CANADA

# DEPARTMENT OF
# ENERGY, MINES AND RESOURCES
# MINES BRANCH

## OTTAWA

# THE REDUCTION TO LIQUID IRON OF COMPOSITE PELLETS OF PEACE RIVER IRON ORE AND WESTERN CANADIAN SUB-BITUMINOUS CHAR

D. A. REEVE AND J. H. WALSH

Canadian Metallurgical Fuel Research Laboratory

ENERGY RESEARCH LABORATORIES

DECEMBER 1974

Price: .75 cents

Mines Branch Research Report R-277

# THE REDUCTION TO LIQUID IRON OF COMPOSITE PELLETS OF PEACE RIVER IRON ORE AND WESTERN CANADIAN SUB-BITUMINOUS CHAR

by

D.A. Reeve and J.H. Walsh**

- - - - - - - - - -

## SUMMARY

Interest in the development of the Peace River iron ore deposit of north-western Alberta has led to preliminary bench-scale reduction studies on the production of liquid iron from composite pellets made from the ore and a western Canadian sub-bituminous coal. A literature survey revealed that smelting composite iron oxide-carbon pellets to yield liquid iron has been successful elsewhere although, in some cases, additional coke was required in the short-shaft furnace or cupola, and agglomerate strength was a problem.

Partial reduction of the iron ore and charring of the sub-bituminous coal was necessary prior to agglomeration to produce composite pellets which did not disintegrate when introduced into a hot environment (>1200°C). Constant-volume studies on single pellets showed that reduction to liquid iron was achieved at temperatures above about 1300°C. The amount of char present had little effect on the dependence of reaction rate on temperature although increased bentonite binder additions had a deleterious effect on this temperature dependence. Constant-pressure studies indicated that sulphur and carbon concentrations in the reduced product were high (S: 0.20-0.25 per cent; C>2 per cent). Appreciable desulphurization with solid CaO could be achieved but lime quantities were required far in excess of the stoichiometric requirement for complete sulphur removal as CaS, indicating that hot-metal desulphurization would probably be required in a steelmaking operation.

Later studies will include smelting of agglomerates made from Peace River iron ore and a low-rank coal in a pilot-scale short-shaft counter-current reactor. These studies are included in Task P2 (Low-Grade Iron Ores) of the National Minerals Research Program.

*Assistant Head, Canadian Metallurgical Fuel Research Laboratory, Energy Research Laboratories, **Senior Adviser Science, Science and Technology Sector, Department of Energy, Mines and Resources, Mines Branch, Ottawa, Canada.

Direction des Mines

Rapport de Recherche R-277

## LA REDUCTION DE BOULETTES COMPOSEES DE MINERAI DE FER DE PEACE RIVER ET DE PRODUIT DE CARBONISATION DE CHARBON SOUS-BITUMINEUX DE L'OUEST CANADIEN, EN FER LIQUIDE

par

D.A.Reeve* et J.H.Walsh**

RESUME

L'intérêt déployé pour l'exploitation du dépôt de minerai de fer de Peace River, dans le nord-ouest de l'Alberta, aboutit à des études préliminaires sur banc d'essai, sur la production de fer liquide des boulettes composées du minerai et d'un charbon sous-bitumineux de l'ouest canadien. Une étude de la littérature sur le sujet a révélé qu'ailleurs la fusion des boulettes composées d'oxyde de fer et de carbone, pour donner du fer liquide, s'est avérée un succès, même si dans certains cas on a dû ajouter du coke dans le bas-fourneau. La résistance de l'aggloméré a, par contre, causé des problèmes.

Il a été nécessaire de faire une réduction partielle du minerai de fer et une carbonisation du charbon sous-bitumineux avant l'agglomération, pour ne pas produire des boulettes composées qui se désintègreraient à une température élevée ($>1200^{\circ}C$) Des études de volume constant sur des boulettes simples ont démontré que la réduction en fer liquide pouvait s'atteindre à des températures supérieures d'environ $1300^{\circ}C$. La quantité de produit

---

*Chef adjoint, Laboratoire Canadien de Recherche sur les combustibles métallurgiques, Laboratoires de Recherche sur l'énergie, **Conseiller principal des Sciences, Secteur de la Science et Technologie, Ministère de l'Energie, des Mines et des Ressources, Direction des Mines, Ottawa, Canada.

de carbonisation a eu peu d'effet sur la dépendance du taux de réaction sur la température, bien que l'addition de bentonite (matière agglomérative) a eu un effet délétère sur cette dépendance de température. Des études de pression constante ont indiqué que des concentrations de souffre et de carbone dans le produit réduit étaient élevées (S: 0.20-0.25 pour cent; C 2 pour cent). On pourrait obtenir une désulfuration appréciable avec du CaO solide, mais des trop grandes quantités de chaux excédant l'exigence stoechiométrique sont requises pour une extraction complète du souffre sous forme de CaS. Ceci indique qu'une désulfuration de la fonte liquide serait probablement nécessaire dans une des opérations de la fabrication de l'acier.

Plus tard, on étudiera la fusion d'agglomérés faits de minerai de fer de Peace River et d'un charbon de classe inférieure dans un bas-fourneau à contre-courant dans un essai pilote à l'échelle semi-industrielle. Ces études sont incluses dans les Tâches P2 (Minerais de fer de classe inférieure) du Programme Canadien de Recherche sur les minéraux.

## INTRODUCTION

The recent renewed interest in the development of the Peace River iron ore deposit of north-western Alberta has led to bench-scale reduction studies on single pellets of the ore and a charred sub-bituminous coal, also from Alberta. These studies were based on a requirement for preliminary information on the smelting of composite pellets of the ore (either raw or beneficiated) and a carbonaceous material to liquid iron in a shaft-type of counter-current reactor. They were a part of a more comprehensive study of the reduction characteristics of composite pellets of iron oxide and carbon which will be reported elsewhere[1] and were a continuation of previous work[2] from this laboratory in which iron oxide-carbon composite pellets, surrounded by a layer of carbon, were reduced to liquid iron in pure oxygen at high temperatures, thereby utilizing the exothermic combustion of carbon monoxide It is also worthy of note that theoretical thermochemical calculations[3] have shown that shaft-type reactors used for smelting composite pellets to liquid iron also may generate a fuel gas having a calorific value up to 200 Btu/ft$^3$, depending on charge and tuyère conditions. This fuel gas may be suitable for power generation using, for example, turbines, or as a preferred fuel for boiler firing and other uses.

A sub-bituminous coal was chosen for these preliminary studies because although coking coal deposits (e.g. at Grand Cache) are reasonably close to the Peace River iron ore deposits, deposits of sub-bituminous coals in Alberta are extensive[4] (proved reserves given as 5341 x 10$^6$ tons recoverable and 10,172 x 10$^6$ tons in-place) and while no plants are operating, the economics of washing these coals to low ash contents have been studied[5]. Also, bentonite

overlies many of the coal seams and this can be used as a binder in the manufacture of composite pellets. Partial reduction of the iron ore was required to obtain pellets of sufficient cohesive strength for the experiments; this problem of the lack of strength of iron oxide and carbon composites is the weak link in this type of pellet technology and further studies are required on the particular case under consideration.

This research report reviews the literature on composite pellet technology and compares the rates of reduction to liquid iron of variously prepared pellets of pre-reduced Peace River iron ore and charred sub-bituminous coal. It was necessary to char the coal to eliminate the effect of volatile products on the constant-volume technique used for the measurement of reaction rates and also to obtain stronger pellets. The effect of bentonite additions on reaction rate was also investigated. The carbon content of pellets, reduced to liquid iron at $1475^{\circ}C$, was measured as well as the degree of desulphurization obtained with increasing additions of lime.

