Dr. J. Convey

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 63-44

INVESTIGATION OF THE SUITABILITY OF TWO MANITOBA SHALES FOR USE IN CLAY PRODUCTS

by

K. E. BELL & L. K. ZEMGALS

MINERAL PROCESSING DIVISION

8P

NOTE: THIS REPORT RELATES ESSENTIALLY TO THE SAMPLES AS RECEIVED. THE REPORT AND ANY CORRESPONDENCE CONNECTED THEREWITH SHALL NOT BE USED IN FULL OR IN PART AS PUBLICITY OR ADVERTISING MATTER.

COPY NO. 10

APRIL 10, 1963

Mines Branch Investigation Report IR 63-44

INVESTIGATION OF THE SUITABILITY OF TWO MANITOBA SHALES FOR USE IN CLAY PRODUCTS

by

K. E. Bell* and L. K. Zemgals**

- - - -

SUMMARY OF RESULTS

Two shale samples from Pembina Mountain were submitted by Mr. Barry Bannatyne, Winnipeg, Manitoba, for evaluation of their suitability for manufacture of sewer pipe and structural clay products.

The physical properties of the raw and fired shales were determined. Differential thermal analysis and temperature gradient methods were employed.

The sample of Morden shale was found highly plastic and tender drying with high drying shrinkage, and to vitrify at low temperature with a short firing range. It contained illitic type clay minerals and large amounts of carbonaceous materials.

The sample of Odanah shale was less plastic, difficult to dry and open firing, and did not vitrify at reasonable temperatures. This siliceous shale also contained an illitic clay mineral and a small amount of carbonaceous material.

A half and half mixture of the two shales showed properties similar to those of the Morden shale.

Neither sample nor mixture thereof is considered suitable for the manufacture of sewer pipe. A mixture comprised of about 80 per cent Odanah shale and 20 per cent Morden shale possibly would be suitable for the manufacture of face brick, common brick, partition tile and drain tile.

---

* Scientific Officer and ** Technician, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

TABLE OF CONTENTS

TABLES

FIGURES

INTRODUCTION

Two shale samples from Pembina Mountain were submitted by Mr. Barry Bannatyne, Industrial Minerals Geologist, Department of Mines and Natural Resources, Winnipeg, Manitoba, for evaluation of their suitability for face brick and sewer pipe manufacture. The samples weighed about one pound each and were identified as follows:

Sample 1 — "Morden shale from Learys (13-6-8 WPM). Composite sample over 20 foot section of nearly horizontally bedded carbonaceous shale."

Sample 2 — "Odanah shale from NE 17-6-8 WPM. Representative of top 30 feet of a thick deposit of hard siliceous shale."

Both samples were tested for unfired and fired characteristics. The approximate mineral compositions and some problems associated with firing were determined by differential thermal analysis (DTA). Furthermore, a mixture of 50 per cent Morden and 50 per cent Odanah shales was made to try to improve the individual characteristics.

PROCEDURE

Temperature Gradient Determinations

The clay was dried and ground to pass a 16 mesh Tyler laboratory screen. The ground clay was tempered with water to a stiff plastic condition. The plasticity and workability were observed, and the amount of water required (water of plasticity) was measured. Hand-moulded test bars (8 x 1 x 1/2 in.) for temperature gradient determinations of the fired properties were made in steel moulds. Similarly, test cones were prepared for determination of heat-softening points (PCE's). The bars were carefully air-dried for 48 hours and then finally dried in a laboratory drier at 100°C (212°F) for 24 hours. The average drying shrinkage was calculated in per cent of wet length. One test briquette was subjected to rapid drying conditions at 85°C (185°F) and the result observed. The PCE was determined.

