WISCONSIN G&NHS MP 83-3

MISCELLANEOUS
PAPER
83-3

POTENTIAL OF A WISCONSIN CLAY FOR BINDING TACONITE PELLETS

by R. DasGupta, R.W. Heins, M.E. Ostrom, and T.D. Tiemann

available from
Geological and Natural History Survey
University of Wisconsin-Extension
1815 University Avenue
Madison, Wisconsin
53705

MISCELLANEOUS
PAPER
83-3

POTENTIAL OF A WISCONSIN CLAY FOR BINDING TACONITE PELLETS

R. DasGupta, R.W. Heins, M.E. Ostrom, and T.D. Tiemann

1983

Available from University of Wisconsin-Extension
Geological and Natural History Survey
1815 University Avenue, Madison, Wisconsin 53705

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

An estimated 4.2 million cubic yards of material containing approximately 1.4 million cubic yards of montmorillonite clay occurs near Hersey, St. Croix County, Wisconsin. This clay material was analyzed to determine its potential for use as a binder in pelletizing magnetite concentrates (taconite). The clay does not meet the requirements for binding purposes in the raw state, however, preliminary tests indicate pellets of suitable strength can be made if the clay is treated with additives.

The clay material contains 65% quartz and 35% clay consisting predominantly of calcium montmorillonite with minor kaolinite. Quartz content was reduced to less than 15% by sedimentation. Various sodium and potassium compounds were used as additives to alter the physical properties of the raw clay. The effect on the 18 inch green drop index, dry compressive strength, and fired strength obtained by varying the additive content within the range of 0 to 5 pounds per ton of magnetite concentrate was studied. The results of these tests indicate that the -200 mess sieve fraction of the untreated Wisconsin clay (no additives) is unsuitable for pellet bonding.

The untreated clay can be used to make pellets with marginally suitable strengths (green, dry, and fired) if the quartz content is decreased from 65% to 28% by extensive settling--but only if 3% of this clay is used in the pellet as opposed to 1% per standard bentonite. The amount of untreated clay required can be reduced to 1% or 0.5% if the following materials are added:

(a) Potassium or sodium compounds (K_2CO_3 and Na_2CO_3 effectively improve the dry strength of the pellets containing 1% Wisconsin clay).
(b) Hydroxyethyl cellulose (a synthetic resin consisting of pure cellulose modified by addition of polymeric ethylene oxide side chains).
(c) Polyox (water soluble, non-ionic, homopolymer of polyethylene oxide).
(d) Guar gum (a natural vegetable colloid).

A combination of 0.5% guar gum and 0.5% Wisconsin clay gives extremely good pellet strengths. By optimizing the proportion of these two binders the Wisconsin clay can be used without a sodium additive.

INTRODUCTION

The purpose of this study was to investigate the potential of a montmorillonite clay which occurs in Pleistocene till near Hersey in St. Croix County, Wisconsin, for use as a binder in pelletizing magnetite concentrates (taconite). The potential of using various sodium and potassium compounds, a synthetic resin, Polyox, and guar gum as additives to improve the bonding properties of the clay for the production of pellets was also investigated.

The use of montmorillonite as a binder for taconite pellets depends on its bonding properties which are a function of its atomic structure and chemical composition. The structure of the basic silicate cell for montmorillonite is a sandwich consisting of two silica tetrahedral sheets enclosing a central alumina octahedral sheet. The tetrahedral sheets are composed of tetrahedra which consist of a single silicon atom (Si^{+4}) enclosed by four oxygen (O^{-2}) or hydroxyl (OH^{-1}) atoms; the octahedral sheets are composed by octahedra which consist of a single aluminum, magnesium, or iron atom enclosed by eight oxygen atoms. The tetrahedral and octahedral sheets combine together into a silicate sandwich or layer. The layers are bonded together by various exchangeable cations such as sodium (Na^{+1}) and calcium (Ca^{+2}). Also present between the layers is water. The thickness of water depends on the nature of the exchangeable cation at a given water-vapor pressure. These also control the ability of the clay layers to separate. Thus, with adsorbed sodium the layers tend to separate completely whereas with calcium the separation is not complete. On this basis, it can be expected that the bonding potential of a sodium montmorillonite such as is found in Wyoming and which is used in the taconite pelletizing process will be greater than that of calcium montmorillonite such as is found near Hersey.

The theoretical chemical formula for montmorillonite without considering lattice substitutions is $(OH)_4Si_8Al_4O_{20} \cdot nH_2O$ and the theoretical composition is SiO_2 66.7 percent, Al_2O_3 28.3 percent, and H_2O 5 percent (Grim, 1953). Differences in this composition are due to substitution within the lattice of aluminum and possibly phosphorus for silicon in tetrahedral coordination and/or magnesium, iron, zinc, nickel, lithium, etc., for aluminum in the octahedral sheet, and to the presence of various exchangeable cations such as sodium and calcium between the layers.

One form of montmorillonite--sodium bentonite from Wyoming--is widely used as a binder, especially in the manufacture of taconite pellets. The advent of taconite pellet manufacturing in iron ore processing, and the vast reserves of taconite in the Lake Superior region, suggest a potential use for the Hersey clay if its bonding properties can be improved. Thus, this preliminary study of certain physical and chemical properties of the Hersey clay deposit was undertaken.

Pellets made with sodium-bentonite satisfy all the requirements of the steel making process. Pellets made with equivalent amounts of other clays are too fragile and too weak to undergo handling, firing, and transportation without fracturing.

Bentonite suitable for pelletizing is found only in certain areas of Wyoming, Montana, and the Dakotas. The cost of transporting it to pelletizing plants in the Lake Superior district can be almost twice the cost of bentonite itself. This problem has led some researchers to seek a substitute. Among the substitutes tried have been clay materials containing substantial amounts of montmorillonite (Aase and Leonard, 1968). An estimated 4.2 million cubic yards of raw material containing approximately 1.4 million cubic yards of montmorillonite clay was identified by the Wisconsin Geological and Natural History Survey in a project to reevaluate the clay resources of the state as a part of its broader program to assess mineral resource potential. The deposit is in St. Croix County, near Hersey (Fig. 1), approximately 100 miles from Wisconsin's only pelletizing plant near Black River Falls. The samples used in this preliminary study to determine the potential for manufacture of pellets were obtained from a representative clay test boring on the Virgil Stang property in Section 31, T.29N., R.15W. of St. Croix County.

Differential thermal analysis of the whole samples indicate that quartz and montmorillonite are the main constituents with a trace of kaolinite. X-ray diffraction analysis (Fig. 2) indicates that montmorillonite and kaolinite are the principal constituents in the less than two micron fraction. Analyses in the files of the University of Wisconsin-Madison Department of Metallurgical and Mineral Engineering (Wiederhoeft and others, 1973) indicate traces of vermiculite and illite are also present. In preliminary tests by A. Tosh (1973) pellets made with raw clay and with 20-minute, 60-minute, and 240-minute decantates of the raw clay had about the same fired strength but very low green and dry strengths as compared with standard bentonites. In lieu of