The next stage of development of the proposed process will be to smelt small quantities of composite pellets in a pilot development shaft furnace; indeed, initial foundry trials with such a furnace have been partially successful[6]. The advantage of the hot-metal process over solid-state direct reduction methods may lie in the availability of near-by sources of reductant and energy, and in the elimination (although it would still be an advantage) of the necessity to beneficiate the ore prior to smelting, if the resulting high slag volume were acceptable. The slag from the steelmaking operation (perhaps based on the oxygen bottom-blowing technique suitable for application to the inevitably high-phosphorus hot metal) could be utilized as a fertilizer source, especially considering the present demand for phosphate fertilizer in western Canada. Hence the value of the slag could be credited to the final cost of the steel although this may not be significant in the final process choice.

LITERATURE REVIEW

## Industrial Developments

Interest in iron oxide-carbon pellet technology has continued for many years without any significant successful application in ironmaking. Although such pellets have been proposed for blast-furnace feed, it is only recently that the recycling of agglomerated pre-reduced in-plant iron oxide fines containing carbon in the form of coke breeze has been attempted. Pre-reduction of recycled waste iron oxides allows the removal of zinc, lead and other volatile metals which are deleterious to blast furnace performance. Several recycling schemes have been proposed which utilize composite pellets, containing bentonite as binder (although fine recycled sponge iron may be acceptable as well) and which achieve metallization in either rotary kilns or on travelling grates. Industrially, the grate-kiln Kawasaki Steel Process[7], which produces a pre-reduced pellet containing between 70 and 80 per cent iron (2 to 3 per cent carbon) from waste dusts, is the largest operation of its kind in the world (monthly capacity for two plants: 26,000 tons). Dominion Foundries and Steel Limited, Hamilton, Ontario, have contemplated the installation of a waste-oxide recovery system in which extrusions of waste oxides and coke breeze are pre-reduced in a rotary hearth furnace[8]. The reduction of iron oxide-carbon pellets to a sponge iron may find increased application in rotary-kiln direct-reduction processes and, indeed, this scheme may be desirable for the utilization of the high-sulphur Illinois coals (accepting the need for external hot-metal desulphurization) and the western Canadian low-sulphur lignites and sub-bituminous coals if washing to a sufficiently low ash content is possible. Such low-rank coals are plentiful and relatively inexpensive.

The above discussion relates to methods of reducing iron oxide-carbon agglomerates to a sponge iron product but, as alluded to in the Introduction, the reduction of such agglomerates to a liquid product may be more attractive both from economic and energy viewpoints. As already mentioned, preliminary pilot-scale tests[6] have indicated the potential advantages of this approach to the Peace River iron ores using a low-shaft furnace or cupola type of operation. A similar approach was proposed by Obenchain[9] using steel plant waste iron oxide products and 15 per cent coke breeze to produce a BOF feed. Recently a patent[10] was granted to Obenchain for a process producing metal from metal oxide pellets in a cupola type vessel. In this process the cupola is loaded with alternate layers of coke and metal oxide pellets containing sufficient internal carbon to reduce the metal oxide of the pellet. However, the use of an oxygen-enriched hot blast may allow the use of pellets containing sufficient carbon to both reduce and melt an iron oxide. The thermal and stoichiometric carbon requirements for the smelting of iron oxide-carbon composites to liquid iron have been calculated by one of the present writers[11]. To reduce completely an iron ore containing 33 per cent Fe (47.1 per cent $Fe_2O_3$) such as that from the Peace River deposit, it must be mixed in a 3:2 ratio with a sub-bituminous coal containing 42 per cent fixed carbon. For the case of an iron ore concentrate containing 66 per cent Fe (94.3 per cent $Fe_2O_3$) and a high-volatile coal containing 60 per cent fixed carbon, the ore:coal ratio by weight is approximately 1:1.

In Europe, a low-shaft furnace process has been developed by the Demag-Humboldt group[12] for the production of liquid iron from composite briquettes of fine iron ores and non-coking coals. One important feature of the process is that devolatilization of the coal in the upper part of the shaft

causes some pre-reduction of the briquettes and produces a reactive carbon which tends to accelerate the smelting to a greater extent than obtained by the intimate mixing of iron oxide and the reductant in the composite briquette. Interest in Australia in iron oxide-carbon pellets started in an attempt to develop a continuous coking process utilizing high-volatile, fluid coals[13, 14]. The addition of iron oxides to such coals prior to flash carbonization at 900-1000°C minimized swelling and produced pellets which promised to give increased production at lower coke rates in the blast furnace. As an extension of these studies, a method has been patented[15] for the smelting of coal-ore pellets in a shaft furnace, carbonization of the coal occurring in the upper part of the shaft by the heat of combustion of volatiles from the lower part of the shaft. The hot calcined ore is mixed with cold coking coal and flux and the mixture is briquetted or pelletized while hot. The temperature of the ore is adjusted in accordance with the proportions of the blend components to bring the coal to its temperature of maximum fluidity. This low-shaft furnace is proposed to be coupled with a steelmaking vessel as a route to continuous steelmaking[16]. Presumably the tuyère air requirement for such an operation will be high relative to the iron blast furnace and a high-temperature oxygen-enriched blast may be required.
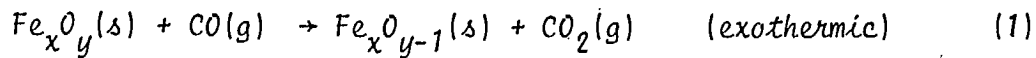
In a British patent assigned to Davies[17], composite pellets (bonded with sodium silicate) containing at least 20 per cent of fixed carbon in excess of the stoichiometric requirement to complete the reduction and formation of carbon monoxide, are charged to a shaft furnace. Heat is provided within the stack by the combustion of the carbon monoxide. It is possible that the 20 per cent stoichiometric carbon excess may not be required for such a process.

Laboratory Studies

Volin, Nigro and Hockings[18, 19] have conducted laboratory and pilot plant studies in which iron oxide pellets are reduced with admixed carbon. As

a reductant, anthracite was found to be better than lignite char and steam coal, but additions had to be limited to 16 per cent for satisfactory pellet strengths. Contamination of the pellets with ash and sulphur from the reductant was the principal shortcoming of the system, although admixed limestone did scavenge some of the sulphur while causing a reduction in pellet strength. Sticking and clustering resulted when the pellets were charged to a shaft furnace; this problem was alleviated by the charging of an equal weight of coke.

It is generally accepted that the reduction of iron oxide in mixtures with carbon proceeds according to the following indirect sequence:

$$Fe_xO_y(s) + CO(g) \rightarrow Fe_xO_{y-1}(s) + CO_2(g) \qquad (exothermic) \qquad (1)$$
$$C(s) + CO_2(g) \rightarrow 2CO(g), \qquad (endothermic) \qquad (2)$$

$$(where \ x = 1, \ 2 \ or \ 3 \ when \ y = 1, \ 2 \ or \ 3)$$

The extent of direct reduction of iron oxide by solid carbon is regarded as being relatively minor, and in the experiments described in this report no attempt was made to prevent secondary reactions occurring by removing CO and $CO_2$ from the reacting pellet. Reaction (2) is the slower and is rate-controlling, assuming the two-stage mechanism. Thus, the reduction of iron oxide-carbon pellets has been related to the gasification of carbon in $CO_2$ (Boudouard or "Solution Loss" reaction). The mechanism of the Boudouard reaction has been studied extensively and, contrary to previously held ideas, it is now thought that CO (reaction product) does not contaminate the carbon surface by chemisorption. Also, the gasification reaction is catalyzed by impurities such as alkalis (which may be present in sufficient quantities in the ash if a coal is the reductant) and these may also catalyze the indirect reduction of iron oxides by carbon.

