Report Title:

PHASE II CALDERON PROCESS TO PRODUCE DIRECT REDUCED IRON RESEARCH AND DEVELOPMENT PROJECT

Report Type: **QUARTERLY** | Reporting Period Start Date: 01/01/2003 End Date: 03/31/2003

Principal Author(s): **ALBERT CALDERON**

Report Issue Date: 04/28/2003 | DOE Award No.: DE- FC22 -95PC92638

Submitting Organization(s) Name & Address

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QUARTERLY TECHNICAL PROGRESS REPORT

PHASE II CALDERON PROCESS TO PRODUCE DIRECT REDUCED IRON RESEARCH AND DEVELOPMENT PROJECT

CALDERON ENERGY COMPANY
COOPERATIVE AGREEMENT NO. DE-FC22-95PC92638

Reporting Period: 1-01-03 to 3-31-03

Date of Report: 4-28-03;

Phase II Award Date: 6-23-00;   Anticipated Completion Date: 12-03-03

Total Project: $ 14,732,316.00   Total DOE Share This Action: $6,457,000.00

Contracting Officer's Representative (COR): Carl Maronde;

Project Director: Albert Calderon

Assistant Project Director: Reina Calderon

Abstract

This project was initially targeted to the making of coke for blast furnaces by using proprietary technology of Calderon in a phased approach, and Phase I was successfully completed. The project was then re-directed to the making of iron units. U.S. Steel teamed up with Calderon for a joint effort which will last 30 months to produce directly reduced iron with the potential of converting it into molten iron or steel consistent with the Roadmap recommendations of 1998 prepared by the Steel Industry in cooperation with the Department of Energy.

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Introduction

The commercialization path of the Calderon technology for making a feedstock for steelmaking with assistance from DOE initially focused on making coke and work was done which proved that the Calderon technology is capable of making good coke for hard driving blast furnaces. U.S. Steel which participated in such demonstration felt that the Calderon technology would be more meaningful in lowering the costs of making steel by adapting it to the making of iron - thus obviating the need for coke.

On page 6 of the July 2002 publication of "Iron & Steelmaker (I & SM)", which covered the International Report on steel for Europe, it was reported that the chairman of the Iron and Steel Institute and president of the German Steel Federation, Mr. Dieter Ameling made reference to the necessity of reducing CO_2. He said the following: "... that in some areas, the burden imposed by politicians has reached the breaking point. During the past year, the discussion about the reduction of CO_2 emissions has intensified. Some policies currently brought forward would deeply affect the steel industry since they would narrowly limit production and market potential to the EAF path. Eventually, oxygen steel production would have to be abandoned completely in Germany, with job losses as a consequence. Some political forces even claim it is about time to initiate a restructuring of the German industry "away from energy-intensive old economy industry sectors"."

The fact that U.S. Steel and Calderon teamed up to jointly work together to demonstrate that the Calderon technology will produce in a closed system iron units from iron concentrate (ore) and coal competitively by eliminating pelletizing, sintering, coking, blast furnace operation and possibly doing away with the BOF and the EAF by making steel directly, a huge reduction in CO_2 generation relating to steelmaking would ensue. Such reduction will restructure the steel industry away from the very energy-intensive steelmaking steps currently practiced.

Accomplishments and Discussion

In the "Conclusion" section of the last quarterly report (page 13), it was stated the following: "All efforts will be concentrated to solve the sticking problem in order to proceed with the 72 hour test. Work will also be directed towards desulfurization in the ladle after killing the heat in order to establish an acceptable practice for managing the sulfur content in the metal, an inherent factor when using coal.

The work performed during the past quarter was consistent with the above statement. Additionally miscellaneous activities directly connected with such work were carried out. The discussion in this report will cover the following:-

Item A - Attempts in Solving the Problem of Sticking;

Item B - Work Relating to Desulfurization of the Metal;

Item C - Other Miscellaneous Related Activities; and

Item D - Coordination of Work with U.S. Steel.

Item A - Solving the Problem of Sticking

The sticking problem affected the following components of the system:-

(i) Sticking in the reactor;

(ii) Sticking in the apron at the discharge of the elbow of the reactor; and

(iii) Sticking in the drums.

Initially the discussion will focus on the approaches taken to overcome sticking in the reactor and in the apron; sticking in the drums will be addressed separately.

The approach to solving the sticking problem continued vigorously by trying other refractories than those that had been tested. Two new candidates were offered by vendors; namely, nitride bonded silicon carbide made by St. Gobain in France, and a chrome-alumina called "Ruby" made by Harbison-Walker in the United States. Coupons of these two materials were imbedded in the X-9 refractory lining which was described in an earlier report, and a 24-hour test run was conducted. Upon checking the results after the unit was taken apart, it was found that the silicon carbide was seriously damaged whereas the Ruby seemed to be unaffected except for some minor blistering caused by direct impingement of oxygen from the lance.

Based on these initial results it was decided to forego the use of silicon carbide as a lining and focus on the Ruby which comes in three different conditions – as a ramming material, as a castable and as a plastic. The Ruby plastic appeared to be most suitable for the application; see photograph #1, showing a block of this material which is wrapped in such a way as to minimize loss of moisture.

To insure proper installation, a form taking the shape of a "doughnut" was installed; see photograph #2 and some X-9 was installed as a bonding medium; see photograph #3. After drying the X-9, the block of Ruby plastic was cut into slices (photograph #4), and gently vibrated into place with a rubber-headed vibrating gun. The surface finish was accomplished by making a water diluted "paint" of the Ruby and painting the vibrated surfaces with a brush to give a smooth finish; see photographs #5 and #6.

