ASSESSMENT OF BLACK LIQUOR RECOVERY BOILERS

PREPARED FOR
THE UNITED STATES DEPARTMENT OF ENERGY
DIVISION OF MAGNETOHYDRODYNAMICS
CONTRACT NO. 01-78-ET 11058.000

May/1979

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EXECUTIVE SUMMARY

In the paper making industry, pulpwood chips are digested and cooked to provide the pulp going to the refining and paper mills. Black liquor residue, containing the dissolved lignin binder from the chips, with a concentration of 12 to 16 percent solids, is further concentrated to 62 to 65 percent solids and mixed with salt cake, Sodium Sulfate (Na_2SO_4). The resulting concentrate of black liquor serves both as a fuel for generating steam in the boiler and also as the mother liquid from which other process liquors are recovered and recycled.

Because the black liquor fuel contains high alkali concentrations, 18.3 percent sodium, 3.6 percent sulfur an amount typical of mid-western bituminous coal, and measurable amounts of silica, iron oxides and other species, the black liquor boiler experience was reviewed for application to MHD boiler technology.

Direct comparison of salient features of black liquor boiler and MHD boiler design are:

1. High alkali concentrations in the combustion gases

   o Carry over of Sodium (Na) in the black liquor boiler is about 0.2 percent by weight of combustion gases compared to 1.0 percent Potassium (K) in the MHD boiler. Corrosion and thermodynamic behavior of K and Na are similar under the same concentrations and operating states.

2. Particulate loading

   o Particulate loading in the MHD combustion gases is about 4 times as high as for the black liquor combustion gases, 77 grains mass flow rate compared to 18. About one tenth of the loading in the MHD cycle is acidic slag particles.

3. Operating States

- MHD gases enter the radiant boiler at 3650°F compared to 2800°F for the black liquor boiler (and 3400°F for conventional coal fired boilers).
- MHD employs fuel rich combustion to limit NOx formation. The resultant reducing atmosphere is corrosive to metal and refractory materials and exists through a high temperature air heater in direct fired systems and through the secondary radiant furnace in the separately fired systems. (This extensive reducing zone occurs because excess air cannot be added until an available injection point is reached after gas temperatures are below 2600°F, otherwise the recombustion could produce additional NOx). Reducing atmosphere in the black liquor boiler occurs only at the hearth (furnace bottom) where maximum reduction of NA_2SO_4 to N_2S is desired.

- Gas temperatures are restricted to 1700°F into the black liquor superheater. This temperature level is high enough to produce superheated and reheat steam and low enough to reduce the concentration of molten salt carryover from the radiant furnace. In the MHD cycle the temperature level into the superheater may be as high as 2400°F and the level does not drop to 1700°F until the exit from the reheater.

- The highly corrosive molten range of the sodium salts in the black liquor boiler is from 1800°F and 1600°F. Potassium salts in the MHD cycle have more complex constituents and the molten range of temperature is higher and more extensive, but the most severe corrosive range extends from 2100°F to 1950°F. In addition, molten range for the corrosive (acidic) slag extends from 3200°F to 2200°F. Since there are operational overlaps of areas which can be contacted by molten alkalies or molten acidic salts material selection is made more difficult in the MHD design.

- Steam temperatures in the black liquor boiler do not exceed 850°F and pressures are 1500 psig. Coal fired MHD/steam cycles where system efficiency is of paramount importance provide superheat and reheat steam to 1000°F at higher pressures.

- Combustion gas velocities in the black liquor boiler are in a 15 to 20 feet per second range. In the MHD radiant boiler velocities which are restricted to allow dwell time for NOx to revert to N_2 and O_2 are at 50 feet per second. Because of cost and performance requirements for MHD boilers, velocities in the other boiler sections approach conventional velocities of 100 feet per second. These higher velocities plus the slag content make MHD combustion gases more erosive than those in the black liquor boiler.

Black liquor boiler design has adopted the following techniques for successful operation of black liquor boilers:

1. In the high temperature, 1800°F, reducing atmosphere at the hearth, a combination of sacrificial studs implemented on diffusion coated tubes, hard face welding protection, "Sandvik" bimetallic tubes, and refractory coating are employed. Compared to carbon tubes with a metallic coating, the increased cost factors for diffusion coating is 5, hard face welding or studs with refractory is 10, and composite tubing is 15.

2. Water cooled deflectors are installed to limit the high temperature impact of the erosive gases on superheater surface. Large pitch, 12 inch lateral spacing, and in-line array to lessen impact area reduce slag buildup. Platen" weld protection reduces erosion and inhibits buildup of slag so that interlocking between adjacent tubes is avoided. Retractable, half length soot blowers allow

easy access to tube surface and increase effectiveness in removing tube deposits.

3. Since the black liquor boiler is a process boiler which also produces plant steam, design features can emphasize utility rather than performance. Input is usually around 300 MWth and even on a relative basis the thermal duty of the furnace is low since combustion gases at the maximum temperature of $2800^{\circ}F$ have to maintain sufficient temperature and enthalpy to superheat steam to $850^{\circ}F$ downstream. Compared to subbituminous coal, the black liquor contains three times the amount of increased Na compounds. This excess lowers the melting point of slag by $300^{\circ}F$. Resulting slagging and fouling in the furnace reduce the effectiveness of the heat transfer surface. In addition, the lower gas temperature in the black liquor furnace reduces the radiative heat transfer (by about 50%) compared to the conventional furnace. For these reasons, heat transfer in the black liquor furnace is about one tenth that of modern conventional furnaces. (MHD furnace unit heat transfer is predicted for first generation MHD plants to be about one third that of modern conventional practice.) Economizer thermal duty, as another design example, is restricted so that outlet gas temperatures are above the condensation of sulfur acids which could cause corrosion.

Review of factors influencing design of the black liquor boiler places it intermediate in difficulty compared to conventional boiler design and MHD boiler design. The increased severity of MHD operating parameters is evidenced in the following table:

TABLE A

Parameter	Black Liquor Boiler	Conventional Boiler	MHD Boiler
Gas flame temperature, ^{o}F	2800 to 3000	3400	3700
Gas inlet to superheater, ^{o}F	1700	2200	2445
Alkali content, % w	0.15 (Na)	traces	1.0 (K)
Particulate loading $\frac{\text{grains}}{\text{Ft}^3\text{-sec}}$	18	7 to 10	77
Molten zone, ^{o}F (highly corrosive)	1600 to 1800 (Na)	2400 to 3100 (slag)	1950 to 2100 (K) 2200 to 3200 (Si)
Steam conditions, ^{o}F, Psig	850, 1500	1000, 2400	1000,2000 to 4000
Reducing Zone (highly corrosive)	Hearth	NA	Topping side substantial section of boilers
System Size, MWt	300	to 2000	2000
Major Design Objectives	Process	Power prod.	Power prod.

The protective techniques and design features which allow successful commercial operation for the black liquor boiler are valid but only as starting points for design of analogous MHD boilers.

The successful design of black liquor boilers provides confidence that the additional steps to satisfactory MHD boiler design can be accomplished technically. Increased cost per square foot of surface for the MHD boilers plus the increased surface requirements for a given duty will create economic challenges. Recent advancements in boiler design for conventional as well as specialized applications, with major application to improved availability, add assurance that if commercial applicability for MHD boilers exists, design problems can be solved.

SECTION 1.0
INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Black liquor is the residual concentrated liquid resulting from cooking pulpwood in an alkaline solution as part of the Kraft (sulfate) process of paper making. In recovery furnaces, heat energy from the combustion of organic liquor constituents is used to produce steam, and inorganic constituents are recovered as molten smelt. The corrosive black liquor recovery furnace may have design application to the Magnetohydrodynamic (MHD) components exposed to corrosive high temperature operating conditions. The report surveys and assesses black liquor design practices and experiences as they might apply to MHD components.

1.2 SIMILARITIES

Commercially operating black liquor recovery boilers and the open cycle MHD system boilers have in common high concentrations of alkali metals in the flue gas. In addition, high corrosion rates in the furnace and slag removal from heating surfaces are major problems for both systems.

The following black liquor boiler design features have been employed to remain operable in the corrosive-erosive environment:

- Sacrificial pin-studs spaced 1/2 inch circumferentially (Ref. 1), on dual wall tubes with a diffusive metallic coating of chromium and aluminum-chromium
- A water cooled furnace screen to shield the superheater from high flue gas temperatures
- Use of a "platen" type, self-drainable, vertical, parallel flow superheater and reheater with a minimum lateral tube spacing of 12 inches. The wider lateral tube spacing is about three times that in the conventional subbituminous coal-fired unit. The platen type membrane wall may prevent the "keying" of the slag, and wider lateral tube spacing may lessen fouling and increase effectiveness of the soot blower.

- Half-length, retractable, steam soot blowers to remove deposits

1.3 DIFFERENCES

The following differences between the systems may constrain direct application to MHD systems:

- A substantially higher MHD plasma temperature of 3650°F (2283°K) compared to the flue gas temperature of 2800°F (1811°K) in the black liquor furnace (at the secondary and tertiary air zones)
- A higher heat absorption rate in the MHD radiant boiler compared to the black liquor furnace (ratio of 3 to 1)
- The higher steam pressure and temperature conditions (3500 or 2400 psig/1000°F/1000° F) proposed by different contractors for the MHD system compared to those in the black liquor system (1500 psig/ 875°F)
- Additional corrosive deposits in the MHD system as iron oxides (Fe_2O_3, Fe_3O_4) and potassium-iron trisulfates [$K_3Fe(SO_4)_3$]

1.4 COST COMPARISON

Since a detailed cost comparison is out of the scope of this study, this section contains only brief, generalized comparisons. Considering a carbon steel tubing with metallic coating as the base coat, diffusion coating costs about five to six times as much, hard face welding or studs with refractory at 10 to 15 times, and composite tubing 11 to 21 times (Ref. 1).

1.5 RECOMMENDATIONS

The black liquor boiler is an intermediate step from conventional boilers to MHD boilers. Turndown, corrosion, and cost increases of black liquor boilers compared to conventional boilers would be analogous to those in going from black liquor boilers to MHD boilers.

Further study of the use of black liquor recovery boiler technology in the MHD system is warranted. To select proper alloys to resist oxidation and corrosion attack, more accurate thermochemical calculations using the Joint Army-Navy-Air Force (JANAF) tables and melting point data on MHD slag are required. In these calculations, governing factors would be temperature, CO/CO_2 ratio, SO_2 content, and combustion gas pressure.

Alternate approaches for MHD design such as gas quenching to eliminate corrosion and adherence problems due to molten seed should also be investigated. (Ref. 2)

SECTION 2.0

COMPARISON OF BLACK LIQUOR AND MHD SYSTEMS

2.1 REVIEW OF BLACK LIQUOR TECHNOLOGY APPLIED TO MHD

For reference, Appendix A contains black liquor boiler installation lists from the three leading manufacturers: Babcock and Wilcox Company (B&W), Combustion Engineering (CE), and Copeland Systems Incorporated subsidiary of Foster Wheeler Development Corporation (FW). Based on these lists, B&W has the most relevant experience. In addition, they have designed the largest capacity unit with the highest steam pressure and temperature (1500 psig/875°F) located at the Union Camp Corporation, Franklin, Virginia, with a firing rate of 1,200 tons/day of sulfate liquor. The consulting engineer on this unit was C.T. Main, Inc. CE has the widest black liquor boiler design experience of all the Engineering Test Facility (ETF) contractors or subcontractors. Their ETF downstream component design reflects black liquor boiler design by low heat absorption rate in the furnace; wider convection surface lateral spacing; three separate furnaces: slag recovery, seed recovery, and final oxidation. Their configurations resemble the three zones in the black liquor furnace: drying, reducing, and oxidizing.

The FW MHD design reflects black liquor boiler design only in the low furnace heat absorption rate (20 percent of the conventional coal-fired value) and a roof-fired, secondary furnace construction which is standard FW furnace design practice for low heating value fuels such as black liquor whose gross heating value is only 6,600 Btu/lb. FW does not appear to have considered the effect of potassium salts (K_2CO_3, K_2SO_4) in their design calculations.

In general, both conceptual designs (AVCO/CE, GE/FW) meet ETF operational goals as defined in their respective design criteria documents. In the CE design, the location of the low temperature air heater (LTAH), the effect of air leakage (to the gas side) on the seed/slag system, most of the selected tube metals, and the separation of dry seed (from slag) at the unbalanced operating conditions should be investigated further. The condensation of seed in the flue gas depends directly upon variables such as partial pressure of potassium compounds, inlet and outlet flue gas and air temperatures, uniform distribution of air to the vertical air heater panels, gas-to-air weight ratio, and predicted-to-actual heat transfer rate. These variables are difficult to define analytically at unbalanced operating conditions, and the design of the recovery furnace will need test verification.

In the FW design as applied to MHD, the following need verification: (1) the flue gas distribution from the spoiler to the radiant boiler, (2) plasma leakage through the dividing wall openings to the "unfired" secondary cavity, (3) the streamlined gas flow distribution at the radiant boiler exit, and (4) the superheater's performance under the variable thermal loads.

2.2 COMPARISON

The black liquor boiler hearth furnace and MHD radiant boiler operate with reducing atmospheres, and sodium (Na) and potassium (K) have similar chemical properties. Table 1 presents the gas constituents for the two systems. Under equal concentrations and the same physical state, potassium compounds are more chemically active and less thermally active (due to higher melting point) than sodium counterparts. While the volatility of potassium sulfate (K_2SO_4) is not as high as sodium sulfate (Na_2SO_4), it is highly volatile compared to other constituents in coal ash. In addition, the ratio of potassium-to-sodium in the coal ash or tube deposit is significant. Potassium has a greater tendency to form complex, molten sulfates which are more corrosive than their sodium counterparts.

TABLE 1

BLACK LIQUOR BOILER AND MHD SYSTEM GAS CONSTITUENTS

BLACK LIQUOR BOILER Furnace Hearth Area	MHD SYSTEM Radiant Boiler Inlet
CO, SO_2, SO_3	CO, SO_2,
Na_2O, Na_2S(solid), $NaCl$,	K_2O(solid), KCl,
KOH	-
H_2O, H_2S	H_2O
Superheater Inlet	Superheater
CO, SO_2, SO_3	CO, SO_2,
Na_2SO_3, Na_2SO_4	K, K_2SO_4(liquid)
Na_2CO_3, $NaCl$	KCl, KOH
	K_2O(solid)

To control fouling and corrosion in the convection surface, a platen type ("pencil" weld) surface with wide lateral tube spacing (minimum 12 inches) is adopted by all the black liquor boiler manufacturers. The lateral tube spacing for coal-fired boilers, black liquor boilers, and MHD-ETF (AVCO and CTE) boiler designs are shown in Figure 1.

Design parameters for a typical black liquor boiler and a number of MHD systems (Gilbert Baseline Plant, ETF-AVCO/CE and GE/FW) are shown on Table 2, and heat transfer surface design details are tabulated on Table 3. Systems operate under positive pressures, and the moisture content is practically the same (about 5 percent by weight). Flue gas temperatures are significantly higher in the MHD system than those in the black liquor boiler. Higher flue gas temperature and the presence

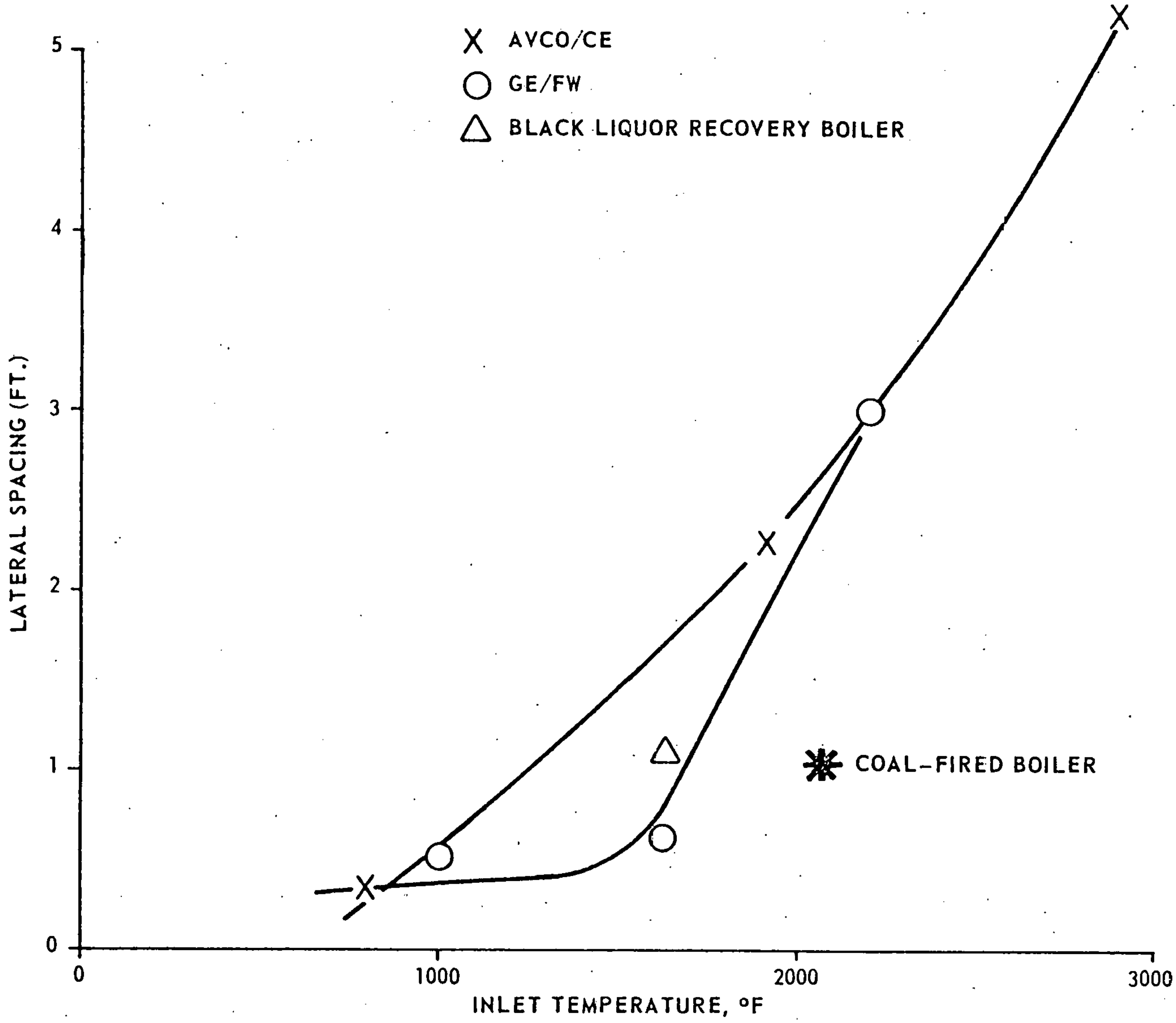


FIGURE 1
ETF CONVECTIVE PASS
TUBE SPACING (REF. 2)

TABLE 2

BLACK LIQUOR BOILER AND MHD SYSTEM DESIGN PARAMETERS

NO.	DESCRIPTION	BLACK LIQUOR SYSTEM (DESIGN RANGE)	MHD BASELINE (REV F)	AVCO/CE ETF DESIGN 2500°F AIR	AVCO/CE ETF DESIGN 3000°F AIR	GE/FW ETF DESIGN MHD/STEAM BOTTOMING	GE/FW ETF DESIGN STEAM BOTTOMING ONLY	REMARKS
1	Thermal Input, MW_t	290	2,000	271.5	299.3	250.0	175.0	
2	Steam Pressure/Temperature, Psig/$^{\circ}$F/$^{\circ}$F	1500/875/-	3690/1000/-	1250/950/-	1250/950/-	3500/1000/1000 2400/943/1000*	3500/1000/1000 2400/943/1000*	At throttle condition
3	Furnace Heat Liberation Rate, Btu/ft^3/hr	7,600 to 15,000	5,275	5,570	5,645	2,310	2,745	*ΔH steam/volume of the furnace
4	Furnace Heat Release Rate, Btu/ft^2/hr	450,000	2,750,000	1,150,550	1,160,800	650,150	744,300	Inlet thermal energy/furnace cross-sectional area
5	Heat Flux (heat available to furnace), Btu/ft^2/hr	30,000 to 42,000	500,000	405,400	415,050	301,000	303,425	*ΔH gas/furnace cross-sectional area
6	Heat Absorption in the Furnace, Btu/ft^2/hr	11,000 to 15,000**	66,000	29,000	29,350	15,175	17,500	*ΔH steam/projected area
7	Furnace Cross-Sectional Area ft x ft	47 x 47	50 x 50	20.8 x 20.8	20.8 x 20.8	18.0 x 36.0	29.5 x 36.0	
8	Furnace Width, ft	22 to 30	50	20.8	20.8	18	29.5	
9	Furnace Residence Time, seconds	3 to 4	1.8	2.0	2.0	2.0	2.0	
10	Radiant Boiler/Furnace Refractory Material	"KROMIGHT"	98% MgO Base + Bubble Alumina	High Magnesia Type (3 in. th.)	High Magnesia Type (3 in. th.)	H.W. Ruby	H. W. Ruby	
11	Maximum Flue Gas Temperature in the Radiant Boiler and Furnace, $^{\circ}$F ($^{\circ}$K)	2800(1811)	3650(2283)	3725(2325)	3700(2311)	3126(1992)	3175(2020)	
12	Flue Gas Temp. Entering Superheater, $^{\circ}$F ($^{\circ}$K)	1700(1200)	2445(1613)	Finishing Superheater 2940(1888) Primary Superheater 1000(811)	Finishing Superheater 2915(1875) Primary Superheater 975(797)	2111(1428) 2915(1875)	2000(1366)	
13	Particulate Loading Entering Superheater, grains/ft^2/sec.	18	77	77	77	77	77	
14	Flue Gas Temperature Leaving Superheater, $^{\circ}$F ($^{\circ}$K)	1300(977)	2080(1411)	800(700)	775(686)	1140(888)	1495(1086)	
15	Ash Fusion Temperature, $^{\circ}$F	1450/1061)	2220(1488)	2220(1488)	2220(1488)	2220(1488)	2220(1488)	
16	Melting Point, $^{\circ}$F ($^{\circ}$K) of K_2CO_3	-	1645(1169)	1645(1169)	1645(1169)	1645(1169)	1645(1169)	
	(under reducing zone) K_2SO_4	-	1955(1341)	1955(1341)	1955(1341)	1955(1341)	1955(1341)	
	Na_2CO_3	1563(1123)***	-	-	-	-	-	
	Na_2SO_4	1625(1158)***	-	-	-	-	-	

*ΔH = change in enthalpy in Btu/hr.
** = 40,000 Btu/ft^2/hr at the burner ports
*** = Under oxidizing zone

TABLE 3

BLACK LIQUOR BOILER AND MHD SYSTEM HEAT TRANSFER SURFACE DESIGN DETAILS

NO.	COMPONENT	BLACK LIQUOR SYSTEM	MHD (BASELINE-REV:F)	AVCO/CE ETF DESIGN	GE/FW ETF DESIGN
1	Radiant Boiler/Furnace				
	Vertical Gas Velocity, ft/sec	20	50	N.A.	15
	Tube Material	SA-226, STUD.	SA-213,T-22 STUD.	Aluminized SA-210C	SA-213,T-22
	Tube O.D.-in., Thickness-in., Spacing-in.	2.0/N.A./3.5	2.0/0.33/4.0	1.25/N.A./1.75	1.5/00.25/1.75
2	Screen Tubes				
	Superficial Gas Velocity, ft./sec.	15	DO NOT EXIST	DO NOT EXIST	DO NOT EXIST
	Tube Material	(SA-209,T-1)			
	Tube O.D.-in., Thickness-in., lateral and longitudinal spacing-in.	3/N.A./24&3.5			
3	Superheater (Parallel Flow)				COUNTER FLOW
	Superficial Gas Velocity, ft/sec.	10	40	N.A.	N.A.
	Tube Material	(SA-209,T-1) (SA-213,T-11)	SA-213,304 S.S.	SA-213,TP-304H T-22,T-11,SA-209 T-1,SA-210A1 SA-178	SA-213,TP-316H
	Tube O.D.-in., Thickness-in., lateral and longitudinal spacing-in.	2.5/N.A./12&3	2.0/0.55/12&3	Initial Superheater .2/N.A./4.5&4.5 Intermediate Superheater .2/N.A./13.5&4.5 Finishing Superheater .2/N.A./62.5&4	2.5/0.38/36&2.5
4	Reheater (Counter Flow)				
	Superficial Gas Velocity, ft/sec.	DO NOT EXIST	50	DO NOT EXIST	N.A.
	Tube Material		SA-213,304 S.S.		SA-213,TP-316H SA-213,T-22
	Tube O.D.-in., Thickness-in., lateral and longitudinal spacing-in.		3.5/0.20/9&6		2/0.165/7.5&2.75
5	Boiler Bank				
	Superficial Gas Velocity, ft/sec.	20	DO NOT EXIST	DO NOT EXIST	DO NOT EXIST
	Tube Material	SA-192			
	Tube O.D.-in., Thickness-in., lateral and longitudinal spacing-in.	2/N.A./6&4			
6	Economizer (Counter Flow)				High Pressure
	Superficial Gas Velocity, ft/sec.	35	33	N.A.	N.A.
	Tube Material	SA-216	SA-213,T-22	SA-178A	SA-209,T-14
	Tube O.D.-in., Thickness-in., lateral and longitudinal spacing-in.	2/N.A./8&4	2.25/0.12/4&4	2/N.A..4.5&4.5	2/0.257/6&4 Low Pressure N.A. SA-210,A-1 2/0.165/4&4

NOTE: N.A. = NOT AVAILABLE

of a liquid hydroxide (KOH) downstream of the superheater exit at 2060°F (1400°K) and a liquid chloride (KCl) downstream of the reheater exit at 1590°F (1139°K) significantly increases corrosion rates. Also, the flue gas entrance velocity to the MHD radiant boiler is about eight times that in the black liquor furnace, resulting in a higher erosion rate. A typical MHD system flow diagram is shown in Figure 2.

