Use of Oxygen-Enriched Gas for the Oxidation of Acid and Fluxed Taconite Pellets

By Larry A. Haas, John C. Nigro, and Robert C. Moe

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu/mt	British thermal unit per metric ton	m	meter
°C	degree Celsius	mg	milligram
°C/min	degree Celsius per minute	min	minute
cm	centimeter	mm	millimeter
g	gram	mt	metric ton
h	hour	pct	percent
kg	kilogram	pct/min	percent per minute
lb	pound	r/min	revolution per minute
lb/mt	pound per metric ton	SL/min	standard liter per minute
lb/p	pound per pellet		

USE OF OXYGEN-ENRICHED GAS FOR THE OXIDATION OF ACID AND FLUXED TACONITE PELLETS

By Larry A. Haas,[1] John C. Nigro,[2] and Robert C. Moe[3]

ABSTRACT

The U.S. Bureau of Mines, in cooperation with Cleveland-Cliffs, Inc. (Hibbing, MN), investigated ways of enhancing the quality (compressive strength, after-tumble and reducibility) of domestic acid and fluxed magnetite pellets by modifying the oxygen content during the preheat and induration periods of the firing operation.

Oxidation of magnetite was best accomplished when sufficient oxygen and time were available before the peak induration temperature was reached. The rate of magnetite oxidation increased directly with the gas oxygen content during the preheat period at 700° C and above. With 30 pct (or more) O_2 and a preheat rate of 200° C/min, most of the magnetite was oxidized during the preheat period.

With laboratory tube and mini-pot furnace tests, oxygen enrichment during the preheat period improved the pellet properties more in the simulated grate-kiln tests than in the simulated straight-grate tests. The longer induration period with the grate-kiln test resulted in more sintering of the residual magnetite and its reaction with the silicon compounds. When flux was present in the pellets, calcium silicates and calcium and magnesium ferrites were formed. More calcium ferrite was formed when the magnetite was oxidized early and less iron was present in the fayalitic calcium silicate slag.

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[1]Research chemist, Twin Cities Research Center, U.S. Bureau of Mines, Minneapolis, MN.
[2]Research supervisor, Twin Cities Research Center.
[3]Metallurgist, Cleveland-Cliffs, Inc., Hibbing, MN.

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INTRODUCTION

To make better use of the Nation's resources, the U.S. Bureau of Mines investigated different technology options that would produce superior domestic iron oxide pellets. Most of the domestic ores utilized are magnetite. Historically, about 99 pct of the domestic iron ore has been produced in the Lake Superior Region. One of the higher production years was 1955, when 68 million mt of iron ore was produced in Minnesota (1-2).[4]

The decrease in the demand of domestic iron ore has been primarily due to the (1) decline in domestic steel consumption, and (2) importing of iron products and iron ore from foreign sources. One means of remaining competitive with foreign suppliers is by developing innovative technologies for producing superior iron ore pellets at lower costs. Pellets with superior properties would have greater value because they would improve the efficiency of the domestic steel industry.

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

STATUS OF PELLET FIRING TECHNOLOGY

One of the factors that can influence a pellet's quality is its thermal history and when the magnetite oxidation occurred. The thermal history usually consists of four distinct periods: drying, preheat, induration, and cooling. Commercial pellets are usually fired in one of three different types of furnaces: shaft, straight-grate, or grate-kiln. Only the last two pelletizing furnaces will be discussed in this report. Typical temperature profiles of the straight-grate and grate-kiln are shown in figure 1 (3). The preheat rate for both furnaces is 200° C/min (conventional rate), but rates as low as 150° C/min and as high as 300° C/min have been reported (4). The induration period for the straight-grate is usually about 10 min, which is the time the on-gas (entering the top of the pellet bed) temperature is the highest. However, the pellets' peak temperature (usually between 1,250° and 1,350° C) may only be held for a few minutes. The induration period for
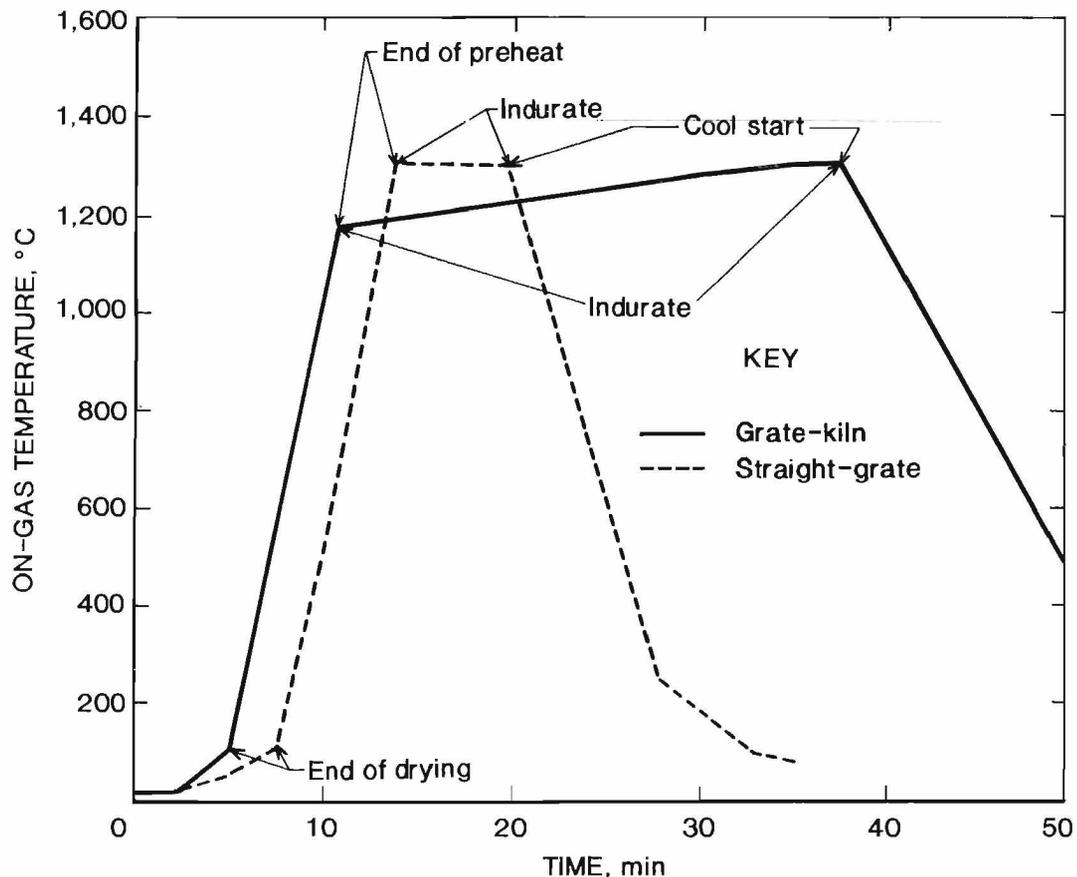
Figure 1.—Temperature profile of grate-kiln and straight-grate.

the grate-kiln is usually about 30 min in the temperature range of 1,200° to 1,350° C. After the pellets are indurated, they are cooled, and these reported rates usually range from 70° to 130° C/min (*3*), but a high rate of 200° C/min (*4*) has also been reported.

The firing operation is a complex process involving the formation of new chemical compounds and changes in the physical structure of the particles. The oxidation reaction of magnetite (Fe_3O_4) to hematite (Fe_2O_3) generates heat, which can result in an increased pellet strength due to increased iron oxide and slag bonding. High-temperature (>1,200° C) sintering of the magnetite and/or hematite grains hardens (indurates) the pellets so less breakage occurs during handling, transportation, and reduction in the blast furnace.

The firing process is highly interactive. For example, it is well known that changing the airflow through the grate can change the pellet temperature profile. This interaction is obvious to the operators, but other process changes have more subtle effects and their overall influence may be more difficult to assess. For example, increasing the grate gas flow may also increase the gaseous oxygen content and more magnetite may be oxidized prior to the induration period. Up to the present time, the importance of the sequence of the oxidation and sintering reactions with different oxygen gas contents has not been completely understood (*5-6*). The preferred final product is slightly sintered hematite. Nonoxidized or partially oxidized magnetite pellets have been known to be weaker with a lower reducibility than completely oxidized pellets.

Considerable heat (4×10^5 Btu/mt) is liberated when magnetite is oxidized to hematite (*7*). This reaction can provide over half of the total heat input to commercial firing operations. The location where the heat is given off can change the heat distribution in the firing operation and thereby influence the final pellet properties and overall process economics (*8*). It is the intent of commercial pelletizing furnaces that most of the magnetite-to-hematite conversion is completed during the preheat period or at least early in the firing process to aid in the heating of the pellets. In a straight-grate, less than half of the magnetite-to-hematite conversion occurs during the preheat period (*9*), and most of the oxidation takes place during the induration period. In a grate-kiln, it has been estimated that about half of the oxidation occurs on the grate, very little (<10 pct) in the kiln (*10-11*), and the rest in the cooler (*7*). When unoxidized pellets enter the cooler, the oxidation causes the pellets to heat up rather than cool down. Over 10 pct more cooling air is needed to attain the same pellet discharge temperature when 50 pct rather than 25 pct of the magnetite is oxidized in the cooler (*12*). About half of this heat is removed in the first-stage cooler and utilized as preheated secondary combustion air. Not all the excess heat is recovered from the cooler (*7*).

Pape, Frans, and Geiger (*7*) reported that the reason that sufficient oxidation is not attained in the preheat portion of the firing operation is the short residence time. Increasing the gaseous reactant (oxygen) concentration during this short time should increase the percentage of magnetite oxidation and thereby permit higher production rates. Previous research at the Bureau showed that strong pellets could be produced at shorter induration periods when the oxygen content of the simulated combustion gas was increased (*13*). In present firing operations, the oxygen content of the cooler inlet gas is about 21 pct (air), but the preheat and induration gases contain combustion gas so the oxygen content is considerably lower. The oxygen content in the kiln has been reported to be between 8 and 13 pct (*11*), which may be similar to that in a straight-grate. In a conventional kiln, most of the gas flows over the top of the pellets, and therefore, the oxygen content in the pellet bed may be lower as oxygen is consumed by magnetite oxidation.

OXIDATION AND SINTERING MECHANISMS

Cooke and Stowasser (*14*) reported that several mechanisms can occur during the firing of magnetite pellets in an oxidizing atmosphere, such as (1) sintering of fragmented magnetite grains (magnetite bonding); (2) formation of fayalitic slag from the reaction between the quartz or silicate(s) with available ferrous ions followed by slag bonding with the magnetite grains (magnetite-slag bonding); and (3) the preferred reaction, i.e., oxidation of the magnetite to hematite, and subsequent sintering of this product (hematite formation and bonding).