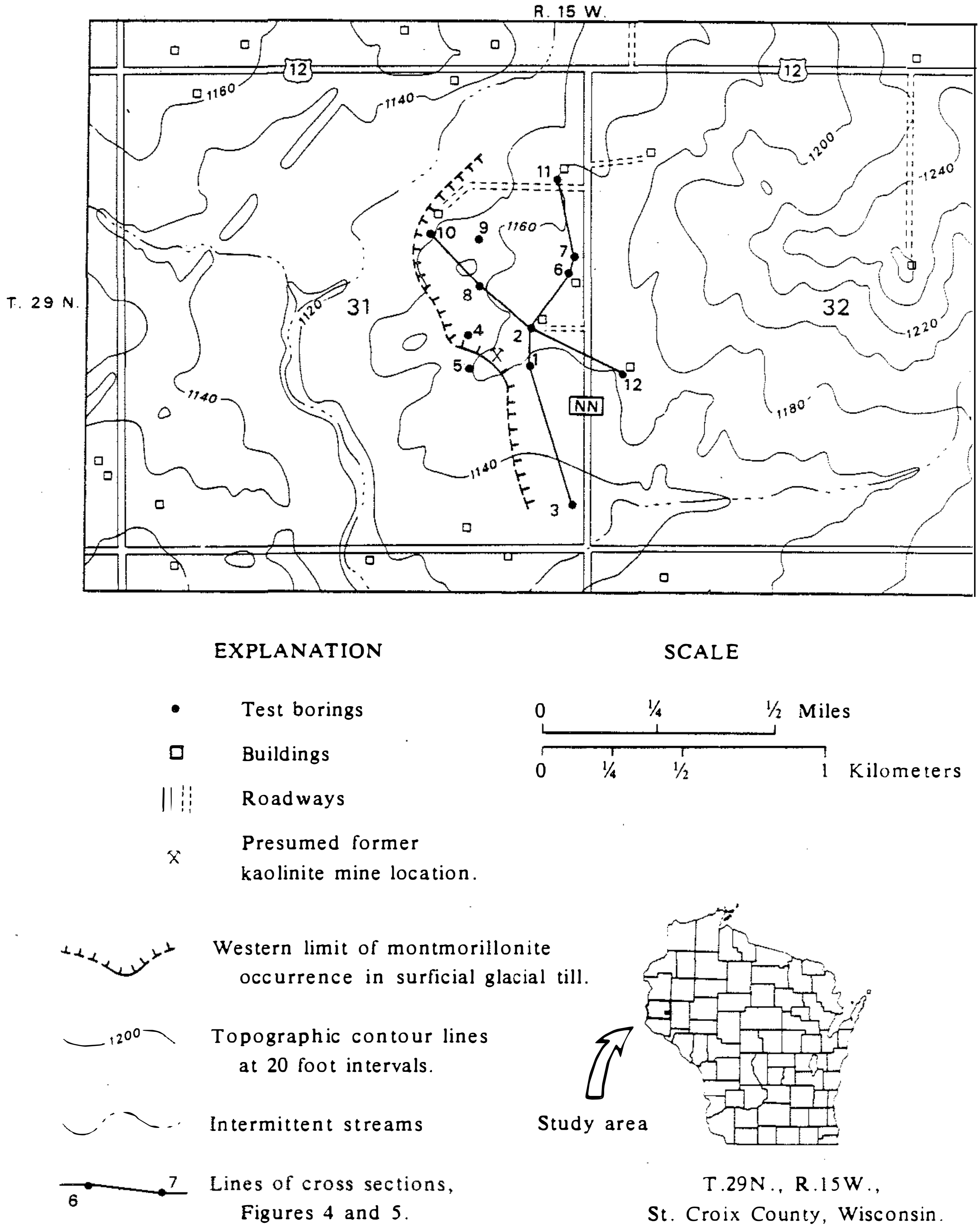

Figure 1. Locations of clay test borings in vicinity of former Superior China Clay Company mine and plant about two miles southwest of Village of Hersey in the E½ of section 31, T.29N., R.15W., St. Croix County, Wisconsin.

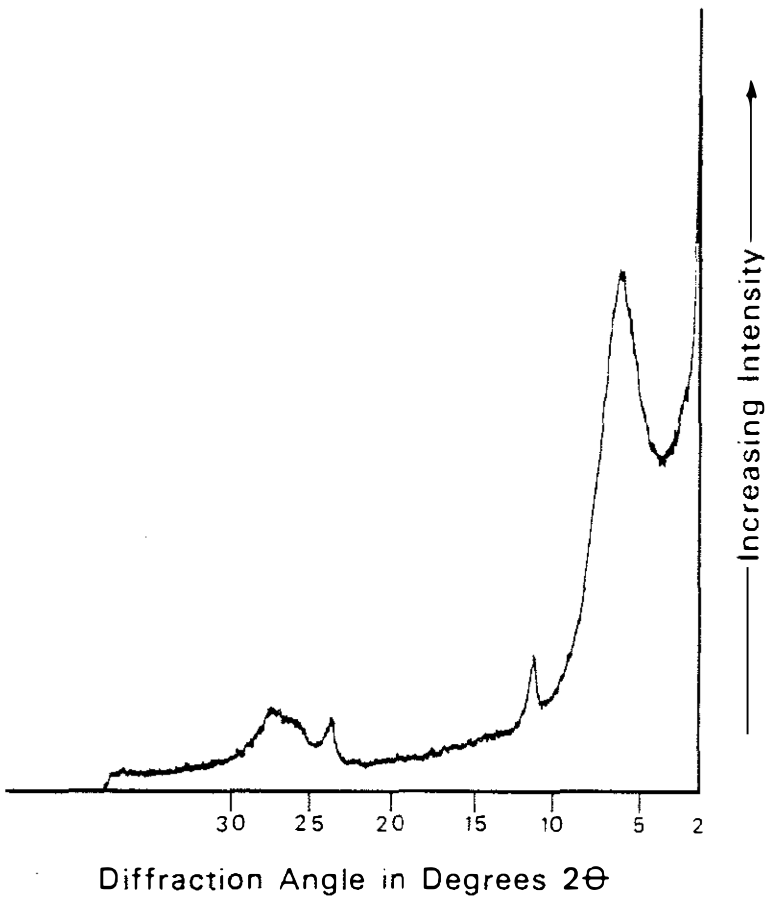

Figure 2. X-ray diffraction curve using Cu Kα source and Ni filter on less-than-2 micron clay fractions between depths of 6 feet and 7 feet from test hole number 7.

adding sodium to the wash water, as had been done by Tosh (1973), sodium was added in this experiment through the balling water in the form of a solution. Tests indicate that plasticity and ballability of the green concentrates are improved by this treatment.

Based on the work of previous researchers, certain other additives which can enhance the green strength were also investigated. Studies were made with potassium compounds, guar gum, Polyox, and synthetic resin. Duplicate experiments were performed with NaOH, NaCl, and Na_2CO_3 to verify the results obtained by other investigators.

DESCRIPTION OF THE DEPOSIT

Buckley (1901) described the occurrence of "kaolin" clay in unconsolidated deposits above bedrock near Hersey in St. Croix County. The deposits are in the E½ of section 31, T.29N., R.15W. (Fig. 1).

Mining of clay in the Hersey area was begun in 1893 by the Superior China Clay Company which operated a plant about 1.5 miles southwest of the village in the SE¼ of section 31, T.29N., R.15W. The plant was one of the largest of its kind in the United States and provided clay used in the manufacture of paper and porcelain. By 1906 it had ceased commercial operation, presumably because the deposit was exhausted.

In 1967 the Wisconsin Geological and Natural History Survey began a restudy of the clay resources of Wisconsin. The Hersey area was selected because of its history of production and because it might still contain useful and valuable clay.

According to Buckley (1901, pages 234-237) the clay in the area is "in irregular beds" and pockets in many places in the western part of Dunn County and in the eastern part of St. Croix County. "In some places it is found near the surface and in others it is covered to a depth of thirty feet or more with boulder clay" (Buckley, 1901, p. 234). The clay in some beds is white, while in others it is deeply stained with yellow iron oxide. It tends to be less stained at depth. Near the surface the clay occurs in lumps and contains more than 50 percent rounded silica sand. At depths below 8 feet it is in horizontally parallel layers varying in thickness from a few inches to two feet or more. The layers near the surface are commonly folded and broken.

Identity of the underlying bedrock in the area is not positively known due to lack of exposures and of drill records. Nearby bedrock outcrops are of Prairie du Chien Dolomite and St. Peter Sandstone, both of Ordovician age. It is presumed that bedrock in the vicinity of the clay deposit is the same.

In the study area, analyses of samples from a limited number of auger holes (Fig. 1; Appendix) indicate the presence of an upper layer rich in montmorillonite clay and a lower layer rich in kaolinite clay. The area of montmorillonite clay coincides with the occurrence of glacial till east of a NNW-trending line as shown in Figure 1. This is likely the "boulder clay" described by Buckley. The glacial till contains montmorillonite with minor kaolinite and locally illite mixed with sand of diverse mineral composition, predominately quartz, and scattered altered pebbles of igneous rocks. Beneath the till, and at the ground surface to the west, is the kaolinite-rich layer. The kaolinite is generally white and locally stained brown with iron oxide and contains primarily rounded quartz sand. Sand and clay of similar character and composition occur to the west in Minnesota in rocks of both Ordovician and Cretaceous age.

Buckley postulated that the kaolinite deposits were formed prior to glaciation and that the advance of the ice crumpled and folded the beds. The findings of this study tend to support those of Buckley to the extent that there are clay deposits of two distinct origins in the Hersey area. The kaolinite deposits are older and likely of Cretaceous age although possibly of Ordovician age. Assignment of these deposits to the Cretaceous is tenuous and is based on their close similarity to Cretaceous rocks in Minnesota (Sloan, 1964, p. 21) and their marked dissimilarity to Pleistocene deposits of the region. The montmorillonite clays are of Pleistocene age and were formed when glacial ice overrode and deformed the older kaolinite deposits, covering them with clay and other material released as the glacier melted. Similar deposits of montmorillonite-rich glacial tills occur elsewhere in west-central Wisconsin (Akers, 1961). In the Hersey area the occurrence of a body of montmorillonite-bearing deposits overlying a body of kaolinite-bearing deposits is clearly shown by x-ray diffraction analyses of samples taken from two auger test holes (Fig. 3; Appendix).

An area of approximately 160 acres in the E½ of section 31 in the vicinity of the former clay mine was selected for examination (Fig. 1). There are no surface exposures. Surficial materials in the W½ of section 32 are clay till with boulders of igneous rocks.

