentiate between the effects of heating and cooling.

Brick

Almost any composition of clay or shale is satisfactory for the manufacture of common brick unless it contains a large percentage of coarse stony material. Further, a high concentration of nonclay material in a silt- size range may cause difficulties by reducing the green and fired strength of the ware. Montmorillonite should be absent or present only in very small amounts as otherwise the shrinkage may be excessive. Clays composed of mixtures of clay minerals with appreciable amounts (25 to 50%) of unsorted fine-grained nonclay minerals, mostly quartz are most satisfactory. Abundant kaolinite tends to increase the temperature required for firing. Large amounts of iron, alkalies, and alkaline earths, either in the clay minerals or as other constituents, are detrimental because they cause too much shrinkage and reduce the vitrification range. Thus, a clay with a substantial amount of calcareous material is not desirable.

Shales and sedimentary clays with a wide range of ages are used in the manufacture of brick. Surficial soil material is also widely used, although the presence of appreciable organic material may make firing somewhat difficult.

Thus, virtually any clay or shale with less than 50% quartz can be fired to a brick-like consistency. Mineral and chemical composition effects the amount of heat required, the amount of shrinkage and the strength of the heated product.

Making a few simple assumptions it is possible to calculate the quartz content of shales from the chemical analyses. The chemical analyses of shales used for making brick indicate that most contain between 20 and 40% quartz; the majority contain 30 to 40%. The quartz tends to reduce shrinkage. Shaw and Weaver (1965) determined that the average quartz content of shales was 30% and that 75% of all shales contain between 20 and 40% quartz. It would seem that the vast majority of shales have the quartz content necessary to make a good brick.

It should also be noted that most brick and ceramic products are not heated long enough to obtain equilibrium assemblages. Thus caution must be used in extrapolating the data based on the firing of bricks. The application of heat for long periods of time will lower the temperature at which most reactions occur. Further, the data on the physical properties of most ceramic products are based on the cooled body and the values may not be applicable to the heated clay.

Bloating

Table 21 (Norton - 1949) list the breakdown temperatures of the most common minor mineral components found in shales. Heating is usually done slowly so that carbon and sulfur gas can escape. If heating is too rapid bloating (formation of cellular structure by gas bubbles) will occur.

Table 21 Breakdown Temperatures of Clay Impurities

	°C.	°F.
$\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeS} + \text{SO}_2$	350-450	660-840
$4\text{FeS} + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$	500-800	930-1470
$\text{Fe}_2(\text{SO}_4)_2 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{SO}_3$	560-775	1040-1430
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	350 →	660 →
$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$	250-920	480-1690
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	600-1050	1110-1920
$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	400-900	750-1650
$\text{FeCO}_3 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2$	800 →	1470 →
$\text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_3$	1250-1300	2280-2370

Bloating is deliberately caused to form lightweight aggregate. The most common substances that evolve gas in shales and slates are limonite, hematite, calcite, dolomite, pyrite, organic matter and vermiculite.

Riley (1951) concluded that the most significant reaction involved in gas generation is the partial reduction of ferric oxide.

Three to 4% Fe_2O_3 is enough to cause bloating. The Fe may occur in a free form or be present in the lattice of silicate minerals. Only 1% by weight of the other minerals listed is necessary to produce bloating. Another requirement is that the bulk material be fusible enough to form an impermeable layer on the outside of the particles to prevent the escape of gas. Heating must be rapid so that fusion starts just before the evolution of the gas. Slates expand from three to seven times their original volume. The expanded particles are composed of small cells separated by glassy walls, the whole being covered by a vitrified, impervious skin (Short and Kinniburgh - 1968).

Apparently most shales will bloat to some degree if gas producing minerals are present. Shales and clays containing more than about 5% iron, alkalies and alkaline earths (fluxes) commonly fuse into a glassy mass at about 900°C rather than from new crystalline phases. Commercial firing is commonly done at 1100 to 1200°C (Grim - 1962).

