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MEMORANDUM

To: Distribution DATE
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SUBJECT Job 6026 - Office of Coal Research
Contract No. 14-01-0001-380

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Attached is Progress Report No. 34 submitted to
the Office of Coal Research.



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Process Development

LJP/pp
Attachment

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RESEARCH & DEVELOPMENT DEPARTMENT

REPORT NO. 34

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RESEARCH AND DEVELOPMENT DEPARTMENT



DEVELOPMENT OF KELLOGG COAL GASIFICATION PROCESS

CONTRACT NO. 14-01-0001-380

May 31, 1967

Progress Report No. 34

APPROVED:


Project Manager

MANAGER

RESEARCH & DEVELOPMENT DEPARTMENT



I. SUMMARY

This Progress Report is the thirty-fourth since the awarding of the contract. It is concerned with the first phase of the contract and summarizes the progress that has been made in the three principal areas now being studied:

- (1) Process Research
- (2) Chemical Engineering Studies
- (3) Mechanical Development

Experiments have been carried out to study sodium carbonate melts containing silica and alumina and the effect of various gases on melt composition. Both carbon dioxide and nitrogen (at one atmosphere total pressure) were used to contact an alumina-sodium carbonate melt. The results, as indicated by a freezing-point depression, showed that with nitrogen as the aeration gas alumina goes into solution fairly quickly. In addition, the solution process can be reversed by switching back to carbon dioxide.

In addition, experiments were carried out with varying concentrations of carbon dioxide in nitrogen in an effort to establish the lower limit of carbon dioxide needed to prevent alumina solubility in sodium carbonate. The results indicate that about 0.4 atmosphere of carbon dioxide is required to effect this, at 1840° F

The effect of steam concentration in the aeration gas on the solubility of alumina was also investigated. Steam was found to greatly affect the freezing point of sodium carbonate (through the formation of sodium hydroxide), although there was no apparent effect on the solubility of alumina.

The presence of silica in the melt was found to greatly affect the freezing point of sodium carbonate with nitrogen as the aeration gas. However, this solubility is quite reversible as the melt freezing point could be raised to its initial level upon contact with one atmosphere of carbon dioxide. As was the case with alumina about 0.4 atmosphere of carbon dioxide in nitrogen was required to prevent silica from dissolving. The addition of steam to the aeration gas indicated that in addition to the freezing point lowering due to sodium hydroxide formation, there is an added depression due to silica solubility.

Some experiments have been made to determine the disposition of sulfur in the melt. Addition of Na_2S to sodium carbonate and subsequent contacting of the melt with carbon dioxide-air and carbon dioxide-steam mixtures resulted in complete conversion of the sulfide to sulfate.



An experiment was conducted to determine the efficiency of ash removal which can be achieved with a melt composition comparable to that used in the commercial design (8 percent ash and 4 percent carbon). The results indicated that in the laboratory apparatus using wash rates and residence times comparable to those proposed commercially, a sodium recovery of about 96% (versus 97.5% assumed in the conceptual design) can be attained.

The Status Report justifying Kellogg's recommendation to proceed to the pilot plant and a Proposal for the cost and schedule of such a pilot plant have been completed. Both of these documents will be forwarded to the OCR during June.

Analysis of the deposits obtained from the melt entrainment tests indicated that they contained 92 to 98% sodium carbonate and 1 to 3% silica. It is difficult to explain these results in terms of volatility, and it appears as though the great majority of the carryout may be attributed to physical entrainment.

Corrosion Test #12, a simulated gasification test, has continued to a total of 340 hours. The test is planned to be terminated at about 500 hours.

An ultrasonic technique has been devised to enable the inspection of Monofrax A for voids and flaws. The method has proven quite successful and it is anticipated that automatic inspection is quite feasible for a commercial operation with currently available equipment.



