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CONCEPTUAL DESIGN OF A BLACK LIQUOR GASIFICATION PILOT PLANT

By
Edward G. Kelleher

August 1987

Work Performed Under Contract No. AC05-80CS40341

For
U. S. Department of Energy
Office of Industrial Programs
Washington, D.C.

By
Champion International Corporation
West Nyack, New York

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Work Performed Under Contract Number:
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Edward G. Kelleher

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SECTION 1

1.0 EXECUTIVE SUMMARY

In July 1985, Champion International Corporation completed Phase II of a study of kraft black liquor gasification and use of the product gases in a combined-cycle cogeneration system based on gas turbines. That study, co-sponsored by the U.S. Department of Energy under Contract No. DE-AC05-80CS40341, indicated that gasification had high potential as an alternative to recovery boiler technology and offered many advantages that included:

- higher energy efficiency than the state-of-the-art conventional technology
- higher output ratio of electrical power-to-steam, better matching mill demands
- modularity, making it feasible to add incremental capacity to mills economically
- significantly improved safety, eliminating the possibility of smelt-water explosions
- significantly reduced air emissions
- reduced capital and operating costs

Champion recommended that development of the technology be continued through a two-step demonstration program. The first step would involve design, construction and operation of a new pilot gasifier which would be used to develop design data for a large-scale demonstration plant. The second step would involve design, construction and operation of the demonstration plant. Champion also recommended that conceptual design of the new pilot gasifier and more detailed investigation of the black liquor feed system, melt discharge system and materials of construction proceed while alternative means of funding the full demonstration program were investigated. This latter recommendation was approved by DOE and is the subject of this report.

The basic requirements established for the conceptual design of a new pilot gasifier were that it be compatible with the existing test facility and that it have sufficiently low heat loss to permit production of readily combustible product gases and highly reduced melt. While the product gas quality could not be equal to that of a commercial unit, it had to be high enough to confirm computer model projections of commercial performance.

The recommended design of the pilot gasifier is a vessel with an internal diameter of about 30 in. and an active height of about 15 ft. Air injection is through two sets of nozzles, one set below the melt surface and the other above the surface but directed downward onto the surface. There are two melt withdrawal points approximately 14 in. and 24 in. above the bottom in order to test the effects of melt depth. The vessel is designed for superficial gas velocities of 2-3.5 ft/s and operation up to 3 atm pressure.

Performance calculations indicate that, at its highest throughput, the new pilot gasifier should operate at black liquor feed rates up to 1254 lb/h, should have a net heat loss from the gasification zone of about 294,500 Btu/h, or about 6% of the energy content of the feed, and should produce gas with a dry higher heating value of about 100 Btu/scf and melt reduced over 90%. The heat loss from the gasification zone of a commercial gasifier would be about 1% of the energy content of the feed, resulting in a higher product gas heating value.

Analysis of the black liquor spray requirements to ensure drying of the black liquor droplets before their entering the gasification zone, but without entrainment in the product gas stream, indicates a need for droplets between 0.2 and 1.4 mm, depending on pilot gasifier operating conditions and the degree of swelling. A review of commercially available nozzles suggests that solid-cone and two-fluid nozzles potentially could deliver the black liquor feed in the desired droplet size range and spray pattern, but testing would be required to confirm this. A novel splash tube spray nozzle was conceived during the study and shown to be feasible based on water testing, but it too requires further experimentation.

Considerable effort was expended in the design of a melt discharge nozzle that could handle a wide range of melt flows without plugging, and a quench system that would operate in a pressurized environment.

A laboratory study of materials combined with a review of available materials data focused on fused-cast refractories for direct contact with the melt pool, castable refractories for intermittent melt contact and contact with the feed and product gases, and metals that could withstand melt contact. As a result, it is recommended that the gasifier be lined with a 2-in.-thick layer of bubble alumina inside the steel shell for thermal insulation and a 6-in.-thick layer of Alfrax 66 castable alumina for general chemical protection. The gasification zone would have a further lining of fused-cast Monofrax M bricks for protection against continuous melt contact and thermally-induced degradation.

Everything found during these studies supports the high potential for gasification as a replacement for the recovery boiler and continued development of the technology is recommended.

SECTION 2

2.0 INTRODUCTION

The investigation of kraft black liquor gasification as a possible alternative to the Tomlinson recovery furnace began in 1982 under Contract No. DE-AC05-80CS40341 between the U.S. Department of Energy and the St. Regis Corporation. When St. Regis merged with Champion International Corporation, the work continued under Champion. Phases I and II of the study indicated that, compared to conventional technology, black liquor gasification and use of the product gases in combined cycle cogeneration systems based on gas turbines had the potential of a higher energy efficiency, a higher ratio of electric power-to-steam outputs, lower costs, lower emissions, greater flexibility, modularity, and greater safety. Champion recommended a two-step demonstration of the technology, the first step involving design, fabrication and testing of a new pilot unit designed specifically for black liquor gasification. On the basis of the very positive results, the D.O.E. contract was modified in 1985 to authorize additional work on the new pilot unit while funding for the full demonstration program was investigated. A brief summary of the Phase II study and the objectives of the additional efforts are presented in this section.

2.1 Summary of Phase II

Under subcontract to Champion, Rockwell International Corporation conducted twenty-three bench-scale tests of air-blown black liquor gasification using its molten salt gasifier.¹ They tested three black liquors (60-65% solids) and the effects of reaction temperature, stoichiometry, and melt depth. The liquor gasified readily and completely to yield product gases with higher heating values over 120 Btu/scf and reductions of sulfate to sulfide in the melt of over 95%. The performance of the gasifier was independent of melt depth and the results correlated well with the process variables.

Two pilot-scale tests were run by Rockwell in an existing unit with a deep melt pool at black liquor rates up to 783 lb/h. This represented a scale-up factor of about 100 over the bench-scale tests. The unit had a high heat loss through its walls that required that it be operated at high air-to-liquor ratios to maintain isothermal conditions; therefore, high heating value product gases could not be expected. The primary objective was to demonstrate operation at this larger scale and study the effects of temperature and stoichiometry. However, Rockwell did use the results in a detailed computer model of the gasifier and gasification process to predict performance in a well-designed commercial unit.

2.1 Summary of Phase II (Continued)

Black liquor gasified readily and completely in the pilot tests. The unit came to steady state quickly and responded rapidly when operating conditions were changed. There was strong evidence that the liquor gasified so readily that some gasified in the gas space above the pool. As a result of this, the high air-to-liquor ratios, and the fact that all feed air passed through the melt pool, the pool likely was in an oxidizing rather than reducing state which caused very low melt reduction. During one of the tests, the liquor gasified as readily with substantially less melt present, and gasification proceeded even as the pool was drained. When the melt level fell below the air nozzles, melt reduction increased substantially.

The gasifier was modified for a third pilot test to reduce the melt pool depth by a factor of more than five and to add air nozzles such that air could be fed both below and above the melt surface. Despite black liquor feed problems caused by high solids and fiber in the liquor, the liquor gasified readily and the melt reduction improved. The modified unit was even easier to operate. Extrapolating the test data to conditions in a commercial unit, performance similar to the bench-scale unit was predicted.

An engineering evaluation of a gas cooling and gas cleaning system resulted in a process scheme that recovers most of the heat energy and much of the chemical value of the product gases. The technology necessary to meet the specifications of the gas turbine manufacturers exists. The turbine manufacturers have run standard gas turbine sets with modified combustors on low-Btu gas fuels similar to the product gases and have no doubt of performance.

In order to evaluate alternative technologies, very detailed computer simulations were developed of overall electric power and steam supply systems. Gas turbines and unfired and supplementary-fired waste heat boilers were integrated with a bark and coal-fired combination boiler and steam turbine to form the overall system. The standard of comparison was a 1500 psig/950°F state-of-the-art system that included a recovery boiler. The efficiency of the base case was significantly higher than a typical operating powerhouse in the kraft industry. The simulations were developed such that both power and steam could be targeted and the objective in all but one case was to meet specified loads. The steam and power loads used were for a 1000-ton-per-day unbleached kraft linerboard mill at two different process power demands, the same mill but targeted for maximum power production from the gas turbine, and a mixed furnish mill typical of a newsprint operation with only partial kraft furnish and a very high electric power-to-steam demand ratio.

2.1 Summary of Phase II (Continued)

In spite of the high efficiency of the base case system, the alternative system met the same loads at even higher overall efficiency in all cases. The efficiency advantage ranged from 0.2% at low power demand to over 10% at high power demand. The efficiency of the base case system decreased at higher power demands as more and more condensing power was required, while that of the alternative systems increased up to the limit of the gas turbine fuel supply.

Budget quality capital cost estimates of the base case systems and the alternative systems indicated that the alternative systems could save substantial capital. Because of the high efficiency of the alternative systems, one case compared the 1500 psig/950°F base case system to a 600 psig/750°F alternative system. The alternative system still met the same process demands at a higher overall efficiency than the base case, and at projected capital cost savings of over \$41 million.

The operating costs of the alternative systems were compared to the base case systems on the basis of coal costs and maintenance; all other operating costs were considered equal. Because of their higher energy efficiency, the alternative system costs were all less than their base case counterparts. In the case cited above, the projected annual savings in operating costs exceeded \$1.6 million.

Two other benefits of the alternative systems should be cited. Black liquor gasification and dissolving of the melt under pressure would eliminate the possibility of a melt-water explosion. Also, for a 1000-ton-per-day kraft mill, two gasifiers appear to be the optimum design. Therefore, the alternative systems offer the possibility of economically providing incremental capacity additions.

Overall, black liquor gasification and use of the product gases in combined cycle cogeneration based on gas turbines shows high potential as an alternative to the recovery boiler. It offers higher energy efficiency, lower costs, safety and environmental benefits.

Champion recommended a two-step demonstration of the technology. The first step would involve design, fabrication and testing of a new pilot unit designed specifically for black liquor gasification. The new unit should have low heat loss and be flexible to enable additional study of the effects of melt depth and air distribution. The second step would involve design, construction, and operation of a demonstration plant at an existing mill site. The plant should include the gasifier, gas cooling and cleaning, and a test stand to verify the applicability of the product gases as a gas turbine fuel.

2.1 Summary of Phase II (Continued)

The high cost of the two-step demonstration program meant that alternative sources of funding had to be investigated. Therefore, Champion proposed and D.O.E. approved that further investigation of the new pilot unit proceed while funding was sought. The results of those further investigations are the subject of this report.

2.2 Objectives

Among the objectives of the pilot unit investigations were the following:

- Develop a conceptual design of a new pilot-scale gasifier. It should be compatible with the existing Rockwell test facility and have a heat loss sufficiently low to permit the production of readily combustible product gases and highly reduced melt. Desired features are continuous melt quenching and above-atmospheric pressure operation.
- Conduct a detailed analysis of the black liquor feed system for a new pilot unit including maintaining a constant feed rate and providing a spray within the desired range of droplet sizes for gasification.
- Conduct a detailed analysis of the melt withdrawal system for a new pilot unit including quenching the melt under pressure.
- Evaluate materials of construction for black liquor gasifiers.

SECTION 3

3.0 PILOT PLANT CONCEPTUAL DESIGN

The unit used for pilot testing of black liquor gasification during Phase II was an existing vessel designed primarily for hazardous waste destruction. It had a high heat loss; heat loss from the melt pool amounted to about 40 percent of the black liquor heating value. Therefore, the black liquor had to be more completely combusted to maintain isothermal conditions and the unit was not expected to produce product gases with a reasonable heating value. Champion proposed that the first step of a demonstration of the technology be to design, build and test a new pilot unit designed specifically for black liquor gasification in order to increase confidence in the technology at reasonable cost and develop design criteria for the Step 2 demonstration unit. Rockwell was requested to develop a conceptual design of the pilot unit, which work is reported on in this section.^{2,3}

3.1 Design Basis

Requirements of Rockwell's conceptual design were that the new unit be compatible with the existing test facility but have sufficiently low heat loss to permit production of readily combustible product gases and highly reduced melt. Also desired was operating flexibility in terms of the melt pool depth, black liquor feed configuration, air feed distribution, and operating pressure. Since the heat losses per unit of feed decrease with increased throughput, it was recognized that the product gas heating value expected in a commercial unit could not be achieved in the pilot unit. Therefore, a target product gas heating value of 85 Btu/scf with over 90 percent melt reduction was established. A complete set of preliminary design criteria was as follows:

- Internal gasifier dimensions - ~30 in. internal diameter by ~15 ft. active height
- Operating pressure capability - ~3 atm
- Gas velocity at maximum pressure - ~ 2 ft./s
- Feed air temperature - 700°F
- Pool depth - 14 in. and 24 in.
- Air injection - 6 in. and 30 in.

