

Effectiveness of Organic Binders for Iron Ore Pelletization

By Larry A. Haas, Jeffrey A. Aldinger, and Robert K. Zahl

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
°C/h	degree Celsius per hour	mL	milliliter
çm	centimeter	mm	millimeter
cm/min	centimeter per minute	mm Hg	millimeter of mercury
сP	centipoise	pct	percent
g	gram	pct/min	percent per minute
g/cm ³	gram per cubic centimeter	ppm	part per million
h	hour	rpm	revolution per minute
in	inch	SLM	standard liter per minute
kg	kilogram	st	short ton
kg/cm ²	kilogram per square centimeter	yr	year
lb	pound	\$/lb	dollar per pound
m	meter	\$/st	dollar per short ton

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EFFECTIVENESS OF ORGANIC BINDERS FOR IRON ORE PELLETIZATION

By Larry A. Haas,¹ Jeffrey A. Aldinger,² and Robert K. Zahl³

ABSTRACT

The U.S. Bureau of Mines investigated the use of organic binders as substitutes for bentonite in agglomerating iron ore concentrate. Over 30 organic binders were evaluated at several dosage levels in laboratory tests. The binder groups producing the greatest green pellet strengths were natural gums (guars), carboxyl methyl celluloses, and gelled starches. The nongelled and alkalized starches, starch acrylic copolymers, wood-related products, and dairy products were less effective but better than bentonite.

The highest wet pellet drop numbers were obtained with binders that had a medium plate water absorption value (>500 and <10,000) in distilled water and a high slurry viscosity (>75 cP) at 6 pct solids. The highest dry compressive strengths were obtained with binders that gave the highest adhesive tensile strength (>4 kg/cm²) on iron oxide lap-joint substrates. Pellets with 0.1 pct organic binder had lower compressive strengths and reduction disintegration indices than those with 1 pct bentonite, but higher reduction rates. Pellets with carboxyl methyl cellulose and gelled starch had higher softening temperatures than those with bentonite. Overall, the most promising binder is gelled starch. Its price makes it more cost effective than carboxyl methyl cellulose, and its pellets have metallurgical properties superior to those of bentonite pellets.

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The majority of domestic iron ore has historically been supplied from the Lake Superior Region of northern Minnesota and Michigan. In 1987, this region accounted for 96 pct of the total domestic iron ore production, with these States responsible for about 71 and 25 pct, respectively (1).⁴

The domestic iron ore production rates have been steadily decreasing. Sixty million short tons of pellets were shipped in 1979 from Minnesota, but because of the severity of the recent slump in demand for domestic iron ore, the estimated production for 1986 was reported as only 25 million st (2). This slump was partly due to the availability of cheaper and superior iron ore pellets from foreign sources and to the decline in domestic steel consumption. The decreased demand had a dramatic influence on the iron ore industry, as shown by the production stoppage (closing) of two of eight pelletizing plants in Minnesota during the last several years (3). To counteract the decreasing production rates and to revitalize the iron ore industry, methods need to be developed for producing domestic iron ore pellets that are economical and have superior metallurgical properties that will result in coke reduction during blast furnace smelting.

Since iron ore concentrates consist of finely divided particles, they must be pelletized (with a binder) for use as blast furnace feed material. Approximately 15 pct of the total pellet cost is attributable to pelletizing. The conventional bentonite binder is mined mainly in Wyoming and shipped to pelletizing plants in the Lake Superior region. Approximately two-thirds of the total binder cost is shipping expenses. Obviously, a sizable savings could be realized if a superior and economical binder could be obtained from sources closer to the pelletizing plants. Additional savings might be realized if pellets made with alternative binders improved the economics of the blast furnace.

Recently there has been a renewed interest by the iron ore companies in replacing relatively inexpensive bentonite with a more expensive organic binder, i.e., carboxyl methyl cellulose (4), because a savings can be realized in the blast furnace operation. This savings is mainly due to the lower acid gangue (aluminum silicates) contamination and the improved pellet metallurgical properties, which have the potential for lowering hot-metal production costs. Also, organic binders are more effective at lower dosage levels, which translates into lower storage and transportation costs. Another advantage of organic binders is that they have low ash contents, and therefore, most of the binder

burns off during the pellet firing operation. An ideal binder should leave behind essentially no residual chemicals after the pellet is fired at temperatures above 1,000° C. The inorganic compounds from the bentonite binder add to production costs by increasing the amount of handling required and by introducing contamination. For example, if 20 lb of bentonite is added per short ton of pellets, this additional noncombustible acid gangue material must be handled throughout the ironmaking operation, which means increased flux requirements and decreased ironmaking throughput capacity; bentonite usually contains about 80 pct aluminum silicates, which in this example decreases the pellets' iron content by 0.8 pct. Treatment of the added gangue from bentonite also requires increased energy. For example, in producing direct-reduced iron (DRI) pellets, de Souza (5) reported that each additional percent of acid gangue present in the pellet decreases the value of prereduced material by over \$2/st.

In the past, many organic binders have been investigated as substitutes for bentonite (4-18). The majority of the binders that have been investigated were synthetic polymers; only a few were inexpensive natural polymers and wastes. Das Gupta (7) reported that there are two reasons why organic binders have not been adopted: (1) their high cost and (2) lack of adequate data on binder effectiveness.

Adequate binder evaluation methods have been one of the major concerns of the iron ore pelletizing industry (19). Standardized quality acceptance tests and specifications for organic binders are currently nonexistent. Quality-control tests with the binder ingredient alone, as well as when mixed with iron ore, are needed. The tests must be relatively simple, fast, reproducible, and meaningful. Historically, the relative importance of some of the suggested binder specifications has not been well defined, and therefore, additional research is required to identify the key binder parameters.

The main binder property specification, presently in use for bentonite is the plate water absorption test (PWAT) (20). Other tests that have been suggested include viscosity and chemical content, which will be used to characterize the binders.

As part of its program to assure an adequate supply of metals and minerals from domestic sources, the Bureau of Mines investigated methods to produce domestic iron ore pellets more competitively, using organic binders for agglomerating iron ore. The goals of this research were (1) to determine the physical and metallurgical pellet properties of pellets made with different types and dosages of organic binders and (2) to relate these pellet properties to the binder properties.

⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

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The authors wish to express their gratitude to Bureau employees Elmer Karlstad, physical science technician, John Moy, metallurgist, and Dean Franke, engineering technician, who helped determine the pellet physical strengths, porosity, and high-temperature softening data, respectively.

MATERIALS

Over 30 organic binders, obtained from commercial suppliers, were divided into six groups: celluloses, dairy wastes, natural gums, starches, starch acrylic copolymers, and wood-related products.

Methyl celluloses were the first group of binders investigated, since a synthetic binder in this group has been recently reported to be very effective for agglomerating iron ore (4). Some of the binders in this group contained considerable quantities of residual sodium chloride, which is one of the products formed when cellulose (fig. 1A) is reacted with sodium hydroxide and monochloroacetic acid to form the anionic hydrophillic polymer, sodium carboxyl methyl cellulose (CMC). The idealized unit structure shown in figure 1B is a CMC with a degree of substitution of 1. The letter "n" in this figure refers to the chain length of the polymers. The carbon and the other chemical analyses, shown in table 1, suggest that the cellulose sample



Figure 1.-Idealized unit structures of starch and cellulose(s).

CMCH was the most pure CMC; the carbon analyses' accuracy was only about ± 5 pct. The sample CMCH also had the lowest chloride content, which suggests that the salt was removed by washing with an organic solvent. The sample CMCP1 contained more sodium carbonate than the others, as verified by X-ray analysis. The binder CMCC1 contained the highest percentage of aluminum and silicon compounds.

Natural materials, such as dairy waste products, have been reported to be inexpensive potential binders (10). Lactose (DLAC) appeared to have lower potassium and sodium concentrations than whey (DWHY) and whey permeate (DWHYP). The phosphorous concentration of whey and whey permeate was high compared with that of most of the other binders. The loss on ignition (LOI) of the dairy materials was slightly higher than the LOI of the CMC's; the temperature at which combustion of the binder occurs may be interrelated with the pellet thermophysical properties.

