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REPORT OF INVESTIGATIONS/1991

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Influence of Reducing Conditions on the Softening-Melting Characteristics of Taconite Pellets

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

UNITED STATES DEPARTMENT OF THE INTERIOR



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**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | | | |
|-------------------|---------------------------|---------|---------------------------|
| °C | degree Celsius | m | meter |
| °C/min | degree Celsius per minute | min | minute |
| cm | centimeter | mm | millimeter |
| g | gram | mm Hg | millimeter of mercury |
| g/cm ³ | gram per cubic centimeter | mt | metric ton |
| h | hour | pct | percent |
| kg | kilogram | pct/min | percent per minute |
| kPa | kilopascal | rpm | revolution per minute |
| kPa · °C | kilopascal degree Celsius | SLM | standard liter per minute |
| lb/p | pound per pellet | | |

INFLUENCE OF REDUCING CONDITIONS ON THE SOFTENING-MELTING CHARACTERISTICS OF TACONITE PELLETS

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

ABSTRACT

The U.S. Bureau of Mines is investigating ways of enhancing the high-temperature softening-melting (HTSM) properties of domestic taconite pellets. These properties, which are important for determining the performance of pellets in blast furnaces, include pellet bed contraction, pressure drop, S-value (area under the pressure-temperature curve), and softening and metal-slag drainout temperatures. Experiments showed that HTSM properties were related to the physiochemical properties (fired strengths and reducibilities) of pellets containing different levels of limestone and dolomite flux. Flux additions resulted in slightly lower green and fired pellet strengths, but improved metallurgical properties, such as reducibility. The influence of reduction conditions on HTSM properties was evaluated by varying the pellet metallization starting temperature and the carbon monoxide content of the CO-N₂ gas mixture. HTSM property change was more sensitive to flux addition levels when metallization was initiated at 1,100° C with 20 pct CO in the gas stream. The S-value and the metal-slag drainout temperature were found to be the best criteria for characterizing HTSM properties. The optimum flux addition level was about 8 pct (4 pct dolomite, 4 pct limestone) or a basicity of about 1. At higher flux levels, a higher metal-slag drainout temperature was obtained.

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INTRODUCTION

As part of the U.S. Bureau of Mines program to make better use of the Nation's resources, it is investigating different technology options that will produce superior domestic iron oxide pellets. Historically, about 95 pct of the domestic iron ore pellet production has been in the Lake Superior Region. In 1989, the total domestic production was an estimated 59 million mt (1),⁴ of which Minnesota supplied about 70 pct (41 million mt) (2). This Minnesota taconite pellet production level is considerably lower than the highest level (54 million mt), which occurred in 1979 (3). Part of this decrease is due to the increase in the quantity of foreign imports. In 1989, 24 pct of the iron ore was imported (1). Importation of superior low-cost foreign ore is one of the greatest threats to the domestic iron ore mining industry. To offset foreign competition, improved innovative technologies must be developed for enhancing domestic competitiveness by producing superior pellets at lower costs.

One means of enhancing the pellet metallurgical performance in the blast furnace is by incorporating basic materials (flux) such as limestone, and/or dolomite, into the pellet mix. Several investigators (4-9) have reported that fluxed pellets have higher reducibility and superior high-temperature softening-melting (HTSM) properties. Kobe Steel, Ltd., has used HTSM properties for characterizing pellets used in its blast furnaces (10).

Blast furnace operators prefer iron oxide feed materials that have a high reducibility, high softening temperature,

and a melting or drainout temperature slightly higher than the softening temperature (4). However, most mineral mixtures have a large (>100° C) interval between the softening and drainout temperatures. Feed materials that have a large temperature interval produce a thicker cohesive layer within the blast furnace. The upper boundary of the cohesive layer is related to the pellet softening temperature and the lower boundary layer to the drainout temperature of the metal and slag. Greater furnace productivity is obtained with thinner cohesive layers, which usually result in higher gas permeabilities and faster, more uniform downward flow rates of the burden.

A comprehensive literature review (11) indicated that the HTSM properties of pellets have been studied under different experimental conditions, but the importance of these conditions is not well known. Some investigators metallize the pellets above 1,000° C with 30 pct CO in nitrogen, while others use 100 pct N₂ and depend on coke to reduce the iron oxide (11). Clixby (5) reported using 40 pct CO to metallize the pellets above 950° C.

This research was initiated to delineate the influence of some of the experimental blast furnace variables on laboratory HTSM properties of taconite pellets. The goals were to (1) investigate the influence of the starting metallization temperature, the carbon monoxide content of the reducing gas, and the flux level on the HTSM indices, and (2) relate these indices to the physical and chemical properties of the pellets.

MATERIALS

The raw materials consisted of taconite concentrate, bentonite, dolomite, limestone, and coke. The chemical analyses of these materials are given in table 1. The sulfur content and ash content of the coke were 0.7 and 7 pct, respectively. The taconite concentrate was obtained from the Mesabi Range in northeastern Minnesota. The dry concentrate density was 4.9 g/cm³, and over 60 pct (by weight) of the particles were finer than 500 mesh. The dolomite and limestone were ground to 100 pct minus 200 mesh.

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

Table 1.—Partial chemical analyses of dried raw materials, percent

| | Taconite | Bentonite | Dolomite | Limestone |
|--|-------------------|-------------------|----------|-----------|
| Fe ^T | ¹ 65.2 | 2.6 | 0.1 | <0.1 |
| SiO ₂ | 5.6 | 63.6 | .2 | .5 |
| Al ₂ O ₃ | <.4 | 20.4 | <.4 | <.4 |
| C | <.3 | .9 | 9.9 | 9.7 |
| CaO | <.5 | 1.2 | 31.4 | 51.9 |
| K | <.10 | .3 | <.1 | <.1 |
| MgO | .5 | 2.5 | 24.6 | .5 |
| Na | .1 | 1.2 | <.05 | <.05 |
| P | <.05 | <.05 | <.05 | .29 |
| S | .01 | .16 | .01 | .06 |
| LOI at 1,000° C ... | -1.7 | 5.9 | 47.3 | 43.2 |
| Fe ^T Total iron. | LOI | Loss on ignition. | | |
| ¹ 21.8 pct ferrous content. | | | | |

EXPERIMENTAL PROCEDURES

A detailed description of the pellet evaluation procedures was reported in previous Bureau publications (12-13), and only the general procedures are described in this report.

PELLET PREPARATION AND PHYSICAL TESTING PROCEDURES

The pellets were prepared by a laboratory batch pelletizing process. Three kilograms (dried equivalent weight) of concentrate was reslurried in distilled water and then filtered. The filter cake was blended for 15 min in a mix-muller while 1 pct bentonite and the other additives were slowly added. About one-tenth of this blended mixture was initially sprinkled into a 0.4-m-diam pelletizing disk rotating at 50 rpm to form seed pellets. Water was sprayed on the seed pellets and more blended mixture was added, as needed, to build up the pellet size. When the pellets reached about 11-mm-diam size, they were removed and the undersize was returned to the disk. The pelletizing procedure was continued until all the blended mixture was added. Only pellets in the size range of minus 13-mm- and plus 11-mm-diam were used in this research.

Immediately after the pellets were made, the average drop number of 20 wet pellets was determined. Also, 20 pellets were dried overnight at 105° C and the dry compressive strength (DCS) was evaluated.

The pellet-firing procedure involved drying about 700 g of the wet pellets at 105° C overnight and then loading them into a fireclay crucible. Numerous 6-mm-diam holes were drilled in the crucible wall to enhance the airflow between the pellets. The loaded crucible was inserted into a preheated muffle furnace for 30 min at 900° C to oxidize the magnetite to hematite, then immediately indurated in a second preheated muffle furnace for 15 min at 1,200° C. Both furnaces had 6 SLM air flowing through them. The hot, covered pellets were cooled in air, and the fired compressive strength (FCS) was determined.

The porosity of the fired pellets was evaluated with a mercury porosimeter at pressures up to 400,000 kPa. The percentage porosity was then calculated from the quantity of mercury that was forced into the open pores.

METALLURGICAL TESTING PROCEDURES

Metallurgical tests were conducted on fired pellets, and these tests consisted of the determination of isothermal reduction rates and HTSM properties. The reduction rates were obtained with a thermogravimetric apparatus described in a previous Bureau publication (14). The tests

were conducted for 6 h at 900° C using 30 pct CO, 0.1 pct H₂, and the balance N₂. The percent reduction was calculated assuming that it was directly proportional to the weight loss of the sample. This was confirmed by chemical analyses.

The HTSM tests were conducted with the equipment shown in figure 1. A cross section of the reactor assembly is shown in figure 2. The reactor tube (99.9 pct alumina) was 10.6-cm OD, 9.8-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, the alumina crucible, and the pellet bed. The preheater contained about 330 g of graphite chips (minus 12 mm, plus 10 mm). The alumina crucible was placed above the preheater to collect the molten pellet products. Above the alumina crucible was a graphite holder that contained a tight-fitting alumina liner (5.7-cm OD, 5.1-cm ID, and 11.0 cm long). The sample bed (6.4 cm high, consisting of about 250 g of minus 11-mm-, plus 10-mm-diam fired pellets) was retained inside the alumina liner. Five-millimeter-thick layers of coke chips (minus 8 mm, plus 3 mm) were placed below and above the pellet bed. A perforated graphite disk (10 holes, 3-mm diam) was placed on top of the layer of coke chips. A graphite foot with four toes was centered above the graphite disk and inside the 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 pressure of 49 kPa on the pellet bed. The thermocouple used for determining the pellet bed temperature was located in the middle of the graphite foot immediately above the pellet bed.

Most HTSM studies (12) have been started with the iron oxide reduced to wustite (Fe_xO, where x = 0.83 to 0.95) at 1,000° C. In this study, the maximum premetallization temperature was adjusted to stay in the wustite zone. This maximum premetallization temperature was 1,000° C initially, but later was increased to 1,100° C. (The reason for this change is explained later in the text.) The conditions with the 1,100° C maximum premetallization temperature are shown by the dashed line A-B-C in figure 3 (15). The furnace was loaded and heated overnight to 750° C with 100 pct N₂ at 8 SLM (figure 3, point A). The furnace temperature was then increased at 3° C/min to 1,100° C (line B-C), with a gas flow of 25 SLM consisting of 24 pct CO, 16 pct CO₂, and 60 pct N₂. After 1,100° C was reached, the wustite metallization period (line D-E) was started by changing the gas to preselected percentages of carbon monoxide in nitrogen and decreasing the heating rate to 1° C/min. These conditions were maintained until the sample drained out or the test was interrupted at some preselected temperature. The

furnace was then shut off, the gas flow changed to 15 SLM of 100 pct N_2 , and the 49-kPa load removed from the pellet bed. After about 1 h, the nitrogen gas flow was decreased to 8 SLM. After approximately 2 h, the temperature reached about 750° C and the gas was shut off.

After the pellet bed cooled down overnight, the final weight and contraction were measured. Representative portions of the samples were analyzed for chemical and mineral contents. Electron microprobe and X-ray diffraction were used to identify the mineral phases.

The temperature, pellet bed contraction, and gas pressure drop were continuously recorded during the test. The pressure drop was measured with both a pressure gauge and a pressure transducer. The pressure tap was located at the bottom of the pedestal (figs. 1-2). The exhaust gas was assumed to be at atmospheric pressure. The overall pressure measurement error for both these instruments

was less than 1 pct. The contraction of the pellet bed was measured with a displacement transducer and a standard depth dial indicator. The contraction value included the total thermoelongation and contraction of the pellet bed as well as that of the bottom and top support columns. The overall measurement error of each of the contraction values was less than 1 pct.

The softening temperature (ST) value was defined as the first major inflection point of the pressure-temperature curve. The drainout temperature (DT) was defined as the temperature at which the pellet bed contraction increased rapidly to nearly 100 pct and the pressure drop decreased rapidly to the softening temperature value. The S-value was defined as the area under the pressure-versus-temperature curve at temperatures between softening and drainout temperatures.