3.1 Design Basis (Continued)

- Black liquor spray nozzles - four feed points
- Heat loss from gasification zone - <600 Btu/lb of feed
- Product gas heating value - >85 Btu/scf higher heating value, dry basis, at maximum throughput

3.2 System Design

A schematic of the overall pilot-scale gasifier system is presented in Figure 3-1. Much of the existing auxiliary equipment can be used with the new unit. Major new equipment items required are the gasifier, quench tank, and product gas separator.

Figure 3-2 shows the overall pilot plant layout including the location of all major equipment. Additional details are provided in Figure 3-3, including the location of the separator and quench tanks relative to the gasifier.

(Gasifier)

The gasifier conceptual design is shown in Figure 3-4; the conceptual internal design of insulation and refractory is shown in Figure 3-5. The insulation should reduce heat loss sufficiently to raise the product gas heating value to targeted levels, while the refractory should provide needed protection against chemical attack by the melt.

Thermal insulation would be provided by a 2-in.-thick layer of bubble alumina inside the steel shell. General chemical protection would be provided by a 6-in.-thick layer of Alfrax 66, a high-purity, high density alumina hydrocast material. Alfrax 66 was selected because it has provided excellent service in other molten salt vessel applications. Fused cast Monofrax M was selected for chemical protection of the lower section of the gasifier where molten salts are actively sparged. Monofrax M has excellent chemical resistance and superior thermal shock resistance, and is significantly lower in cost than Monofrax A which was used in the earlier vessel.

The gasifier has provisions for two melt discharge ports corresponding to melt depths of approximately 14 in. and 24 in. The two ports are 180° apart. Only one discharge port would be used at a time to test the effect of melt depth, and the melt would be discharged into drums for simplicity except when the quench system is being tested.

Figure 3-1. Schematic of Pilot Gasifier System

Figure 3-2. Pilot Plant Layout

3-4

PRELIMINARY-NOT FOR CONSTRUCTION

FACILITIES ENGINEERING			
JAR 68152			
SANTA SUSANA FIELD LABORATORY-BLDG 005			
PHASE I BLACK LIQUOR GASIFICATION			
PILOT PLANT LAYOUT			
DESIGNED BY	DATE	6-1-81	
CHECKED BY	DATE		
APPROVED BY	DATE		
303-005-M72			

Figure 3-3. Test Stand Plan

3-5

PRELIMINARY-NOT FOR CONSTRUCTION

Figure 3-4. Pilot Gasifier

3-6

PRELIMINARY-NOT FOR CONSTRUCTION

REV.	DATE	DESCRIPTION	BY
FACILITIES		Rockwell International Corporation	
ENGINEERING		Atomica International Division	
SANTA SUSANA FIELD LABORATORY - BLDG 005			
PHASE I BLACK LIQUOR GASIFICATION			
GASIFIER			
ENVELOPE CONTROL DRAWING			
APPROVED BY	DESIGNED BY	RELEASE DATE	REV. NO.
	WAT/POWELL	2-3-84	JAR 68152
APPROVED BY	DRAWN BY	DRAWING NO.	REV. NO.
	CHCALD BY	303-005-M74	

Figure 3-5. Refractory Installation

[illegible]

3.2 System Design (Continued)

(Gasifier) - Continued

Two levels of air feed injection are shown. The upper level has six 2-in. nozzles equally spaced circumferentially and angled downward at 45°. The lower level has four equally spaced 2-in. nozzles angled at 30°. A minimum nozzle air velocity of 50 ft./s is planned. The air feed system is valved to permit variation of the fractions of the total air fed below and above the melt surface.

The product gas exit port is located in the center of the head of the vessel. Although this restricts the placement of black liquor feed nozzles, it increases the height of the gas space above the melt pool. This height provides a longer period for drying of black liquor droplets before they hit the melt and also provides a more symmetrical flow pattern for the product gases. The vessel head also contains ports through which black liquor spray nozzles could be inserted.

Finally, the vessel design includes thermocouple wells located every 12 in. vertically in the lower gasifier zone and every 18 in. in the upper zone. These would provide a detailed temperature profile during operation.

(Quench Tank)

The general quench tank design is shown in Figure 3-6. More details on the internals and accessories are discussed in Section 5.2. The quench tank consists of a vertical section designed to receive and shatter melt, and a horizontal section which will contain a pool of green liquor and serve to dissolve the melt particles. It will be located below ground adjacent to the gasifier.

(Product Gas Separator)

The product gas separator, shown in Figure 3-7, serves to remove larger particles of solidified melt and entrained black liquor particles from the product gas stream, primarily during soot blowing. It is not planned to recirculate these particulates in the pilot system as one would in a commercial system. The separator will operate at the gasifier pressure.

REVISIONS					
ZONE	REV	DESCRIPTION	DATE	APPROV.	
		1. HWY BE REMOVED			D P H
		2. SECOND CHAINSE			
		3. BRANCH BE REMOVED 4. NOW SHOT PRACTICE & PUTS BEND ON

2. CORROSION ALLOWANCE: 1/8 IN MIN
3. MATERIAL: CARBON STL SA 915 & 90
B. DESIGN CONDITIONS: PRESSURE, 180 PSIG
TEMPERATURE, 450 °F
1. DESIGN AND CONSTRUCTED IN ACCORDANCE WITH
ASME CODE SECTION VIII DIV 3

[illegible]

Figure 3-7. Product Gas Separator

3-10

PRELIMINARY - NOT FOR CONSTRUCTION

REV	DATE	DESCRIPTION	BY
FACILITIES ENGINEERING		Rockwell International Corporation Atomics International Division	
SANTA SUSANA FIELD LABORATORY BLDG 005 PHASE I BLACK LIQUOR GASIFICATION SEPARATOR TANK ENVELOPE CONTROL DRAWING			
APPROVED BY	DESIGNED BY STEWART/PAWELL	RELEASE DATE 8-9-86	REV. NO. JAR 68152
APPROVED BY	DRAWN BY H. P. GILL	DRAWING NO. 303-005-M76	
APPROVED BY	CHECKED BY		

3.2 System Design (Continued)

(Equipment List)

The principal items of equipment for the black liquor gasification pilot plant that have been identified to date are listed in Table 3-1. Preliminary data on size, capacity and other features are included. Several of the major pieces are available at the site, as is the existing data acquisition and control center. In addition, the following analytical instrumentation would be used in the pilot plant:

- liquid densitometer
- product gas sample station
- gas chromatographs
- oxygen analyzer
- carbon dioxide analyzer
- carbon monoxide analyzer
- hydrogen sulfide analyzer

3.3 Performance Analyses

Process calculations were made to guide the pilot plant design work and to predict the performance of the system selected. The composition of the feedstock and other key process design assumptions used in these calculations are listed in Table 3-2.

The results of the performance calculations are summarized in Table 3-3. To provide a basis for comparing pilot plant performance with that of a commercial unit, the expected performance of a commercial unit is included. The principal characteristics of each case are:

- Case 1 - commercial unit; 233 psia; 2.0 ft/s gas velocity
- Case 2 - pilot unit; 45.0 psia; 2.0 ft/s gas velocity
- Case 3 - pilot unit; 45.0 psia; 2.5 ft/s gas velocity
- Case 4 - pilot unit; 14.7 psia; 2.5 ft/s gas velocity
- Case 5 - pilot unit; 14.7 psia; 3.0 ft/s gas velocity
- Case 6 - pilot unit; 13.7 psia; 2.5 ft/s gas velocity
- Case 7 - pilot unit; 13.7 psia; 3.0 ft/s gas velocity
- Case 8 - pilot unit; 13.7 psia; 3.5 ft/s gas velocity

The latter three cases were included because the altitude at the pilot plant site results in an atmospheric pressure of only 13.7 psia.

These results show, as expected, that the pilot unit will not perform as well as a commercial plant in terms of product gas heating value because of the higher heat loss per unit of feed in the pilot unit. They also show the benefits of operating

TABLE 3-1

Equipment List
(Sheet 1 of 3)

Item	Description or Drawing
VESSELS AND TANKS	
V-1 Gasifier	Figures 3-4, 3-5
V-2 Quench tank	Figure 3-6
V-3 Product gas separator	Figure 3-7
V-4 Vent gas separator	Cyclonic separator approximately 18 in. diam x 36 in. high, tangential entry, bottom drain
V-5 Black liquor tank	9000 gal, 10 ft diam x 10 ft high, 125 psig, 250°F, carbon steel
V-6 Green liquor storage tanks (E)	2 each, 17,500 gal, 12 ft diam x 21 ft high, carbon steel, atmospheric pressure
V-7 Spray nozzle test tank	3 ft diam x 10 ft high, 15 psig, 250°F, with view port, carbon steel
PUMPS	
P-1 Black liquor recirculation pump	100 gpm, 170-ft head, 12 hp, 480 V, 3 phase, 1750 rpm, double mechanical seal, carbon steel
P-2 Green liquor recirculation pump	Same as P-1
P-3 Black liquor return pump	20 gpm, 80-ft head, 3 hp, 480 V, 3 phase, 1750 rpm, single internal mechanical seal, carbon steel
COMPRESSORS AND BLOWERS	
C-1 Feed air compressor (E)	Joy Twistair, 470 cfm at 100 psig, 100 hp
C-2 Induced draft fan (E)	York, R-6837 blower, stainless steel

TABLE 3-1

Equipment List
(Sheet 2 of 3)

Item	Description or Drawing
C-3 Combustor air fan (E)	North American Turbo Blower, 2332-21-2-30, 2000 cfm at 32 psi, 30 hp
FILTERS AND STRAINERS	
S-1 Baghouse (E)	Mikropul Model 495-8-20, stainless with 3-in. insulation, Nomex 14-oz felt bags, 500 ft ²
S-2 Black liquor loop strainer	Rotary strainer, Dorr Oliver, 4 in., 9 rpm, 1/4 hp
S-3 Black liquor feed strainer	Rotary strainer, Dorr Oliver, 2 in., 16 rpm, 1/8 hp
S-4 Black liquor unloading strainer	In-line 3-in. pipe strainer, Y type, coarse screen
S-5 Green liquor product strainer	In-line 1-in. pipe strainer, Y type
S-6 Quench tank strainer	Circulation pump inlet strainer, coarse screen, in tank
S-7 Black liquor tank vent filter	Activated carbon, replaceable canister type, for odor removal, 1-in. pipe connections, 1-atm pressure
S-8 Nozzle test tank vent filter	Same as S-7
S-9 Green liquor storage tank vent filter	Same as S-7
HEATERS, COOLERS, & BURNERS	
H-1 Product gas combustor (E)	Custom J. T. Thorpe, Inc., rated 600-scfm product gas at 150 Btu/scf, inlet temperature 1600 to 2000°F

TABLE 3-1

Equipment List
(Sheet 3 of 3)

Item	Description or Drawing
H-2 Feed air heater (E)	180 kW, 480 V, 3 phase, in-line with SCR controller, 110 psig at 1100°F and 15 psig at 1500°F, ASME Section VIII. Hynes Electric Heating Company
H-3 Melt discharge line burner	75,000 Btu/h, natural gas, 2000% excess air to 30% excess fuel, 50-psig operating pressure
H-4 Black liquor tank heater	40 kW, 480 V, 3 phase in tank with SCR controller, 0 to 250°F, 8 in., A300 flanges
H-5 Black liquor recirculation heater	40 kW, 480 V, 3 phase, in-line heater with SCR controller, 0 to 250°F, 2-in., A300 flanges
H-6 Green liquor heater	15 kW, 480 V, 3 phase, in-line heater with SCR controller, 0 to 250°F, 2-in., A300 flanges
H-7 Vessel preheat burners A&B	Each 1 x 10 ⁶ Btu/h, 2000% excess air, 30% excess fuel, 50-psig operating pressure
H-8 Green liquor cooler	Shell and tube, stainless tubes, 150,000-Btu/h cooling, 70°F cooling water
AGITATORS	
A-1 Black liquor tank agitator	6 hp, 300 rpm, dual-propeller stainless with double mechanical seal, 8 in., A150 flange top entry, 150-psig operation
A-2 Quench tank agitator	Same as A-1

(E) - Existing

TABLE 3-2

Assumptions Used For Performance AnalysesBlack Liquor Composition

C	24.60 wt. %
H	2.37
O	20.32
S	2.63
Na	11.88
K	1.13
Cl	0.06
Inerts	0.05
H ₂ O	<u>36.96</u>
	100.00
Solids, %	63.04
HHV, Btu/lb	4168

Temperature in gasification zone, °F	1750
Temperature of feed air, °F	700
Temperature of feed liquor, °F	220
Drying efficiency in drying zone, %	90
Reduction efficiency of sulfur in melt, %	95
Temperature of dried solids entering gasification zone, °F	220

TABLE 3-3
Results of Gasifier Performance Calculations

	Case							
	1	2	3	4	5	6	7	8
Pressure, psia	223	45.0	45.0	14.7	14.7	13.7	13.7	13.7
Gas velocity, ft/s	2.0	2.0	2.5	2.5	3.0	2.5	3.0	3.5
Black liquor feed rate, lb/h	65,540	982	1,254	338	428	307	391	474
Air, % of theoretical	38.9	45.2	43.6	59.3	54.8	61.5	56.4	53.1
Material balance, lb/lb of black liquor								
Air	1.22	1.41	1.36	1.86	1.71	1.92	1.76	1.66
Product gas	1.94	2.13	2.08	2.58	2.43	2.64	2.48	2.38
Melt	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Product gas								
Volume, scf/lb black liquor	30.8	32.9	32.4	37.8	36.2	38.5	36.7	35.6
Temperature, °F	1,024	956	969	860	887	848	877	898
Water content, %	22.9	23.4	23.3	24.1	23.9	24.2	24.0	23.8
HHV, Btu/scf (dry)	121	101	106	63	74	58	70	78
Composition, % (dry basis)								
CO ₂	14.4	15.1	14.9	16.4	16.0	16.6	16.2	15.9
CO	12.9	10.7	11.2	6.8	7.9	6.3	7.5	8.4
CH ₄	1.9	1.7	1.8	1.0	1.2	0.9	1.1	1.3
C ₂ H ₄	0.18	0.17	0.17	0.15	0.16	0.15	0.15	0.16
H ₂	17.4	14.2	14.9	8.6	10.2	7.9	9.6	10.8
H ₂ S	0.17	0.16	0.16	0.14	0.15	0.14	0.14	0.15
N ₂	53.1	58.0	56.8	67.0	64.4	68.1	65.3	63.4

3.3 Performance Analyses (Continued)

above atmospheric pressure at higher throughput, and of being able to operate at higher gas velocities, which also corresponds to higher throughput. Any change that reduces the heat loss per unit of feed results in improved product gas quality.