Natural gums have been previously used for the laboratory agglomeration of iron ore (7) but have not been adopted by industry, probably because they are more expensive than the CMC's (table 1). The sodium analyses of the guar gums (GG's) and xanthan gum (GX) were lower than those of the CMC's. Samples GG211 and GG211D were unmodified nonionic guars. Sample GG416 was a hydroxyl propyl guar. The xanthan gum is defined as a natural carbohydrate or an exocellular biopolysaccharide. Xanthan had a much higher potassium content than the guars or CMC's.

Several wood-related products were evaluated. Hemicellulose (HC) binders are fairly inexpensive and are presently used to bond together finely divided wood materials. Lignin sulfonates have been used to agglomerate dust particles to prevent them from being fluidized by wind. Two types of lignin sulfonates were investigated: ammonium (LASST), and calcium (LCSG2s or LCSG4s). The small letter "s" at the end of the binder code indicates that the material was used in the slurried form. Two products (LCASFs and LCASFT) were a mixture of both calcium and ammonium lignin sulfonate. Naphthalene sulfonate slurry (NNFS6s) and caustic leonardite (LEST2) were also placed in the wood-related products classification. Both of these binders contained more noncombustible material (ash) than any of the other binders, as indicated by the low LOI at 1,000° C (table 1). The weight loss at 300° C for these two binders was also lower than most of the other binders.

lable 1.	-Partial	chemical	analyse	s of	organic	binders.	percent	on dr	/ basis'
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			Ta	able 1	-Partia	l chemic	al analy	ses of o	rganic b	inders, p	percent	on dry ba	nsis ¹				
Binder name	Code	Al	c	Ca	CI	ĸ	Mg	Na	Р	s	Si		LOI betw	een 75° C	and —		Cost, ²
							-					105° C	300° C	500° C	700° C	1,000° C	\$/lb
Celluloses:										-							_
Methyl carboxyl C1	CMCC1	0.8	27	0.9	8.7	0.06	<0.1	11.3	<0.1	<0.1	0.7	7.1	34.9	54.9	70.7	89.9	0.45
Methyl carboxyl H	CMCH	<.2	33	<.3	.2	<.05	<.1	7.3	.1	<.1	<.5	7.7	53.1	82.5	91.8	94.9	1.00
Methyl carboxyl P1	CMCP1	<.2	26	<.3	9.1	<.05	<.1	17,2	<.1	<.1	<.5	3.8	34.1	40.3	54.8	83.0	.55
Dairy wastes:																	
Lactose	DLAC	<.2	36	<.3	NE	<.05	<.1	<.1	NE	NE	<.5	NE	69.9	99.9	99.9	99.9	.20
Whey	DWHY	<.2	27	.8	NE	2.20	NE	.7	1.4	<.1	<.5	4.4	57.7	91.7	93.3	96.2	.15
Whey permeate	DWHYP	<.2	42	.5	NE	1.60	1.0	1.0	2.4	<.1	<.5	NE	59.1	90.4	91.1	95.1	.05
Gums, natural:																	
Guar 211	GG211	<.2	38	<.3	NE	.17	<.1	.1	<.1	<.1	<.5	8.7	77.0	99.0	99.4	99.8	1.00
Guar 211D	GG211D	<.2	28	.5	NE	.18	<.1	.1	<.1	<.1	<.5	8.5	85.4	99.1	99.5	99.5	1.25
Guar 416	GG416	<.2	34	.3	NE	.05	<.1	.6	<.1	<.1	<.5	7.8	77.6	97.7	97.8	97.8	1.50
Xanthan	GX	<.2	33	<.3	NE	3.00	<.1	2.5	.3	.6	<.5	9.6	66.7	84.4	87.3	91.2	4.00
Wood-related products:																	
Hemicellulose SW	HCSW	<.2	32	1.3	NE	1.60	.3	.8	<.1	.4	<.5	3.9	55.5	91.7	92.8	96.6	.02
Hemicellulose WW	HCWW	<.2	41	1.1	NE	1.55	NE	.8	<.1	.2	<.5	5.1	52.2	92.0	92.7	95.9	.05
Lignin sulfonate:																	
Ammonium SST	LASST	<.2	34	.8	NE	.17	1.0	.1	<1	3.5	<.5	7.2	85.3	94.7	94.9	95.6	.50
Calcium ammonium SFs	LCASFs	<.2	44	4.2	NE	.12	.1	<.1	<.1	4.4	<.5	4.7	62.3	80.8	89.0	89.3	.50
Calcium ammonium SFT	LCASFT	<,2	43	9.2	NE	.13	.2	<.1	<.1	2.6	<.5	6.2	63.1	82.2	86.9	87.1	.50
Calcium SG2s	LCSG2s	<.2	32	4.8	NE	.17	<.1	.6	<1	3.0	<.5	3.5	50.6	73.2	83.3	85.3	.50
Catcium SG	LCSG4s	<.2	NE	4.8	NE	.09	.1	.1	<.1	2.3	<.5	4.9	64.8	NE	87.1	87.6	.50
Leonardite, caustic	LEST2	.7	37	1.9	NE	.10	.5	6.1	< 1	.2	.7	NE	30.6	62.2	74.8	78.4	.05
Naphthlene sulfonate	NNFS6s	<.2	34	<.3	NE	.07	<.1	11.7	<.1	4.7	<.5	10.4	12.2	45.7	64.8	65.4	1.00
Starch copolymers:																	
Acrylic 125	PSA125	<.2	40	<.3	NE	16.90	NE	.1	2.7	<.1	<.5	10.7	58.4	69.6	70.5	83.6	1.25
Acrylic GA	PSAGA	<.2	35	<.3	NE	<.05	1.0	10.6	<.1	<.1	<.5	10.6	50.7	74.4	77.8	88.1	2.00
Acrylic GJ	PSAGJ	<.2	31	NE	NE	.08	1.0	19.3	<.1	<.1	<.5	6.7	22.6	65.5	71.2	78.8	2.00
Starches:																	
Alkalized:																	
Corn Gs	SC-AGs	<.2	31	<.3	NE	<.05	NE	8.9	<1	<.1	<.5	6.8	50.7	74.3	81.3	86.8	.50
Corn Ps	SC-APs	<.2	33	NE	NE	<.05	<.1	NE	NE	NE	.9	NE	NE	63.5	NE	NE	.40
Nongelled:																	
Corn dextrin 06	SC-D06	<.2	36	<.3	NE	<.05	<.1	<.1	<.1	<.1	<.5	3.2	67.7	98.9	98.9	99.9	.30
Corn 71	SC71	<.2	23	<.3	NE	<.05	NE	<.1	<.1	<.1	<.5	10.2	70.8	99.9	99.9	99.9	.10
Corn 806	SC806	<,2	29	<.3	NE	<.05	NE	<.1	<.1	<.1	<.5	8.6	68.8	99.5	99.5	99.6	.25
Gelled:																	
Corn:																	
C5A	SCGC5A	<.2	29	<.3	NE	.19	<.1	8.3	<.1	<.1	<.5	NE	68.7	76.9	79.1	91.1	.45
CTS	SCGCTS	<.2	33	<.3	NE	<.05	NE	<.1	<.1	<.1	<.5	8.3	75.8	99.9	99.9	99.9	.20
ΙΑ	SCGIA	<.2	42	<.3	NE	.05	<.1	.2	.1	<.1	<.5	3.9	72.1	99.4	99.4	99.5	.70
Waxy 08	SCGw08	<.2	33	<.3	NE	<.05	.1	.1	<1	<.1	<.5	5.3	68.9	99.7	99.8	99.8	.45
Waxy 09	SCGw09	<.2	45	<.3	NE	<.05	<.1	.1	<.1	<1	<.5	7.6	61.9	62.1	99.9	99.9	.60
Potato:																	
C10	SPGC10	<2	37	<.3	NE	< 05	<.1	.7	.1	< 1	< 5	NE	79.8	97 9	98.1	98.7	55
S14	SPGS14	< 2	34	<.3	NE	08	< 1		< 1	< 1	<.5	NE	91 4	98.8	QR R	99.7	35
Mhoat	0.0014		54						~	-, .			U ILY	00.0	00.0	33.1	
Corn P	SWCOD	20		12		< 0E	- 1	. 1		. 1	<u>ر ۲</u>	76	£1 0	60 4	00.0	00.0	20
20	SWOOP	~~	-44 N⊏	<.3	NC	<.U0 > 05	2.1	×.1	×.1	S.I.	<.0 / E	1.0	520	04.1	23.3	22.2	.20
20	SWG20	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	NE	×.0		<u>>,00</u> ∠ ^⊑	~ 1	~1	5.1	<. I	<.5 ~ E	0.1 7 F	23.9	33.D	33.3	33.3	.20
70	SW030	~~	NE A4	×.0		<.UD	5,1	51	2.0	<.1	<, 0	1.5	00.8	NE	93.2	98.7	.40
10	30070	~~	41	<u>.</u>	INE	×.05	5.1	5.1	<u> </u>	<u> </u>	¢.>	0.0	09.9	99.2	89.1	99.7	.20

