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A REVIEW OF THE TECHNOLOGY AVAILABLE
FOR THE CONTROL OF
ATMOSPHERIC EMISSIONS FROM OIL SANDS PLANTS

by

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SUMMARY

Dynawest Projects Ltd. has been commissioned by Alberta Environment to provide an overview of the technology available for the control of sulphur and nitrogen oxide emissions from oil sands plants. The study scope is summarized on Table I.

The content of the main sections of the report is summarized below. All economic data is presented in mid 1982 Canadian dollars and refers to process units whose capacity is based on the oil sands upgrading configuration shown in Figure 1.

1. Claus Plant Technology

The Claus process for the recovery of sulphur from gas streams containing hydrogen sulphide is well proven and used throughout the world. Both existing oil sands plants incorporate the process. Different acid gas compositions require alternative process configurations for successful treatment. Acid gas composition and operating procedures are the principal determinants of catalyst deactivation rates. The capital and annual operating costs of the process are shown on Table II.

2. Tail Gas Treatment Processes

Several processes for the recovery of sulphur from Claus plant tail gas are available; none has yet been installed at an oil sands plant. Processes described are listed in Table III which shows the state of development of each, and identifies which processes increase the capacity of the parent Claus plant by recycling material to it.

The capital and annual operating costs of the processes described are shown on Table IV.

3. Flue Gas Desulphurization Processes

A number of processes for the removal of SO_2 from flue gas are available; none has yet been installed at an oil sands plant. Processes described are listed in Table V which shows the state of development of each, identifies principal reagents, byproducts and upper limit (if any) on the SO_2 content of the flue gas to be treated.

Table I. Study scope.

-
-
1. Review briefly bitumen extraction and upgrading technologies.
 2. Review and update Claus sulphur recovery technologies.
 3. Review and update tail gas clean-up technologies.
 4. Review and update flue gas desulphurization technologies.
 5. Review air fluidized bed technologies.
 6. Review coke gasification technologies.
 7. Review control systems for oxides of nitrogen.
-

Table II. Modified-Claus plant costs.^{a,b}

Total installed capital cost	\$39 000 000
Total annual operating cost	\$ 4 400 000

^a Costs are in mid 1982 Canadian dollars.

^b Plant capacity 912 t/d (sulphur).

Table III. Tail gas treatment processes.

Process	State of Development ^a	Removes COS, CS ₂	Residual Sulphur Compound Level in Tail Gas (Volume Fraction x 10 ⁻⁶)	Increases Claus Plant Loading
IFP Clauspol 1500	I	No	1500	No
Sulfreen	I	No	300	No
CBA	I	No	1500	No
Townsend	D	No	1500	No
ASR Sulphoxide	B	No	500	No
MCRC	D/I	No	-	No
SCOT	I	Yes	300	Yes
Beavon	I	Yes	100	No
BSR/Selectox	I	Yes	500	No
Trentham				
Trencor-M	D	Yes	200	Yes
Cleanair	D/I	Yes	50	No
ATS	D/I	Yes	900	No
MCRC (limestone)	I	Yes	50	No
Aquaclaus	D	Yes	100	No
USBM Citrate	D	Yes	100	No
Wellman-Lord	I	Yes	200	Yes
SNPA/Haldor				
Topsoe	D	Yes	500	No
UCAP	D	Yes	250	Yes
Westvaco	D	Yes	-	Yes
Lurgi LUCAS	D/I	Yes	350	Yes
CT 121	D	Yes	-	No

^a B = Benchscale; D = Demonstration unit; I = Industrial unit.

Table IV. Tail gas treatment process costs.^{a,c}

Process	Installed Capital Costs	Annual Operating Costs
Sulfreen	12.0	0.9
IFP Clauspol 1500	15.0	0.9
SCOT	19.0	3.6
BSRP	19.0	3.6
BSR/Selectox ^b	12.0	2.3
Cleanair	19.0	3.6
Trentham Trencor-M	19.0	3.6
Wellman Lord	53.0	9.0
SNPA Haldor Topsoe ^b	36.0	6.0
Westvaco ^b	53.0	7.0
USBM Citrate	17.0	2.4
Aquaclaus	17.0	2.4
Integrated UCAP ^b	49.0	6.0

^a Costs are in millions of mid 1982 Canadian dollars.

^b Denotes unreliable information. Shown for ranking purposes only.

^c Plant capacity 36.5 t/d (sulphur) i.e., Tail gas from a 912 t/d Claus plant operating at 96% efficiency.

Table V. Flue gas desulphurization processes described in this report.

Process	Primary Reagent	Operational Mode	Regenerable	Form of Principal Waste Product	Development Status ^a	Upper Limit on SO ₂ in Flue Gas
Limestone	Limestone	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Lime	Lime	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Alkaline Flyash	Lime/Flyash	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Double Alkali	Soda Ash/Lime	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Sodium Carbonate	Soda Ash	Wet	No	H ₂ O/Na ₂ SO ₃ /CaSO ₄	I	No
CT-121	Limestone	Wet	No	H ₂ O/CaSO ₄	I	No
Aqueous Ammonia	Ammonium Hydroxide	Wet	No	H ₂ O/NH ₄ HSO ₃ /(NH ₄) ₂ SO ₄	D/I	Yes
Wellman-Lord	Soda Ash	Wet	Yes	SO ₂	I	No
Magnesium Oxide	Magnesia	Wet	Yes	SO ₂	D	No
Citrate	Citric Acid	Wet	Yes	Sulphur	D	No
Dry Lime	Lime	Dry	No	CaO/CaSO ₃ /CaSO ₄ /Flyash	I	Yes
Copper Oxide	Copper Oxide	Dry	Yes	SO ₂	B	No
Melamine	Melamine	Wet	Yes	SO ₂	B	No

^a B = Benchscale; D = Demonstration unit; I = Industrial unit.

The capital and annual operating costs of the processes described are shown on Table VI.

4. Residue Gasification

Several processes, most of which were originally developed for the gasification of coal, are available. Table VII summarizes the salient features of those described in the report. Consideration of the potential application of residue gasification in an oil sands plant suggests that an entrained flow gasifier would be more appropriate than either a fixed or fluidized bed. Operating and design considerations for entrained flow gasifiers are described in some detail.

The most probable use of residue gasification in an oil sands complex is for the production of hydrogen. The capital and annual operating costs of a fully integrated hydrogen production plant based on residue gasification are shown on Table VIII.

5. Fluidized Bed Combustion

Fluidized Bed Combustion combines combustion, heat transfer and desulphurization in a single operation. The technology shows a cost advantage over conventional pulverized fuel combustion only when flue gas desulphurization would otherwise be required. Most major processes are still at the development stage with only small industrial units (up to 75 t/h of steam) being offered commercially.

6. NO_x Emission Control

Fuel combustion is the principal source of NO_x emissions from an oil sands complex. Three strategies are available for emission control: operational modifications; equipment design and modification; and NO_x removal. The latter is the most effective and expensive. The technology is well established and its application to oil sands plants presents no special problems.

The Alberta Government has established guidelines limiting the total emission of sulphur from an oil sands operation to 3.2 t per 1000 m³ of bitumen fed to the upgrading process (0.5 long tons per 1000 bbl).

The incremental cost of attaining this standard by progressively increasing expenditure on pollution control equipment is summarized on Figure II which demonstrates the application of the law of diminishing returns as additional technology is added to the basic Claus plant.

Table VI. Capital and operating costs for FGD plants.^{d,e}

Process	Capital Cost ^a	Annual Operating Cost ^b				Total
		Labour	Utilities	Materials	Byproduct Disposal	
Limestone	85.0	1.8	2.7	3.1	2.4	10.0
Lime	80.0	2.1	2.5	6.1	2.1	12.8
Double Alkali	75.0	1.6	2.1	6.7	2.1	12.5
CT-121	65.0	1.8	2.7	2.5	1.5	8.5
Aqueous Ammonia ^c	65.0	1.4	11.4	0.6	3.4	17.0
Wellman-Lord	125.0	1.6	13.3	4.1	0.3	9.9
Magnesium Oxide	92.0	1.6	6.4	1.6	0.3	9.9
Citrate	82.0	1.5	4.8	3.4	0.3	10.0
Dry Lime	83.0	1.8	2.6	8.7	2.6	15.7
Copper Oxide	95.0	2.0	4.3	1.0	0.3	7.6

^a Total installed capital costs.

^b No byproduct credit included.

^c Aqueous ammonia assumed to be available at zero cost. (Commercial cost would add \$3.7 million/a to the materials cost).

^d All costs in mid 1982 Canadian dollars.

^e Data relate to a plant treating 985 t/d (1 370 000 m³/h) of flue gas containing 0.006 mass fraction SO₂.

Table VII. Gasification processes summary.

Gasifier Name	Lurgi	BGC/ Lurgi	Winkler
Reported Cold Gas Thermal Efficiency (HHV)	85% ^a	92% ^a 92% ^b	75%
Operating Temperature, °C	480	1260	800 to 1 000
Operating Pressure, kPa	2410/3100	3100	137
O ₂ , t/t Dry Feed	0.2 to 0.5	0.46 to 0.56	0.35 to 0.6
Steam, t/t Dry Feed	1.0 to 2.6	0.3 to 0.4	0.15
Maximum Commercial Gasifier Capacity, t/d	-	-	263
Expected Date of Commercialization	Commercial	1982	Commercial
No. of Commercial Installations	Several	none	24
No. of Commercial Gasifiers	165	none	70
Scale of Development Unit, t/d	-	350	-
Development Unit start-up	-	1974	-
Type of Gasifier	Fixed Bed	Fixed Bed	Fluidized
Feed Stocks to date	coal/coke	coal/coke	coal/coke
Ash removal	dry ash	liquid slag	hot granulated
Features	<ul style="list-style-type: none"> - cannot process liquids - fluid coke must be sized - cannot process fines - high methane produced - phenol/tar production with reactive feeds 	<ul style="list-style-type: none"> - cannot process liquids - fluid coke must be sized - high methane produced - phenol/tar production with reactive feeds 	<ul style="list-style-type: none"> - low carbon conversion - not tested with liquid feeds - reactive solid feeds required - atmospheric pressure operation

Continued...

Table VII. Continued.

Gasifier Name	High Temperature		
	Winkler	U-Gas	Westinghouse
Reported Cold Gas Thermal Efficiency (HHV)	90% ^b	79%	80%
Operating Temperature, °C	1100	1010/1065	930/1020
Operating Pressure, kPa	1000	70/2450	1500
O ₂ , t/t Dry Feed	0.5	0.55 to 0.68	2.2 to 2.8 (air)
Steam, t/t Dry Feed	0.7	0.2 to 0.6	0.25 to 0.3
Maximum Commercial Gasifier Capacity, t/d	-	-	
Expected Date of Commercialization	1984	1985	1988
No. of Commercial Installations	none	none	none
No. of Commercial Gasifiers	none	none	none
Scale of Development Unit, t/d	13	22	32
Development Unit start-up	1978	1974	1975
Type of Gasifier	Fluidized	Fluidized	Fluidized
Feed Stocks to date	coal/coke	coal/coke	coal/coke
Ash removal	hot granulated	agglomerated	agglomerated
Features	<ul style="list-style-type: none"> - low pressure operation - low carbon conversion - reactive solid feeds required - not commercially proven 	<ul style="list-style-type: none"> - no liquid feed experience - not commercially proven - fines recovery not yet proven 	<ul style="list-style-type: none"> - not commercially proven - no liquid feed experience - high methane production

Continued...

Table VII. Continued.

