



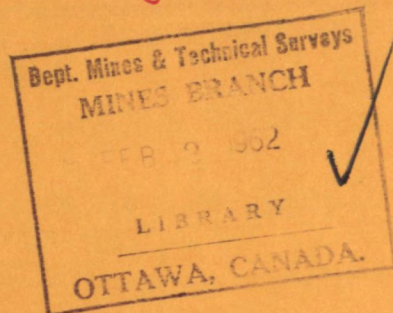
CANADA

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THE NATURE AND PROPERTIES OF SOME WESTERN CANADA CLAYS

J. G. BRADY

MINERAL PROCESSING DIVISION

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THE NATURE AND PROPERTIES OF SOME
WESTERN CANADA CLAYS

by

J. G. Brady*

ABSTRACT

The relation of physical properties to mineralogical composition of five clays from Western Canada which have been used for production of structural clay products is discussed. The clays are from Sidney, Manitoba; Estevan, Saskatchewan; Eastend, Saskatchewan; Alberta Cypress Hills, Alberta; and Sumas Mountain, British Columbia.

It is shown that the Sidney and Estevan clays are heterogeneous mixtures consisting mainly of clay minerals, quartz, micaceous material, calcite, dolomite, and feldspar. As a result, these clays have low melting points and short firing ranges.

The Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 clays are not as heterogeneous as the Sidney and Estevan Buff clays: kaolinite, quartz, and micaceous material are their principal constituents. Consequently, they are more refractory and have a longer firing range for production of clay products than the Sidney and Estevan Buff clays.

It is shown that montmorillonite increases the plasticity of clays but makes drying of clay products very difficult. Conversely, non-plastic ingredients such as quartz, feldspar and coarse mica decrease the plasticity. Kaolinite, chlorite and illite are plastic ingredients.

Clay materials, such as the Estevan Buff, which contain large quantities of calcite and dolomite usually have a short firing range and tend to produce a soft, porous fired product.

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Direction des mines

Bulletin technique TB 21

NATURE ET PROPRIÉTÉS DE CERTAINES ARGILES

DE L'OUEST CANADIEN

par

J.G. Brady*

RÉSUMÉ

Le présent bulletin étudie la relation qui existe entre les propriétés physiques et la composition minéralogique de cinq argiles de l'Ouest canadien qui ont servi à la fabrication de produits d'argile utilisés dans le bâtiment. Ces argiles provenaient de Sidney (Man.), Estevan (Sask.), Eastend (Sask.), collines Cypress (Alb.) et mont Sumas (C.-B.).

Ce bulletin révèle que les argiles de Sidney et d'Estevan sont des mélanges hétérogènes de minéraux argileux, de quartz, de matériaux micacés, de calcite, de dolomie et de feldspath. Il en résulte que ces argiles fondent à des basses températures et ont des gammes de cuisson peu étendues.

Les argiles d'Eastend, des collines Cypress et du mont Sumas n^o 9 ne sont pas aussi hétérogènes que les argiles de Sidney et d'Estevan, car les principaux constituants en sont la kaolinite, le quartz et les matériaux micacés. C'est pourquoi elles sont plus réfractaires et, du point de vue de la fabrication des produits d'argile, elles ont des gammes de cuisson plus étendues que le matériau de Sidney et d'Estevan.

L'auteur démontre que la montmorillonite augmente la plasticité des argiles, mais elle rend plus difficile le séchage des produits d'argile. Inversement, les ingrédients non plastiques tels que le quartz, le feldspath et le mica grossier réduisent la plasticité. Parmi les ingrédients plastiques mentionnons la kaolinite, la chlorite et l'illite.

Les matières argileuses telles que celles d'Estevan, qui contiennent de fortes quantités de calcite et de dolomie, ont ordinairement une gamme de cuisson courte et ont tendance à donner un produit cuit friable et poreux.

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INTRODUCTION

Five clays from Western Canada, which are used by the structural clay products or sewer pipe industries, were selected to show the typical properties and mineralogical compositions of clays from that region. One sample was chosen from Manitoba, two from Saskatchewan, one from Alberta, and one from British Columbia.

These clays were subjected to test procedures employed in the Mineral Processing Division laboratories, Mines Branch, Ottawa, for a full-scale investigation of a clay deposit. The physical properties were determined by several laboratory methods, including measurement of the plastic properties by a plastograph and determination of the fired characteristics by the temperature gradient method. The mineralogical compositions were determined by X-ray diffraction analyses, differential thermal analyses (DTA), and chemical analyses. The effect of the various properties and composition on the manufacture of stiff-mud products is discussed.

SAMPLES INVESTIGATED

Five different materials were selected for study, as follows:

Sidney Clay: The Sidney sample is a low-fusion surface clay

occurring 1/4 mile west of Sidney, Manitoba. It represents a vertical 6- to 8-ft section just below the surface topsoil. This clay has been used as an additive to Winnipeg surface clay in the manufacture of common and face brick.

Estevan Buff Clay: This material has been used for many years at Estevan for the manufacture of brick and tile. It is a low-fusion clay or soft shale which occurs close to the surface in a valley in the southeastern outskirts of Estevan, Saskatchewan.

Eastend Clay: Eastend clay is a stoneware clay of the Whitemud formation. The sample represents a sewer pipe mix and was obtained from the "Dempster" pit, approximately 1 mile northwest of Eastend, Saskatchewan.

Alberta Cypress Hills Clay: This sample is a composite of five separate clay seams representing a 26-ft face, mainly in the Whitemud formation of the Alberta Cypress Hills. The sample, which is somewhat similar to the Eastend clay, was taken from a pit approximately 45 miles southeast of Medicine Hat, Alberta. This clay is used in the manufacture of sewer pipe, flue lining, and buff face brick.

Sumas Mountain No. 9 Shale: The sample of Sumas Mountain No. 9 shale was obtained from an underground mine on Sumas mountain near Kilgard, British Columbia. The shale is used, in

conjunction with other materials, for the manufacture of sewer pipe, flue lining, and face brick.

PROCEDURE

The clays were crushed and pulverized to pass a 16-mesh laboratory Tyler screen. A representative one-pound sample of each clay was taken for a plasticity investigation. Each sample was mixed with an equal weight of potter's flint, in order to reduce the plasticity so that all measurements could be accommodated on the plastograph. A Brabender plastograph was employed to show the relative resistance of the clay-flint mixtures to pugging action. This equipment, which is shown in Figure 1, has been described by Thiess,⁽¹⁾ and its use in testing clays by Marshall.⁽²⁾ Two hundred grams of a dry clay mix were placed in the apparatus, and a continuous curve was obtained of the resistance to shear while water was being added at the rate of 5 cc/min.