Two test bars of each sample, which had not warped while drying, were selected for determining the fired properties by means of a Stone temperature gradient apparatus. The sides of the bars were smoothed and made parallel. Fine reference lines were scribed every half 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 opposite ends of the furnace with the zero ends flush with the cool ends of the tube, thereby providing reference points for locating the exact position of each measured point along the specimens. A temperature gradient of approximately 650°C

(1200°F) from the cold to the hot end of each bar was produced. The centre portion of the furnace, where the temperature is highest, was heated at the rate of 71°C/hr (160°F/hr) to 815°C (1500°F), held there for 6 hours, then heated at the rate of 94°C/hr (200°F/hr) to the finishing temperature, which was held for one hour. A finishing temperature for each sample was selected to vitrify or slightly overfire the bars at the hot end. Five temperature measurements were made at known intervals along the length of each trial piece at the end of the final soaking temperature. A plot was made of temperature versus distance along the bar in order to establish its exact temperature gradient. After cooling, sections were cut at the half inch marks. The fired shrinkage, the water absorption after a 24 hour soak in cold water, the colour and the hardness of each section were determined.

Differential Thermal Analysis

The samples for DTA were ground to pass through a 100 mesh Tyler laboratory screen. DTA curves of each sample were obtained in an air atmosphere. Curves of their heat effects were recorded on a Leeds and Northrup $x_1 - x_2$ recorder using a heating rate of 12°C/min.

RESULTS

The unfired characteristics of the samples are shown in Table 1. Morden shale has a rather high drying shrinkage (7.0 per cent). Both have a tendency to crack with rapid drying. The workability of both shales is good and it can be assumed that they would extrude satisfactorily, although the Odanah shale is slightly gritty. The samples were too small to determine the extrusion properties.

Curves of shrinkage and absorption obtained by the temperature gradient method are shown in Figure 1. Shrinkage values between 0 and minus 2 per cent indicate that there was a residual expansion, while values greater than zero indicate that shrinkage had taken place. A summary of the fired properties - shrinkage, absorption, colour and hardness over appropriate temperature ranges - and the PCE are given in Table 1. The Morden shale and the mixture have very short firing ranges while the Odanah shale is hard to vitrify.

DTA curves are reproduced in Figure 2. Endothermic reactions have peaks pointing down and exothermic reaction peaks point up. The curves show in a general way the temperatures and extent of the various endothermic or exothermic reactions which will take place when the material is fired in a commercial kiln with an oxidizing atmosphere. Normally the reaction temperatures obtained under commercial conditions are slightly lower than the ones shown on the DTA curves because the rate of temperature increase of the DTA is much faster than in a full size kiln.

DTA indicates that both samples probably contain an illitic clay mineral. Confirmation of this would be necessary by X-ray diffraction analysis. Morden shale contains a large amount of oxidizable material, probably carbon and