Sticking at the discharge of the elbow (exit of reactor) see photograph #7, which contributes to excessive increase of hydraulic pressure at the pushing mechanism of the charging system, is caused by heat loss through the collection drum especially during drum change. Irrespective of the high preheat of the drum (about 2000^{o}F) prior to the change, there is a marked difference in temperature between the sintered material at the discharge end (2500^{o}F) and the drum proper. To overcome stickiness in this area, the apron at the discharge was also lined with Ruby; see photograph #8. In addition, to the change in refractory, other changes to the operating practice were added to complement the benefit derived from the Ruby.

From the outset of this project it was assumed that since the iron ore concentrate (see photograph #9) from U.S. Steel has a high moisture content, (see the negative angle of repose shown in photograph #10), the ore would have to be dried in order to minimize the thermal energy required for the high endothermic reactions that would take place in the reactor -- a logical assumption. However, since the process forms an annulus of a mix made up of ore and coal with a coal core being encapsulated within the annulus (see photograph #11), the integrity of the annulus as it is formed in the unique charging system is a very important requirement. In drying the ore, the moisture which served as the binder was absent and therefore the annulus slumped after its formation thereby exposing the refractory wall to direct impingement of oxygen from the lance as oxygen was injected into the coal core. As part of the coal is combusted under substoichiometric conditions to form a very hot tunnel in order to devolatilize the coal into a fissured coke ring (see photograph #12), while producing copious quantities of hot, highly reducing gases, a portion of which flow radially from a hot environment (core) to a colder environment (annulus) through the fissures. This coke ring helps maintain the integrity of the annulus (see photographs #13, and #14), as the annulus is sintered while advancing towards the discharge of the reactor. The remaining reducing gases which flow towards the discharge end of the reactor are combusted in the elbow to form a highly radiant zone which radiates intense thermal energy against the emerging material being pushed out of the reactor. The slumping of the annulus whether it occurs in the elbow or in the reactor causes severe damage to the refractory lining (see photographs #15 and #16) because the lining is unprotected from oxygen impingement from the injecting lance.

To avoid the slumping of the annulus, the drying of the coal was skipped and the ore was used as is; at times the ore in the pile was sprayed with water to keep it moist on purpose. It is well known that when building sand castles at the beach, moist sand is used. The use of moist ore has one additional advantage, it generates steam which reacts with the hot coke to result in the generation of additional reducing gases in the form of water gas ($CO + H_{2}$). Fortunately, the combustion of coal with oxygen in the core provides adequate energy for the reactions to take place despite the charging of moist ore. In maintaining the integrity of the annulus, the annulus does not slump and therefore the lining is protected from overheating thereby preventing the chemical attack of the lining, the main cause of sticking; photographs #17 and #18 show essentially no attack of the lining when the annulus is prevented from slumping.

The collection drum (see photograph #19), as reported previously, has presented the challenge of emptying the material from it by virtue of sticking to its bottom and sides after cool-down.

While running tests, it became standard practice that when exchanging a hot, full drum for an empty drum, a sample of the produced material would be taken out of the full drum (see photograph #20) for the purpose of conducting a grinding test of the sample to predict metallization. As a surprise to all concerned, it was discovered that contrary to general opinion, the sample did not re-oxidize even though it was cooled in open air prior to the grinding test. This realization has led to the decision to try to empty the collection drum while hot to find out if it would be easier to empty its contents. Also, a second decision was made which consisted of lining the drum with ruby with a taper to diverge upwardly to facilitate the discharge of material from the drum. A construction form was made (see photograph #21) to provide such taper; three supports were added to the top of the form in order to suspend the form using the rim at the top of the drum for support (see photograph #22). The ruby plastic lining was then tampered into place with a ceramic blanket for insulation being fastened against the steel shell (shown in photograph #22). Once the ruby was completely installed the form which had been greased for ease of removal, was extracted to result in a high quality lining in place suitable for the severe duty to which the collection drum would be exposed to; (see photographs #23 and #24).

Since the ruby lined drum ended up weighing in excess of 700 lbs it took two people to tip it in order to empty it (see photograph #25); this activity became hot and dangerous, but there was a marked improvement in being able to empty the collection drum while hot. To overcome the problem of exposing the men to heat and bodily injury, a drum tilting device suitable to fit the forks of a lift truck, was acquired (see photograph #26) and the dumping of the collection drum into an unlined drum was greatly facilitated (see photographs #27, #28, #29, and #30). The lessons learned from the work done on the collection drums was very productive because such work has led to the conceptual design of equipment that would be practical when applying the Calderon technology of iron/steelmaking commercially. Scale models of such equipment were constructed in order to get a good understanding of what is required for practical industrial applicability.

Item B - Work Relating to Desulfurization of the Metal

This activity was focused in initiating a procedure for the desulfurization of the molten metal made since high sulfur content in the metal is an important factor when using coal.

To address the sulfur issue a heat was made in the homogenizer (induction furnace) using a heel practice and a stirring plug at the bottom of the furnace, wherein 73 pounds of ingots which had been cast from Calderon material were melted first, and then 80 pounds of Calderon material followed producing a rimmed heat. The melt-in slag was rabbled out of the furnace and a new slag was made while continuously plug stirring in the furnace to cause mixing. Before tapping the heat, sample “A” was taken for analysis, the sample being killed with Aluminum (Al). During the tap (see photograph #31) into a preheated ladle, Al was added to kill the heat first, and an artificial slag made-up of CaC_2 and Spar followed, the analysis of the artificial slag being 66% CaC_2 and 34% spar.

At the completion of the tap, additional stirring was carried out in the ladle with a special injection wand (see photograph #32) to insure proper mixing (photograph #33) and sample “B” was taken for analysis. For convenience nitrogen was used as the stirring gas instead of argon. Next, the killed heat together with the artificial slag were poured back into the furnace for reheating to make up for heat loss; see photograph #34. While re-heating was taking place in the furnace the metal was stirred additionally with the stirring plug at the bottom of the furnace and supplemented by the wand (see photograph #35) until a temperature above 2900°F was reached. At that time the wand was removed from the furnace (see photograph #36) and the heat was slagged-off with a rabble; see photograph #37. Once this was done, a second artificial slag made up of CaC_2 + spar was added to the furnace and additional stirring took place with the plug until the temperature of the metal was reheated to above 2900°F when the heat was tapped through this second artificial slag into the ladle and the heat was poured into molds (see photograph #38); sample “C” was taken during the pour.