Representative 12-pound samples were selected for the determination of the physical properties of the clays. Test bars, 8 by 1 by 1/2 in., were extruded through a laboratory de-airing extrusion machine. The amount of tempering water (water of plasticity) was noted. Two bars from each sample were dried rapidly in a laboratory drier at 185°F, and the results were noted. The remaining ten bars of each specimen were carefully

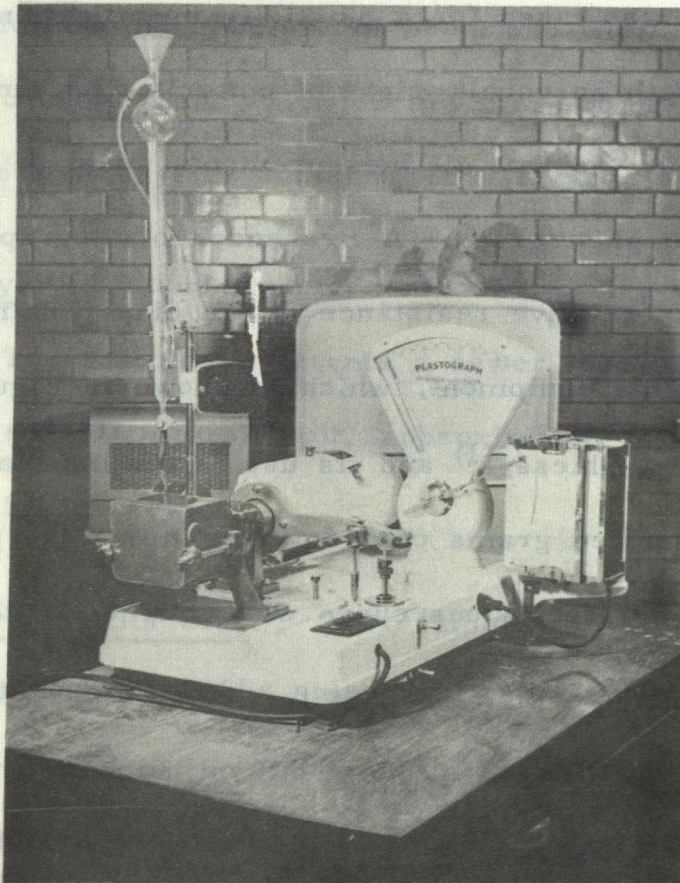


Figure 1. Plasticity apparatus.

air-dried for 48 hours and then finally dried in a laboratory drier at 212°F for 24 hours. The average drying shrinkage was calculated.

Two test bars of each sample that had not warped while drying were selected for determining the fired properties by use of a Stone temperature gradient apparatus. This equipment, shown in Figure 2, has previously been described by Stone,⁽³⁾ and its application to laboratory work on clays by Brady.⁽⁴⁾ Reference lines were scribed every 1/2 inch across the bars. The distances between lines, and the width of the specimen at each line, were very accurately measured. Duplicate bars were placed in the gradient electric furnace, where a temperature gradient of approximately 1200°F from the cold to the hot end of each bar is produced. The centre portion of the furnace, where the temperature is highest, had its temperature raised at the rate of 160°F/hr to 1500°F, held there for 6 hours, then raised at the rate of 200°F/hr to the finishing temperature, which was held for one hour. The finishing temperature for each sample was selected to be high enough to vitrify, or slightly overfire, the bars at the hot end. Temperature measurements were made, along the length of each trial piece, at the end of the final soaking temperature. After cooling, the fired shrinkage, the water absorption, the colour and the hardness were determined at each 1/2-inch mark.

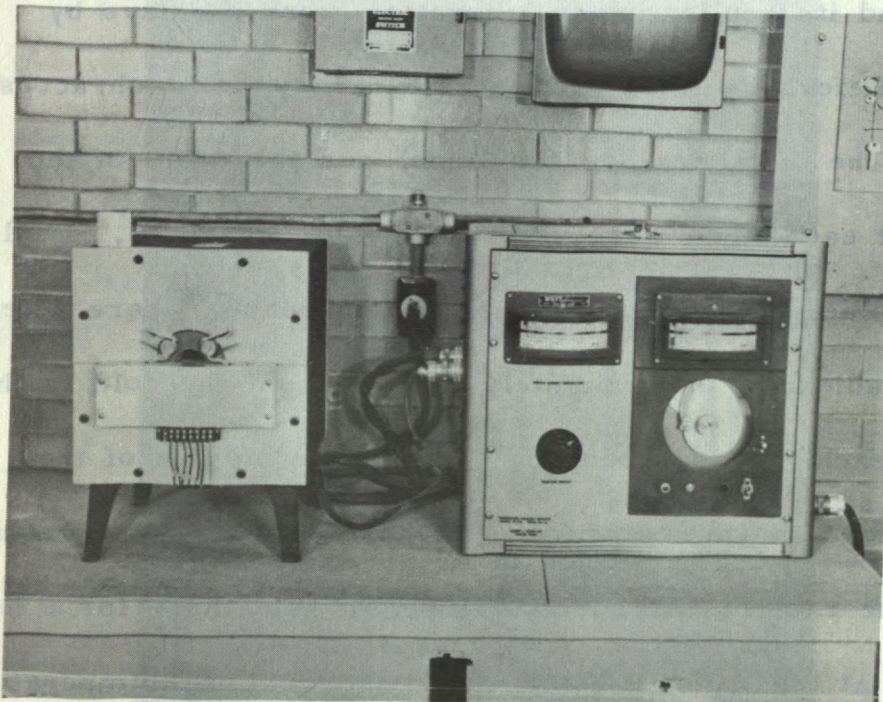


Figure 2. Temperature gradient apparatus.

The pyrometric cone equivalent (PCE), showing the heat softening temperature, and hence the refractoriness, was determined for each sample.

Differential thermal analysis curves of each sample at various appropriate sensitivities were obtained in an air atmosphere. A heating rate of 12°C per minute was used.

X-ray diffraction patterns of the clay were obtained from a Phillips X-ray diffractometer unit. When the presence of an expanding mineral such as montmorillonite was suspected, the sample was treated with ethylene glycol and a second pattern was obtained to confirm its presence. Heat and acid treatment techniques were employed to identify kaolinitic and chloritic clay minerals.

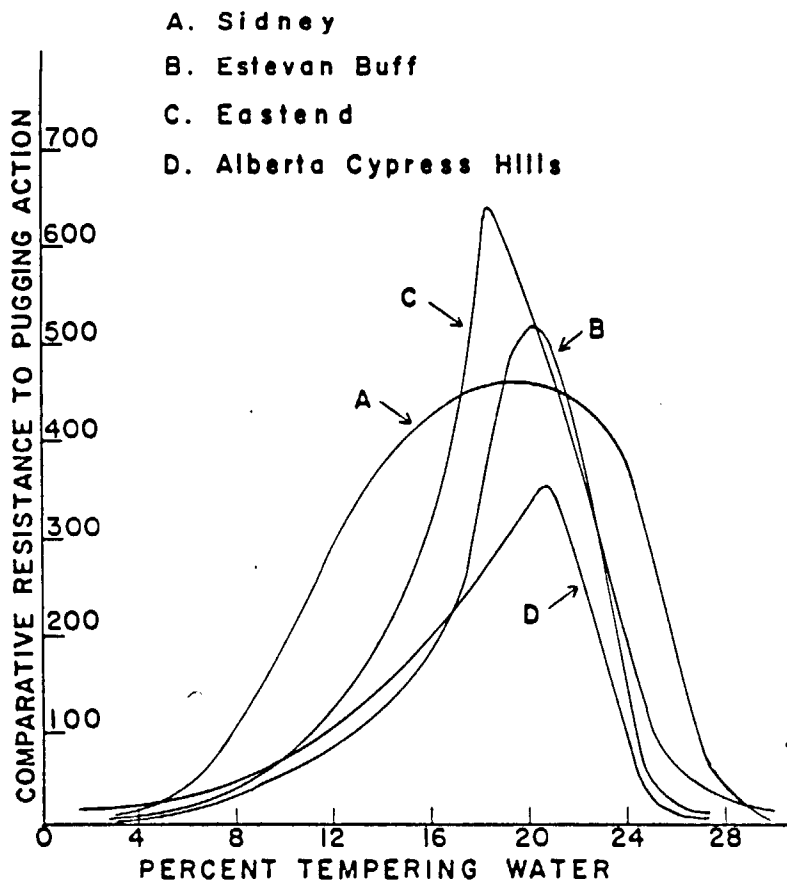
Complete chemical analyses of the samples were made. The analyses were used, in combination with the results of DTA and X-ray diffraction, to determine the mineralogical composition of the samples. Whenever possible the percentages of the various minerals were determined. The total of these percentages was deducted from the total of the chemical analysis for each clay. The value and composition of the remainders varied with the complexity of the clay.