Riley (1951) established that bloating is dependent only on the chemical composition, regardless of the mineral constituents, assuming gas producing minerals are present. Fig. 20 shows the compositional limits established by Riley. Increasing Al content increases refractoriness and decreases bloating (vesiculation). Good "bloaters" contain less than 25% Al_2O_3 . Most clays and shales that contain less than 70% kaolinite should have less than 25% Al_2O_3 . Shales composed largely of illite and chlorite (most Paleozoic and Precambrian shales and slates) are extensively used for the preparation of lightweight aggregate.

Bloating is enhanced in dense, low permeability clays and shales which resist shrinkage during heating thus retarding the release of vapors and gases before fusion; however, montmorillonitic clay can be used to make lightweight aggregate (Dixon and Tyrrell - 1969). Laminated shales bloat better than nonlaminated clays. Bloating is greatest perpendicular to the lamination because of the lesser permeability in that direction. A high quartz content reduces bloating. If the amount of flux is too large, fusion is rapid and the shale becomes extremely fluid (Grim - 1962).

Figure 21 contains some curves showing how the bulk density of bloating shales decreases during heating (Hollenbeck and Tyrrell - 1968). These curves are for Paleozoic shales from east Tennessee and east Kentucky. Tests of lower Paleozoic Chickamauga shale samples indicate they commonly are good bloaters except when they have a high organic content. Conasauga shale samples were not good bloaters.

DIAGENESIS IN SHALES

Mineral and Chemical Changes

Most of the information on the effects of heat on clays is based on laboratory studies of relatively pure clays. The heating rate is high, time is short, and there is little confining pressure. Studies of clay and shale diagenesis in nature indicate the response to heat is more complex. In buried clays significant changes in mineralogy can be observed at temperatures as low as 50°C (lower if amorphous material is present). The most reactive clay mineral is montmorillonite, followed by kaolinite, chlorite and illite. Mineralogic and chemical changes with depth in montmorillonitic clays have been described by Weaver and Beck (1971) and Perry and Hower (1970). The following discussion is taken from Weaver and Beck (1971) who studied both the clay minerals and interstitial water. The reactions described are based on studies of Gulf Coast Tertiary sediments but similar reactions occur in the Pierre shale or any other montmorillonitic shale.

Weathering has caused Al to be concentrated in the hydrolyzates, primarily in the shales. Once the burial cycle has started and temperatures begin to increase, the Al-rich clay suite begins a slow and persistent evolution toward a greater than 300°C to 400°C equilibrium mineral suite of muscovite, chlorite, and quartz.

During the first stage, inherited exchangeable K migrates to the highest charged layers, and inherited interlayer hydroxyl-Al and hydroxyl-Fe becomes better organized and more stable. Most of the calcite is dissolved in this early stage, and the Ca is flushed from the mud. With further temperature increase, the lattice charge of some layers is increased by the reduction of Fe and by the incorporation of some interlayer Al into the tetrahedral layer. K from K-feldspar and perhaps biotite is adsorbed by these newly created high-charge layers increasing the amount of 10⁸ material. Some of the Al from the K-feldspar may move into other interlayers,

increasing the number of dioctahedral chlorite layers. This mechanism presumably accounts for the relatively minor amount of K-feldspar found in most shales and low-rank metamorphic rocks. The resulting mixed-layer clay is composed of montmorillonite, $10\text{\AA}$ "illite," and dioctahedral chlorite layers. These layers form below 100°C . With increasing temperature, the regularity of the interlayering increases with little additional change in the proportion of layers. The interlayer material (K, Al, Fe) is apparently relatively mobile and moves to produce a mixed-layer arrangement that has a high degree of stability. This phase consists of approximately equal parts of the three components.

At a temperature near 150°C , kaolinite starts to decompose, and the Al as hydroxy-Al moves into the interlayer position increasing the proportion of dioctahedral chlorite layers. At this stage some of the chlorite layers form packets with a sufficient number of layers to diffract as the discrete mineral chlorite. Some additional Al may move into the tetrahedral layer at this stage and some packets of $10\text{\AA}$ layers form (the K derived from K-feldspar). Thus, the amount of discrete $10\text{\AA}$ "illite" and dioctahedral chlorite has increased slightly, but the majority of the clay consists of a mixed-layer illite-chlorite with a lesser amount of montmorillonite. In other areas kaolinite may react with dolomite to form chlorite (Muffer and White - 1969).