LOI Loss on ignition. NE Not evaluated. All samples contained <0.3 pct Fe except LEST2 (0.9 pct Fe). ²Approximate costs in truck lot quantities.

Polymeric starch acrylics (PSA's) were investigated because these materials are known to have a high water absorption level, which has been suspected to be an important binder property (20). The chemical analyses indicated that the copolymer PSA125 contained more potassium than the other samples but had a very low sodium content. The PSAG's sodium contents were in the same range as those of the CMC's. PSAGJ contained the most sodium and correspondingly had lower LOI values, or more ash.

Starches were investigated because they are less expensive than the CMC binders and have a similar unit structure (fig. 1). Three types of starches, corn (SC), potato (SP), and wheat (SW), were evaluated. Most of the starches were gelled (i.e., cooked), as designated by the letter "G" in the binder code. In general, the starches contained less sodium than the CMC's; however, one alkalized corn starch (SC-AGs) and one gelled corn starch (SCGC5A) had a high sodium content (>8 pct).

The bentonite used for comparison purposes in this research (not listed in table 1) contained 61 pct SiO₂, 18 pct Al₂O₃, 1.8 pct Na₂O, 1.5 pct CaO, and 0.4 pct K₂O. Other properties of this bentonite were discussed in a previous publication (21), which reported that it was typical of western bentonites.

The iron ore concentrate used in this research was a beneficiated magnetic taconite obtained from the eastern part of the Mesabi Range. It was dried at 105° C overnight. The percentage chemical analyses were 65.2 Fe_T, 21.7 Fe²⁺, 5.6 SiO₂, 0.4 CaO, 0.4 MgO, <0.2 Al₂O₃, <0.1 K₂O, <0.1 Na₂O, <0.01 P, and <0.01 S. The density was 4.9 g/cm², and over 60 pct of the concentrate was finer-than 500 mesh.

EXPERIMENTAL METHODS

Most of the binder and pellet evaluation procedures were described in detail in a previous publication (21), while the more recently developed methods are described in the appropriate sections of this report.

BINDER DIAGNOSTIC TESTS

Prior to testing the binder with iron ore, several diagnostic evaluation tests were conducted on the binder alone. In general, these tests were conducted on the asreceived binders, except for some slurried binders that were first dried at 105° C for the PWAT experiments.

The PWAT experiments were conducted as described by ASTM E946-83 (20), except 0.5 g binder was used in tests of most of the organic binders. For starch copolymers, which had PWAT values greater than 5,000, only 0.2 g was used. Also, a plastic ring (4-cm diam and 4-mm thickness) was placed around the sample to retain the binder on the paper.

It is well known that water quality can influence the water absorption values of some binders. Therefore, three types of water (distilled, tap, and filtrate) were used. The filtrate water was obtained from a 50-pct-solids slurry made from local tap water and the iron ore concentrate. Analyses of the three types of water used in PWAT experiments were, in parts per million:

	<u>Ca</u>	<u>K</u>	Mg	<u>Na</u>
Distilled	4	1	1	1
Tap	22	2	3	7
Filtrate	90	76	1,200	160

The actual water that contacts the binder in a pelletizing operation contains more cations than this filtrate water. The reason for using the three types of water was to conduct some tests on the influence of cations on the PWAT with some of the binders but not to evaluate all cation levels with all binders. The PWAT experiments were conducted with all binders using the standard distilled water, and simplified comparisons were based on these tests.

The slurries for the viscosity and the adhesive tests were prepared by slowly adding the binder to 350 mL of distilled water, which was magnetically stirred at about 600 rpm for 10 min unless otherwise noted. Blending at 14,000 rpm for 5 min was used in some tests when the binder slurry was too thick for magnetic stirring and to determine the influence of high shear. The rate of binder addition was adjusted so all the powder was dispersed before more was added. The viscosities of the slurries were determined with a concentric cylinder Fann⁵ viscometer operated at 600 rpm as specified in reference 21. The apparent viscosities were determined with slurries at 1, 3, and 6 pct solids. Mainly, slurries were made at the 6-pct-solids level, since this is the principal level used by the drilling-mud bentonite industry. However, at this level, the viscosity of some binder slurries exceeded the viscometer's capability (150 cP) and, therefore, lower percent solids were also investigated. All binders were evaluated at the 6-pct-solids level, and this level was used for the simplified conclusive comparative statements.

The lap-joint dry shear adhesive tensile strengths were evaluated by placing a 6-pct binder slurry between two AISI Type C1015 low-carbon, hot-rolled, 16-gauge steel plates (2.5 by 5 cm). Before the plates were used, they were polished on a flat surface with an emery cloth and then scrubbed with a detergent. The dried plates were oxidized in a muffle furnace for 30 min at 500° C. The loose oxide was rubbed off. The bottom portion (2.5 by

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

2.5 cm) of the two oxidized plates was covered with a coating of the 6-pct binder slurry, and the plates were pressed and held together with a 0.2-kg weight for 1 day at ambient conditions. The plates were further dried overnight in an oven at 105° C. Hooks were then inserted into the hole at the top end of each plate and placed in the jaws of a tensile tester. The applied shear tensile force required to rupture the bond was determined at an extension speed of 0.08 cm/min. This is reported as kilogram per square centimeter of lapped area.

GREEN PELLET PREPARATION

The procedure used to evaluate the agglomeration properties of the binders involved mixing dry iron ore concentrate with dry binder and then adding water before pelletizing, unless a different procedure is noted. For example, some slurry binders were used as-received and some dry binders were soaked in water overnight before being added to the dry concentrate; the final letter in the binder code for the slurried binders is an "s". Also, in one test, the concentrate was slurried and then the dry binder (SWG70) was added. This filtered slurry was used for pelletizing, and the binder is coded SWG70F.

When dry concentrate was used, it was difficult to make pellets with high moisture levels (>9 pct), which has also been reported by others (12). This observation could be explained by assuming that dry concentrate does not completely rehydrate during the laboratory pelletizing procedure, which takes less than 2 h. The pellets (minus 1/2 in, plus 7/16 in) made in the laboratory contained only about 8 pct moisture, while commercial pellets usually contain over 9 pct. Commercial pellets are made from concentrate that is ground wet and not dried before pelletizing. Also, in the laboratory pelletizing procedure, more time was needed to make the pellets, and therefore more water was lost by evaporation. Attempts were made to keep the pellet water content about the same in each test. Distilled water was added to the dry iron ore concentrate to obtain the 11 pct level. Only a small quantity (<1 pct) of water was added during the pelletizing process. With some binders, slightly more water was needed in the pelletizing operation because the binders absorbed more. The moisture level was also varied intentionally in some tests to determine the importance of this variable.