Samples A, B & C were sent to Bowser Morner (an outside laboratory) for analysis. The results marked Exhibit 1(A), 1(B) and 1(C) are attached. It is to be noted that the sulfur content is exceedingly high in Sample (A) by virtue of using coal. It is also to be noted as shown in Sample (B) that a carbon pick-up occurred; namely from 1.47% to 2.32%: this was contributed by the carbon in CaC_2 “the artificial slag” which was added to the heat; however, the calcium performed quite efficiently in the removal of sulfur from 0.466%S down to 0.007%S, a major drop; see Exhibit 1(B). To overcome carbon pick-up, an artificial slag devoid of carbon would be necessary. Further, it should be noted that in Sample (C) a carbon pick-up from 2.32% to 2.65% occurred; again, this is caused for the addition of the CaC_2 to form the second slag, but the pick-up of sulfur from 0.007%S in Sample “B” to 0.013% in Sample “C” is an anomaly. The only justification for this irregularity is the belief that such pick-up could have occurred from residual high sulfur slag that had stuck to the furnace walls during the first tap of the metal.

To overcome this problem it would be logical to reheat the metal in the ladle with electrodes instead of pouring the metal back into the furnace where the initial slag was formed. At the present time the project does not have the capability of applying heat to the metal in the ladle; it is intended to explore means capable of achieving this.

Item C - Other Miscellaneous Related Activities

During the past quarter 14 test runs were conducted, lasting a total time of 457.23 hours. The shortest test was 9.00 hrs and the longest 45.88 hrs. By being observant, there was always knowledge that could be gleaned from every test. As for example:- It has been learned that during a drum change it was important to scrape the apron from the bottom of the spool to cause stuck material to be dislodged (see photographs #39 and #40) prior to installing the empty drum to collect material. This simple exercise minimized cumulative build-up and reduced hydraulic pushing pressure.

The installation of a themocouple through the reactor shell (see photograph #41) touching the outer wall of the refractory was included to foretell when the inner lining deterioration (see photograph #42) was taking place by the rise in temperature indicated by the thermocouple.

The making of simple gaskets from ceramic felt to seal the drum to the discharge of the reactor (see photograph #43) and also to seal the entry port of the oxygen lance (see photograph #44) saved the purchase of special gaskets and glands while at the same time features that provide “give” to expansion and contraction caused by heat were incorporated.

The spreading of the metallized material on the concrete floor in furrows and screening of same into +1/4" and -1/4" size (see photographs #45 and #46) gave an idea as to how much material would be recycled commercially, thus having actual data which would enable the incorporation of the appropriate equipment to handle the screenings.

It was also found that a stainless steel water cooled thermocouple wand with a copper tip took the abuse much better than a water cooled thermocouple wand made entirely from copper. Such a wand was made (see photograph #47); it performed trouble free under a hot environment with prevailing flames (see photograph #48) adjacent to it.

Since the Calderon technology is novel and the objective is to make iron/steel direct with the potential of greatly reducing costs, paying attention to details is most critical.

Item D - Coordination of Work with U.S. Steel

U.S. Steel and Calderon cooperated fully during the past quarter. Both parties staying in frequent communication with the immediate objective of running a 72 hour test at a reasonable steady state with the result of obtaining 80% metallization using ore concentrate and coal. As mentioned, 14 runs were carried out during the past quarter, they numbered from #98 to #111 inclusive.

Runs #98, #99, #101, #102, #104, #105, #106, #107, #108, #110 and #111 were shut down as scheduled.

Runs #100, #103 and #109 were shut down on an unscheduled basis because of excessive pushing pressures causing forced shut-downs.

The last five runs #107 through #111 inclusive, exceeded 40 hrs except for run #109 which was aborted after 9 hrs from start-up because of inability to push.

Drum “D” from run #105 was delivered to U.S. Steel Research for analysis of its contents. The results indicated that the metallization was 77.3%, slightly less than the target of 80%. The data sheet of the metallization test is attached and marked Exhibit 2. U.S. Steel informed Calderon that the results so far are encouraging.

Conclusion

It can be concluded that the problem of sticking is gradually being overcome, but it cannot be stated at this time that the problem of sticking has been completely solved as evidenced by the unscheduled forced shut-downs referred to in runs #100, #103, and #109.

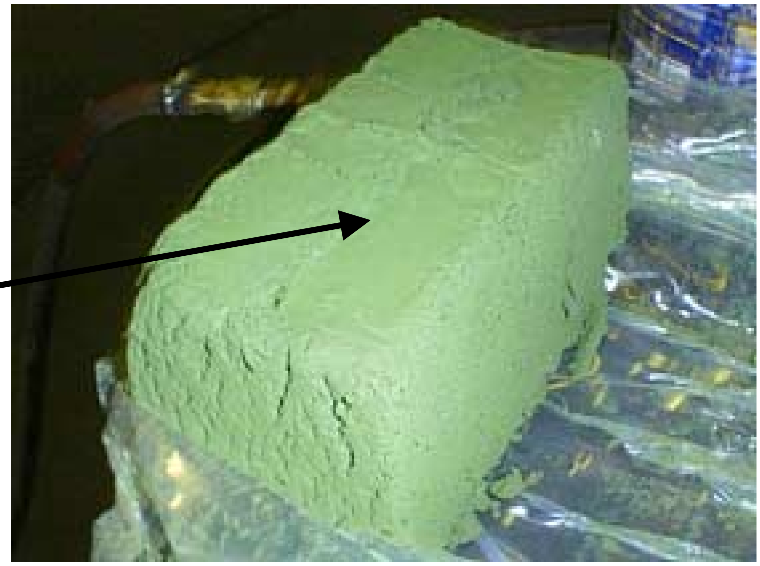
During the next quarter intensive efforts will continue to be applied in order to completely overcome the sticking problem which would lead to the achievement of the 72-hour run at a reasonably steady state with a metallization of 80%.

