

STUDY OF PETROLEUM COKE USED AS REDUCING AGENT IN IRON ORES PROCESSING

Jun M. Lee, Jeffrey G. Rolle, James J. Baker

A. J. Edmond Co., 1530 West 16th Street, Long Beach CA 90813

Marcos de Albuquerque Contrucci, Edmar Saul Marcheze

TECNORED LTDA, Rua Georges Smirnow 305/306 Bairro Boa Vista

CEP 89206-740, Joinville, SC Brasil

James W. Ramming

Tecnored Technologies Incorporated, 100 First Stamford Place, Stamford, CT 06902

Keywords: petroleum coke, iron ores reduction

ABSTRACT

A petroleum coke with a high sulfur content (approximately 7.0 wt %) was tested as reducing agent in iron ores processing. Proprietary TECNORED pellets were prepared by blending of iron ore fines, petroleum coke fines and other additives (binders, fluxing agents, etc.) through a wet-pelletizing process. A pilot-scale reaction system was assembled for the reaction performance study with the petroleum coke and TECNORED pellets, which consists of a packed-bed Inconel reactor with temperature controller and programmer, air, argon and nitrogen gas supply system, effluent product gas sampling system, and gas analyzers. Five screening tests were recently performed and experimental results are presented.

INTRODUCTION

Production of petroleum cokes steadily increased by 51% during the past decade, expecting continuous increase in the coming years, primarily due to declining quality of crude oils [1]. Green petroleum cokes are mostly used as utility fuels (about 73% for fuel grade), and as feedstocks (about 27%) for further upgrading calcination. The calcined petroleum cokes are used in production of specialty products such as aluminum anodes, graphite electrodes, titanium oxide pigments, recarburized ductile irons, etc.

In addition green petroleum coke was often used as an additive in metallurgical coke making, depending on its availability in the market at lower prices than those of coking coals [2]. The performance of metallurgical coke, produced from coking coal blends containing petroleum coke, was successfully tested in several blast furnaces. The maximum limit of petroleum coke in a coal blend for acceptable coke quality was reported to be 5 wt % in Japan. However, elsewhere a higher limit (20 or 40 wt %) was reported. Several properties of coal blends such as particle size, rheological properties, volatile matter and total carbon content are important affecting quality of metallurgical coke. Various instrumental and analytical methods and techniques can be found in the literature to be used to characterize petroleum cokes and coal blends.

TECNORED Process Background and Description

The proprietary TECNORED process (developed by the TECNORED in Brazil) utilizes self-reducing pellets composed of tiny particles of iron ore and petroleum coke, and generating infinite reaction sites, enhances reaction rates of iron ore reduction by more than ten times (residence time 0.5 vs. 6 to 8 hours) [3]. The pellet consists of 70 to 75 wt % iron ore fines, 15 to 20 wt % coke fines and 5 to 10 wt % binders and fluxes, respectively. The process can use 100% petroleum coke without blending with coal or any blends of petroleum coke and coal.

In conventional commercial blast furnace processes [4,5,6], two main reduction steps are involved, requiring 1 to 2 hours residence time for each reduction zone, zone converting wustite ($\text{Fe}_{0.947}$) to solid iron (Fe_s) and zone converting Fe_2O_3 to Fe_3O_4 and further to $\text{Fe}_{0.947}$. Fusion and slagging zones add more residence time after completion of reaction, totaling 5 to 8 hours. Gas residence times are in the order of only 1 second and hence good gas and solid contact is required for efficient operation.

In contrast, the TECNORED process has many advantages in processing iron ores:

- Diversified low-cost raw materials and fuels
 - low-grade iron-ore fines with 60 to 64% Fe
 - low-cost reductant fines with non-coking coals, cokes, petroleum cokes, etc.
 - low-cost binders
 - low-cost solid fuels with non-coking lumps, petroleum cokes, semi-cokes, etc.