GREEN AND FIRED PELLET TESTING PROCEDURES

The drop numbers were determined with freshly prepared wet pellets (called the 25° C samples). The wet and dry (heated overnight at 105° C) compressive strengths of the pellets were determined by standard methods. The wet pellets were stored in sealed containers until they were used in the shock temperature tests.

Selected wet pellets were placed in a preheated muffle furnace for 30 min and shock tested at temperatures of 300°, 500°, 700°, and 900° C. The highest temperature generally investigated with the organic binders was 900° C. This maximum temperature was selected because all the bentonite pellets endured this shock temperature; at $1,000^{\circ}$ C, 11 pct of the bentonite pellets did not survive the test. Each shock test was conducted with 30 pellets in each batch and 5 batches heated at one time. The portion of the pellets that did not break or spall was considered the survival percentage.

The compressive strength dependence on temperature was also evaluated. The 300° to 900° C compressive strengths were determined at room temperature on the unbroken pellets from each shock test. For the 105° C compressive tests, the pellets were heated overnight. The pellets used for the 1,200° and 1,250° C compression tests were dried at 105° C overnight, heated for 30 min at 900° C in a preheated muffle furnace to oxidize the magnetite to hematite, and then immediately placed in another preheated muffle furnace for 15 min at either 1,200° or 1,250° C.

METALLURGICAL PROCEDURES

The metallurgical properties were evaluated with selected pellets fired at 1,200° and 1,250° C. These tests involved determining the pellet reduction kinetics, disintegration, and softening temperatures under reducing conditions.

The reduction kinetics were conducted with a pellet heated in a thermogravimetric apparatus (22) for 6 h at 900° C using 30 pct CO, 0.1 pct H₂, and the balance nitrogen, as described in ISO/DIS 7215 (23). The percentage reduction was assumed to be directly related to the weight loss of the sample.

The low-temperature reduction disintegration index (RDI) tests were conducted by heating 500 g of pellets at 500° C for 1 h using 20 pct CO, 20 pct CO₂, 2 pct H₂, and the balance nitrogen. The reduced product was tumbled for 300 revolutions and screened according to ISO 4696 (24).

The high-temperature softening tests were conducted with the equipment shown in figures 2 and 3. The electric furnace was heated with silicon carbide heating elements. The alumina (99.9 pct) reactor tube was 7.5 cm OD, 6.2 cm ID, and 1.5 m long. An alumina tube (5.0 cm OD, 4.4 cm ID, and 0.6 m long) was used as a pedestal to support the graphite preheater and the pellet bed. The preheater crucible contained about 60 g of graphite chips (minus 12 mm, plus 10 mm). Perforated graphite disks were placed below and above the pellet bed (6.4 cm high and about 250 g); the pellet bed was retained inside an alumina liner (5.7 cm OD, 5.0 cm ID, and 11.0 cm long). A 5-mm layer of graphite chips (minus 8 mm, plus 3 mm) was placed between each disk and the pellet bed. A graphite foot with four toes was centered above the top graphite disk and inside the alumina liner. The top of the graphite foot was inserted into an alumina ram (3.7 cm OD, 3.1 cm ID, and 1.4 m long). On top of the ram, a static load of 8.1 kg was used to apply a force of 0.5 kg/cm^2 on the pellet bed.



Figure 2.-Schematic of high-temperature softening apparatus.

The thermocouple, used for determining the pellet bed temperature, was located in the center of the graphite foot, just above the pellet bed.

Both the gas pressure drop and the bed shrinkage were continuously recorded during the high-temperature softening test. The pressure drop was measured with both a precision pressure gauge and an industrial-type pressure transducer. The overall pressure error for both of these instruments was less than 1 pct. A differential transformer-type displacement transducer and a standard dial indicator were used to measure the shrinkage of the pellet bed. The relative displacement error with both of these instruments was less than 1 pct. Temperature, pressure drop, and relative displacement were recorded with a multichannel strip-chart recorder.

The high-temperature softening test procedure consisted of flushing the reactor with 5 SLM N_2 while heating it up to 500° C, at which temperature the gas was switched to 25 SLM of 24 pct CO, 16 pct CO_2 , and 60 pct N_2 . The heating rate from 500° to 1,100° C was about 150° C/h. At temperatures above 1,100° C, the heating rate was 100° C/h and the gas mixture was 30 pct CO and 70 pct N_2 . This gas composition was maintained until a rapid increase in pressure drop occurred because of the softening of the pellet bed. At this stage, the furnace was shut off and flushed with 15 SLM N_2 until the pellet bed cooled down to about 200° C. The softening temperature value was determined by plotting the pressure and temperature data. This value was defined as the temperature at the intersection of the tangents of the gas pressure drop curve at the point of rapid pressure increase. The bed shrinkage data were also plotted against pellet bed temperature.



Figure 3.--Cross-sectional view of reactor section of high-temperature softening apparatus.

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BINDER WATER ABSORPTION, VISCOSITY, AND ADHESION

The commonly used ASTM bentonite binder water absorption method (PWAT) (20) specifies the use of distilled water, but in this research, two other water types were also investigated to obtain some background data on the influence of cations on some binders. The results (fig. 4) show that bentonite (BEN17) had about the same water absorption value as guar gum GG211 and some of the gelled starches (SWGP3, SWG70, SWG20, and SCGIA) in distilled water. However, in filtrate water, the PWAT value decreased more for the bentonite than for the guars and most of the starches (table 2). The polymeric starch acrylics (PSA's) had the highest water absorption values, which also decreased drastically in filtrate water (table 2, fig. 4). The dairy products (D's), hemicelluloses (HC's), lignins (L's), naphthalene sulfonate (NNFS6), and dextrin (SC-D06) had negative PWAT values, which meant that the binder dissolved during the absorption test. It can be seen from the PWAT data in table 2 that bentonite, celluloses, gums, and gelled starches exceeded the target values. (All the target values were arbitrarily defined and were based on the authors' judgment as to minimum acceptable requirements.)

The apparent viscosities (table 2) of the selected binder slurries were measured at 1, 3, and 6 pct solids. The results indicated that only one binder group (PSA's) had both extremely high viscosities (>150 cP at 1 pct solids) and extremely high PWAT values (>10,000). Guar gum binders also had high viscosities but did not have exceptionally high water absorption values. In general, at 1 pct solids, CMC binders had higher slurry viscosities than the gelled starches. Dextrin and nongelled alkalized starches, lignins, hemicelluloses, and dairy products all had low viscosities (<50 cP at 6 pct binder slurry). These binders showed a smaller relative viscosity change with percent solids change than did the binders that had high PWAT values. The gelled starches had higher viscosities and had PWAT values greater than 600 in distilled water.

The slurry viscosity of one starch (SWG30) at 1 pct solids was very dependent on the type of mixing. When the slurry was mixed with the low-shear magnetic stirrer, the viscosity was greater than 150 cP, but the viscosity was only 40 cP when the slurry was mixed with the high-shear blender. Less shear thinning action was observed with the other binders. The reason for the shear sensitivity of starch may be related to its high phosphorus content (table 1), which has been known to change the rheology of liquids.

The adhesion tensile strengths of some selected binders, in bonding iron oxide strips, were measured. In general, the binders with the best adhesive properties were CMC, guar gum, and gelled starch. The dairy products, hemicelluloses, lignins, and nongelled starches had extremely low adhesive strengths ($<2 \text{ kg/cm}^2$). The tensile strengths of binders have also been investigated by others. Roorda (15) reported that the particle-to-particle bridge tensile strength of CMC could be as high as 1,200 kg/cm².