Gasifier Name	Exxon Catalytic	Koppers- Totzek
Reported Cold Gas Thermal Efficiency (HHV)	90% ^b	75%
Operating Temperature, °C	700	1500
Operating Pressure, kPa	3500	115
O ₂ , t/t Dry Feed	none	0.6 to 1.1
Steam, t/t Dry Feed	1.6	0.0 to 0.5
Maximum Commercial Gasifier Capacity, t/d	-	772
Expected Date of Commercialization	1990	Commercial
No. of Commercial Installations	none	22
No. of Commercial Gasifiers	none	55
Scale of Development Unit, t/d	6	-
Development Unit start-up	1975	-
Type of Gasifier	Fluidized	Entrained Flow
Feed Stocks to date	coal/coke	coal, coke residual oil
Ash removal	hot granulated	quenched slag
Features	- not commercially proven - many novel process steps - high methane production	- well proven process - has processed both liquid and solid feeds - can process unreactive solids - high carbon conversion

Continued...

Table VII. Concluded.

	Shell-Koppers ^c	Texaco	Combustion Engineering
Reported Cold Gas Thermal Efficiency (HHV)	77 to 83%	77%	77%
Operating Temperature, °C	1500	1300 to 1550	1760/950
Operating Pressure, kPa	3500	2000 to 8370	115
O ₂ , t/t Dry Feed	0.6 to 1.1	0.6 to 1.1	4.37 (air)
Steam, t/t Dry Feed	0.0 to 0.5	0.3 to 0.5 ^d	none
Maximum Commercial Gasifier Capacity, t/d	-	910	-
Expected Date of Commercialization	-	commercial for liquids ^e	1984
No. of Commercial Installations	none	75	none
No. of Commercial Gasifiers	none	160	none
Scale of Development Unit, t/d	150	130/180	110
Development Unit start-up	1978	1978	1978
Type of Gasifier	Entrained Flow	Entrained Flow	Entrained Flow
Feed Stocks to date	coal/coke	coal, coke, pitch residual oil	coal/coke
Ash removal	quenched slag	quenched slag	quenched slag
Features	<ul style="list-style-type: none"> - liquid feed experience as Shell process - operates at elevated pressure while maintaining K-T process advantages 	<ul style="list-style-type: none"> - liquid feed experience - high pressure operation - tolerance for wide variety of feeds - high carbon conversion 	<ul style="list-style-type: none"> - not commercially proven - no liquid feeds tested - atmospheric pressure operation - high temperature may cause refractory problems

^a Including liquid by-products.

^b Carbon conversion efficiency.

^c Since April 1982 called Shell coal gasifier. Future development trends unknown.

^d For solid feeds, slurry water replaces steam.

^e 1983 commercialization expected for coal feeds, large number of projects considered.

Table VIII. Residue gasification plant costs.^{a,b}

Total Installed Capital Cost	\$496 000 000
Annual Operating Cost	\$26 000 000

^a Costs are in mid 1982 Canadian dollars.

^b Plant capacity 2050 t/d fluid coke.

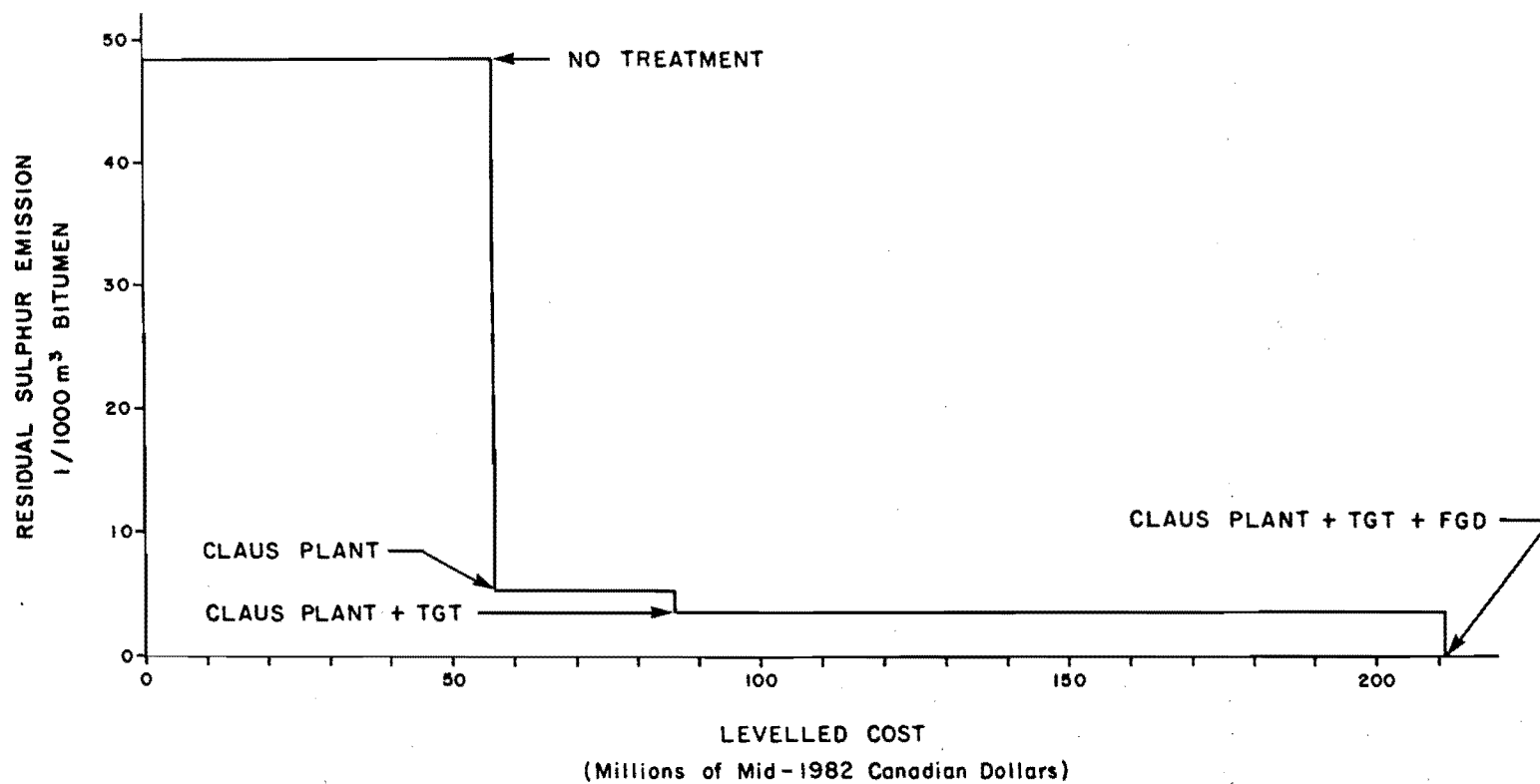


Figure II. Incremental cost of sulphur control technology.

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1. INTRODUCTION

Dynawest Projects Ltd. was requested by Alberta Environment to produce an overview of the technology available for the control of atmospheric emissions of sulphur dioxide and nitrogen oxides from oil sands plants. This report is an update and extension of an earlier study commissioned by Alberta Environment (Western Research and Development Ltd. 1976).

The study scope is summarized on Table 1. Information for the report was collected by reviewing current literature and contacting process licensors. The extent to which information is available for the different technologies varies and this is reflected in the report.

Section 2 of the report provides a brief review of established technology for the extraction and upgrading of oil sands bitumen and is included to place subsequent sections in context.

Most of the processes described in the report have never been applied in an oil sands plant. In order to maintain a consistent approach, our comments have been focussed on the potential application of these processes to an oil sands plant of the capacity defined by Alberta Environment (i.e., 1000 t/d sulphur in the bitumen feed to the upgrading plant).

Section 3 of this report describes how this basic definition was used to calculate the required capacities of the individual processes considered. While much of the report is general in nature, a reasonable definition of required capacity is clearly needed to make sensible extrapolations of the development required to extend a given process from its present proven capacity to that required in a typical oil sands context and also to fix the basis of the process economics.

Sections 4 to 9 describe the individual technologies in detail. The general nature of the report precludes any recommendation as to the best process in a given situation. A far more detailed site specific process study would be necessary to draw such conclusions. However, the particular features, if any, of individual processes which may limit or encourage their application in an oil sands context are noted.

Section 10 shows how sulphur compound emissions can be progressively reduced by increased expenditure on pollution control equipment.

Table 1. Study scope.

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- | |
|--|
| 1. Review briefly bitumen extraction and upgrading technologies. |
| 2. Review and update Claus sulphur recovery technologies. |
| 3. Review and update tail gas clean-up technologies. |
| 4. Review and update flue gas desulphurization technologies. |
| 5. Review air fluidized bed technologies. |
| 6. Review coke gasification technologies. |
| 7. Review control systems for oxides of nitrogen. |
-

2. REVIEW OF ESTABLISHED TECHNOLOGY FOR BITUMEN EXTRACTION AND UPGRADING

2.1 INTRODUCTION

To date, two oil sands plants have been built, the Suncor plant and the Syncrude plant. Two further plants have advanced to the stage of detailed engineering: the Esso Cold Lake project which was put on indefinite hold in July 1981 and the Alsands project which was cancelled in April 1982.

The two production plants and the proposed Alsands plant all use open pit mining of oil sands followed by the Clark Hot Water Extraction process for bitumen extraction from the oil sands. The Cold Lake plant envisaged in situ recovery of the bitumen. All plants upgrade the bitumen to synthetic crude oil by employing a coking operation to enhance the hydrogen to carbon (H/C) ratio followed by hydrotreating to reduce sulphur and nitrogen concentrations to acceptable levels.

The broad outline that follows (Figure 1) is based on the proposed Alsands process with reference to major differences in the two existing production plants as appropriate.

2.2 PROCESS OPERATIONS

2.2.1 Mining

The oil sand is mined using draglines (bucketwheels at Suncor). The mined oil sand is transferred to storage bins using a system of conveyor belts.

2.2.2 Bitumen Extraction

The Clark Hot Water Extraction process is shown schematically in Figure 2. Oil sand from the storage bin is fed to a rotating conditioning drum with water and caustic (to maintain pH of ~ 8.0). The mixture is maintained at $\sim 85^{\circ}\text{C}$ by steam which is sparged into the other end of the drum. The product from the drums is a conditioned pulp together with oversize lumps of rock and clay which are removed by vibrating screens.

The pulp together with make-up water is fed to primary separators where the bulk of the sand settles and is removed from the bottom as tailings. Most of the bitumen rises to the surface and is removed as froth. A further