- full recycling of all dust and fines
- Low-cost and low-investment pelletizing process
 - cold curing in open air yards
 - grinding of coal fines only to minus 140 mesh
 - grinding of ores, if any, only to minus 100 mesh
 - no hot-firing of pellets
 - green pellets with enough strength to bulk handling
- High productivity and energy efficiency in TECNORED furnace
 - 30 to 40 minutes residence time against 6 to 8 hours in blast furnaces
 - no Boudouard reaction on solid fuels due to side feeders
 - CO burning in the upper shaft to heat up and pre-reduce pellets
 - pellets drying in the silos by hot-blast stack off-gases
 - low power requirements due to low shaft height (2-3 m), low-pressure blast and lower elevation of the charge
 - use of blast partially cold
 - cheap top-gas available, if desired
- Low investment TECNORED furnace
 - multi-mode atmosphere concept on a single-vessel unit
 - compact shaft-furnace design with classical units of hot blast, gas cleaning and centrifugal blowers, making even blast furnace conversion possible
 - small working volume due to high productivity
 - no dosing of charge required
 - flow of charge regulated by melting rate solely through the blast
 - simple process control

Summary of Pilot-Scale Tests

The pilot-scale plant tests were performed during July 21-22, 1997 at the Kaiser's Mead Works laboratory of an aluminum smelter, located at Spokane, Washington. Five gas sampling runs were successfully completed as planned by the A. J. Edmond Company (primary contractor - test planning and coordinator), the Kaiser laboratory (subcontractor - testing reactor set-up and operator), and the Am Test-Air Quality, LLC (subcontractor for gas sampling and analysis). Highlights of sampling activities are summarized as follows:

- (1) Nitrogen oxides (NO_x) of five gas samples collected in Tedlar bags were analyzed on-site using a chemiluminescent analyzer, Thermo Environmental Instrument Model 42H, performing the EPA Method 7E. In addition, carbon dioxide (CO₂), carbon monoxide (CO) and oxygen (O₂) were analyzed on-site, performing the EPA Method 3A for CO₂ and O₂, and the EPA Method 10 for CO, respectively.
- (2) Five gas samples for GC/MS analysis of CO, CO₂, H₂ (hydrogen), CH₄ (methane), C_nH_m (speciated volatile organic compounds-VOC), SO₂ (sulfur dioxide), H₂S (hydrogen sulfide), COS (carbonyl sulfide) and N₂ (nitrogen), were collected in 6-L evacuated SUMMA stainless steel canisters. The sample canisters were transported next day to the Atmospheric Analysis and Consulting, Inc. laboratory in Ventura, California, for immediate analysis of gas samples, performing the EPA Method TO-14.
- (3) Five gas samples were withdrawn through a sampling probe. Analysis samples were collected passing through the sampling train device, for IC analysis of Cl₂. The collected samples were transported to the Am Test laboratory, Redmond, Washington, for immediate analysis performing the EPA Method 26.

Details of the experimental procedure for each test are described in the following sections.

RUN OBJECTIVES

The objective of this study is to perform pilot-scale process simulation and variable testing using petroleum coke as a reducing agent of iron ore under operating conditions of a commercial blast furnace process. Specific detail objectives of three Tests A, B and C performed for this study with a petroleum coke and/or iron ore pellets are listed below.

- Test A: To perform a chemical analysis of volatile matter produced from petroleum coke heated at 950 °C for 10 min under non-oxidizing conditions (argon atmosphere) as defined in the ASTM Method D 3175, or equivalent.
- Test B: To perform a chemical analysis of effluent gases produced from combustion of petroleum coke through the injection of air at the base of

the packed column, which is controlled at 1000 °C of the effluent gas temperature.

Test C: To perform chemical analyses of effluent gases produced at three different effluent gas temperatures (500, 900, and 1100 °C, respectively), which are resulting from operation of a column of TECNORED pellets (iron ore blended with petroleum coke) under internally self-generated reduction atmosphere. The column operation is controlled under neutral and non-pressurized argon atmosphere. In addition, to analyze solids product (sintered and clogged pellets) remained in the reactor after heating beyond 1200 °C for composition of carbon, sulfur, and residual FeO present in both metal and slag, which are separated by heating.

EXPERIMENTAL PROCEDURES

Materials Tested

Petroleum coke, a testing sample derived from a refinery located in Texas, with high sulfur content of 7.0 wt %. Approximately 5 kg of sponge/shot coke (60/40 mixture) was prepared with ¼" to ½" (6 to 13 mm) particle sizes by A. J. Edmond Company. The volatile matter content present in this coke was 10.0 wt %.