GREEN PELLET PHYSICAL PROPERTIES

The iron ore pelletizing industry appears willing to accept organic binder pellets with lower green physical properties than those made with bentonite, but no industrial minimum target value is available. With 0.07 pct CMC, de Souza (5) obtained pellet drop numbers of 2.6 at 9.4 pct moisture and dry (105° C) compressive strengths of 3.7 lb per pellet. These values are slightly lower than the arbitrary target values defined in this report; no target value was set for the wet (25° C) compressive strength since this value was found not to be very meaningful in this comparative study. The minimum mean target values for green pellets with organic binders in this research were defined as

drop number = 3.5, and

dry compressive strength = 4 lb.

These values were higher than the results obtained with no binder ("None" in binder type and code column in table 3) but lower than results with 0.5 pct bentonite.

Celluloses

The physical properties of the organic binder green pellets (dried at 105° C or below) were compared with the properties of pellets made with bentonite. The results (table 3) are in general agreement with the literature (5), which indicated that 0.1 pct CMC binder produced green pellets with physical properties comparable to those of about 0.5 pct bentonite (BEN17) but weaker than pellets with 1 pct bentonite.

With several of the CMC's, the target dry compressive strength requirements were met at the 0.1-pct dosage level. At about 8-pct pellet moisture level, the highest drop numbers and dry (105° C) compressive strengths of the pellets made with CMC were obtained with CMCH, which had the lowest chloride content (table 1); pellets were also made at 7-pct and at 9-pct moisture levels to show the importance of this variable. Compared with the other CMC binders, CMCH had the highest PWAT values and the highest viscosity. These results are in agreement with Roorda (15), who reported that CMC's with high viscosities resulted in pellets with high drop numbers. Roorda and Jipping (25) reported that the addition of soda ash improved green pellet properties. A small improvement in the 0.15 pct CMCH pellet was obtained when 0.03 pct Na₂CO₃ was added; this mixture was coded as 0.18 pct CMCHO (table 3). Similar results were obtained with the addition of 0.03 pct NaCl (binder coded CMCHL). Essentially no improvement in the pellet green properties was obtained with the addition of both 0.03 pct NaCl and 0.03 pct Na₂CO₃ to 0.15 pct CMCH (coded as 0.21 CMCHOL). The most improved green properties were obtained when 0.06 pct Na₂CO₃ was added to 0.15 pct CMCH (coded as 0.21 pct CMCHOO).

The method of CMC addition to the iron ore concentrate was also investigated. Essentially, the same dry compressive strengths were obtained whether the CMCP1 binder was added to the wet concentrate either dry or slurried (CMCP1s). However, the drop number was slightly higher using the slurried method, perhaps because the binder reached a higher degree of swelling and absorbed more water.



Figure 4.--Plate water absorption test (PWAT) results for various binders.

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Table 2.-Binder diagnostic data

Binder type		PWAT	value ¹			Viscosity, ² cF)	Tensile
and code	Distilled	Тар	Filtrate	d/f ⁷	1 pct	3 pct	6 pct	strenath.
	water ⁴ (d)	water ⁵	water ⁶ (f)	,	solids	solids	solids	ka/cm ²
Target	≥500	≥500	≥500	NE	≥6	≥10	≥75	≥4.0
Bentonite (BEN17)	940	850	470	2.0	8	19	60	<1.0
CMCC1	1.270	1.290	1.010	1.3	20	86	>150	2.9
СМСН	3,260	3,070	1,990	1.6	90	>150	>150	9.1
СМСНО	2,150	NE	NE	NE	80	>150	>150	8.9
CMCP1	2,550	2,060	1,800	1.4	70	>150	>150	5.5
Dairy wastes:			5 J					
	-120	NE	NE	NE	6	6	6	<1.0
	-100	NE	NE	NE	5	Ý 6	6	1.7
Representation of the second s	-100	INE	INE	INE	0	0	0	<1.0
GG211	1.030	970	910	11	>150	>150	>150	11 3
GG211D	900	850	640	14	>150	>150	>150	10.6
GG416	1 850	1 800	1 730	11	>150	>150	>150	0.5
GX	4 890	4,230	2 890	17	120	>150	>150	29
Wood-related products:	1,000	1,200			120	100	100	2.0
HCSWs	-5	NE	NE	NE	6	NE	10	<1.0
HCWW	-60	NE	NE	NE	6	NE	9	<1.0
LASST	-165	NE	NE	NE	6	NE	6	<1.0
LCASFs	-160	NE	NE	NE	6	NE	7	<1.0
LCASFT	-154	NE	NE	NE	7	NE	7	NE
LCSG2s	-160	NE	NE	NE	6	NE	6	<1.0
LCSG4s	-130	NE	NE	NE	6	NE	7	NE
LEST2	125	50	60	2.1	6	NE	8	<1.0
NNFS6s	-140	NE	NE	NE	6	NE	15	<1.0
Starch copolymers:	44.000	40 700	F 000	• •				
	14,000	13,700	5,390	2.6	>150	>150	>150	3.1
PSAGU	50,500	42,100	9,500	5,3	>150	>150	>150	NE
SC-AGe	520	NE	NE		7	NE	24	17
SC-APs	600	NE	NE	NE	Ŕ	NE	62	4.3
SC-D06	-20	NE	-20	1.0	ĕ	NE	8	<1.0
SC71	110	120	110	1.0	ě	NE	8	<1.0
SC806	50	40	30	1.7	5	NE	8	<1.0
SCGCTS	850	810	830	1.0	7	39	>150	10.8
SCGIA	1,330	1,320	1,230	1.1	9	48	>150	6.1
SCGW08	740	720	670	1.1	10	24	>150	4.9
SCGW09	730	684	550	1.3	11	58	>150	6.3
SPGC10	900	780	650	1.4	13	46	>150	17.5
SPGS14	1,200	880	730	1.6	17	67	>150	10.5
SWCGP	610	530	520	1.2	7	32	135	3.9
SWG20	870	790	750	1.2	11	41	90	6.7
SWG30	3,530	2,680	1,150	3.1	>150	>150	>150	3.1
SWG70	760	710	730	1.0	7	17	90	9.8
SWGP3 ,	970	950	920	1.1	8	23	>150	4.8
Not evaluated. Difference between wet and dry Determined at 600 rpm. Determined after drying the 6-pd Distilled and deionized. Minneapolis, MN, drinking water Filtrate from a 50-pet solids sluri	weight (۵W), o ot binder slurry ry made with i	divided by ini , that was ap ron oxide cor	itial dry weight (\ plied between tw ncentrate and tag	W _{dry}), and m vo iron oxide o water.	ultiplied by 1 substrates.	00.		
PWAT distilled water value divid	ed by filtrate v	vater value.						