TABLE 1

Summary of Physical Properties

CLAY NO.	UNFIRED CHARACTERISTICS	P.C.E.	FIRED CHARACTERISTICS					Remarks
			Temperature °C	Fired Shrinkage % *	Absorption %	Colour	Hardness	
Morden Shale	Dark grey, non-calcareous shale, good plasticity and workability, water of plasticity 36%, cracks slightly with rapid drying (85°C), drying shrinkage 7.0%.	12 (1337°C)	688	-0.4	26.3	light tan	very soft	Common reddish brown firing carbonaceous shale. Short firing range. High drying shrinkage, and high firing shrinkage above 977°C.
			826	-0.2	24.3	light tan	soft	
			938	2.1	20.3	pale salmon	fairly soft	
			977	4.4	16.6	pale salmon	fairly hard	
			1021	8.0	9.0	light brownish salmon	fairly hard	
			1060	11.6	1.5	medium reddish brown	steel hard	
			1096	11.9	0.5	reddish brown	nearly vitrified	
			1123	11.3	0.6	dark reddish brown	vitrified	
			1149	7.8	2.3	dark reddish brown	vitrified-overfired	
			1184	1.5	5.7	dark reddish brown	vitrified-overfired	
Odanah Shale	Grey, non-calcareous shale, fairly plastic, good workability, water of plasticity 41%, cracks with rapid drying (85°C), drying shrinkage 4.3%.	16 (1491°C)	749	—	31.6	pale greyish buff	very soft	Siliceous shale. Difficult to vitrify. Briquettes at 1222°C are still porous. Black specks beginning at approximately 1220°C.
			826	0.5	30.0	pale greyish buff	soft	
			894	1.3	28.2	pale salmon buff	soft	
			1005	3.1	24.0	pinkish buff	fairly soft	
			1055	4.1	21.4	pinkish buff	fairly soft	
			1138	6.7	16.5	light pink	fairly hard	
			1222	7.8	15.0	light brownish pink	fairly hard	
			1249	7.9	14.8	light brown	fairly hard to hard	
			1264	8.3	14.0	medium brown	fairly hard to hard	
			1274	8.6	13.1	medium brown	fairly hard to hard	
Mix of 50% Morden and 50% Odanah shales	Plasticity and workability good, water of plasticity 38%, cracks slightly with rapid drying (85°C), drying shrinkage 5.9%.	14 (1398°C)	760	-0.05	28.6	light tan	very soft	Drying shrinkage slightly above average. Combined shrinkage at 1063°C is too high. Short firing range. Slight improvements over Morden shale.
			839	0.4	27.0	light tan	very soft	
			904	2.0	24.6	pale salmon	fairly soft	
			963	3.1	21.8	pale salmon	fairly hard	
			1015	5.4	17.8	light salmon	fairly hard	
			1063	7.9	11.2	speckled salmon	hard	
			1107	10.2	5.4	light brownish red (buff specks)	very hard	
			1144	11.4	3.6	brownish red (buff specks)	steel hard	
			1192	11.0	2.3	dark reddish brown (buff specks)	vitrified	
			1226	7.7	4.1	—	vitrified-overfired	
			1249	3.4	7.1	—	vitrified-overfired	
			1265	-2.9	9.2	—	vitrified-overfired	