TECNORED pellets (iron ore blended with the coke fines) were made in Joinville, Brazil and forwarded by courier to A. J. Edmond Co. Approximately 15 kg of TECNORED pellets were prepared with 7.5 wt % moisture content and 3.4-6.4 mm particle sizes.

Reaction System

A schematic diagram of the reaction system of the pilot-scale plant is shown in Figure 1. The reaction system consists of argon cylinder, compressed air supply, nitrogen cylinder, pressure regulators, gas mass flow meter and control valves, preheating zone, reactor with temperature controller and programmer, sampling probes and analyzers for Cl₂, NO_x, and other gases (CO, CO₂, H₂, CH₄, C_nH_m (VOC), SO₂, H₂S, COS and N₂). The packed column reactor was made of a 3"φ x 48"H Inconel tube connected at the top to the stainless-steel sampling vent tube (3"φ x 24"H) with three sampling ports. At the mid-point inside the reactor a nickel-chromium screen (16 mesh, #24 wire size) welded to the wall to support the loading of petroleum coke and TECNORED pellets.

Effluent Gas Analyses

The Am Test-Air Quality, LLC (a subcontract service laboratory), Preston, WA performed on-site effluent gas analyses and sampling. Total five grab samples were collected and analyzed as required in this study, employing the analytical methods as described in Section INTRODUCTION, Summary of Pilot-Scale Tests.

Run Procedures

Tests A, B and C were performed under operating conditions closely simulating commercial blast furnace processes, as required by the client, CAEMI International and TECNORED. A 3" Inconel vertical reactor tube was placed in a 3" tube furnace capable of being controlled at 1200 °C of the reaction temperature. The control thermocouple was located at the mid-point outside surface of reactor tube. The effluent gas temperature at the top of reaction zone was not determined, but estimated to be similar within several degrees of this control temperature, based on previous experience with the heating furnace used. The temperature controller was effectively programmed to reach a target temperature within an hour in order to be ready for the next test planned as soon as possible. Effluent gas stream was naturally cooled without condenser through the sampling vent tube before reaching gas sampling probes. The effluent gas temperature at the sampling probe location was periodically measured using a portable thermometer during each test, and ranged from 100 to 350 °C. During the first Run 1, pre-tests were conducted for an integrity check of the reaction system, gas sampling and instrumental analyses, and other pertinent experimental parameters such as temperature, flow rate, etc.

RUN 2 - TEST A

A representative sample of a petroleum coke with 7 wt % sulfur content (approximately 5 kg) was prepared using ASTM Practice D 346 in the range of particle size from ¼" to ½" (6 to 13 mm), and stored in an air tight sample bag until needed for the test. The moisture content of the coke was approximately 0.21 wt %. The reaction test steps were:

- (1) Approximately 312.6 g of the petroleum coke sample was charged into the reactor. The packed-bed height was approximately 4-5".

- (2) Initially the nitrogen gas flow was on for 30 min at 5 liter/min to purge out the reaction system. Then the gas flow switched to argon.
- (3) The argon gas flow slowly increased to 17 liter/min (1000 ± 10 liter/hr). The inlet argon gas pressure to the reactor was set at 70-75 psig.
- (4) The reactor heating furnace was turned on, and the reactor temperature was rapidly increased to 400 °C in 6 min. No sampling was conducted during this preheating period.
- (5) Sampling began at 400 °C and continued heating-up of the reactor from 400 to 950 °C. Three sampling probes were installed and total sampling rate was set at 6.2 liter/min; 4 for NO_x analysis, 2 for Cl₂ analysis, and 0.2 liter/min for GC/MS analysis, respectively.
- (6) The reactor temperature maintained at 950 °C for additional 5 min, and during this period sampling continued. Total sampling time (or reaction time) was 25 min.
- (7) After completion of the gas sampling, the argon gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.
- (8) Solids product remained in the reactor was easily removed without any visible deposits on the wall, when the reactor was sufficiently cooled down, and the reactor was cleaned thoroughly for preparation of the next test.

The material balance showed approximately 9.3 wt % of the petroleum coke converted to volatile matter.