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Binder		Pellet	Wet			Pellet cor	npressive	strength,	lb per pe	llet		900° C
Type and code	Pct	water,	drop				at firing t	emperatu	res			survival,2
		pct	number	25° C ¹	105° C	300° C	500° C	700° C	900° C	1,200° C	1,250° C	pct
Target	≤0.20	8.0	≥3.5	None	≥4.0	≥4.0	NE	NE	NE	≥300	≥300	≥95
None	0	6.6	3.2	3.1	2.3	4.0	12	64	96	284	375	100
Bentonite:												
BEN17	.50	7.0	4.2	1.6	4,9	NE	NE	NE	NE	170	420	NE
BEN17	1.00	7.6	9.2	4.1	20.9	21	80	155	215	527	737	100
Celluloses:												
CMCC1	.10	7.7	3.4	2.1	3.3	9.3	46	88	130	457	NE	100
CMCC1	.30	8.7	6.1	2.6	10.3	12.6	48	72	95	401	NE	100
СМСН	.10	7.0	3.3	2.9	5.2	9.9	5	98	140	443	700	NE
CMCH	.10	7.8	3.9	2.4	5,2	7.2	NE	NE	125	ŇE	698	100
СМСН	.10	9.0	7.0	4.1	7.0	6.8	24	43	74	173	673	100
СМСН	.15	8.1	4.1	2.3	12.6	7.2	NE	NE	NE	280	590	100
CMCHL	.18	8.1	6.6	3.1	13.5	11.9	NE	NE	NE	391	703	33
СМСНО	.18	8.2	5.5	2.9	15.4	13.2	NE	NE	NE	349	697	80
CMCHOL	.21	8.3	5.3	2.7	11.0	11.0	NE	NE	NE	313	682	100
CMCHOO	.21	8.9	14.7	3.0	19.5	7.8	NE	NE	NE	NE	646	NE
CMCP1	.10	8.8	5.5	3.3	4.7	6.7	39	75	100	254	595	100
CMCP1	.15	6.9	3.1	2.8	7.4	NE	NE	NE	NE	NE	668	NE
CMCP1s	.15	8.3	4.1	2.2	7.5	5.1	40	57	61	340	NE	100
Dairy wastes:	1.0	0.0				0.1		<u>.</u>	•	0.0		100
DIAC	.20	74	3.0	20	40	49	4	62	97	423	NE	100
DLAC	1.00	6.8	3.2	20	16.2	7.0	8	62	61	324	NE	93
DWHY	20	7.6	27	17	30	40	5	53	67	371	590	100
DWHYP	10	7.3	31	10	40	50	7	96	111	373	NE	100
DWHYP	1 00	73	3.6	1.6	77	A 1	Å	58	60	458	551	07
Gume natural:	1.00	7.0	0.0	1.0	1.1	4.1	0		03	-100	551	31
GG211	10	07	11 0	29	50	23	21	42	70	240	644	00
GG211D	10	9.7	61	2.0	61	4 1	24	53	70	201	457	90
GG/16	.10	70	0.1	40	57	NE	NE	NE	NE	201	662	NE
GG416	10	0.5	54.6	4.5	12.1	23	22	44	51	233	536	03
GG410	10	9.0	54.0	9.4	12.1	2.0	NE	NE	76	250	NE	100
Wood-related products:	.10	7.0	0.4	£. 4	4.2	14			70	000		100
HOWW	10	77	28	1 4	24	21	20	41	100	347	NE	90
	10	76	2.0	1.4	37	2.1	20	47	79	363	NE	100
	.10	7.0	2.0	20	10.0	16.0	60	1/ NE	10	370	NE	100
LACOT	.00	7.1	9.9	0.0	10.9	10.0	50			040	700	100
	.10	7.0	0.4	2.1	0.9	12.0		64	115	240	700	100
LASSI	.20	7.3	3.5	2.3	9.4	INE	49	INE	115	340	INE E 4 E	100
	.50	7.3	3.2	1.8	11.4	0.1	30	54	54	292	545	100
LUASET	.10	7.4	2.8	2.8	0.3	15.0	54	83	95	289	080	100
	.20	7.8	3.1	NE	7.2	NE	NE	NE	NE	299	475	100
	.24	7.6	3.1	1.4	8.7		NE	NE	83	259	459	100
	.50	8.1	5.8	2.8	21,2	NE	NE	NE	100	394	NE	100
LCSG4s	.45	7,4	4,1	2.8	24.0	NE	NE	NE	49	416	NE	100
LES12	.10	7.6	2,9	1.7	3.4	8.6	32	79	97	401	NE	100
LEST2	1.00	7.4	5.9	3.1	30.7	NE	NE	NE	65	506	NE	100
NNFS6s	.30	7.1	3.2	2.1	16.9	NE	NE	NE	100	456	NE	67
NNFS6s	.40	6.8	4.6	3.5	24.5	24.8	128	150	NE	352	NE	53

Table 3.-Physical properties of pellets made with different binders

See footnotes at end of table.

Binder		Pellet	Wet	Pellet compressive strength, lb per pellet								900° C
Type and code	Pct	water,	drop				at firing to	emperatu	res			survival,2
		pct	number	25° C^1	105° C	300° C	500° C	700° C	900° C	1,200° C	1,250° C	pct
Starch copolymers:								~~~~~				
PSAGA	0.50	12.7	5.8	1.0	1.0	NE	NE	NE	NE	63	262	100
PSAGJ	.20	9.2	5.0	2.8	3.7	NE	NE	NE	NE	204	608	100
Starches:												
SC-AGs	.25	7.3	3.3	2.4	14.9	10.5	34	67	98	382	NE	100
SC-AGs	.53	7.3	4.2	4.0	33.5	NE	NE	NE	NE	303	708	NE
SC-APs	.23	7,7	3.4	2.1	13.3	9.1	NE	NE	80	375	NE	100
SC-D06	.10	7.6	2.9	1.8	3.1	NE	32	NE	108	294	716	100
SC-D06	.30	7.6	3.3	1.7	6.3	NE	NE	NE	109	335	728	100
SC71	.10	8.1	3.2	2.0	5.8	NE	30	71	116	394	NE	100
SC71	.30	8.0	2.9	2.0	6.5	NE	NE	NE	69	258	621	100
SC806	.10	7.5	3.2	2.2	3.2	NE	NE	NE	112	444	NE	100
SCGCTS	.10	6.9	3.6	3.8	9.0	12.1	57	96	135	310	776	100
SCGIA	.10	7.9	3.6	2.1	5.2	5.8	17	76	94	385	NE	100
SCGW08	.10	8.2	4.0	2.0	7.6	NE	29	63	114	359	NE	100
SCGW09	.10	7.8	3.6	1.7	5.0	NE	NE	NE	90	325	NE	100
SPGC10	.15	8.6	3.2	1.4	5.4	NE	NE	NE	58	235	598	100
SPGC10	.30	8.3	9.4	2.5	23	NE	NE	NE	63	238	679	100
SPGS14	,10	7.8	3.2	1.9	4.2	NE	NE	NE	89	373	NE	100
SWCGP	.10	8.1	3.5	1.6	5.9	9	35	69	145	278	729	100
SWCGP	.20	8.6	4.2	1.6	9.4	NE	NE	NE	74	307	673	100
SWG20	.10	6.6	4,4	3.3	11.3	23.2	88	120	185	444	NE	100
SWG20	.30	7.7	10.4	5.2	41.8	20.7	74	121	217	274	647	100
SWG30	.10	7.9	3.2	1.8	3.5	3.8	28	42	85	325	656	100
SWG70	.10	8.5	3.5	1.7	4.0	4.0	32	36	73	276	610	100
SWG70	.20	8.4	4.5	2.6	13.9	7.4	45	58	90	379	NE	100
SWG70	.30	8.4	6.2	2.7	28.6	7.9	37	57	104	338	731	100
SWG70F	.20	10.0	5.8	1.4	6.5	NE	NE	NE	50	205	461	100
SWGP3	.10	8.4	3.4	1.7	4.5	NE	NE	NE	59	257	679	100

Table 3.-Physical properties of pellets made with different binders-Continued

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NE Not evaluated. ¹Wet pellets, ²Percentage of nonbroken pellets after wet pellets were thermally shocked at 900° C for 30 min.

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Dairy Products

Pellets made with 0.2 pct lactose (DLAC) and whey (DWHY) or 0.1 pct whey permeate (DWHYP) did not meet the target value for the drop number, and DWHY did not meet the dry compressive strength target. At the 1-pct binder level, DLAC still did not meet the target drop number but DWHYP did. Whey permeate contains more carbohydrates and fewer proteins than lactose, which may be related to its better results. Whey permeate powder picked up moisture from the air more readily than the other dairy products did, forming hard lumps when exposed to air. This may be another reason why 1 pct DWHYP performed better as a binder. With these dairy products, the dosage level had a more pronounced influence on the dry strengths than on the drop numbers. In general, this was true for all binders having negative **PWAT** values.

Natural Gums

With the guar gum (GG) binders, it was easier to make pellets with higher moisture contents, and consequently, the drop numbers were higher. The guars also had high viscosities, which appear to be indirectly related to the high pellet drop numbers. Guar gum 211D was more dispersible than guar gum 211 but hydrated more slowly. When pellets were made with guar gum 211, it was possible to add more water during the pelletizing procedure, which resulted in higher drop numbers.