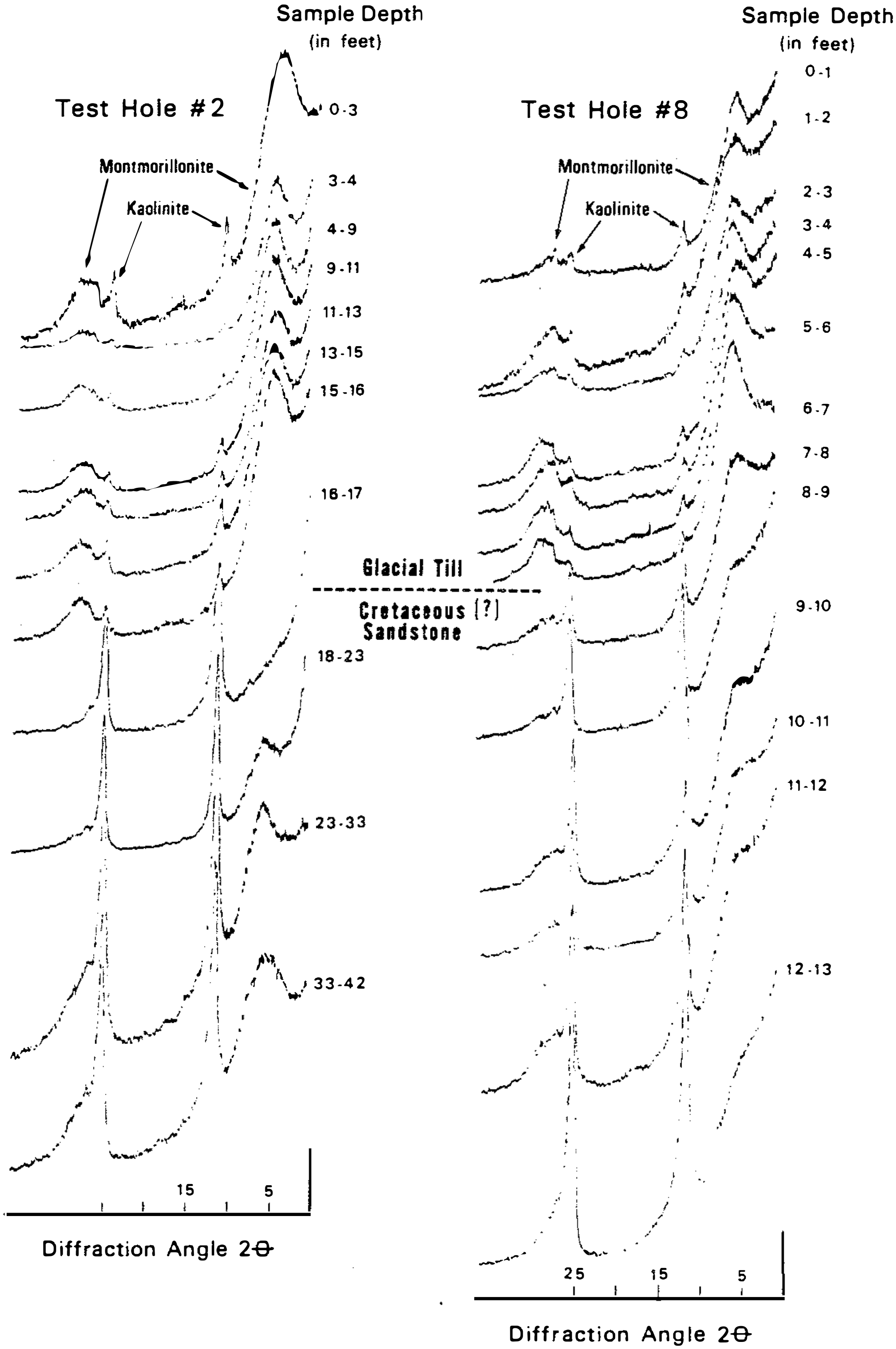

Figure 3. X-ray diffraction curves using Cu Kα source and Ni filter on the clay fraction from test hole numbers 2 and 8, section 31, T.29N., R.15W., St. Croix County, Wisconsin (refer to Fig. 1). Montmorillonite is the primary clay in the glacial till in the upper portion of each hole; kaolinite is the primary clay in what are believed to be Cretaceous deposits in the lower portion of each hole.

A total of 12 test holes were drilled to depths from 9 to 50 feet (Fig. 1). Samples were collected by successively screwing a 4-inch diameter auger from 1 to 2 feet into the clay and then withdrawing. Each lithology was sampled separately from grooves in the auger stem. Care was taken to remove all contaminating material from the outer surface.

Descriptive logs of the test holes are in the Appendix. They indicate the presence within 35 feet of the ground surface of from 9 to 20 feet of montmorillonite-rich clay in an approximately 160 acre area in the E¼ of section 31. In addition, the farm well in the NW¼, NW¼ of section 32 is reported by the owner to contain up to 80 feet of "blue clay" which, on the basis of one analysis of clay from a field in the NW¼, NW¼, NW¼ of section 32, is presumed to consist of montmorillonite.

Preliminary mechanical analyses of the auger samples indicate they contain varying proportions of clay, silt, and rounded quartz sand with scattered igneous rock pebbles in some layers. Visual estimates of the amount of clay versus silt and sand and of montmorillonite versus other clays is given in the descriptive logs in the Appendix.

The subsurface distribution of the montmorillonite-rich clay is shown on cross sections constructed from the testhole logs (Figs. 4 and 5). Distribution of the clay is related to glacial deposition. Its probable western limit is shown on the map in Figure 1; its eastern limit is undetermined.

MATERIALS AND TESTING PROCEDURES

Magnetite concentrate (taconite) from the mine and mill of the Jackson County Iron Company, a subsidiary of the Inland Steel Corporation, located approximately 10 miles east of Black River Falls was selected for testing because it is readily available and is located near the Hersey clay deposit. Sodium bentonite from Wyoming is widely used by industry for pelletizing and was used in this study to provide a basis for control and comparison.

Materials

Materials used for testing were:

1. The Wisconsin clay tested (reference number S73-6) is a combination of materials taken from auger borings from the surface down to a depth of 14 feet in Test Hole Number 7 (Figs. 1 and 3; Appendix).