RUN 3 - TEST B

The reaction test steps were:

- (1) Approximately 302.3 g of the petroleum coke sample was charged into the reactor. The packed-bed height was approximately 4-5".
- (2) Initially the nitrogen gas flow was on for 30 min at 7.5 liter/min to purge out the reaction system. Then the gas flow switched to compressed air.
- (3) The air gas flow was set at low rates, 7.5-8.3 liter/min, in order to closely observe the reactor exotherm. *Note: This lower air flow rate employed was primarily due to the safety consideration of equipment limitation, that is, the Inconel reactor should operate below 1260 °C (maximum operating temperature for Inconel material). The planned air flow rate estimated for complete combustion was 17 liter/min.*
- (4) At the same time the reactor heating furnace was turned on, and the reactor temperature was slowly increased to 920 °C. No sampling was conducted during this preheating period.
- (5) Sampling began at 920 °C and continued heating-up of the reactor from 920 to 1000 °C. Three sampling probes were installed and total sampling rate was set at 5.1 liter/min; 4 for NO_x analysis, 1 for Cl₂ analysis, and 0.1 liter/min for GC/MS analysis, respectively.
- (6) The reactor temperature maintained at 1000-1015 °C for additional 56 min, and during this period sampling continued. The air flow rate was adjusted in the range of 6 to 9.4 liter/min in order to control the reactor exotherm during this period.
- (7) After completion of the gas sampling, the air gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.
- (8) Solids product remained in the reactor was easily removed without any visible deposits on the wall, when the reactor was sufficiently cooled down, and the reactor was cleaned thoroughly for preparation of the next test.

The material balance showed approximately 27.5 wt % of the petroleum coke combusted and converted to various product gases. This low conversion is partly attributed to the oxygen-deficient reaction condition employed in this test with the lower air flow, 6-9.4 liter/min, than 17 liter/min (planned target and estimated stoichiometric flow for complete conversion), and/or partly attributed to possible low reactivity of petroleum coke with air. *Note: The lower oxygen flow (air flow) was employed primarily due to the equipment limitation of Inconel material as discussed in the above (3). This would significantly affect the effluent product composition, resulting in lower content of CO, CO₂, and SO₂.*

RUN 4, 5 AND 6 - TEST C

A representative sample of TECNORED pellets (iron ore blended with coke fines) with 7.5 wt % moisture content was prepared (approximately 15 kg) in the range of particle size from 3.4 to 6.4 mm, and was stored in an air tight sample container until needed for the test. The reaction test steps were:

- (1) Approximately 1200 g of the TECNORED pellets sample was overnight dried in an oven at 100 °C and was charged into the reactor. The packed-bed height was approximately 4-5".
- (2) Initially the nitrogen gas flow was on for 30 min at 15 liter/min to purge out the reaction system. Then the gas flow switched to argon.
- (3) The argon flow was set at 6.9 liter/min. This gas flow was above the sampling rate set in the following (5), <5.1 liter/min.
- (4) At the same time the reactor heating furnace was turned on, and the reactor temperature was rapidly increased to 500 °C in 12 min. No sampling was conducted during this preheating period.
- (5) Sampling began at 500 °C and continued for 60 min with the reactor temperature maintained at 500 °C. Three sampling probes were installed and total sampling rate was set at <5.1 liter/min; <4 for NO_x analysis, 1 for Cl₂ analysis, and 0.1 liter/min for GC/MS analysis, respectively.
- (6) After completion of the gas sampling at 500 °C, three sampling probes were reinstalled, and then the reactor temperature was again rapidly increased to 900 °C. No sampling was conducted during this second preheating period. The argon gas flow rate was set at 6.7 liter/min.
- (7) Sampling began at 900 °C and continued for 30 min with the reactor temperature maintained at 900 °C. Sampling rates were the same as before at 500 °C.
- (8) After completion of the gas sampling at 900 °C, three sampling probes were reinstalled, filters were replaced, and then the reactor temperature was again rapidly increased to 1100 °C. No sampling was conducted during this third preheating period (about 37 min consumed). The argon gas flow rate was set at 6.7 liter/min.
- (9) Sampling began at 1100 °C and continued for 20 min with the reactor temperature maintained at 1100 °C. Sampling rates were the same as before at 900 °C.
- (10) After completion of the gas sampling at 1100 °C, sampling devices were removed, sampling ports were blocked, and then the reactor temperature was again rapidly increased to 1200 °C. No sampling was conducted during this fourth preheating period. The argon gas flow rate was the same as before.
- (11) Without sampling the reactor temperature was maintained at 1200 °C for 60 min before ending the Test C.
- (12) The argon gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.