Submitted by:

Albert Calderon
Project Director

1.

"Ruby"
Refractory Block



2.

Refractory Repair
Form

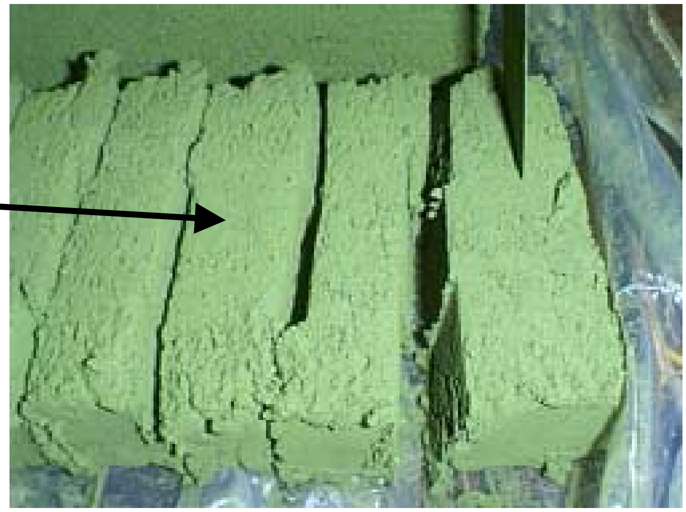
3.

Refractory Repair
Form

X-9 Refractory
Base

4.

Sliced "Ruby" refractory for ease of installation



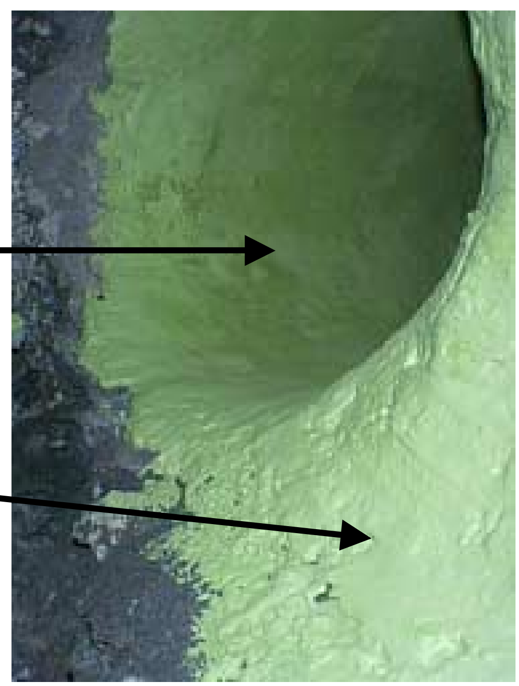
5.

"Ruby" lining installed

6.

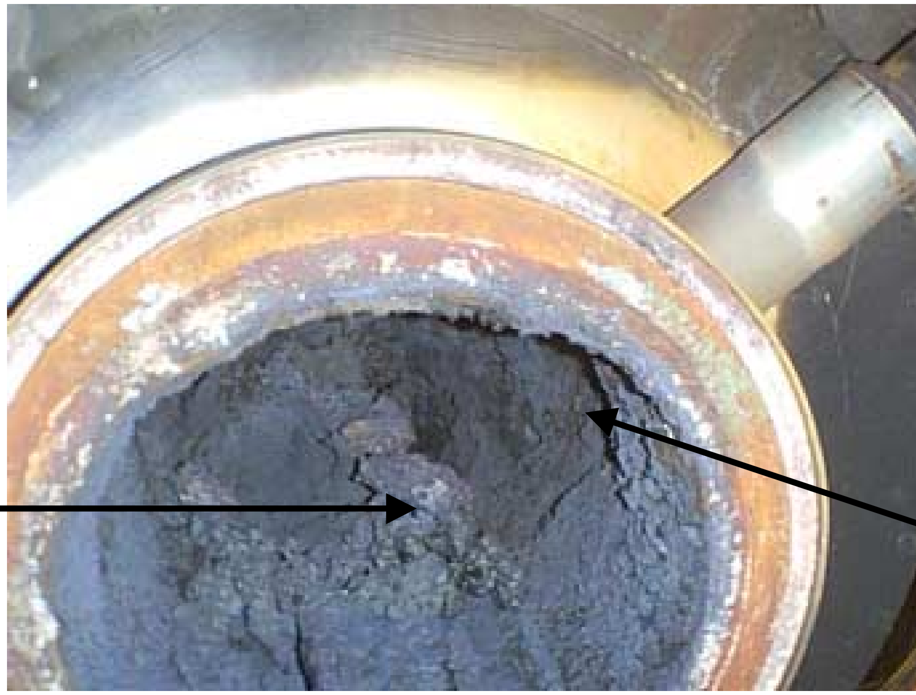
Reactor Discharge, "Ruby" lined

Apron



7.

Frozen material stuck to apron



Reactor Discharge

8.

Reactor Discharge

“Ruby” lining installed in apron

<u>9.</u>

Iron ore
concentrate

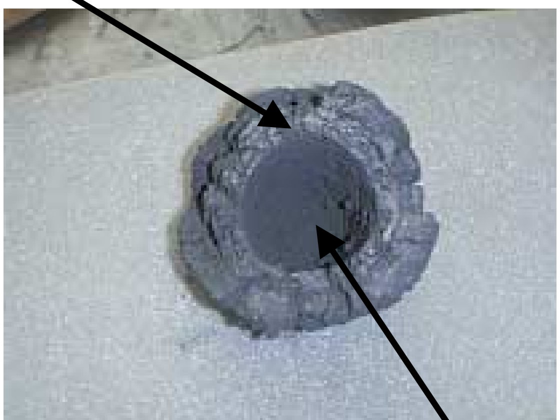
Ore pile

<u>10.</u>

Negative angle of repose


Coal core
Annulus mix (Ore + Coal)

11.