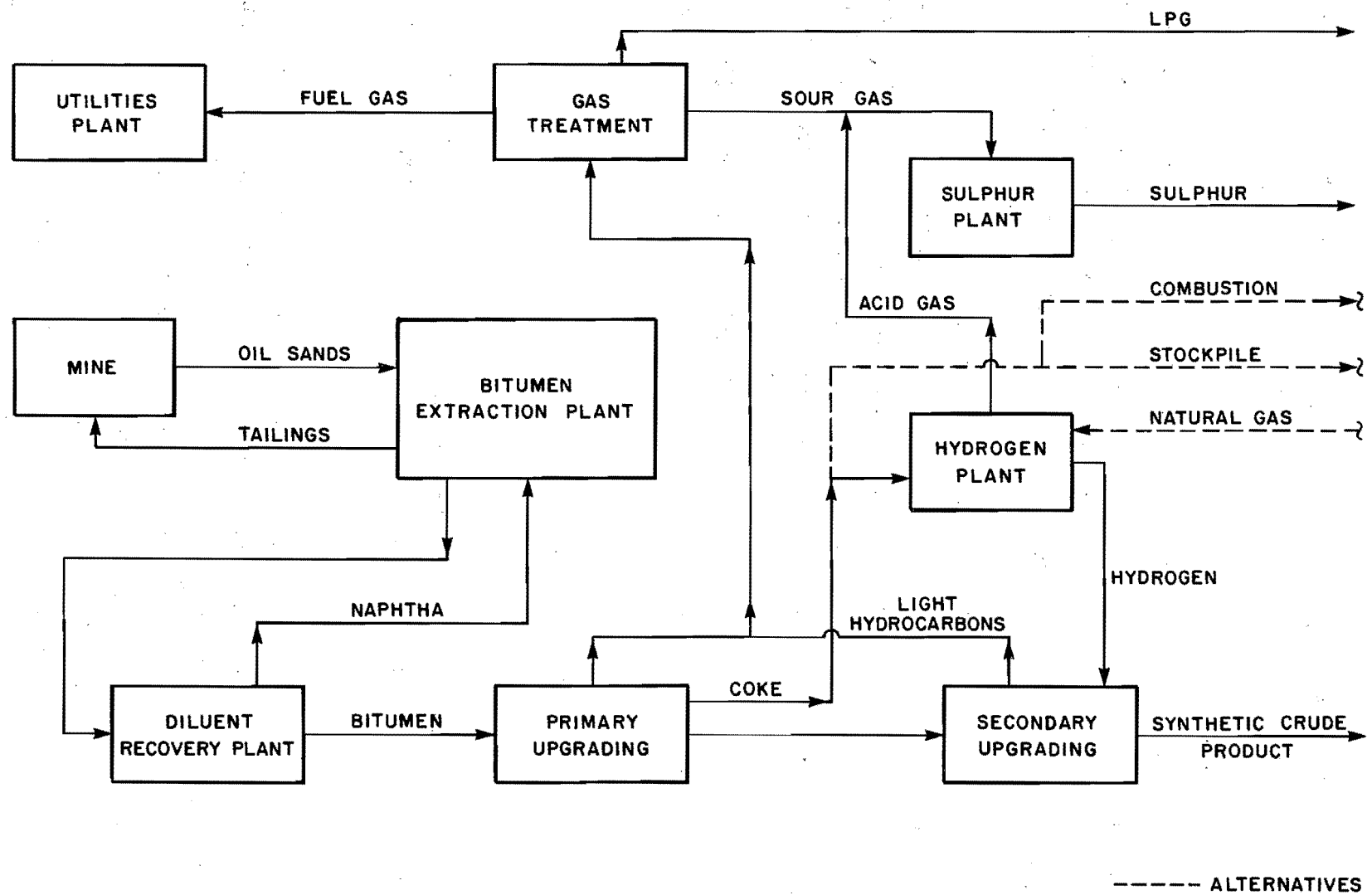


Figure 1. Coker based oil sands bitumen upgrading process configuration.

stream, mainly water with suspended fines and some bitumen, tends to accumulate in the middle of the separator and has to be removed as "middlings" to maintain the operation of the separator. Part of the middlings stream is recycled to the conditioning drum outlet to maintain a pumpable separator feed. The rest is fed to air flotation "scavenging" cells to recover the bitumen content.

The bitumen from the scavenging cells is settled in secondary separators to remove mineral and water. The separator underflow is recycled to the scavenging cells, from which a tailings stream is withdrawn. Tailings from the primary and secondary separators are pumped separately to the tailings pond in the mine area.

The bitumen froths from the primary and secondary separators are deaerated (by live steam injection) and after blending with naphtha to reduce their viscosity, passed to a series of centrifuges to remove water and mineral matter (clay and sand).

The first stage (scroll) centrifuges remove mineral but little water. The second stage (disc) centrifuges are protected by Cuno disc filters. The bitumen product from the disc centrifuges is passed forward to intermediate storage prior to the upgrading operation.

2.2.3 Diluent Recovery

The first upgrading operation is the recovery of the diluent naphtha added in the extraction process. This fractionation also serves to dry the bitumen.

2.2.4 Fluid Coking

In order to reduce the viscosity of the bitumen sufficiently to produce a synthetic crude that can be pumped to a refinery, the H/C ratio has to be increased. This is achieved by reducing the carbon content in a continuous fluid coker (see Figure 3). The Suncor plant employs a delayed coker. This has a lower liquid yield which has precluded its consideration for future plants. It does not, however, produce the SO₂ rich burner gas characteristic of a fluid coker.

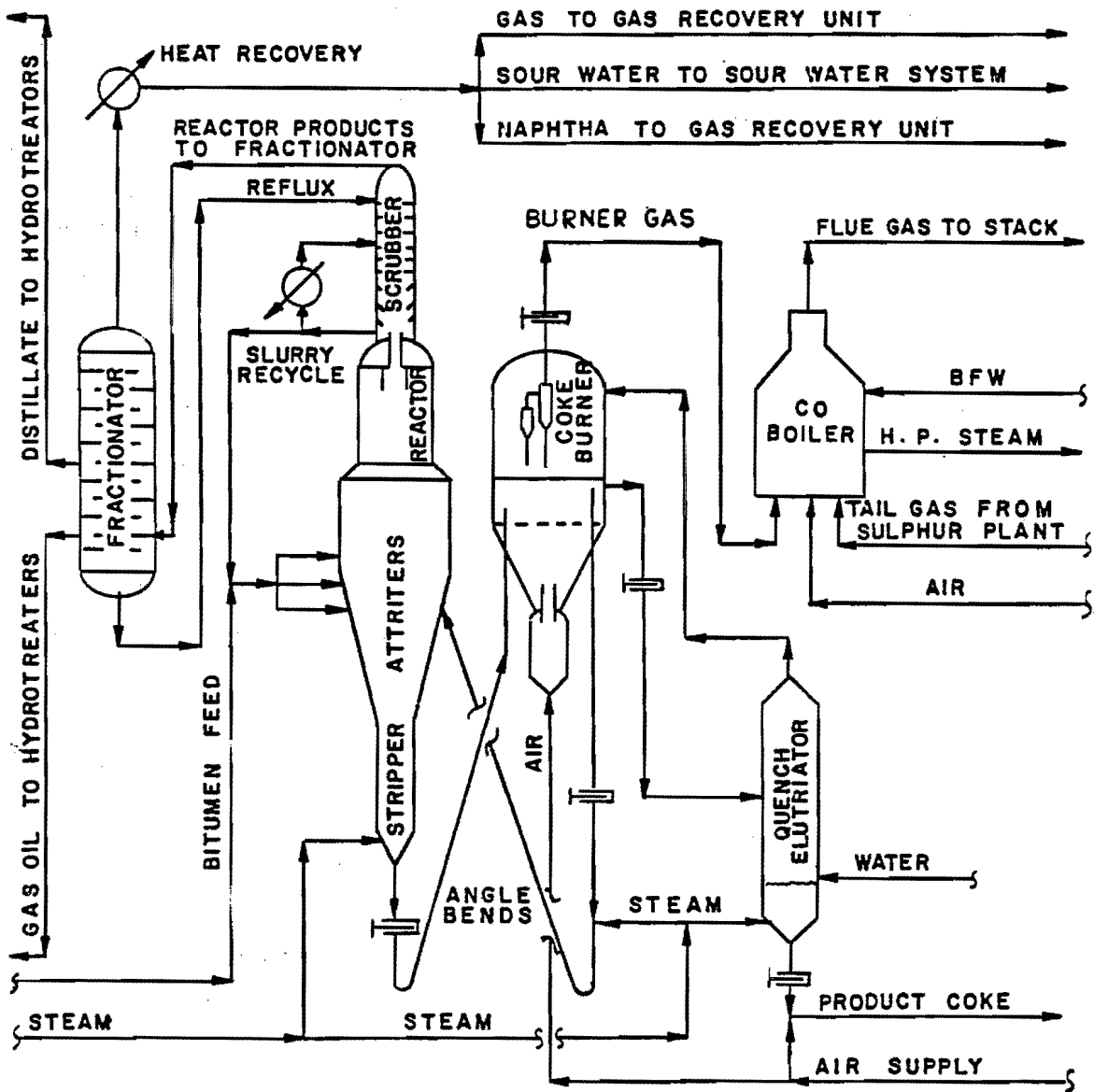


Figure 3. Fluid coker.

2.2.5 Hydrotreating

The hydrocarbon products from the coker are sufficiently mobile for pipeline transportation but contain too much sulphur and nitrogen for direct feed to a conventional refinery. To reduce these compounds to acceptable levels, the material is hydrotreated in fixed bed reactors. Figure 4 shows a typical arrangement.

At least two hydrotreaters are required for separate processing of the naphtha and gas oil fractions. The distillate can be processed with one of the other fractions or alternatively in a third hydrotreater. Using three hydrotreaters reduces hydrogen consumption and increases liquid yield at the cost of higher capital investment and operating and maintenance charges.

The hydrotreated products are the synthetic crude output of an oil sands plant. They are normally blended for pipeline delivery to a refinery.

2.2.6 Coke Treatment

The coke contains upto 0.09 mass fraction sulphur. At the Suncor plant, this coke is burnt in utility boilers and the resultant SO_2 emitted to atmosphere with no treatment. This procedure has not been permitted in any subsequent plants.

The Syncrude plant simply stockpiles coke for potential future use.

For future plants intending to utilize the coke, there are three basic options, viz:

1. Gasify the coke to produce a CO containing gas stream. This stream can be used as either a fuel or a hydrogen source (via a shift reaction). The latter approach was proposed by Alsands (after initial operation in which the coke is stockpiled).
2. Burn the coke in a conventional boiler and use flue gas desulphurization to remove SO_2 prior to atmospheric emission.
3. Burn the coke in an air fluidized bed containing limestone to directly absorb the SO_2 produced.

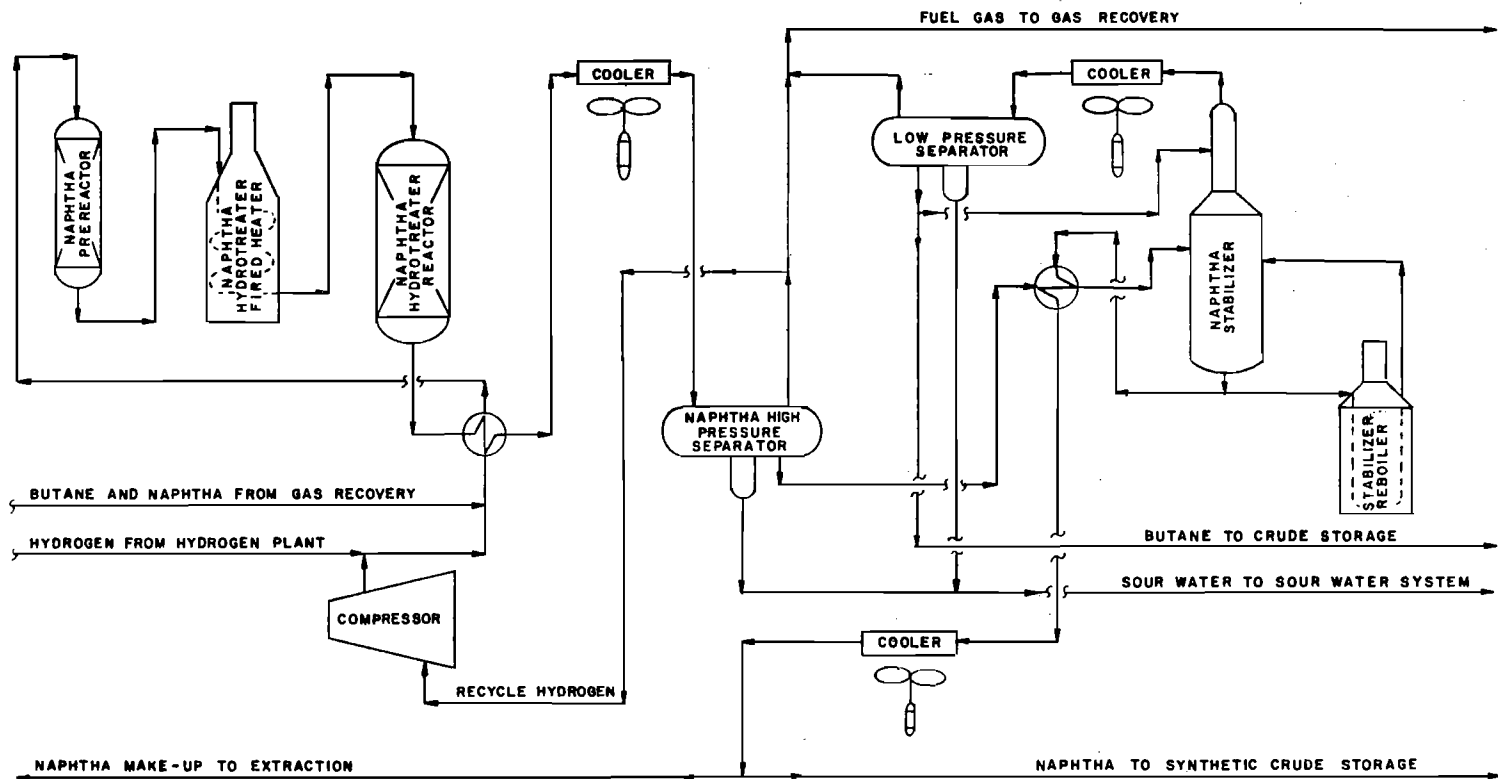


Figure 4. Naphtha hydrotreater.