Rao[20] studied the reduction kinetics of mixtures of hematite and carbon powders in the temperature range 850 to 1087°C using a weight-loss

technique. A kinetic model based upon the Boudouard reaction and described by the equation

$$log(1.743-\theta) = (R/2.303)t + log\ (1.743) \tag{3}$$

where $\theta$ = weight-loss per cent at time $t$

was used to represent the results, and a three stage carbon gasification was indicated. However, reaction times were considerably longer than in work described in this report. More recently Rao[21, 22] developed a physico-chemical model for the reduction of hematite mixed with carbon; CO and $CO_2$ resulting from the Boudouard reaction were transported out of the reacting mixture by mass transfer. Expressions were developed for the fractional weight loss corresponding to the completion of reactions in the reduction sequence: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. The effect of temperature upon reaction rate was of particular interest because the reduced iron acted as a catalyst with maximum activity in the vicinity of $1000^{o}C$. Thus, a temperature profile characterized by a long "temperature reserve zone", as established in the blast furnace shaft, would seem to be advantageous for the reduction of composite iron oxide-carbon pellets to liquid product. Addition of some reduced iron to the composite pellet prior to smelting may also assist in the reduction.

Dobovisek and Lamut[23, 24] have related the reduction of iron oxides to the reactivity of solid fuels and found, in general, that the higher the reactivity to $CO_2$, the higher the degree of reduction obtained. The reactivity of the solid fuel dictates the displacement of its experimental Boudouard equilibrium curve from that calculated theoretically from thermodynamic data at one atmosphere pressure. The position of the Boudouard equilibrium curve determines the minimum temperature for the reduction of iron oxide with carbon monoxide. Ghosh and Tiwari[25] found an activation energy of 18.7 kcal/mole at $900-1100^{o}C$ for greater than 50 per cent reduction for mixed pellets of hematite and lignite-derived char.

The carbonization of mixtures of a medium-volatile coal and iron oxides (30 per cent of $Fe_2O_3$ or $Fe_3O_4$) has been studied at the Brussels Free University[26]. In this work the temperature was raised in $100^\circ$ steps between 350 and $850^\circ C$, with almost complete devolatilization being allowed at the end of each temperature stage. By-product yields and gas compositions were determined at each stage, and the resultant ferrocokes were examined by x-ray diffraction analysis. The iron oxides slightly reduced the yield of tar and increased the yields of water and hydrogen-containing gases at the lower carbonization temperatures, suggesting a catalytic effect. At higher temperatures with progressive reduction of the iron oxides, increased yields of water and oxides of carbon (especially CO) were obtained, and hence a greater total gas yield. The two oxides had different effects in this respect, $Fe_2O_3$ reduction began at about $450^\circ C$ and $Fe_3O_4$ at about $650^\circ C$. Above $850^\circ C$, only free iron and cementite ($Fe_3C$) were present.

A binder may be required in the preparation of iron oxide-carbon composites and Otsuka and Kunii[27] have reported that the reduction of wüstite to iron, during which the "Solution Loss" reaction may also be taking place, proceeds autocatalytically and is influenced by the particle size of ferric oxide and the presence of bentonite. This autocatalysis has been ascribed to the effect of metallic iron produced on the surface of the carbon, and the bentonite is considered to affect in some unspecified way the interaction between the carbon and metallic iron.

Some data on the thermochemistry of iron ore-coal pellet reduction has been published in the Russian literature[28-31]. Storozhev, Telegin and Zavarzin[28] found relationships for the effect of temperature on the specific heat of ore-coal pellets with stoichiometric coal contents. Storozhev et al[29] measured the specific heats, thermal diffusivities, and conductivities at

$500^{\circ}$C. Kozhevnikov and Gul'tyay[30] prepared curves of the variation in temperature at the pellet centre with time during reduction at $1500^{\circ}$C and proposed a relationship to determine the time for 90 per cent metallization, assuming that reduction is inversely proportional to heat flow. The meaning of all the symbols used by Kozhevnikov and Gul'tyay[30] was not clear to the writers. Telegin[31] calculated the heat transfer to ore-coal pellets during metallization for revolving and shaft furnaces.

Both thermal and differential thermal analysis techniques have been used in the present writer's laboratory[2] to measure qualitatively the rate of temperature rise at the centre of composite pellets after introduction of the pellet into a furnace at $1500^{\circ}$C. In the thermal analysis experiments, approximately 60 seconds were required for the pellet centre to achieve the temperature of the furnace. The temperature increased at $48.5^{\circ}$C/sec for the first 20 seconds, slowed to $6.35^{\circ}$C/sec for the next 30 seconds following which the heat transfer rate increased again until the final temperature was attained. In the D.T.A. experiments, an endothermic peak at $280^{\circ}$C was consistently obtained approximately 30 seconds after the introduction of the cold pellet into the hot zone, suggesting that reaction temperatures used in the calculation of activation energies from Arrhenius plots must be treated with caution.

In summary, pertinent points from the rather diffuse literature available on the smelting of composite pellets would seem to be:

(i) Composite pellets can be smelted to liquid iron, but additional coke may be required (Obenchain[10], Volin et al[18, 19]).

(ii) The strength of agglomerate may be related to the amount of carbon present[18, 19].

(iii) The reaction rate may depend on the carbon reactivity[23, 24] as well as the presence of additives such as bentonite[27] or possible catalysts such as sodium and iron itself.

(iv) A long reaction residence time would be an advantage because of the slow rate of heat transfer into the pellet[2] and the catalytic effect of reduced iron on the reaction rate[21, 22].

## MATERIALS

The Peace River iron ore used in these investigations was supplied by Dr. E.F. Bertram of Alberta Research, Edmonton. Comprehensive mineralogical details of the Peace River deposits have been given by Mellon[32]. While the sample used in the present studies was not taken from the bulk sample shipped to Ottawa from Edmonton in 1974 under the Canada-Alberta General Development Agreement to develop the Peace River iron ore deposits, Petruk, Harris and Pinard[33] have presented a mineralogical investigation pertaining to the latter sample. The sample used in the present investigation contained approximately 32.5 per cent Fe, 24 per cent $SiO_2$, 1.8 per cent P, and 0.055 per cent S.

The sub-bituminous coal was from Drumheller, Alberta, available at the Mines Branch. The coal contained 42 per cent fixed carbon, 0.40 per cent sulphur, and 7 per cent ash.

Pelletizing the two components did not provide sufficiently strong pellets to withstand the thermal shock upon introduction into the hot zone of the furnace used in the reduction tests; disintegration resulted. To make acceptably strong pellets, it was found necessary to pre-reduce the iron ore to the magnetite stage in a 20:20:60 $CO:CO_2:N_2$ mixture at $950^\circ C$ (total Fe: 45.56 per cent; $Fe^{3+}$: 33.47 per cent) and remove the volatile matter of the low-rank coal by charring it at $900^\circ C$ under nitrogen (92 per cent fixed carbon and 0.55 per cent sulphur in the char) prior to the pelletizing step.

The reactivity of this char was measured by the per cent weight loss (allowing for ash content) of a 2-g sample (minus 200 mesh) contained in a boat in a horizontal tube furnace at $1000^{\circ}C$ with $CO_2$ (50 ml/min at STP) passing through for one hour. Residual volatile matter had been removed from the char prior to the reactivity test by calcining at $1050^{\circ}C$ under nitrogen. The per cent weight loss obtained was 45.3, which compares with 9.9 for coke from the Athabasca Tar Sands, 19.1 for carbonized eastern Canadian high-volatile coal, and 57.3 for "Fisher" grade willow carbon.