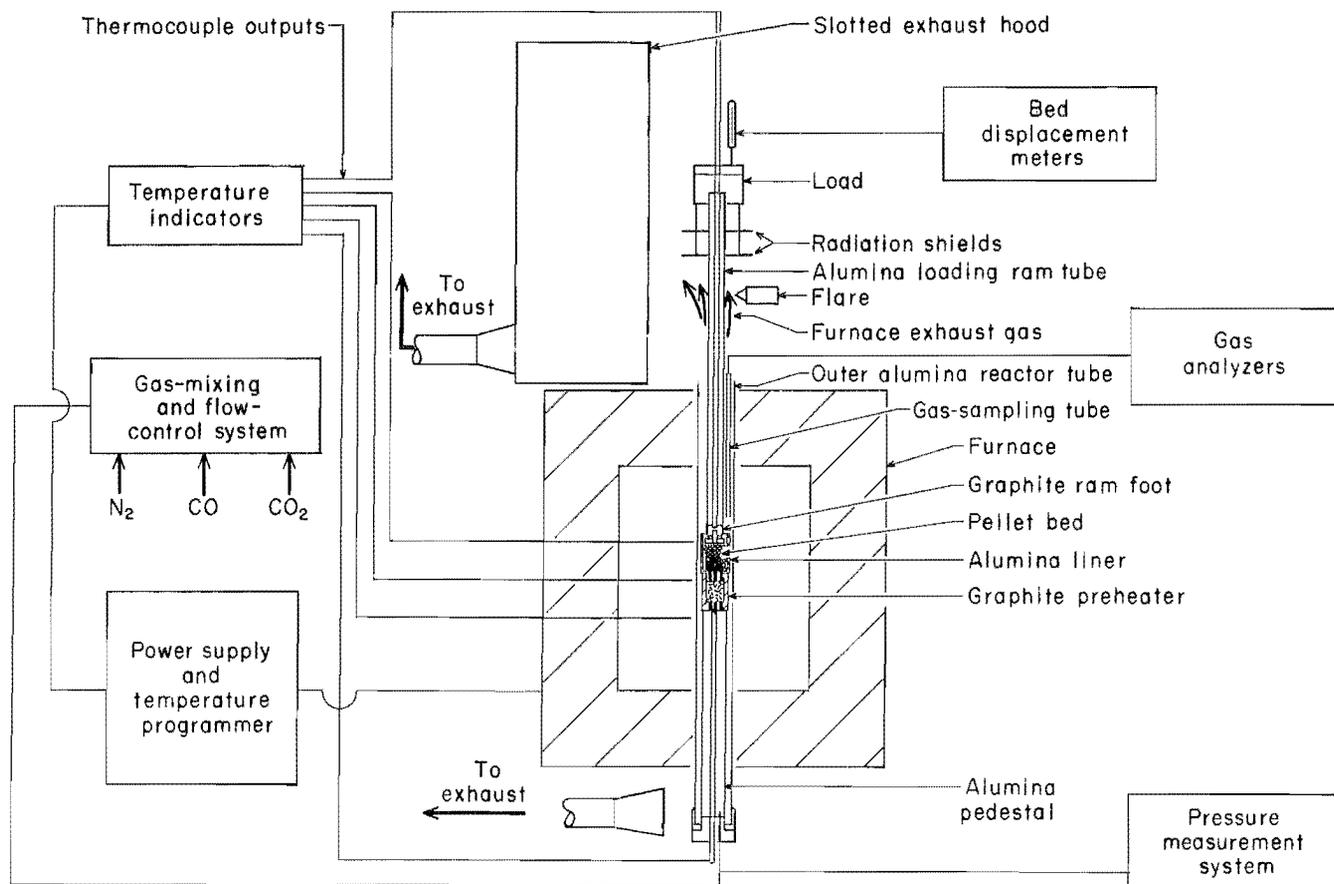


Figure 1.—Schematic of HTSM apparatus.

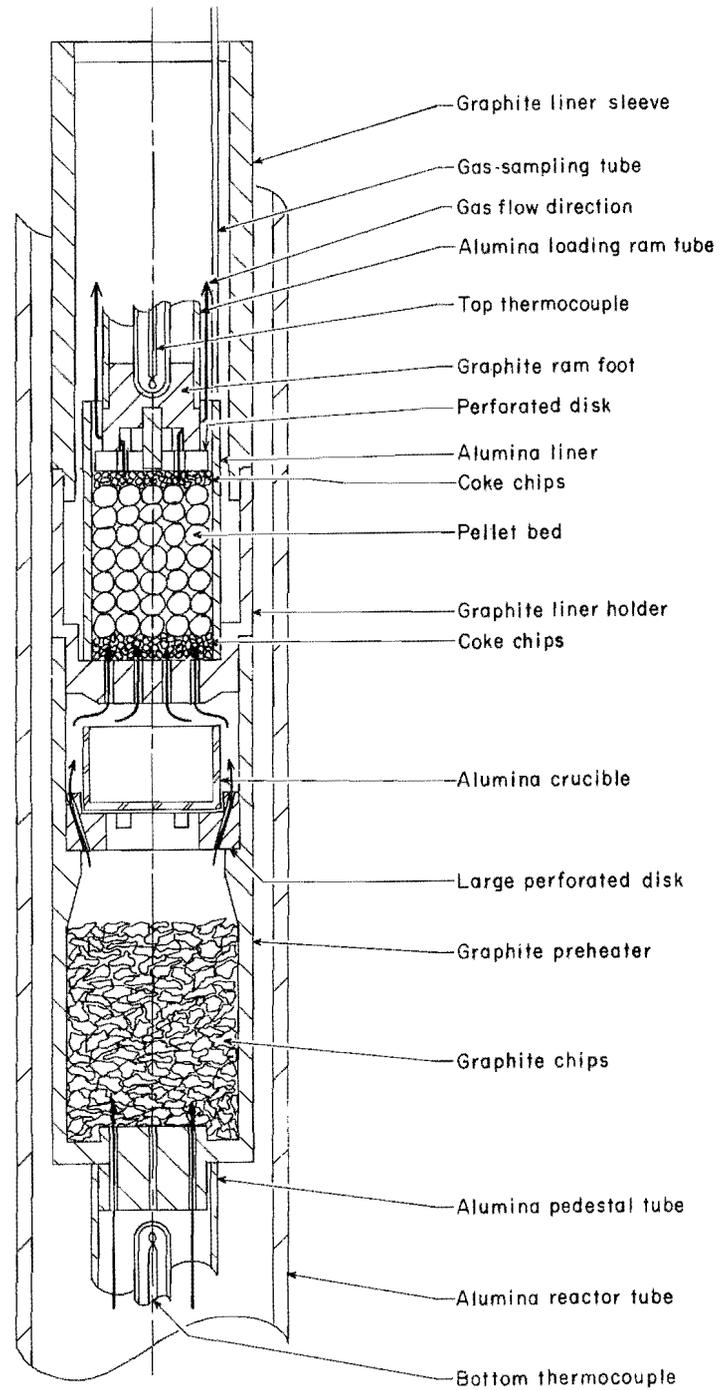


Figure 2.—Cross-sectional view of HTSM reactor section.

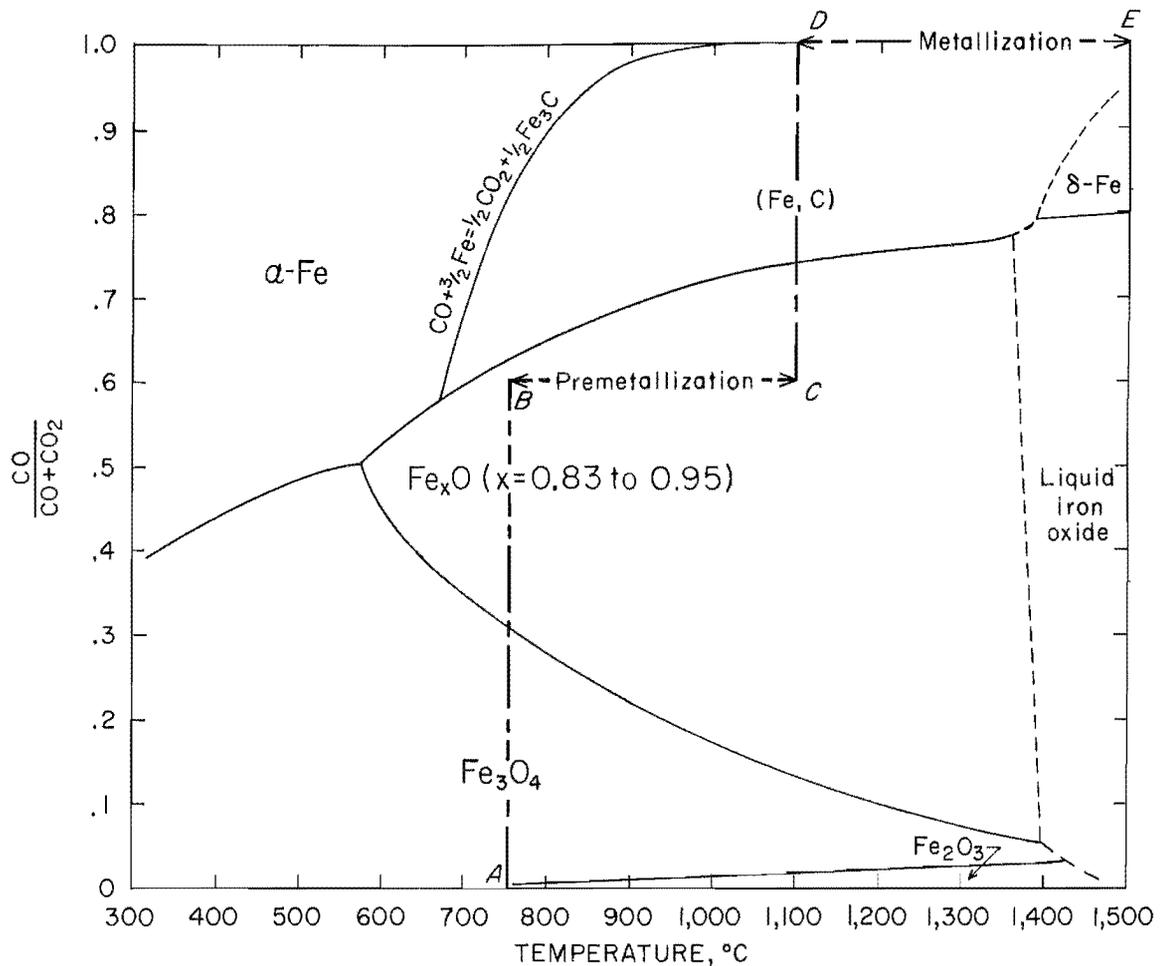


Figure 3.—Equilibrium diagram of Fe-C-O system showing premetallization and metallization conditions. [Adapted from Stephenson and Smailer (15).]

EXPERIMENTAL RESULTS AND DISCUSSION

GREEN PELLET PHYSICAL PROPERTIES

As expected from previous research (6, 12), the average pellet drop numbers were largest with pellets having the highest moisture content. The addition of flux appeared to slightly decrease the average pellet dry compressive strength (table 2).

FIRED PELLET PROPERTIES

Chemical Analyses and Compressive Strengths

The chemical analyses of the fired pellets are given in table 3. Pellets containing dolomite and/or limestone are called "fluxed" pellets, while those without are called "acid"

pellets. The pellet analyses are arranged first in increasing dolomite percentage and second in increasing limestone percentage. The pellet basicity (B) was calculated from the weight ratio of (CaO + MgO) to (Al₂O₃ + SiO₂), which ranged from 0.06 to 1.23. The CaO-to-SiO₂ ratio (C/S) ranged from 0.03 to 1.26.

The ferrous content of fired pellets was less than 0.2 pct when the total flux addition was less than 12 pct, but at the 12 pct level, slightly higher values were obtained. The higher ferrous content may be due to the formation of alkaline earth metal ferrite(s) and/or the endothermic calcination reactions of dolomite and limestone, which may have cooled the pellet sufficiently to retard the oxidation. The flux addition may also have enhanced the high-temperature thermal decomposition of hematite.

The addition of dolomite and limestone (high-melting-temperature oxides) decreased the strengths of the fired pellets. The fired compressive strength of the acid pellets fired at 1,200° C was 630 lb/p, while that of the fluxed pellets averaged only about 450 lb/p (table 2). To

determine the influence of firing temperature on the metallurgical properties, the standard acid pellets were also fired at 1,300° C, and these pellets had a compressive strength of over 1,000 lb/p.