The pilot gasifier performance calculations were based on a net heat loss of 294,500 Btu/h from the gasification zone and 82,000 Btu/h from the drying zone. These losses include heat transfer by conduction through the vessel walls and by radiation between zones and from the walls. The basis for these heat loss figures is summarized in Table 3-4 and is illustrated in Figure 3-8. Calculated gasifier wall temperatures are listed in Table 3-5.

TABLE 3-4
Pilot Plant Gasifier Heat Loss Estimate

Zone	Surface Area, ft ²	Effective Area, ft ²	Q/A Btu/h ft ²	Q Btu/h
Gasification zone				
5-ft vertical cylinder	88	110	895	98,500
gasifier bottom	50	64	703	45,000
radiation loss				<u>151,000</u>
total				294,500
Drying zone				
12-ft vertical cylinder	212	233	867	202,000
gasifier top	27	33	956	31,000
radiation absorbed				<u>-151,000</u>
net loss				82,000

Figure 3-8. Gasifier Thermal Balance Diagram

TABLE 3-5

Pilot Plant Gasifier Wall Temperatures

Location	Temperature, °F			
	Inside Surface	Monofrax/ Alfrax Contact	Alfrax/ Bubble Alumina Contact	Metal Wall
Gasification zone				
5-ft vertical wall	1750	1262	628	356
Gasifier bottom	1750	1099-1262	628-689	282-391
Drying Zone				
Bottom 1-ft vertical	1650	-	501	305
Middle 5-ft vertical	1350	-	660	372
Upper 5-ft vertical	1150	-	577	338
Gasifier top	1000	-	-	369

The thermal conductivities used in the calculations were:

Monofrax M	2.20 Btu/h ft °F
Alfrax 66	1.18
bubble alumina	0.60
carbon steel	25.0

Heat losses from the outside metal shell of the gasifier to the surroundings were estimated based on work reported in W. Trinks, "Industrial Furnaces,"⁴ which combines natural convection and radiation cooling into

$$Q/A = 0.155 \times 10^{-8} (T_s^4 - T_a^4) + 0.28 (T_s - T_a)^{1.25}$$

where Q = heat loss, Btu/h
 A = surface area, ft²
 T_s = surface temperature, °R
 T_a = ambient temperature, °R
 (70°F or 530°R assumed)

3.3 Performance Analyses (Continued)

Heat lost from the gasification zone by radiation upward into the drying zone was estimated by assuming black body radiation across an area equal to the cross section of the gasifier in the gasification zone. A source temperature of 1750°F and a sink temperature of 1100°F were assumed. This approach is conservative.

Heat lost from the gasification zone affects the product gas composition much more than heat lost from the drying zone; the latter affects primarily the product gas temperature. A correlation of the effect of heat lost from the gasification zone with the product gas heating value is presented in Figure 3-9. The calculated cases from Table 3-3 and experimental data from the last pilot unit test are included. The calculated pilot unit cases (Cases 2 to 8) are based on a heat loss from the gasification zone of 294,500 Btu/h, as developed in Table 3-4, while the pilot unit test points are based on an estimated heat loss of 832,000 Btu/h from the gasification zone. The calculated commercial unit case (Case 1) is based on a heat loss of 2,550,000 Btu/h. The position of the experimental data curve relative to that of the calculated cases could reflect less than 90% drying of the black liquor droplets before they entered the gasification zone. This would not be surprising since the feed nozzles used during earlier tests did not perform very well.

Figure 3-9 shows that the tests recommended for the new pilot unit should largely fill the existing gap in data between past experimental work and expected commercial performance. To the extent that radiation losses from the gasification zone have been overestimated by assuming black body radiation, the heating value of the product gases at a given total percent heat loss would be higher.

Figure 3-9. Product Gas Heating Value as a Function of Heat Lost from the Gasification Zone

SECTION 4

4.0 BLACK LIQUOR SPRAYING

The basic requirements of the feed system in the black liquor gasifier are that it be capable of delivering a narrow range of drop sizes with a narrow conical or cylindrical spray pattern, that it operate free from plugging, and that it be scalable to larger units. The importance of these issues and the work to date on determining a good feed system design are described in this section.

4.1 Black Liquor Feed System

A preliminary piping and instrumentation diagram for the black liquor feed system is presented in Figure 4-1. Black liquor delivered to the test site by heated truck would be transferred to a heated tank (V-5) equipped with an agitator and weigh scales. To maintain an available inventory of heated, homogeneous liquor that is free of large solid particles, about 100 gpm would be circulated from the feed tank through a rotary strainer (S-2) and controlled electrical heater (H-5), and back to the liquor tank. Feed for the gasifier, amounting to about 2 gpm, would be withdrawn from the recirculation loop.

The gasifier feed stream passes through a second strainer (S-3) and redundant flow measuring instruments before entering the gasifier. Several types of filter/strainer systems were evaluated. Dorr Oliver's Bantam 2-in. strainer appears to be particularly suitable because of its small size and flexibility. Screens for this unit are available with openings ranging from 0.005 to 0.062 in. The total screen area is 65 in², which provides a nominal capacity of 100 gpm of water at a 1.5 psi drop in pressure. The screens are cleaned continuously by a motor-driven brush.

4.2 Spray Requirements

(Basis for Calculations)

It is desirable that black liquor droplets sprayed into the top of the gasifier be dried thoroughly as they fall through the drying zone, but not be entrained in the rising gas stream. This places upper and lower limits on the allowable drop sizes, which limits are determined by such factors as gas velocity, height of drying zone, black liquor properties, temperature, and pressure.

REVISIONS			
LTR	DESCRIPTION	DATE	APPROVED

NOTES: UNLESS OTHERWISE SPECIFIED ON THIS DRAWING
SEE DWG 174000001

Figure 4-1. Black Liquor Feed System

IN WORK

DOCUMENT NOT RELEASED

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FORM 723P-1 REV. 7-78

4-2

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HEAT TREAT	UNLESS OTHERWISE SPECIFIED: DIMENSIONS ARE IN INCHES AND APPLY PRIOR TO FINISH. 125/ MACH. SURF. ROUGHNESS	CONTR		Rockwell International Corporation Rocketdyne Division Canoga Park, California		
		OWN <i>FALLANDY</i>		DATE		
		CHK		DATE		
		TOLERANCES ON: ANGLES $\pm 0^{\circ} 30'$ DECIMALS .XX $\pm .03$.XXX $\pm .010$ HOLES NOTED "DRILL"				
FINISH	OVER THRU TOLERANCE .0000 .0400 + .0015 - .0010 .0400 .1300 + .0030 - .0010 .1300 .2250 + .0045 - .0010 .2250 .5000 + .0060 - .0010 .5000 .7500 + .0070 - .0010 .7500 1.0000 + .0090 - .0010 1.0000 2.0000 + .0120 - .0010 DO NOT SCALE PRINT	DSGN		<i>BLACK LIQUOR GASIFICATION PILOT PLANT BLACK LIQUOR FEED SYSTEM P#1D</i>		
		MATL				
		STRUCT				
		DESIGN ACTIVITY APVD				
MATL		DATE		SIZE	FSCM NO	DWG NO
				D	02602	1740000004
				SCALE	SHEET	

4.2 Spray Requirements (Continued)

(Basis for Calculations) - Continued

As a basis for calculating the upper and lower limits on the allowable drop sizes, the following parameters were assumed:

- Black liquor feed - 65% solids, 35% water
- Black liquor density - 81.1 lb/ft³
- Gas temperature - 1800 to 1200°F
- Drop surface temperature - 250°F
- Operating pressure - 1, 3 and 15 atm
- Drying zone height - 12 ft (pilot) and 20 ft (commercial)
- Gas velocity - 2.0, 2.5 and 3.0 ft/s
- Gas composition - 43 vol % N₂, 9% H₂, 12% CO, 11% CO₂, 25% H₂O
- Gas molecular weight - 24.92

Since the gas is at a much higher temperature than the droplets at their surface, an arithmetic average temperature is inadequate to represent the boundary layer surrounding the drops. Therefore, following the recommendation of Merriman⁵ in his kraft furnace model, the boundary layer temperature was taken as equal to $T_g/3 + 2T_p/3$, where T_g and T_p are the gas and particle temperatures, respectively, expressed as absolute temperatures. For $T_g = 1960^\circ\text{R}$ (1500°F) and $T_p = 710^\circ\text{R}$ (250°F), the reference temperature (T_{ref}) is 1127°R (667°F). T_{ref} was used in determining the transport properties of the gas.

Gas properties at the nominal composition and reference temperature were estimated to be:

- density (ρ_g)
 - = 0.0303 lb/ft³ at 1 atm
 - = 0.0910 lb/ft³ at 3 atm
 - = 0.4551 lb/ft³ at 15 atm
- viscosity (μ_g) = 0.067 lb/ft h
- heat capacity (C_p) = 0.326 Btu/lb °F
- thermal conductivity (k_c) = 0.285 Btu/ft h °F

The latter two properties are basically independent of pressure.

A schematic representation of black liquor drying is given in Figure 4-2. The maximum allowable drop size can be estimated by equating the residence time in the drying zone with the time required to dry drops of various sizes. The minimum drop size is that which has a terminal velocity equal to the gas velocity in the drying zone, such that the drop will not reach the gasification zone. Changes in drop diameter and density as drying progresses complicate the analysis. Since there are widely different values reported for the expected degree of

Figure 4-2. Representation of Black Liquor Drying

4.2 Spray Requirements (Continued)

(Basis for Calculations) - Continued

drop swelling, cases were calculated assuming zero swelling or no change in diameter and assuming an increase in drop diameter by a factor of two. To simplify the calculations for the case where the diameter doubles over the length of the drying zone, the arithmetic mean drop diameters and densities were used.

(Terminal Velocity, V_T)

For the case of spherical particles falling under the action of gravity, the terminal velocity is given by the equation⁶

$$V_T = (4gd[\rho_p - \rho_g]/3\rho_g C_D)^{1/2} \quad (4-1)$$

where g = gravitational constant
 d = particle diameter
 ρ_p = particle density
 ρ_g = gas density
 C_D = drag coefficient

For Reynolds numbers between 2 and 500, C_D can be approximated by the equation⁶

$$C_D = 18.5/(\text{Re})^{0.6} \quad (4-2)$$

where Re = Reynolds number = $dV_r\rho_g/\mu_g$
 V_r = relative velocity between particle and gas
 μ_g = gas viscosity

At higher Reynolds numbers, C_D is approximately constant at 0.44.⁶

(Convective Heat Transfer)

The convective heat transfer coefficient can be estimated from the equation defining the Nusselt number

$$\text{Nu} = h_c d / k_c \quad \text{or} \quad h_c = \text{Nu} k_c / d \quad (4-3)$$

where h_c = heat transfer coefficient
 k_c = thermal conductivity of the gas
 d = particle diameter
 Nu = Nusselt number

4.2 Spray Requirements (Continued)

(Basis for Calculations) - Continued

The Nusselt number can be related to the Reynolds number using the Ranz and Marshall correlation' to yield

$$Nu = 2.0 + 0.5 Re^{0.5} \quad (4-4)$$

(Incident Heat Flux)

The total heat flux to the surface of each drop will be the sum of the heat transferred by radiation from high-temperature sources and the heat transferred by convective heat transfer from the gas stream:

$$q = \epsilon \sigma (T_r^4 - T_p^4) + h_c (T_g - T_p) \quad (4-5)$$

where

- q = total heat flux per unit area of drop surface
- ϵ = emissivity factor for heat source and drops
- σ = Stephan-Boltzman constant
- T_r = temperature of radiant heat source
- T_p = temperature of drop surface
- T_g = temperature of gas

Radiant heat will be transferred to the drops from the gas, walls, and high-temperature gasification zone. As an approximation, it is assumed that the effective average source temperature is 1600°F, the drop surface is 250°F, and $\epsilon = 0.8$. With these assumptions, radiant heat transfer is the same for all cases (24,300 Btu/h ft²) and generally represents from about one-fifth to one-half of the total heat flux.