From an industrial application viewpoint, the major problem remaining in the materials aspect of composite pellet technology is pellet strength. Indeed as mentioned previously, Nigro et al[18, 19] found that their pellets were of unacceptable strength if they contained more than 16 per cent carbon. In the present study, as mentioned above, pre-treatment of both components prior to pelletizing was required to obtain composites which would not disintegrate during reduction. The explanation for this difficulty requires further study, but pellet weakening could be caused by swelling of the iron oxide during reduction and from cracking caused during the orthorhombic-cubic hematite-magnetite crystallographic transformation. Both of these effects would be minimized by a pre-reduction step.

In a patent describing the production of iron ore-coal briquettes[34], it is claimed that 15 to 30 per cent reduction of specular hematite fines minimized swelling prior to mixing with 5 to 15 per cent cold bituminous coal. The hot, partially reduced iron ore acted as a heat transfer medium to heat the coal into its plastic temperature range to serve as the binder during briquetting.

As well as the industrial use of bentonite as a binder, cold-bonded pellets using cement, as developed in Sweden, or using a mixture of lime and silica flour with autoclaving, as used in the MTU Process[35, 36], and even polymer-impregnated pellets[37], could be considered. Red'ko and Sokolov[38]

investigated methods of strengthening iron ore-coke pellets. Bentonite consumption was reduced by a factor of four by using a 3 per cent aqueous suspension (instead of powder) which still gave a strong pellet, while 8 per cent sponge-iron additions to the pellets also produced a strengthening effect. As noted previously, sponge-iron additions may also increase reduction rates.

Attempts have been made to manufacture a "ferrocoke" in conventional slot-type coke ovens but these have been hampered by brick attack, blending problems, and the difficulty of achieving sufficiently high flue temperatures. Formed coke processes offer an attractive means of producing a composite briquette. Canadian Patent 946327[39] describes a method for producing a formed coke from mixtures of lignite and iron ore fines.

## EXPERIMENTAL

Composite pellets of partially-reduced Peace River iron ore and charred sub-bituminous coal were prepared by weighing appropriate amounts of the components (both minus 200 mesh) for one pellet, including bentonite as binder. After hand mixing in an agate mortar, the mixtures were further blended in rotating bottles. The pellets (5/16-in. dia. x 5/16-in. long) were pressed at 70,000 psi in a cylindrical die.

Rates of reduction of the composite pellets were measured in an inert atmosphere in a constant-volume apparatus which has been described in detail previously[2] and is illustrated below.

Briefly, the pellets, on an alumina tray, were lowered into the hot-zone of an alumina tube fixed vertically in a Globar furnace. Air had been evacuated from the reaction tube and replaced by argon at a pressure of about 400mm Hg. The reduction of the composite pellet was monitored by the increase in pressure within the constant-volume system as measured by a 0-760mm absolute pressure transducer connected to a side-arm in the cool part of the system.
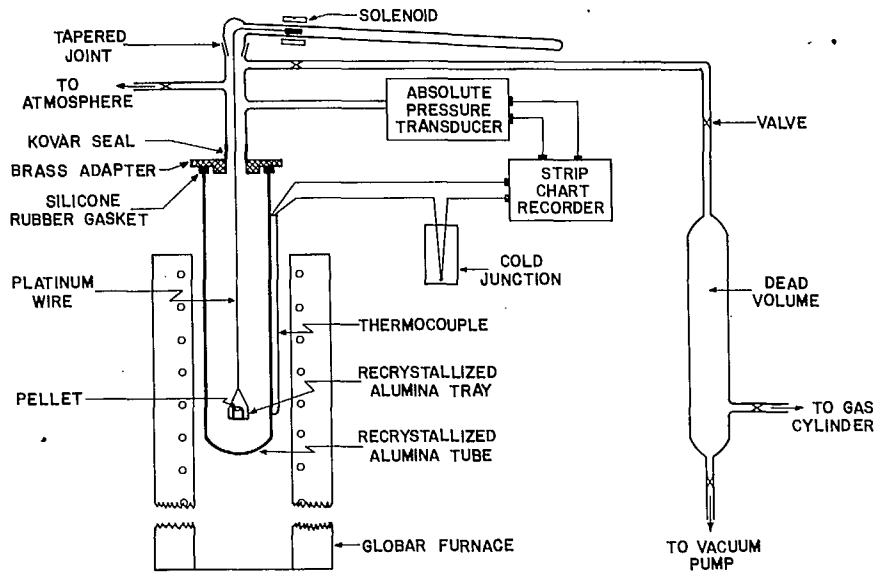
FIGURE 1. Schematic Diagram of the Constant-Volume Apparatus

A starting pressure of 400mm Hg was chosen so that the final pressure within the system after the reduction was completed did not exceed one atmosphere.

Flowing-gas experiments were done at 1475°C in an argon atmosphere with the composite pellets on alumina pedestals in a horizontal Globar tube furnace. These experiments allowed the melting process of the pellets to be observed. The resultant spherical beads were combusted later in oxygen in the same furnace for the determination of carbon and sulphur using Leco analysers.

## RESULTS AND DISCUSSION

In the <u>constant volume</u> studies (Figure 1) rates of pressure increase
in the experimental system were measured during reduction of the composite
pellets at various temperatures above 1300°C; reaction rates below this
temperature were slow and difficult to follow. Results were expressed in fraction
reaction (based on one hundred per cent reaction at the final pressure
attained) versus time curves. Three cases were considered:

    (i)   36 per cent char, one per cent bentonite,

    (ii)  36 " " " , three " " " ,

    (iii) 25 " " " , " " " " .

The theoretical stoichiometric char requirement is 18.4 per cent (based upon
92 per cent fixed carbon) for reduction of pre-reduced Peace River iron ore
containing 46 per cent magnetite. Considerably more than the stoichiometric
requirement was added to the composites for these experiments because in practice
carbon would be required both to reduce and melt the composites[11]. Also, the
effect of bentonite on reaction rate was studied because of the findings
of Otsuka and Kunii[27].

Fraction reaction versus time plots in the temperature range 1200-
1500°C for composites containing 36 per cent char and one per cent bentonite
are given in Figure 2. The curves for temperatures above 1400°C are representative
of composite pellets which yield a molten bead of reduced iron while sponge iron
was obtained at lower temperatures. Melting time was between 1½ and 2 minutes.
The fraction reaction versus time plots for the other two cases were similar
and are not illustrated.