RESULTS

Unfired Characteristics

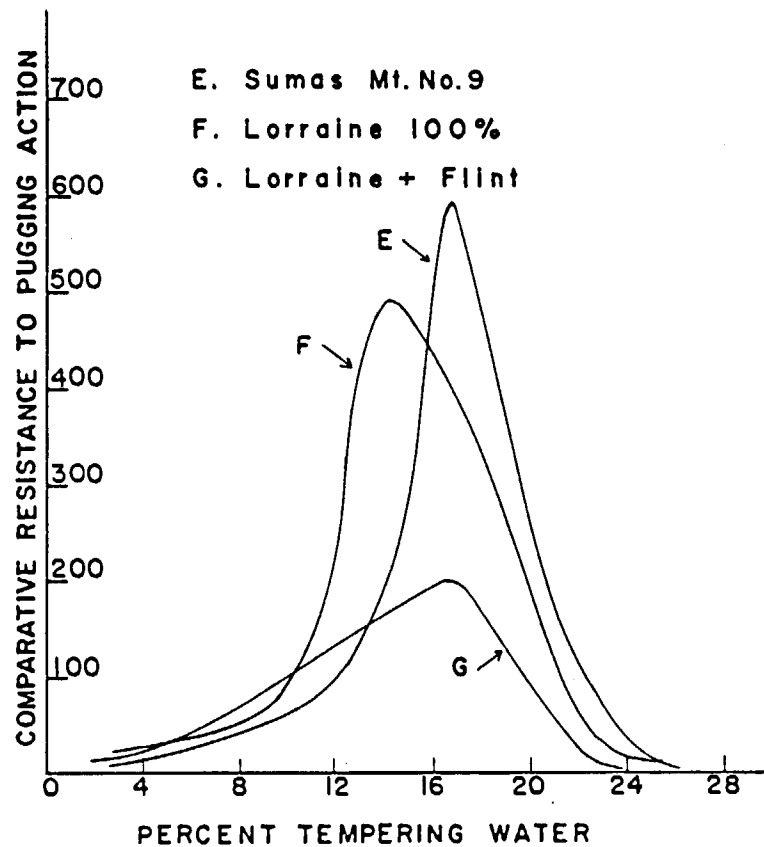
The results of the plasticity experiments on the

clay-flint mixtures are shown in Figures 3 and 4, in which per cent tempering water is plotted against the resistance to pugging action (resistance to shear). Curves of 100% Lorraine shale and a mixture of 50% Lorraine shale and 50% flint are shown in Figure 4 for comparison. The 100% Lorraine (Dundas) shale sample has just sufficient plasticity to extrude satisfactorily in the manufacture of brick and tile. The Lorraine shale-flint mixture would probably not extrude properly and the body would be extremely weak. Neither with minimum water when the test mixture is dry, nor with maximum water when it is in slip form, is there much resistance to pugging action. The peak of each curve indicates the maximum resistance to pugging action or, in effect, maximum plasticity. This corresponds to the tempering condition at which stiff-mud products would be extruded. The 100% Lorraine shale has a maximum resistance of about 500 units. The Sidney, Estevan, Eastend and Sumas Mountain clay-flint mixtures have maximum values almost as high as or higher than the 100% Lorraine shale. The 100% clays would have maximum resistance values much higher than would the mixtures and consequently would have ample plasticity for extrusion. The Alberta Cypress Hills clay-flint mixture has the lowest resistance value of the five Western samples, and the least plasticity. Laboratory trials of 100% Cypress Hills clay indicated that the maximum resistance to pugging action is greater than that of the 100% Lorraine shale.



Note: All Samples Contain 50% Flint

Figure 3. Plasticity Measured by Resistance to Pugging Action.



Note: Samples Contain 50% Flint
 Except Lorraine 100%

Figure 4. Plasticity Measured by Resistance to Pugging Action.

The Sidney clay-flint mixture is very plastic and has a broad range of tempering water at which the resistance to pugging action remains constant. The other mixtures show sharper peaks, and the quantity of tempering water is more critical. The areas under the curves, rather than the amplitudes of the peaks, perhaps give a truer picture of the relative plasticities of the clays.

Additional unfired characteristics are shown in Table 1. All the clays have high drying shrinkages of approximately 6 to 7%. Eastend and Sumas Mountain No. 9 clays dry safely under rapid drying conditions, with Eastend having the best characteristics. Sidney clay is very difficult to dry. Alberta Cypress Hills and Estevan Buff materials have a slight tendency to crack with rapid drying. All samples extruded satisfactorily under vacuum, although the Alberta Cypress Hills test specimens were very weak in the plastic state. This might be expected from the results of the plastograph experiments.

Fired Characteristics

Curves of shrinkage and absorption obtained by the temperature gradient method are shown in Figures 5, 6 and 7. Shrinkage values between 0 and -2 per cent indicate that there has been a residual expansion, while values greater than zero indicate that shrinkage has taken place. A summary of the fired properties --including shrinkage, absorption, colour and hardness, over appropriate temperature ranges, and the PCE--is given in Table 1.

TABLE 1
Summary of Clay Properties

Clay	Unfired Characteristics	PCE	Fired Characteristics					Remarks
			Temperature, °F	Fired Shrinkage*, %	Absorption, %	Colour	Hardness	
Sidney	Calcareous surface clay, plastic, extrudes satisfactorily under vacuum, water of plasticity 22%, cracks badly with rapid drying, drying shrinkage 7%.	4	1840	-0.7	18.4	Salmon	Soft	Difficult-to-dry common clay, with a short firing range.
			1918	-0.3	17.0	Dark salmon	Fairly hard	
			1977	1.1	13.5	Red-brown	Hard	
			2020	4.1	5.9	Red-brown	Very hard	
			2050	5.3	1.8	Red-brown	Vitrified	
Estevan Buff	Very calcareous brown clay, plastic, extrudes satisfactorily under vacuum, water of plasticity 22%, tendency to crack with rapid drying, drying shrinkage 6.5%.	3 1/2	1840	1.0	22.5	Pink-cream	Soft	Very calcareous material which is inclined to be difficult to dry and has a very short firing range.
			1920	1.3	23.3	Pink-cream	Fairly soft	
			1980	3.5	18.0	Cream-pink	Fairly hard	
			2020	11.3	4.5	Light-buff	Very hard	
			2055	13.3	0.3	Buff-green	Vitrified	
Eastend	Stoneware-type Whitemud clay, plastic, extrudes satisfactorily under vacuum, water of plasticity 22%, safe drying, drying shrinkage 6.5%.	19 1/2	1800	0.9	14.9	Cream	Fairly hard	Plastic, easily-dried, stoneware clay with a fairly long firing range.
			1890	2.3	12.2	Cream	Hard	
			1983	4.5	8.0	Yellow-cream	Very hard	
			2065	6.8	3.8	Grey-cream	Steel hard	
			2150	8.3	1.0	Grey	Steel hard	
Alberta Cypress Hills	Stoneware-type Whitemud clay, fairly plastic, extrudes well under vacuum but body is inclined to be weak, water of plasticity 18.5%, slight tendency to crack with rapid drying, drying shrinkage 7%.	20	1893	0.6	12.2	Cream	Fairly hard	Stoneware-type clay with a high proportion of non-plastic material. The plastic portion dries with difficulty. This clay has a long firing range.
			1988	1.5	9.8	Buff	Fairly hard	
			2070	2.4	7.6	Buff	Hard	
			2160	3.5	5.6	Cream-grey	Hard	
			2225	4.1	4.3	Light grey	Very hard	
Sumas Mountain No. 9	Dark grey shale, fair plasticity, water of plasticity 18%, extrudes under vacuum fairly well, will dry under rapid drying conditions fairly well, drying shrinkage 7%.	19	1935	3.3	14.6	Light pink	Fairly hard	This shale has sufficient plasticity to extrude. It has a long firing range. Some care may be required in drying.
			2020	4.9	12.2	Light pink	Hard	
			2097	6.1	9.7	Pink-grey	Hard	
			2163	6.7	8.1	Light grey	Very hard	
			2220	7.0	6.9	Light grey	Very hard	

* A minus sign indicates expansion.