All three of these mechanisms may occur simultaneously, but when the temperature of the pellets is brought up too rapidly, oxygen gas transport to the center of the pellet lags, permitting the interaction between the ferrous ions and the SiO_2-containing compounds. If the ferrous ions in the nonoxidized magnetite are involved in the formation of iron silicates (e.g., fayalite), the iron in the silicates will be more difficult to reduce during the ironmaking process. Fayalite ($2FeO \cdot SiO_2$) formation and/or the sintering of magnetite particles will also decrease the oxidation rate; fayalite particles have a low surface area at the induration temperature because fayalite has a low melting point (about 1,150° C) whereas the melting points of iron oxides are over 1,500° C. Cooke and Stowasser (*14*) also reported that magnetite pellets heated in sufficient oxygen oxidized faster and produced stronger pellets. These results are in agreement with those reported by Wynnyckyj and Fahidy (*15*), who stated that magnetite must be oxidized before the induration temperature is reached to obtain strong, evenly textured pellets. They reported that SiO_2-containing compounds do not react with ferric ions but only with ferrous ions. These investigators have greatly

increased the understanding of the isothermal oxidation of magnetite in air, but very little research has been done at programmed temperatures at different oxygen contents using acid and fluxed pellets.

The purpose of this research was to determine the influence of oxygen content, temperature, and reaction time on the percentage of oxidation of magnetite pellets. Two goals were to determine the relationship between the percentage of pellet oxidation and the physical-metallurgical properties of fired acid and fluxed pellets, and to determine the importance of the sequence of magnetite oxidation and sintering reactions. Another goal was to determine if oxygen-enriched gases can accelerate the magnetite-to-hematite oxidation reaction sufficiently to improve pellet quality and throughput.

ACKNOWLEDGMENT

MATERIALS

Seven batches of wet (green) pellets were obtained from six different commercial taconite operations located on the Minnesota Mesabi Range. The pellets were dried overnight at 105° C (16). The dried pellets were stored in a desiccator; the chemical analyses are shown in table 1. The first six batches listed were referred to as "acid pellets" as they contained less than 2 pct flux (dolomite and limestone). Batch 7 contained about 5 pct each of limestone and dolomite and was referred to as "fluxed pellets." The fluxed pellets contained the highest calcium and magnesium contents and the lowest concentrations of the other major constituents [e.g., total iron (Fe^T), Fe^{2+}, and Si]. The 1,000° C loss on ignition (LOI) was negative for the acid pellets, because the ferrous ions in the magnetite were oxidized to the ferric state and this weight gain was greater than the calcination weight loss. With the fluxed pellets, the weight loss of the carbonate calcination was greater than the magnetite oxidation weight, so a positive value was obtained for the LOI.

The pellet batches were also examined with a Perkin Elmer Thermal Analyzer System 7/4.[5] Pulverized pellet samples (50 mg) were heated at a rate of 25° C/min. Differential thermal analysis (DTA) tests were conducted using a 0.05 SL/min airflow. The results in figure 2 indicate that the highest exothermic temperature (as compared with the baseline) generally occurred at about 350° C. The temperature increase was attributed to the oxidation of magnetite, which was verified by chemical analyses of quenched samples. With all pellet batches, more heat was generated by the oxidation of magnetite than was consumed by the endothermic reactions (e.g., carbonate decomposition). At 375° C, the highest exothermic temperature was obtained with the fluxed pellet sample (batch 7), which may be attributed to the high oxidation rate with these high-porosity pellets (17). Pellet batches 5 and 6 were made from the same concentrate but with batch 6, half of the bentonite (about 10 lb/mt) was replaced with about 1 lb/mt of organic binder. This addition of the organic binder resulted in higher exothermic temperatures, probably because the combustion of the organic produced a porous magnetite pellet, which aided the oxidation reaction.

The pellet and flux powders were also examined with a gas flow of 0.5 SL/min N_2 using a Perkin Elmer Thermogravimetric Analyzer (TGA). It is evident from figure 3 that above 750° C, the weight loss of the dolomite, limestone, and fluxed pellet (batch 7) samples was considerably greater than that of the acid pellet (batch 2) sample. The dolomite and limestone chemical analyses were previously

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[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Table 1.—Partial chemical analyses (percent) of different dried pellet batches[1]

Batch	Fe^T	Fe^{2+}	Si	Al	C	Ca	K	Mg	P	S	LOI[2]
1 ...	67.4	20.6	2.3	0.23	0.5	0.65	<0.05	<0.25	0.020	0.010	-1.9
2 ...	67.4	22.5	2.2	.22	.3	.64	<.05	<.25	.021	.010	-2.6
3 ...	66.3	22.0	2.8	.22	.7	.73	<.05	<.25	.022	.012	-1.6
4 ...	67.0	22.4	2.7	.22	.7	.80	.07	.32	.018	.014	-2.1
5 ...	67.0	21.6	2.5	.26	.5	.11	<.05	.25	.018	.011	-2.2
6 ...	66.4	21.4	2.3	.26	.5	.80	<.05	.25	.017	.013	-2.9
7 ...	62.4	19.0	2.0	<.20	1.6	3.70	<.05	1.00	.022	.010	2.4

[1]Sodium content in all pellet batches was less than 0.05 pct.
[2]Loss on ignition at 1,000° C.

reported (*18*). The greater weight loss of the flux-containing samples was attributed to the decomposition of the carbonates. Above 850° C, the decomposition of the fluxed pellet sample was essentially complete and the weight loss leveled out at 5 pct. The acid pellet sample lost about 1 pct weight due to the decomposition and dehydration of minor constituents (i.e., hydroxides, carbonates, and bentonite).

Figure 2.—Differential thermal analysis of pulverized pellets. Heating rate: 25° C/min; atmosphere: 0.05 SL/min air.

Figure 3.—Thermogravimetric analysis of pulverized pellets and flux samples. Heating rate: 25° C/min; atmosphere: 0.5 SL/min N₂.

EXPERIMENTAL TECHNIQUES

THERMOGRAVIMETRIC FURNACE PELLET PROCEDURES

The pellet oxidation and reduction studies were conducted with a Bureau-designed thermogravimetric laboratory tube apparatus (fig. 4) that was previously described (19). Briefly, this apparatus consisted of a vertical alumina reactor tube (5 cm diam by 1 m long). A platinum wire basket (4 cm diam by 4 cm high) containing the pellet(s) was suspended with a platinum chain inside the tube. In most of the isothermal tests, only one pellet was used. In the temperature-programmed oxidation tests, five pellets were used. In the isothermal tests, a pellet was evaluated from each batch, but in the programmed tests, the acid pellets selected were from batch 2 and the fluxed pellets

from batch 7. The nominal pellet weight and diameter were 2.5 g and 1.1 cm, respectively.

Different nitrogen-oxygen gas mixtures were passed through the tube to simulate different industrial pellet firing conditions; commercial-furnace gases also contain combustion products, such as carbon dioxide and water vapor, but these gases were not added in this research. When 21 pct O_2 was used, it was obtained from a compressed-air supply. In the synthetic gas-mixture tests, nitrogen was purified by passing the gas through a drying reagent and copper turnings at 450° C. The relative total gas pressure in the furnace was 10 cm water.

The percent oxidation was calculated from the weight change and iron analyses. When the sample was calcined prior to oxidation, the percentage of oxidation was directly proportional to the weight gain, which is in agreement with other results (7). In the isothermal oxidation tests, the percentage of oxidation could be calculated to an error of less than 2 pct.

When the calcination and oxidation were conducted simultaneously, the experiments were called programmed temperature tests and no attempt was made to calculate the oxidation level at less than 30 pct. The lower levels of oxidation, calculated from the weight change and the iron analyses, were not very accurate because of the simultaneous calcination-oxidation reactions. The oxidation percentages were calculated to better than 5 pct accuracy at 30 pct or greater.

Isothermal Oxidation Method

In the isothermal oxidation tests, the pellet was first calcined in nitrogen before the oxidizing gas was added. When the furnace reached the desired soak temperature, the pellet was lowered into the hot zone with 100 pct N_2 flowing at 2 SL/min. Unless otherwise stated, the lowering and raising speeds were adjusted so that the pellet heating and cooling rates were 1,000° C/min between 300° C and desired maximum soak temperature. Most of the tests were conducted at soak temperatures of 700°, 850°, and 1,000° C. In general, the pellet was soaked in the furnace hot zone for 5 min in 100 pct N_2 before a four-way valve was switched to the oxygen-containing gas flowing also at 2 SL/min; this flow rate was used by Pape, Frans, and Geiger (7) with a similar apparatus. The pellet was subjected to an oxidizing gas mixture usually for 1 h. The gas was then switched back to nitrogen and the pellet was raised out of the hot zone.

Programmed Temperature Method

In the programmed tests, the oxidation and calcination reactions took place simultaneously. Baseline tests were

1. Nitrogen	15. Cooling coil
2. Carbon monoxide	16. Flare burner in exhaust hood
3. Carbon dioxide	17. Vacuum pump
4. Hydrogen or premix	18. Temperature controller
5. Metering valve	19. Platinum basket
6. Flowmeter	20. Sample
7. Toggle valve	21. Platinum chain
8. Copper turnings	22. Balance flush line
9. Furnace	23. Movable balance platform
10. Magnesium perchlorate	24. Safety screen
11. In-line pressure regulator	25. Holddown clamp
12. Manometer	26. Bell jar
13. Alumina heat exchanger	27. Electronic balance unit
14. Alumina reactor tube	28. Weight loss recorder

Figure 4.—Thermogravimetric apparatus for pellets.

conducted first in 100 pct N_2 to determine the calcined weight loss. Tests were also conducted in 100 pct O_2 to obtain the maximum weight gain at complete oxidation. With these data and chemical analysis, a relationship was developed between the weight change and the percent oxidation.

These tests were conducted with different programmed temperature-time profiles to simulate commercial firing operations. In conventional operations, the pellets are first dried at temperatures up to 300° C before they are preheated, but in this report, both of these operations will be referred to as "preheat." The temperature profiles were defined as preheat from 300° to 1,250° C; induration at 1,250° C; and cooling from 1,250° to 300° C. The preheat and cooling rates were linear between 300° C and 50° C below the induration temperature.

The length of time in the preheat and cooling periods depended on the speed at which the pellets were lowered and raised. The preheat and cooling rates were 200° and 100° C/min, respectively. The time the pellets were at the induration temperature was either 10 or 30 min, which simulated the straight-grate and grate-kiln, respectively (fig. 1).

After firing the pellets at different preheat, induration, and cooling conditions, the fired compressive strength of three cold pellets was determined. Standard methods were used to determine the strength of the pellets (20).

Platinum Basket Reduction Method

The pellets that were oxidized in the thermogravimetric apparatus were also reduced in the same furnace. The procedure was similar to the isothermal oxidation method, but instead of using the oxygen-containing gas mixtures, the mix was 40 pct CO in N_2 at a flow of 3 SL/min, and the pellet temperature was held for 4 h at 950° C. The other operating parameters were similar to those previously discussed (21-22). The percent reduction per minute at 40 pct reduction (R_{40}) was used to express the relative reduction rate (23).

MINI-POT PELLET PROCEDURES

The mini-pot grate research was conducted at Cleveland-Cliffs, Inc., Hibbing, MN. Figure 5 shows a simplified cross section of the apparatus. The oxidation tests involved placing 2 kg of minus 1.3-, plus 1.1-cm-diameter pellets on top of a 2.5-cm-thick layer of ceramic pellets of the same size. The ceramic pellets were used to protect the grate bars. The pellet chamber is 11 cm in diameter and 14 cm high.