(Drying Time)

The time required to dry a drop of black liquor can be estimated by equating the quantity of heat needed to evaporate all of the water in the drop to the quantity of heat transferred to the drop. The amount of water to be evaporated is based on the initial drop size, d_1 , while the heat absorbed is based on the average drop size, d_2 . Therefore

4.2 Spray Requirements (Continued)

(Drying Time) - Continued

$$w\rho_1 h(\pi d_1^3/6) = q(\pi d_2^2)t_D \quad (4-6)$$

heat to evaporate water = heat absorbed through surface

where w = weight fraction of water in the drop initially
 ρ_1 = initial drop density
 d_1 = initial drop diameter
 d_2 = average drop diameter
 h = latent heat of vaporization of water
 t_D = time required for complete drying

The actual drying time will be longer than predicted by the above equation due to thermal resistance within the drop as it dries. Merriman⁵ proposes using a dimensionless correction factor, B , for the drying of black liquor, defined by the equation

$$B = 1.2 + 0.26r \quad (4-7)$$

where r is the particle radius in mm.

If no change in drop size occurs as the particle dries, Equation 4-6 simplifies to

$$t_D = 8w\rho_1 d_1 h/6q \quad (4-8)$$

For the case of 100% increase in drop diameter during drying, $d_2 = 1.5d_1$, and

$$t_D = 8w\rho_1 d_1 h/13.5q \quad (4-9)$$

The actual residence time of a drop in the drying zone will be

$$t_R = L/(V_T - V_g) \quad (4-10)$$

where t_R = residence time
 L = length of the drying zone
 V_T = terminal velocity of particle
 V_g = superficial gas velocity

4.2 Spray Requirements (Continued)

(Drying Time) Continued

The drop size that results in t_R being equal to t_D represents the maximum size that will be dried completely while falling through the drying zone. The minimum particle size that will not be entrained can be estimated by setting the terminal velocity, (V_T) equal to the superficial gas velocity (V_g) in Equation 4-1 and solving for d .

(Drop Size Requirements)

The calculated drop size requirements for a pilot gasifier operating at 1 and 3 atm, and a commercial gasifier operating at 15 atm, without and with drop expansion, are summarized in Table 4-1. Particles larger than the minimum size will be entrained if further swelling occurs in the drying zone after complete dryness has been attained.

The drop residence time in the drying zone, t_R , and time required for drying, t_D , are presented in Figure 4-3 as a function of the initial drop diameter, d_1 . Curves are presented for the case of no drop expansion (Case A) and for 100% drop expansion (Case B), but only for one gas velocity (2 ft/s). The intersection of corresponding t_R and t_D curves represents the maximum size drop that will be completely dried and the time it will be in the drying zone.

TABLE 4-1						
<u>Black Liquor Drop Size Requirements</u>						
Drying Zone Length (ft)	System Pressure (atm)	Gas Velocity (ft/s)	Minimum Feed Drop Size Based on Entrainment (mm)		Maximum Feed Drop Size Based on Complete Drying (mm)	
			Case A*	Case B	Case A	Case B
12	1	2.0	0.20	0.36	1.07	1.53
12	1	2.5	0.24	0.44	1.08	1.55
12	1	3.0	0.28	0.51	1.10	1.57
12	3	2.0	0.26	0.48	1.37	2.04
12	3	2.5	0.31	0.58	1.39	2.08
12	3	3.0	0.37	0.68	1.41	2.12
20	15	2.0	0.39	0.74	3.23	4.81
20	15	2.5	0.47	0.94	3.31	4.94
20	15	3.0	0.55	1.05	3.39	5.09

*Case A - no expansion of drop; Case B - expansion to twice original diameter

Figure 4-3. Residence Time and Drying Time for Droplets as a Function of Drop Diameter and Operating Pressure

4.3 Spray Nozzles

In addition to delivering a narrow range of drop sizes, the other requirements for the gasifier feed system were that the black liquor could be fed in a narrow conical or cylindrical spray pattern, that it be free from plugging, and that it be scalable to commercial size. Commercially available nozzles were reviewed to determine if they could meet all of these requirements.

(Available Spray Nozzles)

Current practices in black liquor spraying are reviewed by McCallum and Blackwell.^a Conical-spray nozzles normally are used on Combustion Engineering (CE) boilers. These nozzles typically contain a helical flow inducer upstream from a circular orifice. They produce a wide-angle hollow-cone spray pattern with an apex angle somewhat greater than 90° using liquor pressures of about 15 to 20 psig. An alternative system for CE boilers involves the use of either flat-spray or splash-plate nozzles.^a While these changes offer advantages for recovery boiler applications, neither the conical-spray nozzle nor the alternative spray nozzle could be adapted to a gasifier.

Babcock and Wilcox (B&W) boilers typically use splash-plate nozzles. This design uses a circular orifice to produce a smooth jet of black liquor that impinges on a splash plate. The angle between the surface of the splash plate and the centerline of the jet is about 135-150°. Splash-plate nozzles produce a flat sheet of relatively large droplets. The wide range of drop sizes and the spray pattern would be unsuitable for gasifier application.

Performance data on several small commercially available pressure nozzles were provided by Spraying Equipment Company and Bete Fog Nozzle, Inc. The data was based on ambient temperature water spraying, which cannot be extrapolated to performance with heated black liquor. While commercial pressure nozzles generally produce a broad spectrum of drop sizes in a broad cone-angle pattern, both companies reported that the increased viscosity of black liquor should decrease the spray angle significantly and increase the drop size. A check of available correlations for predicting pressure nozzle drop size with the performance data indicated that the correlations were not applicable. The nozzles would have to be tested with hot black liquor to determine if they were applicable to the gasifier.

The use of vibratory pulses to augment the natural oscillations in a jet of liquid leaving a nozzle and thereby create a stream of uniform drops has been reported. An equation for predicting

4.3 Spray Nozzles (Continued)

(Available Spray Nozzles) - Continued

the size of droplets is given by Wissema and Davies,¹⁰ and Hill and McCallum¹¹ describe the construction and successful operation of pulse-assisted jet nozzles with as many as 80 individual jets. The pulse jet nozzle concept potentially is viable because of the predictability and uniformity of drop sizes produced. However, it has the disadvantages of requiring a relatively complex pulse generation system and using a large number of small orifices. Scaleup could also be a problem.

The use of multiple jets without the assistance of pulses or vibrations has also been considered. Although mechanically simpler than the pulse jet nozzles, they retain the disadvantage of numerous small orifices, which are subject to plugging. Also, although they provide a more uniform drop size distribution than other simple pressure nozzles, they have a tendency to produce one or more very small satellite drops with each larger drop in the desired size range.

Solid-cone pressure nozzles were used in the past pilot black liquor gasification tests. They have the advantages over hollow-cone nozzles of producing small angle spray cone patterns and providing more uniform coverage of the gasifier cross section. However, they have the disadvantages of restricted internal passages which tend to plug, and the production of a broad range of drop sizes.

Two-fluid nozzles in which an expanding gas (air or steam) atomizes a slower moving stream of liquid generally are used where very fine droplets are required, as in paint spraying. However, they offer several potential advantages for black liquor spraying, such as a narrow spray angle, freedom from plugging due to relatively large liquid flow passages, and the capability for adjustment during operation without changing the black liquor stream flow rate or temperature. If steam is used as the second fluid, it is expected that the tendency for black liquor to dry on the nozzle would be inhibited. The use of a two-fluid nozzle with steam as the atomizing fluid has been reported for black liquor.¹² This application was a brick-lined incinerator in which a single nozzle handled up to 6 tons/h of dry solids in the form of 50% solids liquor. Since the operation of two-fluid nozzles to produce large drops is outside their normal operating envelope, little performance information is available, and published design correlations cannot be expected to be applicable.

4.3 Spray Nozzles (Continued)

(Available Spray Nozzles) - Continued

A summary comparison of the six conventional types of nozzles considered for use in the pilot plant gasifier is given in Table 4-2. It is concluded that two-fluid nozzles (steam and black liquor) and solid-cone nozzles are worth further evaluation for the pilot plant application, and multiple jet nozzles with or without vibratory assistance may be of interest as a longer term development. However, none of the currently available nozzle designs obviously meet all of the requirements for the gasifier feed system.

(Testing of a Splash-Tube Spray Nozzle)

Since none of the commercially available nozzles meet all of the requirements, a special design aimed specifically at the requirements of the pilot unit was developed. The proposed approach has been called a splash-tube nozzle.

A very preliminary experimental evaluation of the splash-tube nozzle concept was conducted using water and visual observations. Three configurations were tested using a nozzle sized for a black liquor feed rate of about 1300 lb/h. The nozzle appeared to give good droplet sizes and a uniform, narrow, hollow spray cone. The spray pattern and droplet size appeared to be much closer to that desired than any commercial nozzles tested similarly. However, further testing is required.

TABLE 4-2

Comparison of Commercially Available Spray Nozzles

Nozzle Type	Advantages	Disadvantages
1. Hollow cone, pressure	<ul style="list-style-type: none"> • Used for black liquor • Fairly large liquid passage 	<ul style="list-style-type: none"> • Wide angle spray pattern • Broad range of drop sizes
2. Splash plate	<ul style="list-style-type: none"> • Used for black liquor • Large liquor passage 	<ul style="list-style-type: none"> • Very poor spray pattern • Broad range of drop sizes
3. Pulse jets	<ul style="list-style-type: none"> • Excellent drop size control • Narrow spray angle 	<ul style="list-style-type: none"> • Subject to plugging • Very difficult to scale up
4. Multiple jets (shower head)	<ul style="list-style-type: none"> • Good drop size control • Narrow spray angle 	<ul style="list-style-type: none"> • Subject to plugging • Difficult to scale up
5. Solid cone, pressure	<ul style="list-style-type: none"> • Medium angle spray pattern available 	<ul style="list-style-type: none"> • Internal passages tend to plug • Broad range of drop sizes
6. Two-fluid (steam/black liquor)	<ul style="list-style-type: none"> • Narrow spray angle • Very large liquid passage • Black liquor drying inhibited • Adjustable during operation 	<ul style="list-style-type: none"> • Second fluid required (steam) • No data available on operation in desired drop size range

SECTION 5

5.0 MELT DISCHARGE

The basic requirements of the gasifier melt discharge and quench system are continuous operation in a pressurized environment at widely varying flow rates, without plugging or serious materials degradation, and with the capability of being scaled up to commercial size. A review of existing discharge systems and the conceptual design of a system for the gasifier are discussed in this section.

5.1 Review of Existing Systems

(Smelt Spout Designs)

The general practice in black liquor recovery boilers is to use short, steeply inclined, water-cooled, metal spouts. Figures 5-1 and 5-2 are typical designs representing the Götaverken^{1,2} and Tampella^{3,4} smelt spouts, respectively. Both of these companies offer water-cooled systems operating at atmospheric pressure or slight vacuum to minimize the mixing of water and smelt in the event of a leak. This is claimed to be a safety feature.

Figure 5-1. Smelt Spout Design Used in Götaverken Recovery Boilers

Figure 5-2. Smelt Spout Design Used in Tampella Recovery Boilers

Corrosion of metal spouts by the flowing smelt is a common problem, and the spouts are therefore designed for ready replacement. The Black Liquor Recovery Boiler Advisory Committee recommends that all spouts be replaced at least once per year.¹⁵ Corrosion of tubes in the boiler wall at smelt spout openings can occur also and is more serious. Local weld repair and spraying the tubes with ceramics are reported to have given good results in one boiler.¹⁶ Another approach used in a recent boiler replacement was to install "form fitting" alloy castings of commercially pure zirconium metal to protect spout opening tubes.¹⁷ Previously, an alloy of 50% Ni and 50% Cr had been used for these castings. These gave 4 weeks of service. The zirconium castings provided about four times the service life. They are considered helpful but not an optimum solution to the problem.