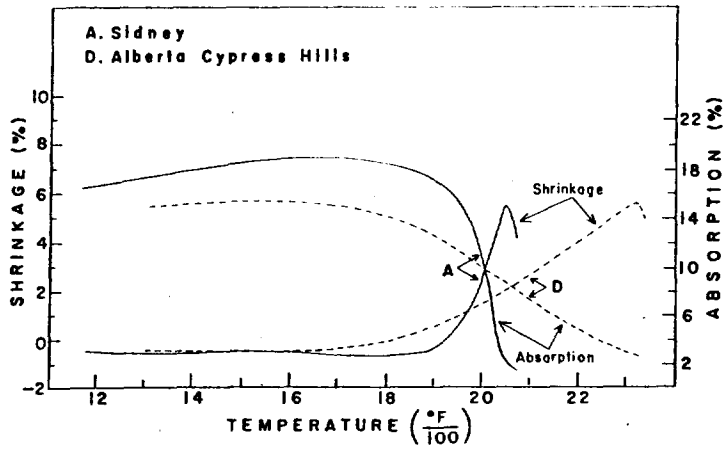


Figure 5. Temperature Gradient Curves of Sidney and Alberta Cypress Hills Clays.

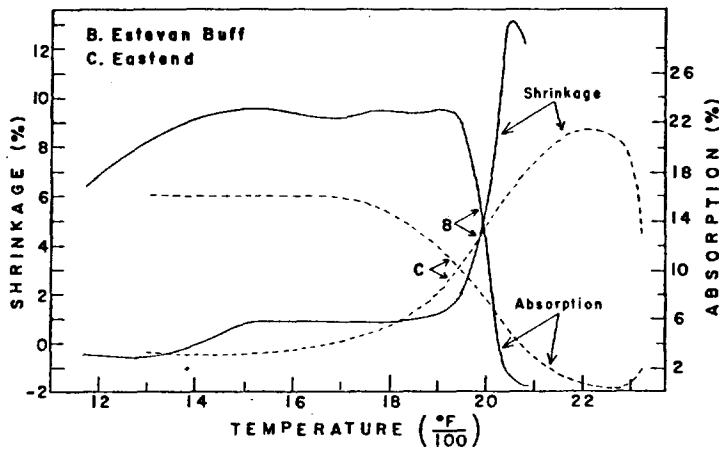


Figure 6. Temperature Gradient Curves of Estevan Buff and Eastend Clays.

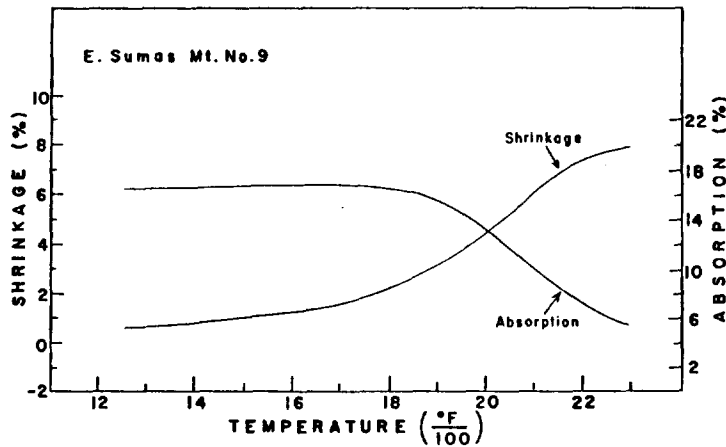


Figure 7. Temperature Gradient Curves of Sumas Mountain No.9 Clay.

The results in Table 1, and the shrinkage and absorption curves, show that Sidney (Figure 5) and Estevan Buff (Figure 6) clays are low-fusion materials having short firing ranges. Both the shrinkage and the absorption change rapidly in the temperature range where a hard-to-very-hard product is obtained. The Estevan Buff has a particularly short firing range.

The PCE's of the Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 materials are 19 or 20, which is in the lower refractory range of a low-duty fire clay. The data in Table 1, and the curves of Alberta Cypress Hills (Figure 5) and Sumas Mountain No. 9 (Figure 7) samples, show them to have a long firing range in which the absorption and shrinkage change slowly in the temperature region where the product is hard to very hard. The Eastend clay (Table 1 and Figure 6) has a firing range shorter than those of the Alberta Cypress Hills and Sumas Mountain No. 9 clays, but much longer than the Sidney and Estevan Buff clays.

Differential Thermal Analysis

The DTA curves are shown in Figures 8 and 9. Standard clay curves of Illite H-36 (Figure 8) and Kaolinite H-4 (Figure 9) are shown with the Western clay curves. The standard clays were obtained from Ward's Natural Science Establishment, Inc., Rochester, N. Y., and are described by Kerr et al. (5) Endothermic peaks point down and exothermic peaks point up.

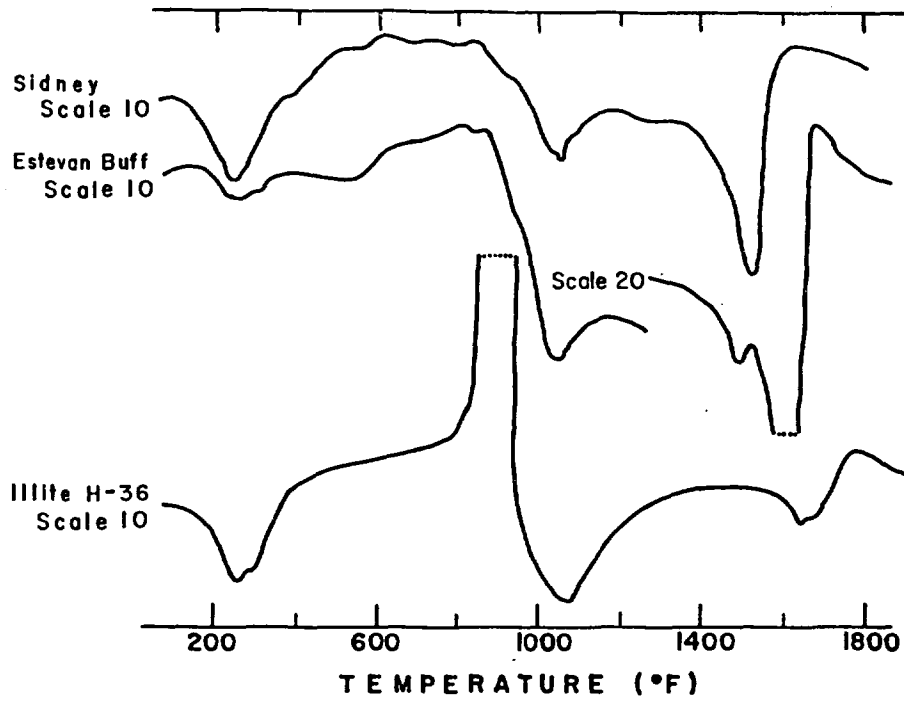


Figure 8. Differential Thermal Analysis Curves.