Air, oxygen, nitrogen, and propane were added to the mini-pot to obtain the desired burner temperatures and to simulate the gas composition and flow rate of commercial straight-grate and grate-kiln pellet firing operations. The down-draft flow rate was adjusted to maintain a 13-cm water pressure across the pellet and hearth layers. Nominally, the flow rate was 850 SL/min during drying and 550 SL/min at other times. Oxygen had to be added to replace air when the desired oxygen content entering the top of the pellet bed was greater than 10 pct. Conversely, nitrogen had to be added to obtain oxygen levels of less than 10 pct.

The quantity of gas to the burner was manually adjusted to obtain average pellet thermocouple (TC) temperatures similar to those shown in figure 1. The temperature of TC-4 was usually about 50° C lower than that of TC-1. The temperature of TC-4 also lagged about 1 min behind TC-1. The TC-1 was held at 260° C for 2 min to dry the wet pellets. The preheat rate was varied from 150° to 300° C/min. The conventional preheat was defined as 200° C/min. The cooling rate was 25° C/min from the peak temperature to 1,200° C and then 50° C/min down to 800° C. The 2- and 30-min high-temperature (>1,200° C) holding periods were used to simulate the induration time in straight-grate and grate-kiln furnaces, respectively. The peak on-gas temperature was held at 1,290° C for acid pellets and 1,320° C for fluxed pellets. Fluxed pellets normally have to be fired hotter than acid pellets to obtain similar physical properties. The 2-min induration time is shorter than that shown in figure 1, but with these mini-pot conditions, pellets were made with properties similar to those made in a conventional straight-grate furnace. In the grate-kiln simulated tests, the induration temperature was increased at a constant rate from 1,200° C to peak temperature over a 30-min period.

KEY

$\triangle P$ Manometer across bed
TC Thermocouple
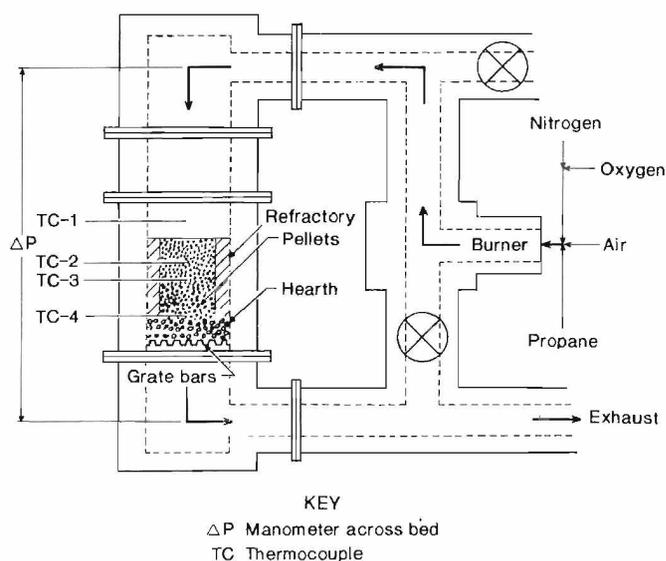
Figure 5.—Mini-pot furnace.

After the pellets cooled, the physical properties were determined. Fifty fired pellets were broken to determine the compressive strength. Because of the limited quantity of pellets, the after-tumble durability determination was made with 650 g of fired pellets, but the other conditions were similar to the 25-lb E279-69 test of the American Society for Testing and Materials (ASTM) (24). This procedure involved tumbling the fired pellets in a drum for a total of 200 revolutions at 24 r/min. After tumbling, the product was screened and the percentage of plus 6.35 mm was determined. This 650-g scaled-down test was more severe than the ASTM test, producing 0.5 pct lower results in the 95- to 96-pct plus 6.35 mm size and 2 pct lower at the 90-pct level.

The relative reducibility was determined with 500 g of fired pellets in a retort furnace by using the standard reduction method (23). The reduction rate was calculated by the same method used in the isothermal reduction tests.

PELLET MICROSTRUCTURE ANALYSIS PROCEDURE

After the pellets were removed from the furnaces, several typical pellets were cut in half and mounted in an epoxy mold. The pellets were polished to expose the desired surface, then examined under optical and electron microscopes. Elemental X-ray distribution mapping was conducted with an energy dispersive spectrometer (EDS).

EXPERIMENTAL RESULTS AND DISCUSSION

THERMOGRAVIMETRIC ISOTHERMAL OXIDATION FINDINGS

To determine the kinetics of the calcination reactions, the pellets were held at different temperatures in a nitrogen gas atmosphere. With acid pellets, a steady-state weight was obtained within 5 min at each isothermal temperature in the range of 700° to 1,000° C (16). With a fluxed pellet at 850° or 1,000° C, the weight loss also leveled out within 5 min, but at 700° C, the calcination of the carbonates was slow and a steady-state weight did not occur even after 90 min in 100 pct N_2 (fig. 6).

When the 100 pct N_2 was replaced with air (zero time in figure 6), an immediate weight gain was obtained. With the acid and the fluxed pellet batches, the weight gain almost leveled off within 10 min after the air was added. The maximum degree of oxidation increased with rising temperature. After 60 min of air oxidation with the fluxed pellets, the degrees of magnetite oxidation at 700°, 850°, and 1,000° C were 74, 94, and 96 pct, respectively (fig. 6); these values were calculated from the batch 7 data in tables 1 and 2. The 850° and 1,000° C data in table 2 indicated that the pellet containing organic binder (batch 6) had a slightly lower ferrous content than the pellet made with the same concentrate and only bentonite binder (batch 5). The DTA results (fig. 2) also indicated faster oxidation (exothermic reaction) of the crushed pellet containing the organic binder (batch 6) than the pellet made with only bentonite binder (batch 5). Faster oxidation was also indicated by the lower ferrous content of the pellet sample with the organic additive and with 21 pct O_2 (table 2). When the organic binder was burned off, it probably produced a pellet with higher porosity. When air was replaced with 100 pct O_2, lower ferrous contents were obtained with all the pellet batches.

Figure 6.—Temperature dependence of calcination and oxidation reactions of fluxed (batch 7) pellets.

Table 2.—Influence of oxygen percentage and temperature on average ferrous content (percent) after 1 h of oxidation

Batch	21 pct O_2			100 pct O_2		
	700° C	850° C	1,000° C	700° C	850° C	1,000° C
1 ...	7.2	1.3	0.8	ND	ND	<0.1
2 ...	8.9	1.2	.5	ND	ND	<.1
3 ...	7.3	1.3	.4	6.9	0.9	<.1
4 ...	6.5	1.2	.8	ND	ND	<.1
5 ...	6.5	1.3	.7	ND	ND	<.1
6 ...	6.4	1.1	.4	ND	ND	<.1
7 ...	6.6	1.4	1.0	ND	.5	.2

ND   Not determined.

With different concentrates, no correlations were possible with the initial pellet analyses and the final ferrous contents (tables 1 and 2). The nitrogen soak times for the results in figure 7 were the same as shown in figure 6, and those above 1,000° C were the same as those at 1,000° C with 21 pct O_2. The maximum deviations of the ferrous contents for duplicate tests with pellets from the same batch are shown by the tie-bars in figure 7. The number of duplicate tests with pellets from the same batch varied from 2 to 10. The ferrous content decreased with increasing temperature, except at 1,300° C; at this temperature, the ferrous content increased, which suggested that hematite decomposed at 1,300° C in air.

The oxidation kinetics that occurred with air at 1,000° C is shown in figure 8. The oxidation rate of the fluxed pellet (batch 7) was slightly lower than that of the pellet containing both organic and bentonite binders (batch 6), but was generally higher than the other acid pellets containing all bentonite binder (batches 1 through 5).

The percentage of oxidation was determined at various oxygen levels with the batch 2 pellets. The degree of oxidation in 1 min increased with increased oxygen content (fig. 9). These results showed that the dependence of the oxidation rate on the gas oxygen content was greater at 1,000° C than at the lower temperatures.

THERMOGRAVIMETRIC PROGRAMMED TEMPERATURE OXIDATION FINDINGS

Acid Pellet Oxidation Studies

Pre- and Postinduration Oxidation Experiments

Since commercial firing furnaces do not oxidize the pellets at isothermal conditions, tests were conducted at various programmed temperature-time profiles to simulate different firing operations. The initial tests were conducted with a 10-min induration period at 1,250° C to simulate straight-grate conditions. The results shown in figure 10 were obtained with five pellets from batch 2 heated in

Figure 8.—Oxidation kinetics of acid (batches 1 through 6) and fluxed (batch 7) pellets. Temperature: 1,000° C; atmosphere: air.

Figure 9.—Influence of oxygen content and temperature on 1-min oxidation of acid (batch 2) pellet.

Figure 7.—Temperature dependence of ferrous content after 1 h of oxidation in air of acid (batches 1 through 6) and fluxed (batch 7) pellets.

Figure 10.—Influence of air addition time on weight gain (oxidation) of acid (batch 2) pellet.

Table 3.—Programmed temperature results using air throughout heating-cooling temperature profile [1]

Batch	Fe^{2+}, pct	Strength,[2] lb/p
Acid pellets:		
1	0.4	530
2	.4	610
3	.5	505
4	.2	430
5	.5	470
6	.2	640
Fluxed pellets:		
7	.6	490

[1] Induration time was 10 min and peak temperature was 1,250° C.

[2] Average compressive strength per pellet.

Preheat Oxygen Experiments

The importance of the preheat oxygen content was determined with the 10-min induration time with pellets from batch 2. As the preheat oxygen content was increased, the final ferrous content decreased (fig. 11). However, the compressive strengths reached a maximum with 21 pct O_2, after which no further strength increase was obtained with increasing oxygen contents.

Programmed temperature tests were also conducted with pellets from batch 2 using a 30-min induration period to simulate the grate-kiln conditions. The goal of these tests was to determine the importance of when magnetite was oxidized during the heating-cooling periods. The gas used for curve A in figure 12 was 100 pct N_2 during the preheat and induration periods and 60 pct O_2 during the cooling period. Under these conditions, essentially all the magnetite was oxidized during the cooling period.

A test was also conducted with 60 pct O_2 during the preheat period but with 100 pct N_2 during the induration and cooling periods. When the 100 pct N_2 gas was turned on, a weight loss was observed, which was explained earlier by hematite thermal dissociation (figure 10, curve C). To prevent hematite dissociation, the data in curves B and C in figure 12 were obtained with at least 2 pct O_2 throughout the tests. Much stronger pellets were produced when the 60 pct O_2 was added before the induration period rather than after the induration period (curve C versus curves A and B). The ferrous contents of these fired pellets were about the same, and therefore, this alone is not a good indicator of pellet strength.

either air or 100 pct N_2. These results indicated that the final oxidation level was 80 pct when air was used only during the cooling period (curve A), but when air was used during the preheat and/or induration periods, essentially all the magnetite was oxidized (curves B through D). The final ferrous contents of the pellets treated by the conditions shown in curves A, B, C, and D were 4.0, 0.8, 0.7, and 0.4 pct, and the compressive strengths were 230, 460, 560, and 610 lb/p, respectively. The high-ferrous pellets were weak because of a duplex structure (shell and core) (25), which will be discussed in a later section. It is evident from these data that the earlier the magnetite is oxidized in the programmed heating tests, the lower the ferrous content and the stronger the pellets. Curve C in figure 10 shows a weight loss when air during the preheat period was followed with nitrogen during the induration period. The reason for this weight loss was the dissociation of hematite to secondary magnetite at 1,250° C in the absence of oxygen (26).