5.1 Review of Existing Systems (Continued)

(Smelt Spout Designs) - Continued

Several companies have evaluated the use of ceramic-lined rather than water-cooled smelt spouts. Domtar, Inc., of Canada has a patent on a refractory-lined spout that incorporates a steam jet to cool the tip and break up the discharged smelt.¹⁸ This concept is shown in Figure 5-3. Termorak Oy of Finland has developed a smelt spout that is ceramic-lined and totally uncooled.¹⁹ They report that ceramic spouts have been installed on boilers at two plants and have demonstrated extremely good durability. One of the installations uses very long spouts (2.2 m). Gas burners are provided to preheat the long spouts to avoid melt solidification; however, during normal operation, when liquid flows continuously, the temperature of the spout remains adequately high and no additional heating is required.

Figure 5-3. Refractory-lined Smelt Spout (Patented by Tremblay of Domtar, Inc. Key features are: 24--steam nozzle, 26--steam passage, 30--steam inlet, 32--insulating brick, 34--plastic refractory, 36--smelt, and 38--discharged stream of smelt.)

5.1 Review of Existing Systems (Continued)

(Shatter Systems)

Steam shatter jets have been found to be more effective than recycled green liquor for breaking up the stream of smelt; however, many installations use both steam and green liquor. The addition of a steam jet to a system that previously employed only recycled green liquor is described in a 1955 paper.²⁰ In this case, the steam shattering plus the addition of a fish-tail nozzle to the green liquor spray line improved operation but did not completely eliminate explosions. In 1958, a Canadian patent was issued covering the concept of directing the steam jet vertically downward into the stream of smelt after it leaves the spout.²¹ The patented configuration is shown in Figure 5-4. For a typical commercial installation, as described in the patent, the steam nozzle is located about 12 in. horizontally from the end of the spout. The smelt stream follows a curved trajectory as it leaves the spout and is impacted by the steam about 6 to 7 in. from the nozzle tip. The nozzle can be fabricated by flattening a 1/2-in. pipe to an elongated tip 1 in. by 1/16 in. with an area of about 0.06 in². Steam flow is on the order of 300 to 500 lb/h with a source pressure of 50 to 150 psi. Under these conditions, the exit velocity approaches the speed of sound. This patent also mentions the use of a horizontal spray of green liquor 4 to 5 ft. below the zone of impact of the vertical steam jet with the smelt to aid in dispersing the smelt particles over the surface of the green liquor pool. The use of near-vertical steam nozzles is currently common practice in recovery boilers.

For economic reasons, it is desirable to minimize the pressure and quantity of steam used. In some installations, low-pressure (10-15 psig) steam has been used for the primary nozzles with higher pressure auxiliary steam nozzles cut in manually when excessive smelt flow occurs. This has not been entirely satisfactory, and the currently preferred mode of operation is to utilize a steam shatter jet powerful enough to effectively break up the smelt stream during both normal and off-normal smelt flow rates. The concept of automatically adjusting steam flow based on smelt flow rate, as indicated by the spout cooling water exit temperature, was patented by Combustion Engineering,²² although apparently this system is not used widely.

Figure 5-4. Steam Jet Shattering System (Patented by Thorson of Babcock and Wilcox. Key features are: 30--vertical steam nozzle, 14--smelt spout, and 24--green liquor nozzle).

5.2 Design of Melt Discharge System

The key design requirements for the pilot unit melt removal and quench system are:

- Operation over a wide flow range without plugging
- Continuous operation in a pressurized environment unattended
- Freedom from serious materials degradation
- Scalable to commercial gasifier applications

In order to meet these requirements, the selected design approach incorporates the following features:

- A simple, straight inclined channel for melt discharge from the gasifier to the quench tank.
- A channel ID large enough to accommodate hot gas flow from the gasifier to the quench tank above the stream of melt. The hot gas is intended to minimize cooling and plugging of the channel by the melt.

5.2 Design of Melt Discharge System (Continued)

- A gas burner firing into the gas space of the melt discharge channel to maintain temperatures above the melting point of the salt at all times.
- A control system to assure positive flow of product gas and/or burner combustion gas into the quench tank and out of the tank via a separate vent line.
- A refractory lining that includes material resistant to attack by flowing melt at the inner surface and thermal insulation between the melt resistant liner and the metal pipe.
- A pressure boundary made up of standard 18-in. steel pipe with a bellows section to accommodate differential movement.
- A mechanical swiper bar under the melt spout, entering the quench tank through a pressure seal to permit stalactites of solidified melt to be dislodged during operation.
- Adequate melt shattering and green liquor mixing capability to prevent any possibility of melt/water explosions.

Additional details of the design are shown in Figure 5-5.

A refractory-lined spout design was selected over a water-cooled design primarily because of the low melt flow rates that will occur during pilot plant operation. Low and intermittent melt flow would be more likely to result in solidification and buildup of solids on an actively cooled spout than on an uncooled refractory-lined unit. In addition, a properly designed water-cooled spout installation requires a relatively complex and expensive water circulation system including the provision of boiler-quality feed water. The use of a refractory-lined melt spout on the pilot plant does not preclude the use of water-cooled designs on later large units since the design of water-cooled spouts is well developed and pilot-scale demonstration is not required.

Melt breakup can be accomplished by the use of either steam or recycled green liquor jets. Steam shatter jets are preferred for black liquor recovery boilers, which produce relatively large streams of melt flowing into an atmospheric pressure quench tank. Since full-size gasifiers will operate at 10 to 15 atm pressure, which is well above the range at which melt-water explosions are known to occur, and since very high

5.2 Design of Melt Discharge System (Continued)

pressure steam would be required to provide high-velocity injection into a 10- to 15-atm system, it appears that steam jets will be neither necessary nor economical for commercial gasifiers. The use of recycle green liquor to break up the melt stream as an aid to dissolving it should be adequate; however, a backup steam system is advisable for use during periods of low-pressure operation of the gasifier/quench system.

Since all or most of the pilot plant operations will be in a pressure range where explosions can occur (1 to 7 atm) and since operational safety is the top priority requirement, a dual steam-green liquor shatter system has been specified for the pilot plant. In accordance with recovery boiler practice, the steam shatter jets will be aimed nearly vertically downward a few inches in front of the point of melt discharge. The green liquor jet will be aimed almost horizontally to impact the falling melt before it reaches the liquid surface in the quench tank. Turbulence is maintained in the green liquor pool by a continuously operating mixer. As an added safety feature, the quench tank is equipped with a high-volume water jet adjacent to the green liquor jet. The water jet will be actuated in the event the recycle green liquor shatter system stops operating.

The quench tank includes a vertical extension that encloses the discharge end of the melt spout and supports accessory equipment. To prevent droplets of melt from adhering to the walls of the extension and to maintain moderate surface temperatures, the inside vertical walls are washed with green liquor supplied by six small nozzles. Radiation from the interior of the melt discharge line, which operates at about 1750°F, to the cooled walls of the extension, operating at about 220°F, is minimized by a radiation shield at the outlet end of the melt spout. The shield is hinged so that it can be raised for inspection or maintenance of the melt flow channel.

The melt discharge line was designed on the basis of the following criteria:

- An inside diameter of at least 6 in. to provide adequate space for gas and melt flow and minimize the possibility of flow blockage.
- A temperature of 600°F or less at the steel pipe pressure boundary to assure adequate strength properties.
- High-purity alumina ceramic or fused cast alumina inner lining in contact with flowing melt to resist melt attack.

5.2 Design of Melt Discharge System (Continued)

- High alumina dense castable refractory behind the inner lining to stop melt flow through cracks.
- A metal melt barrier between the dense castable and insulating refractories if the temperature at the interface is at or near the melting point of the salt (~1400°F).
- An expansion joint in the pressure boundary between gasifier and quench tank vessels.

Thermal calculations were made for several possible configurations, and the design shown in Figure 5-5 was selected. The calculations were based on operation at the reference design conditions and the thermal properties given in Table 5-1.

TABLE 5-1	
<u>Thermal Properties of Materials</u>	
Material	Thermal Conductivity at Mean Temperature (Btu/h ft °F)
Steel	25.0
Alfrax 66 castable refractory	1.18
Alfrax B1 bubble aluminum insulating refractory	0.60
99.9 alumina ceramic	3.60
Air	0.20
	Heat Capacities at Mean Temperature (Btu/lb °F)
Na ₂ CO ₃	0.445
Na ₂ S liquid	0.280
Melt	0.412
Gases (burner and product mix)	0.29

5.2 Design of Melt Discharge System (Continued)

The results of the preliminary thermal analysis for the design configuration are given in Table 5-2. With the gasifier operating at 1750°F and approximately the same temperature inside the discharge line, the temperature of the high alumina dense castable refractory (Alfrax 66) will be 1700°F at its hot face and about 1340°F at its cold face. This is below the freezing point of the molten salt and low enough for a metal alloy barrier to be effective in preventing molten salt attack on the insulating refractory during occasional off-design operating periods. The insulating refractory (Alfrax B1 bubble alumina) has a hot face temperature of 1340°F and a cold face temperature at the steel pipe of 500°F. It is estimated that the 10-in. burner pipe will operate somewhat hotter than the 500°F main discharge pipe and that the flanges and bellows will operate appreciably cooler; however, precise calculation of all surface temperatures will require a more detailed analysis.

TABLE 5-2

Thermal Analysis of Melt Discharge Assembly

Temperatures (°F)	
Inside flow channel	1,750
Alfrax 66 hot face (max)	1,700
Melt barrier tube (max)	1,340
18-in. steel pipe (max)	500
Bellows and flanges (ave)	320
10-in. burner pipe (max)	600
Burner flame (50% excess air)	2,850
Heat losses (Btu/h)	
Main discharge line and bellows	36,000
Burner pipe (burner on)	<u>4,000</u>
Total loss from assembly	40,000
Heat sources (Btu/h)	
Melt cooled 1750°F → 1675°F	8,400
10% of product gas 1750°F → 1675°F	<u>4,600</u>
Total available from gasifier products	13,000
Burner (75,000 Btu/h input)	
Total available heat	<u>27,000</u> 40,000

5.2 Design of Melt Discharge System (Continued)

Heat losses from the melt discharge line and burner assembly are estimated to be about 40,000 Btu/h. This loss can be balanced by using a 75,000-Btu/h burner and permitting the flowing melt and product gas to cool from 1750°F to 1675°F, which is safely above the melt freezing point.

The melt spout at the outlet end of the melt discharge line is not part of the pressure boundary, so its operating temperature is not critical, and efficient insulation is not required. Also, it is in a zone of extreme temperature gradients, which could cause excessive cracking of ceramic or fusion-cast refractory shapes. As a result, the spout has been designed as a simple replaceable unit with a stainless steel casing and a lining of Alfrax 66 high-density alumina castable refractory.

The spout is attached to a metal liner tube that fits loosely inside the bellows and quench tank nozzle and is firmly attached to the 18-in. piping leading from the gasifier. This arrangement allows the quench tank to move relative to the gasifier without disturbing any of the refractory components.

SECTION 6

6.0 MATERIALS EVALUATION

The evaluation of materials of construction for a new pilot gasifier included laboratory corrosion tests and evaluation of manufacturers' data and other research data on the materials. These aspects are reported on in this section.

6.1 Corrosion Tests

Three types of materials were tested in the laboratory: fused-cast refractories for direct contact with the molten salt pool, castable refractories for use as a back up to the fused-cast refractories and as an inner surface in the drying zone, and metals. The tests were carried out in three Lindbergh electric furnaces; furnace temperatures were controlled using Lindbergh SCR controllers. The test salt beds were contained in 99.8% alumina tubes (1.75 in. ID by 18 in. high), which were encased in gas-tight aluminized Inconel tubes. There were provisions for thermocouples, gas flushing and sampling of melt.

The nominal salt composition used in the tests was as follows:

<u>Compound</u>	<u>Wt. %</u>
Na ₂ CO ₃	75
Na ₂ S	20
Na ₂ SO ₄	4
NaOH	1

The test salt baths were prepared using Na₂SO₄ which was reduced in situ to Na₂S using delayed coke. The salts were analyzed at the beginning of each test and the Na₂S content was checked periodically during longer exposure tests. The Na₂S content was maintained at 20-21 wt %. An inert gas atmosphere was maintained over the salt bed using a mixture of about 10% CO₂ and 90% argon; the use of CO₂ prevented decomposition of the Na₂CO₃ in the bed.

Two types of samples of each fused-cast refractory were used: smaller samples for immersion tests and larger samples for tests in which about half the sample was kept below the melt surface. Metal samples were tested half immersed. Castable refractory specimens were prepared in the laboratory following the manufacturer's directions, and were dried and baked prior to testing.

6.1 Corrosion Tests (Continued)

(Fused-Cast Materials)

Three fused-cast materials were tested. Monofrax A, Monofrax E, and Monofrax M are all fused-cast brick materials manufactured by the Carborundum Corporation; their nominal compositions are listed in Table 6-1. The samples were tested at 1750°F for 600 hours. The results are presented in Table 6-2. The low corrosion rates of 0.03-0.08 in./yr for these materials indicate that direct melt corrosion should not be a problem with any of them.