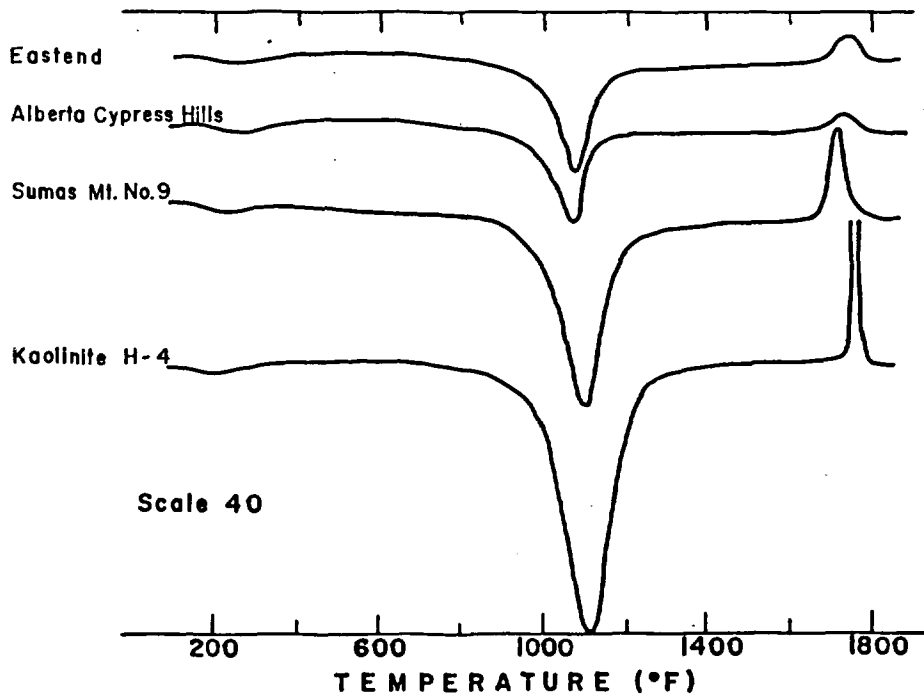


Figure 9. Differential Thermal Analysis Curves.

The Sidney, Estevan Buff and Illite H-36 curves were obtained at a scale setting of 10, which produces peaks four times as large as does the scale setting of 40 that was used for the Eastend, Alberta Cypress Hills, Sumas Mountain No. 9 and Kaolinite H-4 materials.

The presence of illitic material in the Sidney, Estevan Buff and Illite H-36 samples is suggested by two endothermic peaks, one at approximately 250°F due to loss of absorbed water, and a broad one at approximately 1050°F due to loss of combined water from the clay structure. Chloritic material in Sidney clay and Estevan Buff clay would have peaks at approximately the same temperatures and these peaks would likely blend in with the illitic ones. The 250°F Sidney clay endothermic peak is unusually large, which suggests the presence of a calcium montmorillonite as well as illite. The small endothermic dip at approximately 1250°F on the Sidney curve also suggests that a small amount of montmorillonite is present. The small, sharp peak at 1060°F on this curve is caused by the inversion of the low temperature form of quartz to its high temperature form. The endothermic-exothermic change of the Illite H-36 curve at approximately 1700°F is typical of an illitic clay. These reactions are obscured, in the Sidney and Estevan Buff curves, by large endothermic reactions occurring between 1500 and 1700°F, caused by dolomite and excess calcite. The Estevan Buff curves show the presence of a particularly large amount of dolomite and calcite, and the scale sensitivity was reduced from 10

to 20 to retain the peaks on the chart. The double endothermic peak, typical of dolomite, appears in the Estevan Buff curve but not in that of the Sidney clay. Dolomite is indicated in the latter only by the initial shape of the carbonate peak. The sharp exothermic reaction of the Illite-36 curve at 900°F shows that the sample contains a large amount of oxidizable material. Oxidizable substances, chiefly organic material, are also indicated in the Estevan Buff and Sidney clays by the broad exothermic peaks from approximately 550°F to 950°F.

The curves of the Kaolinite H-4, Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 clays are similar. They have a relatively weak endothermic peak at 250°F, due to the loss of absorbed water; a strong endothermic peak at approximately 1100°F due to the breakdown of the clay crystal structure; and an exothermic peak at approximately 1750°F. All reactions are typical of a kaolinitic clay mineral. The exothermic peaks of Eastend and Alberta Cypress Hills are much duller and smaller than the other two. This is probably due to a smaller amount of kaolinite and certain reactive fluxes. There is no evidence of oxidizable material from the appearance of the DTA curves.

X-ray Diffractometry

Smoothed traces of X-ray diffraction patterns of the unfractionated samples are shown in Figures 10 and 11. The only unfractionated sample in which montmorillonite could be detected was the Sidney clay. The small dull peak on the curve of the untreated Sidney sample (Figure 10) at the 14A position has shifted to 16.5A after glycolation, thus confirming the presence of montmorillonite.

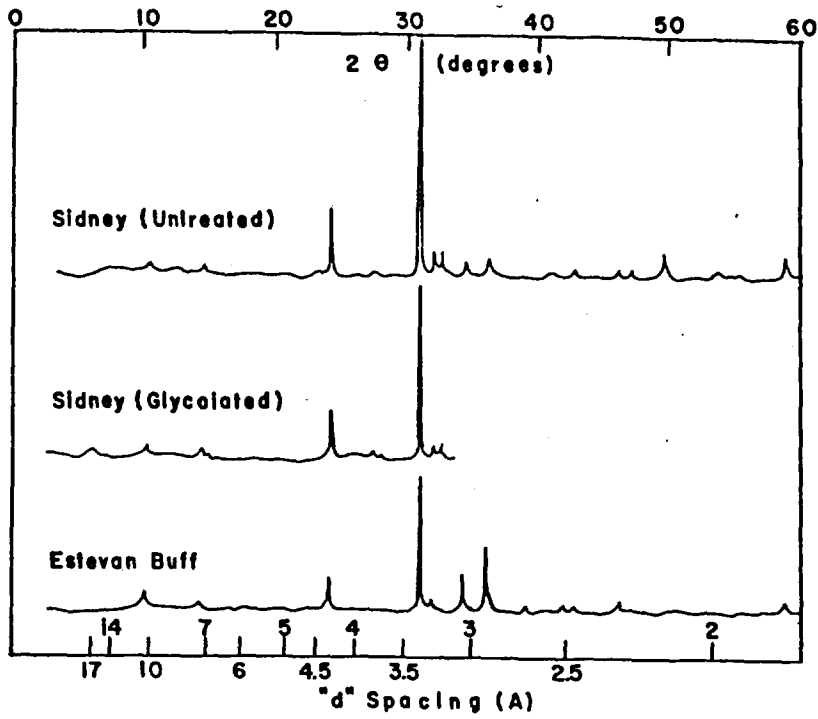


Figure 10. X-ray Diffraction Patterns.