In the MHD system, most of the previous chemical equilibrium composition (CEC) calculations have ignored the effects of tube materials on the gas constituents. Based on CEC (Ref. 4), the pH classifications of gas and slag in the MHD systems are as follows:

	Diffuser Exit	Radiant Boiler Exit	Low Temperature Heater Exit
Gas	neutral	alkaline	alkaline
Slag	acid	neutral	neutral

Acidic silica condenses before alkaline components and produces an increasingly alkaline gas and slag on cooling. In the MHD system, actual chemical reactions between acids and bases form less volatile products and more slag products with complex composition than those predicted by the CEC computer program under equilibrium composition. Big Sky Rosebud subbituminous coal generates a 'lignitic' type ash. With a 2160°F (1455°K) initial deformation temperature (IDT) and 2465°F (1625°K) hemisperical softening temperature (HT), corrosion associated with the formation of metal sulfides is not expected on the surface of the radiant boiler tubes. On the contrary, the surface of the boiler tubes will probably act as a chill surface which will condense solid mixtures of K_2SO_4, K_2CO_3, and KCl, clogging the radiant furnace with bulk deposits. As deposits continue to build up, the thermal conductivity through the deposits will drop until the temperature on the surface of the deposit increases to the melting point of the salts.

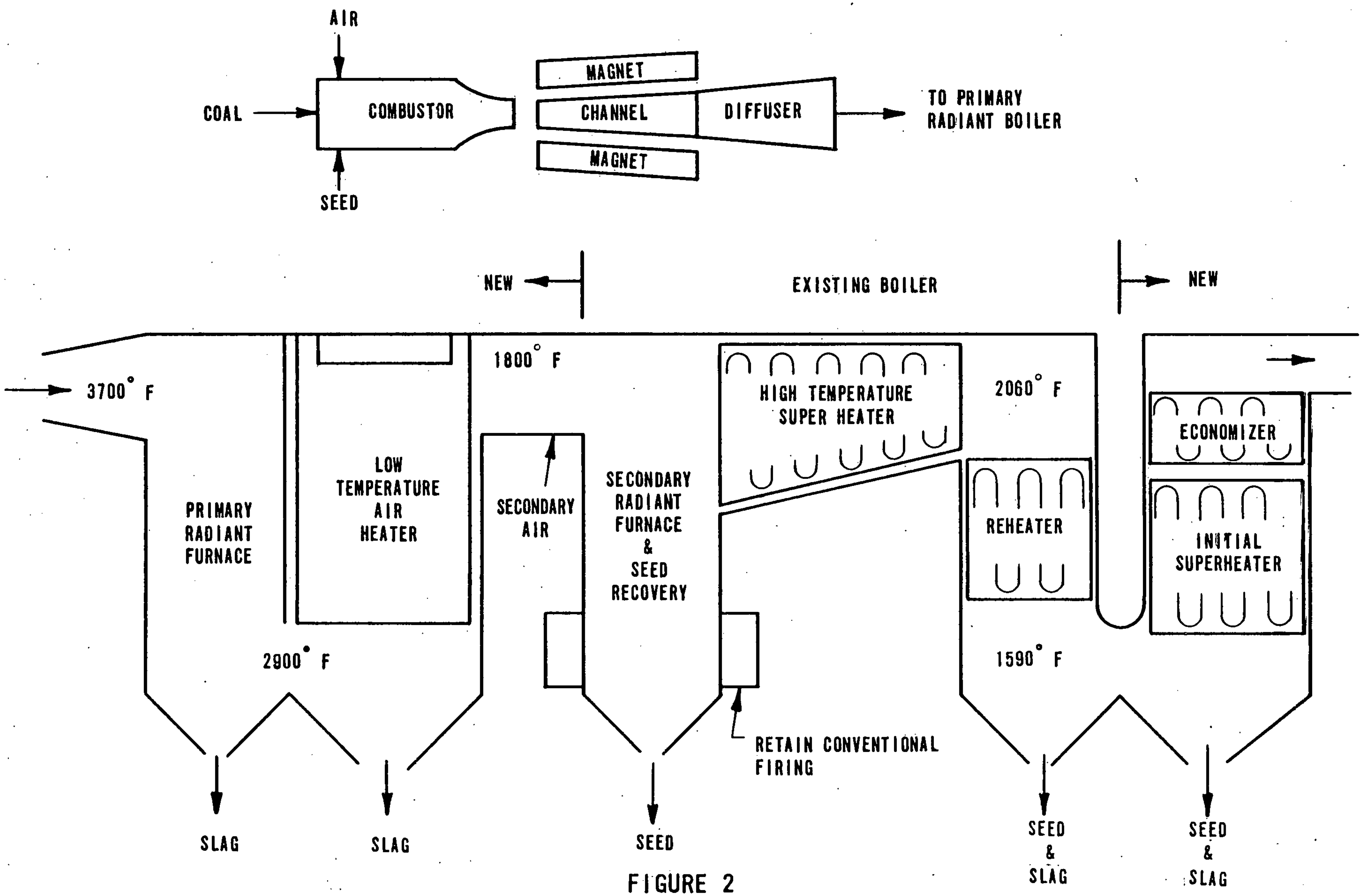


FIGURE 2
A TYPICAL MHD SYSTEM FLOW DIAGRAM (REF. 2)

At this point, any further material condensing out will be a liquid runoff, and no further buildup will occur. According to Rosa's model, when the slag viscosity becomes about 1.5 poise, the shear forces of the gas stream will cause a slag flow. An equilibrium slag thickness is predicted, ranging between 0.43 and 2.8 mm with respective surface temperatures of $3680^{\circ}F$ ($2300^{\circ}K$) and $3590^{\circ}F$ ($2250^{\circ}K$). Under full load operating conditions, the maximum slag layer thickness in the radiant boiler is expected to be about 1 mm. (Ref. 5).

In the MHD radiant boiler and on convection surfaces such as the superheater and reheater, with 95 percent stoichiometric air, formation of elemental sulfur (S) at a temperature of about $3500^{\circ}F$ ($2200^{\circ}K$) is not possible, although 22.0 percent (by weight) of carbon dioxide (CO_2) and 0.09 percent (by weight) sulfur dioxide (SO_2) are present. Corrosion rates of various tube materials (3/4 in. length schedule 40 pipe - 1.05 in. O.D. or 1 in. welded tubing) with seeded (4.4 percent by weight of K_2CO_3 in coal) and unseeded Rosebud Montana coal are tabulated in Table 4.

For the lignitic type ash, fouling on the convection surface will depend directly upon the total percentage of sulfates (Na_2SO_4 and K_2SO_4) in the ash. In the MHD system, the percentage of these sulfates by weight in the total ash is about 84 percent, so that severe fouling can be expected (the high percentage of K_2SO_4; 83.22 percent by weight, is due to seed addition). Steam tubes (mostly located in the superheater, made up of SA-213, 304, or equivalent) operating with a maximum external wall temperature of $1200^{\circ}F$ ($922^{\circ}K$) will act as a cold trap for the potassium and sodium compounds. These constituents will condense on fly ash particles and remain as liquid on the heat transfer surfaces. They will react chemically with fly ash, flue gas, and other deposits to form bonded deposits resulting in additional heat transfer resistance. In the superheater, seed condensation will be substantially complete, and initial deposition on the tubes will form a

TABLE 4

METAL LOSS IN THICKNESS OF CORROSION SPECIMENS IN COMBUSTION GAS WITH UNSEEDED COAL AND IN COMBUSTION GAS WITH COAL SEEDED WITH POTASSIUM CARBONATE (REF. 6)

Material	Metal Temp., °F	Flue Gas Temp. °F	Metal Loss (c) While Burning Unseeded Coal ▲Radius in in.	Metal Loss (d) While Burning Seeded Coal, ▲Radius in in.
Carbon steel (A 106)	800	1800	(a)	0.0075
Croloy 2-1/4	800	1800	0.0000	0.0015
Croloy 5	800	1800	0.0025	0.0075
446 SS	1100	2100	0.0000	0.0000
406 SS	1100	2100	0.0055	0.0035
316 SS	1100	2100	0.0000	0.0000
310 SS	1100	2100	0.0000	0.0000
310 SS	1500	2500	0.0015	(b)
Nickel	1500	2500	0.0035	(b)
Inconel	1500	2500	0.0000	(b)
Haynes 25	1500	2500	(a)	0.0005

(a) Cooling air failure caused loss of specimen.
(b) Completely oxidized after 50 hours.
(c) Duration of test: 83 hours.
(d) Duration of test: 100 hours.

solid coating. Any subsequent deposition will be in the form of low viscosity liquid seed with an interface temperature around 1905°F (1315°K).

In the MHD system, the presence of potassium chloride (KCl) is less than 0.02 percent by weight (not significant to the melting point of slag). However, the pitting effect due to the formation of potassium sulfate (K_2SO_4) is strongly dependent upon the amount of KCl present. The following reactions are predicted over the range of temperature:

$$2KCl + SO_2 + 1/2\ O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$$

(only at low temperature)

This chloride then reacts with the tube metal as follows:

$$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$$

Although elemental chlorine has not been recorded in the MHD CEC run (Ref. 14), it may play a role in the corrosion reaction. Metal oxides (Fe_2O_2) on the tube surface may catalyze the reaction:

$$4FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4Cl_2$$

Under a reducing atmosphere, Fe_2O_3 will probably be converted to Fe_3O_4. The mixed oxide and molten salt layers limit the availability of oxygen and retain chlorine and sulfur within the adherent scale. The corrosion rates of carbon steel in the presence of chlorine and hydrochloric acid are shown in Figure 3.

The melting points of potassium pyrosulfates ($K_2S_2O_7$) and potassium bisulfate ($KHSO_4$) are 575°F (575°K) and 415°F (486°K), respectively, and, even at high temperatures, the following electrochemical reactions are predicted:

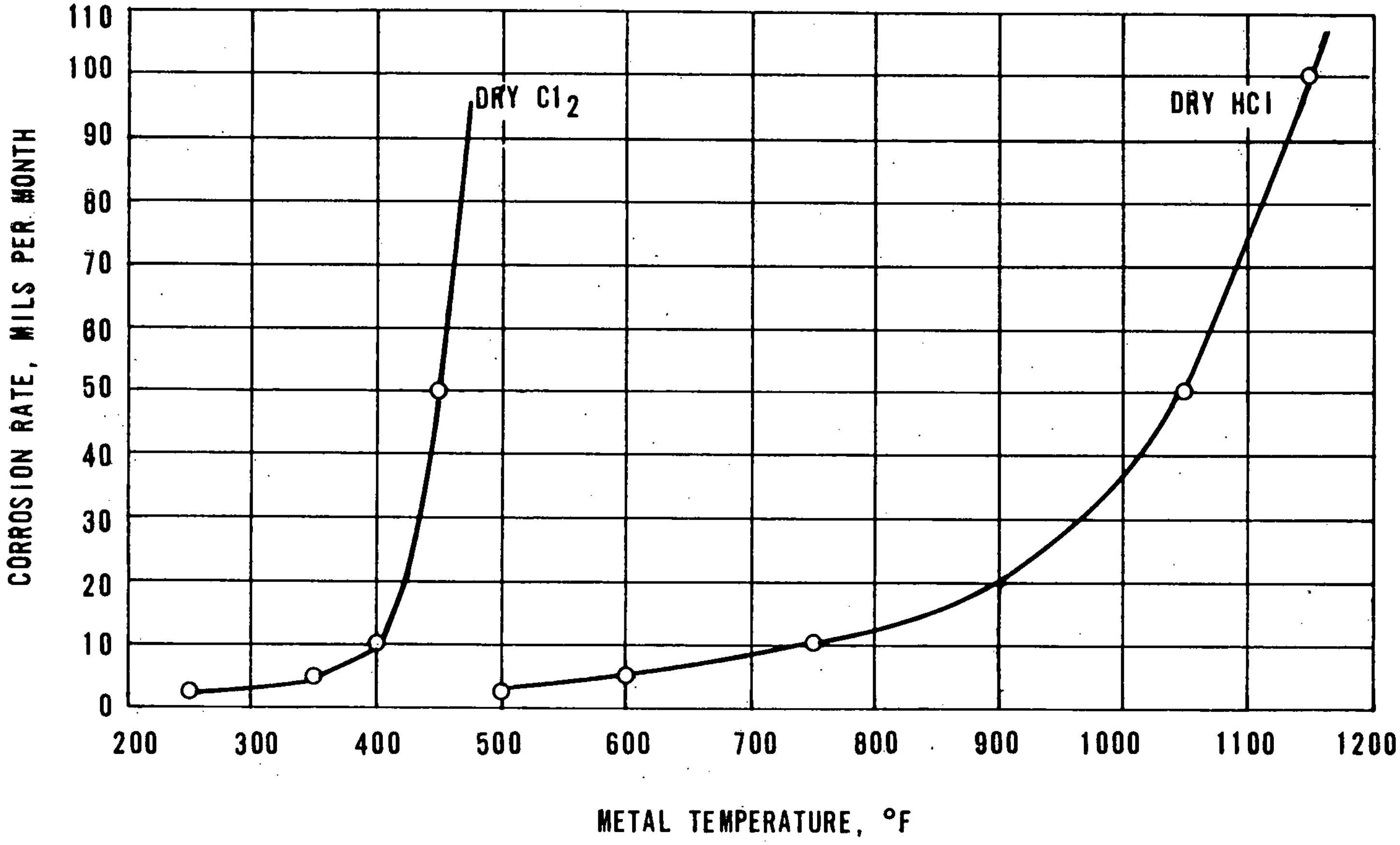


FIGURE 3
CORROSION OF CARBON STEEL IN CHLORINE AND HYDROGEN CHLORIDE (REF. 14)

$Fe_2O_3 + 3K_2S_2O_7 \rightarrow 2K_3Fe\ (SO_4)_3$ (potassium-iron trisulfates)

$Fe_2O_3 + 3K_2SO_4 + 3SO_3 \rightarrow 2K_3Fe\ (SO_4)_3$

These complex sulfates, which form corrosive deposits, then react with the tube metal as follows:

$2K_3Fe\ (SO_4)_3 + 6Fe \rightarrow 3/2\ FeS + 3/2\ Fe_3O_4 + Fe_2O_3 + 3/2SO_2$

SECTION 3.0

BLACK LIQUOR RECOVERY BOILERS

3.1 RECOVERY PROCESS

Figures 4 and 5 are simplified process flow diagrams of typical Kraft (sulfate) pulp and paper mill processes. The function of the recovery unit is the reduction of sodium sulfate (Na_2SO_4) in the black liquor to sodium sulfide (Na_2S) in the furnace. In the recovery furnace, heat obtained from the combustion of the organic liquor constituents dissolved from the wood is used for the production of steam, and the inorganic sodium constituents in the liquor are recovered as molten smelt.

The logs entering the Kraft pulp and paper mill are first debarked (1), reduced to chips (2), and charged into a digester (3), where they are cooked under pressure in a steam-heated, aqueous, digestion solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), known as "white liquor" or "cooking liquor." In the cooking operation, the lignin that binds the cellulose fibers of the wood is dissolved.

After cooling, the cellulose fibers, now called pulp or brown stock, are separated from the spent cooking liquor in the pulp washers (4). The pulp may go through several fiber refining and bleaching processes before being sent to the paper machine. The spent cooking liquor containing the lignin is called black liquor. As the dilute or weak black liquor (15-18 percent dissolved solids) comes from the washers, it is concentrated (45-50 percent dissolved solids) in a multiple effect evaporator (5) by the use of steam. The concentrated or "strong" black liquor then passes to the recovery unit (6,7, and 8). It is further concentrated to "heavy" black liquor in a direct contact evaporator (6) using the sensible heat of the flue gas (62-65 percent dissolved solids). The heavy black liquor then goes to the mix

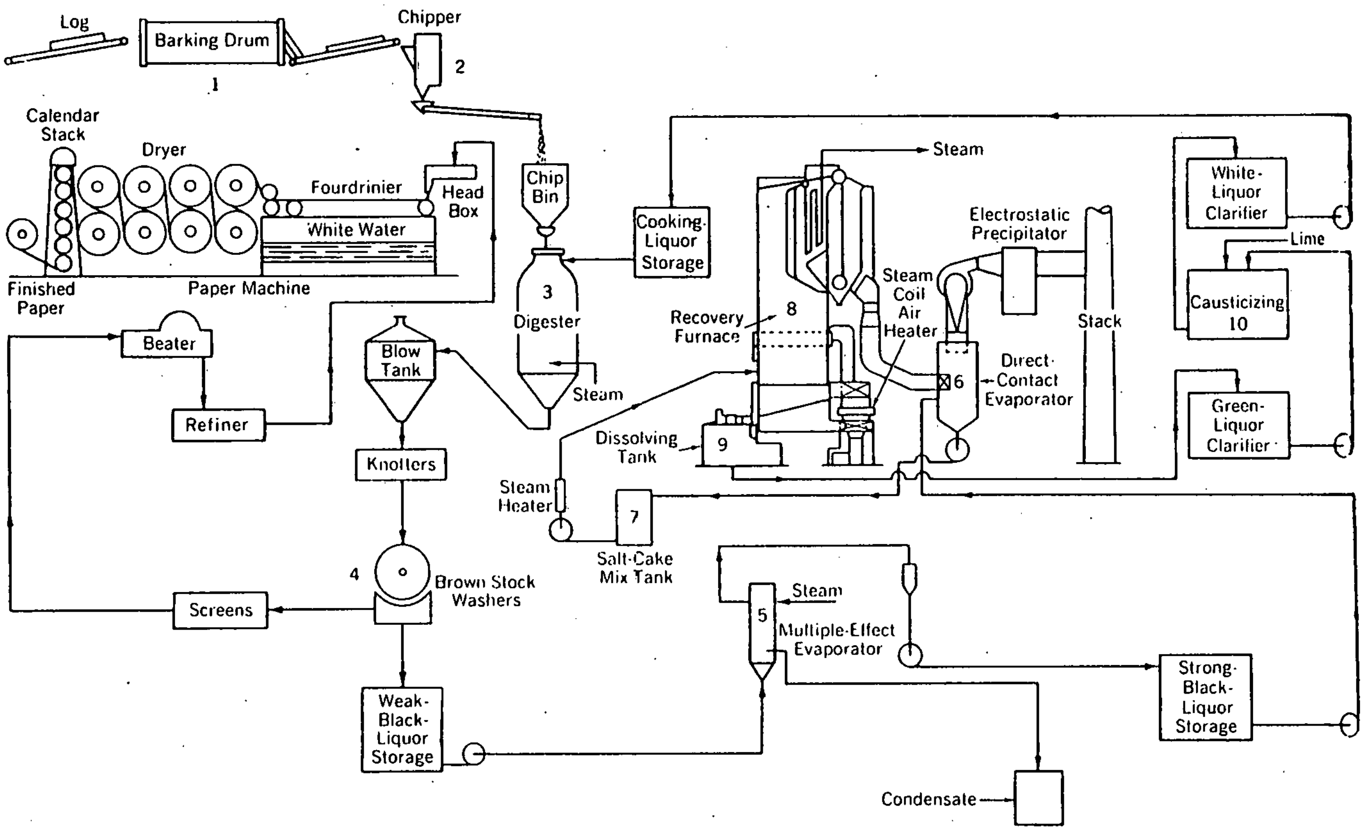


FIGURE 4
PROCESS FLOW DIAGRAM OF A TYPICAL KRAFT PULP AND PAPER MILL (REF. 7)

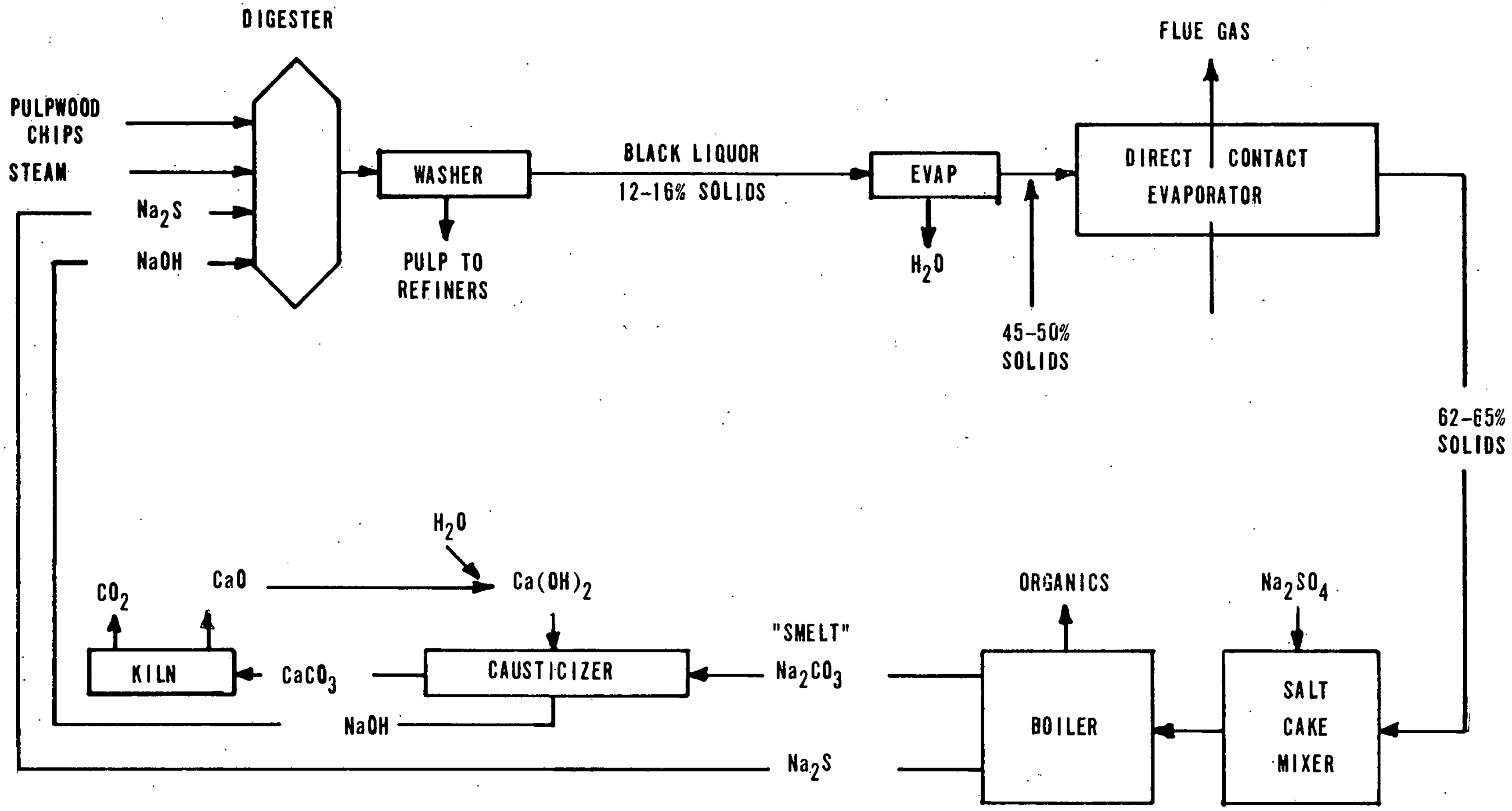


FIGURE 5
KRAFT RECOVERY PROCESS (REF. 1)

tank (7) where sodium sulfate (salt cake) is mixed with the liquor to make up for the chemical losses in the system. Chemical ash recovered from the boiler hoppers and the fume collector following the direct contact evaporator are returned to the liquor cycle. The heavy black liquor with its salt cake burden is heated to lower its viscosity and pumped to the recovery furnace (8). In the furnace, the heavy black liquor is sprayed on the walls for dehydration prior to final combustion of the dried char. Sodium sulfide (Na_2S) is tapped from the furnace and dissolved in water in the dissolving tank (9) to form "green liquor." The green liquor is subjected to a causticizing treatment (10) with slaked lime $Ca(OH)_2$, to convert the sodium carbonate to sodium hydroxide. The sodium sulfide remains unchanged. The liquor, now known again as white liquor, is then ready for reuse as cooking liquor in the digester (3).