Empirical rate constants, expressed in mmHg pressure/second, were
determined from the slopes of the experimental pressure-time plots and
activation energies for the three cases were taken from
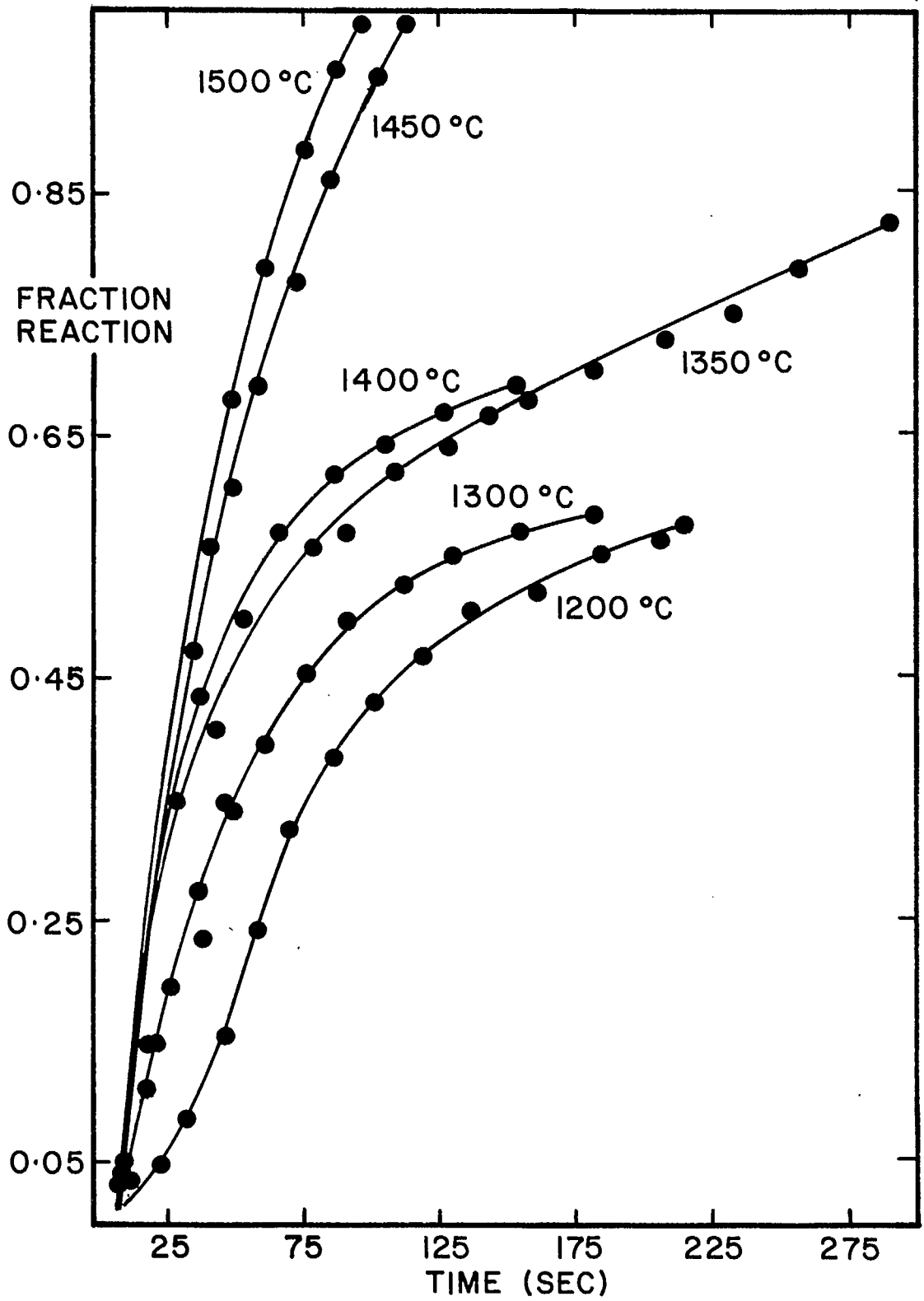
FIGURE 2 - <u>Fraction reaction versus time plots for composites containing 36 per cent char and one per cent bentonite</u>
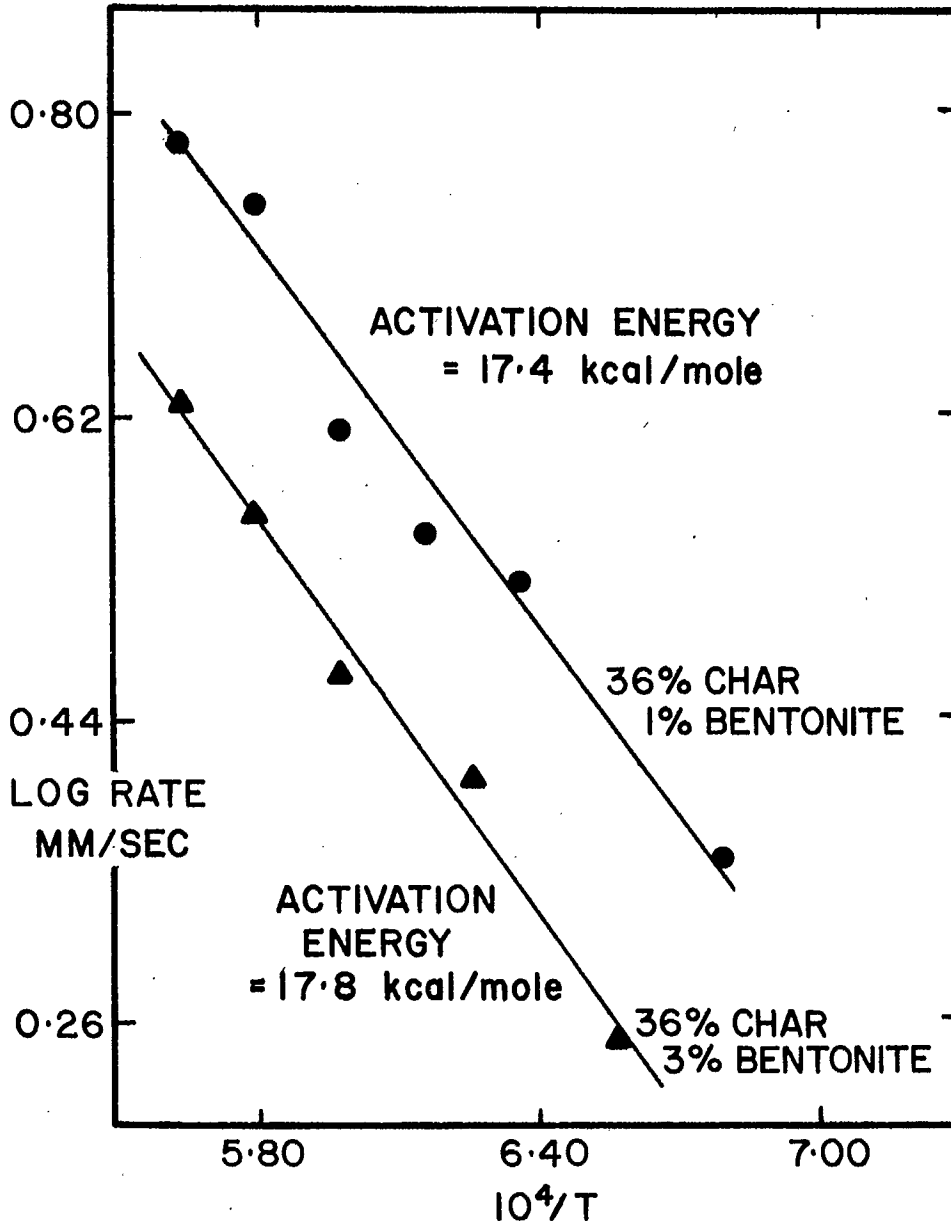
FIGURE 3 - Arrhenius plots for the reduction of composite pellets containing various amounts of bentonite

Arrhenius plots of the logarithm of the rate constant against the reciprocal of the absolute temperature. The Arrhenius plots for cases (i) and (ii) are shown in Figure 3, case (iii) having similar intercepts to case (ii) on both axes. It should be noted that each point in Figure 3 represents one experiment while one experiment is represented by each curve in Figure 2. Activation energies, expressed in kcal/mole and representing the effect of temperature on reaction rate for the three cases, are summarized in Table 1:

TABLE 1. Effect of Temperature on Reaction Rate for Composite Pellets

| Per Cent Char in Composite | Per Cent Bentonite | Activation Energy* (kcal/mole) |
|---|---|---|
| 36 | 1 | 17.4 |
| 36 | 3 | 17.8 |
| 25 | 3 | 16.4 |

(*Ghosh and Tiwari[25] gave an activation energy of 18.7 kcal/mole at 900-1100°C for hematite-lignite char composites)