Table 2.—Physical and reduction properties of green and fired pellets

| Additive, pct | | Green properties | | | | Fired properties | | | |
|----------------|-----------|-----------------------|----------|-----------|----------------------|------------------------------------|--|------------------------------------|---------------|
| Dolomite | Limestone | H ₂ O, pct | Drop No. | DCS, lb/p | FCS, lb/p | R _{3h} ¹ , pct | R ₄₀ ² , pct/min | t ₉₀ ³ , min | Porosity, pct |
| 0 | 0 | 8.2 | 9.7 | 25.3 | 630 | 75 | 0.42 | 256 | 22 |
| 0 | 0 | 8.2 | 9.7 | 25.3 | ⁴ > 1,000 | NA | .34 | 288 | NA |
| 0 | 2 | 10.3 | 23.8 | 19.5 | 659 | 86 | .45 | 196 | NA |
| 0 | 8 | 8.1 | 5.3 | 19.2 | 622 | 86 | .49 | 199 | 30 |
| 0 | 12 | 9.5 | >25.0 | 14.3 | 429 | NA | NA | NA | NA |
| 2 | 0 | 9.4 | 22.9 | 19.4 | 242 | 76 | .38 | 242 | NA |
| 2 | 2 | 10.0 | 19.3 | 22.2 | 433 | 96 | .55 | 158 | NA |
| 4 | 2 | 8.1 | 8.2 | 18.7 | 498 | 92 | .74 | 158 | 29 |
| 4 | 4 | 10.4 | 23.9 | 25.0 | 429 | 95 | .56 | 160 | NA |
| 6 | 3 | 7.9 | 7.8 | 21.4 | 460 | 95 | .68 | 145 | NA |
| 6 | 4 | 8.0 | 7.3 | 19.3 | 476 | 96 | .68 | 145 | 30 |
| 6 | 6 | 9.8 | 13.2 | 18.2 | 378 | 97 | .73 | 142 | NA |
| 8 | 0 | 8.6 | 7.9 | 17.8 | 345 | 92 | .88 | 160 | NA |
| 8 | 4 | 8.1 | 5.7 | 17.6 | 470 | 97 | .74 | 149 | 32 |
| 12 | 0 | 9.5 | 23.2 | 16.4 | 423 | NA | NA | NA | NA |
| ⁵ 0 | 0 | 12.5 | 17.7 | 2.0 | 360 | NA | NA | NA | NA |
| ⁶ 0 | 0 | 12.1 | 4.7 | 11.3 | 178 | NA | NA | NA | NA |

DCS Dry compressive strength.

FCS Fired compressive strength.

NA Not available.

¹Reduction after 3 h.

²Reduction rate at 40-pct reduction.

³Time to reach 90-pct reduction.

⁴Fired at 1,300° C.

⁵12 pct Al₂O₃.

⁶12 pct SiO₂.

Table 3.—Chemical analysis of fired pellets

| Additive, pct | | Analysis, pct | | | | | | CaO-SiO ₂ | Basicity (B) |
|----------------|-----------|-----------------|------------------|----------------------|------------------------------------|---------|---------|----------------------|-----------------|
| Dolomite | Limestone | Fe ^T | Fe ²⁺ | SiO ₂ (S) | Al ₂ O ₃ (A) | CaO (C) | MgO (M) | ratio (C/S) | [(C + M)/A + S] |
| 0 | 0 | 63.8 | <0.2 | 6.0 | 0.7 | 0.4 | 0.5 | 0.07 | 0.13 |
| 0 | 2 | 63.7 | <.2 | 6.2 | .5 | 1.4 | .5 | .23 | .28 |
| 0 | 8 | 62.8 | <.2 | 5.6 | .4 | 4.2 | .5 | .75 | .78 |
| 0 | 12 | 60.2 | <.2 | 5.8 | .7 | 7.3 | .7 | 1.26 | 1.23 |
| 2 | 0 | 63.9 | <.2 | 5.8 | .5 | .7 | .8 | .12 | .24 |
| 2 | 2 | 63.0 | <.2 | 6.2 | .5 | 2.4 | .9 | .39 | .49 |
| 4 | 2 | 62.8 | <.2 | 5.8 | .8 | 1.8 | 1.2 | .31 | .45 |
| 4 | 4 | 61.5 | <.2 | 5.8 | .5 | 4.8 | 1.3 | .83 | .97 |
| 6 | 3 | 61.5 | <.2 | 5.8 | .7 | 3.5 | 1.5 | .60 | .77 |
| 6 | 4 | 61.6 | <.2 | 5.6 | .4 | 3.9 | 1.7 | .70 | .93 |
| 6 | 6 | 60.0 | .3 | 5.6 | .7 | 5.6 | 1.7 | 1.00 | 1.16 |
| 8 | 0 | 59.6 | <.2 | 5.3 | .4 | 3.1 | 2.0 | .58 | .89 |
| 8 | 4 | 60.0 | .3 | 5.6 | .6 | 5.2 | 2.2 | .93 | 1.19 |
| 12 | 0 | 60.8 | .2 | 5.6 | .8 | 4.5 | 2.8 | .80 | 1.14 |
| ¹ 0 | 0 | 57.8 | <.2 | 5.6 | 10.0 | .4 | .5 | .07 | .06 |
| ² 0 | 0 | 58.2 | .2 | 14.1 | .5 | .4 | .5 | .03 | .06 |

Fe^T Total iron.

¹12 pct Al₂O₃.

²12 pct SiO₂.

Isothermal Reduction Kinetics

The isothermal reduction kinetics (fig. 4) of both the acid and fluxed pellets were determined at a temperature of 900° C with 30 pct CO and 0.1 pct H₂ in N₂. The relative reducibilities (table 2) were expressed three different ways: percent reduction in 3 h (R_{3h}), percent reduction per minute at 40-pct reduction (R₄₀), and the time to reach 90-pct reduction (t₉₀). In general, all three of these reduction rates indicated that flux additions increased the reduction kinetics.

The increased pellet reducibility with flux addition appeared to be related to the higher porosity of fluxed pellets (table 2, last column). When the fluxes were calcined, the porosity of the pellet increased, which enhanced mass transfer during reduction. The flux additives may also have enhanced the reduction kinetics by reacting with iron oxide and SiO₂ contained in the gangue. The silicon and calcium elemental maps shown in figure 5 are similar, which suggests that a calcium silicate was formed when

limestone and dolomite were added; the light-colored areas indicate that the element is present. If calcium ties up the SiO₂, it is not available to react with the wustite that is formed when the hematite is reduced. The interaction of wustite and SiO₂ can form a low-melting-temperature compound, fayalite (2FeO · SiO₂) (16), which could decrease the pellet porosity and therefore also the reduction rate.

In the unreduced fluxed pellet (fig. 5A), magnesium appeared to be in the same area as the iron, which suggests magnesioferrite (MgO · Fe₂O₃) was present. Magnesioferrite is known to have a reducibility equal to or greater than that of iron oxides (17). With the acid pellets, very little calcium and magnesium were present (table 3), and some iron appeared to be distributed in the silicon phase in the unreduced pellet bed (fig. 6A). This suggests the presence of iron silicate. Figures 5B and 6B indicate that the magnesium is not in the metallic iron phase of the reduced pellet.

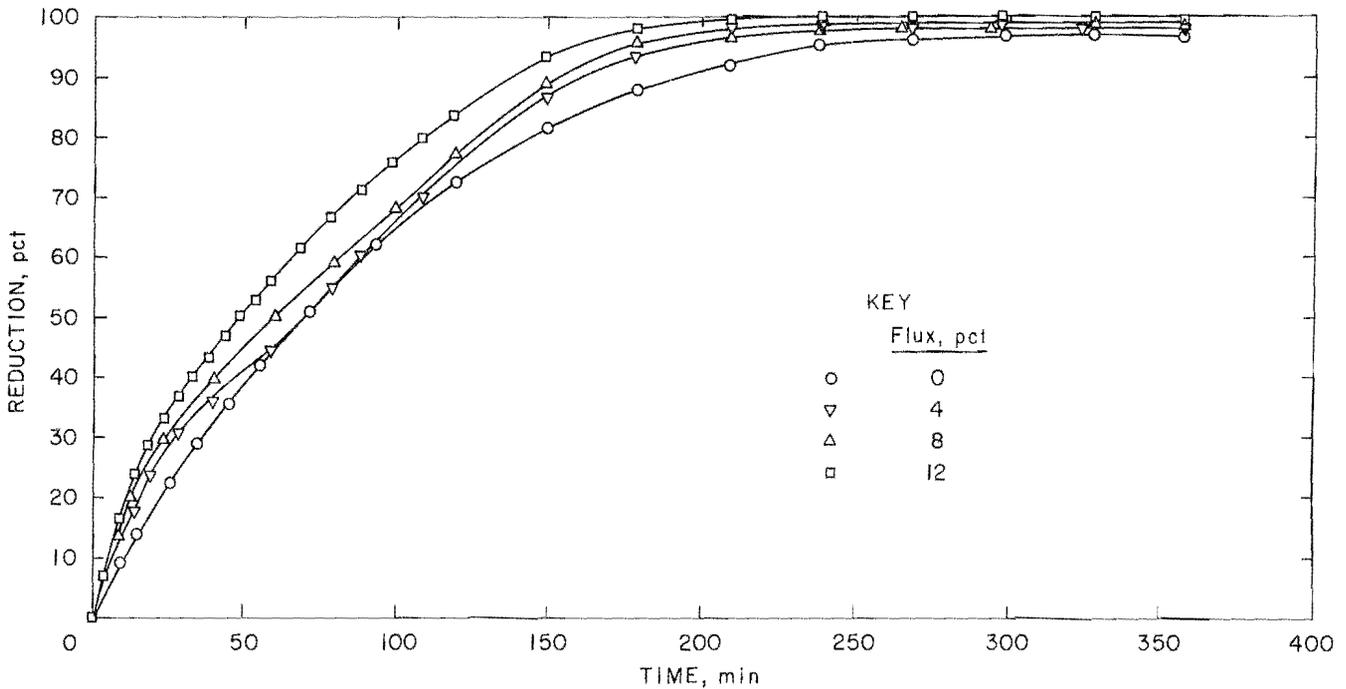


Figure 4.—Influence of flux level on reduction kinetics. (Dolomite to limestone at 1:1 ratio.)

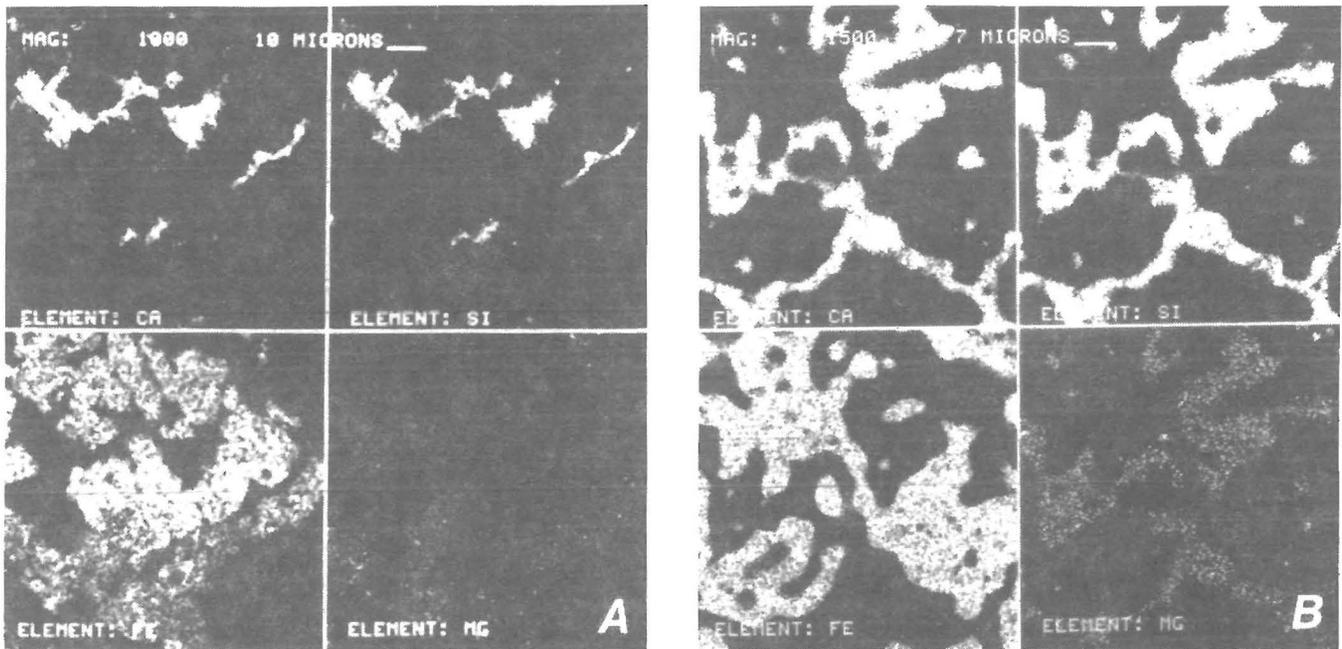


Figure 5.—Electron probe elemental analyses of (A) unreduced and (B) reduced fluxed pellets (8 pct dolomite and 4 pct limestone) (X 160).