TABLE 6-1	
<u>Chemical Composition of Fused-Cast Materials</u>	
<u>Material Identity</u>	<u>Nominal Chemical Composition (Wt. %)</u>
Monofrax A	99% Al ₂ O ₃ (95% alpha alumina and 5% beta alumina)
Monofrax M	95% Al ₂ O ₃ (45% alpha alumina and 55% beta alumina)
Monofrax E	80% Cr ₂ O ₃ , 6% Fe ₂ O ₃ , 14% other

TABLE 6-2			
<u>Results of Exposure Tests on Fused-Cast Materials</u>			
<u>Type of Monofrax</u>	<u>Specimen Number</u>	<u>% of Sample Immersed</u>	<u>Corrosion Rate, in./yr.</u>
A	1	100	0.03
A	2	50	0.04
E	1	100	0.05
E	2	50	0.08
M	1	100	0.07
M	2	50	0.06

6.1 Corrosion Tests (Continued)

(Castable Materials)

Six castable refractory materials were tested to determine their suitability as a back up behind the fused-cast refractory and as an inner surface in the drying zone of the gasifier. Three materials were high chrome content, while three were high alumina content. The nominal chemical compositions of each is listed in Table 6-3.

TABLE 6-3	
<u>Chemical Composition of Castable Materials</u>	
<u>Material Identity</u>	<u>Nominal Chemical Composition (Wt. %)</u>
Harchrome G	44% Al ₂ O ₃ , 24% Cr ₂ O ₃ , 13% MgO, 19% other
Harchrome	Similar to Harchrome G
H. W. Chrome	30% Al ₂ O ₃ , 28% Cr ₂ O ₃ , 16% MgO, 26% other
Cast-O-Last G	94% Al ₂ O ₃ , 6% CaO
Alfrax 66	96% Al ₂ O ₃ , 4% CaO
Jade-Pak 88-P	88% Al ₂ O ₃ , 10% Cr ₂ O ₃ , 2% other

The castables corrosion tests were conducted at 1500°F for 24 hours. In one test, wedging of the samples prevented their immersion to the desired 50% of sample length. For this test, the actual immersion was determined and the percent change in weight is reported based on a linear scaling to 50% immersion. In all other tests, the samples were immersed to the desired 50%. The results are summarized in Table 6-4.

All three high-chrome castables showed evidence of rapid attack at the melt interface and hence do not appear to be suitable for use in the gasifier. The Alfrax 66 did not show specific attack at the melt interface but showed preferential attack of the fine-grained structure leaving a coarse, grainy surface in the portion immersed in the melt. Cast-O-Last G and Jade-Pak 88-P, on the other hand, had a good appearance overall, with the Cast-O-Last G gaining 1.5% in weight and Jade-Pak 88-P losing 1.0% in weight. Thus, it was decided to test the Cast-O-Last G and Jade-Pak 88-P for a period longer than 24 hours to observe the effect of longer melt contact time.

TABLE 6-4

Results of Exposure Tests on Castable Materials

<u>Material Name</u>	<u>Manufacturer</u>	<u>Change (Wt. %)</u>	<u>Remarks</u>
Harchrome	Harbison-Walker	-11.7	Sheared off at melt interface
Harchrome G	Harbison-Walker	-5.9	Attacked at melt interface
H. W. Chrome	Harbison-Walker	-27.8	Attacked both at interface and in melt
Cast-O-Last G	Harbison-Walker	+1.5	Good appearance
Alfrax 66	Carborundum	-5.5	Melt preferentially attacking fine grains leaving coarse surface
Jade-Pak 88-P	A. P. Creen	-1.0	Good appearance

The Cast-O-Last G and Jade-Pak 88-P were tested 50% immersed at 1500°F for 100 hours. Both had a good appearance after exposure. The Cast-O-Last G gained 8.9% in weight while the Jade-Pak 88-P gained 1.6% in weight. Based on these tests, both should perform well.

Even though Alfrax 66 did not perform particularly well in the tests, it has already been proven suitable for backup and gas space service in pilot-scale and demonstration-scale gasifiers. Although the other five refractory samples were fresh material just received from the manufacturers, in the case of Alfrax 66, material that had been on hand for at least 3 or 4 years was used. Although the material was stored in a heavy-wall plastic bag, it is thought possible that some deterioration in binding power may have occurred.

(Metals)

Two tests were carried out on metals to evaluate their possible application in special locations such as a melt barrier between highly resistant fused-cast bricks and less resistant insulating materials. An example of such a use might be in a melt withdrawal nozzle where it is desired to minimize the total thickness of refractory while providing adequate thermal insulation. Nominal chemical compositions of the metals tested are shown in Table 6-5.

TABLE 6-5

Chemical Composition of Metals

<u>Material Identity</u>	<u>Nominal Chemical Composition (Wt. %)</u>
Uniloy	50% Cr, 49% Ni, 1% Ti
Cobalt-Chrome Alloy	80% Co, 20% Cr
LT-1 cermet	80% Al ₂ O ₃ , 20% Cr
Inconel 671	51.6% Ni, 48% Cr, 0.4% Ti
Inconel 601	75.5% Ni, 23% Cr, 1.5% Al
Haynes 25	50% Co, 20% Cr, 15% W, 10% Ni, 5% other

The first metals test involved five specimens: Inconel 601, aluminized Inconel 601, Inconel 671, Haynes 25, and Haynes cermet LT-1. The four metals were suspended on wires so that half of each specimen was immersed in the melt and half above the melt. The cermet sample was small and was fully immersed at the bottom of the melt bed. The samples were tested at 1500°F for 316 hours. When the specimens were removed at the end of the test, it was found that at some point in the test the wires suspending the metal specimens had corroded through and permitted the specimens to drop into the melt and to contact each other. As a result, electrolytic corrosion may have occurred. As shown in Table 6-6, all four metal specimens were badly corroded and easily broken. The cermet sample, on the other hand, showed no visible corrosion and had increased in weight by 0.15%.

TABLE 6-6

Results of Exposure Tests on Metals

<u>Specimen Identification</u>	<u>Corrosion Results</u>
Inconel 601	Badly corroded and broken
Inconel 601, aluminized	Badly corroded and broken
Inconel 671	Badly corroded and broken
Haynes 25	Badly corroded and broken
Haynes LT-1 (cermet)	0.15% weight increase, no visible corrosion

6.1 Corrosion Tests (Continued)

(Castable Materials) - Continued

A second metals test was carried out using a much shorter test time so that the suspension wires would not be subject to failure. In this second test, it was decided to test only those metals that earlier Rockwell tests had shown to have good resistance to high Na_2S -content melts. The resistant metals were Inconel 671, aluminized Inconel 671, and an 80% cobalt and 20% chrome alloy. There was no aluminized Inconel 671 available on hand. There was, however, a specimen of aluminized Uniloy. Uniloy is made by Universal Cyclops Company and is almost identical to Inconel 671 made by International Nickel Company (50% Cr, 49% Ni, and 1% Ti for Uniloy versus 48% Cr, 51.6% Ni, and 0.4% Ti for Inconel 671). Thus, it was decided to substitute Uniloy for Inconel 671, and Uniloy, aluminized Uniloy, and an 80% cobalt-20% chrome alloy were tested. The result of a 1500°F/68-h test of these metals is shown in Table 6-7. The aluminized Uniloy gave the extremely low corrosion rate of 0.001 in./year, Uniloy the low rate of 0.035 in./year, and the 80% cobalt-20% chromium alloy the high rate of 1.87 in./year.

TABLE 6-7		
<u>Results of Corrosion Tests on Metals</u>		
<u>Specimens</u>	<u>Immersion</u> <u>%</u>	<u>Corrosion Rate</u> <u>in./yr*</u>
Uniloy, aluminized	50	0.001
Uniloy	50	0.035
80% cobalt, 20% chrome	50	1.87
*Calculated from weight loss data.		

6.2 Materials Data Review

The objective of this review was to evaluate corrosion data on materials of construction for black liquor gasifiers so as to

6.2 Materials Data Review (Continued)

provide input for the conceptual design of the new pilot unit. The review focused on three locations in the gasifier where refractory materials are needed:

- The inner surface of the gasification zone which is in continuous contact with agitated melt at 1650-1850°F and 1-20 atm pressure.
- The inner surface of the drying zone which is exposed to melt droplets, droplets of partially dried black liquor, and product gases. Temperatures could range from 900°F to 1850°F.
- The surface between the inner surface of the gasification zone and the thermal insulation or metal shell.

The review also included metals since some design concepts could result in direct contact between metal and high-temperature melt.

Although this study is aimed at the evaluation of materials for black liquor gasifiers, a major fraction of the available information was developed in connection with other processes. The most closely related processes are (1) the Molten Salt Coal Gasification Process, which involves conditions of temperature, pressure, and melt composition quite similar to those of the black liquor process; (2) the Aqueous Carbonate Process (ACP) for flue gas desulfurization, which includes an atmospheric pressure reactor in which sodium sulfate is reduced to sodium sulfide under conditions reasonably close to those in a black liquor gasifier; and (3) black liquor incineration, which produces essentially the same melt as gasification. Other processes that are less closely related include molten salt waste destruction, glass manufacturing, and slagging coal gasification. Only those studies believed to be pertinent to the black liquor application were reviewed in detail. The review included unpublished Rockwell data.

(Data on Fused-Cast Refractories)

Early work on the Molten Salt Coal Gasification Process indicated that key requirements for a material to resist attack by a molten sodium carbonate/sulfide mixture at temperature near 1800°F were high-alumina content and low porosity. In these initial studies, Monofrax A, a fused-cast alpha alumina material, was found to have the lowest corrosion rate of 25 commercial refractories.²⁹ More recent work introduced the consideration of such factors as melt penetration and thermal shock in selecting the refractory.

6.2 Materials Data Review (Continued)

(Data on Fused-Cast Refractories) - Continued

The resistance of alumina to corrosive attack is believed due to the formation of a protective film of sodium aluminate, which is quite insoluble in the melt.²⁴ The melt has a very strong wetting ability and readily penetrates cracks and pores in ceramic bodies. As a result, low-density alumina and bricks made by conventional techniques of any composition tested have been found to be attacked by high-temperature melt. High-purity, high-density slip-cast alumina (e.g., Coors AD-998) is at least equal to fused-cast alumina in corrosion resistance and has other properties that are superior due to its uniform fine grain structure. This material would be uneconomical as a lining material for the gasifier vessel, but is useful for specially shaped components where melt resistance is required.

When fused-cast alumina blocks are formed, the outer surfaces, which are in contact with graphite molds, cool more rapidly than the interior material, resulting in the development of a finer grain structure at the as-cast faces. This structure retards melt penetration, causing the as-cast faces to have properties different from cut faces when contacted by melt. This effect is apparent in the data of Table 6-8. The greater expansion at cut faces can lead to bowing of specimens that have cut and as-cast faces on opposite sides. Table 6-8 is based on tests conducted at Rockwell with a melt containing 73% Na₂CO₃, 22% Na₂S, and 5% NaCl, and a cover gas of 80% N₂ and 20% CO₂. The two Monofrax materials listed in the table were manufactured by the Carborundum Company. Their properties and the properties of other Monofrax refractories are summarized in Table 6-9.²⁵

TABLE 6-8					
<u>Corrosion of High-Density Alumina in Carbonate-Based Melts</u> <u>at 1742°F</u>					
<u>Alumina</u>	<u>Melt</u> <u>Impurities</u>	<u>Corrosion</u> <u>Rate</u> <u>(in./yr)</u>	<u>Length</u> <u>of Test</u> <u>(h)</u>	<u>Expansion</u>	
				<u>Face</u>	<u>(%/yr)</u>
Monofrax A	S ⁼ , C	<0.03	500	Cut	1.7
Monofrax A	S ⁼	<0.01	6600	As-cast	0.2
Coors AD-998	SO ₄	<0.002	1500	-	0
Monofrax H	S ⁼ , C	~0.1	500	Cut	10
				As-cast	4

TABLE 6-9

Properties of Monofrax Refractories

	Monofrax				
	A ^a	M ^b	H ^c	E ^d	K-3 ^e
Maximum hot face temperature (°C)	1930	1870	1930	1930	1870
Modulus of rupture (kg/cm ² at 20°C)	411	246	105	400	560
Bulk density (g/cm ³)	3.76	3.4	3.06	4.09	3.9
Porosity (%)	1.1	1.9	4.9	5.4	4.2
Thermal expansion (cm/cm·°C x 10 ⁻⁶ ; 25 to 1400°C)	7.9	7.9	6.4	7.4	7.9
Thermal conductivity (W/m·K at 1477 K)	7.2	4.8	3.5	4.6	2.9
Specific heat (cal/g·°C; 0 to 1400°C)	0.28	0.28	0.28	0.25	0.25
Permeability (air at 25°C)	0	0	0	0	0
Chemical analysis (%)					
Al ₂ O ₃	99.34	94.5	93.9	4.7	60.4
SiO ₂	0.08	1.09	0.18	1.3	1.8
Fe ₂ O ₃	0.06	0.06	0.8	6.1	4.2
CaO	0.13	0.26	0.1	—	—
TiO ₂	—	0.02	0.3	—	—
Na ₂ O	0.39	3.9	5.6	0.1	0.3
Cr ₂ O ₃	—	—	—	79.7	27.3
Other	—	0.15	0.05	8.1	6.0

^aElectrically fused-cast alpha alumina in beta alumina matrix.^bElectrically fused-cast, approximately equal amounts of alpha and beta alumina.^cElectrically fused-cast beta alumina.^dElectrically fused-cast solid solution of chrome-spinel within a complex chrome-alumina spinel matrix.^eElectrically fused-cast solid solution of alumina-chrome within a complex chrome-alumina spinel matrix.