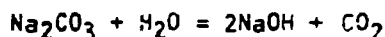
II. PROCESS RESEARCH

A. Accomplishments

1. Study of Na₂CO₃ Melts

The freezing point of Na₂CO₃ with 1 atmosphere of CO₂ was found to be 1567°F (853°C). Changing the atmosphere to 50/50 carbon dioxide and steam at one atmosphere pressure yielded a freezing point of 1521 ± 8°F (3 results). Increasing the steam to give 10% carbon dioxide in 90% steam at 1 atm. pressure produced a melt of 1433 ± 5°F freezing point (2 results).

A 1961 French article in which the sodium hydroxide - sodium carbonate system was studied indicated a 13.4°F change per percent of NaOH present in the Na₂CO₃. Using this correlation, the composition of the melts with 50/50 and 10/90 carbon dioxide to steam correspond to 3.4% NaOH and 10.0% NaOH in Na₂CO₃, respectively. The aforementioned article gave 1569°F for the fusion point of Na₂CO₃, in very good agreement with our result of 1567°F. Equilibrium is established by the reaction:

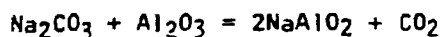


a. Na₂CO₃ - Al₂O₃ System

A Norton Company α - alumina was used to prepare an 8% Al₂O₃ in Na₂CO₃ melt. All tests were made at atmospheric pressure. Initially, carbon dioxide was used to agitate the melt and maintain the Na₂CO₃ at 1840 F, then the freezing point was determined. Nitrogen followed in place of the carbon dioxide and at various time intervals the freezing point was determined. Two rechecks with carbon dioxide then followed. The results are shown in the following tabulation.

<u>Gas Used</u>	<u>Hours at 1840°F</u>	<u>Freez. Pt. °F</u>	<u>Δ°F</u>
CO ₂	0.5	1565	-
N ₂	1.25	1560	5
N ₂	1.25	1558	7
N ₂	17.5	1550	15
CO ₂	1.0	1562.5	-
CO ₂	1.5	1562.5	-

The results indicate that some alumina goes into solution fairly quickly but that the process slows down with time. It also indicates the freezing point lowering for dissolved alumina is low. The overall reaction for dissolving alumina is:





After dissolving some of the alumina, the effect of CO₂ and the reversal of the equation is very pronounced and appears to be rapid. The difference in freezing point between the first 1565°F and the final 1562.5°F cannot be attributed to solubility since it was found that the thermocouple was giving trouble and required replacement.

A melt prepared with 4.9% alumina as sodium aluminate dissolved in sodium carbonate showed a 20°F lowering of the freezing point. Thus in the above experiment after 20 hours, the 8% alumina does not appear to be all dissolved since the freezing point lowering was only 15°F.

The next experiments employed various amount of carbon dioxide in nitrogen at one atmosphere with the intent of establishing the lower limit of carbon dioxide needed to prevent alumina solubility in a melt of 8% Al₂O₃ in Na₂CO₃. The results of these experiments show clearly that about 0.4 atm. of carbon dioxide is needed to prevent alumina from dissolving in sodium carbonate melts.

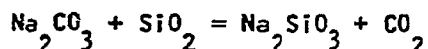
Next, an attempt was made to determine what influence steam would have on the amount of carbon dioxide needed to suppress solubility of alumina. Steam can form some sodium hydroxide which may have a higher rate of reaction with alumina than does sodium carbonate. Also the equilibrium amount of dissolved alumina may be higher. The very large lowering of the freezing point by the formation of some sodium hydroxide was found to be the same as for a melt of Na₂CO₃ indicating little or no alumina solubility. The results are shown in the following tabulation.