Up to this stage of diagenesis, the total chemistry is changed only slightly, if at all. Little further progress toward the muscovite-chlorite-quartz assemblage will occur unless additional ions (mainly K, Mg, Fe) are supplied to the system to balance the high Al content.

With increasing temperature ($\sim 200^{\circ}\text{C}$), either due to deeper burial or increase in heat flow rates, upward-migrating K, Mg, and Fe, derived from the underlying sediments, become sufficiently abundant that the remaining expanded layers are lost, and some discrete $10\text{\AA}$ illite and trioctahedral chlorite formed; however, much of the "illite" at this stage still contains appreciable proportion of dioctahedral chlorite, and the "chlorite" contains some $10\text{\AA}$ layers. This is the typical clay mineral suite found in Paleozoic and Precambrian shales. Detrital mica and chlorite (trioctahedral), derived largely from metamorphic rocks, is also a sizable component of these shales.

Complete unmixing of the mixed-layered minerals requires temperatures on the order of 400°C or a relative high degree of metamorphism (phengite $\rightarrow$

muscovite + chlorite).

The exchangeable cations and interstitial ions also undergo diagenetic changes as the temperature increases and the solid phase changes.

The most notable features of the exchange cations, in addition to a decrease in abundance with depth, is the early loss of Mg to form dolomite in the mud and chlorite in the sands and the dominance of Na in the shallow samples and Ca in the deep samples.

In the surface samples the exchange suite is $Mg > Na$; $Ca > K$; at a depth of 4000 ft, the sequence is $Na > Ca > Mg > K$; at 17,000 ft, the suite is $Ca > Mg > K > Na$. At a relatively shallow depth the exchange cations and exchange sites become more abundant than the cations in the interstitial water. Ion mobility becomes more important than charge, and Na replaces Mg as the major exchange cation. With increasing depth and temperature, interlayer sites tend to become occupied (and unavailable for cation exchange) by K, Al, and Fe, as illitic and chloritic layers are formed. The weakly bonded Na is preferentially removed, and Ca is retained, along with Mg, in the exchange position.

K apparently moves from solid phase (K-feldspar) to solid phase (10 Å layers) without causing a major increase in exchangeable K, though the K content of the water phase is consistently larger than that of seawater.

The preferential Ca retention in the exchange position could explain the increase in the Ca/Cl ratio, with age, of brines from sandstones and limestones. During advance diagenesis, when the last expanded layers are made nonexpandable, Ca may be mobilized to help form the calcite commonly found in veins permeating low-rank metamorphic sediments. The Mg presumably goes to form chlorite.

As the mud section is buried, both interstitial and interlayer water are forced from the muds. The Na content decreases during shallow burial; about 20 percent is adsorbed on the clays in exchange for Mg and about 40 percent migrates from the mud along with Cl. Cl continues to be lost from the mud with increasing burial. Because of the high rate of deposition, SO_4 is not reduced and is concentrated by selective filtration. HCO_3 is formed from calcite and organic material and becomes the dominant anion.

As the water-rich montmorillonite bathyal muds are dewatered, a physical permeability barrier is formed at the top of the mud section and is caused by the relatively rapid loss of water through the overlying sandy shelf sediments. With increased temperature, adsorbed organic material is released from the clay minerals and, along with the ions and water, migrates upward. Due to a decrease in temperature and pressure and an increase in Na and SO_4 , Ca precipitates as calcite increasing the effectiveness of the barrier. The upward migration of water is blocked, and abnormally high water content and pressures develop.

Na migrates upward, systematically decreasing the amount in the deeper muds; Na reaches a maximum in the permeability barrier. Na apparently diffuses through the barrier more easily than H_2O . Cl diffuses through the barrier more easily than SO_4 and HCO_3 .

K and Mg in the interstitial water increases systematically in the deeper samples. This is presumably due to the increased temperature and the increased solubility of the silicate minerals. Some of the K, Mg, and Fe may have been released under deeper, higher temperature conditions and migrated upward from below.