* A minus sign indicates expansion

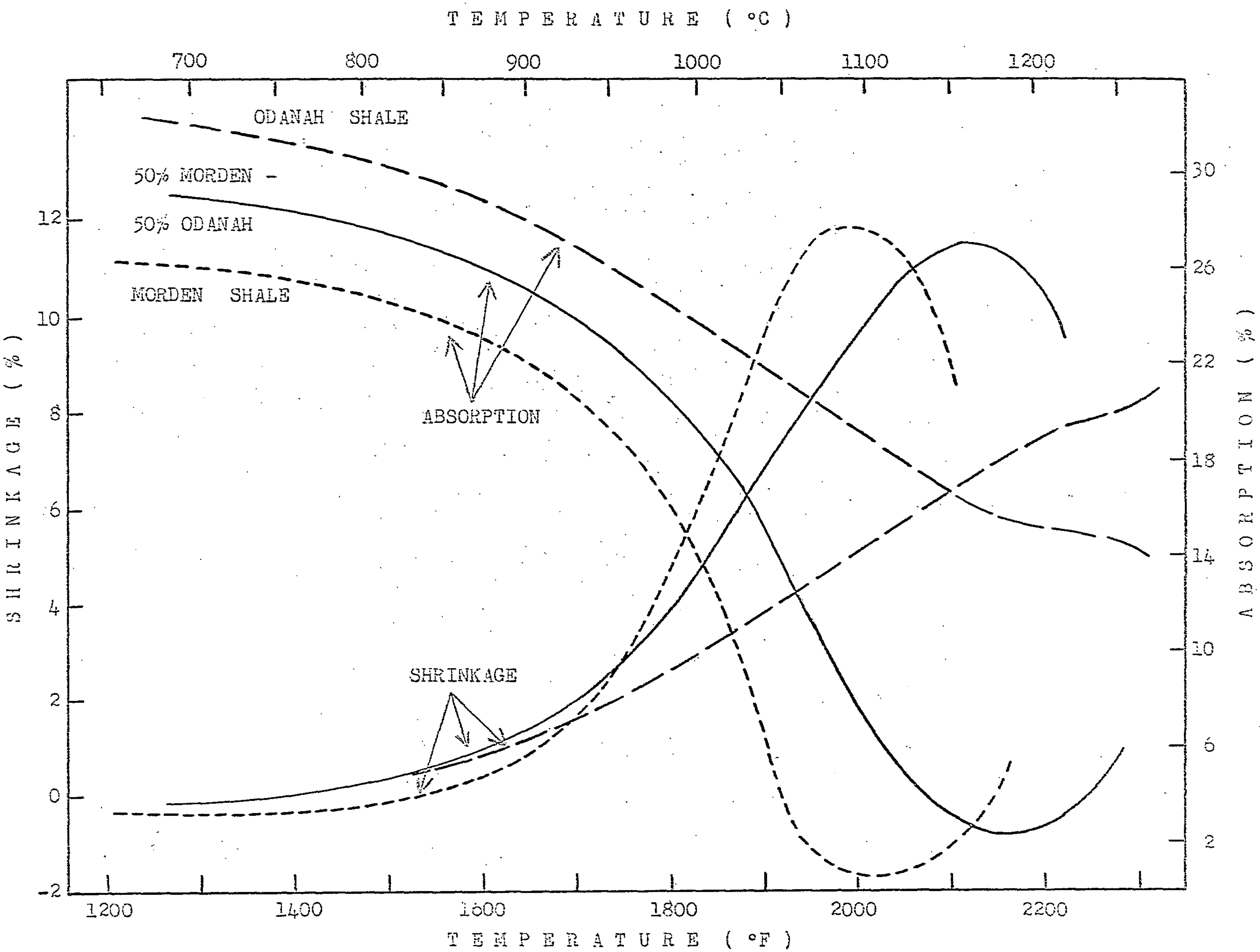

Figure 1. Temperature Gradient Curves.

pyrite, and Odanah shale a small amount of oxidizable material, probably carbonaceous.

TABLE 2

Summary of DTA Results

Sample	Clay Peaks °C	Carbonaceous and other Oxidizable Material Peaks °C	Remarks
Morden Shale	150, 565, 870, 950- Illitic clay mineral	300, 395, 635 - Large amount of carbon (probably coal) and pyrite	The oxidation peak partly obscures the clay peak (565°C). The exothermic peak at 635°C suggests the final burn out of oxidizable material.
Odanah Shale	140, 555, 865, 930- Illitic clay mineral	340, 380 - Small amount of oxidizable material	Medium clay peak at 555°C.
Mix of 50% Morden and 50% Odanah Shales	150, 560, 865, 940- Illitic clay mineral	320, 380, 585 - Large amount of carbon (probably coal) and pyrite	The DTA curve is very similar to the Morden shale curve - there is a smaller oxidation peak

The presence of an illitic clay is usually indicated by a small endothermic peak due to the loss of absorbed water at approximately 120 to 150°C (248 to 302°F), by a broad endothermic reaction at approximately 550 to 600°C (1022 to 1112°F) due to loss of combined water, and by a final endothermic-exothermic reaction in the 875 to 1000°C (1607 to 1832°F) range.

Carbonaceous material usually produces an exothermic reaction in the 300 to 500°C (572 to 932°F) temperature range. Occasionally a very large quantity of high temperature carbon burns out up to 700°C (1292°F) and so interferes with the clay reaction at 600°C (1112°F). Pyrite usually breaks down at approximately 400 to 500°C (752 to 932°F) but its final breakdown usually occurs only after the carbon has been removed.

The peak temperatures are summarized in Table 2.