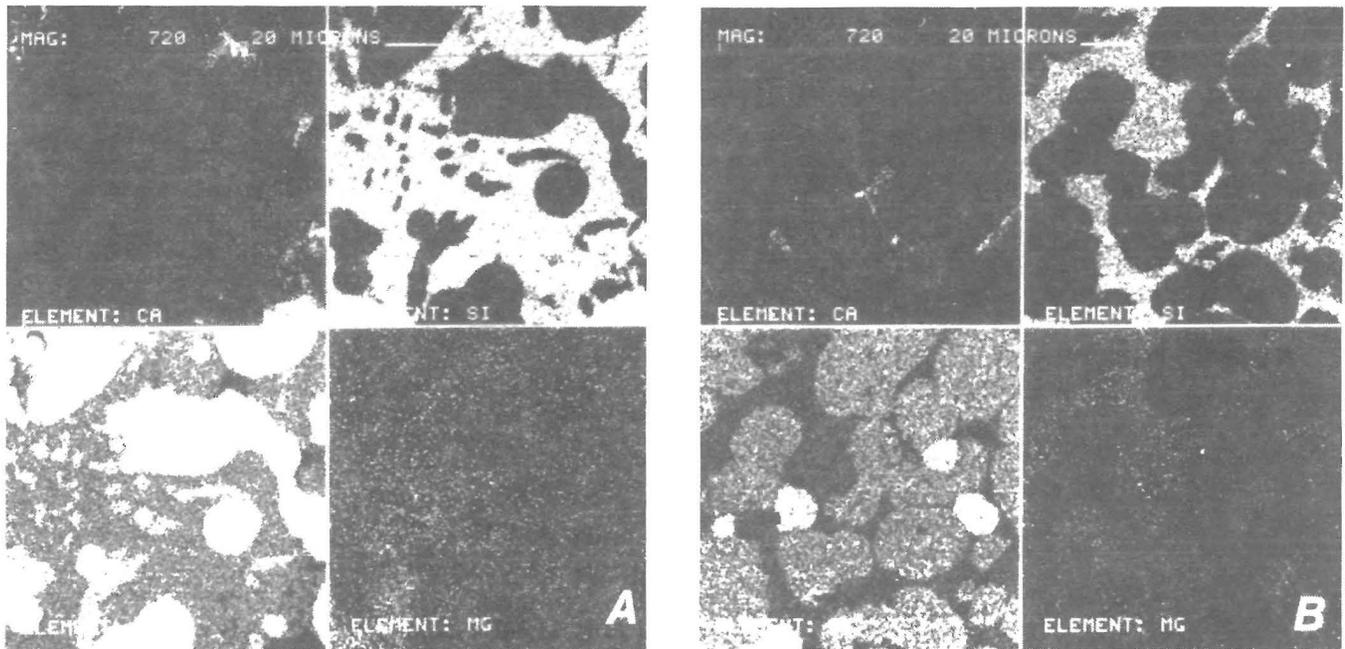


Figure 6.—Electron probe elemental analyses of (A) unreduced and (B) reduced acid pellets (X 160).

HTSM Studies

Premetallization Studies

The initial HTSM experiments (table 4, tests 1-8) were conducted with acid pellets. Test 1 had no metallization period because the premetallization gas composition (24 pct CO, 16 pct CO₂, and 60 pct N₂) was continued up to 1,250° C. At this point, the test was interrupted by shutting off the furnace and replacing the gas with 100 pct N₂. It was evident from the percent reduction, X-ray analyses, and microscopic examination that most of the hematite in the pellet bed had been converted to wustite. This observation was expected because the presence of carbon dioxide at these percentages in the gas mixture is oxidizing to iron at temperatures above 700° C (fig. 3). Some metallic iron (figure 7, light-colored area) was formed, mainly on the top and bottom of the pellet bed where the pellets contacted the coke layers. The fused black area shown in figure 7 appeared to contain fayalite.

Most investigators (11) use a maximum premetallization temperature of 1,000° C. To determine the degree of reduction at this temperature, test 2 was run, which was similar to test 1, except the furnace was turned off at 1,000° C. In test 2, less reduction was observed (table 4) and over half of the iron oxide was wustite.

Metallization Starting Temperature

To determine the influence of the 1,000° C metallization starting temperature, metallization was started at 1,000° C with 40 pct CO until a temperature of 1,275° C was reached and then the bed was cooled in 100 pct N₂ (table 4, test 3). Petrographic analyses of the pellets showed a thick metallic iron shell and a small nonmetallized core. The average metallic iron content of this heterogeneous pellet was 80±10 pct.

Since test 3 resulted in a high percentage of metallization and a low pressure drop (0.2 kPa) at 1,275° C (table 4), test 4 was conducted with a 1,100° C metallization starting temperature. This resulted in a slightly higher pressure drop (0.9 kPa); however, the average metal shell thickness was still >2 mm (fig. 8). With thick shells at this temperature, it is difficult for the carbon monoxide reductant to metallize the unreduced core and for the semi-solid core material to exude through the shell. These results indicate that too much metallization occurred with 40 pct CO during the metallization period regardless of whether the metallization starting temperature was 1,000° or 1,100° C. With 40 pct CO, very little interpellet fusion occurred in this bed compared with the pellet bed shown in figure 7 (no metallization period), which suggests that the degree of metallization does influence the pressure drop or pellet bed permeability.

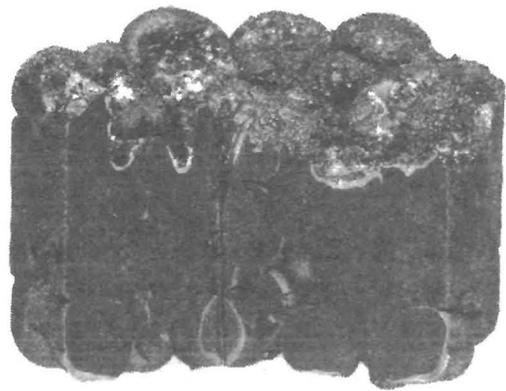


Figure 7.—Acid pellet bed (approximately actual size) without metallization period. (Test was interrupted at 1,250° C.)

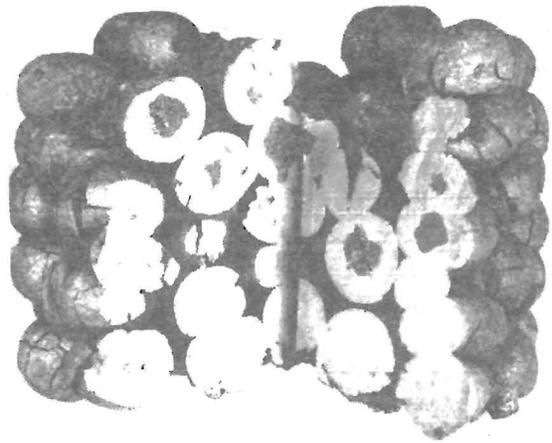


Figure 8.—Acid pellet bed (approximately actual size) with metallization started at 1,000° C using 40 pct CO. (Test was interrupted at 1,275° C.)

To obtain less metallization at temperatures of about 1,250° C, the carbon monoxide content during the metallization period was decreased to 30 pct. In test 5, the metallization period was started at 1,000° C and stopped at 1,300° C. The results in figure 9, curve C, showed that only a small pressure drop occurred at 1,250° C, compared with a larger pressure drop when no metallization period was used (curve A). The pellet bed of test 5 was analyzed, and it showed a high degree of reduction (89 pct) and metallization (75 pct). These results indicated that in order to obtain less metallization, the metallization starting temperature must be increased to 1,100° C. With this procedure, the data of figure 9, curve B, show that the

Table 4.--Softening and melting results of acid and fluxed pellets

| Test | Additive, pct | | CO, pct | 1,275° C contraction, pct | Contraction | | Temperature, °C | | DT - ST | Pressure at 1,275° C, kPa | S-value, ² kPa·°C | Bed metal-lization, ³ pct | Hematite reduction, ⁴ pct |
|-------------------------------------|---------------|-----------|---------|---------------------------|---------------------|--------|-----------------|-------------------|-------------------|---------------------------|------------------------------|--------------------------------------|--------------------------------------|
| | Dolomite | Limestone | | | 50 pct ⁵ | 80 pct | ST | DT | | | | | |
| PREMETALLIZATION STUDIES | | | | | | | | | | | | | |
| 1 | 0 | 0 | 0 | NA | >1,250 | 1,235 | >1,250 | NA | NA | 1,240 | NA | 2 | 36 |
| 2 | 0 | 0 | 0 | NA | >1,000 | >1,000 | >1,000 | NA | NA | >1,000 | NA | <1 | 17 |
| METALLIZATION WITH 40 PCT CO | | | | | | | | | | | | | |
| 3 | 0 | 0 | 40 | 42 | >1,275 | >1,275 | >1,275 | NA | NA | >1,275 | NA | 80 | 94 |
| 4 | 0 | 0 | 40 | 55 | 1,205 | 1,470 | 1,475 | 35 | 35 | 1,215 | .9 | 40 | NA |
| METALLIZATION WITH 30 PCT CO | | | | | | | | | | | | | |
| 5 | 0 | 0 | 30 | 42 | >1,300 | >1,300 | >1,300 | NA | NA | >1,300 | 0.3 | NA | 89 |
| 6 ⁶ | 0 | 0 | 30 | 58 | 1,225 | 1,400 | 1,265 | 140 | 140 | 1,235 | 2.7 | 1,230 | NA |
| 7 | 0 | 0 | 30 | 59 | 1,245 | 1,480 | 1,245 | 235 | 235 | 1,250 | 1.7 | 505 | NA |
| 8 | 0 | 0 | 30 | 61 | 1,245 | >1,275 | >1,275 | NA | NA | 1,250 | 1.9 | NA | NA |
| 9 | 0 | 2 | 30 | 53 | 1,225 | 1,280 | 1,365 | 85 | 85 | 1,250 | .8 | 220 | NA |
| 10 | 0 | 8 | 30 | 43 | 1,345 | >1,360 | >1,360 | NA | NA | >1,360 | .4 | NA | NA |
| 11 | 2 | 0 | 30 | 49 | 1,280 | 1,350 | 1,310 | 45 | 45 | 1,210 | .9 | 65 | NA |
| 12 | 8 | 0 | 30 | 51 | 1,255 | >1,275 | >1,275 | NA | NA | >1,275 | .3 | NA | 70 |
| 13 | 4 | 2 | 30 | 48 | 1,295 | >1,310 | >1,310 | NA | NA | >1,310 | .3 | NA | 65 |
| 14 | 6 | 3 | 30 | 45 | 1,360 | 1,365 | 1,370 | 5 | 5 | 1,365 | .4 | <5 | NA |
| 15 | 6 | 4 | 30 | 44 | 1,315 | >1,325 | >1,325 | NA | NA | >1,325 | .4 | NA | 80 |
| 16 | 8 | 4 | 30 | 41 | 1,335 | >1,350 | >1,350 | NA | NA | >1,350 | .3 | NA | 85 |
| METALLIZATION WITH 5 PCT OR LESS CO | | | | | | | | | | | | | |
| 17 | 0 | 0 | 0 | 69 | 1,225 | 1,300 | 1,205 | 145 | 145 | 1,185 | 20.2 | 1,450 | NA |
| 18 | 0 | 0 | 5 | 64 | 1,215 | 1,330 | 1,200 | 130 | 130 | 1,206 | 6.4 | 490 | NA |
| 19 | 4 | 4 | 5 | 54 | 1,230 | 1,355 | 1,210 | 145 | 145 | 1,200 | 7.8 | 830 | NA |
| 20 | 4 | 4 | 5 | 52 | 1,235 | 1,340 | 1,255 | 95 | 95 | 1,250 | 1.5 | 165 | NA |
| METALLIZATION WITH 20 PCT CO | | | | | | | | | | | | | |
| 21 | 0 | 0 | 20 | 59 | 1,225 | 1,490 | 1,235 | 245 | 245 | 1,225 | 3.3 | 740 | NA |
| 22 ¹¹ | 0 | 0 | 20 | 60 | 1,215 | 1,465 | 1,235 | 230 | 230 | 1,215 | 4.5 | 1,750 | NA |
| 23 | 2 | 2 | 20 | 56 | 1,205 | 1,360 | 1,240 | 120 | 120 | 1,225 | 2.5 | 400 | NA |
| 24 | 2 | 2 | 20 | 60 | 1,185 | >1,340 | 1,250 | NA | NA | 1,245 | 1.9 | NA | NA |
| 25 | 4 | 4 | 20 | 48 | 1,310 | 1,370 | 1,340 | 25 | 25 | 1,255 | .7 | 50 | NA |
| 26 | 4 | 4 | 20 | 50 | 1,275 | 1,355 | 1,325 | 40 | 40 | 1,315 | .5 | 55 | NA |
| 27 ¹² | 4 | 4 | 20 | 41 | 1,350 | NA | 1,495 | NA | NA | 1,410 | .5 | NA | NA |
| 28 | 6 | 6 | 20 | 48 | 1,290 | 1,420 | 1,415 | 5 | 5 | 1,415 | .5 | <5 | NA |
| 29 | 6 | 6 | 20 | 52 | 1,250 | 1,410 | 1,410 | 0 | 0 | 1,410 | .6 | <5 | NA |
| 30 | 0 | 12 | 20 | 48 | 1,295 | 1,420 | 1,425 | 5 | 5 | 1,225 | .8 | 20 | NA |
| 31 | 0 | 0 | 20 | 41 | 1,335 | 1,430 | 1,415 | 15 | 15 | 1,420 | .3 | 5 | NA |
| 32 ¹³ | 0 | 0 | 20 | 60 | 1,190 | 1,500 | 1,290 | ¹⁴ 210 | ¹⁴ 210 | 1,280 | .7 | ¹⁴ >670 | NA |
| 33 ¹⁵ | 0 | 0 | 20 | 71 | 1,210 | 1,455 | 1,235 | 260 | 260 | 1,235 | 4.2 | 1,700 | NA |