CO ₂ /Steam	Melt	°F Fz. Pt. Lowering over pure Na ₂ CO ₃ /1/
50/50	Na ₂ CO ₃	48 ± 6
50/50	8% Al ₂ O ₃ in Na ₂ CO ₃	51
10/90	Na ₂ CO ₃	134
10/90	8% Al ₂ O ₃ in Na ₂ CO	134

/1/ Using one atmosphere of carbon dioxide

b. Na₂CO₃ - SiO₂ System

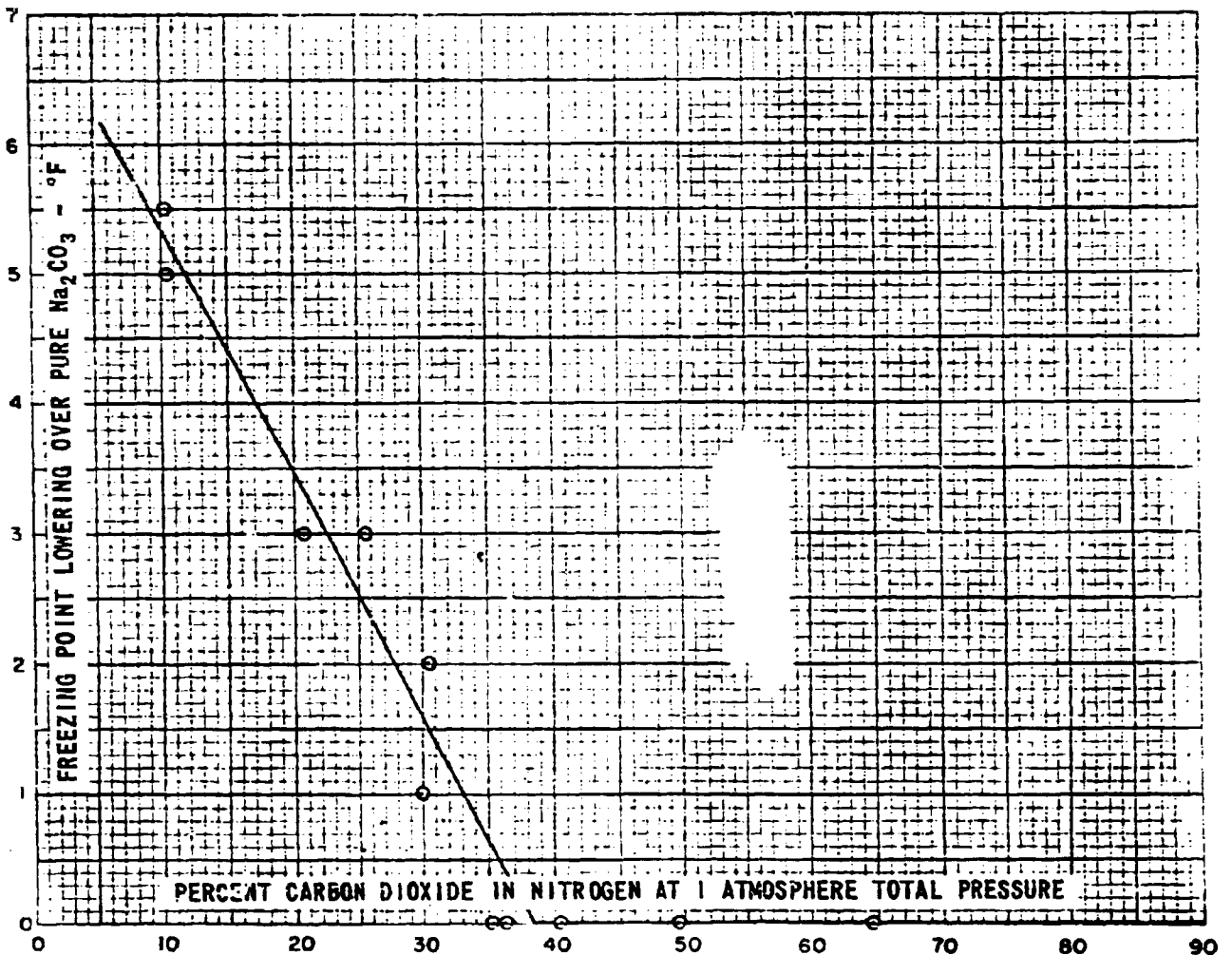
A similar investigation of the SiO₂-Na₂CO₃ system was made. Initially 5% SiO₂ (ex. Davison Co.) in Na₂CO₃ melt was used. Using nitrogen to mix and allow silica to dissolve according to the equation,



gave a freezing point of 1510 ± 4°F, a lowering of 58°F. The freezing point was easily brought back to that of Na₂CO₃ by using 1 atmosphere of carbon dioxide