Thus, within the limits of experimental error, the effect of temperature on reaction rate must be considered the same for all three cases; however, increasing the bentonite concentration lowers the reaction rate for a given temperature, confirming the results of Otsuka and Kunii. Reaction rate (in mmHg pressure/second) as a function of temperature for the three cases is illustrated more clearly in Figure 4. For the general case of iron oxide-carbon pellets, the activation energy for the reduction reaction has been found to be a function of carbon reactivity (to $CO_2$ at 1000°C). This relationship together with the effect of particle size and the reaction and melting mechanism will be discussed elsewhere[1].
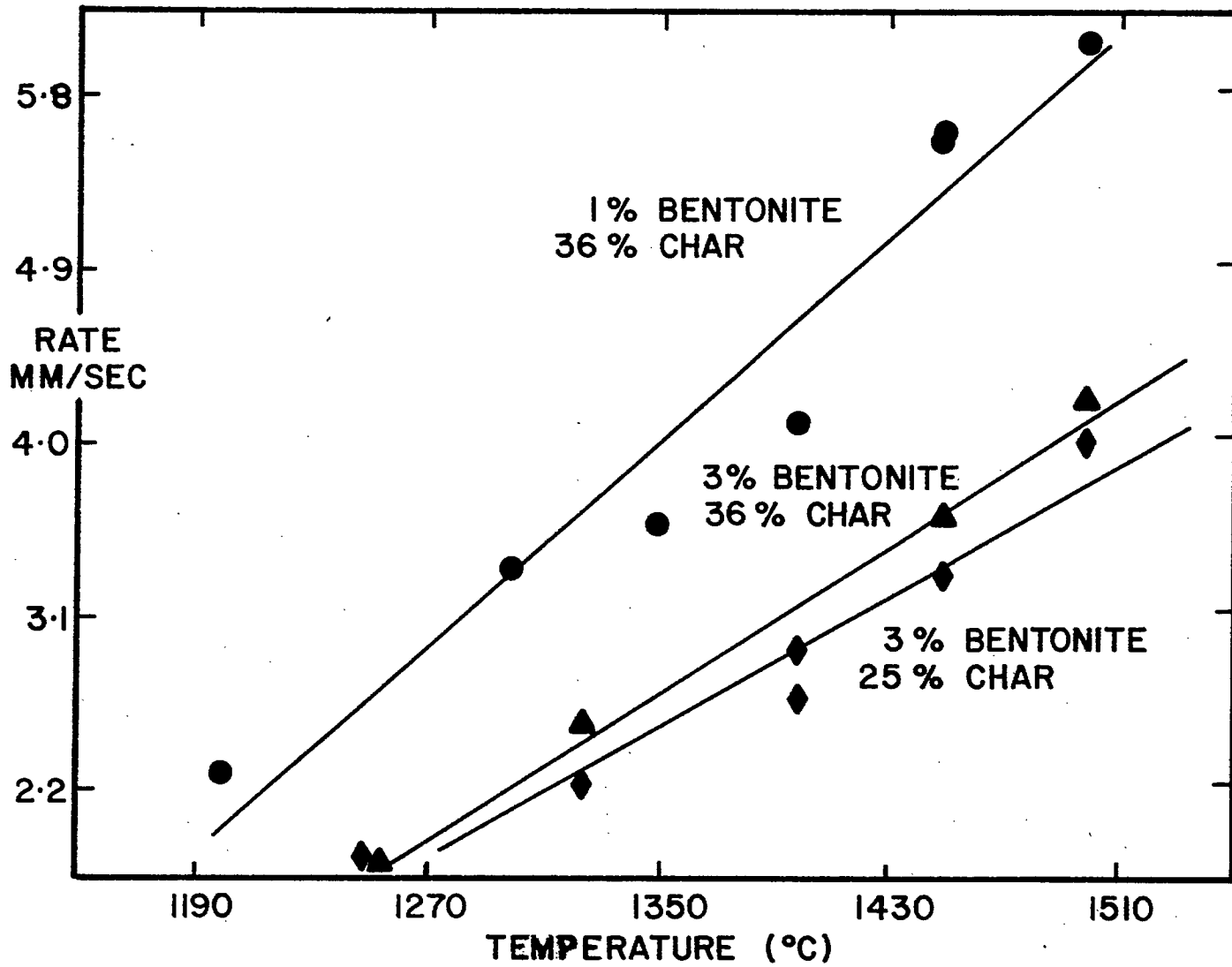
FIGURE 4 - Reaction rate versus temperature plots for the reduction of composite pellets containing various amounts of bentonite

The <u>constant pressure</u> studies (flowing argon atmosphere) at 1475°C (when molten reduced beads were obtained upon reduction of the composite pellets) were done to ascertain the effect of lime concentration on the carbon and sulphur contents of the reduced products. This necessitated two sets of experiments, one each for carbon and sulphur. The stoichiometric lime requirement for complete removal of sulphur (as CaS) from the composite pellets is 0.34 per cent (two per cent bentonite as binder was used in these experiments.

Results are illustrated in Figure 5 in which per cent carbon and sulphur in the reduced product are plotted against per cent CaO; each experimental point is representing an average of between three and five determinations. The sulphur content of the reduced product was in the range 0.20-0.25 per cent and dissolved carbon was high (>2 per cent). The carbon content increased initially to a maximum content close to the stoichiometric lime requirement for sulphur removal. However, at higher lime concentrations, both carbon and sulphur contents decreased with further lime additions, as would be expected from thermodynamic considerations.