Xanthan gum (GX) produced pellets with lower green properties than guar gum pellets. The guar gums had higher slurry viscosities at the 1-pct-solids level and higher adhesive tensile strengths. In general, the experimental results suggest that pellet drop numbers and dry compressive strengths are interrelated with binder slurry viscosities and adhesive strengths, respectively.

Wood-Related Products

With hemicellulose (HC) binders, more than 0.1 pct binder was needed to obtain the drop and dry compressive strength target values. Increasing the dosage levels resulted in a greater relative increase in the dry compressive strength than in the drop number. Lower drop numbers were obtained with all organic binders that had low PWAT values (<500). In general, relatively low drop numbers were also obtained with organic binders that had low viscosities (<75 cP at 6 pct solids).

At the 0.1-pct dosage level, the target drop numbers were also not obtained with the lignin sulfonates (LA's and LC's), but the target dry compressive strengths were obtained. Both the hemicellulose and the lignin binders resulted in pellets with low drop numbers when the binder was added in either the wet or dry form. Naphthalene sulfonate (NNFS6s) slurry was the most effective in this group.

On a comparative dosage level, the drop numbers of pellets made with caustic leonardite (LEST2) were not as

good as those made with the CMC or guar binders but were better than those made with dairy products. Leonardite binder produced pellets with a higher dry compressive strength than did bentonite; however, the drop numbers were lower than those obtained with bentonite.

Starch Acrylic Copolymers

Polymeric starch acrylics (PSA's) produced green pellets that met the target drop numbers, but the pellets had extremely low dry compressive strengths. The low compressive strength values were probably related to the extremely high PWAT values (>10,000). The high expansion of these superabsorbents in wet ore and the corresponding large binder shrinkage during the drying operation may be one reason for the low dry compressive strengths of these pellets.

Starches

At the 0.1-pct dosage level, the target drop number was not met with dextrin (SC-D06) and nongelled starches (SC71 and SC806). This was also true at dosage levels less than 0.3 pct using starches containing alkali (SC-A's). These data were in agreement with results using the dairy and wood-related products, which showed that binders with low PWAT (<100) and low viscosity (<75 cP at 6 pct solids) values resulted in pellets with correspondingly low drop numbers. The highest dry compressive strengths of pellets with these binders were obtained with the alkali starches (SC-A's), which also had the highest adhesive strengths of the low-viscosity binders.

With gelled corn, potato, or wheat starches, the target drop number and dry compressive strengths were generally reached at the 0.1-pct binder dosage level. These starches had PWAT values greater than 500 and slurry viscosities greater than 75 cP at 6 pct solids. Similar results were obtained with the combined gelled corn and wheat starch (SWCGP).

Since starch is added in some flotation circuits before the concentrate is filtered, an alternate pelletizing procedure was also used with one of the starches. Rather than starting with a dry binder and dry concentrate, the dry gelled wheat starch (SWG70) was added to a concentrate slurry, the slurry mixture filtered, and the filter cake pelletized. These pellets had a slightly higher moisture content and thus a higher drop number, but the dry pellet compressive strength was lower because some of the starch was lost in the filtrate. These results are evident from the binder data coded SWG70F in table 3.

FIRED PELLET PROPERTIES

Compressive Strength and Thermal Shock

The temperature dependence of the pellet compressive strength was determined by exposing the wet pellets to temperatures above 105° C. The pellet compressive strength generally increased as the firing temperature was increased, as is evident by the results shown in figure 5 and table 3. With some organic binders (guar gum and hemicellulose at the 0.1-pct dosage level), a local minimum in the pellet compressive-strength-versus-temperature curve was obtained at about 300° C. A minimum in the pellet compressive strengths at this approximate temperature has been observed by Goksel (9).

The fully fired $(1,200^{\circ} \text{ C} \text{ unless otherwise noted})$ target compressive strength for pellets made from organic binders was defined in this report as ≥ 300 lb per pellet. The compressive strength was 170 and 527 lb with 0.5 and 1 pct bentonite, respectively (table 3). These results show that increasing the quantity of bentonite increases the fired strength. Western bentonite contains sodium aluminum silicates and the fusion of this material with iron oxide particles can result in stronger pellets.

The fired target strength was usually met with pellets fired at 1,200° C and made with 0.1 pct organic binders. The binders that contained the most alkalies (Na plus K) generally had the highest strengths; alkali compounds are known to have low melting points, which aid in increasing the sintering strength of pellets. The reason why the pellets made with the PSA binders had low fired strengths was probably related to the high degree of binder swelling. The swelling probably physically moved the iron oxide particles apart, retarding the oxide sintering reactions. With some of the binders, the percent of moisture in the pellet was higher (>9 pct), and this also resulted in weaker fired pellets.

When the target fired strengths were not obtained with some of the binders at the 0.1-pct or higher dosages level, the firing temperature was increased to $1,250^{\circ}$ C. The target strength was then reached with all binders except the starch acrylic copolymer (PSAGA) at a dosage level of 0.5 pct.

The shock survival tests were conducted by inserting wet pellets into a preheated muffle furnace for 30 min at different temperatures and determining the number of unbroken pellets (survivors). Essentially, no pellet breakage was observed at temperatures up to and including 700° C, but at 900° C, some pellets made with organic binders did not survive (table 3). The percentage of pellet survivors decreased as the binder percentage increased. In general, at the 0.1-pct binder dosage level, breakage was observed when the pellets were made with hemicellulose, guar gum, naphthalene sulfonate, or when sodium carbonate or chloride was added to CMCH. With the other binders at this dosage level, all pellets survived the shock temperature test at 900° C. The breakage of the pellets may be attributed to the formation of gaseous products from the combustion of the organics. It is presumed that these gases and the water vapor could not escape fast enough relative to their production rates without building up high internal gas pressures in the pellet. This could especially have been the case with the guar gum binders. They have relatively high viscosites, which could slow down the mass transfer rate of the gases.

Reduction Kinetics

Pellets made with organic binders and fired at 1,200° C had higher reduction rates than those made with 1 pct bentonite. The highest rate at 40-pct reduction (R_{40}) was obtained with pellets made with no binder (table 4). Increasing the firing temperature of the pellets from 1,200° to 1,250° C increased the fired strength of the pellets, but the R_{40} decreased. Pellets made with organic binders and fired at 1,250° C generally had R_{40} values that were higher than those of the 1-pct bentonite pellets fired at 1,200° C (table 4, fig. 6).

The reduction-time dependence data for pellets made with CMC binders fired at 1,200° C are shown in figure 7. It is evident from these results that pellets made with CMC binders reduced faster than pellets made with 1 pct bentonite. When 0.06 pct Na₂CO₃ was added to 0.15 pct CMCH binder, the reduction rate decreased, which suggests that sodium carbonate is a detrimental additive (table 4, binder CMCHOO). The reduction rates of pellets made with all the other organic binders were also higher than the rate of pellets made with 1 pct bentonite (table 4, figs. 8-9). With guar gum binders, a weight gain (decreasing reduction percentage on figure 8) occurred after 4 h of reduction. This suggests that perhaps a carbon deposition reaction (26) occurred with these binders.

The higher reduction rate for organic binders, as compared with bentonite, was probably related to pellet porosity. The open pore porosity, as measured with a mercury porosimeter, was over 23 pct for pellets made with 0.1 pct organic binder but was only 22 pct for pellets made with 1 pct bentonite (table 4).

Low-Temperature Reduction Disintegration

The target for RDI was arbitrarily defined in this paper as ≥ 89 pct for the +6.3-mm size (coarse particles) and ≤ 9 pct for the -0.5-mm size (fines). These target levels were inferior to the values obtained with the 1-pct bentonite binder but were superior to those obtained using pellets made with no binder (table 4). At the 0.1-pct binder dosage level, most of the CMC's and starches met the target level. Most disintegration was generally obtained from pellets with the lowest fired strengths. Pellets made with 1 pct bentonite binder had less disintegration, which may be attributed to fusion of the iron oxide particles with the bentonite.