2.2.7 Coker Burner Gas

The fluid coker burner gas which contains about 7% of the sulphur in the bitumen feed is fed to a CO boiler. On the existing Syncrude plant, the CO boiler vent is discharged directly to atmosphere. This practice is unlikely to be permitted on future projects necessitating either an FGD unit or an alternative approach to upgrading. The Suncor plant with its delayed coker does not have any burner gas.

2.2.8 Gas Sweetening and Sulphur Plant

The gaseous light hydrocarbon fractions from the coker and the hydrotreaters are fed to a gas sweetening plant, typically an amine based unit, where the H_2S , NH_3 and CO_2 are removed. The acid gas from the regeneration unit of the amine plant is fed forward to a Claus plant for removal of the H_2S as sulphur. The basic Claus process will achieve about 96% removal of H_2S in an oil sands environment.

At the Suncor and Syncrude plants, the tail gas from the Claus plant is incinerated and the resultant SO_2 discharged to atmosphere. The proposed Alsands design, which must be regarded as the minimum for future plants, was to further treat the tail gas prior to incineration to achieve an overall removal efficiency of 99.96%.

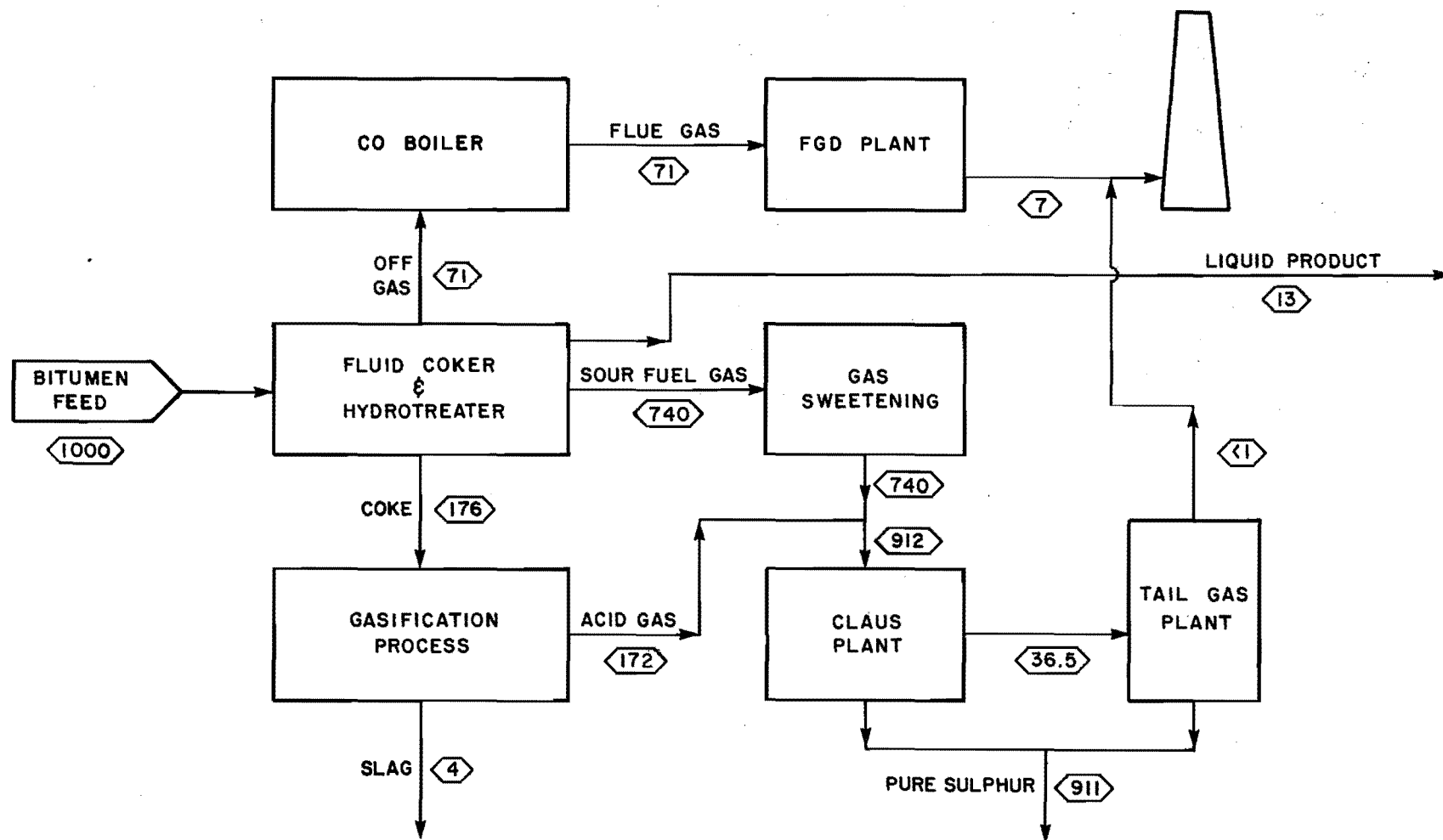
3. DESIGN BASIS FOR PROCESS EVALUATIONS

In order to provide a consistent basis for the comparison of the different processes described in this report, a sulphur content of 1000 t/d in the feed bitumen to the oil sands upgrading plant has been defined for this study.

The sulphur distribution in the upgrading plant has been assumed to follow that described by Kumar (1980) for the Syncrude plant. The capacity of the operations described in the report has then been fixed as follows:

1. Claus plant, based on sulphur recovery from fluid coker sour fuel gas and from the acid gas produced by a presumed coke gasification operation;
2. Tail gas plant, based on 96% sulphur recovery in the Claus plant;
3. Gasification plant, based on coke feed containing 0.087 mass fraction sulphur;
4. Flue gas desulphurization plant, based on treatment of a CO burner flue gas containing 0.006 mass fraction SO_2 .

This information is summarized on Figure 5. Clearly, different assumptions as to either the basic sulphur distribution or arrangement of the units could result in several different combinations of capacities for the different units.



= FLOW OF PURE SULPHUR (t/d)

Figure 5. Upgrading process, sulphur distribution.

4. CLAUS PLANT TECHNOLOGY

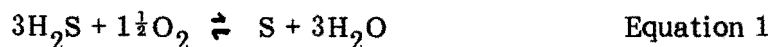
4.1 INTRODUCTION

Environmental regulations relating to sulphur emissions from natural gas plants, oil refineries, oil sands plants, etc., have made the use of some type of sulphur recovery process mandatory. Presently, the modified-Claus process is the most widely used method of sulphur recovery for these types of operations (Grancher 1978). This process is accepted and used on a world-wide scale in many types of fossil fuel processing installations.

The two existing oil sands plants, Syncrude and Suncor, both have modified-Claus plants. The proposed Alsands Project incorporated a modified-Claus plant in its design. The development of a sulphur recovery process able to replace the modified-Claus process does not appear to be imminent.

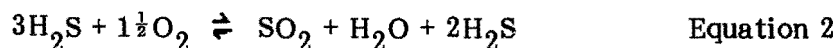
4.2 BASICS OF THE CLAUS PROCESS

The original Claus process produced sulphur by the vapour phase partial oxidation of H_2S over a catalyst according to the following reaction:



Since the reaction is highly exothermic and heat dissipation in the reactor was by radiation only, a space velocity of less than 3 h^{-1} was required in order to achieve a sulphur yield of 80 to 90% (Paskall 1979). The addition of cooling coils or the recycling of cooled gas did not increase the process capacity significantly.

In 1938 a major modification was made to the process by I.G. Farbenindustrie A.G.. In the modified process the vapour phase partial oxidation of H_2S is carried out in two steps. First, one third of the H_2S is oxidized in a furnace to SO_2 . This stoichiometric mixture of H_2S and SO_2 then reacts over a catalyst to form elemental sulphur. The following two reactions illustrate this process.





A simplified process schematic illustrates this process in Figure 6.

The highly exothermic reaction (Equation 2) takes place in the furnace and generates high pressure steam in a waste heat boiler as the gas is cooled to the lower temperature of the converter (catalytic reactor). The sulphur formed in the converter is recovered by passing the gas through a condenser to condense the sulphur. The process operates at a pressure that is close to atmospheric.

Most modern sulphur recovery plants use the modified-Claus process. The use of one converter limits sulphur recovery to approximately 75 to 90%. Since this level of recovery is generally unacceptable, two, three and sometimes four converters are used with sulphur condensers after each converter. The gas is reheated before each converter to prevent sulphur condensation on the catalyst.

Several different process configurations of the modified-Claus process can be used, depending on the H_2S content of the acid and whether there is any NH_3 present. Since the acid gas stream in an oil sands plant has a high concentration of H_2S (typically 0.8 to 0.9 volume fraction), a straight-through configuration is used. This is the configuration shown in Figure 6. If there is NH_3 in the acid gas then it must be destroyed by the use of special burner techniques in the furnace.

A new variation of the modified-Claus process that has developed recently is the Richard Sulphur Recovery Process (RSRP). The RSRP operates at a pressure of approximately 1013 to 1520 kPa. The H_2S and SO_2 are bubbled through the liquid sulphur that condenses in the converter. In a standard modified Claus plant, liquid sulphur in the converter deactivates the catalyst. However, with the RSRP, the catalyst is still active due to the high pressure. This process is presently at the pilot plant stage.

4.3 PROCESS CHEMISTRY

If pure H_2S and O_2 were reacted only SO_2 and H_2O would be obtained as products at a flame temperature of 2450 to 2600°C. However, oil sands acid gas may be expected to contain small amounts of hydrocarbons, H_2 ,