Figure 22 from Muller (1967) summarize the mineralogic changes that take place during increasing depth of burial and temperature. The rate of these reactions is probably measured in thousands rather than millions of years.

Basically, any shale which has not previously been subjected to temperatures greater than 200°C and an illite-chlorite clay suite formed, would be expected to undergo significant mineralogic changes. Changes occur above 200°C but these changes are largely an increase in crystallinity and size of the illite and chlorite.

The changes which take place vertically during burial might be expected to take place laterally, as well as vertically, in the area of the buried canisters. Probably of more concern than the clay mineral changes which take place is the movement of pore water and associated ions. At some distance from the source of heat some of these ions will precipitate forming a relatively impermeable seal and allow the pressure to build-up. In the Gulf Coast calcite, SiO_2 and chlorite precipitate to form the seal.

It seems likely that in the immediate vicinity of the canisters the rapid application of considerable heat will cause a ceramic-type reaction-loss of pore and structural water and partial melting of the minerals. Farther from the canister, after a long period of time, diagenetic reactions should occur. If most of the pore water is flushed from the system early, diagenesis may not occur. However, outside the cavern area the water may not be able to escape from the shales.

Heat Flow Through Sediments

Jones (1968) has discussed the mechanics of heat flow through the thick clay-rich sediments of the northern Gulf of Mexico. The following discussion, slightly modified, is from Jones (1968).

The three modes of heat transport through saturated sediments are (1) conduction through mineral grains and interstitial fluids, (2) convective flow of interstitial fluids, and (3) radiation. Conductive and convective heat flow are important in the low-temperature range common above depths of 10,000 feet (100°C) in the northern Gulf basin. The role of ray transportation increases with increase in temperature. Factors that have a direct bearing on the heat flux include the following:

1. The composition and thermal conductivity of the mineral grains that form the rock skeleton, and of the fluids that occupy the interstices.
2. The specific heat of solid and fluid elements.
3. The porosity, and the hydraulic geometry of the pores.
4. The density, viscosity, and thermal expansion of the fluid elements.
5. The thermal expansion of the solid elements.
6. The absolute temperature.

The thermal conductivity of the mineral grains of sediments is generally 4 to 5 times greater than that of water. For this reason, the thermal conductivity of clay varies inversely with its water content (Langseth, 1965). Lapwood (1948) was the first to consider the possibility of free convective flow in water-saturated porous rock. His studies revealed that, in a horizontal layer uniformly heated from below, convective flow does not occur until the temperature difference across the layer exceeds some minimum value.

Elder (1965), in his analysis of the free convection of a fluid in a porous medium, states that "the motions to be considered arise from the buoyancy forces produced by imbalanced density variations in a field of nonuniform temperature." Elder's calculations assume that density variations of the fluid are important only insofar as they generate buoyancy

forces, and he states that a crude estimate of the thermal conductivity (K_m) of the fluid-saturated medium is given, under conditions of nonisothermal flow, by:

$$K_m = (1-e) K_s + eK_f$$

where e = the porosity (void volume per unit volume of the medium)

K_s = the thermal conductivity of the solid

K_f = the thermal conductivity of the fluid

and the effective thermal diffusivity is given by:

$$k_m = K_m/\rho c$$

where ρ = density of the fluid

c = specific heat of the fluid

Measurement of the heat flow that occurs by free convection in a horizontal slab of homogeneous saturated porous material requires information on its thickness, permeability, and thermal conductivity (K_m); on the density of the fluid and the density change with temperature; and on the specific heat (c) and kinematic viscosity (ν) of the fluid. Satisfactory computations based upon these parameters for the known conditions of temperature were made for the Taupo area of New Zealand by Elder (1965) who asserts that the large heat-flow rates observed in thermal areas are not possible without mass transfer by thermal convection.