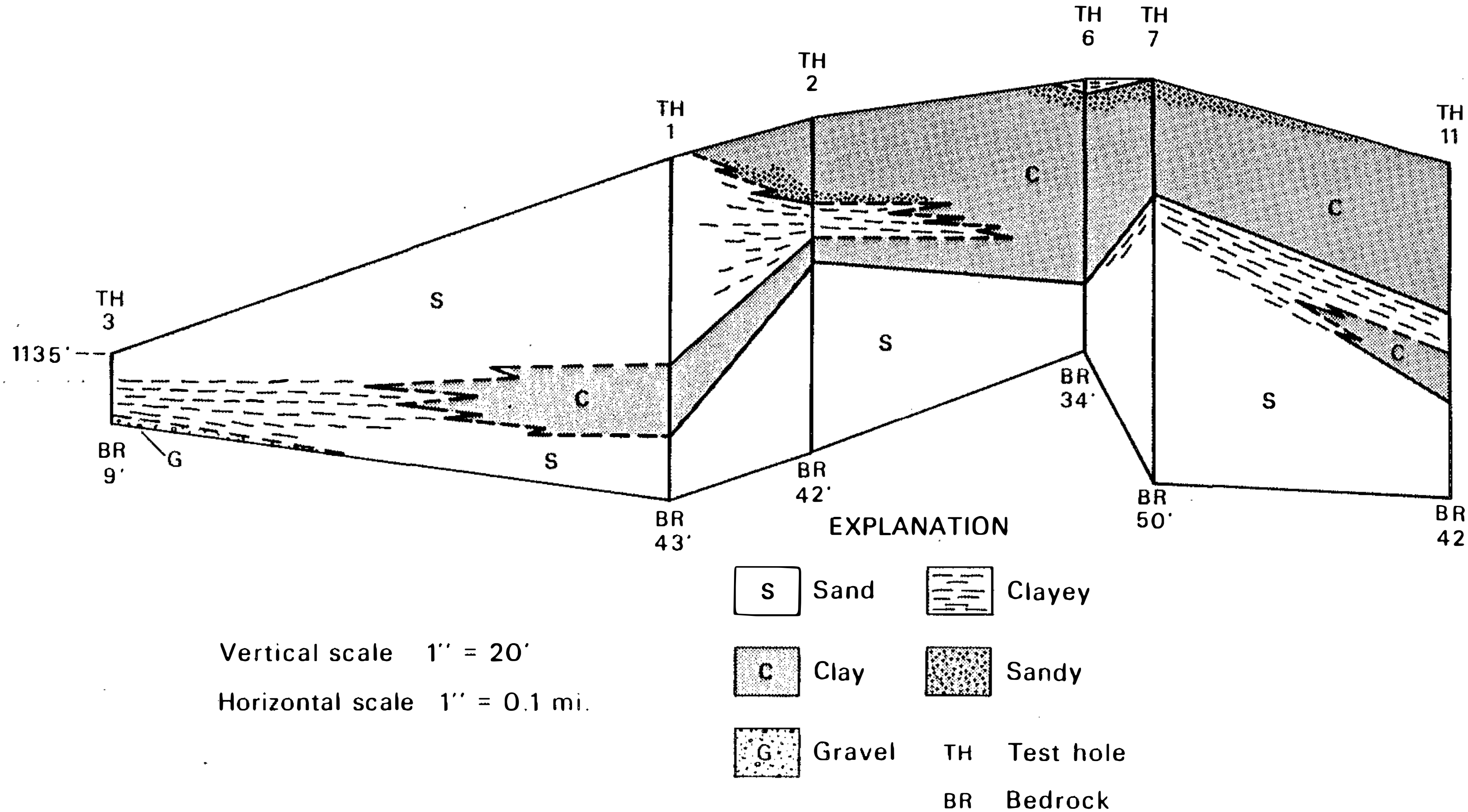

Figure 4. North-south cross section indicating subsurface distribution of clay. Refer to Figure 1 for line of section and to Appendix for detailed description.

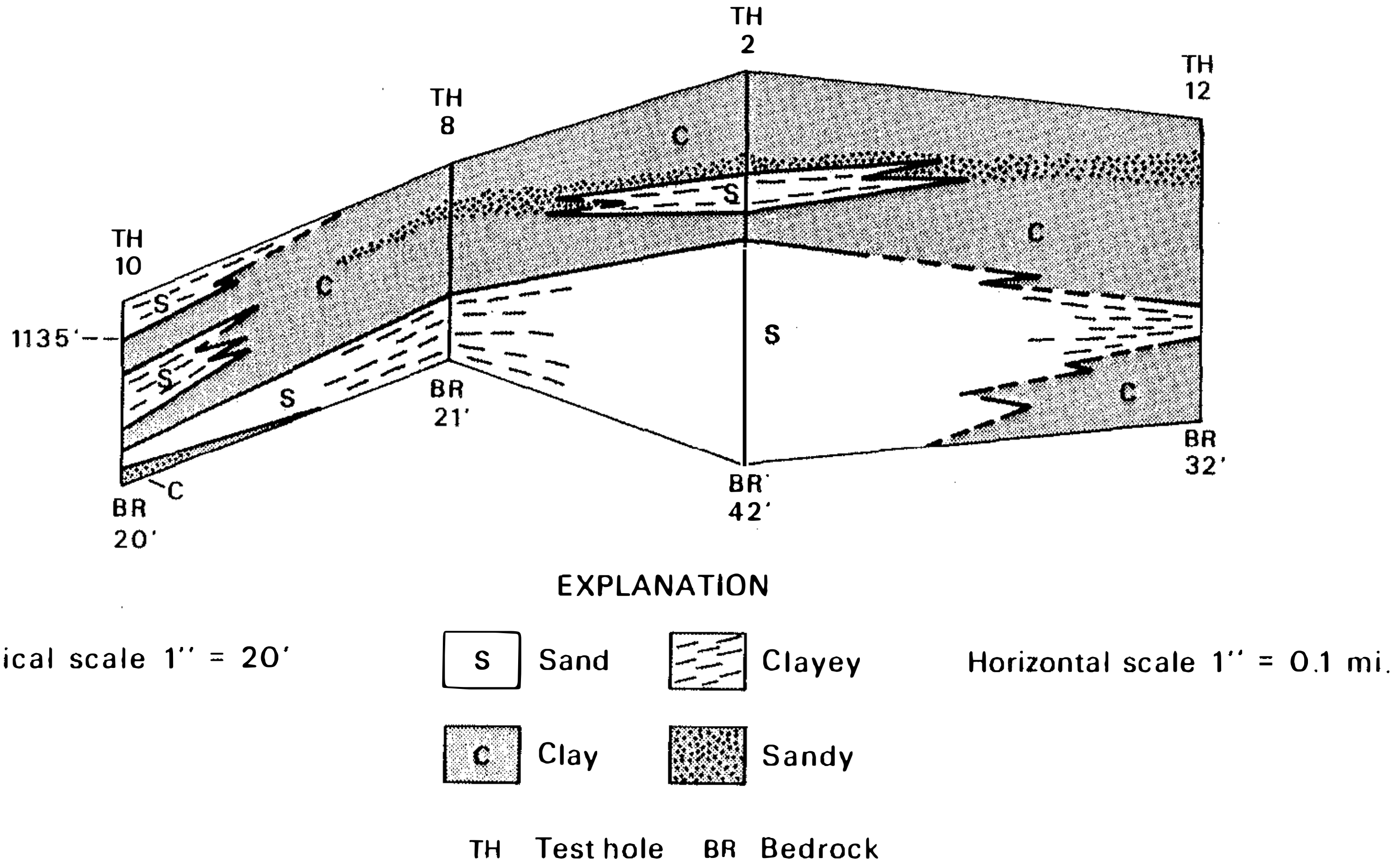

Figure 5. Northwest-southeast cross section indicating subsurface distribution of clay. Refer to Figure 1 for line of section and to Appendix for detailed description.

2. Magnetite concentrate (more than 80% passing a 325 mesh sieve) provided by the Jackson County Iron Company.

3. Standard bentonites, IMC Foundry Grade Bentonite (S73-7) and IMC High Viscosity Bentonite (S73-8), provided by International Minerals and Chemicals Company.

4. Commercial taconite pellets provided by Jackson County Iron Company.

5. Potassium and sodium compounds (K_2CO_3 and Na_2CO_3).

6. Guar gum, essentially a natural vegetable colloid chemically classed as galactomannan, a complex carbohydrate polymer of galactose and mannose. It is typically applied commercially as a non-ionic hydroxyalkyl derivative, e.g., hydroxyethyl guar or hydropropyl guar in which form it is less of a floculant than in the natural state.

7. Hydroxyethyl cellulose, a product of the Union Carbide Corporation, is a modification of pure cellulose by addition of polymeric ethylene oxide side chains. The designations indicate normal dissolving (WP) or rapid dispersing (QP) material. It is available in a wide range of molecular weights with attendant variations in properties.

8. Polyox, a water soluble, non-ionic, homopolymer of polyethylene oxide was supplied by Union Carbide Corporation. It is available in a wide range of molecular weights with attendant variations in properties.

Preparation of Clay Samples

Two untreated clay samples, from depths 0' to 3' and 3' to 14' in Test Hole Number 7 (Appendix), were dried overnight at 80° F (27° C) to remove the absorbed moisture. After drying they were crushed separately in a laboratory jaw crusher and mixed in equal proportions to obtain a composite clay sample number S73-6.

Fifty grams of S73-6 were mixed with 300 ml of distilled water in a Waring blender for 30 minutes. The contents were placed in a 1000 ml graduated cylinder and stirred vigorously by blowing air through a tube placed in the cylinder and subsequently allowed to settle for 20 minutes. This amount of time was found to be satisfactory (Wiederhoeft and others, 1972) for removing 80% of the quartz and was used as a standard for most of the experiments in this study (Table 1, Quartz Distribution).

Table 1. Variation of quartz content in upper 28 cm of suspension using different settling times (Wiederhoeft and others, 1972)[1].

Settling Time (min)	Quartz Distribution(%)[2]	
	Decantate	Sediment
3	33.26	66.74
10	23.44	76.56
20	18.83	81.17
60	8.49	91.51
240	2.55	97.45

[1] Raw untreated clay sample contains 64.12% quartz.

[2] Estimates by examination under a petrographic microscope using oil immersion technique. See also Table 2.

After 20 minutes of settling, the upper 28 cm of turbid clay-water suspension was carefully siphoned off, filtered in a filter press, dried, ground in a ball mill, and sieved through a 200 mesh sieve. Only the -200 mesh fraction was used for testing.

Addition of Additives

Tests were made mixing the additives with the decantate and with the magnetite-clay mixture. An additive of known concentration of sodium or potassium was used as a wash and was mixed with the decantate obtained after 20 minutes of settling. The mixture was then filtered, dried, and tested as a binder. Also, similar additive solutions were combined with magnetite-clay mixtures during the mixing of the magnetite concentrate with the clay just prior to pelletizing.

Pellet Tests

A 500 gram sample of magnetite, the required amount of clay (both 1% or 5 grams and 3% or 15 grams), and an additive (if any) were mixed thoroughly in a Waring blender. Distilled water was then added to adjust the total moisture content to about 9.0%. The wet mixture was further mixed for 5 to 10 minutes before pelletizing.