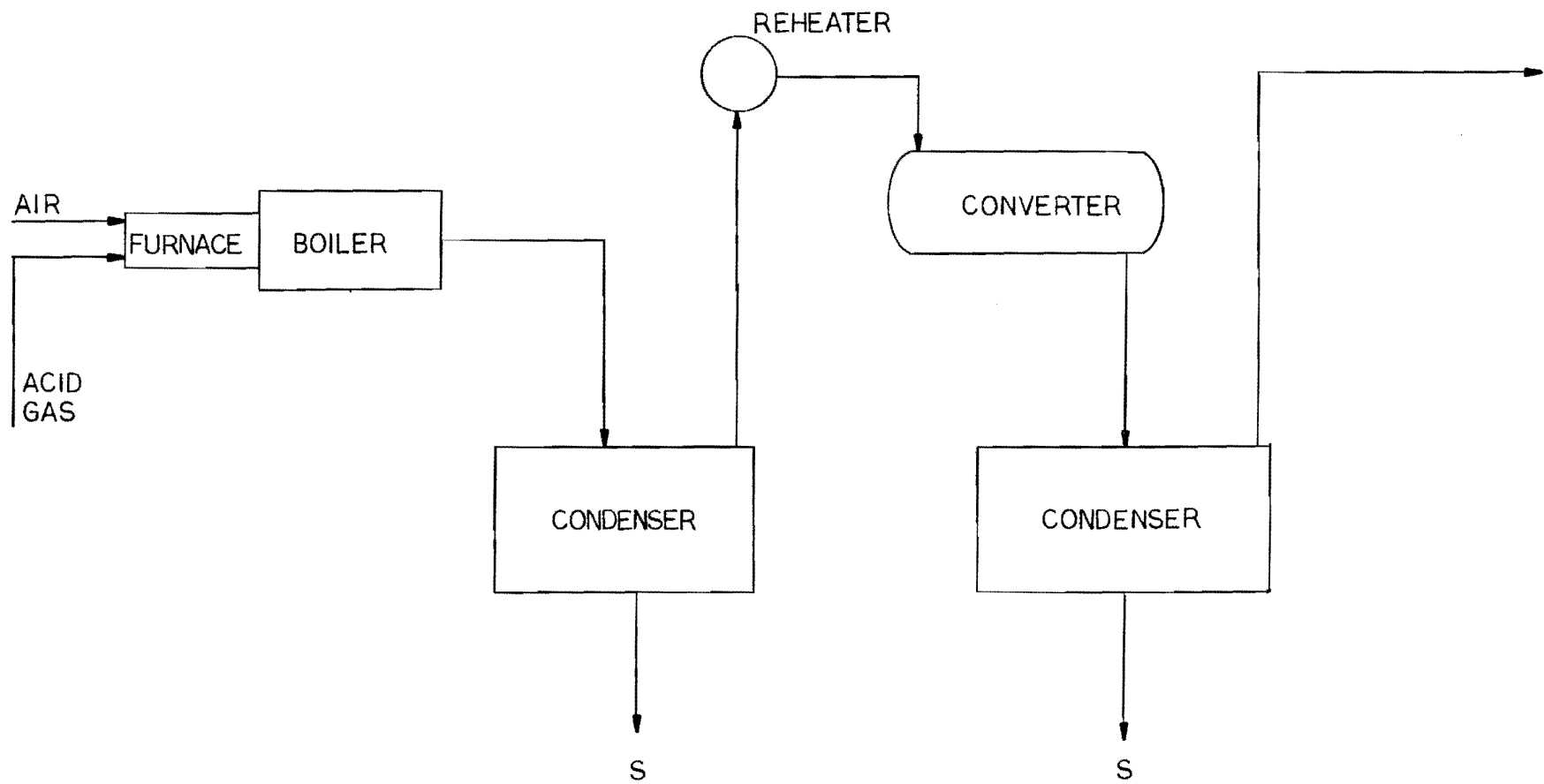
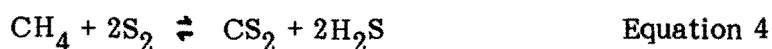


Figure 6 Claus process schematic.

HCN, NH_3 , mercaptans, CO, CO_2 , H_2O and N_2 . The usual source of O_2 is ambient air which contains O_2 , N_2 , Ar, CO_2 and H_2O . As a result, many side reactions occur. Combustibles such as hydrocarbons, NH_3 , etc., tend to increase the flame temperature while diluents such as H_2O , N_2 , etc., decrease the temperature. Since the quantity of diluents is much higher than that of the combustibles, the flame temperature is much lower than ideal, usually in the range of 925 to 1200°C.

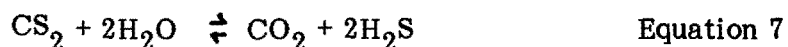
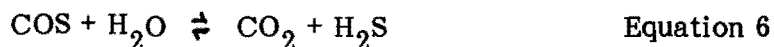
The reactions involving COS and CS_2 are of major concern as up to 8% of total input sulphur has been measured as CS_2 (up to 4.5% COS) in the wasteheat boiler outlet (Western Research 1982). Formation of CS_2 is primarily dependant on the hydrocarbon content of the acid gas, as is shown by the following reaction:



COS is thought to be formed by the reaction of CO and elemental sulphur vapour:



Decomposition of CS_2 and COS is by hydrolysis, usually in the first converter. These reactions are 95 to 100% complete at a temperature of approximately 343°C. The reactions are as follows:



4.4 ACID GAS VARIATIONS

There are many aspects of acid gas quality that can affect the efficiency of the sulphur plant.

4.4.1 H₂S Content

The concentration of H₂S in the acid gas is the major criterion for choosing whether to use a straight-through, split-flow, sulphur recycle or direct oxidation configuration. The high H₂S content of oil sands acid gas allows the use of the straight-through configuration. Paskall (1979) provides a good discussion on the differences in each configuration.

4.4.2 Hydrocarbon Content

The presence of hydrocarbons in the acid gas contributes directly to the formation of CS₂ and, to some extent, COS. The flame temperature in the furnace is also increased by the combustion of any hydrocarbons. Aromatic and cyclic compounds can form a glassy-type carbon that deposits on the catalyst, thereby deactivating it. The quantity of air introduced into the process increases due to need for O₂ to burn the hydrocarbon. This extra volume of air acts as a diluent in the acid gas stream which causes a loss in recovery efficiency. Another implication of having hydrocarbons in the acid gas is that H₂O is produced by the combustion reactions. The extra H₂O tends to drive the sulphur forming Claus reaction back to the left in accordance with the principal of LeChatelier. Thus the sulphur recovery efficiency is reduced. Finally, the hydrocarbon may degrade to carbon and cause the produced sulphur to be different shades of black, brown and even green (Parnell 1981).

The concentration of hydrocarbon in the acid gas is directly related to the gas processed and the type of desulphurization technique used. Acid gases from refineries usually contain more heavy hydrocarbons than acid gas from a natural gas plant. Processes that use physical solvents as opposed to amines lead to acid gases with higher hydrocarbon concentration, up to 0.05 volume fraction (Grancher 1978). Refinery gases processed using amines are expected to have less than 0.005 volume fraction hydrocarbon (Interoffice Memorandum, 1982, J.O. No. 520. 16.11, Dynawest Process File 5.0301). Oil sands acid gas is expected to be much like refinery acid gas.

4.4.3 Ammonia Content

NH₃ in the acid gas stream has the potential to cause several problems. If all or part of the NH₃ passes through the furnace without burning then solid deposits of ammonium salts may occur in the cooler sections of the

plant. Another problem occurs when NO is formed from the NH_3 . In the presence of oxygen, NO catalyzes the oxidation of SO_2 to SO_3 which in turn reacts with water to form sulphuric acid. The acid not only causes severe corrosion problems but also brings about sulphation of the Claus catalyst causing deactivation. Sulphates also cause plugging in the sulphur condenser rundown lines (Fischer 1979).

Oil sands acid gas is expected to contain small amounts of NH_3 . Much of the NH_3 introduced to the sulphur plant is from the sour water strippers. In the past, this sour gas was either flared or fed to the Claus furnace. Development of pollution control laws over the past few years has forced operators to try to dispose of the sour water offgas by a method other than flaring. Initially burning of NH_3 in the furnace was an incomplete process. Fortunately, however, special burner configurations in the Claus furnace, developed over the past few years, have allowed almost complete NH_3 destruction. These burners promote a quick mixing, vortexing action for the reactants which in turn achieves a flame pattern that allows a high concentration of heat in the front end of the furnace, thereby ensuring complete NH_3 destruction. Introduction of this sour water offgas stream is now considered an asset to the modified-Claus process since more sulphur is recovered (Wiley 1980).

4.4.4 Inerts

The major inert compounds are CO_2 , N_2 , Ar and H_2O . These compounds dilute the acid gas by increasing the overall gas volume. This increase inhibits sulphur recovery as more sulphur will remain in the vapour phase while passing through the condensers than with a smaller volume of gas (less inerts). CO and H_2 behave as inerts in the converters and condensers.

4.5 CATALYST

The predominant reaction in the converters is:



This reaction shifts further to the right as temperature is decreased. It is therefore desirable to operate the converters at as low a

temperature as possible. The use of a catalyst lowers the temperature of reaction by decreasing the activation energy and increasing the rate of reaction. Conventional sulphur plants operate from 3 to 14°C above the sulphur dewpoint.

The catalysts generally employed in modern sulphur plants are the activated aluminas and bauxites, although bauxite has been almost completely phased out by the use of alumina. They exhibit high activity, good availability, low cost, high mechanical strength, low resistance to gas flow, high resistance to attrition and are easy to handle.

The activity of a catalyst is dependent on both its chemical and physical properties. It is, therefore, highly susceptible to deactivation due to contaminants in the gas stream, and is very sensitive to operating practices.

4.5.1 Catalyst Deactivation

The mechanisms of catalyst deactivation can be divided into two groups. The first group encompasses actual physical and structural effects on the catalyst due to thermal aging, phase changes, sintering and attrition. This type of deactivation is irreversible; however, it is also generally slow in most modified-Claus plants. These types of deactivation are usually caused by poor start-up and shutdown procedures. Catalyst burnoffs are also detrimental to the activity of the catalyst. The second group of deactivation mechanisms encompasses chemical reactions with simple deposition on the catalyst. Examples of this type are sulphation, carbon deposition, sulphur condensation and salt deposition. These mechanisms are reversible. However, in some cases the catalyst life is shortened by the rejuvenation process. Sulphation is considered to be the largest contributor to deactivation. It is thought to occur by the reaction of O_2 with sulphur that is absorbed on the catalyst. O_2 breakthrough (to the converter) takes place when the furnace does not consume all of the inlet O_2 due to poor mixing in the combustion chamber. The activity of the catalyst decreases because the sulphate blocks off the active sites. In the same manner, operation of the converter at a temperature below the sulphur dewpoint causes liquid sulphur to form on the catalyst, promoting deactivation. Glassy carbon or tar formation from hydrocarbon carry-over completely block off the active sites. Other impurities, such as NH_3 , form unwanted salts.

4.5.2 Catalyst Rejuvenation

The mechanisms in the first group are irreversible but those of the second group (except carbon deposition) may be reversed in the following way. First, the catalyst is subjected to a 24 hour heat soak by operating the converter at a temperature of 60 to 80°C above normal. If the plant load is not reduced at the same time, there will probably be an increase in sulphur emissions. After 24 hours, the O₂ flow to the furnace is cut back to create a reducing atmosphere. The heat soak removes the sulphur while it is the reducing conditions that eliminate the sulphates. After 24 to 36 hours of this treatment the plant is slowly returned to normal (Western Research 1982). A catalyst burn off will eliminate carbon deposits; however, the catalyst life can be severely shortened at the same time. Carbon deposition is normally remedied by digging out and replacing the top 0.15 to 0.30 m of catalyst.

4.5.3 Catalyst Development

The original Claus catalyst was activated bauxite because of its low cost. It has poor mechanical strength and easily deactivated catalytic properties; as a result most sulphur plants now use activated alumina. Alumina has increased macroporosity which results in a more reactant mass (Grancher 1978).

Conversion of CS₂ and COS is achieved in the first converter at a temperature of approximately 315 to 340°C. If these compounds are not hydrolyzed in this reactor then they will pass unaffected through the other lower temperature converters, and possibly through the tail gas treatment unit, to be incinerated and emitted to the atmosphere as SO₂ (some tail gas units recover COS and CS₂). Several new catalysts that enhance CS₂, COS conversion have been developed in the last few years. One such catalyst is a promoted alumina catalyst that does not suffer the same degree of sulphation as a standard alumina catalyst (Pearson 1981). It is reported to have a higher degree of CS₂, COS conversion even after several years of aging. A certain number of the new catalysts require the process gas to be free of oxygen (Grancher 1978). Otherwise, under sulphating conditions, conversion can be less than for a standard alumina catalyst.

Protection of standard alumina catalyst from deactivation by sulphation may be achieved by use of a covering layer of newly developed AM

catalyst over each converter bed (Grancher 1978, Chute 1977). This catalyst eliminates the trace amounts of oxygen and SO_3 that lead to sulphation.

4.6 DESIGN CONSIDERATIONS AND OPERABILITY

4.6.1 Furnace and Waste Heat Boiler

The temperature of the furnace ($\sim 1200^\circ\text{C}$) necessitates lining the vessel with firebrick or castable refractory to reduce the skin temperature to approximately 240 to 300°C . The lining protects the carbon steel walls of the furnace from the effects of high temperature acid gas. The skin temperature must be kept above 240°C to prevent acid condensation and subsequent corrosion problems. An aluminum cowling is used on the furnace to provide an insulating layer of air to reduce heat loss. In this way energy is conserved for recovery in the waste heat boiler.