CONCLUSIONS

The Canadian Standards Association specification for Vitrified Clay Pipe (CSA Standard [illegible]0) limits absorption to a maximum average of 8 per cent.

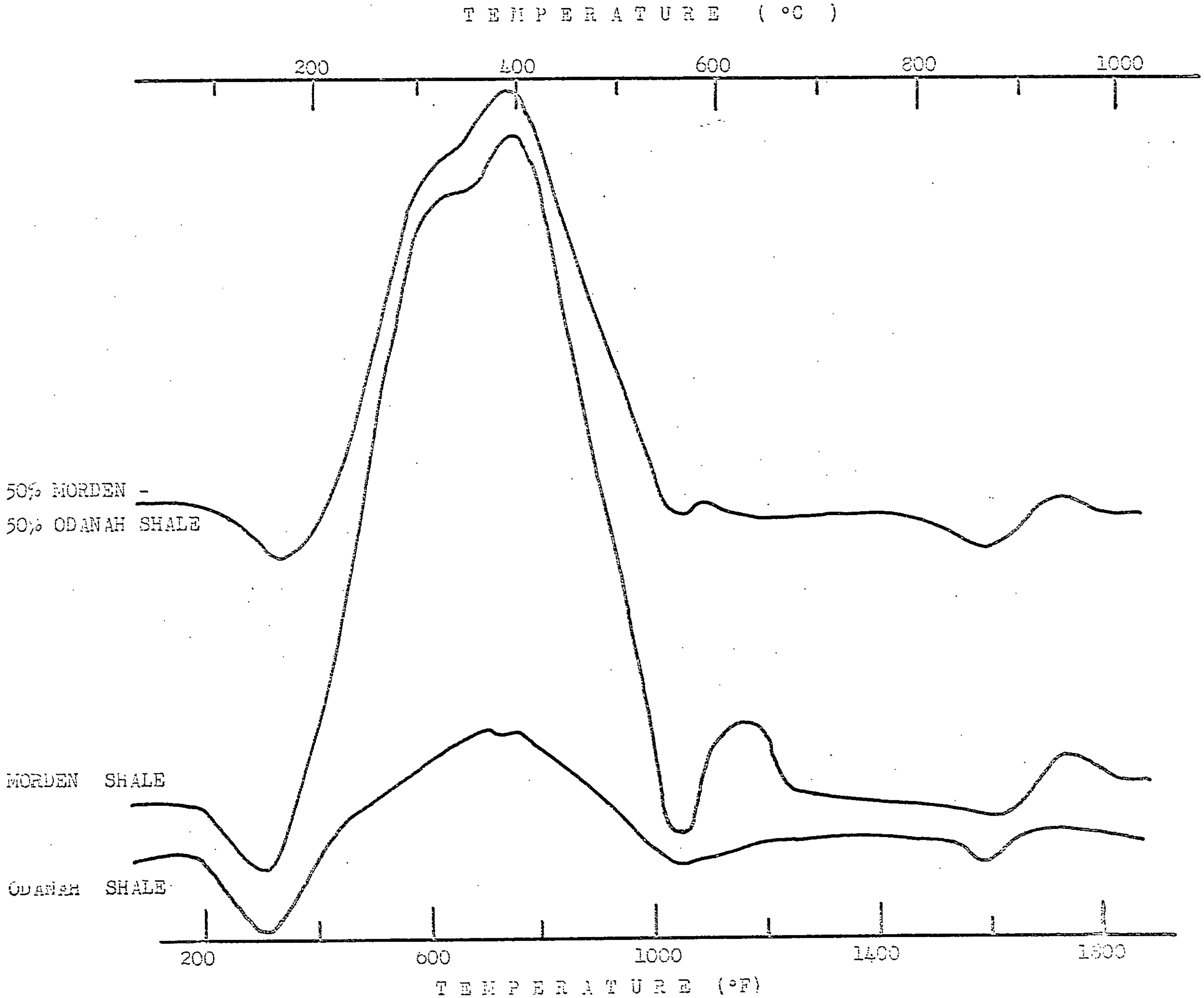

Figure 2. D T A Curves.