Table 3 gives the properties of all the pellet batches when the tests were conducted using the same conditions shown in curve D of figure 10 (air used throughout the programmed test). The compressive strengths and ferrous contents varied with different pellet batches, but no interrelationships between the physical and chemical properties were evident.

Figure 11.—Influence of preheat oxygen content on properties of acid (batch 2) pellets.

KEY

Curve	O_2, pct (P-I-C)	Strength, lb/p	Fe^{2+}, pct
A	0-0-21	230	4.0
B	6-0-21	430	1.9
C	11-0-21	440	1.9
D	21-0-21	550	0.7
E	30-0-21	550	0.4
F	100-0-21	510	0.3
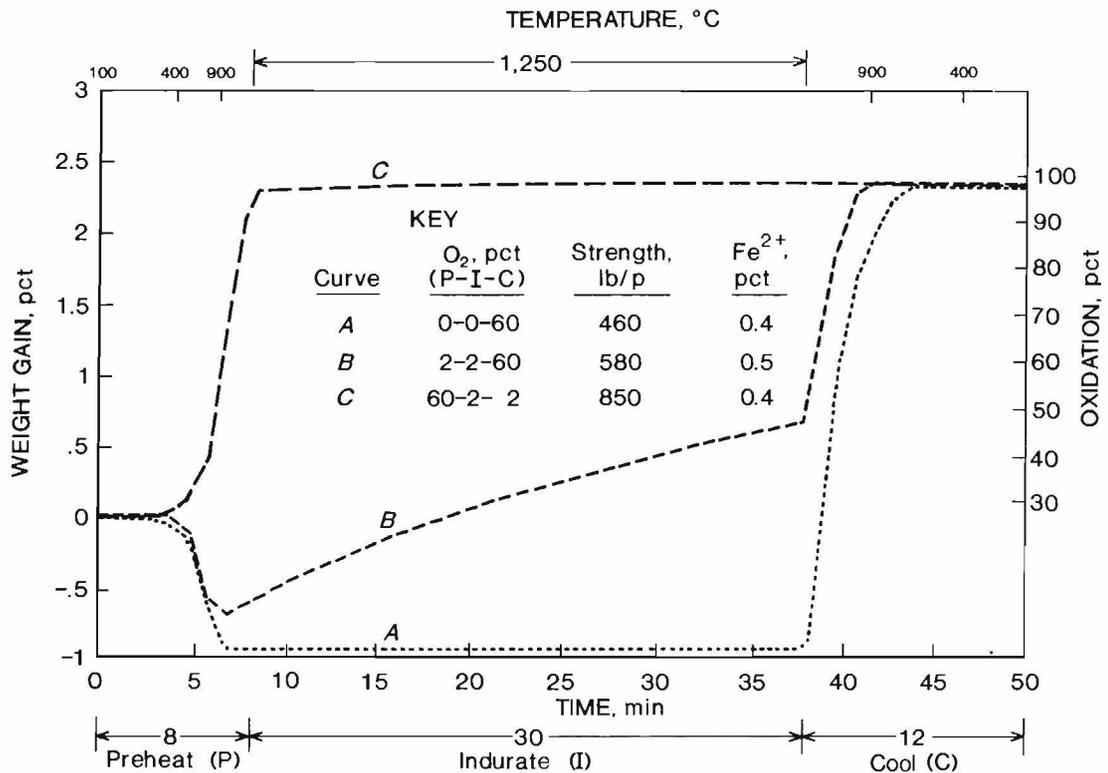
Figure 12.—Influence of pre- and postinduration oxidation on properties of acid (batch 2) pellets.

KEY

Curve	O_2, pct (P-I-C)	Strength, lb/p	Fe^{2+}, pct
A	0-0-60	460	0.4
B	2-2-60	580	0.5
C	60-2- 2	850	0.4

Fluxed Pellet Studies

Pre- and Postinduration Oxidation Experiments

The importance of adding oxygen early or late in the firing operation was evaluated with fluxed pellets (batch 7) using the 30-min induration period, since this time was found to be critical with the acid pellets. The results in curve A of figure 13 were obtained with 60 pct O_2 during preheating, 100 pct N_2 during indurating, and 21 pct O_2 during cooling. When a temperature of about 600° C was reached during the preheat period, a weight gain was obtained, but a loss was obtained above 800° C. These results indicated that the oxidation of magnetite starts at a lower temperature than the decomposition of the carbonate flux; similar results were observed with the DTA and TGA results (figures 2 and 3, respectively). At 1,250° C, the pellets kept losing weight during the next 30 min because of the decomposition of hematite as shown by curve A in figure 13.

When 100 pct N_2 was used during the preheat period, all the carbonate was decomposed during the 8-min preheat period (figure 13, curves B and C). When 60 pct versus 21 pct O_2 was added during the cooling period, more pellet oxidation (lower ferrous content) occurred and stronger pellets were obtained (curve B versus curve C, respectively). However, these pellets were still weaker than those preheated with 60 pct O_2 (curve A). These data indicated that the best results were obtained when the pellets were oxidized early.

Preheat Oxygen Experiments

In general, the results in figure 14 indicated that the greater the oxygen content during the preheat period, the greater the compressive strength. The ferrous content with 60 pct O_2 during the preheat was the same as with 30 pct O_2, but the former pellets were stronger so the ferrous content was not the sole contributing factor (curves A and B, respectively). The results indicated that higher pellet strengths and lower ferrous contents were generally obtained with increasing preheat oxygen levels. The weight loss (carbonate decomposition) reaction was faster than the weight-gain (magnetite oxidation) reaction, as evidenced by the preheat data between 900° and 1,250° C (figure 14, curves A through D).

MINI-POT PELLET OXIDATION FINDINGS

Preheat Ferrous Content Studies

In order to determine the percentage oxidation at different temperatures, tests were interrupted during the
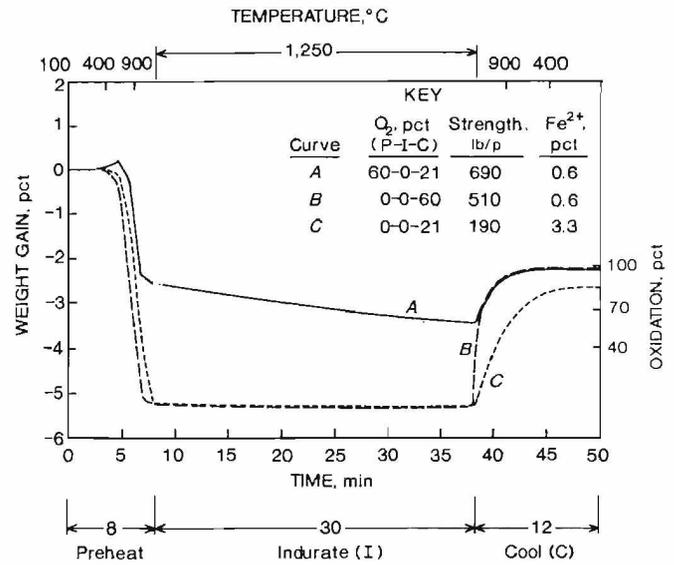
Figure 13.—Influence of pre- and postinduration oxidation on properties of fluxed (batch 7) pellets.
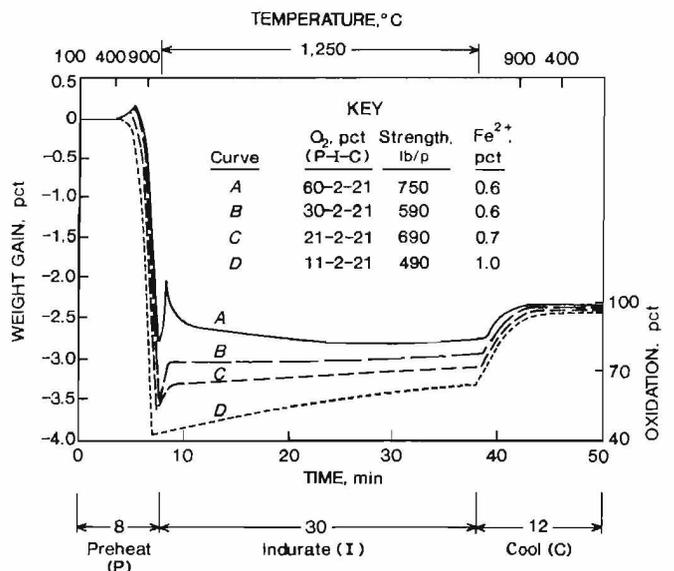
Figure 14.—Influence of preheat oxygen content on properties of fluxed (batch 7) pellets.

preheat period. When the desired temperature was reached, three pellets were removed and quenched in water; this sampling technique involved sliding out the mini-pot part of the furnace and exposing the top layer of pellets to ambient conditions.

The quenched pellet analyses were compared with the charged analyses. The ferrous content of the dried, non-fired fluxed pellets was nominally 20 pct and the carbon (mainly carbonate) content was 1.6 pct. The ferrous content of the acid pellets was about 2 pct higher. The carbonate content of the pellets did not decrease appreciably

until the pellet temperature was above 700° C (table 4). At the lower temperatures, the fluxed pellets oxidized slightly faster than the acid pellets, which was possibly due to the higher porosity of the fluxed pellets. At 1,150° C, the ferrous contents of both the acid and the fluxed pellets were 7.8 pct (tests 2 and 5, respectively). At 1,000° C, the ferrous content was considerably higher when the preheat gas contained 15 pct rather than 30 pct O_2 (test 3 versus test 4), but the carbonate decomposition rate was not appreciably influenced by the oxygen content as evident from the carbon analyses. At 1,150° C, 75 pct of the carbonate was decomposed but only 65 pct of the magnetite was oxidized (test 5). These results, along with the data in figure 14, indicated that the high-temperature carbonate decomposition reaction was faster than magnetite oxidation in 30 pct (or less) O_2.

The length of time needed to oxidize the magnetite and to decompose the carbonates was also determined. At 1,000° C, over 5 min was required to decrease the ferrous content to 1 pct (or less) with 15 pct O_2 (table 5, tests 6 and 8), but with 30 pct O_2, less than 5 min was required (tests 7 and 9). Again, fluxed pellets oxidized more readily than acid pellets (tests 6 through 9). No further change in the carbon analysis was noted beyond 5 min, which again

indicates that the carbonate decomposition reaction was faster than the oxidation reaction. These results are in fair agreement with the laboratory tube furnace data.

Two-Minute Induration Studies

Acid Pellet Experiments

The straight-grate was simulated with a mini-pot pellet induration time of only 2 min at a peak temperature of 1,290° C but the time above 1,000° C was about 10 min. With a preheat rate of 200° C/min and 6 pct O_2 throughout the test, the average compressive strength of the acid pellets was only 380 lb/p and the ferrous content was 4.1 pct (table 6, test 10); a low percentage of O_2 was selected so that some magnetite would remain unoxidized. Earlier isothermal oxidation studies showed that oxygen enrichment may be most effective at about 1,000° C. To substantiate this finding, the 6 pct O_2 content was increased to 30 pct for 5 min after a 1,040° C preheat temperature was reached. This enrichment produced stronger pellets (580 lb/p) with a lower (0.2 pct) ferrous content (test 11); the ferrous gradient difference between the top, middle, and bottom was less than 0.5 pct.