Steam produced by the waste heat boiler has, in the past, been in the 2100 to 2700 kPa range. There are, however, some designers who consider that the benefits of steam in the 4100 to 4800 kPa range justify the higher metallurgical and structural costs required (Western Research 1982).

4.6.2 Converters

The thermodynamics of the Claus reaction show that more sulphur is produced as the temperature in the converter is reduced. But it is also important that no sulphur condenses on the catalyst, as this causes catalyst deactivation. It is desirable to operate as close to the sulphur dewpoint as possible while ensuring that the temperature never drops below it. In a well controlled plant it is feasible to operate 3 to 6°C above the dewpoint. A margin of 8°C is generally considered to be realistic although somewhat conservative. The exception is the first converter which must operate at a temperature of approximately 340°C (well over dewpoint) in order to promote CS_2 and COS hydrolysis.

The design of the converter must include provisions for ensuring proper gas distribution at the inlet. The inlet is at the top of the converter and, if the gas is fed in unhindered through a simple nozzle, the catalyst will probably shift. This situation will result in poor catalyst yields and will not

allow for good sulphur desorption during a period of catalyst rejuvenation. To avoid this problem, a distributor should be installed in all the converters.

4.6.3. Condensers

Improper design of the condensers can result in a loss of sulphur recovery efficiency due to the formation of both sulphur mist and sulphur fog. Sulphur fog occurs when sulphur vapour condenses in midstream, as opposed to condensation on the tubes. This situation is due to an excessive temperature gradient in the condenser tubes. Sulphur mist is entrained droplets of liquid sulphur, caused by a high gas velocity in the condenser. Installation of mist extractors in the coalescing chamber eliminates most of the mist.

Another problem that has already been mentioned, is that of plugging due to deposits of ammonium salts. Elimination of NH_3 in the reaction furnace is the preferred way to treat this problem. However, failing this, if temperatures are kept above 150°C , plugging may be avoided with only a slight loss in recovery efficiency (Western Research 1982).

Formation of "sulphur-crete" can be a problem in some plants. Sulphur-crete is a mixture of catalyst fines and sulphur that forms an extremely hard, solid material which collects in low spots. This sulphur-crete is extremely difficult to remove.

4.6.4 Reheaters

The gas leaving the condensers must be reheated before entering the next converter. In general, the different methods of reheat may be classified in two groups, indirect and direct reheat.

Direct reheat methods involve mixing a hot gas stream with the process stream. There are three methods of direct reheat:

1. acid gas fired inline burner;
2. fuel gas fired inline burner;
3. hot gas bypass.

In the first method, some acid gas is bypassed around the converters to be burned and remixed with the process gas. This method must be carefully monitored to prevent O_2 breakthrough. Recovery efficiency drops slightly as a result of passing reactants around the converters.

Fuel gas fired burners are not as common as acid gas burners. They must be operated at a substoichiometric level of air to prevent O_2 breakthrough. At the same time, however, hydrocarbon breakthrough must be prevented to eliminate the possibility of carbon deposition.

Hot gas bypass methods typically involve bypassing 5 to 15% of the furnace product gas around the converters and remixing with the process gas. One of the most detrimental aspects of this process is that CS_2 and COS are bypassed around the first converter, where the rest of the CS_2 and COS is hydrolyzed. This can lead to efficiency losses of 1 to 3%. Sulphur in the bypass stream increases loading on the downstream converters, increasing the sulphur dewpoint and thereby forcing an overall higher operating temperature which results in a loss of efficiency.

Indirect methods of reheat involving the use of heat exchangers are:

1. steam reheat;
2. fuel gas fired indirect heater;
3. gas-gas heat exchanger.

All these methods are highly recommended from an operational viewpoint as they do not have any of the problems of the direct methods. One disadvantage to these methods is that they are generally more expensive than the direct methods.

4.7 START-UP AND SHUTDOWN

Starting up a sulphur plant usually involves slowly heating up the reaction furnace and converters with fuel gas, air and steam before acid gas is introduced. The fuel gas is burned substoichiometrically to prevent O_2 breakthrough, unless the catalyst is new (no sulphur condensed on new catalyst). An oil sands plant should not use its own product gas because it will likely have a variable composition, thereby making a substoichiometric burn very difficult.

In recent years a new method has been tried. The burned fuel gas is vented from the waste heat boiler until the furnace is up to temperature. The converter beds are then fed process gas. The Claus reactions generate the energy needed to bring the converters up to temperature. This is called "cold startup". This method is not yet widely used.

Scheduled shutdowns should be preceded by a 24 hour heat soak to remove sulphur from the beds. The load is slowly reduced and fuel gas added to the burners. Once there is no more sulphur being produced, the acid gas is shut in. The plant is left to cool naturally or by the use of N_2 , CO_2 or steam purge.

Emergency shutdowns must be carried out such that no O_2 reaches the catalyst beds because they are loaded with sulphur. To ensure this, the acid gas and air inlets are closed and blinded off. Nitrogen is then used to purge the system.

4.8 PROCESS ECONOMICS

Based on the defined inlet sulphur rate of 1000 t/d (in the bitumen) to the oil sands plant, the sulphur plant will have a capacity of approximately 912 t/d. Capital and operating costs for a sulphur plant this size are shown in Table 2.

Cost data for the RSRP is not available as the process is only at the pilot plant stage. Since the pressure is so much higher, it is reasonable to assume that the unit equipment costs would be higher.

4.9 APPLICABILITY TO OIL SANDS PLANTS

The applicability of the modified-Claus process to an oil sands plant has already been shown to be very good: the two existing oil sands plants, Suncor and Syncrude, both successfully use the process. The sulphur plant is expected to operate in a manner similar to that of a modified Claus plant in a refinery. The variability of the feed rate and the feed composition will cause some design and operation problems; none, however, that have not been previously encountered. In the same way impurities in the feed are expected to be a problem.

Feed variability and the need for a split ammonia burning furnace make operation of an oil sands modified-Claus plant more difficult than for a sour gas modified-Claus plant and require a somewhat more sophisticated control system. In order to try to minimize catalyst deactivation, the use of special catalysts (even for a thin protective layer) should be examined.

Overall sulphur recovery from a Claus plant processing natural gas can reach 99%. This level has not been achieved at oil sands plants where recovery of 96% can be obtained in a three stage unit (Alsands 1978).

Table 2. Modified Claus plant costs.^{a,b}

Total installed capital cost	\$39 000 000
Total annual operating cost	\$ 4 400 000

^a Costs are in mid 1982 Canadian dollars.

^b Plant capacity 912 t/d.

5. TAIL GAS TREATMENT

5.1 INTRODUCTION

The increasingly demanding sulphur emission standards of the last ten years have made it necessary for many companies to utilize tail gas treatment processes. As a result, many such processes have been developed and are now commercially available. Although most of these processes were developed primarily for use in the natural gas processing and oil refining industries, their potential for application in oil sands installations appears to be quite good. Since many of the unit operations performed in an oil sands plant upgrading section are the same as those in an oil refinery, such as hydrotreating, amine treating and Claus sulphur recovery, the tail gas produced in an oil sands plant is similar to that produced by a refinery. The only way to definitively prove the applicability of one of the processes would be to monitor its performance in an oil sands plant. This approach is not possible as the two existing oil sands plants, Syncrude and Suncor, do not have tail gas treatment facilities. Neither of the plants are expected to install such facilities in the near future. The proposed Alsands project incorporates two SCOT units in its sulphur recovery system (Alsands Project Group 1978).

There are three principal approaches to tail gas treatment:

1. Continuation of the Claus reaction at lower temperatures on a solid catalyst or in a liquid media.
2. Catalytic hydrogenation/hydrolysis of SO_2 , COS, CS_2 and other sulphur compounds to H_2S , which is recovered by absorption.
3. Oxidation of tail gas to convert all sulphur compounds to SO_2 , followed by treatment through an SO_2 control system.

The processes described in this section are listed on Table 3 together with their state of development and typical performance.

5.2 CLAUS EXTENSION PROCESSES

5.2.1 Institut Francais du Petrole (IFP) Clauspol 1500 Process

5.2.1.1 Process description. This process is based upon the use of a liquid reaction medium and catalyst system (Figure 7). The liquid is polyethylene

Table 3. Tail gas treatment processes.

Process	State of Development ^a	Removes COS, CS ₂	Residual Sulphur Compound Level in Tail Gas (Volume Fraction x 10 ⁻⁶)	Increases Claus Plant Loading
IFP Clauspol 1500	I	No	1500	No
Sulfreen	I	No	300	No
CBA	I	No	1500	No
Townsend	D	No	1500	No
ASR Sulphoxide	B	No	500	No
MCRC	D/I	No	-	No
SCOT	I	Yes	300	Yes
Beavon	I	Yes	100	No
BSR/Selectox	I	Yes	500	No
Trentham				
Trencor-M	D	Yes	200	Yes
Cleanair	D/I	Yes	50	No
ATS	D/I	Yes	900	No
MCRC (limestone)	I	Yes	50	No
Aquaclaus	D	Yes	100	No
USBM Citrate	D	Yes	100	No
Wellman-Lord	I	Yes	200	Yes
SNPA/Haldor				
Topsoe	D	Yes	500	No
UCAP	D	Yes	250	Yes
Westvaco	D	Yes	-	Yes
Lurgi LUCAS	D/I	Yes	350	Yes
CT 121	D	Yes	-	No

^a B = Benchscale; D = Demonstration unit; I = Industrial unit.

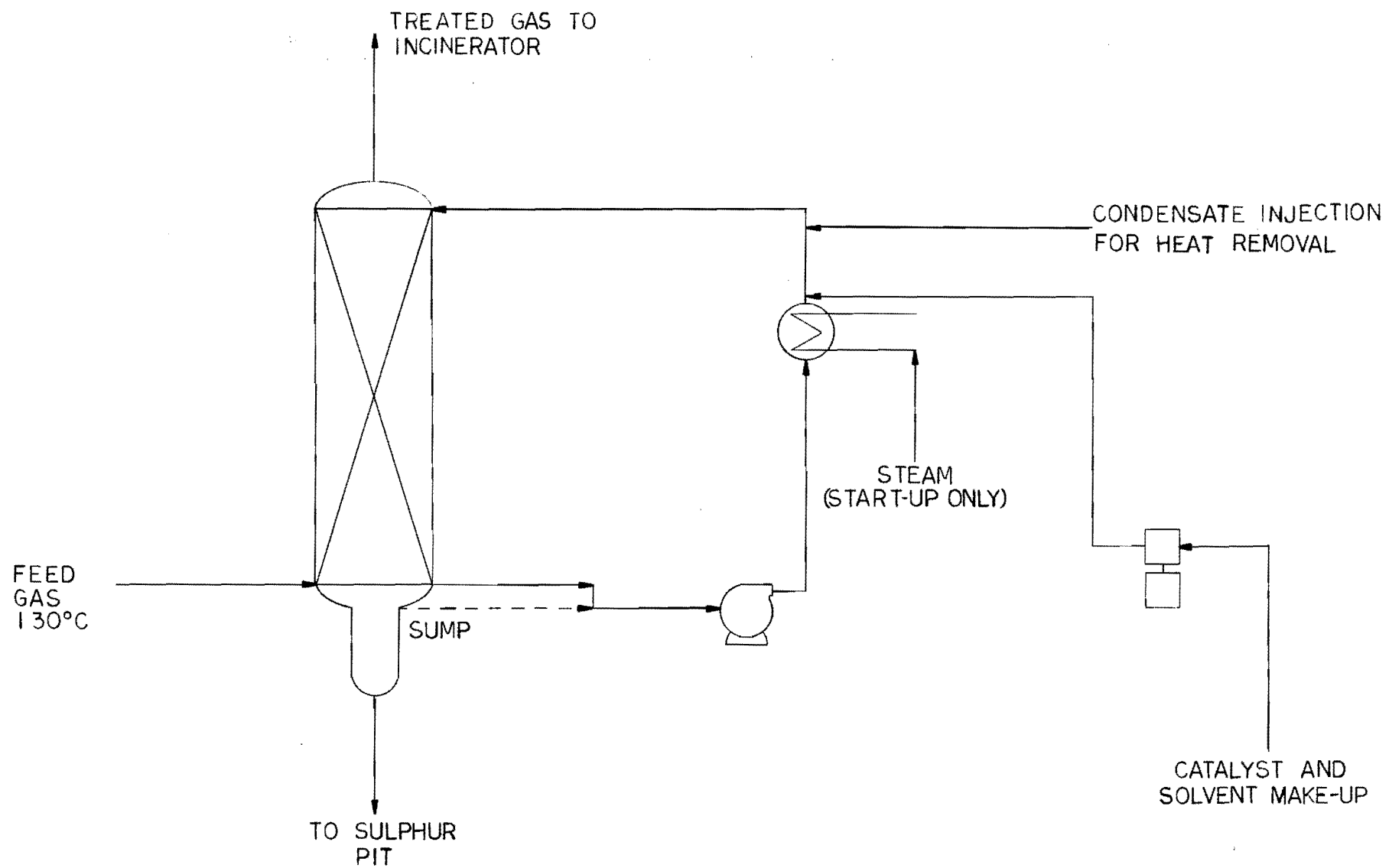


Figure 7. IFP Clauspol 1500 process.