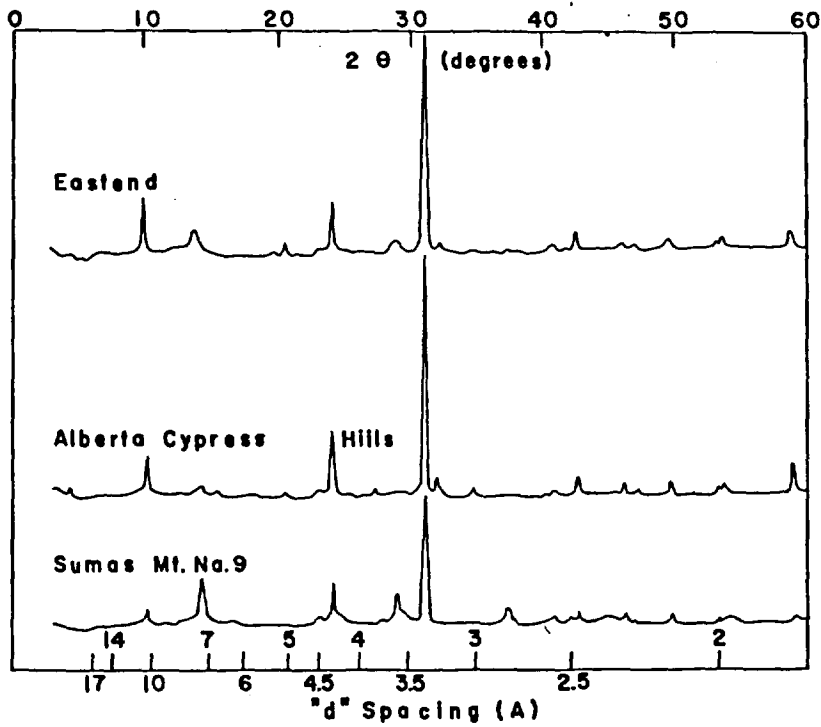


Figure 11. X-ray Diffraction Patterns.

Separate studies on the fine fractions allowed the identification of a mixed layer illite-montmorillonite in Estevan Buff and of montmorillonite in Alberta Cypress Hills, Eastend and Sumas Mountain No. 9. The fine fraction of the Sidney clay was found to contain a small amount of illitic material interlayered with montmorillonite.

Thermal and acid-dissolution studies reveal the presence of a normal chlorite in the fine fraction of the Estevan Buff sample. The fine fraction of the Sidney clay contains a 7A mineral which is soluble in hot concentrated hydrochloric acid and yet fails to yield a typical chlorite response to heat treatment, i. e., show a 14A peak after heating to 1100° F. This material was tentatively identified as a chamosite or septechlorite (Nelson and Roy⁽⁶⁾).

The curves of all samples have a 7A peak which results from the presence of kaolinite except in the case of Sidney and Estevan Buff. The 7A peak of the latter is due partly to kaolinite and partly to chlorite. The 7A peak of the Sidney clay is due partly to a very small amount of kaolinitic material and a probable septechlorite.

All samples contain quartz as indicated by the principal peaks at 3.34A. Secondary quartz peaks occur in most of the curves at 1.81, 1.98, 2.13, 2.28, 2.46, and 4.17A.

All samples contain micaceous material, as indicated by the 10A peaks. This material could be either micas, such as muscovite and biotite, or an illitic clay mineral.

Small quantities of feldspar are present in the Sidney clay (Figure 10), as indicated by peaks at 3.19 and 3.29A; in Estevan Buff (Figure 10), at 3.24A; in Eastend (Figure 11), at 3.19A; and in Alberta Cypress Hills (Figure 11), at 3.24A. Feldspar cannot be detected by DTA, but small quantities are readily revealed by X-ray diffraction.

The X-ray patterns of Sidney and Estevan Buff indicate the presence of calcite (3.03A) and dolomite (2.89A). These peaks are highest on the curve for the Estevan Buff clay. Siderite is present in the Sumas Mountain No. 9 clay, according to the peak at 2.79A. The decomposition peaks of the siderite on the DTA curve were obscured by the large kaolinite peak at 1100°F.

Chemical and Mineralogical Analyses

The chemical analyses are shown in Table 2. These figures were used, in combination with the results of DTA and X-ray diffraction, to determine the mineralogical composition of the five samples. A mineralogical balance showing the approximate mineralogical composition is outlined in Table 3.

The crystalline silica percentages shown in Table 3 were obtained by the Trostel and Wynne method,⁽⁷⁾ and agree closely with quartz percentages obtained by DTA. Usually the DTA values, if different, were slightly smaller.

TABLE 2

Chemical Analysis of Western Clays

Clay	SiO ₂ %	FeO %	Fe ₂ O ₃ %	TiO ₂ %	Al ₂ O ₃ %	CaO %	MgO %	Tot. C %	Organic C %	S %	L.O.I. %	H ₂ O at 110°C %	CO ₂ %	H ₂ O +110°C %	Na ₂ O %	K ₂ O %
Sidney	65.00	0.58	3.57	0.47	10.86	5.23	2.24	1.37	0.24	0.018	9.64	1.67	4.15	3.17	1.29	1.92
Estevan Buff	44.96	1.03	2.29	0.44	10.44	14.32	5.14	4.31	0.27	0.162	19.17	0.67	14.8	2.95	0.48	2.19
Eastend	67.56	0.64	1.86	0.59	18.78	0.14	0.46	0.11	0.08	0.023	7.33	0.95	0.40	5.75	0.17	2.57
Alberta Cypress Hills	72.32	0.19	1.64	1.17	16.54	0.12	0.05	0.13	0.10	0.012	5.95	0.77	0.12	4.51	0.40	2.59
Sumas Mountain No. 9	52.12	5.08	2.22	1.09	24.52	0.59	0.23	1.14	0.12	0.019	12.90	0.72	3.74	8.48	0.13	0.55

TABLE 3
Mineralogical Balance

Clay	Minerals	Total %	SiO ₂ %	FeO %	Fe ₂ O ₃ %	TiO ₂ %	Al ₂ O ₃ %	CaO %	MgO %	Organic Carbon %	S %	CO ₂ %	Na ₂ O %	K ₂ O %	H ₂ O at 110°C %	H ₂ O +110°C %
Sidney		100.40	65.00	0.58	3.57	0.47	10.86	5.23	2.24	0.24	0.018	4.15	1.29	1.92	1.67	3.17
	Crystalline Silica (SiO ₂)	47.80	47.80													
	Dolomite	4.00						1.22	0.87			1.92				
	Calcite	5.10						2.87				2.23				
	Remainder - feldspar, montmorillonite-illite mixed layer clay, probably septechlorite, and trace of kaolin group clay	43.50	17.20	0.58	3.57	0.47	10.86	1.14	1.37	0.24	0.018	-	1.29	1.92	1.67	3.17
Estevan Buff		100.14	44.96	1.03	2.29	0.44	10.44	14.32	5.14	0.27	0.162	14.80	0.48	2.19	0.67	2.95
	Crystalline Silica	28.10	28.10													
	Calcite	17.57						9.82				7.75				
	Dolomite	14.80						4.50	3.25			7.05				
	Remainder - feldspar, kaolinite, micaceous material, chlorite, and illite-montmorillonite mixed layer clay	39.67	16.86	1.03	2.29	0.44	10.44	-	1.89	0.27	0.162	-	0.48	2.19	0.67	2.95
Eastend		99.97	57.55	0.64	1.86	0.59	13.78	0.14	0.46	0.08	0.023	0.40	0.17	2.57	0.95	5.75
	Crystalline Silica	41.40	41.40													
	Kaolinite	35.00	16.30				13.80									4.90
	Remainder - feldspar, micaceous material, and minor montmorillonite	23.57	9.85	0.64	1.86	0.59	4.98	0.14	0.46	0.08	0.023	0.40	0.17	2.57	0.95	0.85
Alberta Cypress Hills		100.53	72.32	0.19	1.64	1.17	16.54	0.12	0.05	0.10	0.012	0.12	0.40	2.59	0.77	4.51
	Crystalline Silica	49.90	49.90													
	Kaolinite	27.00	12.60				13.70									3.70
	Remainder - feldspar, micaceous material, and minor montmorillonite	23.63	9.82	0.19	1.64	1.17	3.84	0.12	0.05	0.10	0.012	0.12	0.40	2.59	0.77	0.81
Sumas Mountain No. 9		99.61	52.12	5.08	2.22	1.09	24.52	0.59	0.23	0.12	0.019	3.74	0.13	0.55	0.72	8.48
	Crystalline Silica	21.60	21.60													
	Siderite	8.20		5.08								3.12				
	Kaolinite	55.00	25.60				21.70									7.70
	Remainder - micaceous material, minor montmorillonite, and carbonate	14.81	4.92	-	2.22	1.09	2.82	0.59	0.23	0.12	0.019	0.62	0.13	0.55	0.72	0.78