McNitt (1965) with reference to the Wairakei area of New Zealand, states that: "There is a rapid increase in temperature with depth down to the base of the confining mudstone. At this point, temperatures are close to, or above, the boiling point corresponding to the theoretical hydrostatic pressure for this depth below the water table The temperature gradient through the aquifer is much reduced"

In geopressured reservoirs of the northern Gulf of Mexico basin the formation water is commonly at temperatures greater than 120°C at depths

ranging from 10,000 to 14,000 feet. The geothermal gradients are large in the clay beds overlying the reservoirs, and very much reduced in the aquifers. There can be no doubt that, by checking the upward flow of water from the "waterlogged" sediments beneath them, sealing clay beds of geopressured reservoirs have caused reduction of the geothermal flux above and overheating of the sediments below. In this geotemperature regime, dehydration of montmorillonite occurs at relatively shallow depths. Liberation of intracrystalline water (endothermic reaction) in clay beds of geopressured zones increases the pressure of fluids in them and reduces their thermal conductivity by increasing their porosity.

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FIGURE 1 Average shale-density curves. (After Skeels.)

PROFILE = 018420-C05 JAN. 28, 1976
ACCOUNT = THRESHOLD WT. C0000

DATA BASE SEARCHED. NSA V 32.12

GROUP	TERM NO.	TYPE	WEIGHT	TERM
G001	1	TXT	CC000	THERMAL CONDUCT*
G001	2	TXT	CC000	THERMAL PROPERT*
G001	3	TXT	CC000	HEAT*
G001	4	TXT	CC000	THERMOPHYSICAL PROPERT*
G001	5	TXT	CC000	THERMAL EXPAN*
G001	6	TXT	CC000	THERMAL DIFFUS*
G001	7	TXT	CC000	TRANSPORT PROCESS*
G001	8	TXT	CC000	DENSIT*
G001	9	TXT	CC000	WATER CONTENT*
G001	10	TXT	CC000	POROSIT*
G001	11	TXT	CC000	PERMEABILIT*
G001	12	TXT	CC000	THERMAL INSULAT*
G001	13	EIT	CC000	THERMAL CONDUCTIVITY*
G001	14	EIT	CC000	THERMAL VARIABLES MEASUREMENT*
G001	15	EIT	CC000	THERMAL EFFECTS*
G001	16	EIT	CC000	THERMAL DIFFUSION, SOLIDS*
G001	17	EIT	CC000	HEAT TRANSFER*
G001	18	EIT	CC000	SPECIFIC HEAT, SOLIDS*
G001	19	ISH	CC000	THERMAL CONDUCTIVITY
G001	20	ISH	CC000	THERMAL DIFFUSIVITY
G001	21	ISH	CC000	THERMAL CONDUCTIVITY MEASUREMENT
G001	22	ISH	CC000	THERMAL VARIABLES MEASUREMENT
G001	23	ISH	CC000	HEAT
G001	24	ISH	CC000	THERMAL EXPANSION
G001	25	ISH	CC000	THERMAL CONDUCTIVITY OF SOLIDS
G001	26	ISH	CC000	TRANSPORT PROCESSES
G001	27	ISH	CC000	THERMAL DIFFUSION
G001	28	ISH	CC000	HEAT TRANSFER
G001	29	ISH	CC000	THERMAL INSULATION
G001	30	ISH	CC000	HEAT CONDUCTION
G001	31	ISH	CC000	SPECIFIC HEAT
G001	32	ISH	CC000	DENSITY
G001	33	ISH	CC000	POROSITY
G001	34	ISH	CC000	PERMEABILITY
G001	35	ISH	CC000	THERMODYNAMIC PROPERTIES
G001	36	CAS	CC000	069002
G001	37	CCR	CC000	069002
G001	38	CCC	CC000	20M
G001	39	NST	CC000	THERMAL CONDUCTIVITY*
G001	40	NSC	CC000	04909
G001	41	NST	CC000	THERMAL CONDUCTION*
G001	42	NST	CC000	THERMAL DIFFUSION*
G001	43	NSC	CC000	04910
G001	44	NST	CC000	THERMAL DIFFUSIVITY*
G001	45	NST	CC000	THERMAL EXPANSION*
G001	46	NSC	CC000	05863
G001	47	NST	CC000	THERMAL INSULATION*
G001	48	NSC	CC000	04913
G001	49	NST	CC000	POROSITY*
G001	50	NSC	CC000	03714
G001	51	NST	CC000	PERMEABILITY*
G001	52	NST	CC000	DENSITY*
G001	53	NSC	CC000	01302
G001	54	NST	CC000	HEAT TRANSFER*
G001	55	NSC	CC000	02050
G001	56	NST	CC000	SPECIFIC HEAT*
G001	57	NSC	CC000	04542
G001	58	TXT	CC000	THERMODYNAMIC PROPERT*
G002	59	TXT	C1000	CLAY*
G002	60	TXT	00010	SHALE*
G002	61	TXT	-CC100	COMPACTED SOIL*
G002	62	TXT	01000	ILLITE*
G002	63	TXT	01000	KAOLINITE*
G002	64	TXT	C1000	MONTMORILLONITE*
G002	65	TXT	C1000	SMECTITE*
G002	66	TXT	01000	KAOLIN*
G002	67	TXT	01000	CHLORITE*
G002	68	EIT	-00100	SOILS, COMPACTION*
G002	69	NST	01000	CLAYS*
G002	70	NST	00010	SHALES*
G002	71	NSC	01000	01082
G002	72	NSC	00010	06885