glycol, which dissolves both H_2S and SO_2 but is neither a sulphur solvent nor itself soluble in molten sulphur. The catalyst is a sodium or potassium salt of an ester of a polycarboxylic acid with the solvent. The tail gas is countercurrently contacted in a packed tower by the polyethylene glycol and dissolved catalyst. The tower is specially designed for low pressure drop in an attempt to minimize or eliminate the need for a booster fan immediately following the Claus plant. H_2S and SO_2 are dissolved in the liquid where sulphur is formed. The treated gas is incinerated and then vented to atmosphere. The product sulphur separates from the solvent and is collected from a sump at the bottom of the tower. The sulphur is 99.9% pure (Hydrocarbon Processing 1982). The clean tail gas has 1.5×10^{-3} volume fraction SO_2 .

5.2.1.2 Principal chemical reactions. The process is simply an extension of the standard Claus reaction, shown below:



The possible presence of ammonia does not have any detrimental effect upon the process efficiency.

5.2.1.3 Design considerations and operability. One of the major advantages of the Clauspol 1500 is the good turndown ratio. Satisfactory results are obtained at 30% of design capacity and up to 30% overload (Anonymous 1974). The process operates at a sufficiently low temperature (130°C) that carbon steel may be used as the main construction material. The plant itself is regarded as fairly simple in design and operation (Goar 1975) and therefore, would be expected to have a minimum of maintenance and operating problems. There are no byproducts that must be dealt with.

There are disadvantages to this process as well. Carbonyl sulphide and carbon disulphide in the tail gas are not removed by the process. These compounds contribute significantly to the overall sulphur emissions. The efficiency depends, to a great extent, on having an $\text{H}_2\text{S}:\text{SO}_2$ ratio of 2.0 to 2.4. This ratio can be disturbed by an upset in the acid gas supply, thereby causing an oxygen deficiency in the Claus furnace. This situation causes a

stoichiometric imbalance and subsequent loss of efficiency. Special instrumentation, generally an ultraviolet spectrometric device connected to a sophisticated automatic control system, is needed to prevent this problem (Anonymous 1974).

The commercial viability of this process has been demonstrated in many instances. Presently there are 32 units in operation for Claus plants with capacities of 30 to 800 t/d as well as two units under construction (Hydrocarbon Processing 1982).

5.2.2 Sulfreen Process (Lurgi Apparate - Technik GmbH)

5.2.2.1 Process description. The Sulfreen process makes use of a solid alumina catalyst in a fixed bed reactor (Figure 8). H_2S and SO_2 react to form elemental sulphur via the standard Claus reaction at a temperature below the dew point of sulphur. The reaction takes place in the reactor where the sulphur condenses and is absorbed by the catalyst. When the pressure drop through the reactor reaches a certain maximum value, thereby indicating a large sulphur holdup, the sulphur is recovered by desorption with a hot gas. The unit usually has several reactors operated in a cyclic manner. In the process shown in Figure 8, one reactor is in desorption service and the other two are in adsorption service. In the newer designs the hot desorption gas is a heated slipstream of treated tail gas (Morin and Philardeau 1977). The clean tail gas has less than 0.3×10^{-3} volume fraction SO_2 .

5.2.2.2 Principal chemical reactions. Like the Clauspol 1500 process the major reaction is the standard Claus reaction (see equation 4). Since equilibrium conversion increases as temperature is lowered, higher sulphur recovery is possible than in a normal Claus converter.

5.2.2.3 Design considerations and operability. The Sulfreen process generally is most attractive for large Claus plants, mainly due to the possibility of eliminating the third stage Claus converter. The low process temperature and use of alumina catalyst permit carbon steel construction. The ratio of H_2S to SO_2 can be varied to some extent without significantly effecting the efficiency of the process.

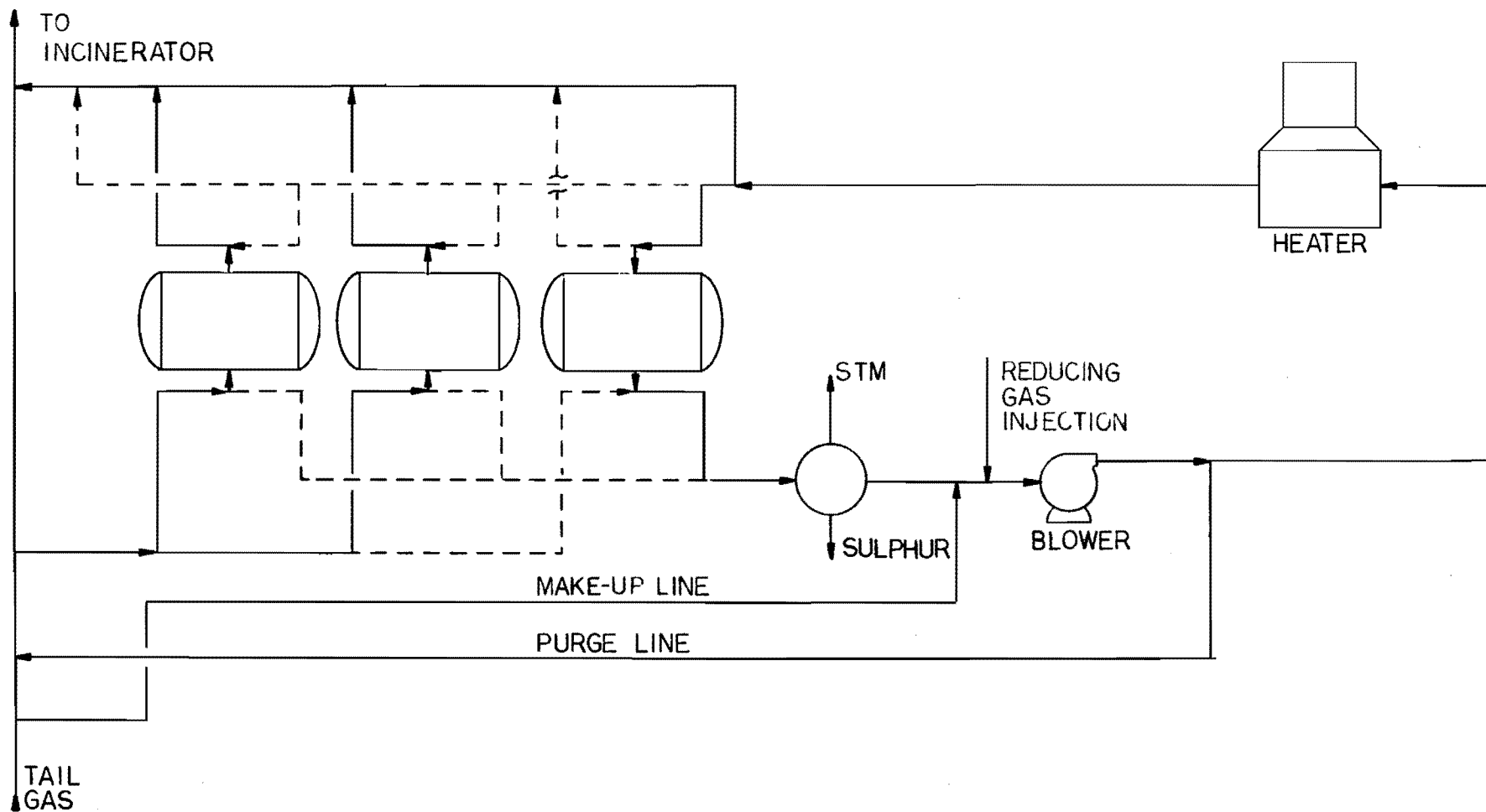


Figure 8. Sulfreen process.

Like the Clauspol 1500 process, Sulfreen does not recover COS and CS₂. Sulphate formation on the catalyst has been a problem with previous designs. To alleviate this problem, a reducing gas is injected into the regeneration gas circuit at the end of the desorption cycle. In some cases, this reducing gas is an H₂S slipstream. The use of AM proprietary catalyst has also been suggested as a way to avoid decreased efficiencies due to sulphation (Grancher 1978b).

Since the catalyst is solid and there are no byproducts formed, there are no significant waste disposal problems. Operating problems are not anticipated since the process is fairly simple and there are over 19 such plants operating throughout the world (Hydrocarbon Processing 1979).

5.2.3 Cold Bed Adsorption (CBA) Process (Amoco Production Co. Ltd.)

5.2.3.1 Process description. The Cold-Bed Adsorption (CBA) process (Figure 9) is designed to be an integral part of the Claus plant. It provides for a final catalytic converter at a low temperature (130°C) in order to achieve a higher conversion with the standard Claus reaction. Unlike the standard Claus converters, the sulphur condenses and is adsorbed onto the catalyst. Hot regeneration gas recovers the sulphur. In the process shown, CBA Reactor 2 is being regenerated by hot gas from the first Claus converter. Following regeneration the reactor is cooled by gas from the second Claus converter. Overall the process is very similar in concept to the Sulfreen process. The clean tail gas has 1.5×10^{-3} volume fraction SO₂. Overall sulphur recovery is reported to reach 99.3% for Claus unit plus CBA converters (Interoffice memorandum, 1980, J.O. No. 13798, Dynawest Process File 5.0301).

5.2.3.2 Principal chemical reactions. The chemistry is the same as for the Sulfreen process. Refer to section 5.2.2.2.

5.2.3.3 Design considerations and operability. The CBA process is very easy to operate because it is a simple configuration that ties directly into the Claus plant operation. No waste disposal problems exist since the catalyst is solid and no byproducts are formed. The CBA Process does not have sulphate formation problems since the regeneration gas is the gas from the first Claus converter.