Sulphur removal by CaO is shown in Figure 6 as per cent desulphurization versus CaO content - zero per cent desulphurization refers to the quantity of sulphur in the reduced product when CaO was not present in the starting mixture. Considerably more than the stoichiometric CaO requirement was needed to effect desulphurization to any significant extent (e.g. approximately seven times the stoichiometric requirement produced only 30 per cent desulphurization). The reason for this excess lime requirement was not clear, but this effect has been observed in other situations (e.g. the addition of lime to bituminous coal blends to remove inorganic sulphur while carbonizing in slot-type coke ovens) and must be ascribed in general terms to surface
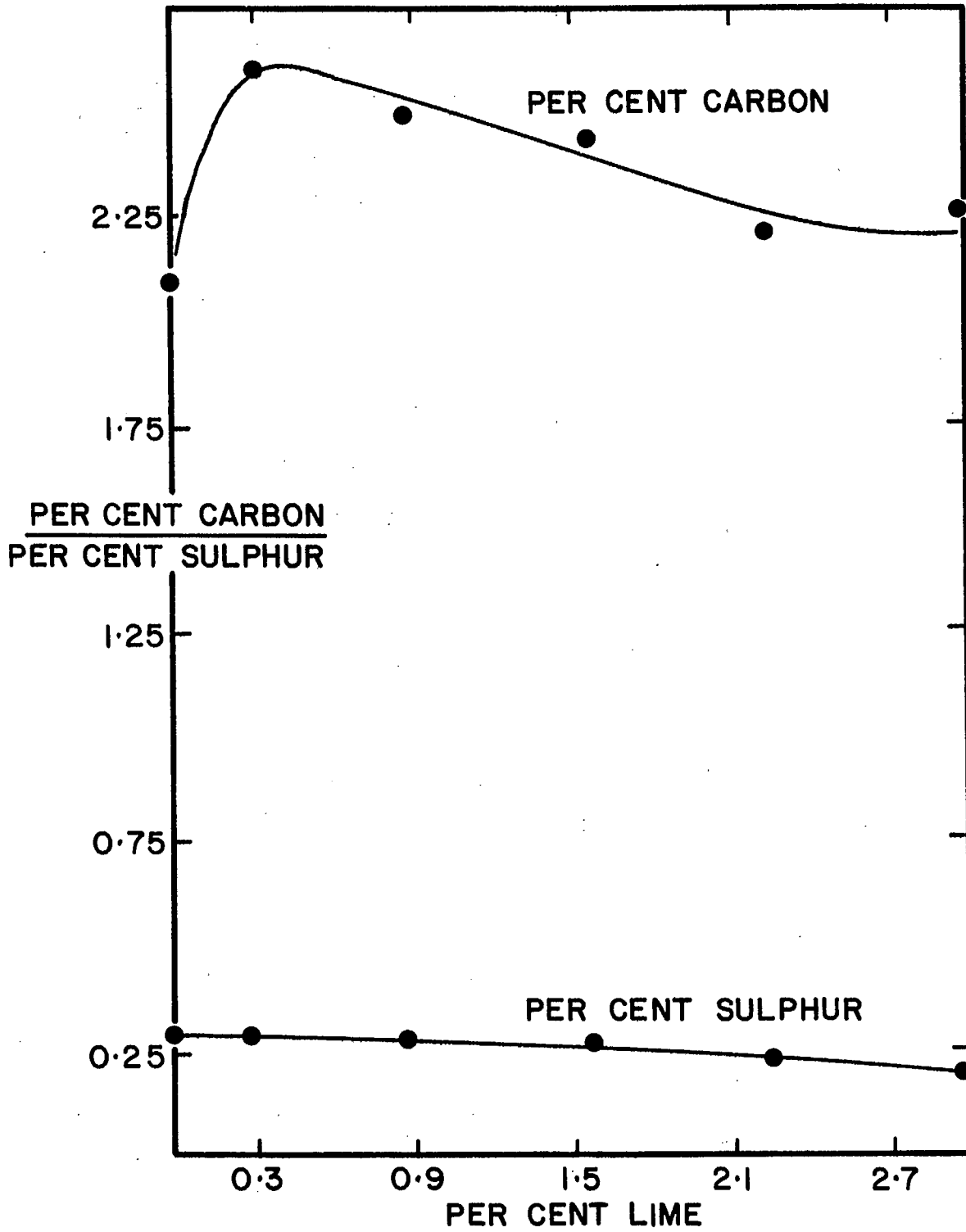
FIGURE 5 - Per cent carbon and sulphur versus per cent lime addition for pellets reduced at 1475°C
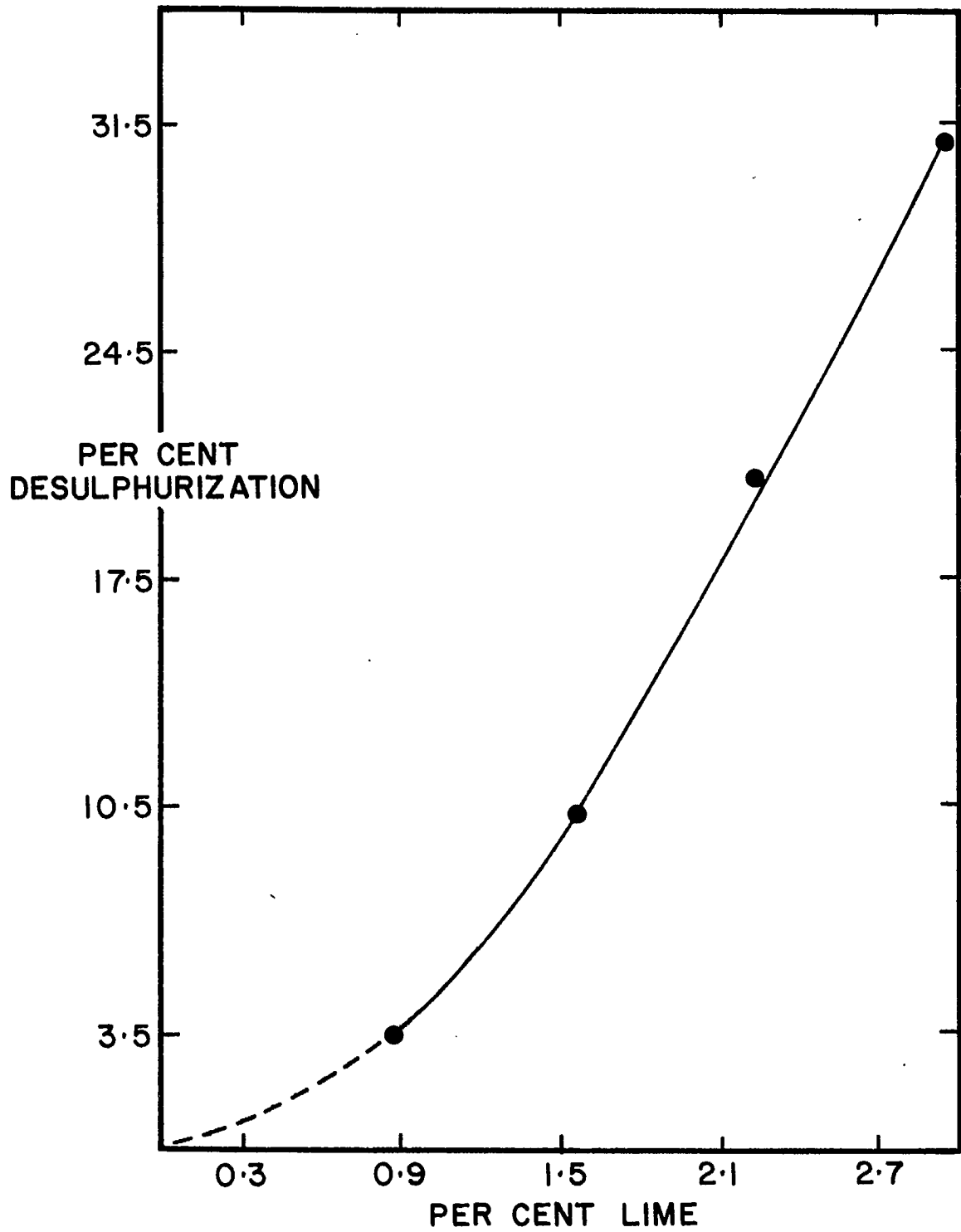
FIGURE 6 - <u>Per cent desulphurization versus per cent lime addition
for pellets reduced at 1475°C</u>

interactions of the sulphur species and carbon. The detailed mechanism of sulphur removal by solid CaO from iron oxide-carbon pellets has been studied elsewhere[40]. As mentioned previously, Volin et al[18, 19] reported that limestone additions cause a reduction in pellet strength. Because of this difficulty, it would seem, therefore, that hot metal made from composite pellets of Peace River iron ore and a sub-bituminous char would require a desulphurization treatment prior to transfer to the steelmaking operation.

Although the effect of lime on reduction rate was not studied with these materials, analogous studies[1] would indicate that reduction rate would diminish with increased lime concentrations.

## CONCLUSIONS

1. A literature survey on the reduction of iron oxide-carbon composite pellets to liquid iron reviewing both industrial type trials and laboratory scale studies indicated that composite pellets have been smelted successfully in the past. However, additional coke requirements have been necessary in some cases to achieve reduction and lack of agglomerate strength has caused problems.

2. Composite pellets derived from Peace River iron ore and a western Canadian sub-bituminous coal as starting raw materials can be smelted to liquid iron at temperatures above approximately 1300°C.

3. Pre-treatment of the raw materials by partial reduction of the ore and removal of a part of the volatile matter from the coal may be required before agglomerates of sufficient strength can be made to withstand the high-temperature reduction conditions in shaft furnaces.

4. For composite pellets containing considerably more than the stoichiometric fixed carbon requirement, the amount of char present had little effect on the variation of reduction rate with temperature.

5. Increasing the binder concentration (in the form of bentonite) lowered the reduction rate increase with temperature.

6. Sulphur and carbon concentrations in the reduced iron products were high (S: 0.20 - 0.25 per cent; C>2 per cent).

7. Desulphurization by lime additions to the composite pellet starting materials requires quantities of desulphurizing agent far in excess of the stoichiometric requirement calculated on the basis of the removal of all inorganic sulphur present as CaS.

8. Hot-metal desulphurization would probably be required prior to steelmaking.

## ACKNOWLEDGEMENT

## REFERENCES

1. Reeve, D.A., Ramey, N.J., and Walsh, J.H., "The Reduction of Iron Oxide-Carbon Composites to Liquid Iron - The Effect of Iron Oxide and Carbon Type". For presentation at an international symposium on "Metal-Slag-Gas Reactions", Electrochemical Soc., Toronto, May 1975.