During the heating-up period to 1200 °C for the pre-melt and slag-off test, trickling and slipping-down noise was noticed inside the reactor tube. It appeared that the wire-mesh screen welded to the reactor wall (for support of pellets and petroleum coke loading inside the reactor) was loosened and fell down to the bottom section of the reactor. The test was not successfully completed for further analysis of solids remained.

RESULTS AND DISCUSSION

Table 1 summarizes analysis results of gas samples collected for this study. Some of Runs 4 to 6 results are proprietary data. Therefore, ratio values of N₂, CO, CO₂ and H₂ compositions were calculated for comparison. Run 5 data were used as basis.

Devolatilization and Pyrolysis of Petroleum Coke under Argon Atmosphere

A study of pyrolysis of petroleum cokes under nitrogen inert atmosphere showed that the volatile matter significantly released in the plastic range of a given coal (400-500 °C) [2]. Maximum evolution of volatile matter (about 40 to 49% of total) was observed in the range of 500-750 °C, and then the volatile matter release decreased in the range of 750-1000 °C. Based on this literature information, in Run 2 - Test A gas sampling was performed for 25 min in the temperature range of 400-950 °C. The weight loss determined after the test showed 9.3 wt %, and

similar to the volatile matter content (10.0 wt %) determined by ISO 562, which is equivalent to ASTM Method D 3175.

The gas analysis data for Run 2 – Test A at 400-950 °C (in Table 1) shows that the effluent product gas consists of H₂, CH₄, CO₂ and CO. In addition a significant amount of H₂S is present in the gas sample produced primarily due to the high sulfur content of the petroleum coke (7.0 wt %) tested for this study. Other trace gases are NO_x, C_nH_m (VOC), and insignificant amounts of Cl₂ and SO₂ plus COS.

Combustion of Petroleum Coke with Air Flow

During the start-up (heating-up) period in Run 3 – Test B, the oxygen deficient reaction condition was employed as mentioned in Section RUN 3 – TEST B, in order to control highly exothermic reaction (combustion), $C + O_2 \rightarrow CO_2$, occurring below 930 °C (1200 K) [4]. When the reaction temperature reaches above 930 °C, the controlling reaction changes to highly endothermic reaction (gasification), $CO_2 + C \rightarrow CO$. The low flow rates of air, 6-9.4 liter/min, coupled with slow heating-up of the reactor enabled to closely control the reactor exotherm. The estimated stoichiometric flow of air for complete conversion was 17 liter/min. Without increasing the flow rate of air for complete conversion, gas sampling started at 920 °C when the governing reaction changes from combustion to gasification and continued for 60 min at 1000-1015 °C (most of time).

The material balance showed approximately 27.5 wt % of the petroleum coke combusted and converted to various product gases. This low conversion is partly attributed to the oxygen-deficient reaction condition employed in this test with the lower flow rate of air, and/or partly attributed to possible low reactivity of petroleum coke with air. The low conversion would significantly affect the effluent gas product composition, resulting in low content of CO, CO₂, and SO₂. The on-site gas analysis data showed an insignificant amount of O₂, 0.2%, present in the gas sample, indicating most of oxygen in the air converted to oxides and depleted in the reaction zone.

The gas analysis data for Run 2 – Test B at 1000-1015 °C (in Table 1) shows that the nitrogen-free effluent product gas consists of H₂, CH₄, CO₂ and CO. A significantly reduced amount of H₂S is present in the gas sample, and the SO₂ plus COS content significantly increased by oxidation, compared to the result of Run 2 – Test A. Other trace gases are NO_x, C_nH_m (VOC), and insignificant amount of Cl₂.