3.2 BOILER DESIGN

In black liquor, organic sulfur compounds are present in combination with sodium sulfide, sodium carbonate, sodium sulfate, salt, silica, traces of lime, iron oxide, alumina, and potash. An approximate analysis of a typical black liquor is shown in Table 5.

TABLE 5

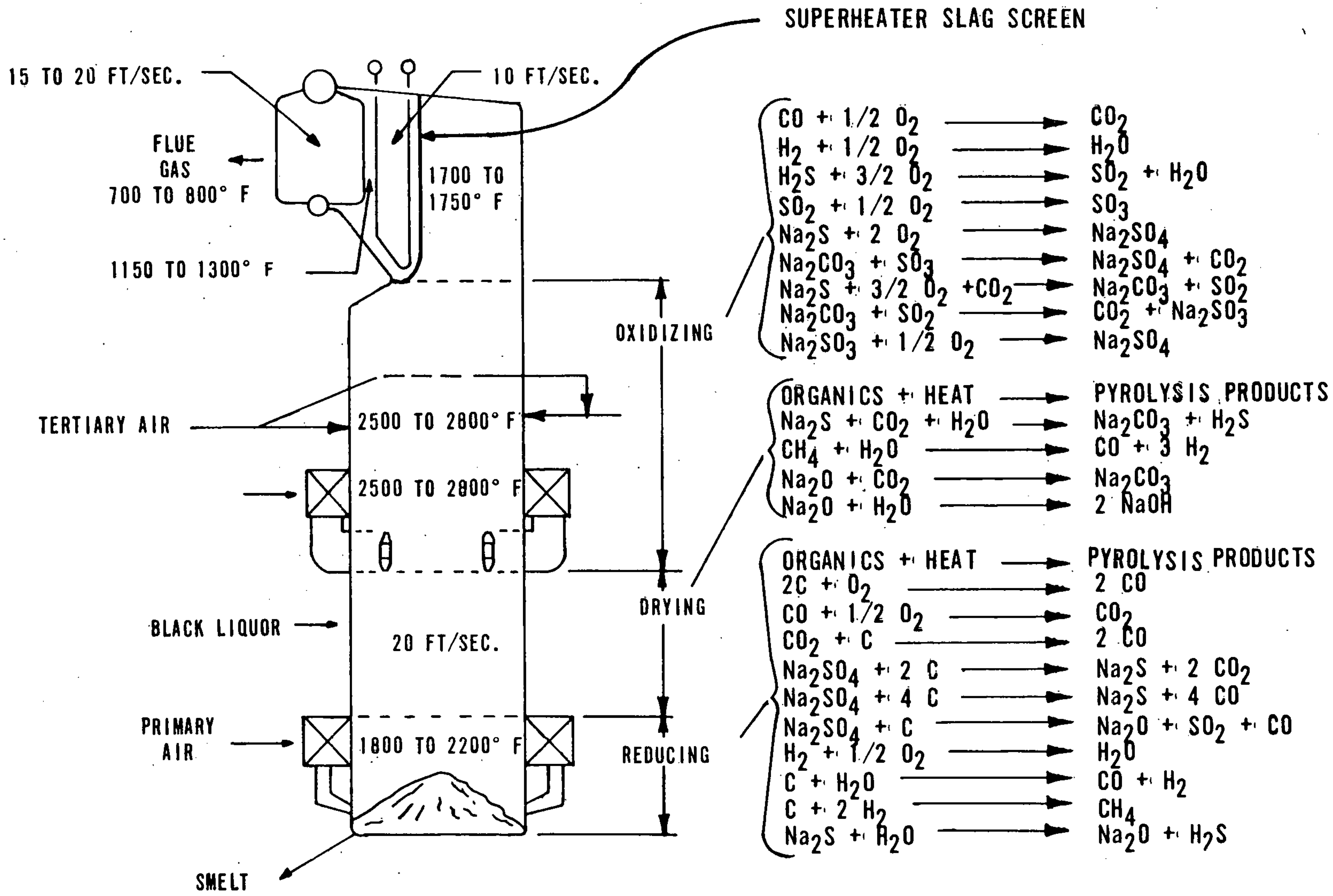
ANALYSIS OF TYPICAL BLACK LIQUOR

Element	Inorganic	Organic	Total Black Liquor Solids
Na	18.3	-	18.3
S	3.6	-	3.6
C	0.4	42.2	42.6
H	0.5	3.1	3.6
O	10.0	21.7	31.7
N	-	0.2	0.2
Total	32.8	67.2	100.0
		Gross Heating Value = 6,600 Btu/lb.	

The black liquor at (200^{0}F) and combustion air (15 percent excess air at 280^{0}F) are fired in the furnace at an approximate ratio of 1 to 5.3 by weight. The total air is distributed as 40 percent primary air, 30 percent secondary air, and 30 percent tertiary air (B&W design) or 50 to 60 percent of the total air as primary air and the balance as secondary air (CE design). Typical recovery unit chemical reactions and their points of occurrence are shown in Figure 6. The reactions listed occur simultaneously in each of the zones.

In the recovery furnace, a drying zone is required, so that the residual water in the black liquor can be evaporated as the first step in the drying process. The controlled reducing atmosphere at the hearth burns dehydrated char falling from the walls to effect a maximum reduction of sodium sulfate to sulfide in the smelt. Typical gas temperatures (^{o}F) at various points in the unit are:

Location	^{o}F
Primary Air Port Level	1800 - 2200
Secondary Air Port Level	2500 - 2800
Tertiary Air Port Level	2500 - 2800
Superheater Inlet	1700 - 1750
Boiler Bank Inlet	1150 - 1300
Boiler Bank Outlet	700 - 800
Economizer Outlet	550 - 600
Cyclone Evaporator Outlet	325



$CO + 1/2\ O_2 \longrightarrow CO_2$
$H_2 + 1/2\ O_2 \longrightarrow H_2O$
$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O$
$SO_2 + 1/2\ O_2 \longrightarrow SO_3$
$Na_2S + 2\ O_2 \longrightarrow Na_2SO_4$
$Na_2CO_3 + SO_3 \longrightarrow Na_2SO_4 + CO_2$
$Na_2S + 3/2\ O_2 + CO_2 \longrightarrow Na_2CO_3 + SO_2$
$Na_2CO_3 + SO_2 \longrightarrow CO_2 + Na_2SO_3$
$Na_2SO_3 + 1/2\ O_2 \longrightarrow Na_2SO_4$

$\text{ORGANICS} + \text{HEAT} \longrightarrow \text{PYROLYSIS PRODUCTS}$
$Na_2S + CO_2 + H_2O \longrightarrow Na_2CO_3 + H_2S$
$CH_4 + H_2O \longrightarrow CO + 3\ H_2$
$Na_2O + CO_2 \longrightarrow Na_2CO_3$
$Na_2O + H_2O \longrightarrow 2\ NaOH$

$\text{ORGANICS} + \text{HEAT} \longrightarrow \text{PYROLYSIS PRODUCTS}$
$2C + O_2 \longrightarrow 2\ CO$
$CO + 1/2\ O_2 \longrightarrow CO_2$
$CO_2 + C \longrightarrow 2\ CO$
$Na_2SO_4 + 2\ C \longrightarrow Na_2S + 2\ CO_2$
$Na_2SO_4 + 4\ C \longrightarrow Na_2S + 4\ CO$
$Na_2SO_4 + C \longrightarrow Na_2O + SO_2 + CO$
$H_2 + 1/2\ O_2 \longrightarrow H_2O$
$C + H_2O \longrightarrow CO + H_2$
$C + 2\ H_2 \longrightarrow CH_4$
$Na_2S + H_2O \longrightarrow Na_2O + H_2S$

FIGURE 6
TYPICAL RECOVERY UNIT SHOWING CHEMICAL REACTIONS AND WHERE THEY OCCUR (REF. 8)

Velocities (feet/sec.) through the unit are in the order of:

Location	Feet per sec
Furnace	20
Superheater	10
Boiler Bank	15-20
Economizer	20-35

The dried black liquor collects as char on the hearth, forming a pile to which a controlled amount of air (primary air) is supplied. This determines the amount of heat released in this section and the composition of the gas atmosphere. Sufficient heat must be released to maintain an incandescent char bed, furnish the heat required for endothermic reactions, smelt the inorganic chemicals, supply heat to the drying process, and allow for the heat absorbed by the furnace walls. The water cooled furnace walls fabricated from carbon steels (SA-192 or SA-226) are protected from corrosion as described in Section 3.6, "Heating Surface Protection." Under steady state conditions, the furnace wall tube mean metal temperature will be about 100°F (55°K) higher than the inside water temperature.

Black liquor is an extremely poor fuel because of its high ash content and low ash fusion temperature (approximately 1450°F). Large furnaces produce the low gas temperature (approximately 1700°F) needed in the superheater. This low gas temperature weakens the corrosion attack, reduces the fly ash carryover, and facilitates the operation of the soot blower. Superheaters are normally arranged for parallel flow of gas and steam. When steam temperatures are above 825°F, the superheater reqires alloys, such as SA-209, T-1 and SA-213, T-11.

Superheaters supplying lower temperature steam utilize carbon steel tubes such as SA-192 and SA-226. The parallel flow superheater arrangement keeps the hottest gas in contact with the coolest metal, reducing metal wastage due to corrosion.

The economizers are vertical, bare tube, modular type, baffled to establish cross-flow of gases. To avoid external corrosion (due to formation of sulfuric acid, H_2SO_4), the effectiveness of the economizer is kept low. For high sulfur (3.6 percent by weight) black liquor, the mean metal temperature is limited to about 250^oF.

Retractable steam soot blowers are continuously in use when a modern recovery unit is operated at or near rated capacity, and, consequently, no hand lancing is required to keep gas passages open. However, as load increases from partial load to full load on a unit, mechanical entrainment of ash and sublimation of sodium compounds increase and invariably lead to cleaning problems. In addition to excessive quantities of ash in the flue gas, velocities and temperatures at all points in the unit are increased, and ash deposits become more difficult to remove. All the furnace designs incorporate a sloping floor to minimize smelt pool formation. (Ref. 2)

3.3 CORROSION

Corrosion in the black liquor boiler occurs in the furnace at the "hearth" zone (0.03 in/yr or 0.76 mm/yr) near the window face of the furnace wall tubes and at the upper parts of the furnace (0.01 in/yr or 0.25 mm/yr). Figure 7 charts these corrosion rates. Since flue gas temperature entering the superheater is limited to 1700^oF, corrosion rates in the convection surface zones (the superheater and boiler bank) are minimum. The corrosion rates measured on carbon steel (SA- 192) samples at 700^oF (with both synthetic smelt and actual unit smelt)

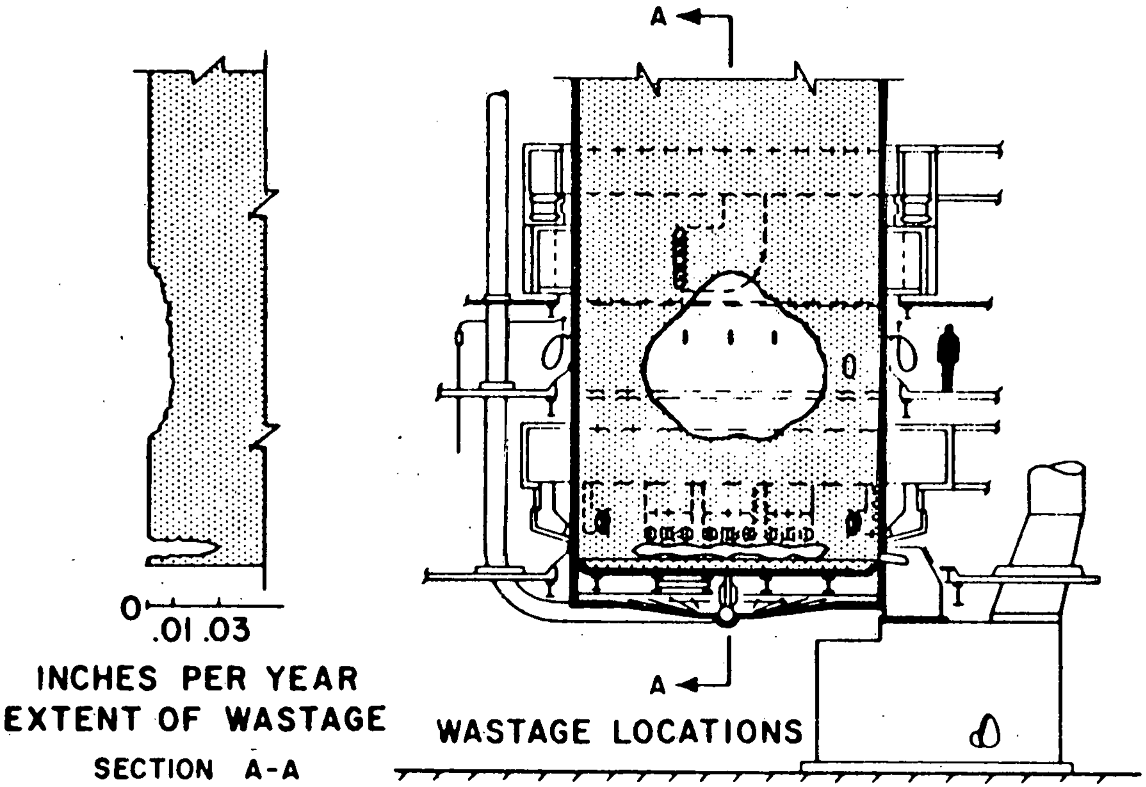


FIGURE 7
TYPICAL RECOVERY UNIT CORROSION (REF. 1)

obtained from a unit operating with 22 percent sodium chloride in various furnace atmospheres, i.e., air, nitrogen, and carbon dioxide are listed below:

TABLE 6

CORROSION RATES ON SA-192 AT 700°F (REF. 1)

Atm.	Synthetic Smelt (Weight loss/week)	Actual Unit Smelt (Weight loss/week)
N_2	28.7×10^{-6} lb/in^2 (2.0 mg/cm^2)	52.9×10^{-6} lb/in^2 (3.7 mg/cm^2)
Air	30.9×10^{-6} lb/in^2 (2.1 mg/cm^2)	50.7×10^{-6} lb/in^2 (3.5 mg/cm^2)
CO_2	29.4×10^{-6} lb/in^2 (10 mg/cm^2)	90.5×10^{-6} lb/in^2 (6.3 mg/cm^2)

Corrosion rate is strongly affected by skin metal temperature, type of atmosphere (reducing or oxidizing), gas constituents, and tube metal composition. It is further complicated by operating pressures, high velocities, and erosive particle impingement. The corrosive gases and salts contain low melting NaCl and sulfur compounds such as sodium sulfate (Na_2SO_4), sodium thiosulphate (Na_2SO_3), and sodium pyrosulphate ($Na_2S_2O_7$). Gases, such as sulfur dioxide (SO_2), sulfur trioxide (SO_3), hydrochloric acid (HCl), and chlorine (Cl_2), play a major role in the corrosion process. Appendix B contains a detailed description of corrosion in black liquor boilers.

3.3.1 Material Test Results

Laboratory test results of the wastage of a carbon steel (SA-192) sample (1-1/2 x 1-1/2 bar) kept at 700° F (644 K) for one week are tabulated below:

TABLE 7

WASTAGE ON SA-192 AT 700°F (REF. 1)

Carbon steel tubes (at the primary zone)	0.03 in/yr (0.76 mm/yr)
Carbon steel tubes (liquid spray gun area)	0.01 in/yr (0.25 mm/yr)
Carbon steel with chromium	no measurable wastage
Carbon steel with chromium + aluminum	no measurable wastage
Compound tubes (304 s.s. over carbon steel)	0.0026 in/yr (0.066 mm/yr)
410 stainless steel	0.0026 in/yr (0.066 mm/yr)
Weld overlay tubes*	0.039 in/yr (0.99 mm/yr)

*Tubes with extra welding material on the surface.

In a simulated recovery furnace, corrosion rate versus metal temperature data for carbon steel (SA- 226) is shown in Figure 8. Type 304 stainless steel has exhibited the best resistance to corrosion and is virtually corrosion-free in the range of 110^{o}F (316^{o}K) to 950^{o}F (783^{o}K), as shown in Figures 9 and 10. Type 304 stainless steel provides satisfactory protection from gas and smelt corrosion due to the formation of a tight and firm surface film containing sulfides and oxides of iron, chromium, and nickel. Firmness of the film is sufficient to resist mechanical actions within the furnace, and tightness of the film is adequate to minimize diffusion of corrodents through the film, thus limiting the corrosion rate to a low value of 1 to 1.5 mills per year. Higher alloyed steels offer no better protection against fireside corrosion.

Type 309 stainless steel applied as a flame sprayed protection layer does not have the necessary mechanical strength to stand up to the stresses used by firebox and temperature cycling. Type 309 stainless steel is applied as a weld overlay on a carbon steel tube and forms a martensitic zone. This zone, with its associated hardness peaks, acts as a stress raiser. These hardness peaks are shown in Figure 11 (Ref. 10).