Pellets were made from pastes prepared in a laboratory disc-pelletizer constructed with a pneumatic drive and a brass pan edged with a small rim (Fig. 6). This device could be operated at variable speeds and at an angle of 25 degrees to the horizontal.

Green drop tests from a height of 18 inches were carried out according to the procedure described by Stone (1967). The test is designed to assess the ability of green pellets to withstand the drop encountered at conveyor belt transfer points in transit from the balling plant unit to the firing unit. In this test, a green pellet is dropped from a height of 18 inches onto a half-inch thick steel plate, and the number of drops the pellet can withstand before breaking is noted. The number of green drops recorded is the average of drops required to break 20 pellets. A drop number of about 8 is considered satisfactory (Marothy, 1967). Too low a value indicates a brittle ball and too high a value would give a poor bed permeability. It appears that good green strength is also associated with good ballability.

For dry compressive tests, the green pellets were dried in an oven at 230° F (110° C) overnight and compression tests were carried out in an Instron machine using the "C" load cell (capacity 200 pounds). Cross-head speed was maintained at 0.1 inches per minute. The dry compressive strength should be about 10 pounds (Marothy, 1967).

For fired compression tests, the dried pellets were first preheated from room temperature to 1800° F (982° C) in a muffle furnace in one and one-half hours, after which they were transferred to a Glo-bar furnace at 2300° F (1260° C) and held at this temperature for 30 minutes. They were then removed from the furnace and air cooled. Compression tests on these pellets were run in an Instron machine using the "F" load cell (capacity 10×10^3 pounds). The cross-head speed was maintained at 0.1 inches per minute. A fired compressive strength of 500 pounds or more is considered good (Marothy, 1967).

Results of Tests

The naturally occurring Wisconsin clay from near Hersey consists principally of quartz (65%) and high calcium montmorillonite with traces of vermiculite, illite, and kaolinite. Certain specific determinations are summarized below:

1. X-ray diffraction analysis. X-ray diffraction analysis of the Wisconsin clay by International Minerals and Chemical Corporation revealed quartz as the major constituent and montmorillonite as a medium to minor constituent (written communication, Schumacher to Hanson, December 19, 1972). Analyses done by M.E. Ostrom at the Wisconsin Geological and Natural History Survey indicate that the less than two micron fraction consists of montmorillonite with trace amounts of kaolinite.

2. Flame photometer analysis. Flame photometer analysis of raw clay was conducted by John Philosophos of Allis Chalmers. Results indicate:

CaO	1.70 percent
Na_2O	0.55 percent
K_2O	1.37 percent

3. Particle size analysis. Particle size distribution was determined using the Andreason Pipette method and the hydrometer method. Tests were conducted (Wiederhoeft and others, 1972) to determine the particle size distribution by plotting cumulative percent versus the particle size. These results are shown in Table 1 and Figure 7.

4. Chemical analysis of the magnetite concentrate. The magnetite concentrate (taconite) provided by the Jackson County Iron Company has the following chemical analysis for selected components (Amer. Iron Ore Assoc., 1973):

Fe*	P	SiO_2	Mn	Al	CaO	Mg	Moisture
64.84	0.015	5.75	0.06	0.06	0.34	0.23	0.68

* The iron occurs principally as magnetite (Fe_3O_4 = 89.5%) calculated from the analysis.

5. Effect of settling on quartz removal. The effect of settling on the variation in quartz content and distribution was studied by Wiederhoeft and others (1972). Their observations are summarized in Tables 1 and 2. The results show the decrease in quartz content which can be obtained with increased settling time.

6. Effect of quartz content on pellet strength. The effect of the quartz content of Wisconsin clay on green, dry, and fired pellets was studied by Tosh (1973). His results are summarized in Table 3. These tests suggest that any reduction in quartz content below 27.5% (20 minutes settling time) has very little effect on pellet strength (the standard bentonite contains about 5% quartz).

7. Wisconsin clay versus standard bentonites. The results of the pelletizing experiments using the standard bentonites and Wisconsin clay are summarized in Table 4. Foundry grade bentonite is more effective than the high viscosity bentonite or the bentonite used at the Black River Falls plant. All three of these bentonites are western. The Wisconsin clay showed greater fired compression strength than all others tested, however, it tested significantly lower in all other categories.

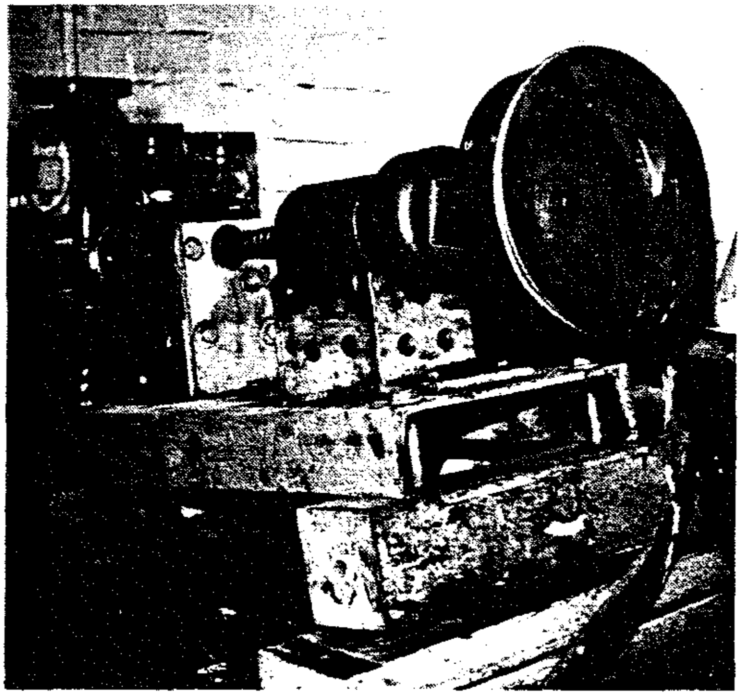

Figure 6. Disc-pelletizer

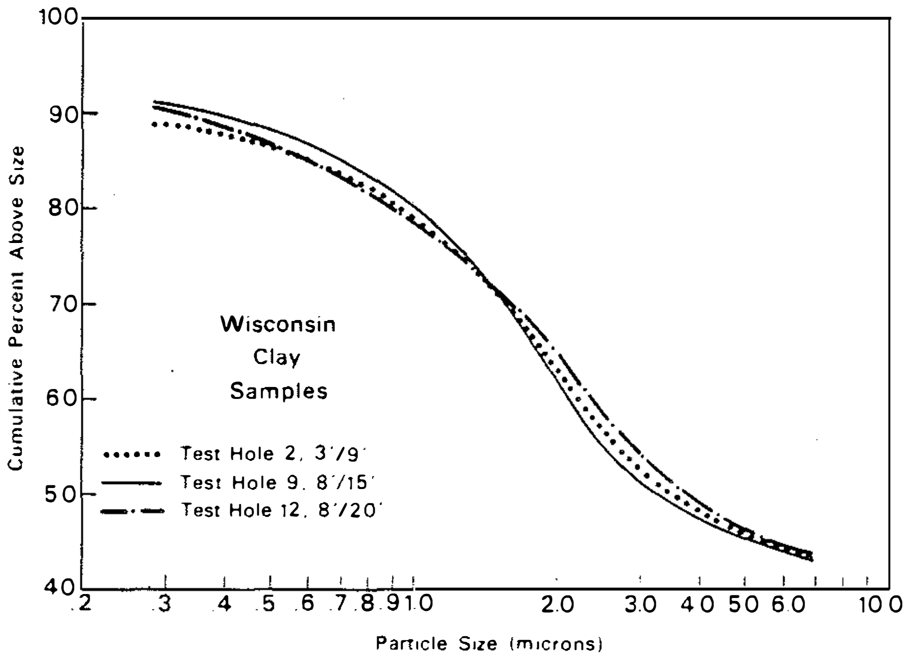

Figure 7. Particle size distribution of raw clay samples from test hole numbers 2, 9, and 12.

Table 2. Estimation of total quartz content[1] and distribution from petrographic microscope analysis data (Wiederhoeft and others, 1972).

		Settling Time (min.)				
		3	10	20	60	240
Quartz Content and Distribution	Quartz (%) in Sediment (A)	98.0	93.5	92.0	92.0	87.5
	Weight (%) of Sediment (B)	45.02	53.18	56.32	63.74	68.63
	Quartz (%) subtotal from Sediment (A x B)(C)	44.12	49.72	51.81	58.64	60.05
	Quartz (%) in Decantate (D)	40.0	32.5	27.5	15.0	5.0
	Weight (%) of Decantate (E)	54.98	46.82	43.68	36.26	31.37
	Quartz (%) subtotal (F) from Decantate (D X E)	21.99	15.22	12.02	5.44	1.57
	Total Quartz Content (%), (C + F), (G)	66.11	64.94	63.88	64.08	61.62
	Quartz Distribution (%): In Sample (set G=100)	100.00	100.00	100.00	100.00	100.00
	In Sediment (C/G x 100)	66.74	76.56	81.17	91.51	97.45
	In Decantate (F/G x 100)	33.26	23.44	18.83	8.49	2.55

[1] Average Quartz Content -- 64.12%

Table 3. Results of strength tests on green, dry, and fired pellets (Tosh, 1973).