The combustion reaction with air produced much higher amounts of CO₂ and CO, while reducing CH₄ composition, compared to the result of Run 2 – Test A. The high hydrogen content observed suggests a possibility of pyrolysis reaction still present under the oxygen deficient condition. The reactor temperature profile was not measured in this study, which might provide better understanding of reaction mechanism.

TECNORED Pellets Reduction under Argon Atmosphere

In Runs 4 to 6 – Test C, TECNORED pellets were processed under argon atmosphere at three different reaction temperatures, 500, 900 and 1100 °C, sequentially. Ratio values were used for comparison of proprietary data (compositions of N₂, CO, CO₂ and H₂). Other gas composition data are reported as measured (carrier gas-free basis) in Table 1.

Run 6 at 1100 °C shows the highest CO composition in the gas sample among three runs, indicating that a significant gasification reaction occurs above 930 °C with TECNORED pellets present. The CO content is several times higher than the CO₂ content at this condition. This suggests that gasification is the controlling reaction, $CO_2 + C \rightarrow CO$, and TECNORED pellets generate self-reducing environment.

In Run 5 at 900 °C, the CO content is similar to the CO₂ content. Both combustion and gasification are competing and important at this temperature. Again this indicates that TECNORED pellets generate self-reducing environment.

Relatively small, insignificant amounts of CO and CO₂ were observed at the lower reaction temperature of 500 °C. A small degree of devolatilization might be mainly happening at this temperature without presence of self-generated combustion and gasification reactions.

Other trace gases produced at 900-1100 °C are CH₄, H₂S, SO₂ plus COS, NO_x, C_nH_m (VOC), and insignificant amount of Cl₂.

SUMMARY

Five screening tests with high sulfur petroleum coke and TECNORED pellets were successfully completed under process conditions of iron ores reduction. Effluent product gas analyses suggest that:

- TECNORED pellets generate self-reducing environment for iron ores processing at 900-1100 °C.
- The high CO production at 1100 °C with TECNORED pellets provides an evidence of gasification reaction controlling at this temperature.
- Minimum or insignificant amounts of trace gases (H₂S, SO₂ plus COS, NO_x, C_nH_m (VOC) and Cl₂) were produced at 900-1100 °C with TECNORED pellets.
- TECNORED pellets effectively reduce sulfur compounds emission in the gas stream through internal scavenging actions with addition of additives in the pellets, even though a high-sulfur petroleum coke fines (7 wt %) was used in pelletizing.
- Reactivity of petroleum coke under combustion and gasification condition seems significant and sufficient enough in its application for iron ores processing.