DT Drainout temperature.
 NA Not available.
 ST Softening temperature.
¹Percent CO in metallization period above 1,100° C.
²Area under pressure-versus-temperature curve between ST and DT.
³Calculated from chemical analysis (100 Fe°/Fe¹⁺).
⁴Calculated from weight loss.
⁵Furnace shut off at temperature preceded by "greater than" symbol (>).
⁶No metallization period, premetallization stopped at 1,250° C.
⁷No metallization period, premetallization stopped at 1,000° C.
⁸Metallization started at 1,000° C.
⁹Temperature held at 1,000° C for 1 h.
¹⁰Drainout product.
¹¹Pellets fired at 1,300° C; standard firing temperature is 1,200° C.
¹²No coke added.
¹³12 pct Al₂O₃.
¹⁴Pellets became molten but did not drain completely.
¹⁵12 pct SiO₂.

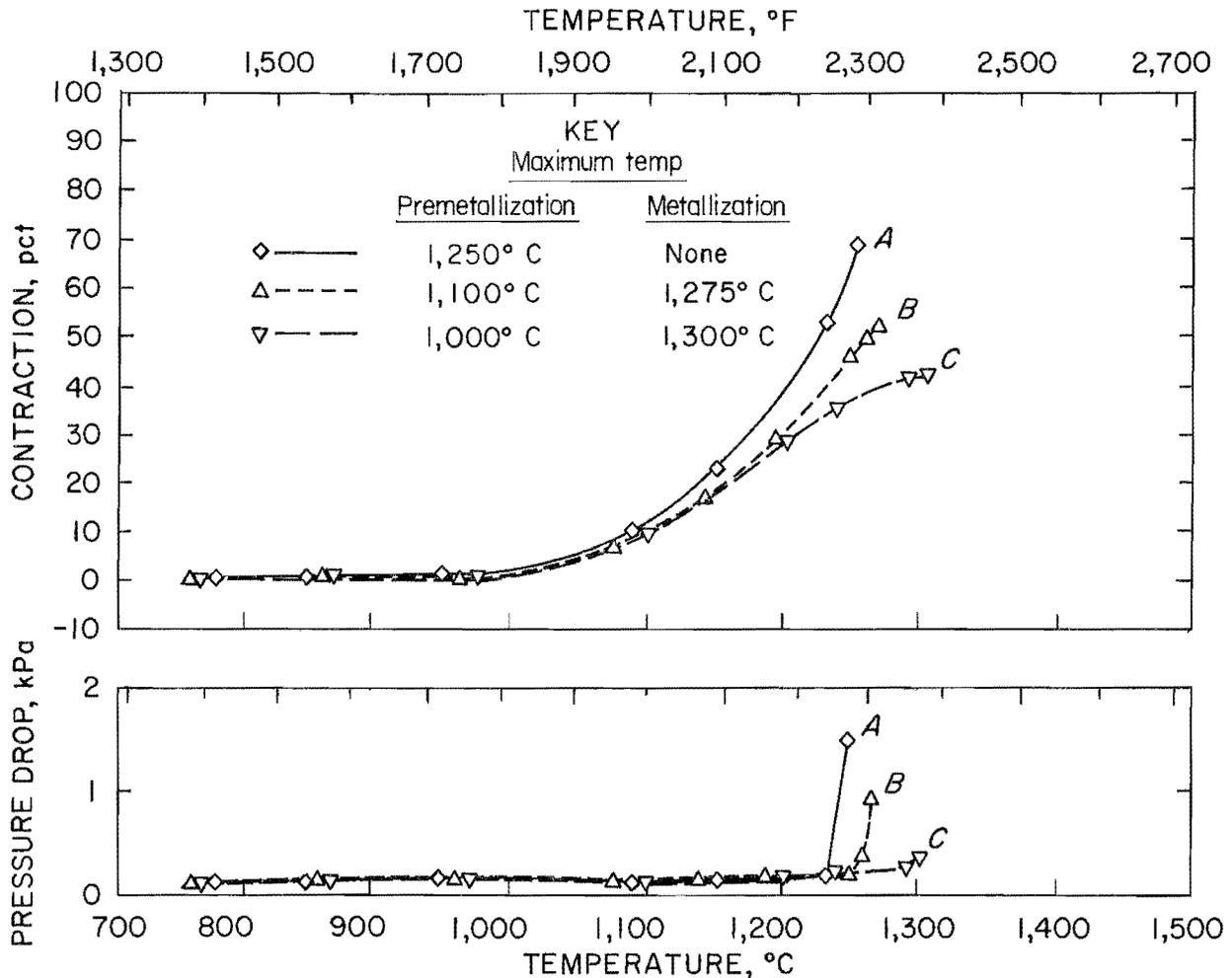


Figure 9.—Interrupted tests showing influence of maximum premetallization temperature on HTSM properties of acid pellets using 30 pct CO during metallization period.

pressure buildup, or softening temperature, occurred at about 1,260° C, which is in agreement with other investigators (5, 18).

Although not easily visible in the top graph of figure 9, the contraction decreased slightly at temperatures up to about 1,000° C, owing to thermal expansion and pellet swelling. Above this temperature, the contraction then increased with increasing maximum premetallization temperature, owing to the plastic deformation of the pellets. This deformation was most likely due to the formation of a mineral phase with a low melting temperature. Since wustite is the main constituent in the premetallization period, it probably reacted with SiO_2 to form fayalite, which has a low melting temperature (16). At higher maximum premetallization temperatures, more wustite reacted with SiO_2 . The 1,100° C maximum premetallization (or starting metallization) temperature appeared to

produce contraction results similar to those obtained by other investigators (5, 18-19).

Influence of Carbon Monoxide

Since most previous investigators have used either 30 or 40 pct CO, the influence of these carbon monoxide levels on the pressure drop and contraction was determined at a 1,100° C metallization starting temperature. With 40 pct CO, the pressure buildup with temperature was gradual (fig. 10), but this made it difficult to determine a precise pressure-temperature inflection point (softening temperature). With 30 pct CO, a sharp pressure buildup occurred at about 1,255° C, which is similar to that obtained by Mu (18). The drainout and 80-pct contraction temperatures with 40 and 30 pct CO were about the same.

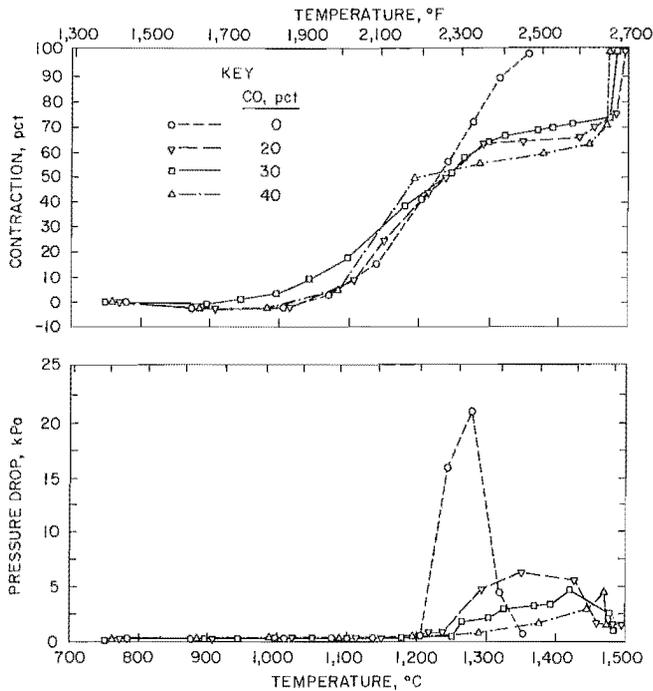


Figure 10.—Influence of metallization carbon monoxide content on HTSM properties of acid pellets.

The pressure drop between 1,250° and 1,300° C with 0 and 20 pct CO was higher than that with 30 and 40 pct CO (fig. 10). With 0 pct CO, complete drainout occurred at 1,350° C and the contractions were extremely high above 1,275° C (table 4, test 17). These results indicate that the reducing gas potential is very important, and the most meaningful results were obtained with a metallization gas containing either 20 or 30 pct CO. The latter was selected for the next set of tests because most previous investigators (11) used this concentration.

Metallization With 30 pct CO

Acid pellets with different thermal histories were evaluated with 30 pct CO during the metallization period. In test 6, the premetallization period was extended by soaking the pellets at 1,000° C for 60 min and then continuing the test. With this long soak, a considerably larger pressure drop was obtained at about 1,350° C and the 80-pct contraction and drainout occurred at lower temperatures (figure 11; table 4, tests 6-7). It is well known that wustite in the presence of iron oxide gangue sinters at about 1,000° C which could result in a decrease in the degree of reduction during the metallization period. The higher pressure drop with the 60-min soak (test 6) is probably due to the formation of a fayalitic slag. Fayalite melts at about 1,150° C, and the molten slag could decrease the gas permeability through the acid pellet bed.

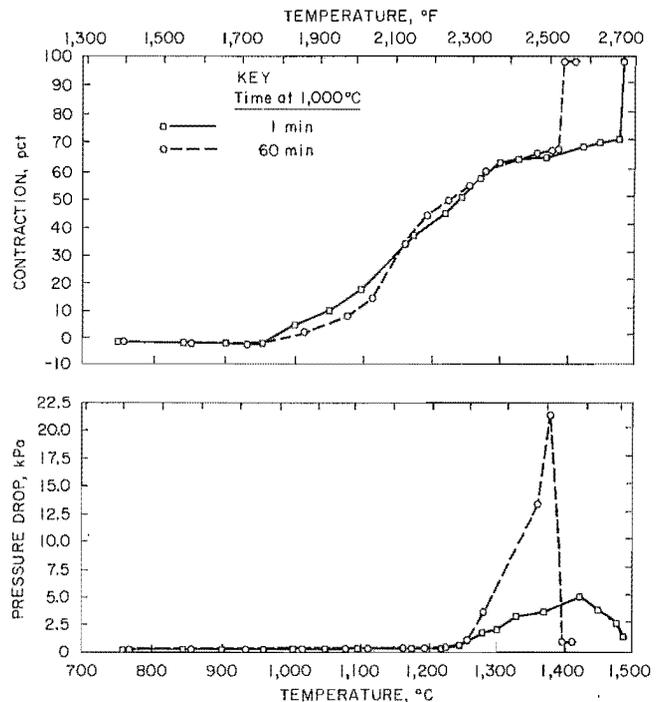


Figure 11.—Influence of 1,000° C soak time during premetallization period on HTSM properties of acid pellets using 30 pct CO above 1,100° C.