Fissured coal
Core Tunnel (End)

12.


Mix
Core tunnel
Fissured coke

13.


Mix
Core
Coke

14.

15.

Stuck Material

Refractory damage caused by oxygen impingement

16.

"Ruby" lining

17.

Clean undamaged discharge after use. "Ruby" lined.

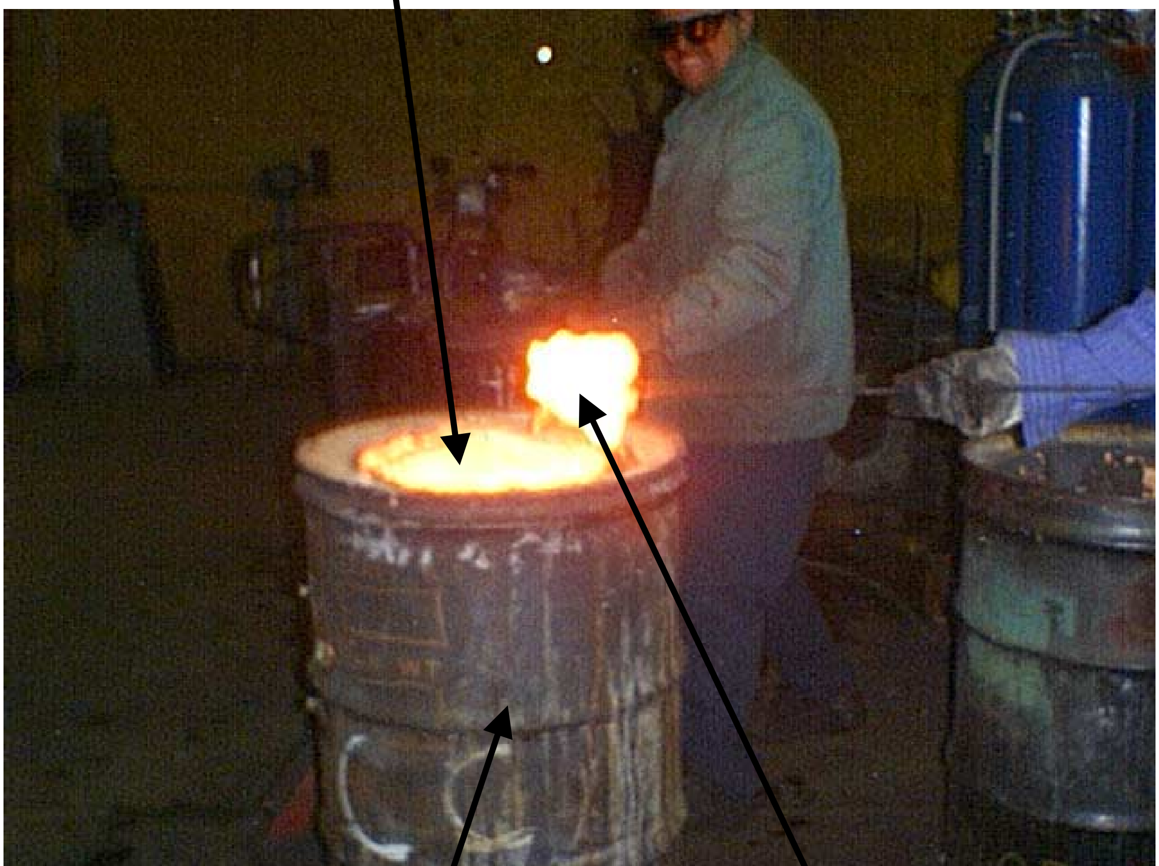
"Ruby" lining

18.

Clean undamaged discharge after use. "Ruby" lined.

19:

20.



21.

Relining form being greased

Ceramic blanket insulation

22.

Relining form in place

Ceramic blanket insulation

23.

Relined drum with "Ruby" refractory

24.

Relined drum

Taper

25.

Hot drum being tilted manually

26.

Drum tilting device

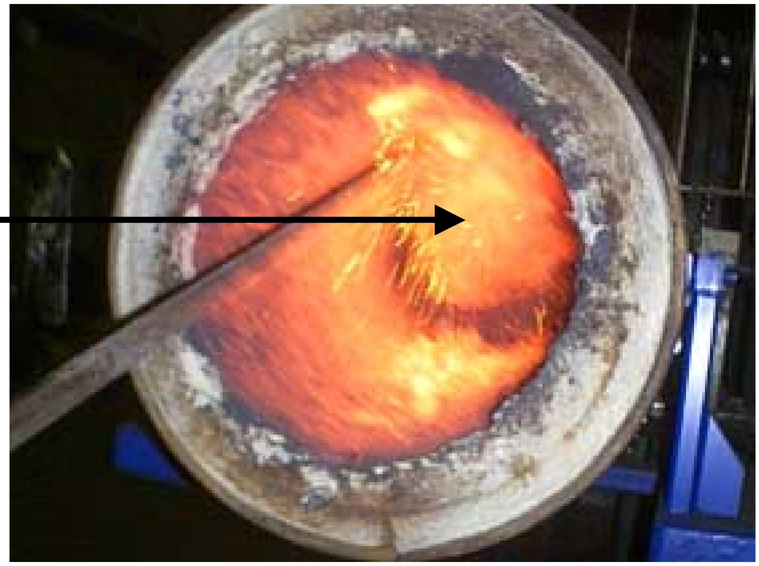
27.