FIGURE 8
CORROSION RATE VS. METAL TEMPERATURE FOR CARBON STEEL (SA-226) (REF. 3)

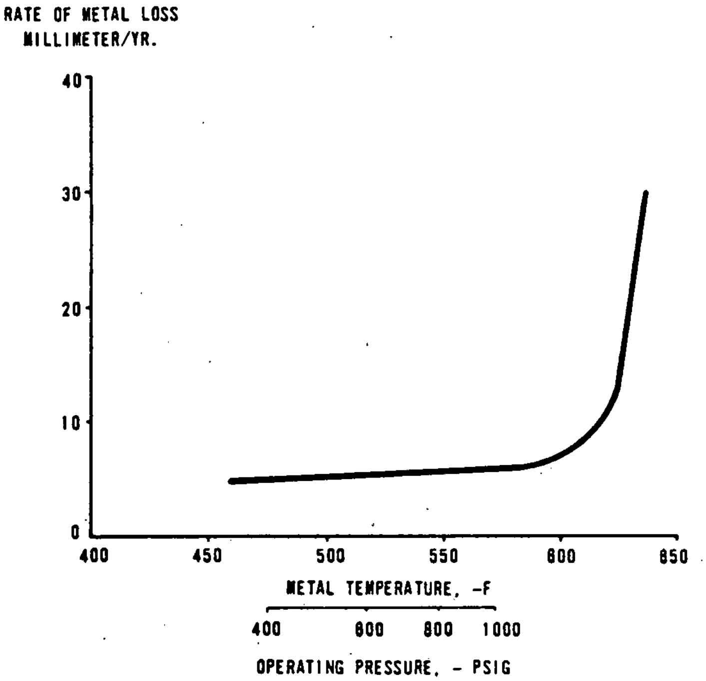


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FIGURE 9
TYPE 304 STAINLESS STEEL CORROSION RATE (REF. 10)

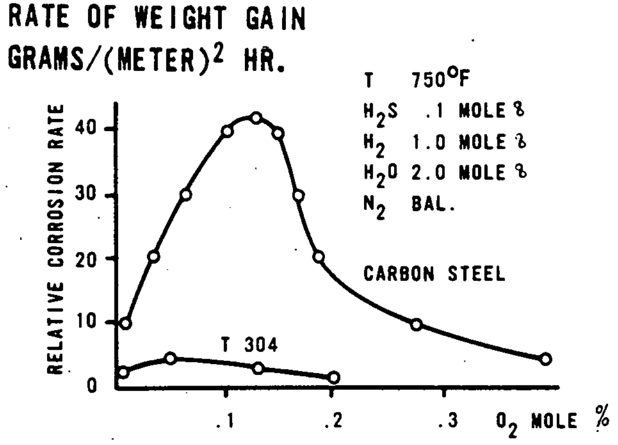

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FIGURE 10
TYPE 304 STAINLESS STEEL WEIGHT GAIN VS. TEMPERATURE (REF. 10)

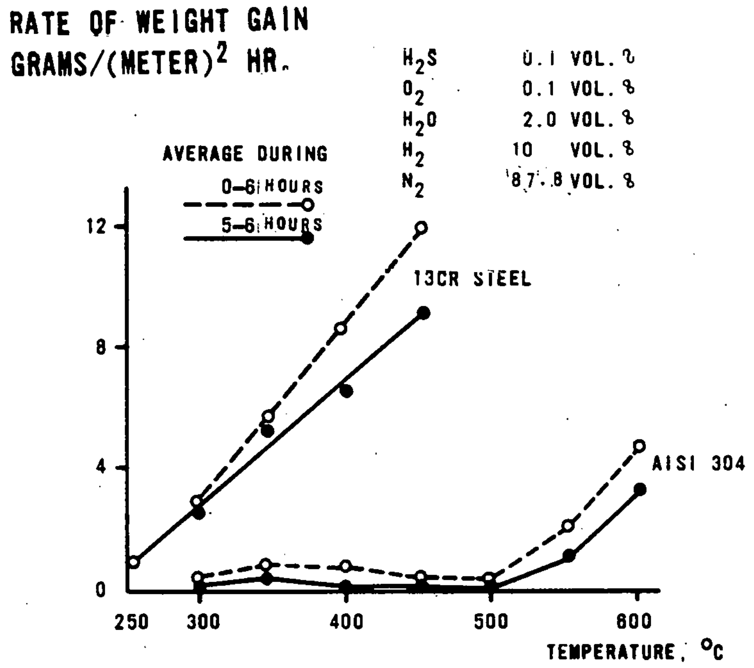

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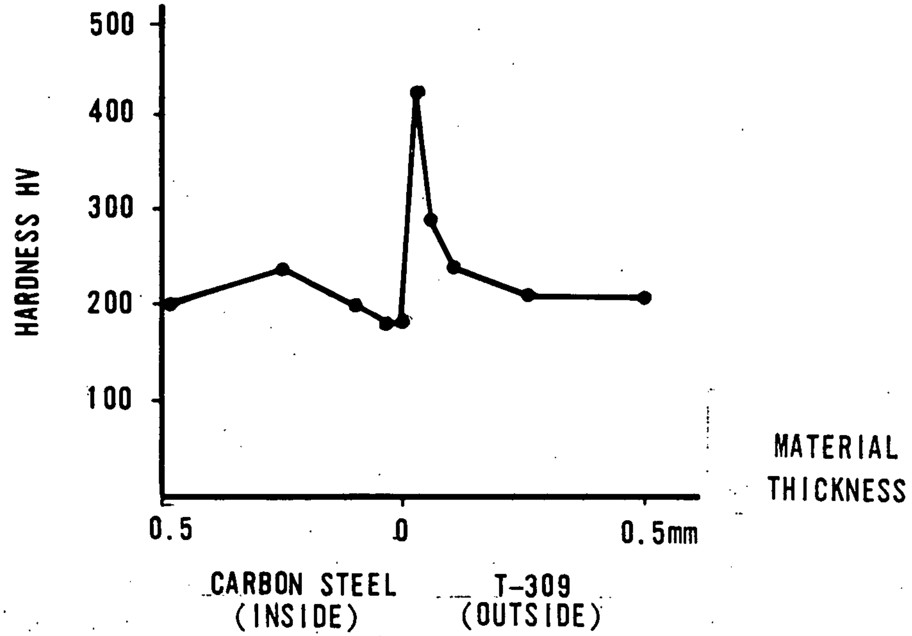
FIGURE 11
HARDNESS PEAKS OF TYPE 309 CARBON STEEL (REF. 10)



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3.4 FIELD OPERATION AND EXPERIENCE

Several paper companies were contacted to determine user experience in the field. The major problem areas were corrosion of the waterwall tubes in the lower part of the furnace and fouling in the superheater sections. The possibility of explosions occurring due to smelt/water reactions caused by tube leakage in the lower furnace dictates frequent boiler inspections. The majority of users inspect boilers twice annually, with one company inspecting three times annually. Inspection shutdowns require three to four days (minimum) for inspection alone. During the shutdown water/steam tubes are inspected utilizing ultrasonic and radiographic techniques. Occasionally, the front rows of superheater tubes require cleaning due to the buildup of hard deposits formed by molten/sticky salts during load fluctuations. Most users keep superheater slag screen entrance temperatures in the 1400-1600°F range to limit buildup problems, but occasional shutdowns are required. (The inlet gas temperatures to the superheater are not monitored, but settings are established by monitoring superheater exit gas temperatures.)

In contrast to the practice followed by most users, the Hudson Pulp & Paper Company (Palatka, Florida) has a relatively new CE boiler (1250 psi, 900°F steam) that is operated at rated load continually. At load conditions, slag screen entrance temperature is 1900°F, and superheater entrance temperature is 1650°F (CE design values). The boiler was operated from December 1976 to December 1977 with no shutdowns. During the inspection period, hard deposit layers were removed from the slag screen and the initial bank of superheater tubes, which would indicate that liquid smelt had been present on the tubes during operation. No fouling problems were encountered during the one year operational period, but the reason this could not be determined from the users or from the manufacturer. The superheater and soot blower design does not differ markedly from older designs that reportedly have fouling problems.

To minimize furnace waterwall tube corrosion, the industry feels that duplex tube configurations are necessary for steam pressures in excess of 850 psi. The "Sandvik" dual wall tube is the industry choice; the "Sandvik" tube consists of a carbon steel inside tube for pressure carrying and a 316 stainless steel outside shell for corrosion resistance.

3.5 BOILER EXPLOSION

The smelt/water chemical reactions in the unique environment of the recovery boiler produce rapid generation of steam and are potentially explosive. The sequence of chemical reactions resulting in catastrophic explosions is not yet known.

The various causes of smelt/water explosions are (Ref. 11):

- firing weak black liquor or chemical solutions
- using water in an unsafe manner
- overheating pressure parts
- adding heavy black liquor to smelt bed
- using air lances improperly
- corrosion and erosion
- leaking smelt
- leaking water cooled parts

To prevent explosion, the following precautions are recommended (Ref. 12):

- maintenance of oxygen and combustible analyzers
- proper use of air lances
- thorough periodic checking of the furnace from the standpoint of erosion and corrosion
- monitored auxiliary fuel burners
- application of boiler feedwater treatment system

- maintenance of liquor pump and standby pump, so that the load can be immediately picked up (otherwise condensate is formed in a direct contact secondary liquor heater)
- accurate measurement of percent solids fired
- ensuring that the smelt bed is adequately cooled before water washing of boiler to facilitate fireside inspection or repair
- use of an auxiliary fuel firing facility
- design of good control and instrumentation systems to rapidly drain the recovery boiler under emergency conditions to a level 8 feet above the bottom (8 feet depth of water will avoid the overheating and thermal stresses set up in dry hot tubes due to the hot char and the smelt bed)
- opening of a vent valve, following a time delay of 2 minutes longer than the time to drain to the 8 feet level as described above (the objective of this precaution is to reduce the flow of water in the event there is a pressure part failure below the 8 feet level.)

3.6 HEATING SURFACE PROTECTION

The commercial methods of water cooled wall construction to protect it from corrosion are as follows:

- A sacrificial, pin studded tube (up to tertiary windbox level) is used to reduce the potential for corrosion by retaining a solidified layer of smelt adjacent to the tube. This provides a position barrier to the fluid smelt, elemental sulfur, and corrosive gases of the hearth zone. Sometimes, B&W PCO "KROMIGHT-GUN" refractories (at 1500^{o}F, refractory's average temperature, thermal conductivity, 12 Btu/sq.ft,hr,^{o}F/in) are also applied.
- Metallic coatings with chrome steel (13.5 percent Cr) are applied to sand blasted tube walls.

- Application of multiple coats of flame spraying with nickel aluminide (Ni_3Al_4), 300 series stainless steel and aluminum (respectively from inside to outside layers).
- Spray coating with chromium nickel titanide plasma.
- Application of diffusion coatings of chromium and aluminum chromium.
- Providing hard face welding protection over the lower 6 to 9 feet hearth zone.
- The use of "SANDVIK" bimetallic compound tubes, fabricated from carbon steel inside for pressure carrying and 315 stainless steel outside for NaCl corrosion resistance; approximate thickness ratio of carbon steel to stainless steel required is 4-to-1, especially when the steam pressures are in excess of 850 psig.

The success of each of the above methods depends upon operating conditions and quality of the manufacturing process.

To control fouling and corrosion in the superheater surface, a platen type ("pencil" weld) surface with wide lateral tube spacing (minimum 12 inches) is adopted by all the manufacturers. The technique of tangent tube construction minimizes the projected surface area perpendicular to the gas flow and, as a result, reduces the fouling and erosion/corrosion problem. (Ref. 1). The platen type tube surface prevents the circular (360°) formation of slag (keying) and, thus, makes it easier to remove slag by soot blowers.

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38. Cyclone Manufacturers Surveyed:

a. Fisher-Klosterman, Inc., Louisville, Kentucky
b. Ducon Company, Inc., Mineola, New York
c. Aerodyne Development Corp., Cleveland, Ohio
d. AGET Manufacturing Company, Adrian, Michigan
e. Hammond Machinery Builders, Kalamazoo, Michigan

f. Peerless Mfg. Company, Dallas, Texas
g. Envirotech Corporation, Houston, Texas
h. General Electric Company, Schenectady, New York
i. Enviro-Systems & Research Inc., Roanoke, Virginia
j. W.W. Sly Manufacturing Company, Cleveland, Ohio
k. Joy Manufacturing Company, Los Angeles, California
l. Dyna-Therm Corporation, Houston, Texas
m. Shell Development Company, Houston, Texas
n. Van Tongeren, Reynoldsburg, Ohio
o. Donaldson Company, Minneapolis, Minn.
p. Dixie Manufacturing Company, Baltimore, Md.
q. W.C. Wiedenmann & Son, Inc., Kansas City, Mo.
r. Seneca Environmental Products, Tiffin, Ohio
s. Aerex Corporation, Scottstown, Quebec
t. Environmental Elements Corporation, Baltimore, Maryland

39. AVCO Everett Research Laboratory. Engineering Test Facility Conceptual Design. Everett, MA. 1978.

40. Westinghouse. MHD Conceptual Design. 1978.

APPENDIX A
BLACK LIQUOR BOILER
INSTALLATION LISTS

BABCOCK & WILCOX CO.
BLACK LIQUOR UNITS WITH CYCLONE EVAPORATORS

Contracts	Customer	No. of Units Sold	B&W Ton Rating	Oper. Press (Psig)	Temp. °F
S-9906	Hudson Pulp & Paper Co., Palatka, Fla.	1	250	460	725
S-9950	W. Va. Pulp & Paper, Charleston, S.C.	1	360	1525	880
S-9952	Crown Zellerback Corp., Camas, Wash.	1	350	400	700
PR-35	Packaging Corp. of America, Filer City, Mich.	1	300	600	750
PR-42	W. Va. Pulp & Paper co., Luke, Md.	1	500	1525	880
PR-49	Bowaters Carolina Corp., Catawba, S.C.	1	450	850	825
PR-55	Continental Can Co. Nixon, Ga.	1	400	875	900
PR-56	Rayonier Corp., Hoquiam, Wash.	1	550	620	750
PR-57	Fibreboard Paper Products, Antioch, Cal.	1	400	600	715
PR-67	Downingtown Mfg. Co. for: Seshasayee Pulp & Paper Ltd., India	1	66	150	Sat.
PR-77	Spruce Falls Pwr. & Paper Co., Kapuskasing, Ont.	1	200 (MgO)	100	560
PR-83	Olin Mathieson Chemical Corp., W. Monroe, La.	1	450	640	750
PR-84	Crown Zellerbach Corp., Bogalusa, La.	1	800	450	730
PR-85	Crown Zellerbach Corp., St. Francisville, La.	1	600	600	730
PR-86	Scott Paper Co., Mobile, Ala.	1	450	575	750
PR-87	Champion Papers, Inc., Canton, N.C.	1	900	450	725
PR-88	Georgia Pacific Corp., Woodland, Me.	2	350	875	850
PR-89	Continental Can Co., Nixon, Ga.	1	400	875	900
PR-90	Crown Zellerback Corp., Eureka, Cal.	1	800	600	750
PR-91	Bowaters Carolina Corp., Catawba, S.C.	1	600	850	900
PR-92	Weyerhaeuser Co., Cosmopolis, Wash.	1	196 (MgO)	860	825
PR-93	Crown Zellerbach Corp., Wauna, Ore.	1	800	600	750
PR-94	Celulose Billeruds, Portugal	1	350	1025	896
PR-97	Alabama Kraft Co., Mahrt, Ala.	1	900	875	825
PR-105	Int. Paper Co., Vicksburg, Miss.	1	1000	1020	900
PR-108	Owens-Illinois, Orange, Texas	2	550	885	835
PR-112	Int. Paper Co., Bastrop, La.	1	1100	1275	925
PR-113	Int. Paper Co., Pine Bluff, Ark.	1	1100	1275	925
PR-114	Int. Paper Co., Georgetown, S.C.	1	900	1020	825
PR-115	Int. Paper Co., Springhill, La.	1	700	850	825
PR-116	Int. Paper Co., Camden, Ark.	1	500	850	825

BABCOCK & WILCOX CO.
BLACK LIQUOR UNITS WITH CYCLONE EVAPORATORS
(continued)

Contracts	Customer	No. of Units Sold	B&W Ton Rating	Oper. Press	Temp. °F
PR-118	Boise Cascade Corp., St. Helens, Ore.	1	450	250	725
PR-122	Siam Kraft Paper Co., Bangkok, Thailand	1	66	600	750
PR-123	Kimberly Clark de Mexico, Orizaba, Mexico	1	95 (Soda)	250	Sat.
PR-124	Great Northern Paper Co., Millinocket, Me.	1	600 (MgO)	1275	855
PR-127	Publishers Paper Co., Oregon City, Ore.	1	200 (MgO)	635	750
PR-128	U.S. Plywood-Champ. Papers, Inc., Courtland, Ala.	1	600	450	550
PR-130	Boise Cascade Corp., DeRidder, La.	1	1000	900	825
PR-140	Southwest Forest Industries, Snowflake, Ariz.	1	500	1225	850
PR-141	Kopparfors A/B, Gavle, Sweden	1	300	854	842
PR-144	Int. Paper Co., Texarkana, Texas	1	750	700	750
PR-146	U.S. Plywood-Champion Papers, Canton, N.C.	1	900	425	750
PR-148	Int. Paper Co., Mobile, Ala.	1	700	1475	925
PR-158	U.S. Plywood-Champion Papers, Pasadena, Tex.	1	550	400	725
PR-169	Champion Celulose, S.A., Mogi Guacu, Brazil	1	575	450	644
PR-170	International Paper Co., Springhill, La.	1	700	450	765
PR-176	Gulf States Paper Corp., Demopolis, Ala.	1	600	600	750
PR-179	Western Kraft, Hawesville, Kentucky	1	300	250	530
PR-180	Champion International, Courtland, Alabama	1	1000	450	550
PR-186	International Paper, Texarkana, TX	1	1200	1075	935
PR-193	Gulf States Paper, Tuscaloosa, AL	1	700	875 (fut)	925 (fut)

Cyclone Evaporators:

The cyclone evaporator is a vertical cylindrical vessel with a conical bottom. The strong black-liquor (45 to 50% solids) from the storage tank enters the cyclone evaporator and is dried by flue gas (to 62 to 65% solids). The flue gas is admitted through a tangential inlet near the bottom. Black liquor is sprayed from the top across the gas outlet to obtain contact of liquor with gas.

BABCOCK & WILCOX CO.
BLACK LIQUOR UNITS WITH CASCADE EVAPORATORS*

Contracts	Customer	No. of Units Sold	B&W Ton Rating	Oper. Press	Temp. °F
S-9949	R. Gair for Continental Can, Hodge, La.	1	300	1250	900
S-9953	Scott Paper Co., Mobile, Ala.	1	300	600	725
PR-30	Champion Paper & Fibre, Pasadena, Texas	1	550	1500 fut.	900
S-9965	Container Corp. of America, Brewton, Ala.	1	390	880	830
PR-33	Container Corp. of America, Fernandina Beach, Fla.	1	300	900	825
PR-61	Scott Paper Co., Mobile, Ala.	1	300	600	750
PR-70	Southern Land Timber & Pulp, Cedar Springs, Ga.	1	666	850	900
PR-71	Parsons & Whittemore for Edfu, Egypt	1	108	625	700
PR-72	Downingtown Mfg. Co. for Ledesma, Argentina	1	94 (Soda)	625	797
PR-79	Container Corp. of America, Brewton, Ala.	1	390	880	830
PR-103	Great Southern Land, Cedar Springs, Ga.	1	666	850	900
PR-117	Eastex, Inc., Evadale, Texas	1	534	610	750
PR-132	Gilman Paper Co., St. Marys, Ga.	1	500	650	750
PR-154	Pan African Paper, Kenya	1	225	600	750

Cascade Evaporators:

In the cascade evaporator, spaced tubular elements arranged horizontally are supported between two circular side plates to form a wheel that is partially submerged in a bath of hot-liquor contained in the lower position of the evaporator housing. Slow speed rotation turns the welded tubes into the gas stream; as the tubes rise above the liquor bath, the surface coated with black liquor contacts the gas stream flowing through the wheel above the liquor level. The number and arrangement of the wheels to provide the amount of total contact surface required, depends on the weight and temperature of the gas and the weight of water that must be evaporated from the liquor. It can concentrate the black liquor up to 65% solids.

BABCOCK & WILCOX CO.
BLACK LIQUOR UNITS WITH VENTURI SCRUBBER - EVAPORATORS

Contracts	Customer	No. of Units Sold	B&W Ton Rating	Oper. Press	Temp. °F
S-9905	Western Kraft Corp., Millersburg, Ore.	1	117	250	Sat.
S-9912	Potlatch Forests Inc., Lewiston, Idaho	1	300	600	750
S-9915	Int. Paper Co., So. Kraft, Natchez, Miss.	1	250	650	750
S-9925	Watervliet Paper Co., Watervliet, Mich.	1	30 T. Smelter	120	Sat.
S-9930	Owens Ill. Glass Co., Big Island, Va.	1	40 T. Smelter	185	Sat.
S-9931	Int. Paper Co., So. Kraft, Mobile, Ala.	2	360 ea.	450	725
S-9932	Northwest Paper Co., Cloquet, Minn.	1	300	600	750
S-9958	Mead Corp., Lynchburg, Va.	1	108 (NSSC)	600	750
PR-34	Gulf States Paper Corp., Demopolis, Ala.	1	330	600	750
PR-36	Int. Paper Co., So. Kraft, Panama City, Fla.	1	360	1275	900
PR-37	Int. Paper Co., So. Kraft, Pine Bluff, Ark.	2	390 ea.	1275	900
PR-38	Western Kraft Corp., Millersburg, Ore.	1	165	250	580
PR-40	Buckeye Cellulose Corp., Foley, Fla.	1	550	600	750
PR-41	American Can Co., Naheola, Ala.	1	390	875	825
PR-43	Eastern Corp., Lincoln, Me.	1	165	635	650
PR-44	Hoerner-Waldorf Corp., Missoula, Mont.	1	300	600	750
PR-45	Champion Int. Paper, Lawrence, Mass.	1	66	400	600
PR-48	Int. Paper Co., Ticonderoga, N.Y.	1	150	425	700
PR-52	Boise Cascade Corp., Walla Walla, Wash.	1	165	250	580
PR-58	Hoerner-Waldorf Corp., Missoula, Mont.	1	300	600	750
PR-59	American Can Co., Naheola, Ala.	1	390	875	825
PR-60	Int. Paper Co., So. Kraft, Pine Bluff, Ark.	1	390	1275	900
PR-63	Thilmany Pulp & Paper Co., Kaukauna, Wisc.	1	390	620	825
PR-64	Boise Cascade Corp., Wallula, Wash.	1	250	260	580
PR-65	Bengal Paper Co., Calcutta, India	1	94	475	725
PR-66	Southwest Forest Products, Snowflake, Ariz.	1	250	1200	900
PR-69	D. M. Bare Paper Co., Roaring Springs, Pa.	1	122	615	730
PR-73	Kimberly-Clark Corp., Anderson, Cal.	1	150	600	600
PR-74	Int. Paper Co., Springhill, La.	1	500	870	825
PR-75	South Carolina Industries, Florence, S.C.	1	410	650	760
PR-76	S.D. Warren Co., Cumberland Mills, Me.	1	250	570	720
PR-81	Int. Paper Co., Georgetown, S.C.	1	900	1020	825
PR-82	Int. Paper Co., Natchez, Miss.	1	600	1250	925
PR-89	Continental Can Co., Nixon, Ga.	1	400	875	900
PR-95	Green Bay Pulp & Paper Co., Opello, Ark.	1	250	250	Sat.
PR-96	Owens-Illinois Glass Co., Big Island, Va.	1	40 (NSSC)	185	Sat.
PR-98	Hammermill Paper Co., Riverdale, Ala.	1	450	650	760
PR-99	TJK Corp., Riceboro, Ga.	1	450	650	760
PR-100	Western Kraft Corp., Albany, Ore.	1	165	250	580

BABCOCK & WILCOX CO.
BLACK LIQUOR UNITS WITH VENTURI SCRUBBER - EVAPORATORS

Contracts	Customer	No. of Units Sold	B&W Ton Rating	Oper. Press	Temp. °F
PR-102	Hoerner-Waldorf Corp., Missoula, Mont.	1	500	600	750
PR-104	Central Pulp Mills, Poona, India	1	122	625	750
PR-106	American Can Co., Naheola, Ala.	1	390	875	825
PR-107	Brown Co., Berlin, N.H.	1	466.5	850	760
PR-109	Olin Kraft, Canoas, Brazil	1	108	600	705
PR-110	Georgia Pacific Corp., Port Hudson, La.	1	690	875	825
PR-111	Container Corp. of America, Cali, Colombia	1	150	700	750
PR-129	Western Kraft Corp., Hawesville, Ky.	1	225	250	550
PR-152	Rigesa S.A., Tres Barras, Brazil	1	178	600	700
PR-164	Punalur Paper, Kerala, India	1	200	500	750
PR-173	Container Corp. of America, Cali, Colombia, S.A.	1	200	250	460

Venturi Scrubber - Evaporators:

The venturi evaporator-scrubber is a device that collects the fume from the waste gas and also provides contact of the gases with the black liquor for concentration by evaporation. This scrubber depends on the collision of fume particles with liquid droplets. The liquor is concentrated by cooling the gas to about 180°F. The liquor is recirculated from the cyclone separator sump to the Venturi throat nozzles at a concentration of 60-70% solids. Fume collection coefficiencies of 90 to 94% are continuously maintained.