The 30-pct-CO method was also evaluated with pellets containing dolomite and limestone flux. A lower pressure drop at 1,275° C was obtained with fluxed (tests 9-16) than with acid pellets (tests 7-8), but only a small difference was obtained with the low flux additions (tests 9 and 11) compared with the higher flux additions (tests 10, 12-16). A fluxed pellet bed (test 12) indicated that about 70 pct metallization was obtained at temperatures of 1,275° C, which appears to be too much metallization. A lower carbon monoxide content is needed to evaluate the HTSM properties of fluxed pellets with the slow heating rate (1° C/min above 1,100° C) used in this research. Higher heating rates were not possible with the furnace that was used. Most other investigators (11) used heating rates between 3° and 10° C/min during the metallization period, but Bjorkvall and Thaning (19) used 1° C/min.

Metallization With 20 pct (or Less) CO

With 4 pct dolomite plus 4 pct limestone added to the pellets, a much higher softening temperature was obtained with 20 pct CO than with 5 pct CO (table 4, tests 19, 25-26; figure 12). Also lower contractions were obtained with 20 pct than with 5 pct CO. From these results, it was decided to use the 20-pct-CO gas composition for the remaining tests.

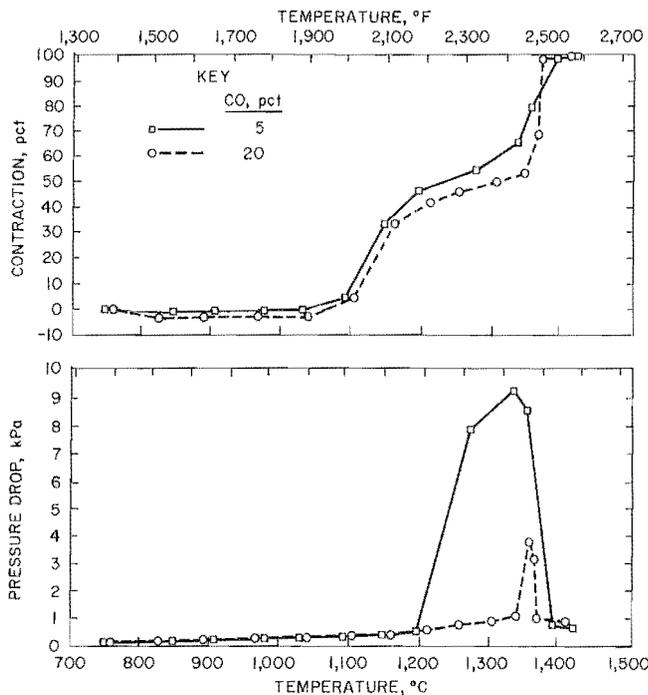


Figure 12.—Influence of 5- and 20-pct-CO gas contents during metallization on HTSM properties of fluxed pellets (4 pct dolomite and 4 pct limestone).

The influence of thermal history was evaluated with acid pellets with 20 pct CO during the metallization period. Acid pellets were intentionally overfired at 1,300° C (test 22) and compared with similar green pellets fired at the standard induration temperature of 1,200° C (test 21). These results and those in figure 13 show that the 1,300° C fired pellets had a higher pressure drop and the 80-pct contraction value occurred at a lower temperature. This behavior would be expected because the overfired pellets had a lower reduction rate (table 2, second row), which would suggest that more wustite would have been present between 1,250° and 1,450° C. These data indicate that this metallization method produces HTSM results that are sensitive to the physical, chemical, and metallurgical properties of acid pellets.

The 20-pct-CO metallization method was also used with pellets containing different levels of flux at dolomite-to-limestone ratios of 1:1. Figure 14 and table 4 show that the pressure inflection temperature (or softening temperature) was higher with increased flux additions. The temperature required to reach drainout (>80 pct contraction) approached a minimum at around 4 to 8 pct total flux addition.

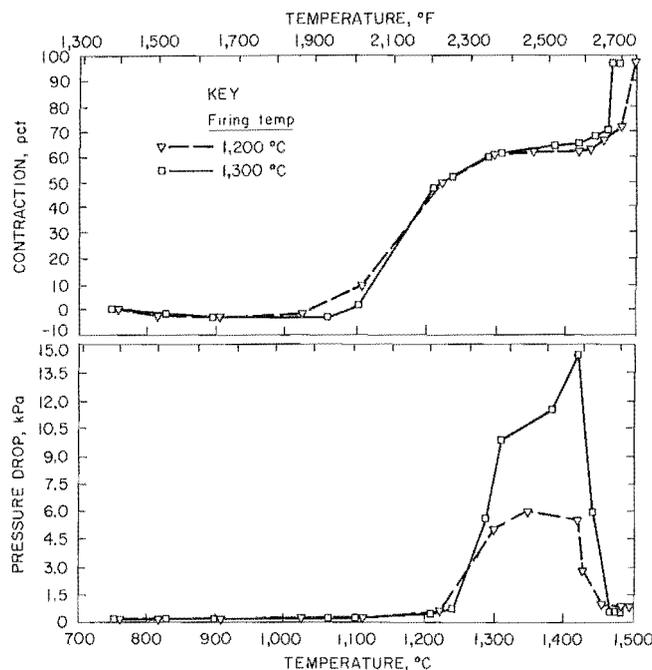


Figure 13.—Influence of firing temperatures of acid pellets on HTSM properties using 20 pct CO above 1,100° C.

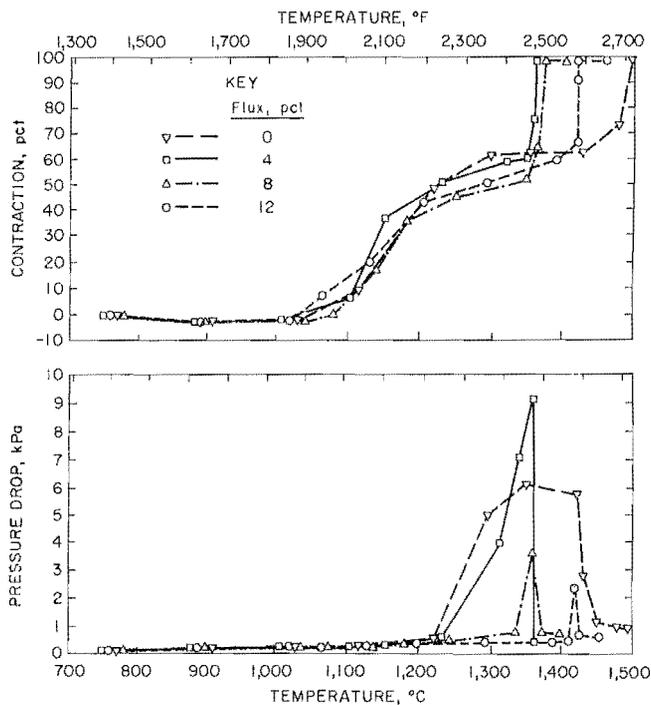


Figure 14.—Influence of flux percentage on HTSM properties using 20 pct CO above 1,100° C. (Dolomite to limestone at 1:1 ratio.)

HTSM Indices Evaluation

Several indices have been used to characterize the HTSM properties of pellets, but the most common index is the contraction at 1,100° C (5, 8), because this index can be determined with relatively inexpensive equipment. Other indices have been used, such as temperature for 10-pct contraction (18), pressure drop (12), softening temperature (19), drainout temperature (10, 12, 18); drainout-to-softening temperature interval (DT - ST) (12, 18); and S-value (19-21).

Pressure-Related Indices

Three pressure-related indices were considered in evaluating the HTSM data with both acid and fluxed pellets. The first index evaluated was the pressure drop at 1,275° C. The pressure drops at this temperature decreased with increasing flux additions (fig. 15), as would be expected. The lower pressure drop with fluxed pellets is partially the result of less pellet deformation or contraction. The pressure drops were very dependent on the metallization conditions. For example, the 20-pct-CO curve appeared to reach a plateau at about the 8 pct flux addition level, but the 30-pct-CO curve appeared to be less dependent on the flux level (fig. 15).

The second index was the temperature at which the pressure drop reached 0.7 kPa (5 mm Hg). This temperature increased with increasing flux additions (tests 21, 23-26, 28-29). This is consistent with the first index, which indicated that less gas flow resistance was obtained with pellets that have less deformation. However, these two indices are not very useful because they are dependent on the absolute pressure, which is dependent on the experimental loading technique.

The third index, softening temperature, is dependent on the relative change of pressure drop and varied fairly similarly to the second index because, in most cases, the softening temperature was about the same magnitude as the temperature required to obtain a pressure drop of about 0.7 kPa (table 4). However, the softening temperature appeared to be a slightly better index because it depended on a relative pressure drop change and therefore was less influenced by the charge packing technique. This index appears to be a good criterion to characterize the softening properties of the pellets, but in order to predict the overall blast furnace burden behavior, the index must also include a variable that is related to the pellet draining properties.

Draining-Related Indices

The metal-slag drainout temperature appeared to have a minimum between 4 and 8 pct flux (fig. 16). The initial decrease of the drainout temperature with the low flux

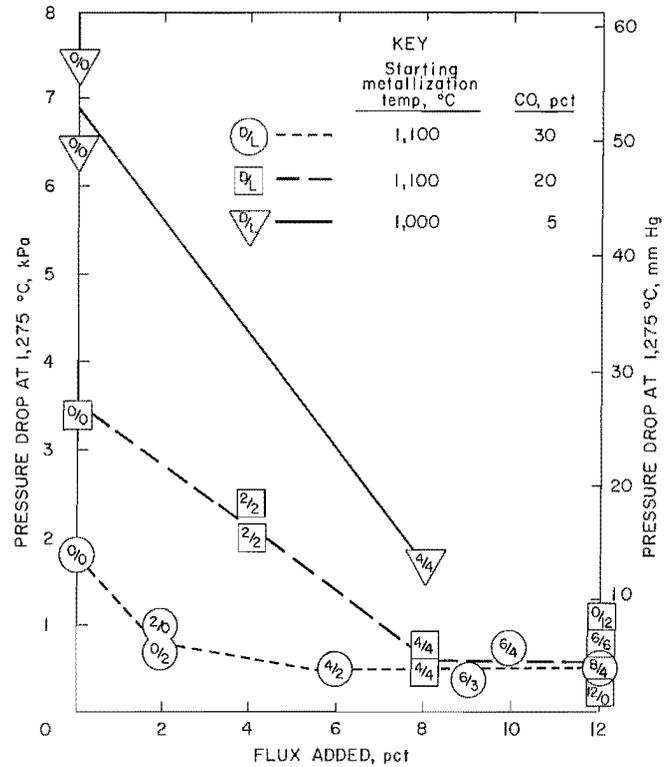


Figure 15.—Influence of metallization conditions and flux addition on pressure drop at 1,275° C. (D/L = ratio of percent dolomite to percent limestone.)

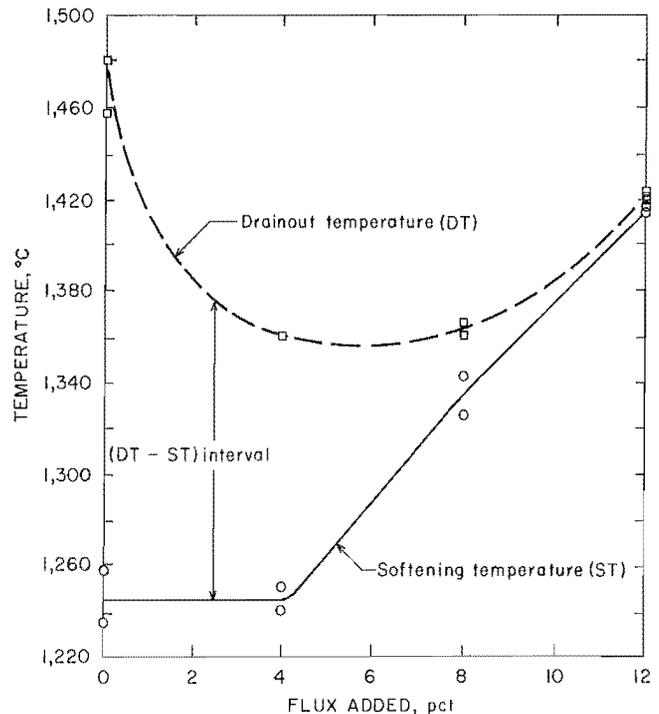


Figure 16.—Influence of flux percentage on softening and drainout temperatures using 20 pct CO above 1,100° C. (Dolomite to limestone at 1:1 ratio.)

additions was expected because flux is known to be a good fluidizer. The increase of the drainout temperature at high flux levels was also expected because refractory oxides can increase the dissolution temperature of wustite (22). The $\text{SiO}_2 \cdot \text{CaO}$ phase diagram indicates that low melting eutectics are formed between 35 and 55 pct CaO. Low liquidus temperatures probably enhance the reaction rate of carbon with iron oxide and later with iron to form a low-melting iron-carbon alloy, which is the main drainout product.