FIGURE 1
EFFECT OF CARBON DIOXIDE IN NITROGEN ON FREEZING POINT
OF
8% ALUMINA IN Na_2CO_3 MELT





for 1.5 hours. Addition of 3 more percent of silica to give a total of eight and mixing with N_2 for two hours, lowered the freezing point to $1469^\circ F$, a $99^\circ F$ lowering. This was not a linear response to the additional silica. Silica solubilization had a greater effect on the lowering of the freezing point than did alumina ($58^\circ F$ vs. $20^\circ F$ for 5% solubilization).

The next experiments employed varying amounts of carbon dioxide in nitrogen at one atmosphere with intent of establishing the lower limit of carbon dioxide needed to prevent silica solubility in a melt of 8% SiO_2 (ex: Berkley Sand Co.) in Na_2CO_3 . The results are shown in Figure 2. Again the curve shows, just as with alumina in Figure 1, that 0.4 atmosphere of carbon dioxide is needed to prevent solubilization of silica in sodium carbonate melts.

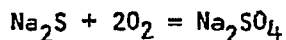
The attempt was now made to determine what influence steam would have on the amount of carbon dioxide needed to suppress solubility of silica. The results, shown in the following tabulation, indicate that besides the influence of hydroxide formation from the steam, there was a significant lowering due to silica solubility.

<u>CO₂/Steam</u>	<u>Melt</u>	<u>°F Fz. Pt. Lowering over pure Na₂CO₃</u>
50/50	Na ₂ CO ₃	48
50/50	8% SiO ₂ in Na ₂ CO ₃	84
10/90	Na ₂ CO ₃	134
10/90	8% SiO ₂ in Na ₂ CO ₃	175

During some of the silica - Na_2CO_3 studies, other freezing points were observed at $1680 - 1650^\circ F$. A check of the literature indicated this may have been due to sodium disilicate.