C-E recovery unit orders

CASCADE EVAPORATOR SYSTEMS

CUSTOMER NAME LOCATION	DRY SOLIDS CAPACITY LBS/DAY	PRESSURE – PSI S. HO. TEMP. °F
Allied Paper Jackson, Ala.	1,700,000	400/700
Chesapeak Corp. of Virginia West Point, Va.	2,700,000	1,225/900
Churchill Forest Industries Manitoba, Canada	1,450,000	775/825
Comp. Portuguesa De Celulosa Cacia, Portugal	800,000	910/797
Consolidated Paper Co. Wisconsin Rapids, Wisc.	1,200,000	1,275/900
Crown Zellerbach Camas, Wash.	1,980,000	415/525
Federal Paperboard Riegelwood, N C.	2,100,000	850/825
Westvaco Corp. Covington, VA	3,968,000	650/750
Westvaco Corp. Luke, MD	3,450,000	645/720
Georgia-Pacific Corp. Port Hudson, LA	3,000,000	900/825
Great Lakes Paper Co. Thunder Bay, Ontario	3,000,000	900/900
International Paper Co. Natchez, Miss	2,700,000	600/750
International Paper Co. Panama City, Fla.	2,700,000	450/450 (2 units)
Longview Fibre Longview, Wash..	3,300,000	850/750
New Zealand Forest Products Kinleith, N Z	2,500,000	350/490
St. Joe Paper Co. Port St. Joe, Fla.	3,180,000	1,300/900
Union Camp Corp. Savannah, Ga	4,050,000	1,375/925
Canadian Cellulose Prince Rupert, B.C.	2,640,000	625/650
Canadian International Paper La Tuque, Que.	3,000,000	400/500
Eastex, Inc. Evadale, Texas	3,300,000	625/750
Hudson Pulp & Paper Palataka, Fla.	3,600,000	1,300/900
Kimberly-Clark Corp. Coosa Pines, Ala.	2,700,000	575/750
Kimberly-Clark Corp. of Canada Terrace Bay, Ontario	2,400,000	875/900
Northwestern Pulp & Paper Hinton, Alberta	2,400,000	625/750
Proctor and Gamble Grand Prairie, Alberta	3,300,000	910/800
Scott Paper Co. Skowhegan, Me.	3,000,000	900/850
Sociedade Industrial De Cullulose Setubul, Portugal	1,186,800	925/878
Weyerhaeuser Co. Everett, Wash.	1,000,000	620/710
Weyerhaeuser Co. Plymouth, N.C.	4,500,000	875/825

EXTENDED ECONOMIZER SYSTEMS*

CUSTOMER NAME LOCATION	DRY SOLIDS CAPACITY LBS/DAY	PRESSURE – PSI S. HO. TEMP. °F
Arkansas Kraft Morrilton, Ark.	2,000,000	615/735
ish Forest Products St. Felicien, Que.	3,000,000	625/750

LAMINAIRE AIR HEATER **

CUSTOMER NAME LOCATION	DRY SOLIDS CAPACITY LBS/DAY	PRESSURE—PSI S. HO. TEMP. °F
Boise Cascade St. Helens, Ore.	2,100,000	400/750
Boise Cascade Wallula, Ore	2,100,000	400/750
Continental Can Hodge, La.	3,700,000	1,275/900
St. Regis Tacoma, Wash.	2,590,000	450/725
Weyerhaeuser Co. Valliant, Okla.	4,500,000	1,300/925

* See following page for note.
** See following page for note.

* EXTENDED ECONOMIZER SYSTEMS:

The types of extended surfaces are cast iron or aluminum gill rings, spiral fins and small metal studs welded to the tubes. The extended surface economizers have economic advantages over bare tube surface in lower first cost and smaller space required for installation. Extended surface tubes are normally installed horizontally in a staggered pattern. They are suited for units without air heaters.

** LAMINAIRE AIR HEATER:

This regenerative type air heater is of two types: (1) rotating plate and (2) rotating duct connections. In the rotating plate type regenerative air heater, heat storage plate elements are heated progressively in a flowing gas stream, and then progressively rotated by mechanical means into a flowing air stream where the stored heat is released to the air before the plates are returned to the gas stream. In the rotating duct connections plates are stationary. Depending upon the gas and air inlet and outlet temperatures, two or three types of heating surface metals with ceramic coating are used.

COPELAND SYSTEMS INCORPORATED
(SUBSIDIARY OF FOSTER WHEELER DEVELOPMENT CORPORATION)
BLACK LIQUOR UNITS WITH DIRECT CONTACT EVAPORATORS

NO.	PURCHASER, LOCATION, OPERATION	MATERIAL PROCESSED	TECHNOLOGY	YEAR OF START-UP
1	Domtar Fine Papers Ltd. Cornwall, Ontario 600 tpd bleached Kraft board and specialties	200 tpd equivalent Kraft black liquor with chemical recovery (Na_2SO_4-34%/Na_2CO_3-66%)	Kraft overload recovery by fluidized bed combustion at 32% liquor solids with 60,000 lbs/hr steam generation at 250 psig/Sat.	1975

DIRECT CONTACT EVAPORATORS:

In the direct contact evaporator, the liquor and flue gas are brought into intimate physical contact, and there is a mass transfer of water vapor from the liquor to the gas across the liquor-gas interface.

The direct contact evaporator used in the recovery unit is of the cyclone, cascade or Venturi type which were described previously.

APPENDIX B

CORROSION IN BLACK LIQUOR BOILERS

The corrosion rate is strongly affected by skin metal temperature, type of atmosphere (reducing or oxidizing), gas constituents, and tube metal composition. It is further complicated by operating pressures, high velocities, and erosive particle impingement. Cyclic operation also increases the potential for corrosion, due to accelerated exfoliation of semiprotected scale. Corrosion follows a parabolic relationship with time, i.e. corrosion tends to "drown" in its own waste products unless they are removed by spalling due to thermal cycling or other causes.

Knowledge of the action of the gas constituents on the principal and minor elements of the tube metal, along with the relative thermodynamic stability of the various metal compounds that could be formed, are necessary to determine corrosion. The gas constituents may be oxidizing (H_2O, CO, CO_2), carburizing (CO, CO_2, CH_4), sulfidizing (SO_2, H_2S, COS), or nitriding (N_2, NH_3). The tube metal is principally composed of Fe, Ni, or Cr, with minor additions of Si, Mn, Cu, Ti, Al, Mo, etc. The metal compounds that could be formed are oxides, sulfides, carbides, and nitrides, simple or complex. As a result of chemical reactions, new species, including S_2, O_2, C, HS, COS, and SO_3, will be formed. At any given pressure and temperature, the gas will shift composition to approach equilibrium. The radiant furnace zone, especially at the hearth area, incurs extensive corrosion compared to the convection surface zones (superheater and boiler bank). (Ref. 13)

At higher operating pressures, sulfur and oxygen partial pressures are similar, but carbon activity increases significantly. Depending upon changes in sulfur and oxygen activity through the predominant scale, other reaction products may form. If the sulfur activity at the interface of a chromium oxide (Cr_2O_3) scale surface falls below the value at which the sulfide is in equilibrium with the metal, only the oxide will form, and the sulfides will not grow beneath the scale. The penetration of any protective oxide scale system by sulfur is inevitable, and, eventually, that scale will be destroyed by the undergrowth or internal formation of sulfides.

The equilibrium mixture changes significantly when the pressure is changed. As for example, when the pressure is changed from one atm. to 68 atm., sulfur and oxygen pressures are similar, but carbon activity is increased by a factor of over 50. A shift toward equilibrium for CO/CO_2 may be established in seconds, where as the CH_4/H_2 equilibrium shift has a half life of over seven minutes. That is, the methane content will be reduced to half its initial value in this time span. Nickel-NiS slags are liquid above 1193^oF (918 K) while Fe-FeS-FeO slags are liquid above 1697^oF (1198 K). Melting of Fe-FeS-FeO slags on Fe-Al-Cr is at temperatures as low as 1650^oF (1172 K). Sulfide melting temperature is of major importance in determining the use of stainless steels and high temperature alloys. (Ref. 13)

In black liquor boilers, the phenomenon of corrosion has been observed at the following locations:

- The window face of the furnace wall tubes. The attack is limited to an area between the primary air ports from six to eight inches above and below the ports. This high heat relase area (since the heat absorption rate is nearly twice (40,000 Btu/hr/sq.ft.) as high as the average rate for (containing localized concentrations of CO_2, O_2 and S compounds) are major reasons for attack. Under the furnace conditions, the gases always generate sodium hydroxide (NaOH) vapor by the following reaction:

  $$2\ Na_2S + H_2O + 2O_2 \rightarrow Na_2S_2O_3 + 2\ NaOH$$

  This NaOH vapor penetrates the porous wall structure into the small closed space. Here, the vapor condenses due to the considerably cooler tube surface. This causes a vacuum which draws additional NaOH vapor. The additional components such as Na_2CO_3 and Na_2SO_4, lower the melting point of NaOH still further. Thus, the NaOH appears as a smelt at higher boiler pressure. This molten NaOH reacts with oxidized steel (ferric oxide-Fe_2O_3) forming sodium hypoferrite ($NaFeO_2$) as follows:

$$2NaOH + Fe_2O_3 \rightarrow 2NaFeO_2 + H_2O$$

If removed, the generated $NaFeO_2$ exposes the unattacked tube metal (Fe) for further corrosion attack by concentrated NaOH. $NaFeO_2$ in the presence of O_2 transforms to sodium ferrate (Na_2FeO_4).

- In the reducing atmosphere in which sodium sulfide (Na_2S) along with high metal temperatures results in a fire side corrosion of the flat studs (corrosion starts at 570°F and maximizes above the 750°F). Burn-through of the flat stud barrier above and below the primary air ports accelerates the penetration and deposit of alkaline salts in back of the furnace wall tubes.

- At the upper parts of the furnace (above the furnace zone), due to the following reactions, elemental S is generated:

$$H_2S + 1/2\ O_2 \rightarrow H_2O + S$$
(known as "sulfide" corrosion)

$$Na_2S + 2\ CO_2 \rightarrow Na_2CO_3 + S + CO$$

$$2Na_2S + 3\ SO_2 \rightarrow 2Na_2SO_3 + 3S$$

The principal corrosion product is formed by the reaction:

$$Fe + S \rightarrow FeS$$

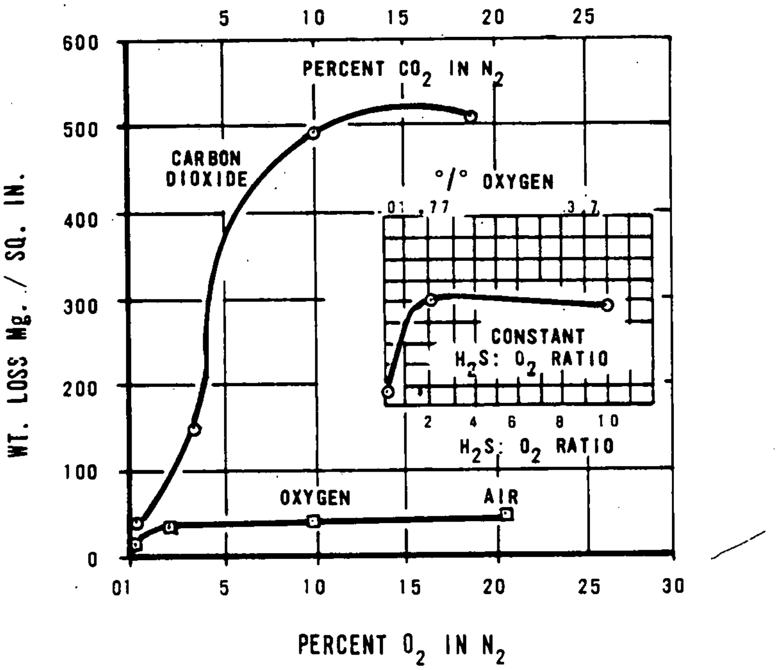
The formation of iron sulfide (FeS) in the corrosion scale suggests that the oxygen pressure beneath the scale may be in the order of 10^{-14} atmospheres. At higher SO_2 or O_2 pressures, iron oxides form, and, in the presence of oxides on iron surfaces, higher sulfur pressures and moistures are needed to form iron sulfide (FeS). (Ref. 14)

The corrosion caused by the furnace gases is dependent on the varying ratio between H_2S and O_2 due to lack of combustion air, overloading of the boiler, high sulfidity, and sulfur losses. The corrosion is diminished by proportional increase of oxygen as well as by an increase of water vapor and SO_2. In the area near the tube walls below the primary air ports, the furnace gas analysis in recovery units show large amounts of carbon dioxide (7 to 9 percent) and small amounts of sulfur dioxide (0.05 percent or less). The effect of concentrations of CO_2 on the corrosion rate is shown in Figure 12.

- At the smelt level, the corrosiveness of the smelt depends primarily the amount of sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) present. The resulting corrosion can be so severe that a bare stainless steel tube cannot stand a steam pressure higher than 1200 psig.

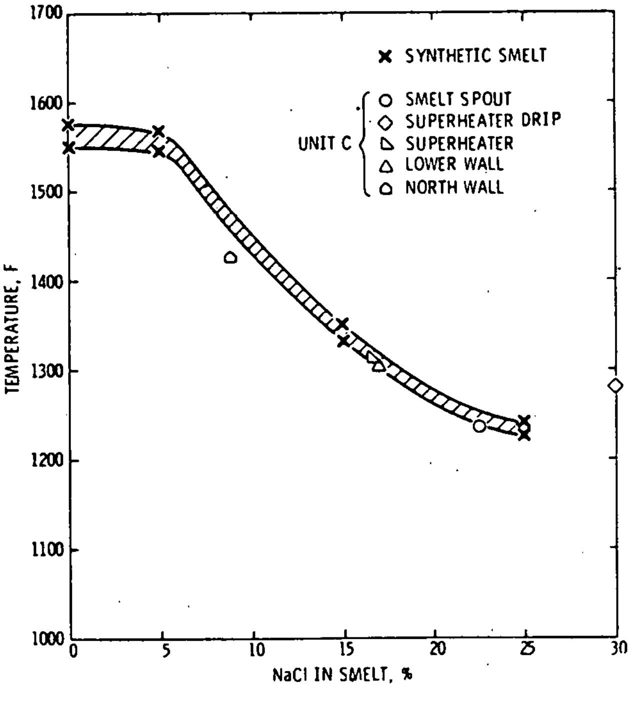
As shown in Figure 13, the melting point of the smelt (mostly Na_2S) decreases as the concentration of sodium chloride (NaCl) increases. Based on hot corrosion screening tests for two mixtures of NaCl and Na_2SO_4, corrosion rates on IN- 738 and UDIMET-500 are plotted in Figures 14 and 15. Chloride stress corrosion has cracked the solid stainless steel tubing. It is advisable to retain a carbon steel tube as the pressure-bearing tube. Chloride stress corrosion conditions may arise in the furnace during shutdown and waterwash operation in the boiler. The origin of chlorides may be either sea water or bleach plant

FIGURE 12
EFFECT OF FURNACE GAS COMPOSITION ON CORROSION (REF. 8)



AESD-79-0228

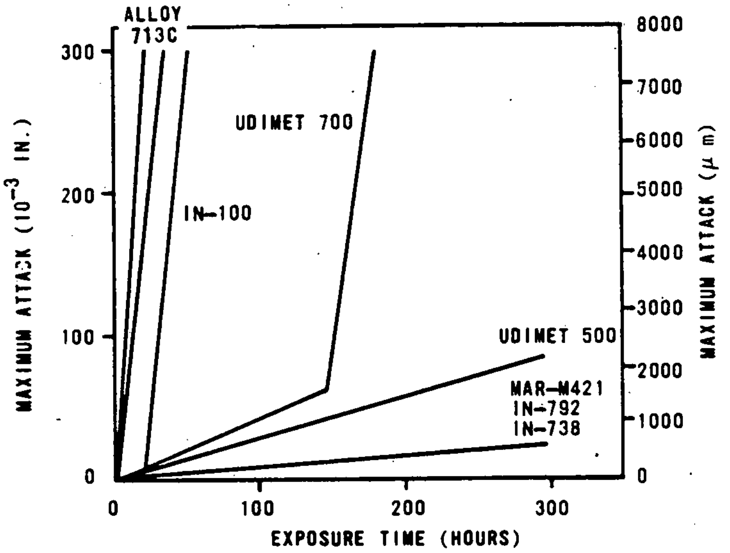
FIGURE 13
EFFECT OF SODIUM CHLORIDE ON THE MELTING POINT OF SMELT (REF. 8)



AESD-79-0229

FIGURE 14

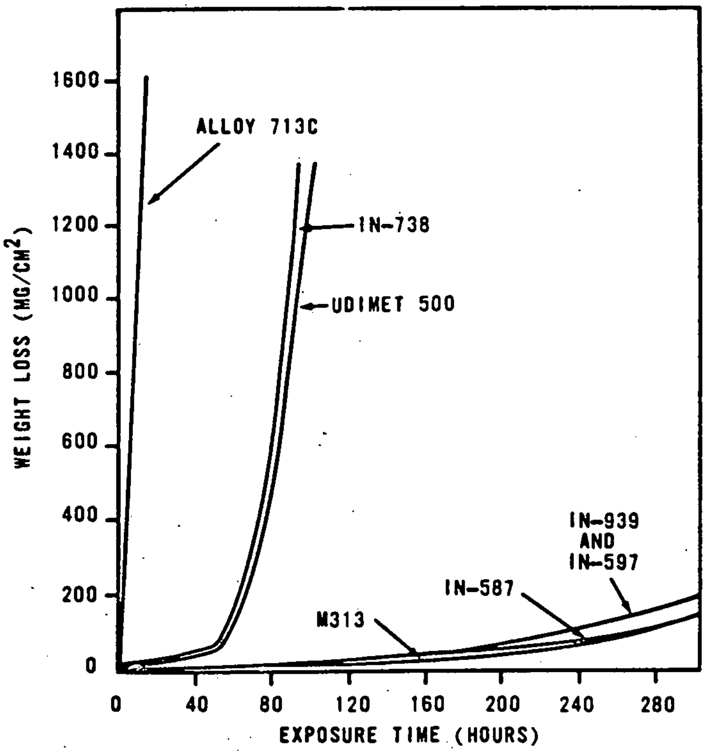
COMPARISON OF SUPERALLOY PERFORMANCE IN 90 PERCENT Na_2SO_4 –10 PERCENT NaCl CRUCIBLE TEST AT 927° C. (REF. 15)



AESD-79-0230

FIGURE 15

COMPARISON OF SUPERALLOY PERFORMANCE IN 75 PERCENT Na_2SO_4 – 25 PERCENT NaCl SALT SHOWER TEST AT 900°C (REF. 15)



AESD-79-0231

recycle water. Relatively lower melting points of sodium thiosulphate (Na_2SO_3) and sodium pyrosulphate ($Na_2S_2O_7$) result in high corrosion rates. The expected reaction is:

$$Fe_2O_3 + 3Na_2S_2O_7 \rightarrow 2Na_3Fe(SO_4)_3$$

Sodium sulfide (Na_2S) is corrosive in air, and sodium thiosulfate (Na_2SO_3) is extremely corrosive in nitrogen. The sodium sulfide is much more corrosive than the thiosulfate in the furnace gas atmosphere. Above 950°F (738 K), corrosion of studs has been recorded due to polysulfides and chlorides in the smelt.

Mechanical Technology Incorporated

Research and Development Division

MTI 78TR112

COMMERCIAL BOILER SYSTEM AND CYCLONE SEPARATOR TECHNOLOGY FOR MHD

Prepared For:
Department of Energy

November, 1978

MECHANICAL TECHNOLOGY INCORPORATED
968 Albany-Shaker Road
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ABSTRACT

Current conceptual designs of Magnetohydrodynamic (MHD) Electrical Power Generating Stations are open cycle systems which include the use of a Rankine cycle bottoming system in combination with the MHD loop. The high temperatures and presence of significant amounts of alkali metal compounds are items of concern for the Rankine cycle equipment. In this report, currently available commercial boiler systems and cyclone separations are reviewed. The applicability of this technology to an MHD system is assessed, and development requirements identified. This report is divided into three sections: 1.0 Black Liquor Boilers, 2.0 Slag Tap Boilers, and 3.0 Cyclone Separators.

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1.0 BLACK LIQUOR RECOVERY BOILERS

1.1 Introduction

Black liquor recovery boilers utilized in the paper industry operate with significant quantities of sodium sulfate (Na_2SO_4), which is chemically similar to potassium sulfate compounds that will be encountered in the MHD system. Fouling and corrosion problems encountered in the Black Liquor System are indicators of the problems to be expected in the MHD system. Techniques to minimize these problems in black liquor boilers and their applicability to MHD are examined in this section.

1.2 Summary and Conclusions

There are certain features employed in black liquor boilers which have merit regarding applicability to the MHD steam tube banks. Designs by major manufacturers incorporate wide lateral spacing in the tube banks to minimize plugging due to fouling. Spacings similar to black liquor recovery boiler practices are desirable for the MHD system. The technique of tangent tube construction in the superheater region to minimize the projected surface area perpendicular to the gas flow should reduce fouling and corrosion/erosion problems. Tube rows in the black liquor superheaters are in line (not staggered), to similarly minimize projected area perpendicular to the gas flow. This technique should be considered for the MHD system. Parallel flow superheaters are used in black liquor units to ensure that the hottest gases encounter the coolest metal tube temperatures. This practice should also be considered for the MHD system.

Corrosion of water-wall tubes is typically encountered in the furnace hearth area. The severity is apparently little affected by application of refractory coating in this area, but rather is minimized by maintaining low tube wall temperatures.

One manufacturer's design, Combustion Engineering, (CE) permits superheater screen inlet temperatures in the range of 1900°F (1040°C). At these temperatures, molten sodium compounds would be present on the tubes at the front of the superheater, and "sticky" deposits would occur further into the tube banks. Operation under these conditions apparently does not markedly effect either tube corrosion or fouling problems. The Babcock and Willcox design on the other hand, is based on a 1700°F superheater screen inlet temperature to minimize liquid/sticky deposits. Similar operating conditions are contemplated for the MHD superheater/reheater components.

The most critical concerns of the MHD system relative to the black liquor boiler are:

- Higher gas side and steam temperatures as envisioned in the ECAS and ETF studies. The possibility for corrosion, especially during transient periods of unbalanced steam/gas flow operation, is increased.
- The presence of coal slag constituencies also increases corrosion potential.
- Increased particulate loading. Fouling problems will be more severe due to loading on the order of 5 times higher in the MHD system.
- Presence of molten and sticky seed on the superheater tubes. Corrosion potential is enhanced with liquid seed, and fouling problems become more severe with "sticky" seed.

The following recommendations are made to increase the probability of success of the superheater-reheater-low temperature MHD component designs.

- Conduct small scale tests in a simulated MHD atmosphere.
- Continue the search for improved materials.
- Investigate the feature of gas quenching to eliminate either molten seed, or "sticky" seed problems as an alternative approach to current conceptual designs.
- Consider alternate means of seed removal, other than deposition on heat exchanger surfaces.
- Consider steam temperatures and pressures lower than ECAS and ETF levels for initial test train evaluation.

These recommendations point to the need for a greatly expanded data base for the MHD heat recovery equipment. Testing conducted to date has not duplicated the actual MHD operating conditions; hence, very little materials data and essentially no fouling information is available. It is important that such information be obtained as soon as practical, utilizing such facilities as Argonne National Laboratory's TCTDF [12] test facility, UTSI and Mississippi State University Test Programs, and the coal combustor development facility at Pittsburgh Research Center.

1.3 Discussion

1.3.1 Black Liquor Process Description[1]

Black liquor is the solution resulting in the sulfate pulping process from dissolving the lignin binder which molds the cellulose fibers together in wood chips. The wood chips are "cooked" under pressure with steam, sodium hydroxide, and sodium sulfide. During this cooking process, the lignin is dissolved in the cooking solution, which is then known as black liquor. The black liquor is then recycled for repeat use as a cooking liquor through several processes shown in the schematic in Figure 1-1. The boiler serves to burn off the organic compounds in the black liquor and convert the sodium sulfate (Na_2SO_4) to sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S).