The $\text{SiO}_2 \cdot \text{CaO}$ phase diagram also helps to explain the constant softening temperature between 0 and 4 pct flux. The solidus temperature does not increase until the CaO percentage approaches the SiO_2 percentage. The softening temperature curve does not increase appreciably until more than 4 pct flux is added. Part of this increase may be attributed to the increased reduction rate with flux. The higher reduction rate results in a thicker metallic iron shell and a smaller ferrous iron core. This prevents the pellet from softening until a higher temperature is reached.

The drainout-to-softening temperature interval is the difference between the drainout and softening temperatures. The drainout-to-softening temperature interval decreased with increasing flux levels (figure 16; table 4, tests 21, 23-26, 28-29). Previous literature (18) suggests that a small interval is preferred by blast furnace operators because it should result in a thin cohesive zone. Although the interval appears to be a good index, it can be deceiving. This research indicated that a fairly low interval was also obtained with acid pellets, using 0 pct CO and 100 pct N_2 during the metallization period (test 17). The low drainout temperature in this test can be attributed to the reaction of wustite with SiO_2 to form fayalite. In this test, essentially no metallization occurred before melting and a low temperature drainout was obtained. The pressure drop was also very high just before drainout. An index is needed that can differentiate between metallized and non-metallized pellet beds. Therefore, these results indicate that the interval does not appear to be a good index by itself.

The S-value appeared to be a better index than the drainout-to-softening temperature interval because it included the interval plus the magnitude of the pressure drop. The S-value decreased with increasing flux levels (fig. 17), and it did not appear to be strongly dependent on the dolomite-to-limestone ratio. Ranade and Nora (21) suggested that an S-value less than 40 $\text{kPa} \cdot ^\circ\text{C}$ is acceptable for blast furnace burden materials. In this research, this approximate value was obtained at flux percentages of about 8 or greater.

With both acid and fluxed pellets, the S-value decreased with increasing carbon monoxide content (figs. 17-18).

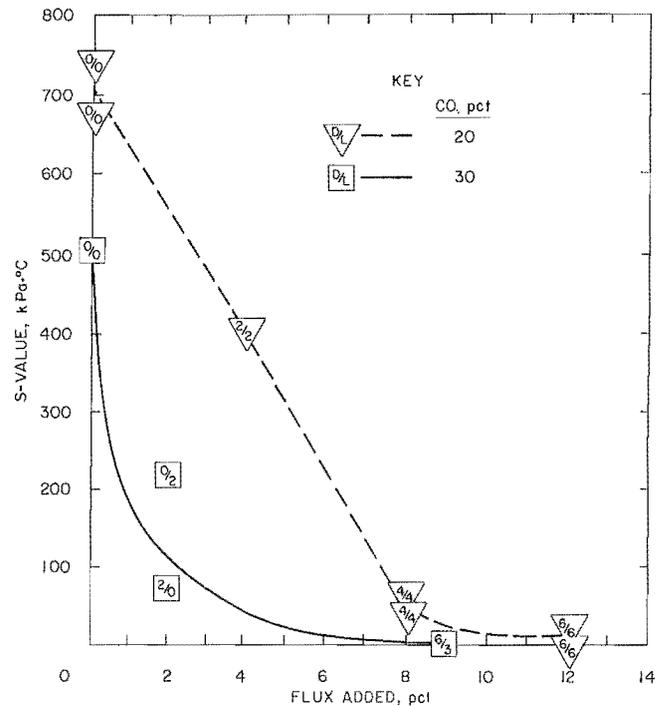


Figure 17.—Influence of flux addition and carbon monoxide percentage on S-value. (D/L = ratio of percent dolomite to percent limestone.)

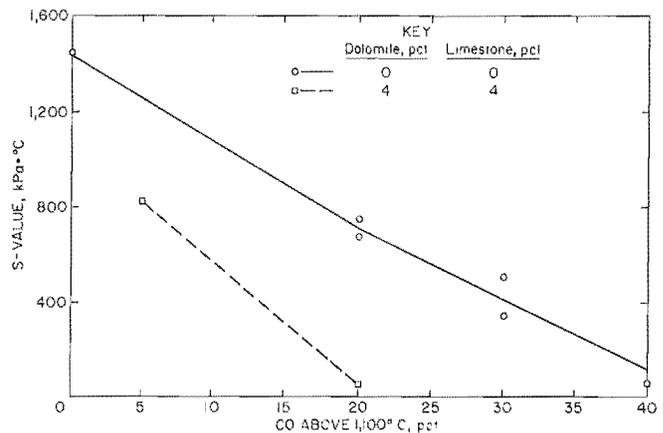


Figure 18.—Influence of metallization carbon monoxide content on S-value.

This would be expected because high carbon monoxide content should result in more wustite reduction to metallic iron, and therefore, less fayalite should be formed. Since fayalite has a low melting temperature, its presence decreases the pellet bed permeability and thereby increases S-value.

It was not possible with the S-value alone to determine when excess (about 12 pct) flux was added. The

drainout temperature and the S-value had to be used together to determine which pellets would have the best HTSM properties. Zuke (4) reported that blast furnace burdens should have a high softening temperature and a slightly higher drainout temperature. However, pellets with excess flux have a high drainout temperature, requiring the blast furnace to operate at a higher temperature and therefore increasing operating costs.

When the additive was 12 pct acid oxide (silica or alumina) instead of 12 pct basic oxide (dolomite or limestone), lower softening temperatures and higher drainout temperatures were obtained (table 4, tests 30-33; figure 19). The lower softening temperatures have been previously attributed to the formation of low-melting iron silicates and aluminates. The reason for the higher drainout temperatures and the higher S-values with acid oxides is probably that they form anionic compounds. These silicates and aluminates can have a relatively high viscosity, which has been attributed to their chainlike structure in the liquid phase (23).

The contraction, pressure drop between 1,200° and 1,350° C, and S-value were higher with 12 pct limestone than with 12 pct dolomite (table 4, tests 30-31; figure 19). This can probably be explained by the lower melting temperature of the phases formed with the limestone additive.

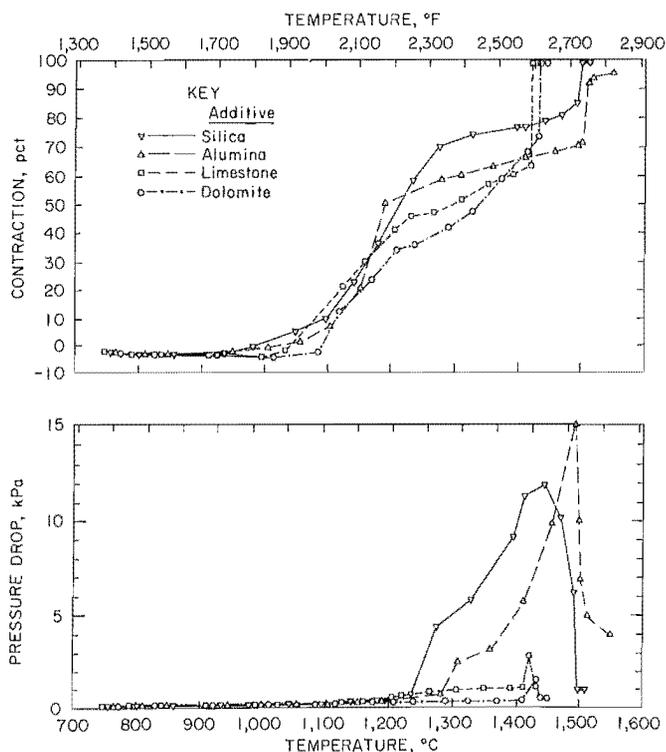


Figure 19.—Influence of 12 pct pellet additives on HTSM properties using 20 pct CO above 1,100° C.

Contraction-Related Indices

The three contraction indices selected for evaluation in this study were contraction at 1,275° C and temperatures at 50- or 80-pct contraction. The 10-pct contraction temperature (18) was rejected because it was too close to the baseline contraction value. The contraction at 1,100° C (8) was also not meaningful in this study because this is the temperature at which metallization was started. Instead, the contraction at 1,275° C was selected because this temperature was between the pressure buildup of acid and fluxed pellets. An index is needed to show why fluxed pellets work better in blast furnaces. The pressure buildup at this temperature appears to be useful to differentiate between acid and fluxed pellets.

The 50-pct contraction temperature was selected since this contraction value approximately corresponds to the disappearance of all the interpellet voids. The 80-pct contraction was selected because it corresponded to the temperature at which rapid drainout occurred.

The contraction at 1,275° C decreased and the temperature for 50-pct contraction generally increased with increasing flux levels (tests 21, 23-26, 28-29). However, neither of these two indices appear to be as effective in characterizing the HTSM behavior as the 80-pct contraction value. The 80-pct contraction temperature is almost the same as the drainout temperature (table 4). The drainout temperature would appear to be a fair indicator of the start of dripping from the bottom of the cohesive zone. The drainout temperature and the S-value were found to be better measurements than the contraction values for characterizing the HTSM properties of pellets. The contraction values were very dependent on the experimental technique, such as the pellet and coke packing.

Influence of Coke Addition

In most HTSM studies, a coke layer is placed above and below the pellet bed to simulate blast furnace charges. A test was performed in which the coke layers were replaced with nominal 7-mm alumina chips and beads. The alumina liner was replaced with a straight-walled alumina cup with 6-mm-diam holes drilled into the bottom. Also, most of the bottom of the graphite liner holder was bored out so that the molten pellet bed would not come in contact with graphite. With fluxed pellets (4 pct dolomite and 4 pct limestone) and no coke, no drainout was obtained at 1,550° C. The furnace was then turned off and the sample cooled. The pellets had melted, and more slag splattering and alumina dissolution were observed than when coke was present. The bed contractions were higher when coke was present (table 4, tests 25-27; figure 20), which could be due to the interaction of coke with the pellet bed.

Without coke, the molten mass did not drain out but was retained in the conchoidal alumina chips and beads. The nonmagnetic fraction of the sample contained 22 pct Fe^T, of which less than 10 pct was metallized. With coke present, complete drainout occurred at 1,365° C and the sample contained about 95 pct Fe^T and 4 pct C. These analyses suggest that when coke is present, an iron-carbon alloy is formed. With no coke, more unreduced iron is present in the molten phase, which results in more slag splattering and alumina dissolution.

The gas analyses data also helped to elucidate what reactions may have occurred. In the test with no coke, only the carbon monoxide was available to carburize the iron. At temperatures above 1,000° C, this reaction is very slow (24). This explains why essentially no iron-carbon alloy was formed during the no-coke test. The top portion of figure 20 shows that some carbon monoxide and dioxide were formed just before the bed reached the drainout temperature of 1,365° C when coke was present. This suggests that the conversion of the iron compounds from the solid to the liquid state enhances the mass transport mechanisms between the pellets and coke.

Softening-Melting Phases

Examination of the components of samples from the interrupted tests was helpful in postulating what reactions occurred. Microscopic and chemical analyses indicated that wustite and fayalite were formed above 1,200° C with acid pellets. The literature indicates that the melting points of fayalite and wustite are 1,150° (16) and 1,369° (25), respectively. These data indicate that the lowest melting constituent is fayalite, which can be formed from the SiO₂ and wustite. More uncombined SiO₂ is available in the acid pellets because essentially no flux is present to combine with the SiO₂ to form calcium and magnesium silicates. During metallization, pellets with low reducibility have more uncombined wustite available for a longer period, which will enable it to more readily react with SiO₂.

Half-sections of typical acid and fluxed (4 pct dolomite and 4 pct limestone) pellet beds are shown in figure 21. Both tests were interrupted at 1,300° C. It is evident from figure 21A that a molten phase moved above the acid pellet bed, while no sign of a molten phase movement or slag splashing was observed with the fluxed pellet bed (fig. 21B).