Table 4.—Influence of temperature on ferrous and carbon content of pellets fired in mini-pot

Test	Preheat, °C/min	Oxygen, pct	Fe^{2+}, pct[1]				C, pct[1]			
			600° C	700° C	1,000° C	1,150° C	600°C	700° C	1,000° C	1,150° C
Acid pellets:										
1........	200	30	20.9	ND	10.2	ND	ND	ND	ND	ND
2........	200	30	ND	19.1	ND	7.8	ND	ND	ND	ND
Fluxed pellets:										
3........	200	15	16.8	ND	11.0	ND	1.4	ND	0.8	ND
4........	200	30	16.4	ND	9.6	ND	1.6	ND	.8	ND
5........	200	30	ND	15.6	ND	7.8	ND	1.3	ND	0.4

ND Not determined.
[1]Pellets were removed during preheat portion, quenched in water, dried, and analyzed.

Table 5.—Dependence of ferrous and carbon content on time of pellets fired at 1,000° C in mini-pot

Test	Preheat, °C/min	Oxygen, pct	Fe^{2+} at 1,000° C, pct[1]				C at 1,000° C, pct[1]			
			0 min	5 min	10 min	15 min	0 min	5 min	10 min	15 min
Acid pellets:										
6........	200	15	13.6	4.3	1.0	0.3	ND	ND	ND	ND
7........	200	30	9.7	.8	.4	.2	ND	ND	ND	ND
Fluxed pellets:										
8........	200	15	11.3	1.6	.2	.2	0.7	0.2	0.2	0.2
9........	200	30	11.2	.3	.2	.2	.6	.1	.1	.1

ND Not determined.
[1]Pellets were removed during preheat portion, quenched in water, dried, and analyzed.

Table 6.—Mini-pot results using 2-min induration time

Test	Preheat, °C/min	Peak temp, °C	Oxygen, pct	AT,[1] pct	Strength,[2] lb/p	Fe²⁺,[3] pct
		ACID PELLETS—OXYGEN CONTENT				
10 ..	200	1,290	6	97.0	380	4.1
11 ..	200	1,290	[4]6	96.4	580	.2
		ACID PELLETS—PREHEAT RATE				
12 ..	150	1,290	15	96.1	640	0.6
13 ..	300	1,290	15	96.4	540	.8
		FLUXED PELLETS				
14 ..	150	1,320	15	96.2	600	0.8
15 ..	300	1,320	15	95.9	545	1.2
16 ..	300	1,320	30	95.0	625	.3

[1]Percentage plus 6.35 mm after-tumble (AT) test.
[2]Average compressive strength per pellet.
[3]Analysis after test.
[4]Oxygen increased from 6 to 30 pct for 5 min after preheat temperature of 1,040° C.

Strong (640 lb/p) and fairly well oxidized (0.6 pct ferrous content) pellets were obtained (test 12) with 15 pct O_2 throughout the test and at a lower preheat rate of 150° C/min. However, with this oxygen percentage at the higher preheat rate of 300° C/min, a lower pellet strength (540 lb/p) and a slightly higher ferrous content (0.8 pct) were obtained (test 13). These results indicated that with 15 pct O_2 the pellet strength decreased at the higher preheat rate. In a commercial operation, a higher preheat rate could result in a higher pellet production rate.

The after-tumble differences in table 6 were within the experimental error so no correlations were made from these data. These values indicate the abrasion resistance of the pellets.

Fluxed Pellet Experiments

With fluxed pellets using 15 pct O_2 during the preheat and induration periods, the pellet strength decreased and the ferrous content increased when the preheat rates were increased from 150° to 300° C/min (table 6, test 14 versus test 15), which was similar to the results observed with acid pellets (tests 12 and 13). When the oxygen content was increased to 30 pct with the 300° C/min preheat rate, the pellet strength increased and the ferrous content decreased as would be expected (test 15 versus test 16). These data indicated that, at the high heating rate, the best results were obtained with 30 pct O_2.

Thirty-Minute Induration Studies

Acid Pellet Experiments

In a grate-kiln firing process, the pellet induration time is longer than in a straight-grate operation; therefore, tests were also conducted with an induration of 30 min. When the oxygen preheat percentage was increased from 5 to 30 pct, the acid pellet after-tumble values and pellet compressive strengths increased while the ferrous contents decreased as expected (table 7, tests 17 through 19).

When the preheat rate was increased from 150° to 250° C/min, the acid pellet compressive strengths dropped from 830 to 570 lb/p and the ferrous contents increased from 0.2 to 0.6 pct as expected (tests 19 and 20, respectively). When the preheat oxygen content was decreased from 30 to 15 pct at preheat rate of 250° C/min, the compressive strength and the after-tumble values decreased and the ferrous content increased (tests 20 and 21, respectively). However, when the oxygen content during the induration period was increased from 5 to 10 pct while using 15 pct O_2 during the preheat period, the pellet compressive strength and the after-tumble value increased and the ferrous content decreased as expected (tests 21 and 22, respectively).

The higher preheat rates had a bigger influence on the acid pellet compressive strengths with the 30-min rather than with the 2-min induration time (table 7, tests 19 and 20 versus table 6, tests 12 and 13). With the longer induration period, some residual magnetite was present at high temperatures (above 1,200° C) long enough to sinter it sufficiently and retard its oxidation. This may be one of the reasons for the duplex structure of partially oxidized pellets. The center of the 30-min indurated pellets appeared to have larger and more sintered grains.

Fluxed Pellet Experiments

Fluxed pellets were also indurated for 30 min and cooled in air in the mini-pot (table 7, tests 23 through 28). In tests 24, 26, and 28, the preheat oxygen content was increased from 15 to 30 pct O_2 for 3 min after 1,040° C was reached. The increased oxygen content increased the compressive strength and after-tumble values at all the heating rates (tests 23 through 28). The greatest oxygen-enrichment benefit was observed at the highest preheat rate (300° C/min), which was expected (fig. 15).

The oxygen-enrichment benefit with fluxed pellets was more apparent with the 30-min than with the 2-min induration time. With 2-min induration time, increasing the preheat rate from 150° to 300° C/min with 15 pct O_2 resulted in no appreciable decrease in the compression strength (table 6, tests 14 through 15). With the 30-min induration time, a significant decrease in compressive strength was obtained when the preheat rate was increased from 200° to 300° C/min (table 7, tests 23, 25, and 27). However, with 30 pct O_2, only a small decrease in compressive strength was observed when the preheat rate was increased from 200° to 300° C/min (tests 24, 26, and 28).

Table 7.—Mini-pot results using 30-min induration time

Test	Preheat, °C/min	Oxygen, pct[1]		AT,[2] pct	Strength,[3] lb/p	Fe^{2+},[4] pct	Porosity, pct	R$_{40}$,[5] pct/min
		Preheat	Indurate					
ACID PELLETS—PREHEAT OXYGEN CONTENT								
17	150	5	5	45.0	200	8.3	21.2	0.60
18	150	15	5	75.8	300	3.6	23.9	.65
19	150	30	5	97.9	830	.2	24.3	.85
ACID PELLETS—HIGH PREHEAT RATE								
20	250	30	5	97.7	570	0.6	27.0	0.84
21	250	15	5	95.7	350	1.5	27.2	.86
22	250	15	10	98.5	730	.4	24.8	.83
FLUXED PELLETS—PREHEAT OXYGEN CONTENT								
23	200	15	5	98.9	805	ND	ND	ND
24	200	[6]30	5	99.0	875	ND	ND	ND
25	250	15	5	98.1	755	ND	ND	ND
26	250	[6]30	5	98.8	835	ND	ND	ND
27	300	15	5	96.9	630	ND	ND	ND
28	300	[6]30	5	98.7	810	ND	ND	ND

ND   Not determined.
[1]Pellet bed was cooled in air.
[2]Percentage plus 6.35 mm after-tumble (AT) test.
[3]Average compressive strength per pellet.
[4]Analysis after test.
[5]Reducibility rate at 40-pct reduction.
[6]Oxygen increased from 15 to 30 pct for 3 min after preheat temperature of 1,040° C.
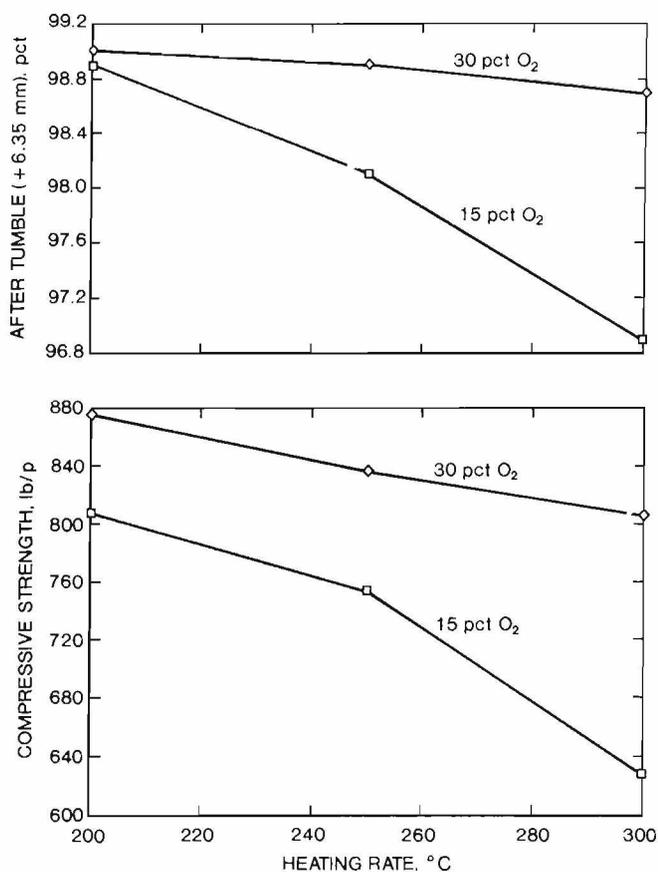
Figure 15.—Influence of mini-pot preheat rate and oxygen content on tumble durability (top) and compressive strength (bottom) of fluxed (batch 7) pellets.

REDUCTION FINDINGS

Acid Pellet Studies

Platinum basket furnace reduction studies were conducted on both pre- and postinduration oxidized pellets. The results in figure 16 indicate that the postinduration oxidized pellets (curves A and B) had lower reduction kinetics (i.e., R$_{40}$ values) than preinduration oxidized pellets (curves C and D). Preinduration oxidation resulted in the strongest pellets, and stronger pellets are usually more difficult to reduce, so this finding was encouraging. Decreasing the pellet induration time from 30 to 10 min decreased the pellet strength, but the R$_{40}$ value increased as would be expected (curves C and D, respectively). The induration time had no influence on the reducibility with the postinduration oxidized pellets (curves A and B).