The per cent kaolinite for the Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 clays was obtained from DTA. The calculation of SiO_2 , Al_2O_3 and H_2O from the kaolinite content was based on kaolinite having a composition of SiO_2 46.3%, Al_2O_3 39.8%, and H_2O 13.9%. The small quantities of kaolinite present in Sidney and Estevan could not be determined by this method, because the reaction peaks were obscured by those of other clay minerals.

All carbon dioxide (CO_2) in the analyses of Sidney and Estevan Buff was assigned to calcite and dolomite. In the case of the Estevan material, the necessary CO_2 was arbitrarily assigned to all available CaO . This assumption is not necessarily valid, but the resultant percentages of dolomite and calcite obtained by this method are approximately correct for clays of this type. The remaining CO_2 was assigned to MgO and the percentage of dolomite was then calculated from the resulting MgO value. The per cent calcite was calculated from the CaO remaining after deducting the CaO in dolomite from the total CaO in the Estevan Buff clay. This procedure was not satisfactory for the Sidney clay, because in the initial step 4.10% out of a total of 4.15% CO_2 was taken up by the entire CaO of 5.23%. The remaining 0.05% CO_2 could be assigned to a minute quantity of dolomite. On the basis of DTA and X-ray diffraction, however, there was

an appreciable quantity of dolomite. Consequently, from the results of these methods the amount of dolomite was arbitrarily set at 4%. The remaining CO_2 in the Sidney clay was then assigned to calcite.

The remainders in the cases of Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 are mainly micaceous material and a small amount of montmorillonite, with the first two also having feldspar. Sidney has a remainder made up of feldspar, montmorillonite (montmorillonite-illite mixed layer), a probable septechlorite, micaceous material, and a kaolinitic mineral. The remainder for Estevan Buff consists of feldspar, kaolinite, micaceous material, chlorite, and illite-montmorillonite. Special separation techniques would be necessary to arrive at a quantitative estimate of the constituents in the remainder fraction.

Micaceous material in the form of illitic clay enhances the plasticity, but mica, especially coarse mica, is a non-plastic component. Very fine mica would probably act as a flux. The 10A peaks are particularly strong in the X-ray diffraction curves for the Alberta Cypress Hills and Eastend clays (Figure 11). Microscopic examination of the coarse fraction (+200 mesh) revealed that there was some mica in these two clays. The small quantity of H_2O at $+110^\circ\text{C}$ in the "remainders" (Table 3) suggests that the amount of illitic clay is small. This factor probably contributed to the low strength, in the unfired state, of

the Alberta Cypress Hills clay. No coarse mica was visible in the Sumas Mountain No. 9 and Estevan Buff samples. The Estevan Buff sample is fairly plastic and, therefore, the majority of micaceous material in it is probably an illitic clay. No such inference could be drawn for the Sumas Mountain No. 9 clay. The Sidney clay has a small amount of mica in the coarse fraction, while the mixed layer mineral in the fine fraction contains a small number of illite layers.

DISCUSSION AND CONCLUSIONS

The relative plasticity of the samples has been shown by the plasticity curves. The relatively high and very broad peak of the Sidney clay indicated that it is very plastic. Materials of this type are difficult to dry and such is the case with the Sidney material. The montmorillonite content of the Sidney clay is chiefly responsible for the high plasticity (Marshall⁽²⁾) and the difficulty in drying. The montmorillonite layers in the mixed layer illite-montmorillonite clay in the Estevan Buff sample, and the montmorillonite in the Alberta Cypress Hills sample, are probably responsible for the difficulty in drying these clays rapidly. The Sumas Mountain No. 9 and Eastend samples do not contain sufficient montmorillonite to cause difficulties with drying.

Montmorillonite is frequently found in the clays of Manitoba, Saskatchewan, Alberta and British Columbia, and as a

result many of them are very plastic and difficult to dry. A small, controlled amount of montmorillonite (bentonite) may aid the plasticity of a non-plastic material, but an uncontrolled, substantial amount of montmorillonite will cause drying and shrinkage difficulties.

Kaolinite, chlorite and illite, being clay minerals, are responsible for imparting a degree of plasticity to clay materials. They do not increase plasticity or adversely affect the drying properties in the same manner as montmorillonite, unless their particle size is extremely small.

The Alberta Cypress Hills clay is fairly plastic. However, the body strength is weak after extrusion, probably because of the high content of non-plastic material such as quartz, feldspar and coarse micaceous material.

The Sidney and Estevan Buff clays are heterogeneous mixtures of quartz, calcite, dolomite, feldspar, clay minerals, and micaceous material. The amounts of CaO, MgO, Na₂O, K₂O and Fe₂O₃ are relatively high, particularly CaO and MgO. These materials are active fluxes in conjunction with SiO₂ and Al₂O₃, with the result that the clays have a low melting point and a short firing range. The Estevan Buff, with a total dolomite and calcite content of about 32.4%, is a good example of a clay having these properties.

The Estevan Buff fires to a buff colour at the temperature range in which the product becomes hard. A buff colour in a clay of this type may be attributed to a high percentage of CaO and

MgO relative to the FeO and Fe₂O₃ content. While the CaO and MgO content of the Sidney clay is fairly high, the ratio of these oxides to FeO + Fe₂O₃ is much lower than in the Estevan Buff. Consequently, the Sidney clay fires to a salmon or red-brown colour. If the CaO and MgO contents were appreciably higher, particularly the CaO per cent, then the clay would likely fire to a buff colour. Calcareous common clays of the Sidney or Estevan Buff type are frequently encountered in Western Canada.

Kaolinite is a very refractory material, commonly found in refractory or semi-refractory clays such as the Eastend, Alberta Cypress Hills and Sumas Mountain No. 9. Illite, montmorillonite and chlorite are less refractory materials and are found frequently in common clays such as Sidney and Estevan Buff. Quartz, which was found in all the Western clays investigated, is a refractory material that forms low-temperature eutectics with fluxing ingredients.

The Eastend, Alberta Cypress Hills and Sumas Mountain No. 9 materials are not as heterogeneous as the Sidney and Estevan Buff clays. Quartz, kaolinite, and micaceous material are their principal constituents. Their combined totals of CaO, MgO, K₂O, Na₂O, FeO and Fe₂O₃ are considerably lower than those of the Estevan Buff and Sidney clays, while the Al₂O₃ contents are considerably higher. These factors are largely responsible for the more refractory nature of the Eastend, Alberta Cypress Hills

and Sumas Mountain No. 9 clays. The feldspar and some of the micaceous material would likely provide some fluxing action in the Eastend and Alberta Cypress Hills clays. The fluxes appear to be more active in the Eastend clay, which vitrifies at a much lower temperature than does the Alberta Cypress Hills. The Sumas Mountain No. 9 contains a substantial proportion of FeO and Fe_2O_3 , which with some of the micaceous material would likely reduce the refractoriness of this clay despite its high Al_2O_3 content.