6.2 Materials Data Review (Continued)

(Data on Fused-Cast Refractories) - Continued

Some applications of these materials involve melts containing sodium hydroxide which may be formed in situ by the reaction of steam with the carbonate. High concentrations of hydroxide markedly increase the corrosion of alumina, as shown in Table 6-10.²⁶

TABLE 6-10			
<u>Corrosion of Alumina in Melts Containing Sodium Hydroxide</u>			
Alumina	NaOH (Wt. %)	Corrosion Rate (in./yr) ^a	
		650°C	800°C
Monofrax A	100	-	1.4-2.3
	14 ^b	0.1	0.1-0.2
Coors AD-998	100	-	0.9-1.5
	14 ^b	0.01-0.1	0.01-0.1

^aextrapolated from 200-h data

^b25 wt % CO₃⁼, 34 wt % SO₄⁼, 27 wt % Cl⁻, 14 wt % OH⁻

The somewhat higher corrosion rate for Monofrax A reported in Table 6-2 compared to Table 6-8 may be attributed to the 1% NaOH in the initial melt of the recent tests. Comparing the data of Tables 6-8, 6-2 and 6-10, there is a definite trend of increased corrosion as the concentration of NaOH increases.

The amount of NaOH in black liquor gasifier melt will depend to a considerable extent on the efficiency of drying in the drying zone since the NaOH concentration is limited by equilibrium in the reaction

6.2 Materials Data Review (Continued)

(Data on Fused-Cast Refractories) - Continued

A high CO_2 concentration inhibits NaOH formation and, therefore, corrosion by this mechanism. Water vapor and CO_2 concentrations predicted for the gasification zones of black liquor gasifiers are expected to result in an NaOH concentration of about 1% in the melt.

An extensive research program was conducted by Rockwell to evaluate alternative refractories and investigate the possible benefits of modifying known refractory compositions. In preliminary screening tests, several types of MgO and SiN refractories and a fused-cast alumina refractory containing CaO (Corhart SR-504C) were compared to Monofrax A in a 1,000-h test in 1832°F melt. The MgO and SiN refractories were severely attacked after 100 h of testing. The two alumina refractories showed a similar very low corrosion rate, but microscopic examination indicated significantly greater melt penetration into the Monofrax A than into the Corhart SR-504C (0.6 mm versus <0.1 mm after 1,000 h).²⁷

The effect of CaO in the Corhart refractory appeared to be to reduce the grain size and modify the composition of the grain boundary phase. Additional testing was therefore conducted to evaluate this effect.²⁸ Special modifications of Monofrax A were prepared by the Carborundum Corporation, and these were tested together with SR-504C and Monofrax M. The compositions of materials tested are given in Table 6-11 together with the indicated corrosion rates based on 5,000 h immersion in sodium carbonate melt containing 23% Na_2S at 1832°F .

All of the materials except the high-calcia modified Monofrax A exhibited corrosion rates that would be low enough for commercial application if surface attack represented the only form of deterioration. However, microscopic examination showed some intergranular penetration in all but the SR-504C samples. Many cracks that had not been present prior to testing were visible in the calcia modified Monofrax A samples. The main conclusions of this work were that (1) SR-504C is the most resistant fused-cast alumina, showing about the same corrosion rate and much less melt penetration than Monofrax A, and (2) Monofrax M has an acceptably low corrosion rate and can be considered as a replacement for Monofrax A based on cost and thermal shock resistance.

The thermal shock resistance of refractories for lining slagging coal gasifiers was evaluated by J. P. Singh et al. of ANL.²⁹ These refractories are exposed to high operating temperatures (2552 to 3182°F) and a very corrosive molten slag in a reducing gas atmosphere. Thermal transients during initial heatup and cooldown periods as well as process upsets

TABLE 6-11

Evaluation of Modified Fused-Cast Alumina RefractoriesCompound (Wt. %)^a

Refractory Trade Name	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	CaO	MgO	TiO ₂	Fluorides	Corrosion Rate (in./yr)
SR-504C	97.6	0.1	0.1	0.4	1.5			0.2	0.06
Monofrax M	94.5	1.09	0.08	3.9	0.26	0.15	0.02		0.08
Monofrax A	99.35		0.08	0.06	0.39	0.13			0.04
Modified Monofrax A Low calcia	98	0.24 ^a		0.42 ^a	1.57 ^a				0.06
Modified Monofrax A high calcia	97	0.42 ^a		0.37 ^a	2.7 ^a				0.15

^aCompositions are nominal except values with symbol (a) which represent determinations by Rockwell.

6.2 Materials Data Review (Continued)

(Data on Fused-Cast Refractories) - Continued

cause high thermal stresses that can lead to failure by cracking, spalling, and disintegration. In general, chromia-based refractories were found to have better corrosion resistance but poorer thermal shock resistance than alumina-based refractories in the slagging gasifier environment. A recently developed ribbon test was used to investigate thermal shock resistance by cycling sample specimens in the 363 to 1832°F temperature regime. It was found that the parameter R_{st} is very useful in evaluating thermal shock resistance:

$$R_{st} = (Y/\alpha^2 E)^{1/2}$$

where Y = fracture surface energy
 α = coefficient of thermal expansion
 E = elastic modulus

This parameter is proportional to the minimum temperature difference required to initiate the stable propagation of large cracks under thermal shock conditions. The considerations in refractory material selection are strongly influenced by the microstructure of the material. Materials of fine microstructure are used to arrest fracture initiation. However, this results in large stored energy at the time of fracture, which causes dynamic crack propagation and extensive damage. To minimize the extent of crack propagation, a material of low strength and high elastic modulus should be selected.

Thermal cycling of fusion-cast refractories was investigated by Chan and Nicholson (McMaster University, Canada).³⁰ The objective of the work was to determine the minimum temperature for the relaxation of thermal-induced stresses by the microstructural glass component of the refractory and thus to establish guidelines for the prevention of thermal stress failure. An alpha-alumina and an alumina-zirconia-silicate refractory were investigated. A threshold temperature (T_{th}) was determined above which the glassy phase viscoelastically damps out stresses induced by thermal cycling. For alpha-alumina, T_{th} was in the range of 1652-1742°F; for alumina-zirconia-silicate refractory, T_{th} was in the range 1112-1202°F.

6.2 Materials Data Review (Continued)

(Data on Fused-Cast Refractories) - Continued

The Carborundum Company supplied information on the critical threshold temperatures of various Monofrax refractories:

Monofrax	T _{th} (°F)
A	1652-1742
M	1202-1292
E	1292-1382
K-3	1562-1652

Monofrax A must be heated with great care to 1652-1742°F to avoid structural damage and the probability of thermal shock failure is much reduced if the refractory is cycled above that temperature range. Monofrax M has superior thermal shock resistance since T_{th} is only 1202-1292°F.

(Data on Castable Refractories)

Castable refractories were initially tested as candidates for the primary lining in contact with high-temperature molten salt. Among those tested were bubble alumina, Alfrax 66, and Alfrax 34492D, manufactured by the Carborundum Corporation, and Green Cast 97, manufactured by A. P. Green Corporation. After only 1 h of immersion in melt at 1800°F, the bubble alumina specimen had disintegrated, the Alfrax 34492D had gained about 33% in weight and cracked, while the Alfrax 66 and Green Cast 97 remained intact but had each gained about 13% in weight. After 18 h immersion, all specimens showed signs of disintegration.

Although these and other tests demonstrated that available castable refractories could not tolerate continuous immersion in hot melt, several were found to be resistant to intermittent melt contact, particularly at intermediate temperatures, and to be highly resistant to attack by low-Btu gas. The results generally indicated that high-alumina, high-density castables offered the most promise, and these were used successfully in the early molten salt test vessels in the gas space and as backup material for the more melt-resistant fused-cast refractories.

Cup slag tests, in which the refractory is tested while in the form of a thick-walled cup containing a small amount of melt, indicated that the melt penetrates a high-alumina castable without significantly affecting its integrity. Some volume expansion was noted, and it is believed that this may aid the performance of a castable by closing cracks and porosity at the surface.

6.2 Materials Data Review (Continued)

(Data on Castable Refractories) - Continued

The corrosion resistance of castable refractories for dry ash coal gasifiers was investigated by L. Y. Sadler et al. (U.S. Bureau of Mines).³¹ Gas environments included steam, H₂, CO, and typical high- and low-Btu gas mixtures. Exposure pressures ranged from 100 to 1000 psig, temperatures from 932 to 2012°F, and exposure periods from 50 to 2000 h. In some exposures, sodium and/or potassium hydroxide were introduced to simulate a high alkali environment. It was found that intermediate and low-alumina refractories had better resistance than high-alumina refractories. Alkali attack was not a serious problem.

The recent tests described in Section 6.1 confirmed the superiority of high-alumina castable refractories over high chrome materials with regard to melt contact resistance. A composition containing about 10% chromium oxide and 88% aluminum oxide also showed promise in these tests for short-term contact with melt at a temperature of 1500°F.

(Data on Metals)

A considerable effort has gone into the evaluation of metals, cermets, and metal coatings for service in molten salts. Metals and cermets tested at Rockwell include Uniloy 50491, Inconel 671, Inconel 600, Inconel 617, Inconel 625, Inconel 702, Inconel 706, Incoloy 800, Haynes 25, Haynes LT-2 cermet, 347 SS, 310 SS, 304 SS, 406 SS, Carpenter 20, Hastelloy G, Hastelloy N, Hastelloy X, Hastelloy F, Hastelloy B, Hastelloy C, Zircaloy-2, Kanthal A-1, chromium, tantalum, molybdenum, cobalt, and platinum.³² In addition, tests have been conducted on alloys coated by the Alonizing and Aluminizing processes and on several experimental alloys produced specifically for molten salt service.

The results of work with various iron, nickel, chromium alloys showed that resistance to corrosion in sulfide-containing melt improves with increased chromium content. Nickel was found to be superior to iron as an alloying agent, although the possible formation of NiS, which melts at 1467°F, is of concern for very high nickel alloys. The most promising alloy in this series was found to be one containing approximately 50% chromium and 50% nickel. This was offered commercially as Uniloy 50491 and Inconel 671, both of which contain a small amount of titanium in addition to the chromium and nickel. These alloys are no longer available as standard products; however, Inco Alloys offers an alloy consisting of approximately 40% chromium and 60% nickel (Inconel 72) in the form of welding wire, and it is

6.2 Materials Data Review (Continued)

(Data on Metals) - Continued

anticipated that the 671 alloy could be made available on special order. The 40/60 chrome-nickel alloy is marketed as an arc-aprayed coating to protect recovery boiler tubes.²³

The early tests showed Uniloy 50491 to have a corrosion rate less than about 0.05 in./year in sulfide-containing melts at temperatures below about 1472°F and to have erratic corrosion behavior at higher temperatures. The recent tests with simulated black liquor melt generally confirmed these findings, with a rate of 0.035 in./year at 1500°F.

In view of the indicated resistance of Al_2O_3 and chromium metal to corrosion by sulfide-containing melts, efforts have been made to gain the benefits of these materials by incorporating them into coatings and cermet materials.

The coating studies involved diffusing a film of aluminum or chromium into the surface of alloys. Although both types of coating showed some promise, the aluminum coatings gave the best results and were tested on numerous base alloys. As expected, the most corrosion-resistant base alloy (Uniloy 50491 or Inconel 671) gave the best results when coated. In one test series, Inconel 671 samples aluminum-coated by the Alonizing process showed a corrosion rate of only 0.09 in./year when tested for 250 h in a melt containing 62.5% Na_2CO_3 , 13.5% Na_2S , 9.5% Na_2O , and 14.6% ash and other salts. The tests reported in Section 6.1 confirm the value of aluminum diffusion coatings in reducing the corrosion rate of the Uniloy alloy. The protection afforded by these coatings is attributed to the formation of aluminum oxide on the surface.

The combination of Al_2O_3 and chromium metal in the form of a cermet gave outstanding results. The alloy tested contained 23% chromium and 73% Al_2O_3 and was produced by the Haynes Stellite Division of Union Carbide Corporation (now the Stellite Division of Cabot Corporation). Although this cermet is no longer manufactured, the test results are of value in showing that a resistant material of this type can be made, if required for future gasifier components. In early corrosion tests, the material showed corrosion rates of only a few mils per year at temperatures as high as 1832°F. Its resistance to simulated black liquor melt is confirmed by the recent tests.