c. Na₂S - Na₂CO₃ System

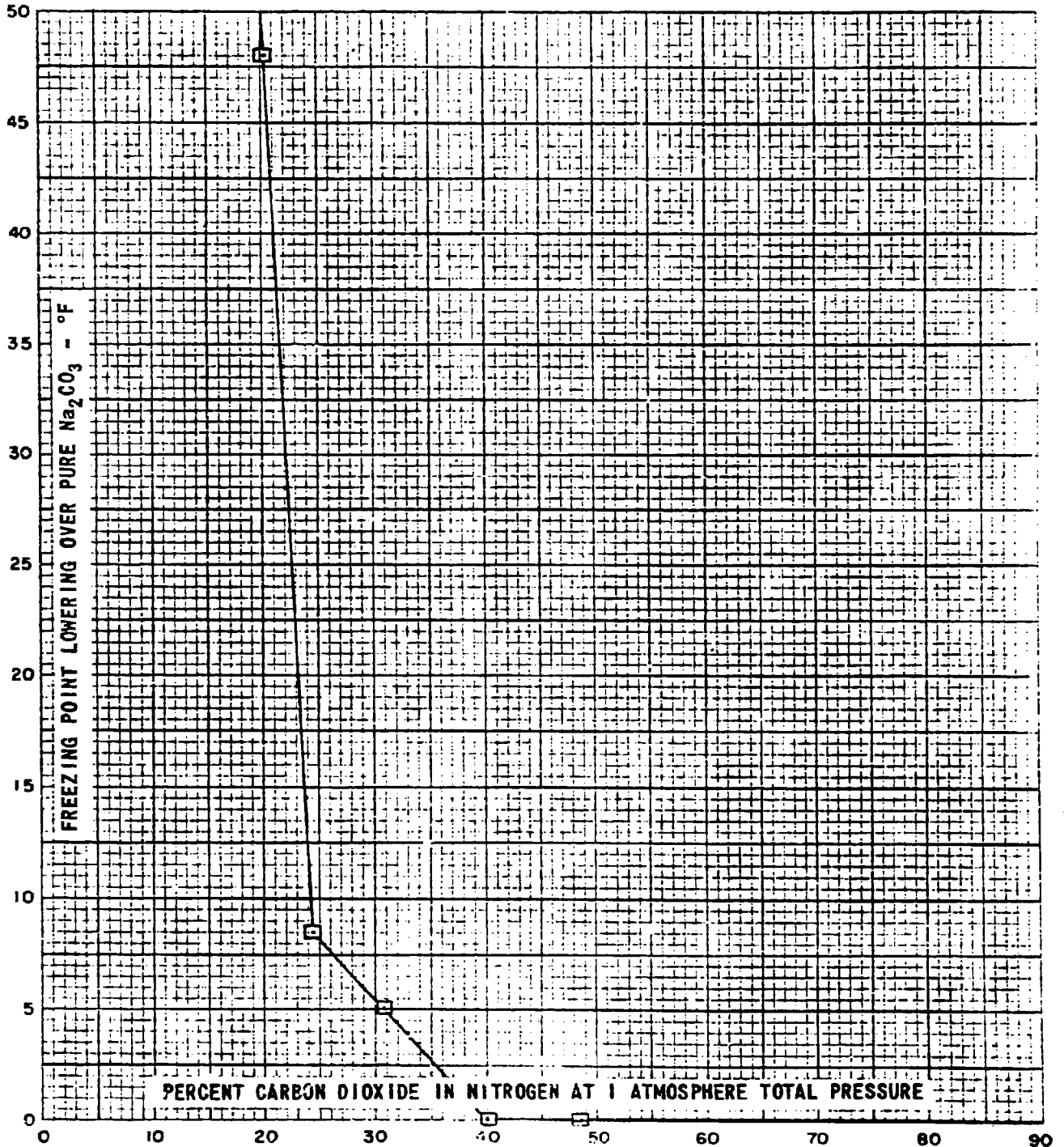
A melt of 8% Na_2S in Na_2CO_3 was prepared and found to have a freezing point in N_2 of $1508^\circ F$, a $59^\circ F$ lowering from that of pure Na_2CO_3 . Addition of 40% carbon dioxide in air for two hours raised this freezing point to $1548^\circ F$. A sample of the melt, removed at $1840^\circ F$ and immediately frozen, showed no sulfide - only sulfate was present. It was concluded that oxidation of sodium sulfide occurred by the oxygen in the carbon dioxide-air mixture:



Another melt of 5% Na_2S in Na_2CO_3 was treated with 50/50 carbon dioxide to steam which showed no hydrogen sulfide was evolved and that all the sulfide had been oxidized to sulfate. Oxidation of the sulfide occurred by either the steam or the carbon dioxide or both. This point will be investigated.



FIGURE 2
EFFECT OF CARBON DIOXIDE IN NITROGEN ON FREEZING POINT
OF
8% SILICA IN Na_2CO_3 MELT





From these experiments, it appears that the sulfide that gets into the melt from the coal in the gasification reactor may be oxidized to sulfate even before it reaches the combustion reactor where it certainly will go to sulfate. Based on this, consideration has been given to removal of sulfate from the melt which goes to the ash removal section.

2. Recovery of Sodium in Ash Removal

A melt was prepared of 440g. Na_2CO_3 , 40g. of Island Creek bituminous coal ash and 20g. of 20/40 mesh coke from Island Creek bituminous coal to give 8% ash and 4% carbon in the melt. This was held at 1900°F for 1/2 hour after introducing the coke and with 1 atm. of carbon dioxide being used for mixing. The melt was frozen, ground to powder, and used in the following.

a. 100 grams was treated with 9% NaHCO_3 at 6/1 liquid/solid ratio for a 10 minute boiling period and filtered. The residue was dried, weighed and analyzed.