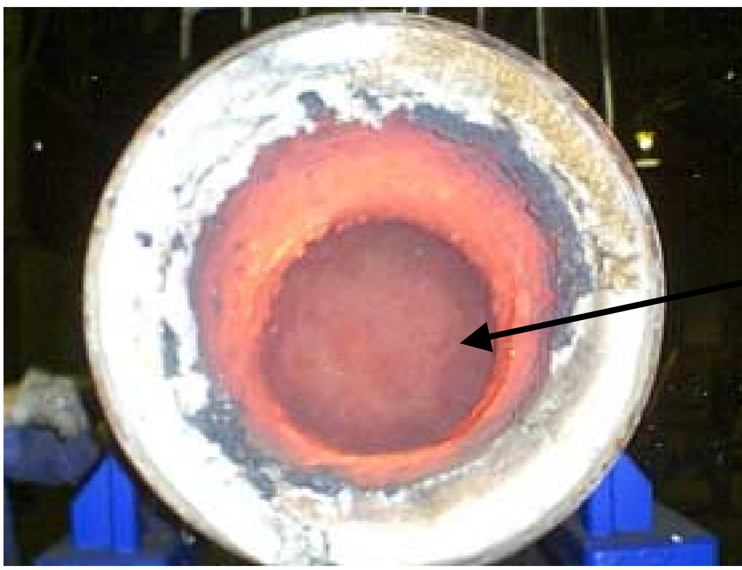
Drum tilting device

Emptying of hot drum using tilting device

28.

Material in bottom of drum being dislodged



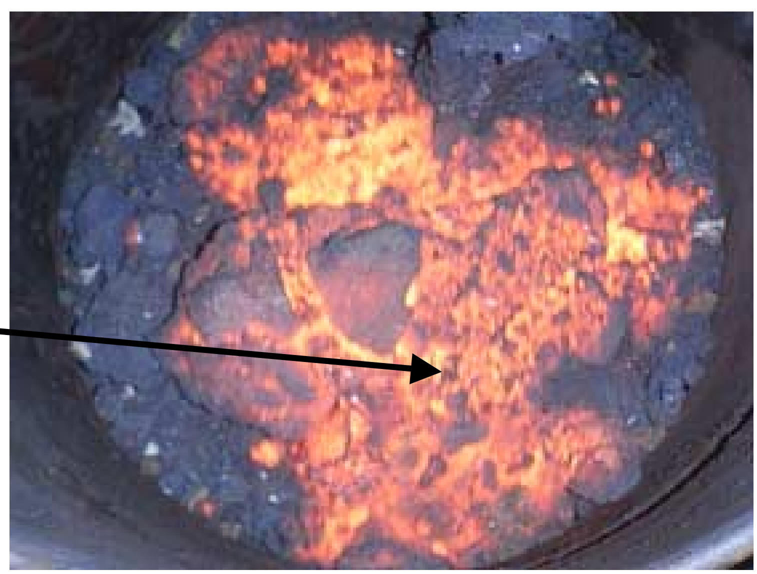


29.

Clean empty drum after being dumped

30.

Hot material in unlined drum after transfer from lined hot drum



Desulfurization of Metal

Rimmed heat being tapped into a ladle which had been reheated

31.

Injection stirring Wand

32.

Metal being stirred in ladle

33.

Metal being poured back into furnace for raising temperature

34.

Desulfurization of Metal (cont'd.)

35.

Additional metal stirring of killed heat while reheating

36.

Stirring wand removal

37.

Slagging with a rabble

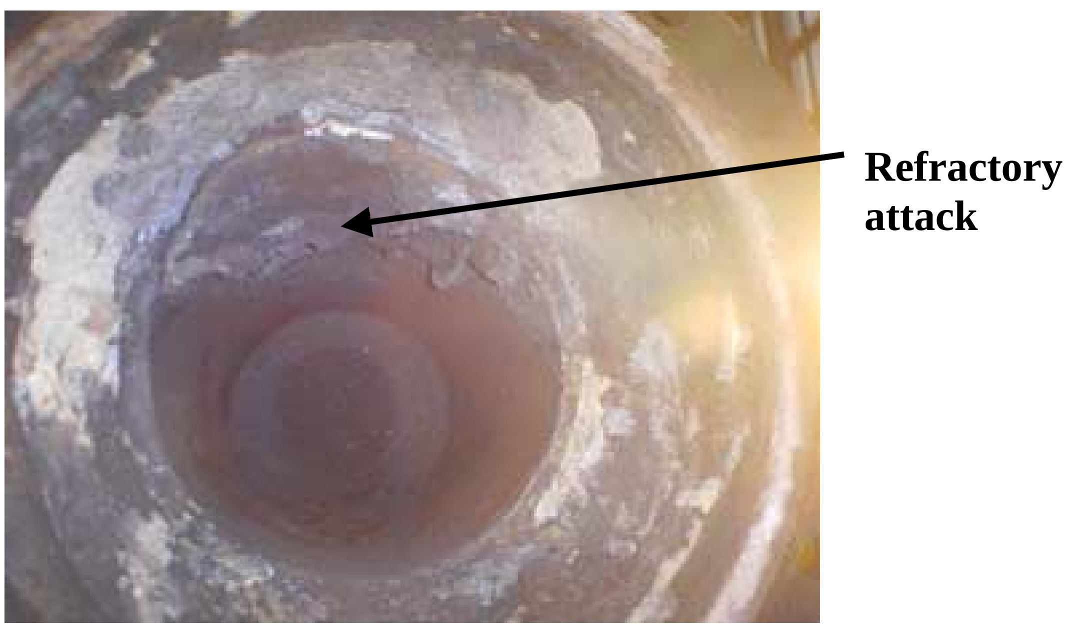
<u>Desulfurization of Metal</u> (cont'd.)