With the mini-pot oxidized pellets, higher reduction rates with higher pellet strengths were also obtained with increasing preheat oxygen contents (table 7, tests 17 through 19). The higher reducibility was probably due to the higher porosity because of the lower ferrous content. When the oxygen level was low during the preheat period, the magnetite probably reacted with the silicon compounds to form low-melting (1,150° C) iron silicates (i.e., fayalite). Fayalite formation may be the reason for low pellet porosities when low oxygen contents were used during the preheating period. However, other factors influence the reducibility, because when the preheat rate was increased

from 150° to 250° C/min (tests 19 and 20, respectively), the porosity increased but the reducibility did not.

At a preheat rate of 250° C/min, essentially no change in the reducibility was obtained when the preheat oxygen content was decreased from 30 to 15 pct (table 7, tests 20 and 21, respectively). Increasing the oxygen content from 5 to 10 pct during the induration period decreased the porosity but did not significantly increase the reduction rate (tests 21 and 22, respectively). Again, the increase in pellet strength without a significant decrease in reducibility was a positive finding.

Fluxed Pellet Studies

The platinum basket furnace reduction tests with fluxed pellets were similar to those of acid pellets, in that the preinduration oxidized pellets reduced faster than the postinduration oxidized pellets (fig. 17). The time to obtain a fractional reduction of 0.9 was 125 min with the postinduration oxidized fluxed pellets, while only 80 min was required with the preinduration oxidized pellets. This 90-pct reduction level was used as the comparison level because this reduction rate difference was greater with the pre- and the postinduration oxidized pellets than it was at the 40-pct reduction level. These flux results, along with the acid data, indicated that pellets that were oxidized early during the firing operation have higher reducibility.

PELLET MICROSTRUCTURE FINDINGS

The photographs discussed in this section were taken of typical pellets indurated in the platinum basket furnace for 10 min at a peak temperature of 1,250° C unless otherwise stated. Figure 18 shows acid pellets that were partially oxidized using 5 pct O_2 throughout the entire firing cycle. Figure 18A shows a pellet with a grayish (hematite) shell and a black (magnetite) core. Pellets with this type of duplex structure usually had concentric cracks (27), which probably resulted from the difference in the thermal expansion coefficient of hematite and magnetite grains (28). Also, the core was more sintered and sometimes appeared to shrink away from the shell.

Figure 18B depicts an enlargement of a portion of the pellet core in figure 18A near the shell-core interface. It shows that the oxidation occurred preferentially on a specific magnetite (grayish area) crystal plane to form hematite lamella (white areas).

Partially oxidized pellets are also shown in figure 19 but these pellets were indurated at a higher temperature

(1,300° C rather than the normal 1,250° C). This higher temperature resulted in more rounding of the edges, which was probably due to the softening of the hematite and magnetite grains (fig. 19A). Figure 19B is a different area of the pellet shown in figure 19A, and it shows more silicate slag (black area).
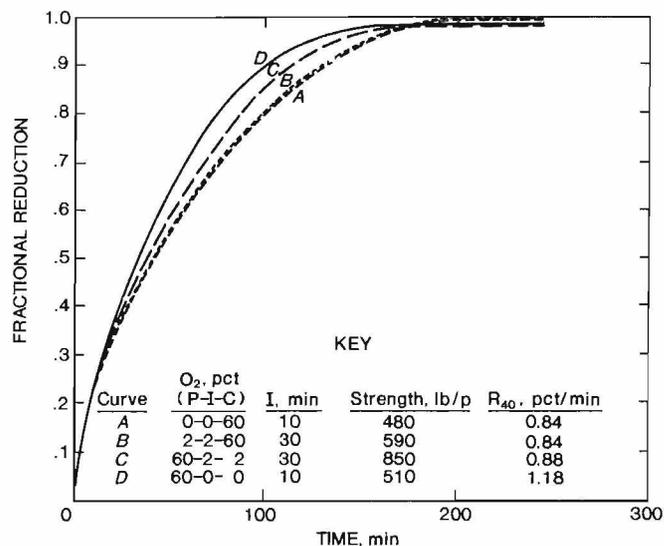
Figure 16.—Influence of pre- and postinduration oxidation on reduction of acid (batch 2) pellets. P, Preheat; I, Induration; C, cooling.
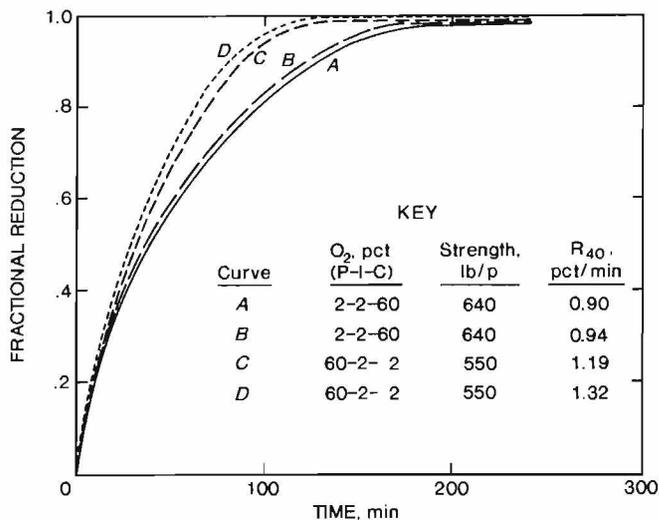
Figure 17.—Influence of pre- and postinduration oxidation on reduction of fluxed (batch 7) pellets. P, Preheat; I, Induration; C, cooling.
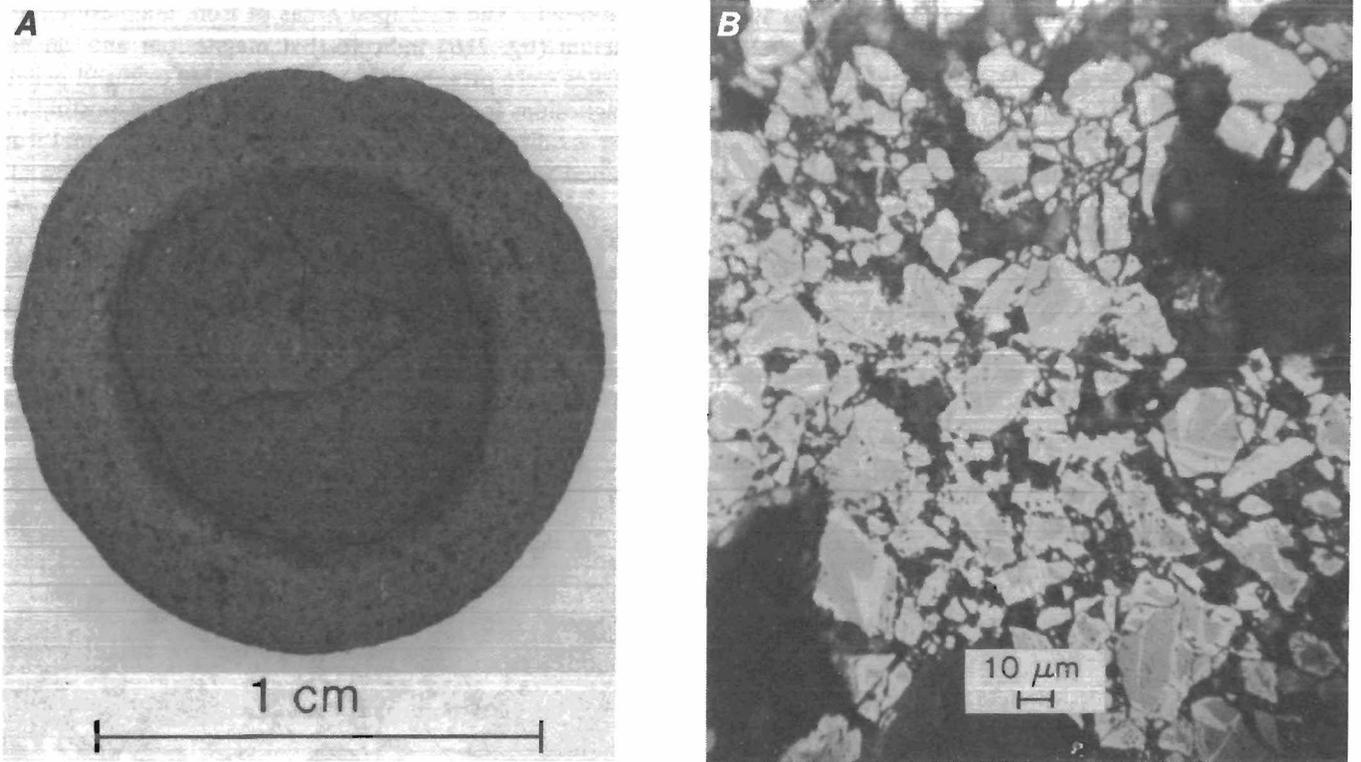
Figure 18.—Partially oxidized acid (batch 2) pellets. A, Pellet shell and core; B, hematite (white) lamella in magnetite (gray) near shell-core interface.
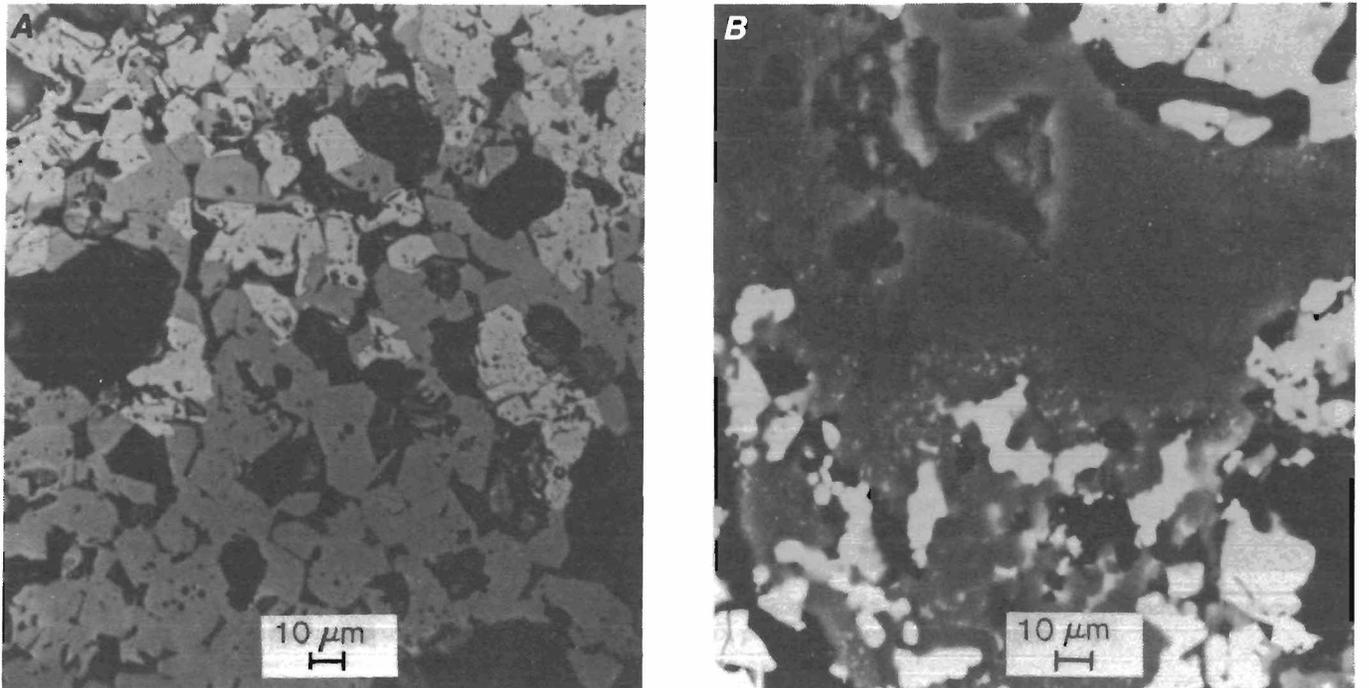
Figure 19.—Partially oxidized acid (batch 2) pellets indurated at high temperature (1,300° C). A, Rounded hematite (white) and magnetite (gray) grains; B, large slag (black) area containing hematite (white) grains.