Clay			18-Inch Green Drops[1]		Compressive Strength (pounds)	
Type	Symbol	%	Number Drops to Break	% Water in Pellets	Dry	Fired
IMC Foundry Grade bentonite	S73-7	1	18	10.9	--	860
		3	55	11.1	34.4	998
IMC High Viscosity bentonite	S73-8	1	27	10.5	12.2	778
		3	--	--	33.4	919
Composite Sample Stang #2 0'-14'	S73-6	1	4.8	9.3	2.1	668
		3	7.1	9.6	5.1	798
20 Min Decantate of S73-6	S73-6A	1	6.0	9.6	4.6	957
		3	9.8	9.6	12.8	847
60 Min Decantate of S73-6	S73-6B	1	5.9	8.9	4.4	1002
		3	7.9	9.5	11.9	1060
240 Min Decantate of S73-6	S73-6C	1	6.7	9.5	3.6	952
		3	14	9.7	18.8	1030
Black River Falls	Nt[3]		Nt[3]	Nt[3]	Nt[3]	650

[1] Average of 10 pellets

[2] Average of 5 pellets

[3] Not tested (Nt)

Table 4. Comparison of the results of strength tests on pellets made using Wisconsin clay and standard bentonites.[1]

			18-Inch Green Drops[1] Number Drops to		Compressive Strength (pounds)	
Magnetite	Type of Clay	% Clay	Crack	Break	Dry	Fired
Black River	Foundry grade bentonite	1%	5	23	23	520
	Bentonite used at the Black River Falls Plant	1%	9	17	16	611
	High viscosity bentonite	1%	7	15	14	496
	Black River Falls Commercial Pellets	0.9% approximately	Nt[2]	Nt[2]	7	516
	Wisconsin clay (with 20 min. settling)	1%	1	2	5	665
		3%	1	2	10	576

[1] Results are average of 15 pellets.

[2] Not tested (Nt).

The 18-inch green drop of the pellets with 1% western bentonite is about 15 to 23 drops and that with the Wisconsin clay (1% and 3%) is 2 drops. The dry strength with 1% western bentonite is about 14 to 23 pounds as against that with 1% Wisconsin clay of 5 pounds and 3% Wisconsin clay of about 11 pounds.

8. The effect of additives on pellet strength. Experiments on the effect of additives on pellet strength were carried out during the earlier part of the investigation. The decantate obtained after 20 minutes settling was washed with various sodium compound solutions in order to replace the calcium ions with sodium ions. The clay was subsequently dried and used as a binder for pelletizing.

Montmorillonite is composed of a basic cell unit made up of two silica tetrahedral sheets which enclose a central alumina octahedral sheet. The tetrahedral and octahedral sheets combine to form a silicate sandwich or layer. Exchangeable cations such as sodium and calcium plus water are located between the layers. Sodium ions occupying the interlayer sites of the montmorillonite lattice increase the capacity of the clay to absorb moisture. This enhances the ease with which the clay particles can be deformed or elongated. The particles thus elongated form a network of the binder throughout the magnetite mass. On drying the pellets, the excess moisture evaporates, but the network of clay minerals holds the magnetite particles firmly. Calcium ions on the other hand reduce the capacity of montmorillonite to absorb moisture and consequently, the ease with which the clay particles can be deformed. Hence their presence lowers the dry strength.

The results of pellet strength tests using various additives are shown in Table 5. Solutions of NaCl, NaOH, and Na_2CO_3 were used and the sodium concentration of the solutions with 20% NaCl, 18.2% Na_2CO_3 and 13.73% NaOH was the same.

The results in Tables 4 and 5 indicate that the addition of sodium or potassium improves green strength, but not to acceptable levels. Neither does washing the Wisconsin clay with NaOH and NaCl significantly improve the dry strength. However, dry strength is improved with the addition of 18.2% Na_2CO_3 and 3% Wisconsin clay (Table 5). This is reflected in the amount of sodium and potassium absorbed by the 20-minute settling sample of Wisconsin clay from the different washing agents. This is shown by the following comparisons:

Table 5. The effect on green, dry, and fired strengths of pellets made with Wisconsin clay washed with various additives and mixed with Black River Falls magnetite.

Na or K[1] Compound	% of Na or K Compound	% Clay in Pellets	18-Inch green Drops[2] Number Drops to Crack	18-Inch green Drops[2] Number Drops to Break	PELLET STRENGTH Compressive Strength (pounds) Dry	PELLET STRENGTH Compressive Strength (pounds) Fired
NaCl	6%	1%	2	5	4	597
		3%	2	9	9	535
NaCl	20%	1%	2	18	5	525
		3%	2	21	8	615
Na_2CO_3	18.2%	1%	4	27	7	476
		3%	3	33	15	535
NaOH	13.73%	1%	2	12	5	542
		3%	4	19	8	639
KCL	20%	1%	3	15	4	497
		3%	3	18	7	599
K_2CO_3	18.2%	1%	2	29	8	521
		3%	5	31	17	516
KOH	13.73%	1%	1	11	7	479
		3%	3	16	12	623

1) Compounds added to the decantate

2) Results are average of 15 pellets

Table 6. The effect on green, dry, and fired strengths of pellets made when additives were combined with Black River Falls magnetite and Wisconsin clay through water used in balling process.

Na or K[1] Compound	Pounds of K or Na Compound Per Ton of Magnetite	% Clay in Pellets	18-Inch Green Drops[2] Number Crack	Drops to Break	Compressive Strength (pounds) Dry	Fired
NaCl	1.3	1%	1	23	5	586
	2.6		1	21	5	638
	3.9		1	20	4	510
	5.2		2	29	5	575
NaCl	1.3	3%	2	28	7	592
	2.6		2	27	8	628
	3.9		2	31	9	615
	5.2		1	28	6	558
Na_2CO_3	1.04	1%	1	28	9	610
	2.08		3	28	8	452
	3.12		3	34	8	587
	4.16		1	31	7	612
Na_2CO_3	1.04	3%	1	38	17	515
	2.08		1	37	18	496
	3.12		2	34	17	610
	4.16		3	39	17	596
KCl	1.3	1%	1	21	5	476
	2.6		1	20	5	515
	3.9		1	18	6	644
	5.2		1	24	7	415
KCl	1.3	3%	1	25	6	586
	2.6		3	25	7	515
	3.9		3	22	5	476
	5.2		4	27	7	610

Table 6. (cont'd)

Na or K[1] Compound	Pounds of K or Na Compound Per Ton of Magnetite	% Clay in Pellets	18-Inch Green Drops[2] Number Crack	Drops to Break	Compressive Strength (pounds) Dry	Fired
K_2CO_3	1.04	1%	2	25	8	525
	2.08		2	31	9	616
	3.12		4	33	9	610
	4.16		2	36	8	585
K_2CO_3	1.06	3%	1	31	17	596
	2.08		1	33	19	475
	3.12		4	37	16	575
	4.16		5	35	18	616

[1] Compounds added to balling water.

[2] Results are average of 15 pellets.

Chemical Analyses of Washed/Dried Clay (percent)

Washing Agents	Na_2O	CaO	K_2O	Na_2O/CaO Weight Ratio
20% NaCl	1.15	1.72	1.88	0.67
18.2% Na_2CO_3	2.00	2.41	1.87	0.83
water	0.42	2.41	1.87	0.174

It has been noted that the Na_2O-to-CaO ratio of a clay is an important factor in deciding the dry strength of the pellets. The higher the Na_2O-to-CaO ratio, the greater is the possibility of getting a better dry strength.

Another set of experiments was run with various potassium compounds (Table 5). Solutions of KCl, K_2CO_3 and KOH were used for washing the clay and the potassium ion concentration of the solutions (20% KCl; 18.2% K_2CO_3; and 13.75% KOH) was the same. It was observed that with the exception of K_2CO_3, the dry strength of the Wisconsin clay washed with KCl and KOH does not improve. Results, however, also indicate that K_2CO_3 helps to significantly improve the green strength.

The strength of green, dry, and fired pellets of magnetite and Wisconsin clay to which additives were added during the balling process was also tested. Additives tended to increase the green strength of the magnetite-clay mixture. A measured quantity of potassium and sodium compounds was added, respectively, through balling water during mixing of clay and magnetite. The additives tried were NaCl, Na_2CO_3, KCl, and K_2CO_3 (Table 6). The sodium and potassium salt addition improved the plasticity and ballability of the green concentrate.