The basic principles of operation of a typical boiler are depicted in Figure 1-2.[2] Black liquor (65 percent solids) is sprayed on the furnace wall for drying to evaporate the water remaining in the solution. The dried solids fall to the hearth area of the furnace for combustion. A reducing atmosphere is maintained in the hearth area to accomplish conversion to sodium sulfide. Additional air is added in other sections above the hearth in different locations to complete combustion and promote drying of the black liquor sprayed onto the furnace walls. The chemical reactions that occur in given areas are also shown in Figure 1-2.

1.3.2 Design Features

1.3.2.1 Furnace. There are several different philosophies utilized for the recovery boiler furnace design. The Foster-Wheeler Copeland Systems design[3]

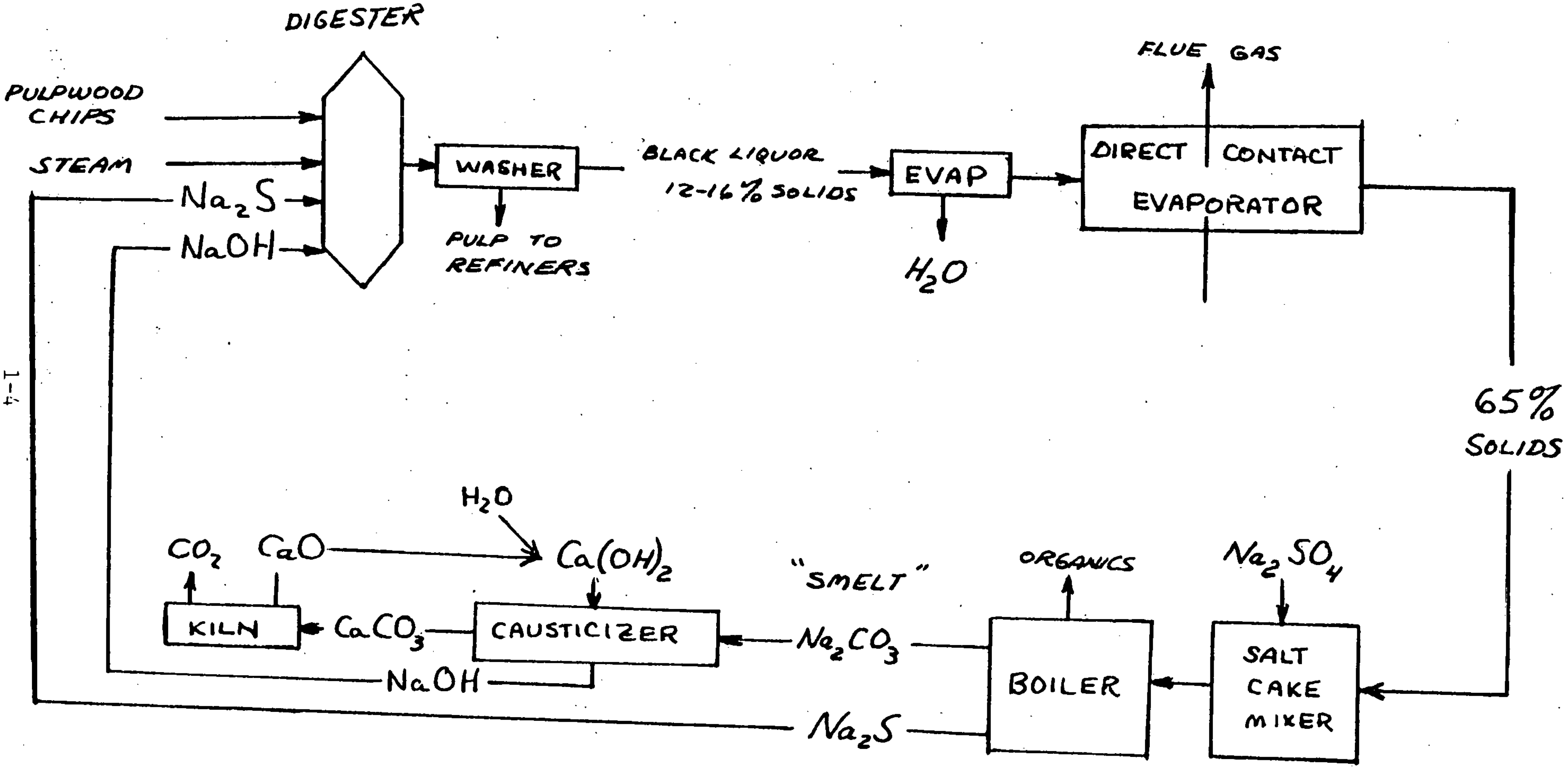

Fig. 1-1 Kraft Recovery Process

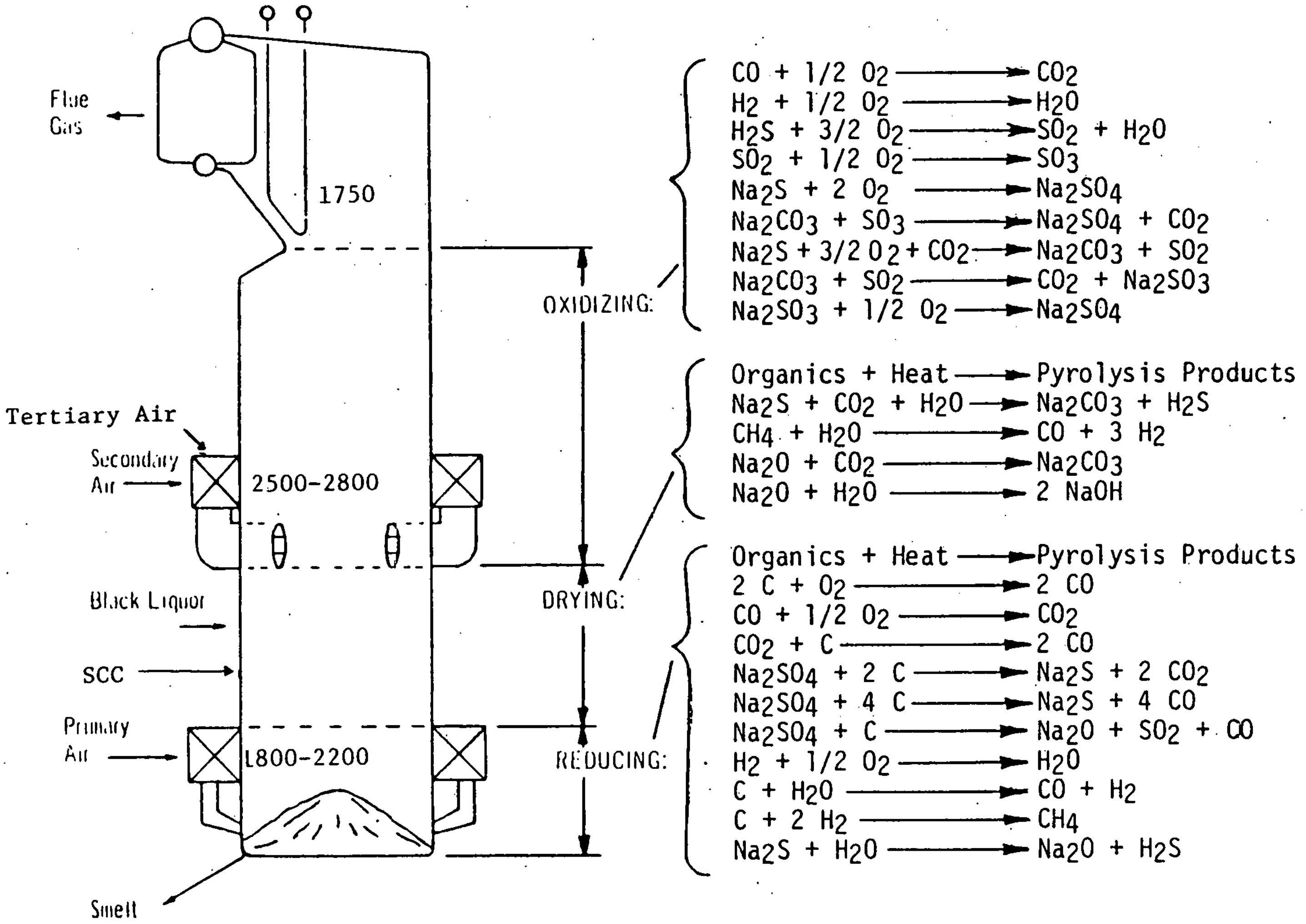

Fig. 1-2 Typical Recovery Unit Showing Reactions and Where They Occur, Reference [13]

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All designs incorporate a sloping floor to minimize smelt pool formation.

1.3.2.2 Tube Banks. The different design features are shown below in Table 2-2.

TABLE 1-2

	B & W [5,6]	CE [4]
S/H (Spacing, Lateral/Fore & Aft)	12"/3"	12"/0 (tangent tube)
Boiler Bank	6"/4"	9"/5 1/2"
Economizer	8"/4"	4"/7 1/2" finned
Steam Flow	Parallel	Parallel
Temperature in:		
Superheater (Slag Screen)	1700	1900
Boiler Bank	1300	1200
Economizer	750	700-750

Similar wide lateral spacings are used in the superheater designs by both manufacturers to minimize the possibility of fouling when ash deposits build up. The CE superheater design incorporates a tangent tube construction (tube wall surfaces in contact in the direction of gas flow) to minimize projected surface area perpendicular to the gas flow. This philosophy was chosen because the most severe ash deposition usually occurs on surfaces perpendicular to the gas flow due to impingement. Gas velocities through the superheater are on the order of 10 ft/sec for all designs. The most significant design feature of the CE unit is the superheater inlet temperature level. At the 1900°F inlet temperature, deposits on the initial rows of the superheater slag screen tubes are liquid. (The tube wall temperatures are on the order of 700-800°F so that, later, a solid ash is maintained adjacent to the tube surface.) Further into the superheater bank, the gas temperature passes through the ash solidification temperature of ∿ 1600°F. For several rows thereafter, sticky ash deposits result. The deposits apparently do tend to fall off (with soot blower assistance) before fouling occurs. The soot blowers actually blow upstream to enhance removal of the deposits. In the economizer bank, the CE design incorporates finned tubes (in the gas flow direction) to direct the flow and minimize ash deposition. The gap between fins is approximately 1/2 inch.[4]

1.3.3 Field Operation and Experience

Several paper companies were contacted (see References 13-18) to determine user experience in the field. The major problem areas were corrosion of the waterwall tubes in the lower part of the furnace and fouling in the superheater sections. The possibility of explosions occurring, due to smelt/water reactions caused by tube leakage in the lower furnace, dictates that frequent boiler inspections be made. The majority of users inspect boilers twice annually, with Crown-Zellerbach inspecting thrice annually on major holidays. Inspection shutdowns require three to four days (minimum) for inspection alone. All water/steam tubes are inspected during the shutdown, utilizing ultrasonic and radiographic techniques. Occasionally the front rows of superheater tubes require cleaning during shutdown due to buildup of hard deposits formed by molten/sticky salts during load fluctuations. Most users attempt to keep superheater slag screen entrance temperatures in the 1400-1600°F range to avoid such problems but occasional load fluctuations cause higher inlet temperatures and occasional shutdowns are required due to fouling. (It should be noted that the inlet temperatures to the superheater are not monitored, but settings are established via monitoring superheater exit temperatures.)

In the contrast to the practice followed by most users, the Hudson Pulp & Paper Company (Palatka, Florida) has a relatively new CE boiler (1250 psi, 900°F steam) that is operated at rated load continually. At rated load conditions, slag screen entrance temperature is 1900°F, and superheater entrance temperature is 1650°F (CE design values). The boiler was operated from December 1976 to December 1977 with no shutdowns. During the inspection period, hard deposit layers were removed from the slag screen and initial bank of superheater tubes, which would indicate that liquid smelt had been present on the tubes during operation. No fouling problems were encountered during the one year operational period.

The reason for the difference in fouling experience with this boiler, relative to other boilers, could not be determined from the users or from the manufacturer. The superheater and soot blower design does not differ markedly from older designs that reportedly have fouling problems. A more detailed investigation into specific boiler and soot blower operational procedures would be required to ferret out the differences.

Insofar as furnace water-wall tube corrosion is concerned, the industry feels that duplex tube configurations are necessary for steam pressures in excess of 850 psi. The Sandvik tube would be selected by the industry for these conditions. It consists of a carbon steel inside tube for pressure carrying and a 316 stainless steel outside shell for corrosion resistance.

1.3.4 MHD Requirements

The principal differences between the Black Liquor Recovery Boiler Systems and the contemplated MHD designs are listed in Table 1-3 below and discussed in the following paragraphs.

TABLE 1-3

Item	Black Liquor	MHD Steam Cycle (ETF/ECAS)
Steam Temperature/Pressure	to 925°F/1500 psi	1000°F/3700 psi
Primary Ash/Constituents Slag	Na Compounds	K compounds and coal slag
Maximum Gas Temperature	2800°F	3650°F
Gas Temperature to Steam Tubes	1900-2000°F	to 3000°F (ETF/ECAS)
Particulate Loading into S/H Grains/ft^2/sec	18	77
Melting Point °F	$Na_2\ CO_3$-1563 $Na\ SO_4$-1625	K_2CO_3-1645 K_2SO_4-1955

The increased steam requirements for the MHD system create concern for steam tube corrosion in the superheater region. The limited available data indicate that corrosion of tube materials at metal temperatures in excess of 1100°F in the presence of smelt, similar to that anticipated in the MHD system, could be extremely severe [7, 8, 9, 10, 11]. Any transient unbalances which either increase the heat load to the steam tubes, or decrease the heat transfer rate on the steam side, will increase corrosion potential. The higher gas temperature also increases the potential for corrosion during temporary steam side imbalances.

The presence of coal slag in the MHD system, in addition to the potassium compounds, adds further complexity to the corrosion problems due to several factors such as effects on the potassium compound melting temperatures and presence of additional trace elements in the system. There is a meager data base available to understand and predict the reaction of tube materials in the MHD environment for lengthy exposures and with cyclic effects caused by startup and shutdown that would be expected in the operation of the system.

Superheater fouling problems in the MHD system can be expected to be more severe than those encountered in black liquor boiler operation. The particulate loading in the MHD system is anticipated to be much higher than the black liquor boiler, as noted in Table 1-3. Although the fouling tendencies of K_2SO_4-K_2CO_3 are not clearly defined, again due to lack of data, it is expected that it will exhibit tendencies similar to the deposits in the Black Liquor Systems. Experiences in the Russian MHD effort and at the Pittsburgh Energy Research Center have indicated that severe fouling problems can be anticipated.[7] In addition to the quantity of ash, the temperature range of the gas in the superheater/reheater banks will result in formation of molten and "sticky" deposits as the gas temperature falls through the K_2SO_4-K_2CO_3 solidification temperature.

1.3.5 Technology Voids and Development Requirements

There are several areas where technology advancements or alternate approaches may be required for the MHD system, namely: (1) new materials, (2) deposit removal techniques, (3) recycle gas mixing systems, and (4) development of alternate seed removal techniques other than by deposition on steam tube surfaces. It would appear that scaled tests should be conducted at the earliest possible time to confirm or deny the need for these development items.

From the standpoint of materials corrosion in the steam tube banks, the data can be accumulated, prior to the testing of a full steam train system, by utilizing facilities at the Pittsburgh Energy Research Center (PERC) currently being used for the development of an MHD coal combustor. Tube material sample tests have been conducted in the past in this facility, and could again be conducted as an add-on item to the current program. The test component and technology development facility at Argonne National Laboratory ANL, currently under construction, is targeted to conduct tests of tube type heat exchangers in simulated MHD atmosphere in the near future. Early sample testing in the PERC facility could provide guidance to the ANL program.

As an alternate to the current conceptual design approach with liquid and sticky seed deposits in the steam tube banks, it is recommended that the concept of recycle gas mixing be pursued. In the event that corrosion and deposit removal in the sticky form are severe problems, gas quenching temperatures on the order of 1700°F could provide relief. Conceptual development of a quenching process utilizing recycled stack gas should include an economic assessment to evaluate additional power requirements, increase in heat exchanger surface requirements, and overall cycle effects.

An additional alternate approach to the seed deposition problem would be via removal of seed by techniques that do not involve the use of heat exchanger tube materials. Conceptual designs could be developed to utilize devices such as cyclones, expansion wave techniques, or moving bed filters. The applicability of any of these approaches is dependent on characterization of the deposit and again emphasizes the need for testing at an early date. The economics of the alternate removal techniques, as in the case of gas quenching, must also be assessed.

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2.0 SLAG TAP BOILERS

2.1 Introduction

Slag tap boilers are coal-fired systems which operate with liquid slag in the furnace. Liquid coal slag will also be present in the radiant boiler section of the MHD Downstream Heat Recovery System. A review of existing slag tap boilers was conducted to define current problem areas, and identify technology requirements for the MHD radiant boiler.

2.2 Summary and Conclusions

Slag tap boilers operate successfully in utility atmospheres with a one-year operational period between shutdowns. The combustion gas in the MHD System, however, is expected to be more corrosive and may require more frequent shutdowns. Based on industry experience and materials testing, it is anticipated that corrosion problems can be minimized by control of waterwall tube temperatures through steam cycle selection. Experimental testing should be conducted to ascertain the magnitude of the corrosion problem. Slag tap boiler construction/design techniques that should be retained for the MHD System are sloping furnace floor and studded wall construction.

2.3 Discussion

2.3.1 Furnace Design

There are two basic types of slag tap boilers - pulverized-coal-fired and cyclone furnaces. These two designs are discussed in the following paragraphs.

2.3.1.1 Pulverized-Coal-Fired Boilers.[1,2] The concept of coal pulverization was initiated with the desire to promote a more rapid, fully mixed combustion process than that normally obtained in grate-fired, crushed-coal furnaces. The coal is pulverized to a fine "dust" and pneumatically injected into the furnace, with the finer coal particle size and turbulence created by injection, enhancing the combustion process. The formation of a liquid slag pool in the furnace occurred as an incidental result of this design, due to the higher combustion temperatures obtained. It was discovered that the liquid slag pool was desirable as a result of reduction of ash carry-over to the exhaust stack (40-50 percent for the pulverized coal furnace compared to 80 percent for typical dry-ash boilers). New furnace problems arose, however, with the formation of a liquid slag pool: 1) increased corrosion resulted in the hearth area, and 2) techniques had to be developed to achieve effective liquid slag removal. The problem of corrosion still exists but is minimized through use of sacrificial stud walls, refractory coatings and maintenance of tube wall temperatures in the area of 600°F. Slag removal problems have been decreased by the use of a sloping floor in the furnace, enlarged slag taps, and location of the pulverized-coal injectors so that the coal is fired directly at the slag tap hole. This last technique ensures that the maximum furnace temperature occurs at the tap to provide the lowest possible slag viscosity for removal purposes. Even with these precautions, occasional tap hole plugging occurs with high-slagging coals. In the final analysis, the pulverized-coal-fired furnace suffered from two undesirable features - tap hole plugging and use of a substantial amount of power required to pulverize the coal, thereby degrading overall station efficiency. These two drawbacks led to the development of the cyclone furnace discussed in the following paragraph. With the cyclone furnace successfully developed, production of pulverized-coal furnaces was terminated. Several of these furnaces are still in service at present.

2.3.1.2 Cyclone Furnace. [1,2,3] The cyclone furnace was conceived to overcome two deficits of the pulverized coal furnace: 1) to eliminate the need for pulverization, and 2) to provide better slag removal. The cyclone furnace operates with crushed coal, thereby reducing the coal sizing power requirements. Increased fan power is required, however, with the resultant auxiliary net power about equal to that of pulverized-coal furnaces. The design of the cyclone furnace is illustrated conceptually in Figure 2-1. Coal is injected tangentially at the head of the furnace, along with combustion air. Swirl and turbulence in the cyclone furnace promote effective mixing and result in higher combustion temperatures than those obtained in the pulverized-coal furnaces. A liquid slag pool is formed in the cyclone and runs off into the main boiler, as shown in Figure 2-1. The cyclone is constructed with water-cooled walls, and utilizes a ceramic wear liner for protection. Both corrosion, due to liquid slag, and erosion, due to coal particle abrasion, are experienced

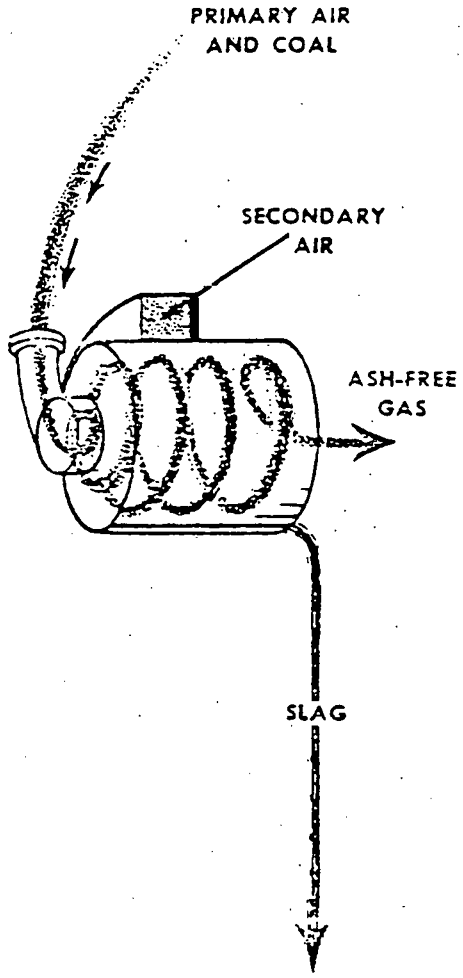

Fig. 2-1 Cyclone Furnace Design

in the cyclone. The wear liner is designed for a continuous one-year furnace operational period. During the annual shutdown/maintenance interval, the liner is simply replaced. The main boiler section experiences corrosion problems similar to those encountered with the pulverized-coal furnaces. Here again, studded wall construction is used and refractory linings are applied. The cyclone furnace operates with approximately 10 percent excess air overall. Locally, however, under the slag layer, the atmosphere is reducing.[4] Several utility companies have experimented with various refractory coatings to enhance corrosion resistance, but all have found that the lining is completely consumed in the one-year operating period. Regardless of lining consumption, the unit does normally operate for one year without shutdowns. The waterwall tube corrosion is mainly controlled by sacrificial studs and maintenance of ~600°F maximum tubewall temperatures, as for the pulverized-coal furnaces.[5]

The temperatures encountered in the cyclone furnace are usually on the order of 3200°F in the cyclone and 3000°F+ in the boiler furnace. It should be noted here that, although these temperatures are somewhat higher than those encountered in the pulverized-coal furnaces, the overall corrosion effects are similar. The materials of construction for both furnaces are the same, and both units operate for one year between shutdowns.

2.3.1.3 Convection Passage Design Philosophy. In coal-fired furnaces of all types, the ground rule used for the boiler design is to lower the radiant (water-walled) furnace gas temperature to a level below the initial deformation temperature of the particular coal being burned. There are two reasons for this approach. First is the concern for heat exchanger surface fouling. Reduction of the gas temperature below the initial deformation temperature of the coal ash is desirable, so that the ash deposited on the tube banks will be non-sticky and, hence, easier to remove. Secondly, there is concern for corrosion with the presence of fluid ash on heat exchanger surfaces at elevated temperatures.[5,7,8] Experience has indicated that presence of liquid slag on heat exchanger metallic surfaces, at temperatures in excess of 1000°F, causes corrosion severe enough that this practice is avoided in commercial installations.