b. 100 grams was treated similarly except the residue was reslurried in 50cc of hot water and refiltered. The residue was dried, weighed, and analyzed. The results are tabulated in the following:

	<u>MELT</u>	<u>RESULT a</u>	<u>RESULT b</u>
% Na	36.5	11.8	12.8
% SiO_2	2.35	23.27	22.32
% Al_2O_3	3.05	22.66	25.25
Weight-gms.	100.0	11.8116	11.4850
g. Na	36.5	1.39	1.47
g. SiO_2	2.35	2.75	2.56
g. Al_2O_3	3.05	2.68	2.90
% Na Loss	-	3.81	4.03

It can be concluded that reslurry of the ash residue after retracting the Na_2CO_3 had no effect on further sodium removal. Thus 96% Na recovery was achieved with a melt composition comparable to commercial operation. Further investigation of this will be made.

Another 40 gram sample of the melt prepared above was intentionally held 3 hours at the boiling point of the extracting 9% NaHCO_3 solution instead of the standard 10 minutes. The dry residue of ash weighed 4.7178 grams and contained 5.27% of the total sodium. Thus the sodium recovery is now only 94.7%

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indicating a disadvantage to prolonged extraction time.

B. Projections

The effect of more than one atmosphere total pressure of steam and carbon dioxide on solubilization of silica and alumina will be studied. Some freezing point studies on melts containing coal ashes will be made.

Investigations on the overall sulfur disposition in the process have been initiated and will continue. Sulfate removal from the system and recovery of sulfur will also be investigated.



III. Chemical Engineering Studies and Development

A. Accomplishments

1. Pilot Plant

Efforts during May were directed towards preparing a Status Report justifying Kellogg's position to proceed to the pilot plant and also a proposal for the cost and schedule of such a program. This proposal has been completed in its final form and the Status Report has been completed in draft form.

B. Projections

1. Pilot Plant

Both the Status Report and the Proposal for the gasification pilot plant will be forwarded to the OCR by mid-June.

In addition, work will begin to prepare a complete "Process Release" for the pilot plant. Items to be incorporated in this release include a complete process flow diagram, process load sheets for furnaces, exchangers, machinery and special equipment, analytical sketches of reactors, drums, and towers, recommendations for materials of construction, and utilities requirements.

2. Flowsheet Studies

Efforts will be made to complete the hydrogen flowsheet in its final form so that the complete "process package" for hydrogen can be submitted.



IV. MECHANICAL DEVELOPMENT

A. Accomplishments

1. Mechanical Characteristics Testing

The analysis of deposits found in Test #3, conducted to determine entrainment in the aeration gas exiting a sodium carbonate melt bed has been completed. Table 1 below shows the analysis of four samples of deposits taken from the exit line cooler and filter. The term "inlet" refers to the piping from the reactor exit to the first bottom elbow of the cooler. The term "bottom" refers to the bottom pipe of the cooler including the two elbows. The outlet line includes the remainder of piping to the filter.

Table 1

<u>Location</u>	<u>Deposit Wt.</u>	<u>% Na₂CO₃*</u>	<u>% SiO₂*</u>	<u>% Misc.*</u>
Inlet	3.74 gms.	96.6	1.90	1.5
Bottom	3.62 gms.	95.9	2.84	1.26
Outlet	1.6 gms.	92.0	2.18	5.82
Filter	<u>3.72 gms.</u>	98.2	0.96	0.84
	12.68 gms.			

Aeration Gas - Carbon Dioxide
Bed Height - 2 Ft. 6 In.
Bed Superficial Velocity 2.0 Ft./Sec.

(* Dry Basis approximate.)

The melt bed contained 8% ash. Analysis shows this ash to contain 38.3% SiO₂. The deposits appeared to be uniformly distributed on the walls of the exit pipes and it would appear from the data that the great majority of carry-over resulted from physical entrainment in the exit gas. Volatile carry-over could not be reasonably predicted by this test.



2. Corrosion Testing of High-Temperature Materials

Run #12, as described in the last report, has been restarted and has now been in operation for approximately another 200 hours, for a total of some 340 hours to date. It is anticipated that this test will be terminated at 500-hour point and the total corrosion rates determined.