Green strength is an extremely important property for pelletizing and unless the green bonding properties of the Wisconsin clay are improved it cannot be successfully used as a binder in the pelletizing industry. Experiments with guar gum and synthetic resin are of significant importance in this respect. The results are tabulated in Tables 7 and 8, respectively.

A combination of 0.5% guar gum and 0.5% Wisconsin clay gives extremely good strength properties. By optimizing the proportion of these two binders the Wisconsin clay can be used without any sodium compound as an additive.

From Table 8 it can be inferred that 2% of any synthetic resin without the addition of Wisconsin clay gives good strength properties. A combination of 1% resin (any kind) and 0.5% Wisconsin clay also yields very good strength properties. The fired strength, however, seems to be relatively independent of any additive added.

Table 7. Effect of guar-gum on pellet strength.

% Guar Gum	% Clay	18-Inch Green Drops[1] Number Drops to Crack	Break	Compressive Strength (pounds) Dry	Fired
0.5	None	More than 35		49	520
0.4	None	More than 35		32	525
0.3	None	More than 35		22	511
0.2	None	More than 35		11	465
0.1	None	More than 35		5	485
0.5	0.5% Wisconsin Clay (20 Min. Set.)	More than 35		31	686
0.0	0.5% Wisconsin Clay (20 Min. Set.)	2	5	7	790

[1] Results are average of 10 pellets.

Table 8. Effect of organic additives on pellet strength.

Type of Organic Additive (%)	% Clay and Type	18-Inch Green Drops[1] Number Drops to Crack	Break	Compressive Strength (pounds) Dry	Fired
Hydroxyethyl cellulose QP-52000 W-193-X (high)					
0.25	None	1	4	35	465
0.50	None	1	6	21	438
0.75	None	2	6	21	513
1.00	None	9	25	25	496
1.00	0.5 (20 Min. Settled)	More than 35		25	496
2.00	None	More than 35		52	586
Hydroxyethyl cellulose WP-02 W-1602-R (high)					
0.25	None	2	7	24	431
0.50	None	2	6	20	513
0.75	None	2	9	21	565
1.00	None	2	6	18	478
1.00	0.5 (20 Min. Settled)	More than 35		31	528
2.00	None	18	35+	46	492
Polyox (Synthetic resin) WSRN-80 1001-C					
0.50	None	4	6	28	415
0.75	None	2	5	17	551
1.00	None	2	7	24	418
1.00	0.5 (20 Min. Settled)	More than 35		33	467
2.00	None	More than 35		40	422

[1] Results are average of 10 pellets.

CONCLUSIONS

The results of pellet tests are summarized in Tables 3 through 8. The results indicate that:

1) The raw montmorillonite-bearing Wisconsin clay from near Hersey, Wisconsin is unsuitable in its natural state for pellet bonding due to the high calcium content of the clay and to the presence of abundant very fine quartz particles.

2) Removal of some of the quartz from the raw clay by settling improves the green and dry strength of the pellets to a small extent. However, these strengths are below acceptable levels.

3) Addition of a sodium or potassium compound to the separated clay by mixing improves pellet green strength.

4) Addition of NaCl, KCl, NaOH, or KOH to the separated clay does not appreciably improve pellet dry strength.

5) Addition of K_2CO_3 and Na_2CO_3 effectively improves the dry strength of the separated clay to acceptable levels.

6) Neither clay content nor additive content of the pellets had an effect on fired strength within the range investigated.

7) Green strength of the pellets made with the separated clay can attain acceptable levels by the addition of a small quantity (0.5%) of guar gum and also by using a small amount of hydroxyethyl cellulose (a synthetic resin).

ACKNOWLEDGEMENTS

This investigation was funded in part by financial assistance from the University-Industry Research program of the Graduate School, University of Wisconsin. This and related studies of the St. Croix County clay deposits are products of a broad program of the Wisconsin Geological and Natural History Survey begun in 1966 to assess Wisconsin clay resources and their potential uses.

Thanks are due Dr. John Philosophos of Allis-Chalmers, Mr. L. Olson, General Superintendent and Mr. G.A. Vase, Senior Mining Engineer, Jackson County Iron Company, and to Mr. J.A. Schumacher of International Minerals and Chemical Corporation for their suggestions, interest, and for providing samples of clay and magnetite.

Appreciation is also extended to Messrs. Gary Wiederhoeft, Andrew Slagle, A. Gholkar, A. Tosh, Dr. A. Hayatdavoudi and Daniel Marchant for their investigations and much of the data. Also, to the Society of Mining Engineers of the American Institute of Mining, Metallurgical and Petroleum Engineers for granting permission to publish materials originally contained in a preprint issued by the Society (Clum, and others, 1976).

Special appreciation is to property owners who permitted access for drilling and sampling, namely Messrs. Eitland, Ellefson, Stang, and Thompson and their families.

REFERENCES

Aase, James H., and Leonard, George E., 1968, Field investigation and testing of a Minnesota clay resource for iron ore pellet bonding: U. S. Bureau of Mines Report of Investigations No. 7206, 17 p.

Akers, Ronald H., 1961, Clay Minerals of glacial deposits of west-central Wisconsin: Unpublished Master's thesis, University of Wisconsin-Madison, 69 p.

American Iron Ore Association, 1973, Iron Ore: Cleveland, Ohio, p. 72.

Buckley, Ernest R., 1901, Clays and clay industries of Wisconsin: Wisconsin Geological and Natural History Survey Bulletin No. 7, p. 234-237.

Clum, James A., Heins, Robert W., and Tiemann, Theodore D., 1976, Substitutes for western bentonite in magnetic taconite pellets: Society of Mining Engineers of American Institute of Mining, Metallurgical, and Petroleum Engineers Preprint No. 76-B-11, p. 29.

Gholkar, A.G., 1974, An investigation of a bentonite clay as a binder for the production of blast furnace pellets from magnetite concentrates: Unpublished Master's thesis, University of Wisconsin-Madison, 59 p.

Grim, Ralph E., 1953, Clay Mineralogy: McGraw-Hill Book Company, Inc., New York, 384 p.

Marothy, G. Majar, 1968, Pellet binders, bentonites versus substitutes: 29th Annual Mining Symposium, Minnesota Section, American Institute of Mining, Metallurgical, and Petroleum Engineers, Duluth, Minnesota, p. 153-157.

Sloan, R.E., 1964, The Cretaceous System in Minnesota: Minnesota Geological Survey Report of Investigations 5, 64 p.

Stone, R.L., 1967, Relation between zeta potential of bentonite and the strength of unfired pellets: Transactions of the Society of Mining Engineers of the American Institute of Mining, Metallurgical, and Petroleum Engineers, vol. 238, no. 9, p. 284-292.

Tosh, A., 1973, Analytical records in files of Department of Metallurgical and Minerals Engineering, University of Wisconsin-Madison.

Wiederhoeft, Gary, Slagle, Andrew, and Marchant, Daniel, 1972. Analytical records in files of Department of Metallurgical and Minerals Engineering, University of Wisconsin-Madison.

APPENDIX

Logs of augered test holes drilled to determine location, character, and extent of clay deposits in Sections 31 and 32, T.29N., R.15W., St. Croix County, Wisconsin.

Test Hole #1

Located 700 feet west and 800 feet south of NE corner of the SE¼, Section 31, T.29N., R.15W., St. Croix County.

0 - 26'	Quartz sand, light yellow brown, medium- and fine-grained. Trace of clay, primarily kaolinite with minor montmorillonite.
26 - 35'	Clay, dark brown gray to light yellow brown; less than 5 percent quartz sand. Clay primarily montmorillonite with minor to no kaolinite.
35 - 43'	Quartz sand, yellow brown, medium- and fine-grained. Trace of clay consisting of about equal amounts of kaolinite and montmorillonite.
--------	Refusal

Test Hole #2

Located 700 feet west and 350 feet south of NE corner of the SE¼, Section 31, T.29N., R.15W., St. Croix County.

0 - 9'	Clay, brown mottled and streaked yellow brown, very plastic; 5-10 percent quartz sand; few rock fragments and little white chert; plant fragments 3 to 4 feet. Clay is montmorillonite with trace of kaolinite.
9 - 11'	Clay, brown gray and yellow brown; 30 percent quartz sand. Clay is montmorillonite with trace of kaolinite.
11 - 15'	Quartz sand, light yellow brown, medium- and fine-grained; 10 percent clay; scattered fragments of white chert to ½ inch. Clay is montmorillonite with trace of kaolinite.
15 - 16'	Clay, gray mottled yellow brown, plastic, waxy. Clay is montmorillonite with trace of kaolinite.
16 - 18'	Clay, gray brown; sandy with chert fragments to ½ inch. One fragment oolitic chert indicative of Ordovician Prairie du Chien Group dolomites. Clay is kaolinite with trace to no montmorillonite.
18' - 42'	Quartz sand, light brown gray, medium- and fine-grained; minor white clay; few fragments of oolitic white chert 38-42'. Proportion of kaolinite to montmorillonite estimated to be 7:3.
--------	Refusal

Test Hole #3

Located 600 feet north and 150 feet west of SE corner of Section 31, T.29N., R.15W., St. Croix County.