2. Reeve, D.A., and Walsh, J.H., "Fundamental Studies Relating to the Development of the Smelting Reduction of Iron Oxide and Carbon - Constant Volume Studies", Can. Met. Quart., 12(1), 115-24, (1973).

3. Walsh, J.H., and Reeve, D.A., "Iron Reduction with Concurrent Production of Fuel Gas in Shaft Reactors", For presentation at a special symposium on "Energy Utilization and Conservation in the Metal Industry", AIME Annual Meeting, New York, February, (1975).

4. Horachek, J., Venter, R.H., and Gilchrist, R.D., "The Appraisal of Coal Resources in Alberta", CIM Bulletin, 67, 103-112, 1974.

5. Symonds, D.F., and Norton, G., "The Economics and Problems Associated with Washing Low-Rank Coals in Western Canada", CIM Bulletin, 67, 92-97, (1974).

6. J.E. Rehder, Private Communication.

7. Saito, F., "Key to New Kawasaki Plant is Special Pellet Formula", Am. Metal Market, April 6, 1973.

8. Stanlake, R.C., Nicks, G.D., Gordon, R.A., Becken, W., Hampson, A.J., and Wilson, J.C., "Reduction of Waste Oxide for Zinc Removal", Symposium on Waste Oxide Recycling, McMaster University, Hamilton, May 16 and 17, 1974.

9. "New Pelletizing Technique for Iron", Foundry, June 1973.

10. "Process for Producing Metal from Metal Oxide Pellets in a Cupola Type Vessel", Obenchain, R.F., U.S. Patent 3,832,158, (1973).

11. Reeve, D.A., "The Thermal and Stoichiometric Carbon Requirements for the Smelting of Iron Oxide-Carbon Composites to Liquid Iron", Mines Branch, Metals Reduction and Energy Centre, Divisional Report MREC 74/2, Dept. of Energy, Mines and Resources, Ottawa, (1974).

12. Reinfeld, H., "Low-Shaft Furnace Process as Developed by the Demag-Humboldt Group", Iron and Coal Trades Review, 175, 1139-48, November 9, (1956).

13. Innes, J.A., Gregory, J.A., and Worner, H.K., "Coke and Iron Coke Pellets", The B.H.P. Technical Bulletin, 7(1), 9-13, (1963).

14. Innes, J.A., "Metallized Pellets from Ore-Coke Mixtures", J. Metals, 15, 294-7, April, 1963.

15. "Shaft Furnace Smelting of Oxidic Ores, Concentrates, or Calcines", Conzinc Riotinto of Australia, Ltd., Brit. Pat. 1,261,127, (1972).

16. Baker, F.H., and Worner, H.K., "WORCRA Iron and Steelmaking", Alternative Routes to Steel, 99-106, The Iron and Steel Institute, London, (1971).

17. "Improvements in the Smelting of Iron Ores", Davies, W., Brit. Pat. 1,164,96 27 May, 1968.

18. Nigro, J.C., "Reduction Requirements for Hematite Pellets Reduced with Internal Carbon", paper presented at the AIME-SME Fall Meeting and Exhibition, Minneapolis, Minnesota, September 18-20, (1968).

19. Volin, M.E., Nigro, J.C., and Hockings, W.A., "Laboratory and Pilot Plant Study of Iron Ore Pellets Reduced with Internal Carbon", paper presented at the International Meeting on the Production and Utilization of Reduced Ores, Evian, France, 29-31 May, (1967).

20. Rao, Y.K., "The Kinetics of Reduction of Hematite by Carbon", Met. Trans., 2, 1439-47, (1971).

21. Rao, Y.K., "A Physico-Chemical Model for Reactions between Particulate Solids Occurring Through Gaseous Intermediates-I. Reduction of Hematite by Carbon", Chem. Eng. Sci., 29, 1435-45, (1974).

22. Rao, Y.K., and Chuang, Y.K., "A Physico-Chemical Model for Reactions Between Particulate Solids Occurring Through Gaseous Intermediates-II. General Solutions", Chem. Eng. Sci., 29, (1974) - In Press.

23. Dobovisek, B., "Direct Reduction of Iron Oxides and Reactivity of Solid Fuels", Rudarsko-Metalurski Zbornik, No.1, 87-100, (1971).

24. Dobovisek, B., and Lamut, J., "Influence of Solid Fuel Reactivity on the Reduction of Hematite Ore", ibid, No. 3-4, 375-386, (1969). (English Translation, p. 67-79).

25. Ghosh, P.C., and Tiwari, S.N., "Reduction of Pellets of Iron Ore plus Lignite Coke", J.I.S.I., 255-7, March 1970.

26. Cypres, R., et al., "Study of the Pyrolysis of Mixtures of Coal and Iron Oxides at Different Isothermal Levels", Ann. Mines Belg., No. 4, (1973).

27. Otsuka, K., and Kunii, D., "Reduction of Powdery Ferric Oxide Mixed with Graphite Particles", J. Chem. Eng. Japan, 2(1), 46-50, (1969).

28. Storozhev,Yu.I., Telegin, A.S., and Zavarzin, V.P., "Determination of the Specific Heat of Ore-Coal Pellets during Metallization", Steel in the U.S.S.R., 331-2, May, 1971.

29. Storozhev,Yu.I., Telegin, A.S., Kudryavtsev, V.S., and Pchelkin, S.A., "Thermochemical Properties of a Bed of Ore-Coal Pellets", ibid, 763-4, October, 1971.

30. Kozhevnikov, I. Yu., and Gul'tyay, I.I., "Thermochemistry of Ore-Coal Pellet Reduction", Russian Metallurgy (Metally),No. 3, 5-9, (1969).

31. Telegin, A.S. Kitayev, B.I., Shvydkiy, V.S., Storozhev, Yu.I., and Kazantseva, N.M., "Calculation of the Heat Transfer to Pellets During Metallization", Russian Metallurgy (Metally), No. 6, 5-7, (1971).

32. Mellon, G.B., "Petrology of Upper Cretaceous Oolitic Iron-Rich Rocks from Northern Alberta", Economic Geology, 57, 921-40, (1962).

33. Petruk, W., Harris, D.C., and Pinard, R.G., "A Mineralogical Investigation of Samples from the Clear Hills Oolitic Iron Deposit, Peace River Alberta", Mines Branch Investigation Report IR 74-33, July 1974, Dept. Energy, Mines and Resources, Ottawa.

34. "Method of Making Ore Briquettes", Johnson, R.T., U.S. Patent 3,295,952, (1967).

35. Mathias, W.M., and Goksel, M.A., "Cold Bonded Pellets, Solid Waste to Raw Material in Steel Mills", Presented at the 57th National Open Hearth and Basic Oxygen Steel Conference, Atlantic City, N.J., April 29, 1974.

36. Goksel, M.A., "Treatment of Zinc Rich Steel Mill Dusts for Reuse in Steel Making Processes", U.S. Patent 3,770,416, Nov. 6, 1973.

37. Nigro, J.C., and Prasky, C., "High Strength Iron Oxide Pellets by Polymer Impregnation", Proceedings of the 12th Biennual Briquetting and Agglomeration Conference.

38. Red'ko, A.N., and Sokolov, V.S., "Methods of Strengthening Ore and Ore-Coke Pellets", Steel in the U.S.S.R., (8), 587-9, 1972.

39. Fischer, K.O.P., "Process for Coking Lignitic Coal", Canadian Patent 946327, Nov. 22, 1971.

40. Adams, C.J., Ph.D. Thesis, McMaster University, Hamilton, Ontario. In preparation.