2.3.2 MHD Requirements

Current conceptual designs for the MHD Heat Recovery System call for a radiant boiler section immediately downstream of the MHD Channel-Diffuser Exit. The conditions of the combustion stream at this point are more severe than normally encountered in existing commercial coal-fired boiler systems. The major concerns are: 1) higher temperatures, and 2) a more complex and corrosive slag. The MHD radiant boiler entrance temperatures are expected to be on the order of 3700°F, 600-700°F hotter than cyclone boiler furnace temperatures. The atmosphere in the boiler will be reducing, similar to conditions under the slag layer in the cyclone furnace. However, the increased potassium salt content of the gas stream is of concern from the corrosion standpoint. The planned MHD steam conditions of 3800 psia and 1005°F will require steam temperatures of 800°F at exit from the radiant boiler.[6] This will result in waterwall tube metal surface temperatures in excess of 800°F. Experience has indicated that corrosion of carbon steel tubes at this temperature will be a problem, and raises concerns relative to life characteristics of the MHD System.

Based on industry experience with existing systems, it seems advisable to adopt techniques which have been proven successful commercially. The concept of studded wall construction should be maintained to minimize the amount of corrosion experienced on tube waterwalls, utilizing the studs as sacrificial material. The sloping floor concept should also be maintained to enhance slag drainage and prevent slag-pool buildup. Finally, industry waterwall tube corrosion experience as a function of steam cycle selection should be reviewed, and the MHD desired conditions as envisioned in the ECAS studies should be revised as necessary, as development progresses to ensure successful MHD System commercial life.

2.3.3 Technology Voids and Development Requirements

The technology voids identifiable for the MHD radiant boiler section, compared to current coal-fired boilers, are corrosion oriented. Materials and coatings with increased corrosion resistance are desirable for the MHD System. As noted earlier in this report, the corrosion anticipated for the MHD radiant boiler is expected to be essentially a function of the selected steam conditions. To ascertain this, it is recommended that tests be conducted as early as possible to guide the overall MHD program. Tests planned at UTSI, Mississippi State, and Argonne National Laboratory are expected to provide this needed information. Additional data could be obtained utilizing the coal combustor development facility at the Pittsburgh Energy Technology Center.

There are additional, unique requirements for the MHD radiant boiler that are not addressed in current boilers. High NO_x concentrations are anticipated in the MHD System, and current conceptual designs utilize the radiant boiler to decompose NO_x through controlled cooling rates. Preliminary data from tests at UTSI indicate that NO_x emissions are controllable in this manner; however, additional testing would be helpful to determine the effect of variables such as scaling, stoichiometry, and combustion temperatures. The attainment of slag removal and seed separation in the boiler through temperature control is also a concern. Economic studies have indicated that on the order of 95 percent of the seed material must be recovered for recycling purposes. Testing must be conducted to verify that this separation can be achieved.

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3.0 CYCLONE SEPARATORS

3.1 Introduction

This report is a survey of cyclone equipment feasibility for liquid and solids removal in the MHD steam bottoming plant. Cyclone theory is reviewed, potential uses for cyclones are discussed, the capabilities of currently available equipment are assessed, and recommendations for development are presented.

3.2 Summary and Conclusions

Standard cyclones lack capability to effectively separate particulate matter with particle sizes of five microns or less. Development of modified cyclones that utilize aerodynamic or mechanical means of separation enhancement could be of interest to the MHD system in two areas, (1) seed separation prior to superheater entrance, and (2) flyash/seed separation at the econometer exit. Seed separation at the superheater entrance could be attractive to decrease superheater tube plugging. However, the elevated temperatures, corrosive atmosphere, and small particulate sizes anticipated would indicate that extensive development would be required. Development of improved efficiency collectors for flyash/seed collection at the economizer outlet could be helpful in reducing the load on electrostatic precipitators. The economic impact of these devices should be assessed if development is contemplated.

3.3 General Cyclone Theory [3,4]

The basic principle of operation of cyclones is to impart a spin to the gas stream, creating a vortex to separate solids by centrifugal force. A sketch of a typical cyclone is shown in Figure 3-1.

Air enters through the tangential inlet, spirals downward, and exits upward through the discharge duct in a strong vortex. Particle separation that can be achieved in a cyclone is dependent primarily on the following factors:

- Particle size
- Particle density
- Gas viscosity
- Vortex spin speed

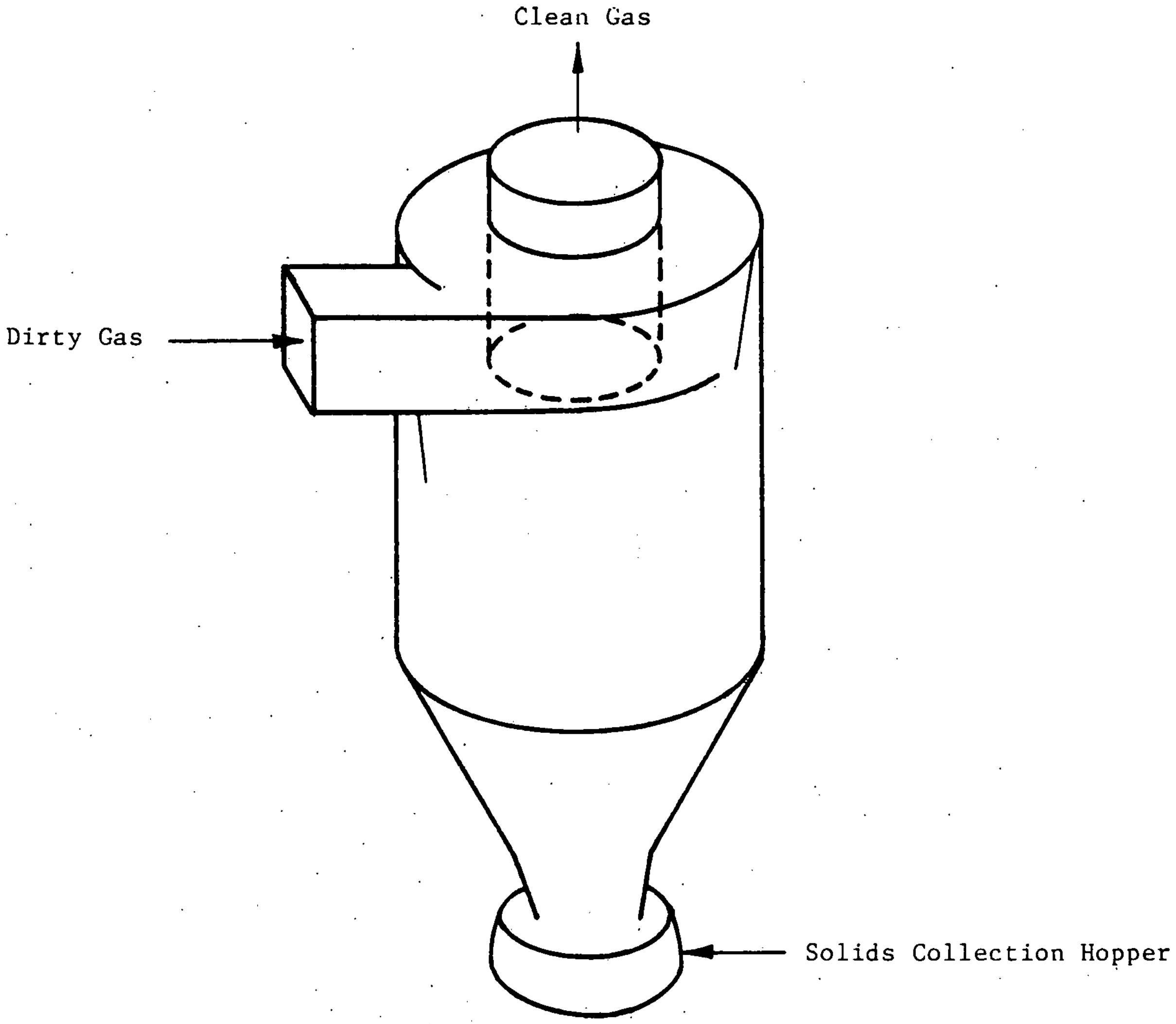


Fig. 3-1 Typical Cyclone Configuration

Theoretically, for a given cyclone design with a fixed particle density, gas density, and gas viscosity, there is a minimum particle size (referred to as the "cut" size) that can be collected. The "cut" size is determined by calculating viscous drag and centrifugal forces acting on the particles, and determining the particle size at which these forces are equal. All smaller particles will drift inward with the gas flow and will escape, whereas all larger particles will be separated. The "cut" size calculation is illustrated below:

> <u>Spin Speed</u>: The centrifugal force generated in a cyclone is a function of the spin speed, which is in turn a function of throughput mass flow, and cyclone geometry. For a selected geometry, and flow rate, the cyclone spin speed has been experimentally determined to be represented by two different relationships as shown in Figure 3-2.

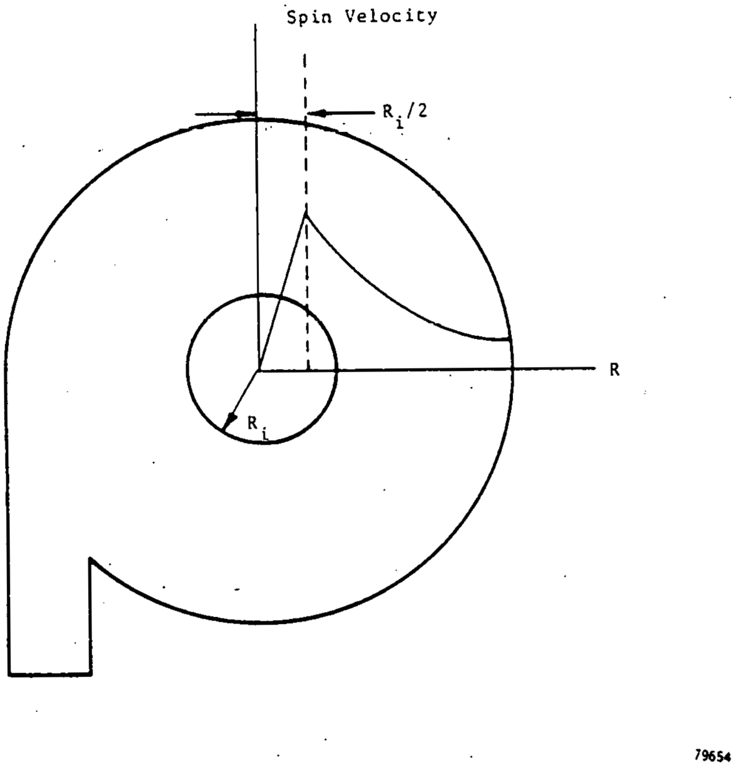


Fig. 3-2 Cyclone Spin Speed

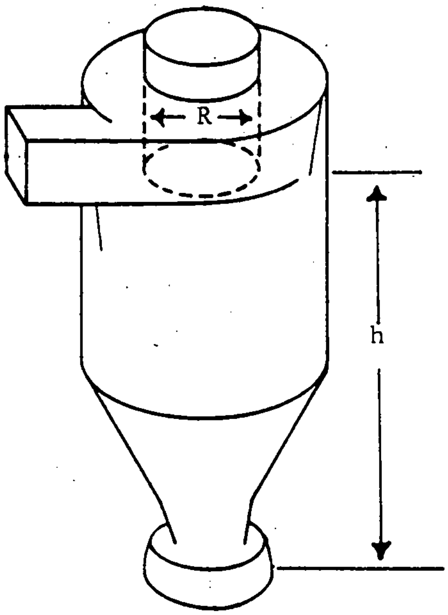
The inner core gas spins at constant angular velocity, and the outer gas according to the relationship U^2R = Constant.

Centrifugal Force - The centrifugal force generated = $\frac{U_T^2}{R}$, and is a maximum at R/2.

Inward Drift Velocity - The inward drift velocity is a function of mass-flow rate and cyclone geometry, and is calculated as follows:

$$W = \rho^{AV}$$

$$V = \frac{W}{\rho A} = \frac{\dot{m}}{2\pi \frac{R}{2} \cdot h}$$



Cut Size Calculation - At the location where maximum centrifugal force is generated, (R/2 in the preceding figure) the drag force on the "cut" size particle, due to the inward drift, will be exactly equal and opposite to the centrifugal force. The situation is analogous to one wherein a drag force counterbalances a gravitational field of magnitude equivalent to the centrifugal force. The cut size particle, then, in $\boxed{\text{a 1g}}$ field would free fall at the velocity $V_{FF} = \frac{V_{Inward}}{\text{Cent Force(gs)}}$

one G field

At free fall conditions (V=K)

Drag = Gravitational Force

$$6\pi\mu r_p = ma = \rho \frac{4}{3}\pi r_p^3 a$$

Therefore, for a given particular density, the "cut" size is determined. The theoretical separation should then be 100 percent for all larger particles and 0 percent for all smaller particles. Due to particle collisions and agglomerations, however, some smaller particles will be collected, and conversely, due to secondary flow fields and wall bounce effects, some larger particles will escape. The resultant collection efficiency curve, then, is shown typically in Figure 3-3.

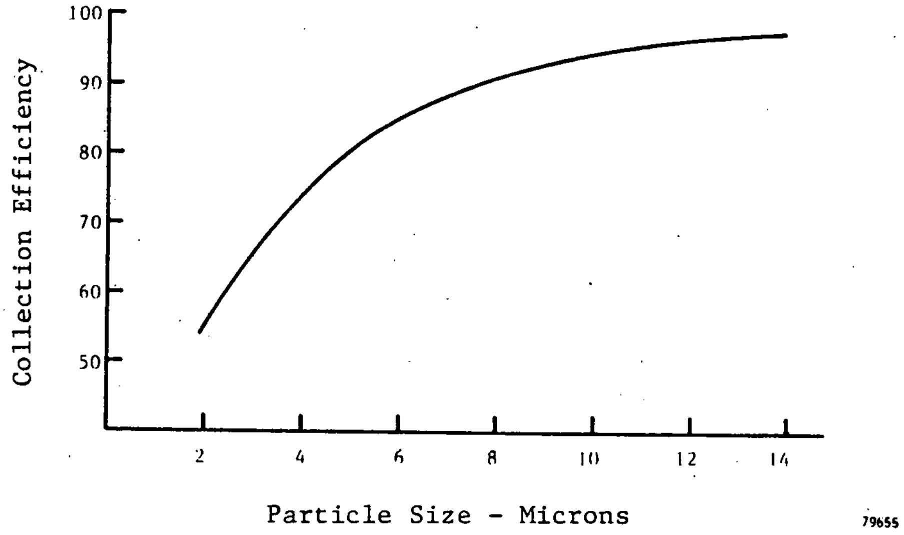


Fig. 3-3 Cyclone Fractional Collection Efficiency

The effect of various design parameters on the collection efficiency curve is presented qualitatively in Table 3-1.

TABLE 3-1

Parameter Increase	Efficiency
Particle Density	Increases
Cyclone Diameter	Decreases
Gas Viscosity	Decreases
Inlet Velocity	Increase then Decrease

3.4 Cyclone Applications in the MHD System

3.4.1 Summary

There are several requirements for liquid and solid material separation in the MHD System. These requirements and the probable application of cyclones are summarized in Table 3-2 and are discussed in detail in the following sections.

TABLE 3-2

MHD SEPARATION REQUIREMENTS

Separation Requirement	Temperature Range	Cyclone Potential	Problem Areas
Slag (liquid)	3000-3700	No	No cyclones available for this temperature.
Seed (liquid)	2060-3200	No	No cyclones available for this temperature.
Seed (solid)	~1700°F	Yes	Particle size
Emission Control	200-400°F	Yes	Particle size
Coal	200°F	Yes	Particle size

3.4.1.1 Slag Separation - The criteria of separate slag and seed recovery dictates that slag removal must be accomplished at temperatures above the point where the seed vapors begin to condense. Current MHD system conceptual designs utilize a radiant boiler at the MHD channel exhaust to condense and remove the coal slag carried over from the combustor.

Use of a cyclone to achieve slag separation at this location presents several problems. First, the MHD channel exhaust temperatures currently contemplated are in the order of 3600-3800°F. At this temperature, as much as 20 percent of the coal slag carried over into the radiant boiler[1] could still be vaporized (Figure 3-4) and would not be separated; therefore, this approach is considered impractical. Alternatively, the gas temperature could be reduced to ~3000°F, by quenching, to achieve slag condensation while leaving the seed in the vapor state.

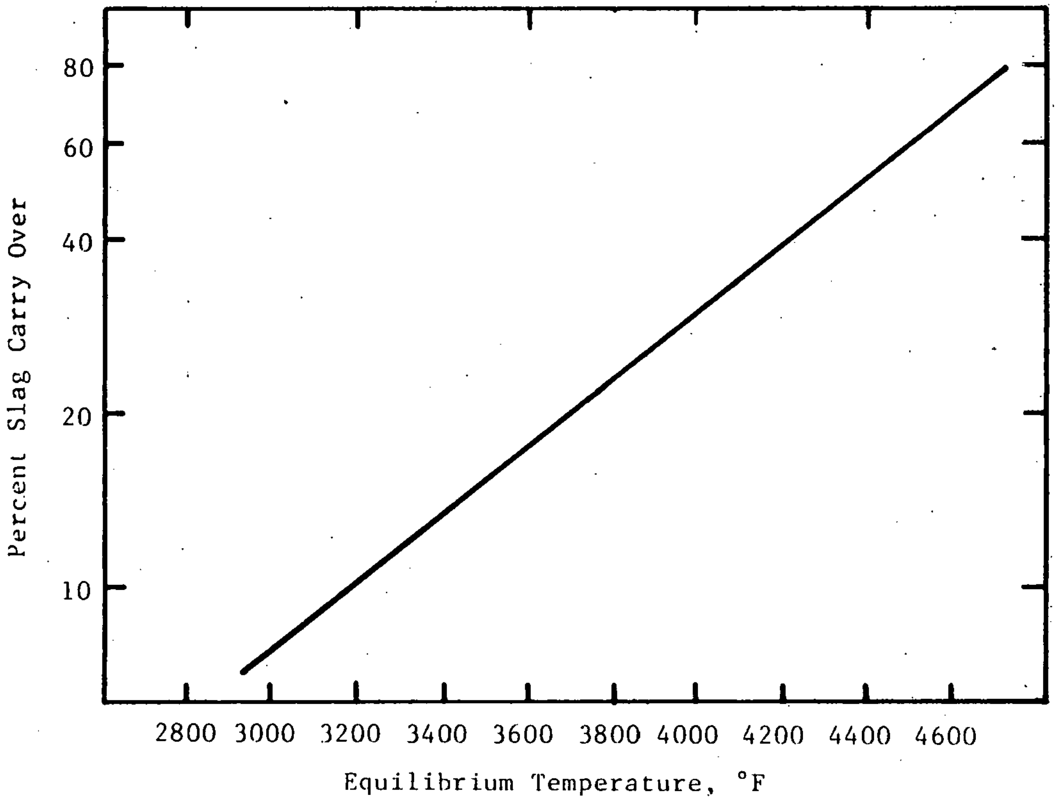


Fig. 3-4 Percent Slag Carryover as Vapor as a Function of Temperature

However, NO_x control is achieved in current design concepts through decomposition with residence times of 2-3 seconds at temperatures in excess of 3000°F. Quenching to 3000°F would not allow the required residence times and would result in NO_x control problems.

If NO_x control could be achieved by other means, such as utilization of a decomposition chamber prior to radiant boiler entry, then quenching to 3000°F could be accomplished to promote slag condensation. However, there are no state-of-the art cyclones capable of operating at 3000°F. Development would be required in the event that this approach is used.

It is concluded that the use of cyclones for slag separation in MHD systems is not practical for currently contemplated MHD systems. Alternate methods of NO_x control and cyclone development for temperatures of 3000°F would be required.

<u>3.4.1.2 Seed Separation</u> - Seed separation/removal from the gas stream is currently contemplated in both liquid and solid forms in the downstream sections of the stream bottoming plant (superheater, reheater, and low temperature air heater units). It is anticipated that removal of the deposited seed from the heat exchanger surfaces may be difficult and that corrosion may be a concern. Removal of seed by use of cylcones would reduce potential heat exchanger fouling problems and provide potentially easier-to-clean surfaces.

With base line plant operation at radiant boiler exit temperatures in the range of 2500-3000°F, the combustion gas exiting the boiler will be essentially slag-free but will contain seed in the vapor state. The gas then must be quenched to get the seed into a liquid or solid form for separation. A temperature of ~2000°F would be required to condense the seed vapor in a liquid form, and a temperature of ~1700°F would be required to sub-cool the particles in a solid state to the point where tackiness would not be a problem. Rapid gas quenching, however, may produce sub-micron, fume-like particles which would be difficult to separate. In addition, with quenching, the heat exchanger surface requirements are increased, but this approach may be attractive if heat exchanger seed removal is a serious problem.

The use of cyclones in this temperature range appears to be feasible. Several manufacturers have built cyclones for unique applications at temperatures ~1800-

1900°F. However, it is predicted that seed particles will be small and collection will be difficult.

3.4.1.3 Exhaust Stack Cleanup - For some plant designs,[6,7] the flue gas exiting the economizer section of the boiler is exhausted directly to the atmosphere. The flue gas will contain both flyash and seed particles which must be removed from the gas stream to enable effective seed recovery and reduce exhaust stack emissions. Here again, as in the case of seed removal further upstream, the particulate size and loading is as yet undetermined, but it is thought that the loading will be quite heavy, with small-to-medium size particles (50 percent 12-15μ)[1] or (50 percent 3-10μ)[5]. With EPA standards permitting a maximum of .1 lb particulate emissions per 1 m Btu fuel input, collection efficiencies on the order of 99 percent will be required. A cyclone alone cannot provide sufficient removal to meet the standards, but it could be used to reduce the load on the prime collection mechanism (ESP or baghouse).

Other designs [2, 6, 7] utilize the stack gas exiting the economizer for coal drying and transport. In this case, flyash/seed must be removed at the economizer exit, and coal particles must be separated from the flue gas after drying. The flyash/seed separation problem remains unchanged in this concept. The separation of coal particles presents an additional process requirement. The particulte loading will be very heavy and particle sizes relatively large. To separate as much of the coal as possible, a cyclone in series with a baghouse will most likely be used. This approach is attractive because most of the coal is removed in the cyclone, minimizing maintenance requirements associated with baghouse operations.

3.5 Existing Cyclone Capability

3.5.1 Cyclones and Multi-Clones

The principle of cyclone separation is dependent overwhelmingly on the balance between viscous and centrifugal forces. Conventional cyclone designs that utilize tangential entry, reverse flow, and center tube discharge do not vary markedly in collection efficiency, regardless of design details such as tailored inlet scroll passages, cone angles, etc. For throughput sizes on the order of 20,000 ACFM, collection efficiencies on the order of 80-90 percent can be achieved for particles sizes of five microns. Several manufacturers utilize a multi-clone design to enhance separation of finer particles. This concept consists of clustering several small cyclones (tube diameters generally less than one foot) in a common enclosure. Both tangential and vertical inflow with swirler vanes are utilized. Units of this size are prone to plugging in the collection vessel area with sticky and/or large particles. Generally, the collection efficiency improvements with these configurations (relative to standard cyclones), at particle sizes of 2 microns or less, is minimal. Illustrated on Figure 3-5 are fractional collection efficiencies from several sources. A general assessment of collection efficiency is provided by "typical" curves from references 3 and 4. Also presented on the curve are manufacturers' quotes for a range of throughput sizes. As would be anticipated, the smallest unit has the highest collection efficiency. The efficiency differences between units is probably due to pressure drop allowances and minor design differences. For all units, however, the effectiveness drops off rapidly below 5 micron particle size. It can be concluded that standard cyclones are effective for stack cleanup only when particle sizes are expected to be in excess of 5 microns.