G003 73 EIT 01000 CLAY, THERMAL*
G003 74 EIT 00010 SHALE, THERMAL *
G003 75 EIT 01000 CLAY, SPECIFIC HEAT*
G003 76 EIT 00010 SHALE, SPECIFIC HEAT*

75

BCOL.EXP.(G001*G002)+G003

NUMBER OF CITATIONS

0

FIGURE 2. Density-porosity relationship. Wet density = dry density $\times .615 + 1.04$.
This is a poor substitute for the method of obtaining wet densities at the well.
(After Skeels, Standard Oil Company of New Jersey.)

FIG. 3 'Natural' density and dry-bulk density of rocks from Barberton, Ohio, core hole no. 3 as a function of sample depth, lithology, and stratigraphic position.

FIG. 4 -Density versus depth of Isleton rocks. Carbonate content of each sample noted in percentage by weight. Rock densities in upper part of graph with their corresponding grain densities in lower part.

FIG. 5 --Porosity versus depth of Ireton rocks. Carbonate content shown in percentage by weight on axis perpendicular to page. Curves represent surface of best fit.

Fig. 6 Ocean sediment. Thermal conductivity (at 1 atm) versus water content by weight.

Fig. 7 Ocean sediment. Diagram for assessment of thermal conductivity at 4°C and 1 atmosphere. Add 1 per cent per 1000 fathoms and 1 per cent per 4°C temperature increase.

Fig. 8 Wet granular material. Thermal conductivity (at 1 atm) versus water content by volume.

Fig. 9 Thermal conductivity of calcite, marble, limestone, dolomite, halite and slate.

Sl ₁	Slate, Penn., ⊥ bed-plane.
L ₁	Limestone, Penn., ⊥ bed-plane.
L ₁₁	Limestone, Penn., bed-plane.
L	Limestone, Solenhofen.
M ₁	Marble, Vermont, ⊥ bed-plane.
M ₁₁	Marble, Vermont, bed-plane.
Ca ₁	Calcite, single crystal, ⊥ optic-axis.
Ca ₁₁	Calcite, single crystal, optic-axis.
Do	Dolomite, Penn.
NaCl	Halite.

Fig. 10 Schematic Illustration of Variations in Thermal Conductivity Through a Castable Wall Heated on One Side Only, And Not Insulated.

FIG. 11 Linear shrinkage and rate of shrinkage for a kaolin.

FIG. 12. Dimensional changes on firing kaolinite and illite, after Kiefer (1952).

FIG. 13. Dimensional changes on firing muscovite, after Kiefer (1957).

FIG. 14 Dimensional changes on firing kaolinite (flint clay), halloysite, and montmorillonite, after Kiefer (1957).

FIG. 15 Vitrification characteristics of *A*, a kaolinite clay and *B*, an illitic shale, after Stone (1957).