(Pilot and Demonstration Plant Materials Experience)

The unit used for the past pilot tests of black liquor gasification is a brick-lined vessel about 4-ft OD by 15-ft high. It has been used for a variety of test operations

6.2 Materials Data Review (Continued)

(Pilot and Demonstration Plant Materials Experience) - Continued

including combustion, gasification and reduction reactions. Table 6-12 summarizes the operations experienced by the existing lining of the vessel. The lining in the lower 8 feet was installed in September, 1975. It consists of 6-in.-thick Monofrax A blocks installed with a thin layer of 3449-2D mortar between blocks and backed up by a 1/2-in.-thick layer of Alfrax 66XF castable refractory between the Monofrax blocks and the stainless steel shell. The top 5 feet of the vessel was added to the unit early in 1978 and lined with a 6-in.-thick layer of Alfrax 66 castable, which was baked out during the pre-heat phase of the test of 24 March through 3 May, 1978.

The lining has experienced extremely severe service with 17 separate heatups and cooldowns during which the rate of temperature change greatly exceeded the $<100^{\circ}\text{F}/\text{h}$ recommended for Monofrax A. A variety of salts have been used with sulfur compounds constituting up to about 50% of the melt in some tests. Melt temperatures reached 2000°F . In the two film combustion tests, temperatures well in excess of 2000°F were attained prior to draining. Most of the tests were conducted under reducing conditions, but some were conducted under oxidizing conditions.

Although a quantitative assessment of refractory condition has not been done, visual inspection indicates that both the Monofrax and exposed Alfrax 66 generally are intact and serviceable. Some surface spalling has occurred on the inner surfaces of the Monofrax blocks. It is estimated that the spalling has reduced the thickness of the blocks by 1/2 to 2 in. over the total period of service with the greatest damage near the bottom of the vessel.

Molten salt coal gasification was tested in a larger development unit, which was built by Rockwell in 1978 and operated in a series of nine runs during the period November 1978 through June 1981.³⁴ A schematic of the unit is presented in Figure 6-1. The principal construction materials in contact with molten salt were Monofrax A and Alfrax 66. Coal was gasified at feed rates up to 1.0 ton/h using air at pressures up to 20 atm.

The initial Monofrax lining was severely damaged in May 1979 when water inadvertently entered the gasifier during operation, causing a very rapid cooldown and solidification of the melt inventory. Attempts to remelt the solidified pool by use of a coke/air burner lance were not successful. Very high temperature transients were generated during this operation, which undoubtedly contributed to brick damage. The frozen material was finally jackhammered from the vessel, a procedure

TABLE 6-12

Operations of Existing Pilot Unit With Present Lining

Dates	Type of Test	Total Operating Time (h)	Time of Melt in Vessel (h)		
			Total	Above 1300°F	Above 1700°F
10/22-11/07/75	Sodium sulfate reduction	388	20	15	5
01/21-02/08/76	Film combustion in Na_2CO_3	566	146	146	129
06/07-07/17/76	Sodium sulfate reduction, coal gasification, and water combustion	932	760	721	619
10/05-10/30/78	Sodium sulfate reduction	593	113	113	103
06/13-06/24/77	Film combustion in Na_2CO_3	276	108	108	100
07/12-07/21/77	Offgas system test (Na_2CO_3)	220	78	78	24
08/31-09/12/77	Waste combustion in Na_2CO_3 / K_2CO_3 mix	283	150	145	62
03/24-05/03/78	Sodium sulfate reduction	888	216	216	192
02/08-02/20/79	Sodium sulfate reduction	293	168	168	156
02/29-03/07/80	Sodium sulfate reduction	168	96	96	96
06/22-06/26/80	Sodium sulfate reduction	156	84	84	84
03/02-03/06/81	Sodium sulfate reduction	108	108	108	108
03/16-03/18/81	Liquid injection test Na_2CO_3 / NaCl mix	108	60	60	60
07/13-07/17/81	Waste combustion Na_2CO_3 / NaCl mix	108	88	88	88
07/21-07/25/84	Black liquor gasification	97	45	45	45
08/10-08/15/84	Black liquor gasification	120	53	53	53
04/12-04/18/84	Black liquor gasification	136	47	47	47
		5512	2340	2291	1971

Figure 6-1. Molten Salt Coal Gasification Development Unit

6.2 Materials Data Review (Continued)

(Pilot and Demonstration Plant Materials Experience) - Continued

that probably caused additional damage. Inspection of the wall following cleanup indicated that spot repairs would be impractical; therefore, all of the Monofrax blocks except those in the melt withdrawal chamber were replaced.

The initial liner had been assembled without mortar; however, some edge spalling was observed after the initial heatup cycle (without melt). This was identified as pinch spalling caused by excessive stresses at points of block-to-block contact. As a result, the second lining was installed with mortared joints. In addition, the new blocks were cast with a curved back face to provide a smooth slip surface against the castable refractory backing material.

The new lining was used for all of the remaining runs, which totalled 629 h of operation with high temperature molten salt in the gasifier. The salt was primarily sodium carbonate with 0 to 13% Na_2S and 0 to 25% coal ash. Melt pool temperatures during steady-state operation were in the range of 1750 to 1950°F. The vessel was exposed to atmospheric air at ambient temperature between runs. Inspection of the lining after each of the runs revealed no pinch spalling, indicating that the design changes were effective in preventing this form of damage; however, some face spalling was evident. Several flat sheets of Monofrax approximately 1/4 in. thick were found at the bottom of the vessel after each run indicating that some brick damage had occurred; however, the total quantity of spalled material did not represent a significant fraction of the Monofrax A lining. It is believed that the observed face spalling was caused primarily by the rapid thermal transients, primarily cooling, known to have occurred during the runs, augmented by melt attack in zones of crack formation.

The Alfrax 66 castable on the interior of the gasifier above the Monofrax A lining and on the gasifier head showed excellent resistance to the product gas and entrained melt droplets. In general, both refractories endured the molten salt gasification environment during the five test runs without significant damage.

Prior to the last run, Monofrax A in the melt withdrawal chamber was removed and replaced with Monofrax M. Limited inspection after the run, which included only 83 h of operation with high temperature molten salt, indicated the interior to be in good condition.

6.2 Materials Data Review (Continued)

(Pilot and Demonstration Plant Materials Experience) - Continued

Additional experience with refractories was gained during the operation of Rockwell's Aqueous Carbonate Process demonstration plant for sodium sulfate reduction. The plant was built at a Niagara Mohawk power station for the purpose of demonstrating a new process for desulfurizing flue gas, and included an 11-ft. diameter atmospheric pressure reactor. Sodium sulfate produced during SO₂ absorption is reduced to sodium sulfide by contact with carbon and air in a molten sodium carbonate medium. General arrangement of the refractory lining in the reactor is shown in Figure 6-2. Ten tests were conducted over a period of 2 years, including 172 days with high temperature melt in the reactor. In addition to heatup and cooldown, operation involved numerous short thermal cycles and several periods of temperature operation above 2000°F.

The vessel lining was inspected several times during the operating period. In general, the Monofrax A lining exposed to the melt pool was in satisfactory condition near the top; however, extensive damage was observed in the lower, highly agitated region of the pool. The main types of refractory damage were cracking, surface spalling, and abrasion. A thorough examination after the termination of the tests led to the assessment below.

The Monofrax A portion of the lining suffered unexpectedly severe deterioration, especially near the bottom of the conical vessel, where almost 50% of the 14-in. lining was lost. The wear experienced was much greater than expected on the basis of laboratory tests that measured chemical corrosion. It was indicated that cracking, erosion, and spalling combined with chemical corrosion caused most of the extensive wear.

The observation of cracks indicated strongly that thermal shock played an important role in the overall wear process and reduced the resistance of the ceramic to abrasion by circulating debris. When crack propagation advanced to the point that cracks parallel to the hot face met behind the face, spalling took place. Propagation of the cracks possibly was accelerated by the formation of beta-alumina on the crack surfaces. Since beta-alumina has a higher specific volume than the bulk material, the buildup of the beta-alumina layer could tend to widen the crack.

Figure 6-2. ACP Demonstration Plant Reducer Vessel

6.2 Materials Data Review (Continued)

(Pilot and Demonstration Plant Materials Experience) - Continued

The block orientation may have been a contributing factor to the observed degradation. Shrinkage cavities (vugs) formed during casting had been filled with Alfrax 66 and located on the upper faces of the blocks. Melt penetrated the mortar between bricks and the Alfrax filling and was then able to attack the interior of the Monofrax blocks, particularly in those areas in which thermal cracks had formed. This kind of damage probably could have been reduced by locating the shrinkage voids on the back side of the blocks rather than on the horizontal faces.

Since thermal-shock-induced crack formation was identified as the main mechanism initiating wear, a study was conducted to model significant thermal events that occurred during heatup or operation. It was shown that thermal shocks exceeding 100°F/h penetrated 3 to 5 in. deep into the Monofrax blocks, thus supporting the proposed mechanism for spalling described above.

Typical cracking patterns in refractories exposed to thermal shock are shown in Figure 6-3.²⁵ Sudden cooling causes cracks at a right angle to the block's surface. Contraction of the outer surface causes tension that can lead to failure. Sudden heating often produces cracks at an angle of approximately 45° to the heated surfaces. This causes compression balanced by interior tensile stresses. Shear induced by the compression may cause surface spalling.

Figure 6-3. Typical Cracking Patterns in Refractory Bricks Exposed to Thermal Shocks; Cooling on Left, Heating on Right

6.2 Materials Data Review (Continued)

(Pilot and Demonstration Plant Materials Experience) - Continued

Other failure mechanisms, especially corrosion, absorption of melt, or penetration of melt into cracks and mortar, aggravated the refractory deterioration but were not the initiating mechanisms. Corrosion or chemical attack of the bulk refractory was limited to the first 1 in. of material inward from the hot face; up to 0.3 wt. % sulfur was detected in this regime. With the exception of areas adjacent to cracks, sulfur concentration was on the order of hundreds of parts per million in the rest of the ceramic bricks.

The main conclusion of this evaluation was that the observed damage was caused by the formation of thermal shock cracks in the Monofrax A blocks followed by salt penetration and the formation of beta-alumina over the inside cracked surfaces. The resulting volume expansion probably accelerated the propagation of cracks. Erosion by circulating debris in the lower portion of the melt pool may have been a contributing factor. Another factor may have been the formation of sulfate compounds on the hot surface. This material absorbed moisture when the vessel was cooled down, and the absorbed water may have accelerated deterioration. It was further concluded that such damage could be minimized by (1) improving control of heating and cooling transients to avoid thermal shocks, (2) eliminating vugs or locating them on the cold face, (3) incorporating a debris sump in the vessel bottom to reduce abrasion wear, and (4) keeping the vessel warm at all times to minimize moisture absorption by the residual salts.

SECTION 7

7.0 CONCLUSIONS AND RECOMMENDATIONS

All of the objectives of this extension to Champion International Corporation's Phase II study of black liquor gasification have been met. Conclusions reached and recommendations offered are summarized in this section.

7.1 Conclusions

On the basis of the work done during this phase of the effort, it is concluded that:

- A new pilot gasifier has been conceptually designed to be used at the existing Rockwell International test site, which gasifier will have a throughput sufficiently high and a heat loss sufficiently low to permit production of product gases with a heating value of up to about 100 Btu/scf on a dry basis and melt with reduction of sulfate to sulfide of up to about 90%.
- It is possible with the new pilot gasifier and existing auxiliaries to operate at pressures up to about 3 atm.
- Two types of commercially available spray nozzles - solid-cone and two-fluid nozzles - potentially could deliver black liquor feed droplets within the required range of diameters and spray pattern. In addition, a novel splash tube spray nozzle has been conceived to meet the specific requirements of black liquor gasification and its basic feasibility has been demonstrated with a water feed.
- A melt discharge and quench system has been designed and incorporates special features to prevent plugging of the melt transfer line and to shatter the melt in a closed pressurized environment.
- Materials of construction for the new gasifier are available which should offer good thermal insulation and good resistance to chemical corrosion and thermally-induced degradation.
- Everything found during these studies continues to support the conclusion that black liquor gasification shows high potential as an alternative to recovery boiler technology.

7.2 Recommendations

On the basis of the work done during this phase of the effort, it is recommended that:

- Development of black liquor gasification technology should continue. The first step should involve detailed design, construction, and operation of the new pilot gasifier to be followed by a demonstration of the technology on a significantly larger scale.
- Operation of the new pilot gasifier system at as high a pressure as possible within reasonable economic constraints should be investigated.
- Potentially applicable black liquor spray nozzles should be evaluated experimentally.

SECTION 8

8.0 REFERENCES

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