3.5.2 Modified Cyclones

Four modified cyclones were identified in the industry survey conducted. Both aerodynamic and mechanical enhancement techniques have been utilized. The performance quoted for these units is presented in Figure 3-6, compared to the range of standard cyclone performance presented on Figure 3-5. In all cases, the quoted efficiencies exceed that of the standard cyclones. The four units are discussed in the following subsections.

3.5.2.1 Aerodyne "SV" Collector - The SV collector utilizes a secondary gas flow to augment the inlet (dirty) gas flow as indicated in Figure 3-7. The manufacturer claims collection efficiencies of 100 percent at 6 microns and 92 percent at 2 microns. Westinghouse has tested the unit under cold flow conditions and has been unable to verify these claims, measuring collection efficiencies on the order of 50 percent at five microns. General Electric has planned to utilize an aerodyne unit in a combined gas turbine/fluidized bed combustor unit, using part of the bed exit gas for the secondary inlet. Tests at one atmosphere and low

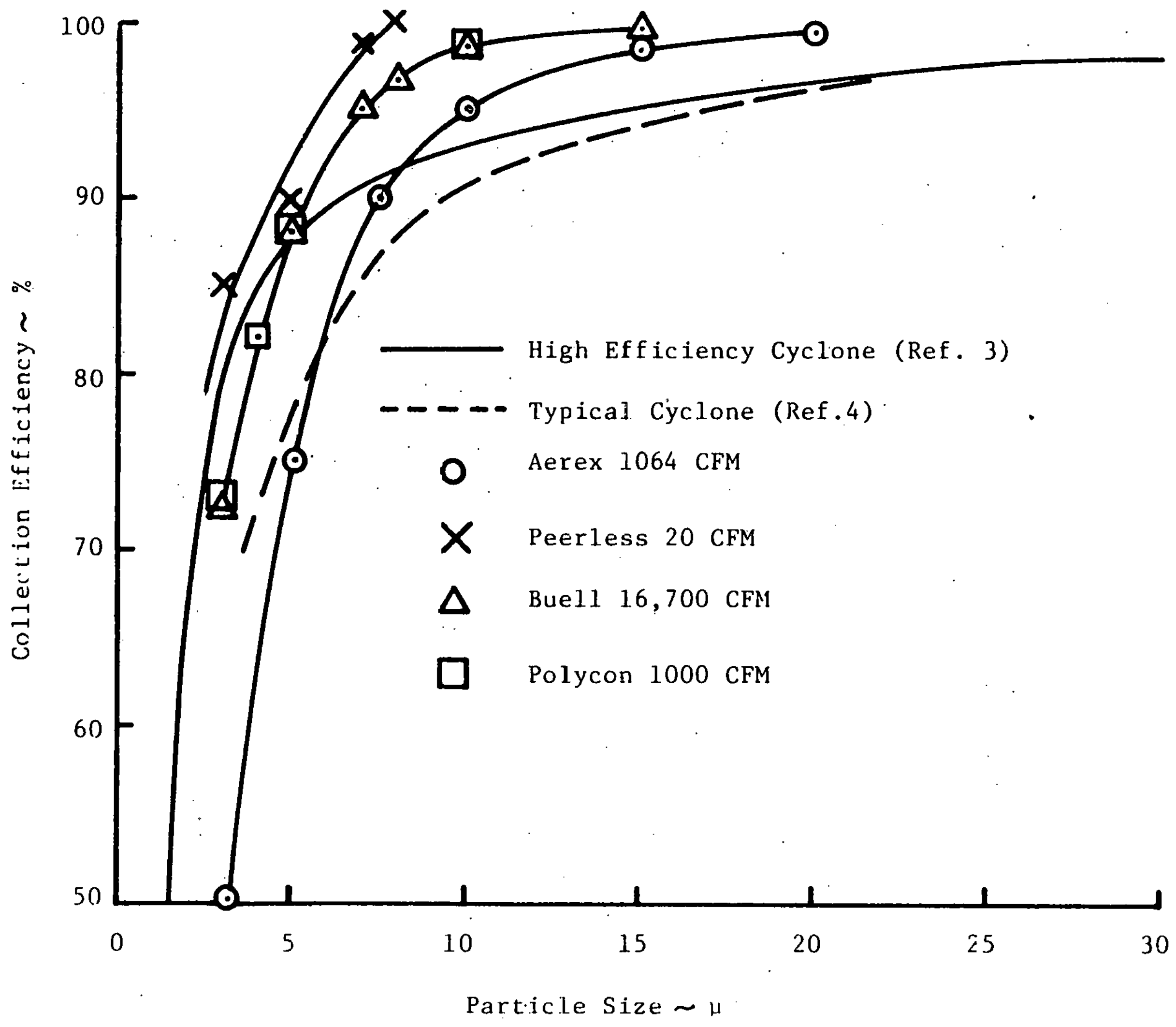


Fig. 3-5 Cyclone Performance Comparison

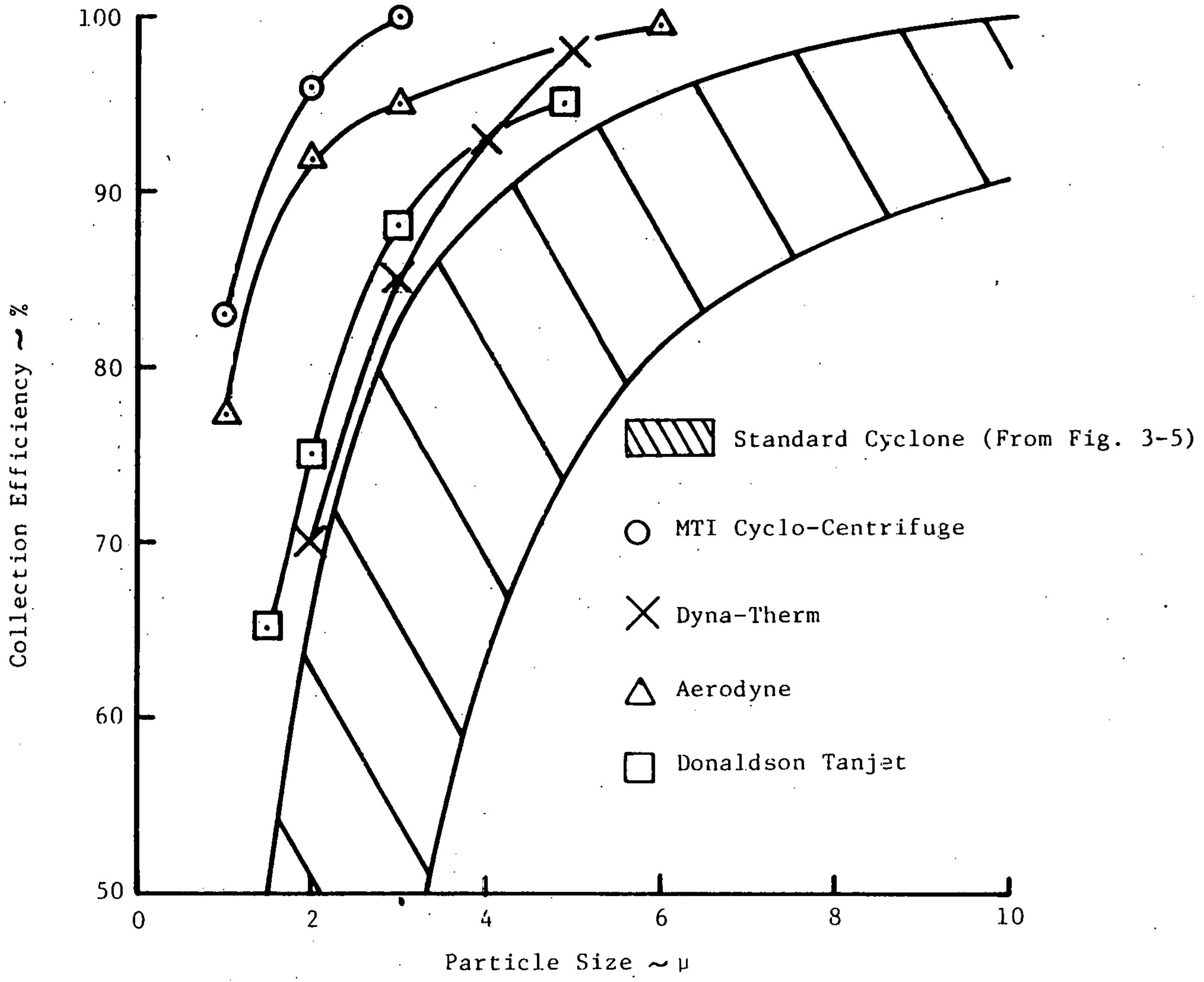


Fig. 3-6 Modified Cyclone Performance

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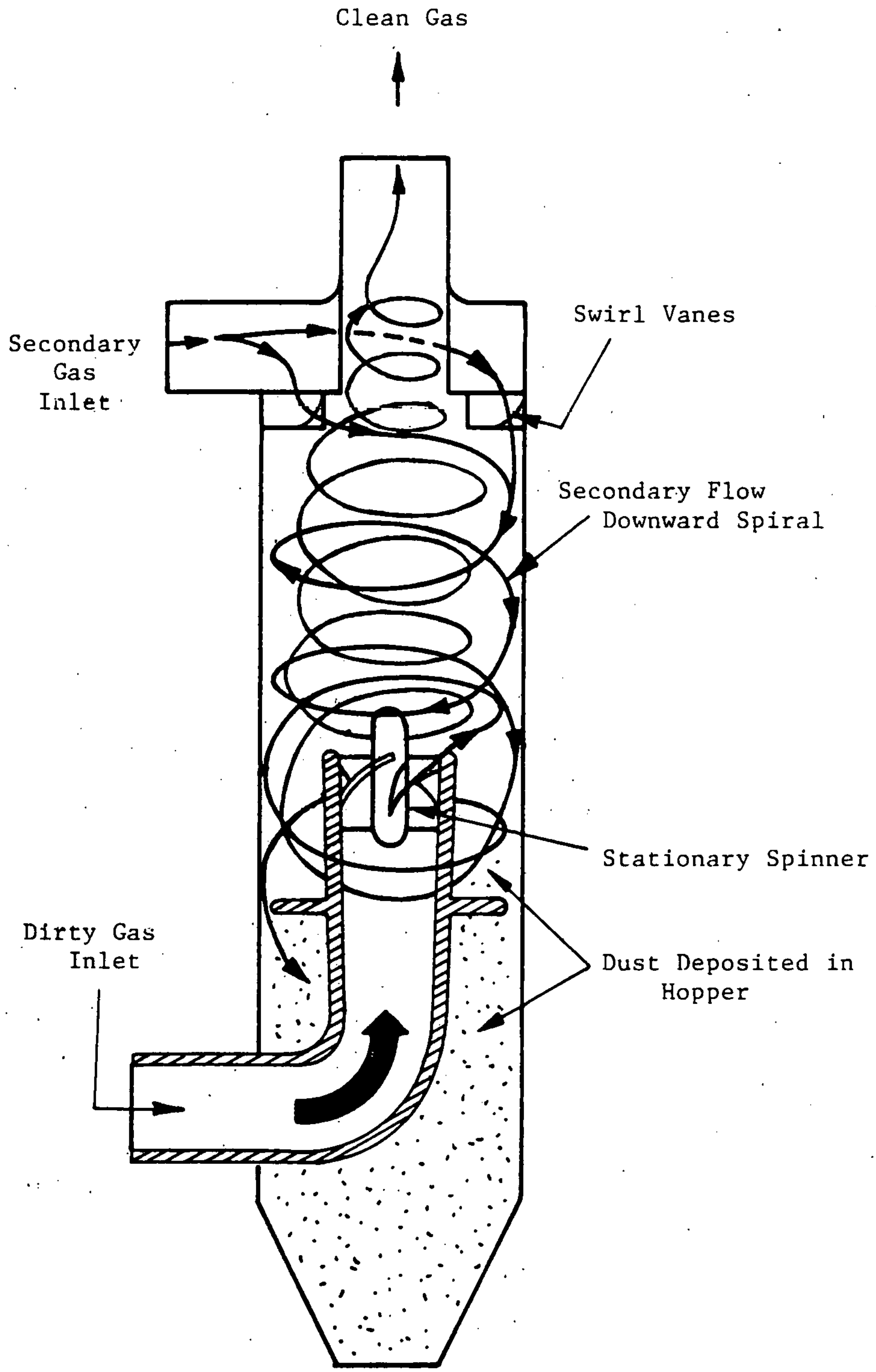

Fig. 3-7 Aerodyne Dust Collector

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temperature have indicated poor collection efficiencies (60 percent). Particle size distribution of 0-100 microns, with a mean particle size of 30-35 microns, was utilized in this test. It has been noted that many large particles escape from the collector and that no measurable improvement is evident at the smaller particle diameters.

3.5.2.2 Donaldson Tanjet - The tanjet utilizes a high energy tangential injection system on the O.D. of the inner collector tube. This tangential injection enhances the vortex strength and, in theory should improve separation capability. The vortex thus created is strong enough so that tangential inflow is not required. Development work on the tanjet was suspended due to a lack of market potential, resulting from the power requirements associated with the secondary air source supply. Also, problems were encountered with re-entrainment of particles due to the vortex strength. It is currently planned to continue the development program started in August 1978.

3.5.2.3 MTI Cyclocentrifuge - The cyclocentrifuge utilizes a rotating, bladed center tube to enhance vortex strength (Figure 3-8). The predicted collection efficiency is approximately 94 percent at 2 microns for 125,260 SCFM at 250 psia and 1000°F inlet temperature. This device is in the development stage with initial cold flow tests scheduled to begin in July 1978, with subsequent follow-on hot testing at Morgantown Energy Research Center.

3.5.2.4 Dynatherm Solids Separator - The Dynatherm Solids Separator, Figure 3-9, incorporates several design features that are a departure from the standard cyclone design. The initial flow is upward, a separator element is added to the center tube, and a third tube is added for clean gas exit. Efficiency claims state that 100 percent collection will be achieved at particle sizes of five microns and larger, and that 90 to 95 percent of particles, 1 micron in size or larger would be removed. Several units are currently in operation at catalytic cracking facilities at temperatures up to 950°F. A visit was made to the Dyna-Therm Corporation to examine the design and investigate the collection efficiency claims. The "Whirl-Away" separation element is typically a stamped louver unit claimed to

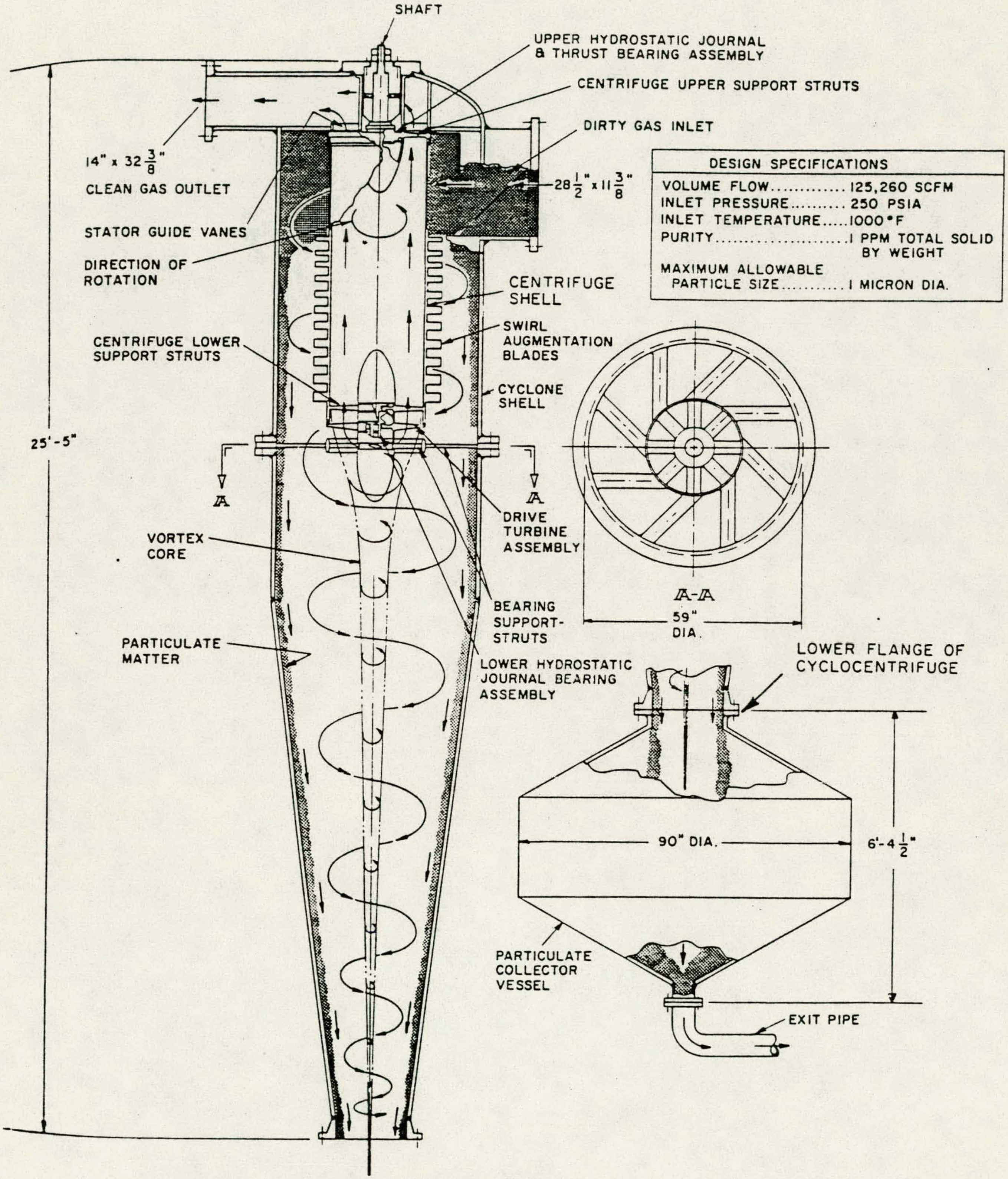

Fig. 3-8 Cyclocentrifuge, General Arrangement

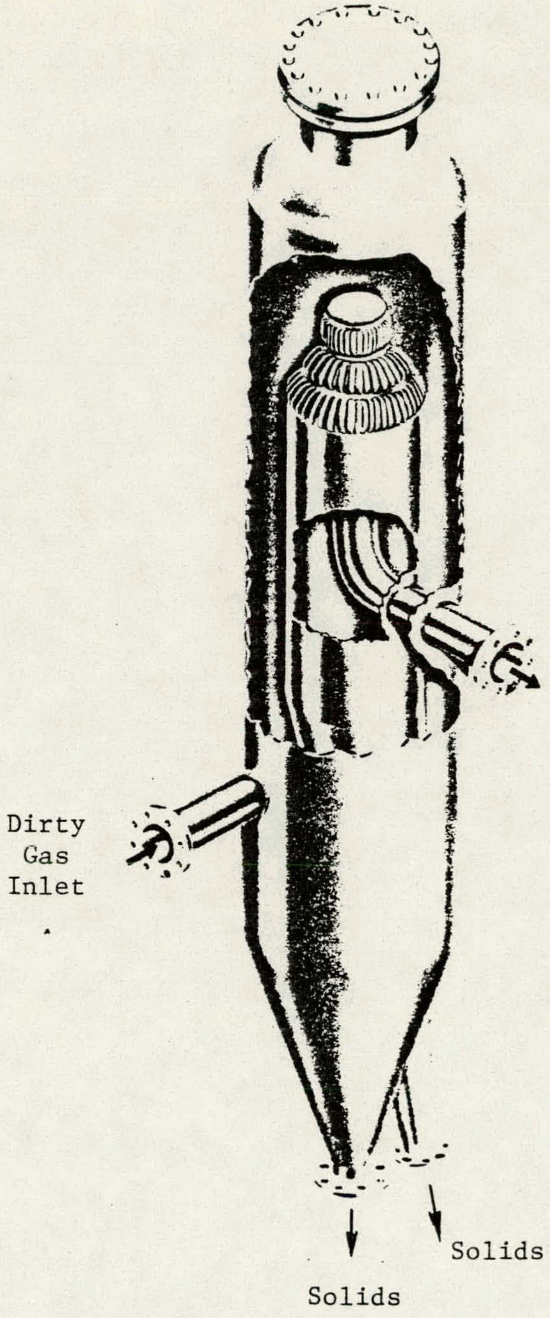

Fig. 3-9 Dynatherm Solids Separator

direct the incoming gas flow along the inner collector tube outer wall. Collection efficiency claims could not be documented by the Dyna-Therm Corporation, although it is claimed that University of Florida tests were used to determine collection efficiency levels. The Dyna-Therm Corporation does not build hardware nor do they have facilities to test their product. It is recommended that this device be tested to verify or dispute the efficiency claims.

3.6 Technology Voids and Development Requirements

Current standard cyclone devices lack the potential to achieve effective particulate separation for particle sizes of less than five microns. It is conceivable that modified cyclone devices could be developed and used to reduce fouling tendencies in the superheater/reheater sections and also to reduce particulate loading on the exhaust cleanup system prior to coal dyring. There are two prime areas which must be addressed. First, in the superheater region, corrosion problems can be anticipated. Materials development (metals and refractory coatings) would be required to achieve successful sustained operation. Second, for stack cleanup or for removal of flyash and seed material, prior to coal drying, the prime development requirement is to enhance collection efficiency of small particles. For the separation of pulverized coal after the coal drying process, standard cyclones would appear to provide sufficient collection capability due to the expected large particle size.

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    c. Aerodyne Development Corp., Cleveland, Ohio
    d. AGET Manufacturing Company, Adrian, Michigan
    e. Hammond Machinery Builders, Kalamazoo, Michigan
    f. Peerless Mfg. Company, Dallas, Texas
    g. Envirotech Corporation, Houston, Texas
    h. General Electric Company, Schenectady, New York
    i. Enviro-Systems & Research Inc., Roanoke, Virginia
    j. W.W. Sly Manufacturing Company, Cleveland, Ohio
    k. Joy Manufacturing Company, Los Angeles, California
    l. Dyna-Therm Corporation, Houston, Texas
    m. Shell Development Company, Houston Texas (No Reply)
    n. Van Tongeren, Reynoldsburg, Ohio (No Reply)
    o. Donaldson Company, Minneapolis, Minn.
    p. Dixie Manufacturing Company, Baltimore, Md. (No Reply)
    q. W.C. Wiedenmann & Son Inc., Kansas City, Mo (No Reply)
    r. Seneca Environmental Products, Tiffin, Ohio (No Reply)
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    t. Enviromental Elements Corporation Baltimore, Maryland

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