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Acid pellets that were indurated for 30 min in 100 pct N_2, preinduration oxidized with 60 pct O_2, and cooled in air were less sintered than those that were postinduration oxidized with 60 pct O_2 (figures 20A and 20B, respectively). This is in agreement with previous investigations, which reported that magnetite reacts more readily with silicon compounds than hematite to form low-melting iron silicates (15, 29-30). Kokal (31) reported that the formation of slag and the recrystallization of magnetite was undesirable.

The fluxed pellets were examined with an electron probe. Figures 21A and C are composite pictures, while figures 21B and D are X-ray images of the boxed-in areas of the composite pictures. In the elemental X-ray maps, the greater the quantity of the element present, the lighter the image. Figures 21A and B show an area in a pellet that was oxidized before it was indurated, while figures 21C and D show an area that was oxidized after it was indurated. The K-shaped areas of iron, magnesium, and calcium (fig. 21B) indicate that magnesium and calcium ferrites were present in the preinduration oxidized pellets. Magnesium ferrite was also formed with the postinduration oxidized pellets, and is shown as a channel-iron-shaped area (middle bottom of iron and magnesium elemental maps of figure 21D). The iron and calcium maps only indicated the presence of calcium ferrite in the preinduration oxidized pellet.

Areas of the pellets were also examined with an energy dispersive spectrometer and higher peak intensities were obtained with higher cation concentrations. More calcium ferrite was again indicated with the preinduration than with the postinduration oxidized pellet (figure 22C and figure 23B, respectively). These results suggest that calcium oxide reacted more readily with hematite than magnetite. In the calcium silicate slag area, the iron peak heights were slightly higher in the postinduration oxidized pellet
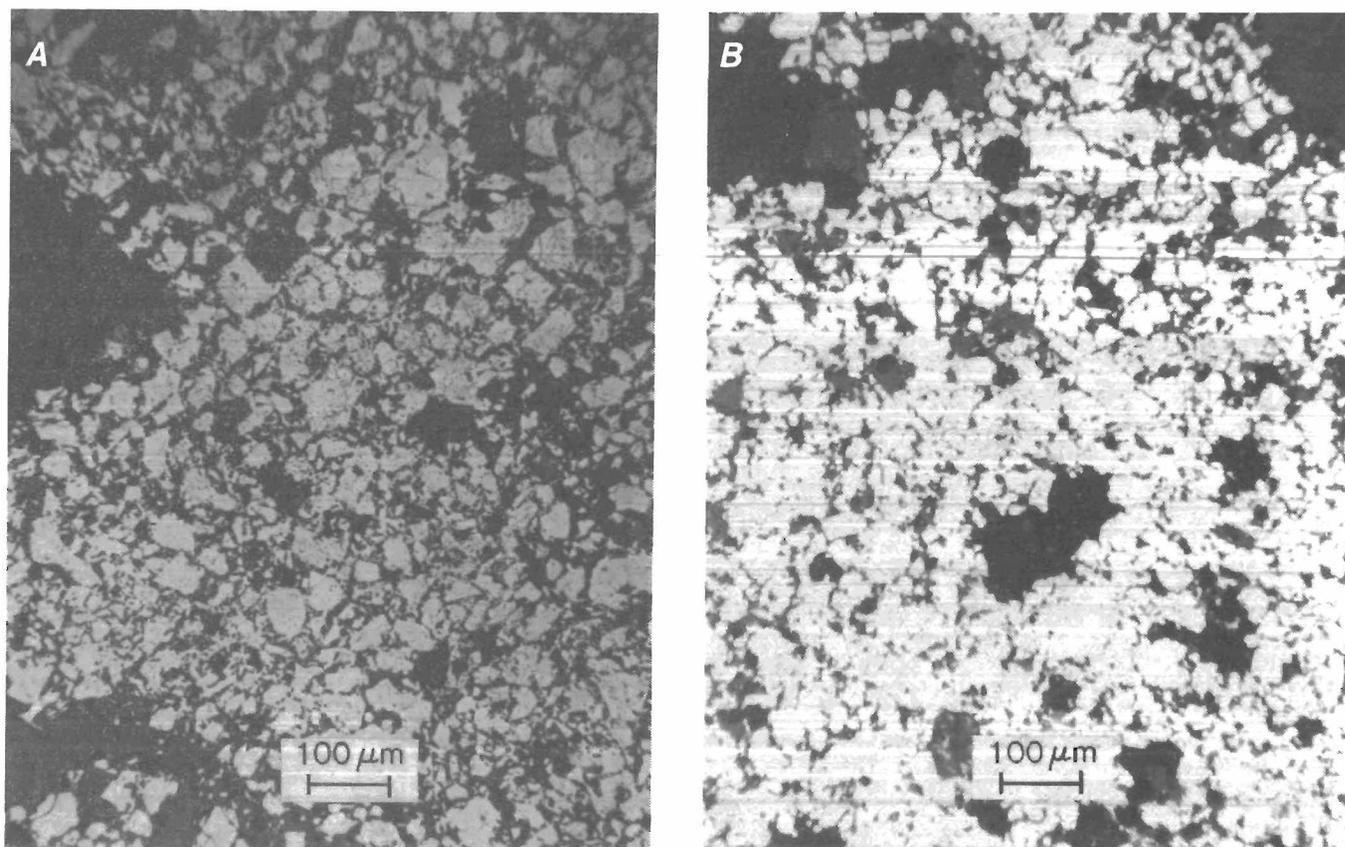
Figure 20.—Oxidized acid (batch 2) pellet. A, Preinduration oxidized; B, postinduration oxidized.
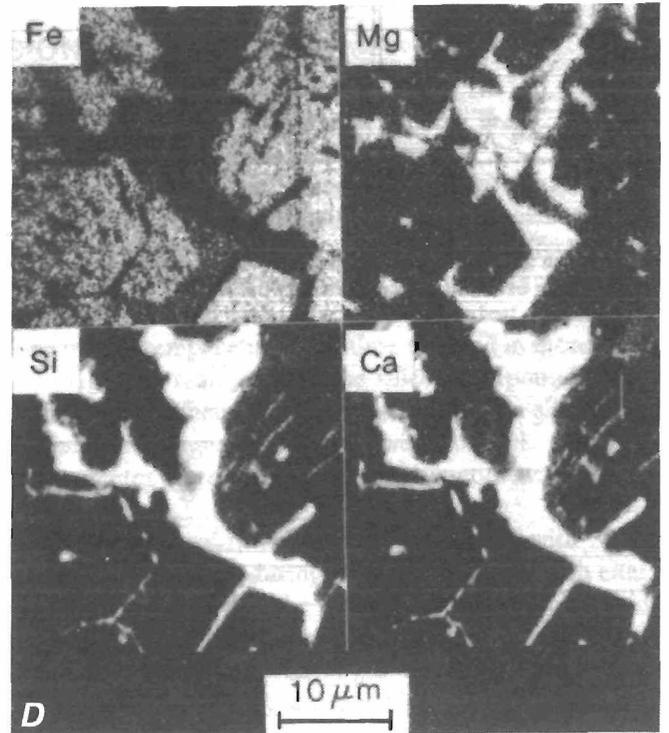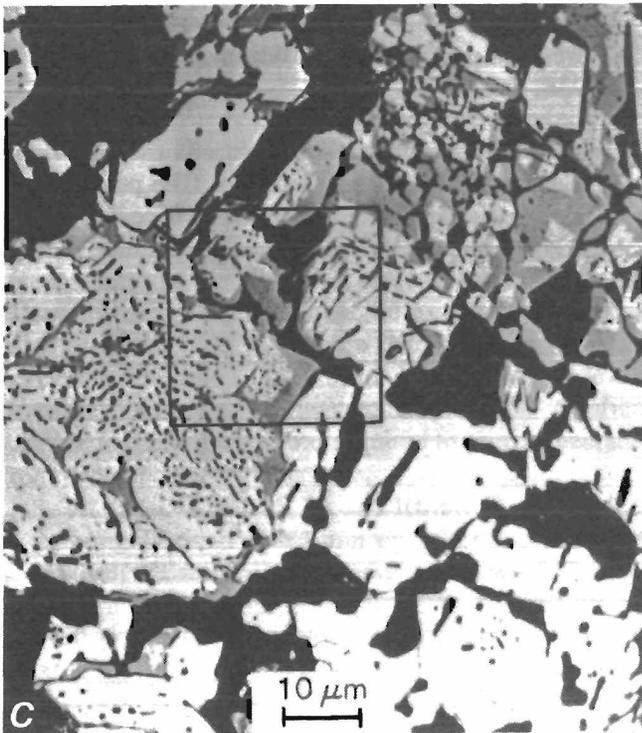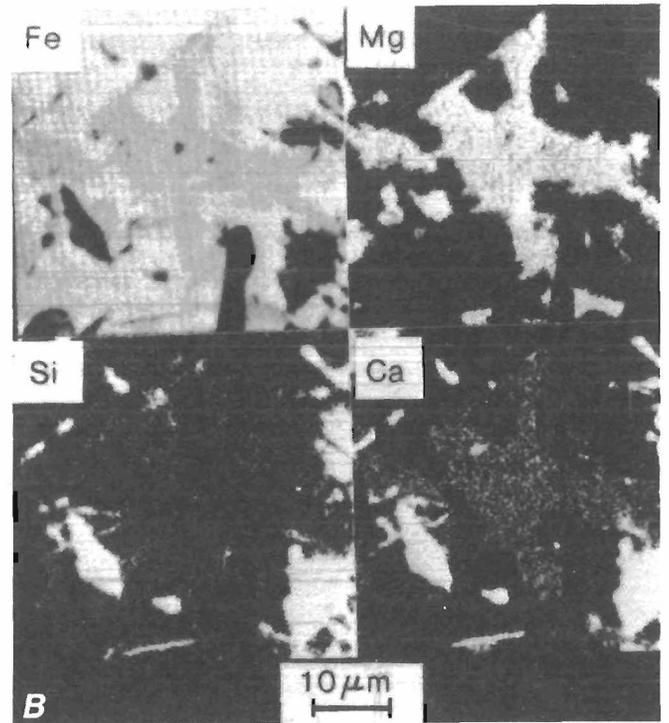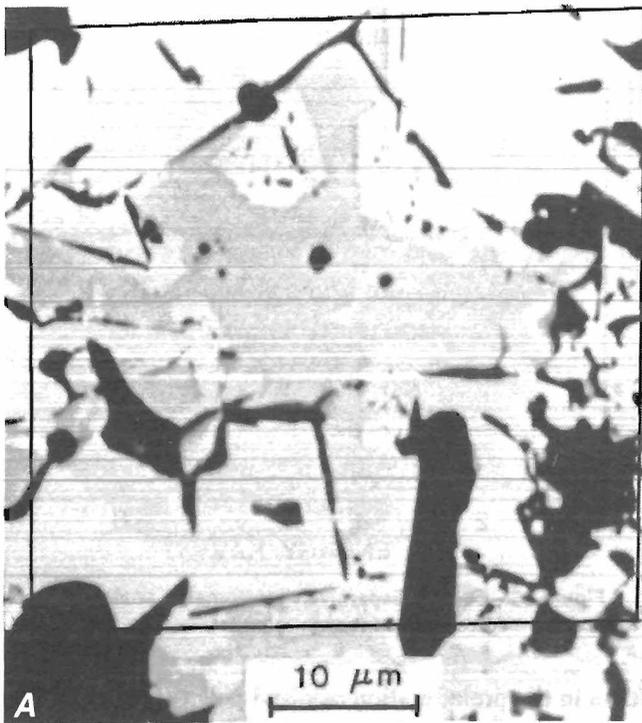
Figure 21.—Electron probe photographs of pre- and postinduration oxidized fluxed (batch 7) pellets. *A*, Preinduration composite; *B*, preinduration X-ray elemental maps; *C*, postinduration composite; *D*, postinduration X-ray elemental maps.
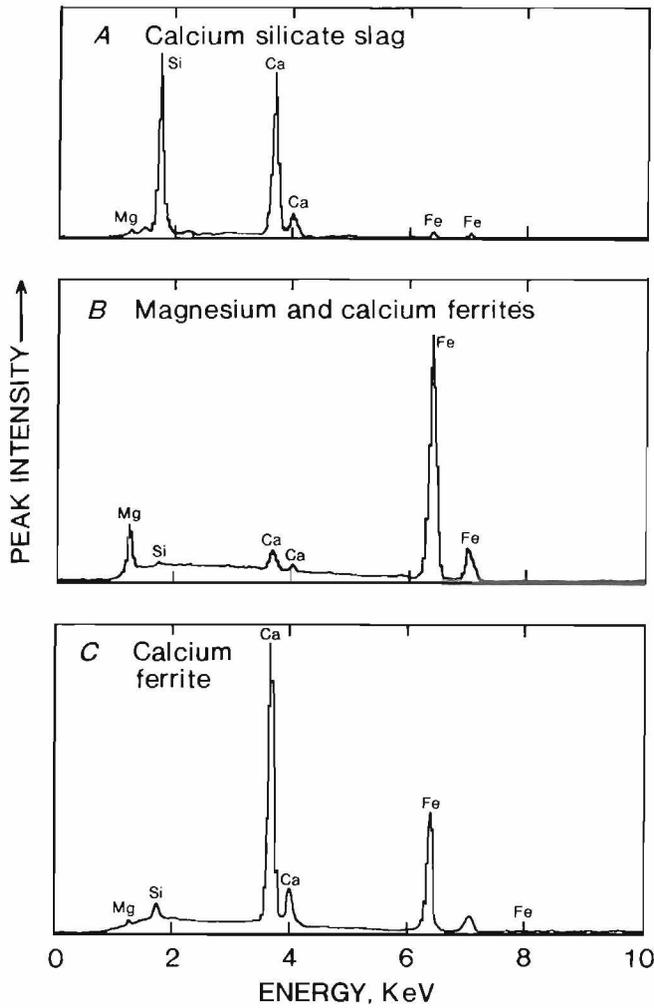
Figure 22.—Energy dispersive spectrometric analyses of pre-induration oxidized fluxed (batch 7) pellet.
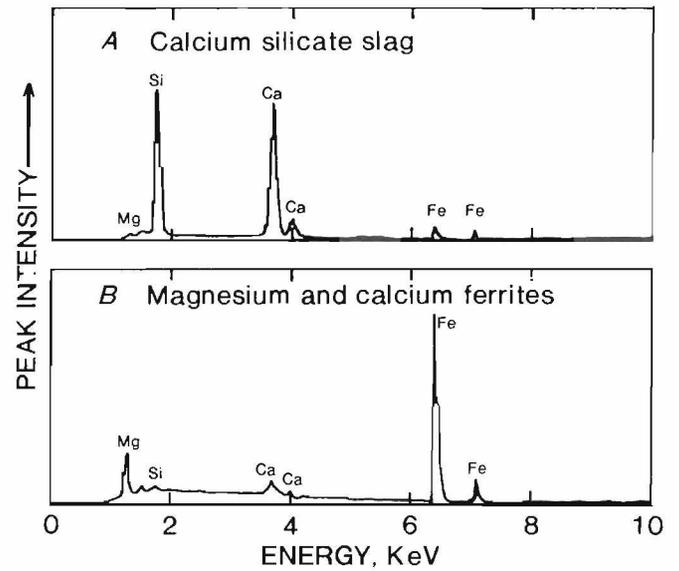
Figure 23.—Energy dispersive spectrometric analyses of post-induration oxidized fluxed (batch 7) pellet.