Softening Properties of Reduced Pellets

Softening temperatures were determined only with pellets made with either 1 pct bentonite, 0.1 pct gelled starch (SWG70), or 0.1 pct CMC (CMCH). These binders were selected because (1) when the dairy, wood-related, and nongelled starch binders were used, the pellets did not meet the target physical properties, and (2) the guar gum binders did not meet the target shock temperature and

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Figure 5.-Effect of temperature on compressive strength of pellets made with 0.1 pct organic binder or 1 pct bentonite.

TEMPERATURE, °C

Table 4.-Metallurgical properties of pellets

Binder			t/min ¹	t ₉₀ ,	min ²	RDI,	pct ³	Porosity,
Type and code	Pct	1,200° C	1,250° C	1,200° C	1,250° C	+6.3 mm	-0.5 mm	pct
Target	≤0.20	≥0.50	≥0,50	≤250	≤250	≥89.0	≤9.0	≥23.0
None	.00	.80	.69	150	178	82.0	11.5	25.6
Bentonite:	.00	,			110		11.0	20.0
BEN17	50	56	35	206	260	00.8	34	
BEN17	1 00	.50	.00	250	203	02 1	26	21.0
Celluloses	1.00	.40	.01	LUL	200	30.1	2.0	21.9
Centrioses.	10	NE	50	NE	010	00.0	0.0	00.0
	.10	NE	.50		210	90.9	8.8	23.2
	.15	.83	.46	163	241	NE	NE	28.0
CMCHOO	.21	.59	.40	204	261	NE	NE	NE
CMCHOL	.21	.72	NE	174	NE	NE	NE	25.0
CMCP1	.10	.71	NE	178	NE	91.3	7.2	24.9
Dairy wastes:								
	.20	NE	NE	NE	NE	87.2	7.1	NE
DLAC	1 00	73	NE	163	NE	86.2	75	NE
DWHYP	1.00	59	NE	106	NE	89.0	6.4	NE
Gump paturali	1.00	.00		130		00.0	0.4	
Goott	10	NIC	40	NIT.	000	04.0		A 100
00211	.10		.48	NE	222	84.2	9.1	NE
GG211	.30	NE	.59	NE	194	85.8	7.4	NE
GG416	.10	.53	NE	202	NE	87.4	4.5	NE
Wood-related produ	cts:							
HCSWs	.50	.69	NE	178	NE	90.9	6.1	NE
LASST	.10	NE	NE	NE	NE	90.2	6.4	NE
LCASFs	.50	.74	NE	167	NE	89.7	6.8	NE
LCASET	.10	NF	NE	NF	NE	88.3	7.4	NE
10862	50	70	NE	201	NE	NE	NE	NE
LEGT2	10	69	NE	100	NE	94.5	9.4	NE
	1.00	.00	NE	102		04,5	0,4	
	1.00	10.	INE	190	INE		NE	NE
ININPODS	.40	80,	NE	178	NE	93.7	2.9	NE
Starches:								
SC-AGs	.25	.58	NE	199	NE	93.2	3.8	NE
SC-AGs	.23	.61	NE	196	NE	NE	NE	NE
SC-D06	.30	.73	NE	161	NE	NE	NE	NE
SCGW08	.10	.74	NE	160	NE	93.0	4.0	NE
SCGW09	.10	.77	NE	149	NE	NE	NE	NE
SCGCTS	.10	70	NF	174	NF	ŃE	NE	NE
SPG100	.30	70	NE	167	NE	NE	NE	NE
SWCGP	10	73	NE	167	NE	NE	NE	NE
SWCGP	.10	.70	NE	107			NE	07.0
	.20	./9		103				27.9
30020	.10	10,	NE	199	NE	89.2	3.0	23.6
SWG20	.30	.75	.51	170	240	90.9	3.6	NE
SWG30	.10	.70	NE	165	NE	NE	NE	NE
SWG30	.30	.76	.45	163	225	NE	NE	NE
SWG70	.20	.65	NE	179	NE	93.1	5.9	26.2
SWG70	.30	.73	NE	162	NE	92.0	5.7	NE

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NE Not evaluated. ¹Reduction rate at 40-pct reduction. ²Time required to obtain 90-pct reduction. ³Pellets fired at 1,200° C.

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Figure 6.-Dependence of reduction rate on firing temperature of pellets made with different binders.



Figure 7.—Reduction rate comparisons of pellets made with carboxyl methyl cellulose (with and without soda ash) and bentonite binders.



Figure 8.--Reduction rates of pellets made with guar gums, starches, and bentonite binders.



Figure 9.-Reduction rates of pellets made with slurried organic and dry bentonite binders.



Figure 10.—Temperature dependence of bed shrinkage and gas pressure drop of pellets with different binders. (Duplicate tests were conducted with bentonite.)

fired compressive strength values at 1,200° C. The results (fig. 10) indicate that comparable pellet bed shrinkage was obtained over the entire temperature range tested with either bentonite or organic binders. Duplicate tests with bentonite were conducted, and good repeatability was obtained. For these binders, the pellet shrinkage below 55 pet is not a sensitive indicator of the pellet performance in

the blast furnace. However, the gas pressure drop data were different. From the pressure-temperature data, the softening temperature was calculated and was found to be about 30° higher for pellets made with organic binders than for those made with bentonite. High softening temperatures are preferred in ironmaking operations (27).

SUMMARY AND CONCLUSIONS

Over 30 different organic binders were evaluated for agglomerating iron ore concentrate. The binders were divided into groups. The most effective groups in order of decreasing green pellet physical properties were natural gum (guar), CMC, and gelled starch. The less effective binders were dextrin, nongelled and alkalized starches, starch acrylic copolymers, wood-related products, and dairy products. The most effective organic binders for producing pellets with physical properties exceeding the minimum target values had medium PWAT values (>500 and <10,000) in distilled water, high slurry viscosites (>75 cP at 6 pct solids), and high adhesive tensile strengths $(>4 \text{ kg/cm}^2)$. Pellets made with 0.1 pct of binders with these characteristics generally met the target drop number and dry compressive strength values; the only binders that failed were the starch acrylic copolymers, whose PWAT values were over 10,000. These copolymers were the most

sensitive to the type of water used. In general, binders with high PWAT values were the most sensitive to the cation content of the water.

When wet pellets were shock temperature tested by being heated rapidly to 900° C, generally the only pellets that did not meet the target value were those made with 0.1 pct guar gum or hemicellulose and with 0.15 pct CMCH when 0.03 pct Na₂CO₃ or NaCl was added. With the other binders, essentially no breakage or spalling occurred during the shock temperature tests.

The 1,200° C target fired compressive strength was usually met by all the pellets made with 0.1 pct organic binder; the lowest compressive strengths were obtained with guar gum. At higher dosages, a firing temperature of 1,250° C was sometimes required to reach the target compressive strength value. For organic binders with little or no alkali, the fired strength decreased with increasing binder addition; a slightly higher induration temperature can compensate for this decreased strength.

Slightly more reduction disintegration occurred for pellets made with organic binders than for those made with bentonite, but CMC, and gelled starch binders met the minimum target disintegration indices.

The addition of sodium carbonate to CMC binder decreased the reduction rate of the pellets. The rate for all organic binder pellets was higher than for bentonite pellets. For example, with 0.1 pct CMCH or gelled wheat starch (SWG70), the reduction rate at the 40-pct level (R_{40}) was over 30 pct greater than with 1 pct bentonite.

The softening temperatures for pellets made with these organic binders were also about 30° C higher than with bentonite.

This study shows that the most promising overall binder results were obtained with CMC or gelled starch binders. Even though the pellets made with gelled starch had slightly lower drop numbers than those made with CMC, the starch's lower price appears to make it more cost effective. Gelled starch costs more than bentonite, but the pellets have superior metallurgical properties. Large-scale testing will be required to confirm these laboratory results.

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