FIG. 16 Stresses in a brick heated at one end. (J. Amer. Ceram. Soc.)

FIG. 27 Stresses in a brick heated on one end and one-third of the distance up the side.
(J. Am. Ceram. Soc.)

FIG. 18 Stresses in a wall. (J. Am. Ceram. Soc.)

FIG. 19 Cracks in a sphere suddenly cooled. (*J. Am. Ceram. Soc.*)

FIG. 19 Cracks in a sphere suddenly heated. (*J. Am. Ceram. Soc.*)

HEATED END

FIG. 19 Cracks in a brick suddenly cooled. (*J. Am. Ceram. Soc.*)

HEATED END

FIG. 19 Cracks in a brick suddenly heated. (*J. Am. Ceram. Soc.*)

Fig. 20 Composition diagram of major oxides showing area in which clays fire to a mass viscous enough to insure good bloating. The unlabeled points are from the analyses by Conley, Wilson, and Klinefelter (see footnote 8). Dashed line represents limits of bloating.

FIGURE 21 - Preliminary Quick-Fire Bloating Curves for Several Eastern Tennessee Samples.

Listed below are some thermal conductivity values for clay-rich sediments from Romania (Demetrescu - 1973)

Age and Lithology	Thermal Conductivity (m cal/cm sec °C)
Miocene	
Shale (2543 m)	10.30
Clayey Marl (1803 m)	4.01
Clayey Marl (2201 m)	3.32
Cretaceous	
Clayey Marl (1005 m)	3.53
Marly Clay (1210 m)	4.09
Marly Clay (2237 m)	2.51

Walsh and Decker (1966) made calculations that show the observed thermal conductivity for dry rock samples of low porosity may differ (lower) by more than 15% from the conductivity that the rocks had in place - saturated and under hydrostatic pressure (For porous rock conductivity can increase by a factor of 2 or more). They reasoned that error in the apparent conductivity arises because cracks form effective barriers to the flow of heat when rocks are dry but have a negligible effect when the rock is saturated or when the cracks are closed by stress. Formulas are presented for estimating the possible error.

Their discussion is based on granites and marbles but would probably apply to low porosity shales.

Long, Neglia and Rubino (1970) have calculated that by the time a clay is compacted to 33% porosity it should have no intercrystalline (pore) water but only intracrystalline (interlayer and surface adsorbed)

Fig. 22 Relationship of mechanical and mineralogical-chemical changes occurring in argillaceous sediments during diagenesis with depth of burial, pressure, temperature, and duration of burial.

APPENDIX I

Thermal Properties of Clays and Shales

Dr. Charles E. Weaver

Horai (1971) measured the thermal conductivity of 166 rock forming minerals, unfortunately he did not include any clay minerals (except glauconite). The specimens were pulverized into fine powders, mixed with water and conductivity values measured by the needle-probe method. Values for some sheet structure silicates are listed below:

Mineral	Density g/cm ³	Thermal Conductivity (m cal/cm sec °C)
Muscovite	2.83-2.87	5.3 - 6.0
Glauconite	2.85	3.9
Biotite	2.89-3.08	4.1 - 5.6
Pyrophyllite	2.83	19.4
Talc	2.80-2.82	12.4 - 16.7
Chlorite	2.64-2.86	10.4 - 14.8
Serpentine	2.60-2.66	5.6 - 12.7

Thermal conductivity of minerals increases as the density and atomic weight increases (though there are numerous exceptions). Horai states that the latter two values can be used to estimate the thermal conductivity of rocks. He also discusses the relation of thermal conductivity to Si - O bonding and the amount of isomorphous substitution. Conductivity decreases with an increase in the number of Si - O bonds and an increase in Fe.

water. More heat should be required to remove non-ore water than pore water. If pores are not present it would be most difficult to remove the interlayer water. However, as the swelling clays contract and release their interlayer water, pores would be created.

Thus, at shallow depth clays should have both pore water and intracrystalline water. During shallow burial pore water is lost. With deeper burial intracrystalline water is lost and new pore water and pores are created. Permeability should be less in the deep porous shale.

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