than in the preinduration oxidized pellet (figures 22A and 23A, respectively). These results suggest that the magnetite dissolved more readily than hematite in the calcium silicate slag. The magnesium peaks were small with both the pre- and postinduration oxidized pellets (figures 22B and 23B, respectively).

The preinduration oxidized fluxed pellet expanded more during reduction than the postinduration oxidized pellet did (figures 24A and B, respectively). The postinduration oxidized pellet expanded less; probably it contained more fayalitic slag and the strong slag bond prevented the pellet from swelling.
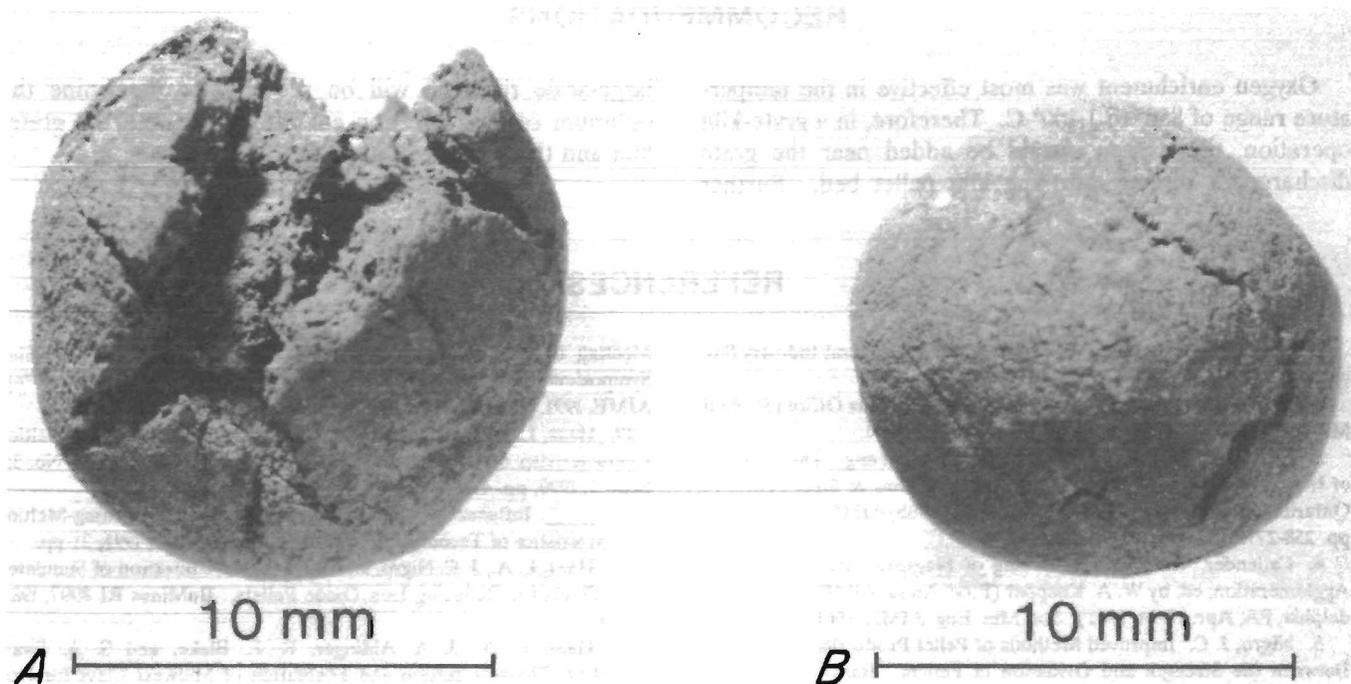
Figure 24.—Reduced fluxed (batch 7) pellets. *A*, Preinduration oxidized; *B*, postinduration oxidized.

CONCLUSIONS

1. The maximum level of magnetite oxidation increased both with increasing oxygen content and temperature below 1,300° C. At 850° C and below, complete oxidation was not obtained in 1 h even with 100 pct O_2.

2. The initial oxidation rate was dependent on both the temperature and the oxygen content. Oxygen was most effective for enhancing the magnetite oxidation at temperatures of about 1,000° C. Below 700° C, oxygen was not very effective. Above 1,200° C and at low oxygen levels, hematite decomposed to magnetite. At 1,250° C, about 2 pct O_2 in the pellet bed was required to prevent hematite from decomposing to magnetite.

3. At 1,000° C with 15, 30, and 100 pct O_2, the degrees of isothermal oxidation in 1 min were 25, 40, and 100 pct, respectively. Essentially the same results were obtained with the mini-pot furnace. For example, with 30 pct O_2, over 90 pct of the magnetite was oxidized in 5 min at 1,000° C.

4. Three minutes of preheat between 650° and 1,250° C was required to oxidize over 80 pct of the magnetite in the programmed-temperature thermogravimetric furnace tests with 30 pct O_2. With 100 pct O_2, less than 2 min was required.

5. The pellet physical and metallurgical qualities improved directly with the degree of magnetite oxidation prior to the induration period. The beneficial effects of the early magnetite oxidation were greater with the simulated grate-kiln test than with the straight-grate test, because the longer high-temperature soak time resulted in more residual magnetite reacting with the silicon compounds in the former test. When flux was present, calcium silicate and calcium and magnesium ferrites were formed. More calcium ferrites were formed when magnetite was oxidized early.

6. Higher quality pellets were produced with 30 pct rather than 15 pct O_2 during the preheat period with either acid or fluxed pellets in the simulated grate-kiln tests using a mini-pot furnace at high preheat rates. Enriching the oxygen content of the preheat gas may permit greater pellet production rates by using a higher preheat rate and thereby a shorter preheat time.

RECOMMENDATIONS

Oxygen enrichment was most effective in the temperature range of 850° to 1,100° C. Therefore, in a grate-kiln operation, the oxygen should be added near the grate discharge or directly into the kiln pellet bed. Further large-scale research will be required to determine the optimum oxygen injection conditions for both the grate-kiln and the straight-grate.

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