When tests using 20 pct CO or more were interrupted at about 1,350° C, the top of the acid pellet beds next to the coke layer usually had irregular metallic formations protruding upward (fig. 22). This metallic phase may have

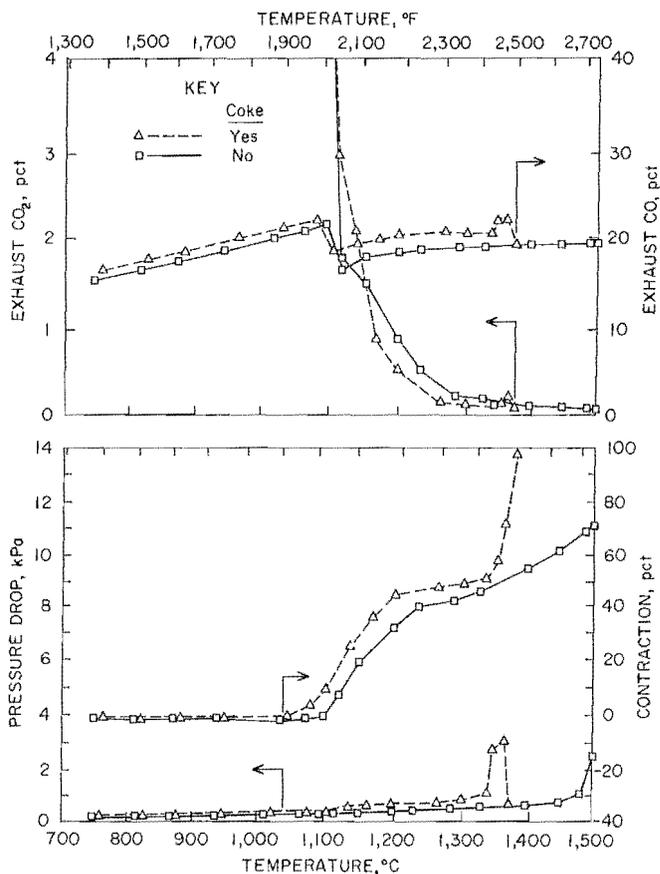


Figure 20.—Influence of coke on HTSM properties with fluxed pellets (4 pct dolomite and 4 pct limestone) using 20 pct CO above 1,100° C.

formed when the gas flow pushed up the molten fayalite into the coke, where it reacted to form a low-melting iron-carbon alloy. For tests interrupted above 1,300° C, the metallized pellet beds as well as the metallic drainout materials for all tests contained between 1 and 4 pct C. The literature (15) indicates that dissolved carbon in iron decreases the melting point of the alloy almost linearly from 1,535° to 1,153° C with 0 to 4 pct C, respectively. This suggests that the softening phase in an acid pellet bed is fayalite, which then reacts with coke to form a low-melting iron-carbon alloy. Fluxed pellets formed less fayalite and more pure iron in the bed, and therefore, less contraction and pressure drop occurred at similar temperatures.

With tests interrupted at 1,300° C, acid pellets contained denser, less permeable, metallic iron outer shells (figure 23A, light-colored areas) than did fluxed pellets (fig. 23B). The smaller metallic iron grains formed with

A

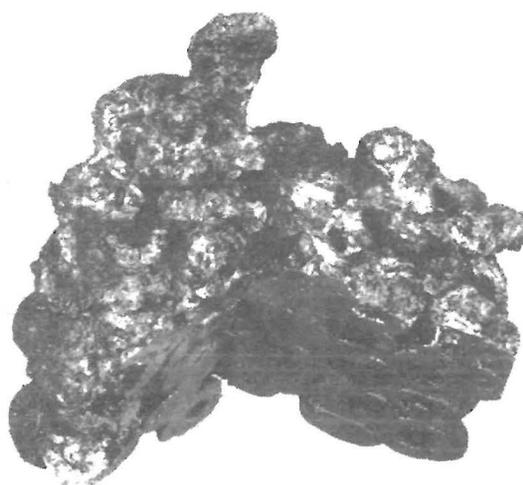


Figure 22.—Acid pellet bed (approximately actual size) showing metallic protrusion on top. (Above $1,100^{\circ}\text{C}$, 20 pct CO was used; test was interrupted at $1,350^{\circ}\text{C}$.)

B

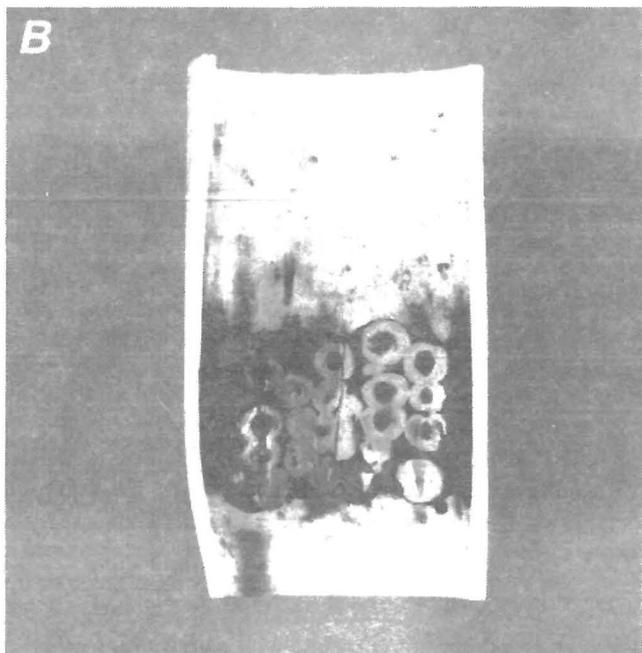


Figure 21.—Acid (A) and 4 pct dolomite and 4 pct limestone fluxed (B) pellet beds in liners (approximately half size). (Above $1,100^{\circ}\text{C}$, 20 pct CO was used; tests were interrupted at $1,300^{\circ}\text{C}$.)

the fluxed pellets were probably the result of the flux separating the metallic iron grains, thereby decreasing the grain growth. Acid pellets had cores inside the shells that were larger than those in fluxed pellets. The cores of the pellets appeared to be a liquid wustite-rich slag similar to that previously reported (26). With greater relative core-to-shell volume, more contraction under load occurred during the metallization period.

In the temperature range between $1,200^{\circ}\text{C}$ and $1,450^{\circ}\text{C}$, the contraction leveled out in the range of 40 to 70 pct with acid pellets. This phenomenon has been called "reduction retardation" by Onoda (9). This retardation has been attributed to the decrease in the porosity of the shell, which retards gas diffusion and indirect reduction.

Acid pellets had more reduction retardation than fluxed pellets (fig. 14) because the acid pellet shell was denser (fig. 23) and therefore less permeable. The addition of flux increased the liquidus temperature of the fayalitic slag so less deformation and pressure drop occurred, thereby allowing the gaseous reactants and products to pass more readily through the shell. With fluxed pellets, the drained-out slag was generally olive green, indicating that olivine was formed, as suggested by others (10).

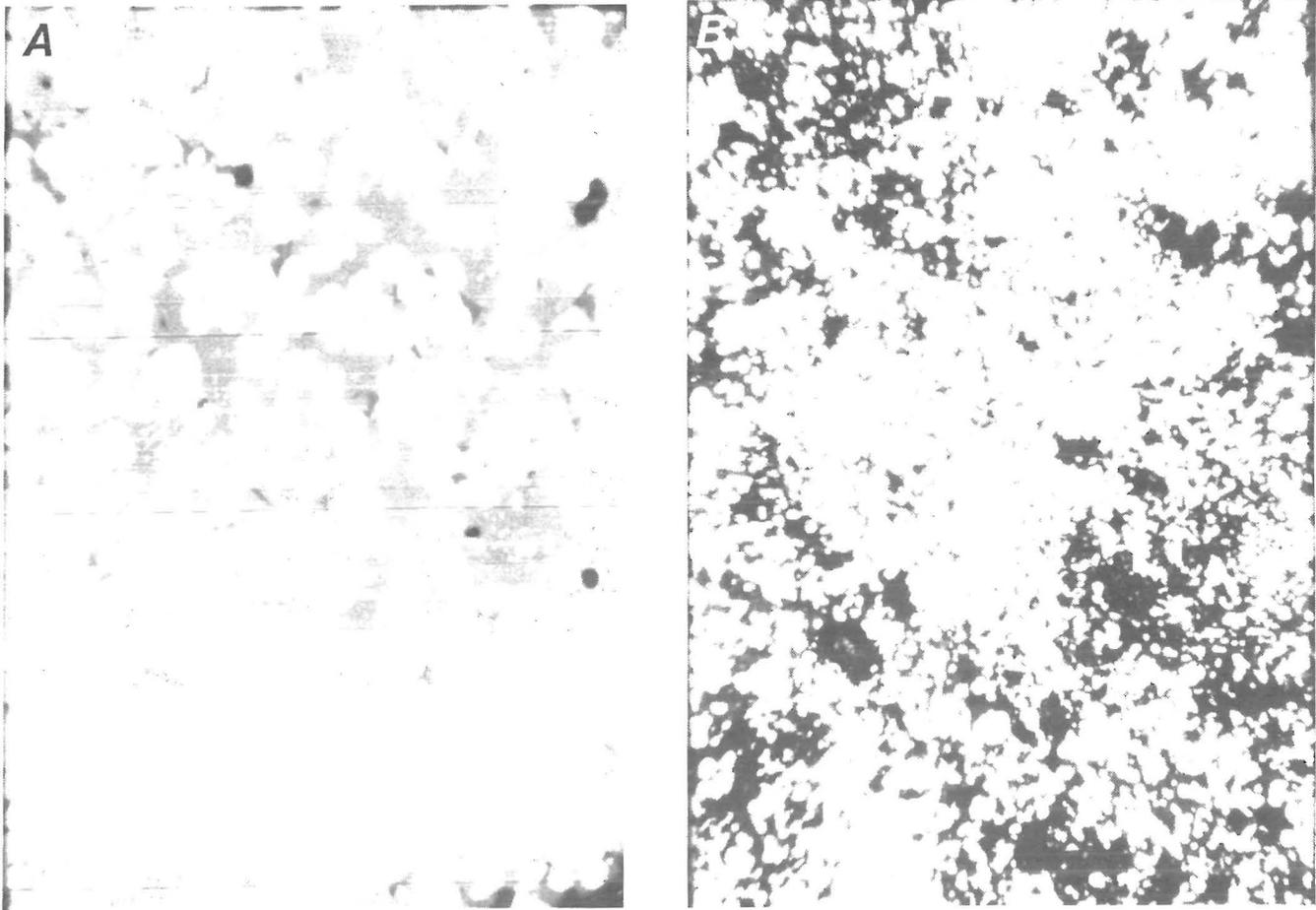


Figure 23.—Shells of acid (A) and fluxed (B) pellets (X 160). (Above 1,100° C, 20 pct CO was used; tests were interrupted at 1,300° C.)

CONCLUSIONS

1. A method was developed for determining the HTSM properties that are sensitive to the physiochemical properties of both acid and fluxed pellets.

2. The addition of flux improved the pellet reducibility and the HTSM properties. This effect is probably because the iron oxides passed through the wustite phase at a faster rate with fluxed than with acid pellets. This faster reduction rate decreased the chance of forming low-melting-temperature fayalite, which increases pellet contraction or deformation.

3. The pellet bed contraction and pressure drop at temperatures above 1,200° C were very dependent on the experimental metallization conditions. With the equipment and procedures used, the metallizing condition for the best HTSM property correlation with the physiochemical properties of the pellets was 20 pct CO in N₂ above 1,100° C at a heating rate of 1° C/min.

4. At lower metallization starting temperatures and with a higher carbon monoxide percentage, the softening temperature increased and the optimum flux level was more difficult to determine.

5. The contraction, or absolute pressure drop values alone, appeared to be too dependent on the experimental technique and did not correlate well with the flux addition level and reducibility of the pellets.

6. The drainout-to-softening temperature interval index also was not an ideal index because it did not contain a pressure magnitude value and gas permeability is known to be an important variable in blast furnace operation.

7. The S-value and the drainout temperature were found to be the best means for characterizing the pellet HTSM properties. Using these two HTSM indices, the experimental results indicated that 8 pct flux was about the optimum level, which corresponds to a basicity of about 1.

The S-value was about 50 kPa·°C and the drainout temperature was 1,365° C.

8. When the flux constituent was 12 pct limestone alone, the S-value, contraction, and pressure drop above

1,200° C were slightly higher than with 12 pct dolomite or mixtures of limestone and dolomite. This indicates that dolomite may be a better additive than limestone.

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