<u>38.</u> **Pouring the heat into molds.**

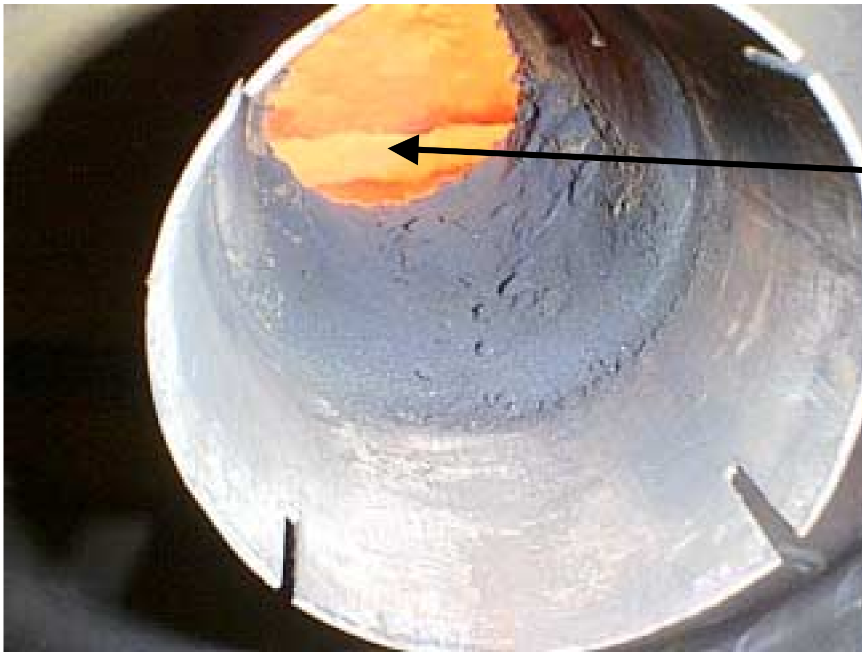
39. **Scraping the apron from the bottom of the spool**

40. **Hot material scraped from the spool falling on concrete floor**

<u>41.</u> **Thermocouple through the shell of reactor to measure the temperature of refractory in order to foretell internal attack**

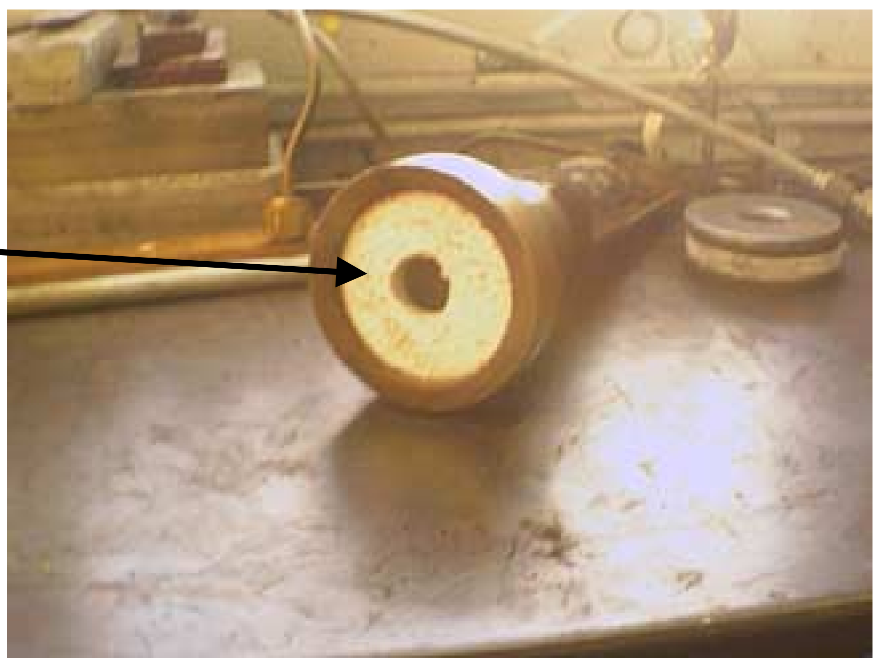


<u>42.</u> **Internal attack of refractory caused by oxygen impingement**



Ceramic blanket seal between drum and spool

43.