Because the percentages of FeO and Fe_2O_3 in the Eastend and Alberta Cypress Hills clays are relatively low, these clays burn to cream or buff colour. Buff-firing, non-calcareous, plastic materials of this type are usually classified as stoneware clays and have much longer firing ranges than do the buff-firing calcareous clays of the Estevan Buff type. Stoneware-type clays occur in all four Western provinces. Although Sumas Mountain No. 9 has relatively high FeO and Fe_2O_3 contents, it burns to a pink-grey colour. Usually, shales containing such large amounts of iron will burn to a salmon or red colour. According to Searle,⁽⁸⁾ however, the iron oxides in material of this type probably react with the alumina from the decomposed clay to form a lighter colour than the red which might ordinarily have been expected from the amount of iron present.

Differential thermal analysis (DTA) serves to compare the amount of oxidizable material, such as organic matter

and pyrite, in clay samples. If these substances are present in substantial quantity, provision must be made for oxidizing them during the firing schedule. The DTA curves (Figures 8 and 9) indicate that all the Western samples contain little organic matter or pyrite. There is a suggestion of a pyrite peak at 850°F on the Estevan Buff curve. The broad exothermic peaks on the Sidney and Estevan Buff curves at 550 to 850°F are due principally to a very small amount of organic material. The chemical analyses of all samples, in Table 2, indicate that the organic carbon contents are low, the highest being in the Sidney and Estevan Buff clays. The samples contain only minor amounts of sulphur, except the Estevan Buff which contains a small quantity due probably to pyrite. The greater proportion of the oxidizable material burns out in a narrow range--mainly at 800 to 850°F--in the Estevan Buff material, and excess oxygen should be present when this occurs.

Large quantities of carbonate in a clay usually produce a porous, soft product during firing. Since calcite and dolomite, particularly the former, are common constituents of heterogeneous clays, they are the worst offenders in this respect. The Estevan Buff clay illustrates well the effect of a large amount of calcite and dolomite on the absorption characteristics. The temperature gradient curve of this material (Figure 6) shows that the absorption is 22.5% up to approximately 1930°F, after which it

drops very rapidly to 2.5%. Slight under-firing of a clay of this nature produces a very soft, porous product. Sidney clay, which contains approximately one-third as much carbonate as the Estevan Buff clay, behaves in a similar manner, although the variations with a slight change in firing temperature in the critical range are not so severe.

Siderite decomposes at a much lower temperature than does dolomite or calcite, causing a rather high initial absorption in the Sumas Mountain No. 9 shale. This latter effect is overcome long before the proper firing temperature is reached.

During the firing of clays containing excessive dolomite and calcite, a residual expansion occurs which is rather high in the Estevan Buff and Sidney clays (Figures 5 and 6). These residual expansions are partly due to the decomposition of the carbonates and possibly to the resultant formation of crystalline compounds.

Quartz commonly occurs in all clays. It is present in large quantities in the Sidney, Eastend and Alberta Cypress Hills samples. This mineral has a reversible expansion at 1060°F. Part of the residual expansion, which is shown on all the temperature gradient curves except that of the Sumas Mountain No. 9, results from the quartz. Quartz in the fired material causes severe cracking if the ware is cooled too rapidly through the inversion point. Usually, clays high in free silica cause difficulty in this respect. Trouble from expansion may result from excessive

movement during rapid heating of the ware, particularly if there is an uneven temperature distribution. The very large amount of quartz in the Alberta Cypress Hills sample may account, in part, for the very long firing range.

Expulsion of the combined water, shown by the endothermic peaks on the DTA curves at approximately 1100°F, may also cause some expansion.

Feldspar, which occurs in small amounts in all samples except the Sumas Mountain No. 9, is a very active flux and contributes to glass formation during firing.

The Sumas Mountain No. 9 clay is unusual, because it is high in kaolinite, has a moderate amount of quartz, and is relatively low in CaO, MgO, Na₂O and K₂O. In this respect it is similar to a fire clay. However, the FeO, the Fe₂O₃ and some of the micaceous material apparently reduce the refractoriness to Cone 19, which is in the low duty range. It is plastic for a shale and has an excellent firing range. The long firing range is probably due to the high kaolinite content. Some care may be required in firing during the period when the siderite decomposes.

SUMMARY

The effects of various minerals on the properties of some typical Western clays have been discussed.

Clays (such as the Sidney sample) that contain a rela-

tively small amount of montmorillonite commonly occur in Western Canada. They are very plastic and are difficult to dry from the plastic state. Materials (such as the Alberta Cypress Hills sample) that have some plasticity and extrude fairly well, tend to produce a weak body because of their high content of non-plastic ingredients.

Chlorite was identified in the Estevan Buff and tentatively identified in the Sidney clay. Chlorite enhances plasticity much in the same manner as illite and is usually found in non-refractory clay materials.

Clays (such as the Estevan Buff) that contain the commonly occurring minerals calcite and dolomite in large quantities have very short firing ranges. Products from this type of material are apt to be soft and porous when underfired; or hard, glassy and deformed when overfired. Very close control of the firing temperature is necessary.

Heterogeneous mixtures (such as the Sidney and Estevan Buff samples) have a low heat softening temperature (PCE). Clays or shales (such as the Eastend, Alberta Cypress Hills and Sumas Mountain No. 9) which contain kaolinite as the principal clay mineral, and only relatively small amounts of CaO, MgO, Na₂O and K₂O, are more refractory than the heterogeneous mixtures and usually have long firing ranges.

Quartz is commonly found in all clays and shales. In the Alberta Cypress Hills sample it constitutes almost 50% of

the material. Quartz, as well as dolomite, calcite and the expulsion of combined water, can be a principal cause of residual expansion in fired ceramic products.

Micaceous material was found in all the samples, and feldspar in most of them. Feldspar acts as an active flux. The effect of micaceous material may vary considerably. If it is in the form of illitic clay, the plasticity will be increased, but if it is in the form of mica, such as muscovite or biotite, the plasticity will probably be reduced. The degree of fluxing by mica will vary according to the particle size. Large flakes of mica usually do not react readily.

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REFERENCES

1. L. E. Thiess, Method of Recording Plastic Properties of Porcelain Bodies. *J. Amer. Ceram. Soc.* 22, 286-289 (1939).
2. Claude L. Marshall, A New Concept of Clay Plasticity. *Bull. Amer. Ceram. Soc.* 34, 54-56 (1955).

REFERENCES - Concluded

3. R. L. Stone, Temperature Gradient Method for Determining Firing Range of Ceramic Bodies. *J. Amer. Ceram. Soc.* 36 (4), 140-142 (1953).
4. J. G. Brady, Preliminary Evaluation of Clays and Shales for Clay Products. *J. Can. Ceram. Soc.* 29, 7-17 (1960).
5. P. F. Kerr, J. L. Kulp and P. K. Hamilton, Reference Clay Minerals API Research Project 49. Pub. by Columbia University, New York, N. Y., 1951.
6. Bruce W. Nelson and Rustum Roy, New Data on the Composition and Identification of Chlorites. *Proceedings of the Second National Conference on Clays and Clay Minerals, 1953*, Columbus, Miss., NAS-NRC Pub. 327 (Washington, D. C.), p. 338 (1954).
7. L. J. Trostel and D. J. Wynne, Determination of Quartz (Free Silica) in Refractory Clays. *J. Amer. Ceram. Soc.* 23, 18-22 (1940).
8. A. B. Searle, *Modern Brick Making*. Fourth Edition (Ernest Benn Limited, London, 1956), p. 24.

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