The absorption of the fired Odanah shale exceeded this limit at all temperatures investigated, hence this material would not be suitable for the manufacture of sewer pipe.

The Morden shale met this requirement when fired between about 1030°C (1875°F) and 1090°C (1995°F). This firing range is considered sufficiently wide for adequate control. Practical considerations, however, dictate that shrinkages should be sufficiently low to preclude cracking and warping of the pipes during processing. The normal maximum allowable shrinkage would be 10 to 12 per cent, about equally divided between drying and firing. Total shrinkage of the Morden shale, through the above firing range, was from about 16 to 19 per cent, greatly exceeding the practical limits. Furthermore, this variation in shrinkage would cause differences in length of fired pipes in excess of the maximum allowable (2.1 per cent) of CSA Standard A60. Thus, the Morden shale is not considered suitable for the manufacture of sewer pipe.

The half-and-half mixture showed characteristics similar to those of the Morden shale and is considered unsuitable for the same reasons. The total shrinkage corresponding to 8 per cent absorption was 15 per cent, increasing with increase in firing temperature to almost 18 per cent. The evaluation of other mixtures was precluded by the small sizes of the samples. However, mixtures containing significantly larger proportions of Odanah shale could be expected to show absorptions in excess of the maximum allowable.

The specifications for facing brick, building brick, partition tile and drain tile are progressively less restrictive than those for sewer pipe. CSA Standard A82.7 provides for first quality (Grade SW) facing brick having absorptions of up to 17 per cent (determined by the method of boiling for 5 hours; probably equivalent to a value of about 15 per cent determined by the cold soaking method of this investigation). Highly porous brick of this type has been shown to give satisfactory service under the climatic conditions prevailing in the prairie provinces.

The absorption of the fired Odanah shale remained above the desired 15 per cent level until the firing temperature of 1230°C (2246°F) had been reached. This temperature is considerably higher than those usual for burning brick (about 1025°C to 1125°C - 1875°F to 2050°F) and would result in excessive fuel costs.

Conversely, the absorption of the Morden shale reached the desired level at about 990°C (1815°F). However, the total shrinkage at this temperature was 12.5 per cent and increased rapidly with increasing temperature. To control the size of the fired bricks within limits acceptable to the trade (about 3 per cent) it would be necessary to limit the firing range to about 33°C (60°F), which presents many practical difficulties. Furthermore, the total shrinkage at the top of the range (1023°C - 1875°F) was 15.5 per cent. Brick shrinking to such an extent could crack under the load of a normal brick setting, or differential shrinkage due to unequal temperature distribution over the cross-section of the setting could result in an unstable condition and cause the setting to collapse.

The half-and-half mixture of the shales showed characteristics only slightly improved over those of the Morden shale; the firing range was short, or, through a firing range sufficiently wide for convenient control (50°C, 90°F), the shrinkage was excessive - about 15 per cent, total.

By interpolation from the curves of Figure 1, the best mixture appears about 20 per cent Morden shale, 80 per cent Odanah shale. Such a mixture, fired in a range from about 1090° to 1140°C (about 1990° to 2080°F) could be expected to have absorptions varying from about 15 to 11 per cent and total shrinkages of about 12 to 13.5 per cent.

Facing brick, common brick, partition tile and drain tile could possibly be manufactured from this mixture. The inclusion of 20 per cent Morden shale should improve the plastic properties of the Odanah shale, and perhaps improve the drying characteristics. Careful control of the drying process would be required to prevent cracking. This small proportion of Morden shale would probably not cause serious difficulty during the oxidation or carbon burn-out period of the firing cycle. The firing shrinkage would be rather high and kiln facilities and firing procedures should be designed to ensure uniform heating over the cross-section of the setting.