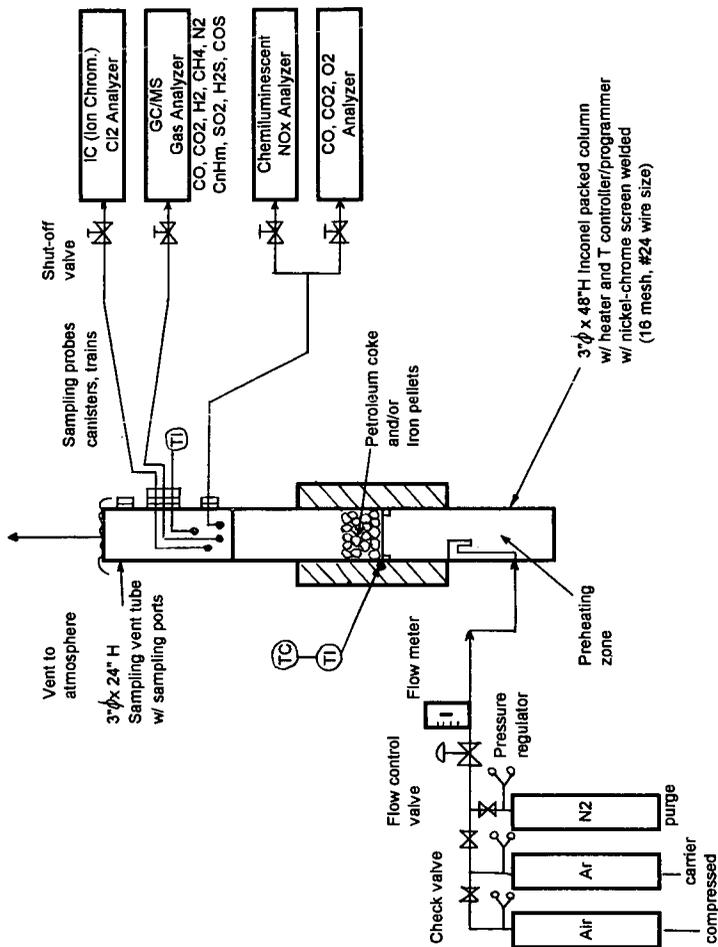
ACKNOWLEDGMENT

The project was sponsored by North Star Steel and Tecnored Technologies, Stamford, Connecticut and TECNORED LTDA, Joinville-SC, Brazil. Messrs. Mark Wyborne and Randy Czikall, Kaiser laboratory, Spokane, WA, are acknowledged for their participation and efforts in testing reactor set-up at the Kaiser laboratory and successful operation of the reactor. Mrs. Karen Kumke, A. J. Edmond Company, Texas City, TX, provided the petroleum coke sample used for this study.

REFERENCES

1. J. M. Lee, J. J. Baker, R. Llerena, J. G. Rolle, 214th American Chemical Society National Meeting, Las Vegas, Preprints of Symposia, Division of Fuel Chemistry, Vol. 42, No. 3, 844-853 (1997).
2. J. A. Menendez, et. al., Energy & Fuels, Vol. 10, No. 6, 1996, 1262-1268.
3. J. W. Ramming, M. Contrucci, E. Marcheze, TECNORED process data published (1997).
4. J. G. Peacey, The Iron Blast Furnace: Theory and Practice (1979).
5. McGraw-Hill Encyclopedia of Science and Technology, 7th Ed., 423 (1992).
6. Kerk-Othmer Encyclopedia of Chemical Technology, Volume 9, 7th Ed., 829 (1995).

Figure 1. SCHEMATIC DIAGRAM OF REACTION SYSTEM



**Table 1. EFFLUENT PRODUCT GAS ANALYSES
(Carrier Gas-Free Basis)**

Based on argon (carrier gas)-free in Runs 2, 4 to 6, & nitrogen-free in Run 3.

	Run 2 <u>Test A</u>	Run 3 <u>Test B</u>	Run 4 <u>Test C</u>	Run 5 <u>Test C</u>	Run 6 <u>Test C</u>
<u>Operating Conditions</u>					
Reaction temperature (°C)	400-950	1000-1015	500	900	1100
Reaction/sampling time (min)	25	60	60	30	20
<u>Raw material charge (gr)</u>					
Petroleum coke	312.6	302.3	---	---	---
TECNORED pellets (dried)	---	---	1200 ^a	1200 ^a	1200 ^a
<u>Gas flow (L/min)</u>					
Argon (carrier gas)	17	---	6.9	6.7	6.7
Air (reactant gas)	---	6-9.4	---	---	---
<u>Effluent Gas Composition (vol %)</u>					
			<i>Relative ratio to Run 5 data^b</i>		
N ₂ (nitrogen)	---	---	2.1	1	0.7-1.0
CO (carbon monoxide)	<0.1-1.2	8.5	<0.01	1	2.9
CO ₂ (carbon dioxide)	<0.1-2.1	15-24	0.0-0.5	1	0.9
H ₂ (hydrogen)	---	---	1	1	0.6-0.8
CH ₄ (methane)					
C _n H _m (C ₂ -C ₆ hydrocarbons)					
C _n H _m (VOC) (ppmv)			DETERMINED BUT NOT DISCLOSED		
(volatile organic compounds)			DUE TO CONTRACT AGREEMENT		
H ₂ S (hydrogen sulfide) (ppmv)			(HYDROGEN TO CHLORINE ANALYTICAL DATA)		
SO ₂ (sulfur dioxide) plus					
COS (carbonyl sulfide) (ppmv)					
NO _x (nitrogen oxides) (ppmv)					
Cl ₂ (chlorine) (ppmv)					
Undetermined (H ₂ O, etc.)					

NOTE: Most of data were determined using GC/MS analysis of SUMMA canister samples

a Initially charged in Run 4, and Runs 5 and 6 continued without replacement.

b Ratio values of some of Runs 4 to 6 results (proprietary) were used for comparison.