0 - 3'	Soil and sand. Sand has variable mineral composition and is medium- and coarse-grained; 6 inches of brown clay at base. Likely glacial deposit.
3 - 8'	Sand, brown, fine- and medium-grained, mostly quartz, clayey, few pebbles. Clay about equal proportions of kaolinite and montmorillonite.
8 - 9'	Gravel or weathered bedrock, dolomitic.
--------	Refusal

Test Hole #4

Located 600 feet south and 1400 feet west of NE corner of the SE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 1'	Soil
1 - 6'	Quartz sand, yellow brown, fine- to medium-grained. Little clay and few limonite pebbles from 3 feet to 6 feet. Clay about equal proportions of kaolinite and montmorillonite; little illite 4 feet to 6 feet.
6 - 8'	Clay, predominantly yellow brown with some light green to white. Yellow brown is slightly streaked with light green and contains silt and little very fine sand. Pale green clay only slightly silty with no sand. Both contain pebbles of limonite and sandy limonite. Clay is montmorillonite and illite in about equal proportions with trace of kaolinite.
8 - 11'	Quartz sand, brown and red brown, medium- and fine-grained, slightly clayey. Clay is kaolinite and montmorillonite in approximate proportion of 7:3.
11 - 12'	Gravel and sand, slightly clayey, and sand as above. Pebbles of sandstone up to 1 inch. Clay is kaolinite and montmorillonite in about equal amounts.
--------	Refusal

Test Hole #5

Located 800 feet south and 1400 feet west of NE corner of the NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 2'	Clay, white, silty. Clay is kaolinite with only slight trace of illite.
2 - 3'	Clay and sand, dark gray brown. Clay consists of approximately equal proportions of kaolinite, montmorillonite, and illite.
3 - 15'	Quartz sand, light gray, fine- and medium-grained. Little clay consisting of kaolinite and montmorillonite in approximate proportion of 6:4.
15 - 18'	Clay, red brown with partings of pale green clay, silty; little quartz sand; few pebbles of limonite in lower foot. Trace white clay. Clay consist of about equal proportions of kaolinite and montmorillonite.
18 - 24'	Quartz sand, red brown, medium- and fine-grained, abundant sandstone pebbles in lower 2 feet; very clayey in lower 1 foot. Clay primarily montmorillonite.
--------	Refusal

Test Hole #6

Located 200 feet west and 280 feet north of SE corner of the NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 2'	Clay and sand, yellow brown, plastic. Clay predominantly montmorillonite with little kaolinite.
2 - 5'	Clay, yellow brown, plastic with little quartz sand. Clay predominantly montmorillonite with little kaolinite.
5 - 26'	Clay, yellow brown and gray, plastic with trace to little quartz sand. Plant fragments 17 feet to 18 feet. Clay more than 90 percent montmorillonite.
26 - 34'	Quartz sand, yellowish gray, medium- and fine-grained. Little clay consisting of more than 90 percent montmorillonite.
--------	Refusal

Test Hole #7

Located 150 feet west and 400 feet north of SE corner of the NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 3'	Clay, dark brown gray, slightly sandy with pebbles. Clay predominantly montmorillonite with little kaolinite.
3 - 14'	Clay, light yellow brown and gray grading downward to dark gray to light yellow brown, plastic; trace of sand. Clay predominantly montmorillonite with little kaolinite.
14 - 18'	Quartz sand, light yellow brown, medium- to fine-grained; little clay. Clay predominantly montmorillonite with trace kaolinite.
18 - 50'	Quartz sand, light yellow brown, fine- to medium-grained. Not sampled.
--------	Refusal
	Interval to 14 feet tested

Test Hole #8

Located 1320 feet west and 50 feet north of SE corner of the NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 2'	Clay, dark gray brown and yellow brown, plastic; trace of sand. Clay montmorillonite with trace of kaolinite.
2 - 3'	Clay, brown gray, plastic. Clay montmorillonite with trace of kaolinite.
3 - 6'	Clay and quartz sand, light brown gray; trace of white chert in lower foot. Clay is montmorillonite with trace of kaolinite.
6 - 9'	Clay, light yellow gray, plastic, slightly sandy. Upper foot montmorillonite; lower 2 feet montmorillonite and kaolinite in about equal proportions.
9 - 14'	Clay and quartz sand, light yellowish gray. Clay is montmorillonite and kaolinite in about equal proportions; kaolinite locally more abundant.
14 - 21'	Sand and clay; clay white and gray, plastic. Clay is kaolinite and montmorillonite in approximate proportion of 5:1.
--------	Refusal

Test Hole #9

Located 1400 feet west and 660 feet north of SE corner of NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 4'	Sand and clay, brown; few chert pebbles. Clay is montmorillonite with little kaolinite.
4 - 5'	Clay, brown, plastic; trace of quartz sand. Clay is predominantly montmorillonite with little kaolinite.
5 - 8'	Quartz sand and clay, brown. Clay is predominantly montmorillonite with little kaolinite.
8 - 15'	Clay, gray and brown gray, plastic; trace of quartz sand. Clay is montmorillonite with trace of kaolinite.
15 - 18'	Quartz sand, yellow brown and brown gray. Trace of clay consisting of predominantly montmorillonite with trace of kaolinite.
18 - 26'	Clay, gray brown, plastic; little quartz sand; few chert pebbles in upper foot. Clay is montmorillonite with trace to little kaolinite.
--------	Refusal

Test Hole #10

Located 1800 feet west and 680 feet north of SE corner of NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 4'	Quartz sand and clay, brown. Clay is montmorillonite with trace of kaolinite.
4 - 8'	Clay, brown mottled light gray, plastic; trace of quartz sand in upper 2 feet. Clay is montmorillonite with trace kaolinite.
8 - 14'	Sand and clay, light yellow gray and brown. Clay is kaolinite and montmorillonite in approximately equal proportions.
14 - 16'	Clay, gray, plastic. Clay is montmorillonite with trace of kaolinite.
16 - 17'	Quartz sand with trace of clay, light yellow brown. Clay is montmorillonite with little kaolinite.
17 - 19'	Clay, light yellow brown; little quartz sand. Clay is montmorillonite with little illite and trace of kaolinite.
19 - 20'	Clay and quartz sand, brown and reddish brown; few igneous rock pebbles. Clay is montmorillonite with little illite and kaolinite.
--------	Refusal

Test Hole #11

Located 1300 feet north and 120 feet west of SE corner of NE¼ of Section 31, T.29N., R.15W., St. Croix County.

0 - 15'	Clay, yellow brown with gray streaks, plastic; slightly sandy; few pebbles. Clay is montmorillonite with less than 10 percent kaolinite.
15 - 19'	Clay, gray with some yellow brown, sandy to very sandy in lower 2 feet. Clay montmorillonite with trace of kaolinite.
19 - 24'	Quartz sand, light yellow brown to yellow gray, medium- to fine-grained, slightly to moderately clayey. Caly is montmorillonite with trace of kaolinite.
24 - 30'	Clay, gray, plastic, slightly sandy. Clay is montmorillonite with trace of kaolinite.
30 - 42'	Quartz sand, light yellow gray, medium- and fine-grained. Trace of clay consisting of montmorillonite with only slight trace of kaolinite. Lower 6 inches very clayey and contains igneous rock pebbles. Clay in lower 6 inches is montmorillonite with little kaolinite.
42'	Refusal

Test Hole #12

Located 950 feet south and 330 feet east of NW corner of SW¼ of Section 32, T.29N., R.15W., St. Croix County.

0 - 3'	Clay, yellow brown, plastic, silty at top to sandy at base. Clay is montmorillonite with trace of kaolinite.
3 - 7'	Clay with abundant gravel consisting of igneous rock pebbles. Clay is predominantly montmorillonite with trace of kaolinite.
7 - 20'	Clay, gray streaked with light yellow brown, plastic, slightly sandy in upper foot. Clay is montmorillonite with trace to little kaolinite in lower 2 feet.
20 - 23'	Quartz sand with clay, yellow brown. Clay is montmorillonite with trace of kaolinite.
23 - 32'	Clay, gray and yellow brown with trace red brown; slightly sandy 26' to 30'; igneous rock pebbles in lower foot. Clay is montmorillonite with only slight trace of kaolinite.
-------	Refusal