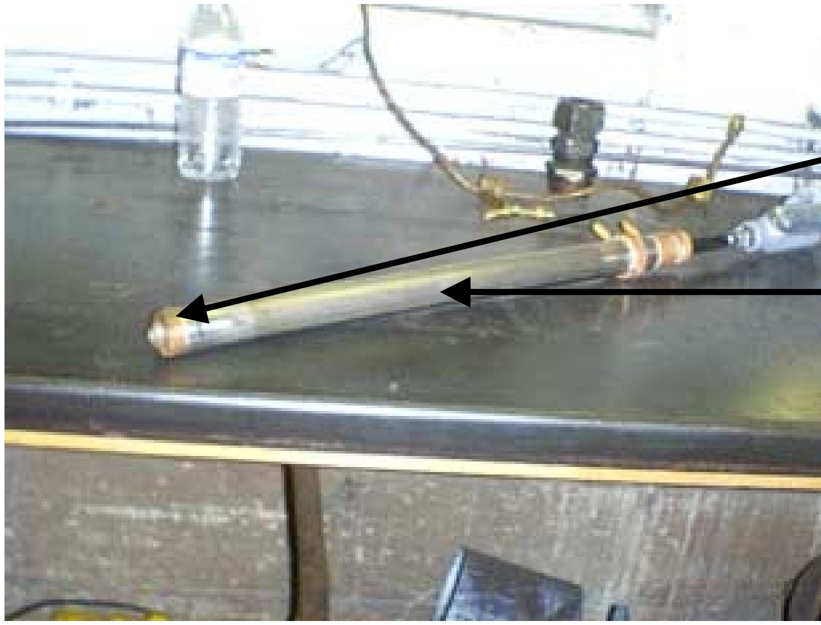


Pliable seal for oxygen injection lance

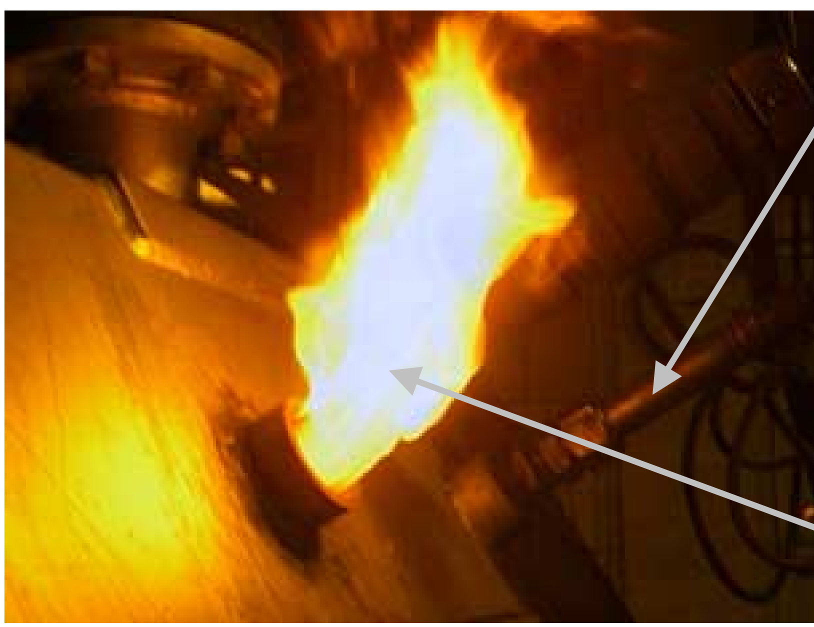
44.

45. **Metalized material screened at + 1\4" & - 1\4"**

46. **Furrows of material organized for visual inspection and comparison from various runs**



47. **Water-cooled thermocouple**



48. **Water-cooled thermocouple exposed to hot environment**

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EXHIBIT 1(A)

LABORATORY REPORT

TO: BRUCE B.
CALDERON ENERGY COMPANY
500 LEHMAN AVE.

BOWLING GREEN, OH 43402

Report Date: 02/18/03
Job Number : 10010382
Group No. : 41696
Sample No. : 301411
Auth/P.O.# : PDU/DRI-1449

Sample Identification: HEAT #2016 - SAMPLE A

Date Sampled: Date Received: 02/17/03

Analysis Description	Result	Units	Method
Carbon	1.47	%	BMI 34-065
Sulfur	0.466	%	BMI 34-065

[redacted]

Submitted by,

Thomas M. Ryan

Thomas M. Ryan, Senior Chemist
Analytical Services Division

A2LA/9786/

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EXHIBIT 1(B)

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LABORATORY REPORT

TO: BRUCE B.
CALDERON ENERGY COMPANY
500 LEHMAN AVE.

BOWLING GREEN, OH 43402

Report Date: 02/18/03
Job Number : 10010382
Group No. : 41696
Sample No. : 301412
Auth/P.O.# : PDU/DRI-1449 B

Sample Identification: HEAT #2016 - SAMPLE B

Date Sampled: Date Received: 02/17/03

Analysis Description	Result	Units	Method
Carbon	2.32	%	BMI 34-065
Sulfur	0.007	%	BMI 34-065

Submitted by,

Thomas M. Ryan

Thomas M. Ryan, Senior Chemist
Analytical Services Division

A2LA/9786/

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EXHIBIT 1(C)

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937-236-8805
937-237-9947 FAX

LABORATORY REPORT

TO: BRUCE B.
CALDERON ENERGY COMPANY
500 LEHMAN AVE.

BOWLING GREEN, OH 43402

Report Date: 02/18/03
Job Number : 10010382
Group No. : 41696
Sample No. : 301413
Auth/P.O.# : PDU/DRI-1449 B

Sample Identification: HEAT #2016 - SAMPLE C

Date Sampled: **Date Received: 02/17/03**

Analysis Description	Result	Units	Method
Carbon	2.65	%	BMI 34-065
Sulfur	0.013	%	BMI 34-065

Submitted by,

Thomas M. Ryan

Thomas M. Ryan, Senior Chemist
Analytical Services Division

A2LA/9786/

EXHIBIT 2

Attn: Mr. Calderon

Calderon DRI Sample : Operation of Feb. 18, 2003

	Weight, lb.	%				
Uncrushable	13.50					
+1/4 Inch	46.50	30.41				
- 1/4 Inch	92.90	60.76				
Total	152.90	100.00				
Uncrushable						
Fe Total	95.60					
Fe Met*	95.60					
(*assumed all metallic)						
C	0.022					
S	0.514					
+ 1/4 Inch	+100 Mesh	-100 Mesh	Composite			
%	63.10	36.90	100.00			
Fe Total	95.60	53.90	80.21			
Fe Met	95.60	13.80	65.42			
C	0.022	14.070	5.206			
S	0.514	0.914	0.662			
- 1/4 Inch	+100 Mesh	-100 Mesh	Composite			
%	44.90	55.10	100.00			
Fe Total	95.60	59.70	75.82			
Fe Met	95.60	19.70	53.78			
C	0.022	12.870	7.101			
S	0.514	0.822	0.684			
Overall						
	Wt. Fraction, %	Fe Total	Fe Met	% Met	C	S
Uncrushable	8.83	95.60	95.60	100.00	0.022	0.514
+1/4 Inch	30.41	80.21	65.42	81.56	5.206	0.662
- 1/4 Inch	60.76	75.82	53.78	70.93	7.101	0.684
Composite	100.00	78.90	61.01	**77.33**	5.900	0.662
Fe Balance						
No. of Pushes	70					
Blend/Push, lb.	3.50					
Tot Blend, lb	245.00					
Tot Fe Charged, lb	110.39	(2.26% Moisture, 46.1% Fet)				
Tot Fe Recovered, lb	120.64	(Tot Wt. X Fet in Composite)				