An attempt has been made to ultrasonically inspect the Monofrax "A" for voids and flaws. A sample of the results appear as Figures 3 and 4. Figure 3 is the trace obtained when examining a flawless, two-inch-thick block of Monofrax "A" using ultrasonic techniques. Figure 4 is the same except the Monofrax has a flaw at the midpoint, i.e., one inch below the surface. In both cases, the trace obtained is clear and easy to interpret, so that ultrasonic inspection of the refractory material would seem quite feasible. Discussions with the vendors of ultrasonic equipment have indicated that this material lends itself to good ultrasonic inspection with no problems or special techniques required. Automatic inspection is quite possible with currently available equipment.

B. Projections

1. Mechanical Characteristics Testing

Further testing will be undertaken to better demonstrate the carry-over that may be expected. This information will aid in design of the pilot plant overhead piping.

2. Corrosion Testing of High Temperature Materials

Run #12 will be continued to approximately the 500-hour point. The test will be terminated and the specimens examined at this point. The results of this test will help to determine the future course of the test program.

To date, all the Monofrax "A" tested has been from ordinary blocks of Monofrax, and, as such, have had a wide variety of grain size and structure as well as internal voids and cracks. In the near future, testing will begin on DCL Monofrax "A", which should have a far more uniform internal structure, and thus, even better corrosion resistance. This DCL Monofrax "A" will further be inspected ultrasonically prior to testing to insure a uniform quality of test sample. This technique has not been used on the previous test specimens.

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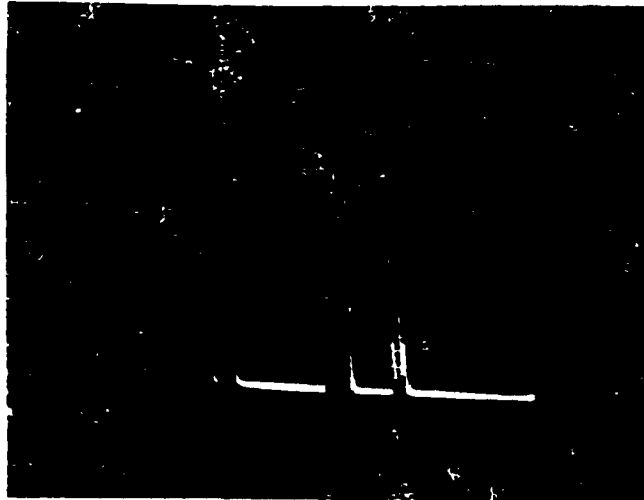


Figure 3

ULTRASONIC TEST 2-INCH MONOFRAX "A" BLOCK
NO FLAWS BOTTOM SCALE XI

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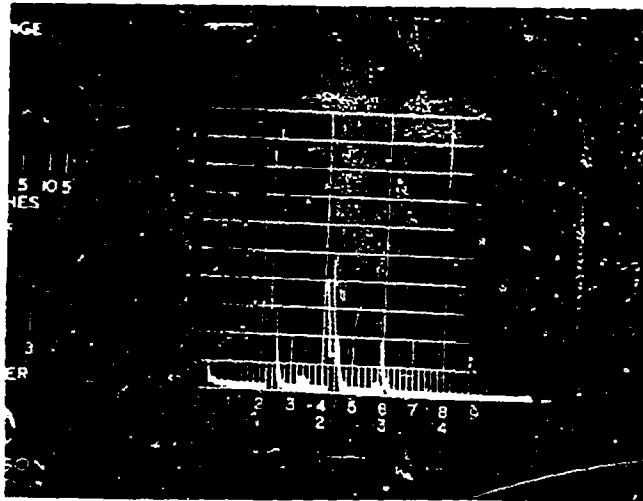


Figure 4

ULTRASONIC TEST 2-INCH MONOFRAK 'A' BLOCK

ONE INCH BELOW SURFACE

BOTTOM SCALE XI