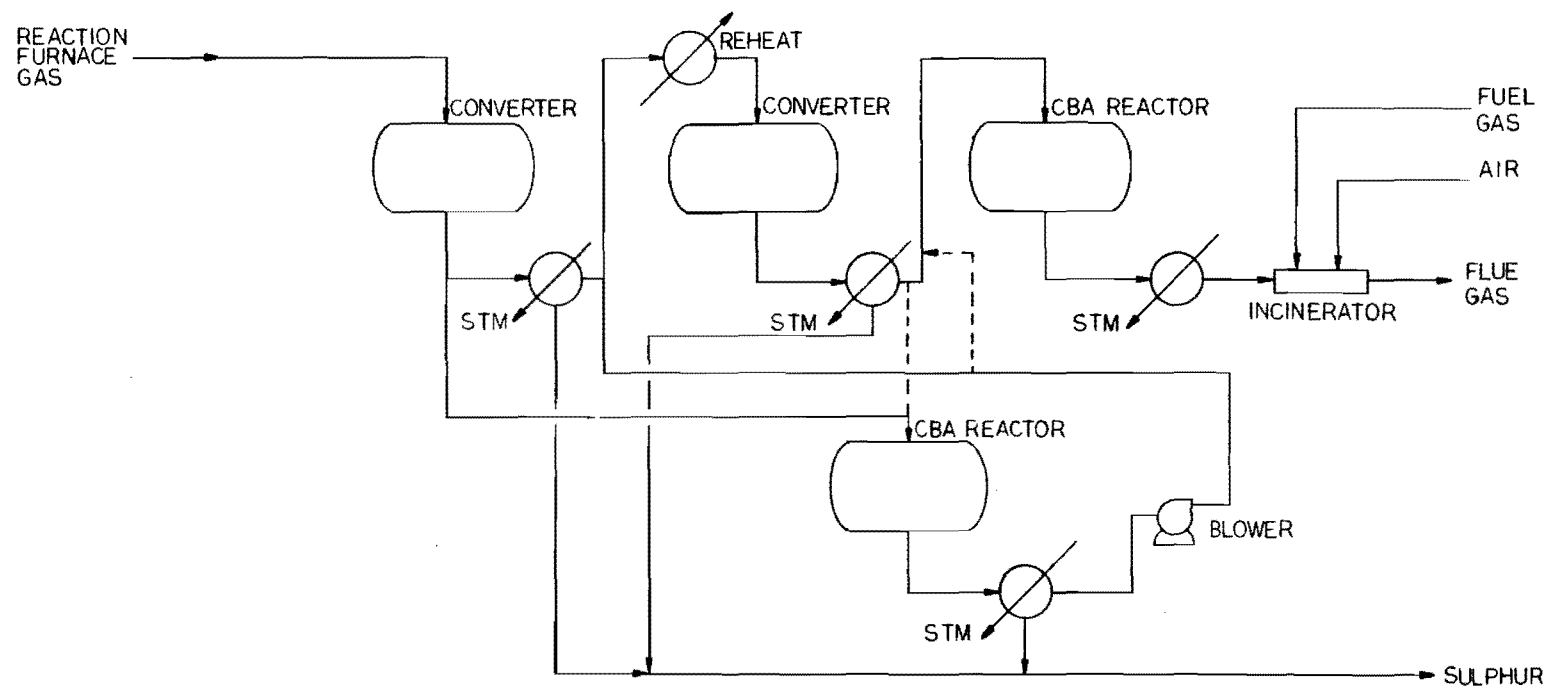


Figure 9. Cold bed absorption process.

This gas contains H_2S which reduces the sulphate. As with the Sulfreen process, the possibility of eliminating the third Claus converter makes this process attractive.

The CBA Process was first applied commercially at Amoco's East Crossfield plant near Calgary, Alberta. Presently there are ten CBA units in design or operation with total Claus capacities ranging from 2 to 1440 long tons of sulphur per day.

5.2.4 Townsend Process

5.2.4.1 Process description. The Townsend process operates on the same principal as the IFP Clauspol 1500 process in that it uses an organic solvent (triethylene glycol) to allow the standard Claus reaction to take place. It does not remove COS or CS_2 and thus cannot produce very low sulphur concentration tail gas. Sulphur recovery is very similar to the Clauspol 1500 process.

5.2.5 Alberta Sulphur Research (ASR) Sulphoxide Process

5.2.5.1 Process description. This process was first developed in 1972 by Alberta Sulphur Research Ltd. (ASR) (Hyne, J. B. and W.J. Rennie, 1972). It can produce a clean gas stream with less than 0.5×10^{-3} volume fraction sulphur residual compounds (COS, CS_2 and H_2S). The process has never been commercialized although it has been operated at the laboratory bench-scale level. Presently all work on the process has been suspended by ASR (telephone conversation March 4, 1982 with Dr. J.B. Hyne, ASR, Calgary, Alberta).

5.2.6 Mineral and Chemical Resources Company Process (MCRC) (Delta Projects)

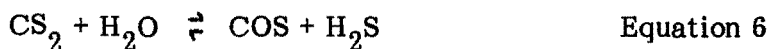
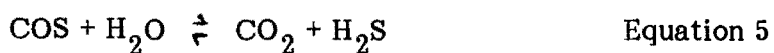
5.2.6.1 Process description. The Mineral and Chemical Resources Company (MCRC) process is the newest subdewpoint adsorption process in terms of commercialization. The process configuration and operation is very similar to that of the Sulfreen process (Section 5.2.2). Presently there is one unit in operation.

5.3 CATALYTIC HYDROGENATION/HYDROLYSIS PROCESSES

5.3.1 Shell Claus Offgas Treating (SCOT) Process (Shell Development Co Ltd.)

5.3.1.1 Process description. The Shell Claus Offgas Treating (SCOT) process was first developed in 1972 (Goar 1975). The process consists of three stages; reduction, alkanolamine absorption and amine regeneration (Figure 10). Initially the Claus tail gas is heated to 300°C in a gas fired furnace and mixed with a hydrogen rich reducing gas. All sulphur and sulphur compounds are converted to H₂S in the reactor over a cobalt/molybdenum catalyst. The reactor gas is first cooled in a heat exchanger and then quenched in a water quench tower. The H₂S rich gas is sent to an absorber where the H₂S is absorbed by a solution of di-isopropanolamine (DIPA). Clean tail gas is fed to the incinerator and the rich amine is sent to a regeneration column. DIPA is regenerated by reboiling against steam with the resulting H₂S and CO₂ rich offgas being recycled to the front of the Claus plant. Sour water from the quench tower is sent to a sour water stripper. Sour gases from the stripper are sent to the Claus plant. The clean tail gas can have an SO₂ concentration of less than 0.3 x 10⁻³ volume fraction.

5.3.1.2 Principal chemical reactions. The major hydrogenation/hydrolysis reactions are shown below.



The catalyst used has the dual purpose of promoting both the hydrogenation and the hydrolysis reactions.

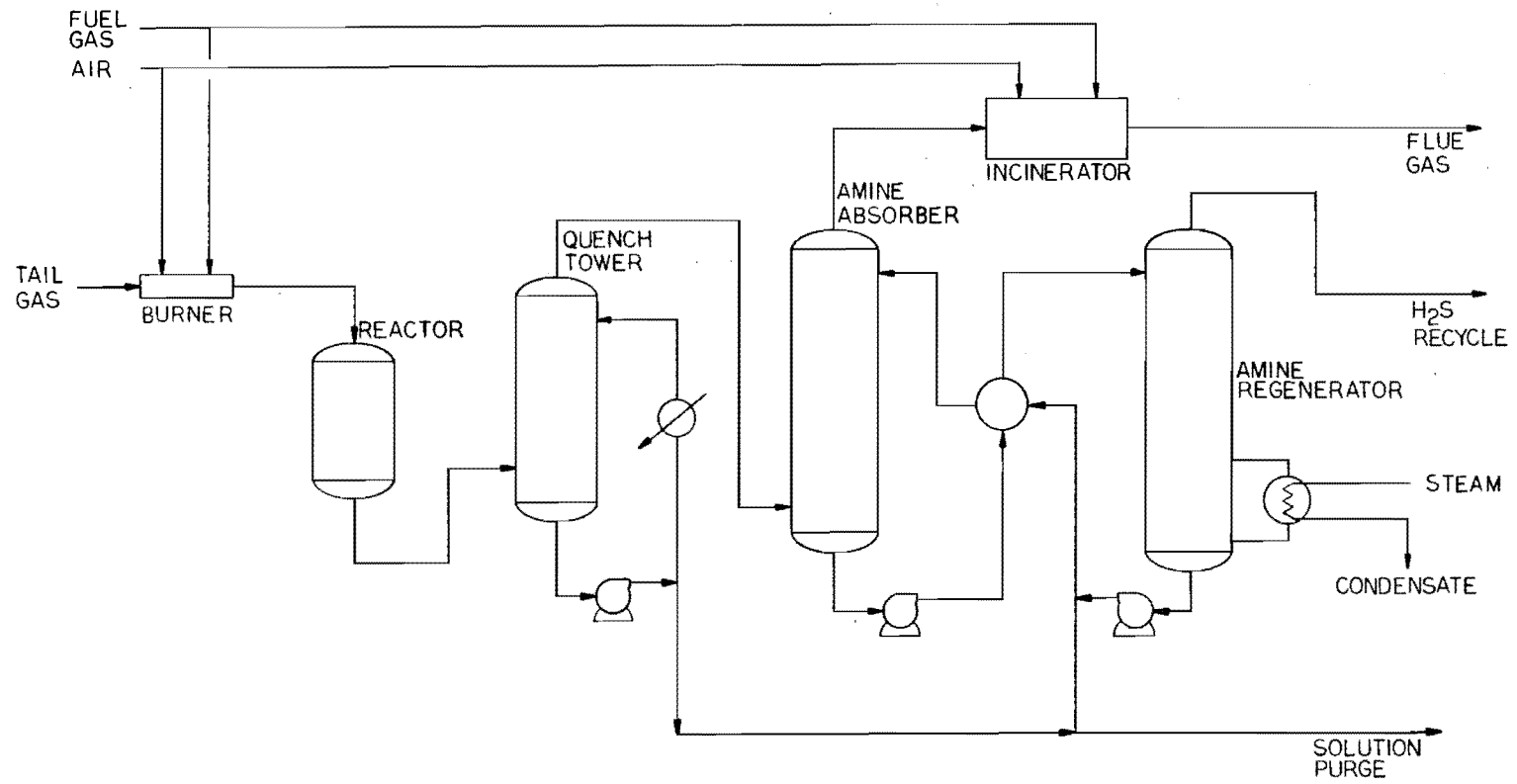


Figure 10. SCOT process.

5.3.1.3 Design considerations and operability. The SCOT process has a high flexibility to cope with variations in the Claus plant operation. Changes in the tail gas composition do not have a large effect on the overall sulphur recovery. A turndown of 40% is easily accomplished, however, designs of up to 20% turndown have been made (Hydrocarbon Processing 1979). The DIPA typically coabsorbs 20% to 30% of the CO_2 present in the tail gas. If the feed to the Claus plant has 0.1 to 0.2 volume fraction CO_2 , the effect of the inert CO_2 absorbed is of no great consequence. However, if the Claus plant feed gas contains 0.3 to 0.5 volume fraction CO_2 , then the SCOT process is not believed to be a good choice. Recycling of the CO_2 back to the Claus unit can cause the CO_2 to build up to such high levels that H_2S and CO_2 react to form and deposit a polymeric carbon on the catalyst and thus plug up the reactor (specifically, the third converter) (telephone conversation March 4, 1982 with Dr. J.B. Hyne, ASR, Calgary, Alberta). At high CO_2 levels, a loss in Claus efficiency is also attributed to CO_2 occupying active sites on the catalyst, although the affinity of the alumina catalyst for SO_2 as opposed to CO_2 is 40 to 1. Furnace flame stability is also adversely affected by high concentrations of CO_2 . Partial solutions to this problem include using another solvent such as methyl diethanolamine or a mixture of solvents.

Regeneration of the amine may be done in a separate stripper. However, if the same amine solutions are being used in the upstream treating facilities then a considerable saving in capital cost may be realized by combining the regeneration facilities.

As with most alkanolamine absorption systems there is expected to be a small problem with amine degradation. If this is the case then the amine system would have to be purged and a makeup stream introduced.

The SCOT process is one of the most widely used tail gas treatment processes as there are approximately 85 units in operation, design or construction on a world wide basis. SCOT units have been used with Claus plants that range in capacity from 10 t/d to 3000 t/d (Goar and Sames 1982).

5.3.2 Beavon Sulphur Recovery Process (Union Oil Co of California)

5.3.2.1 Process description. The Beavon Sulphur Recovery Process (BSRP) consists of two distinct phases (Figure 11). In the first phase, the tail gas is

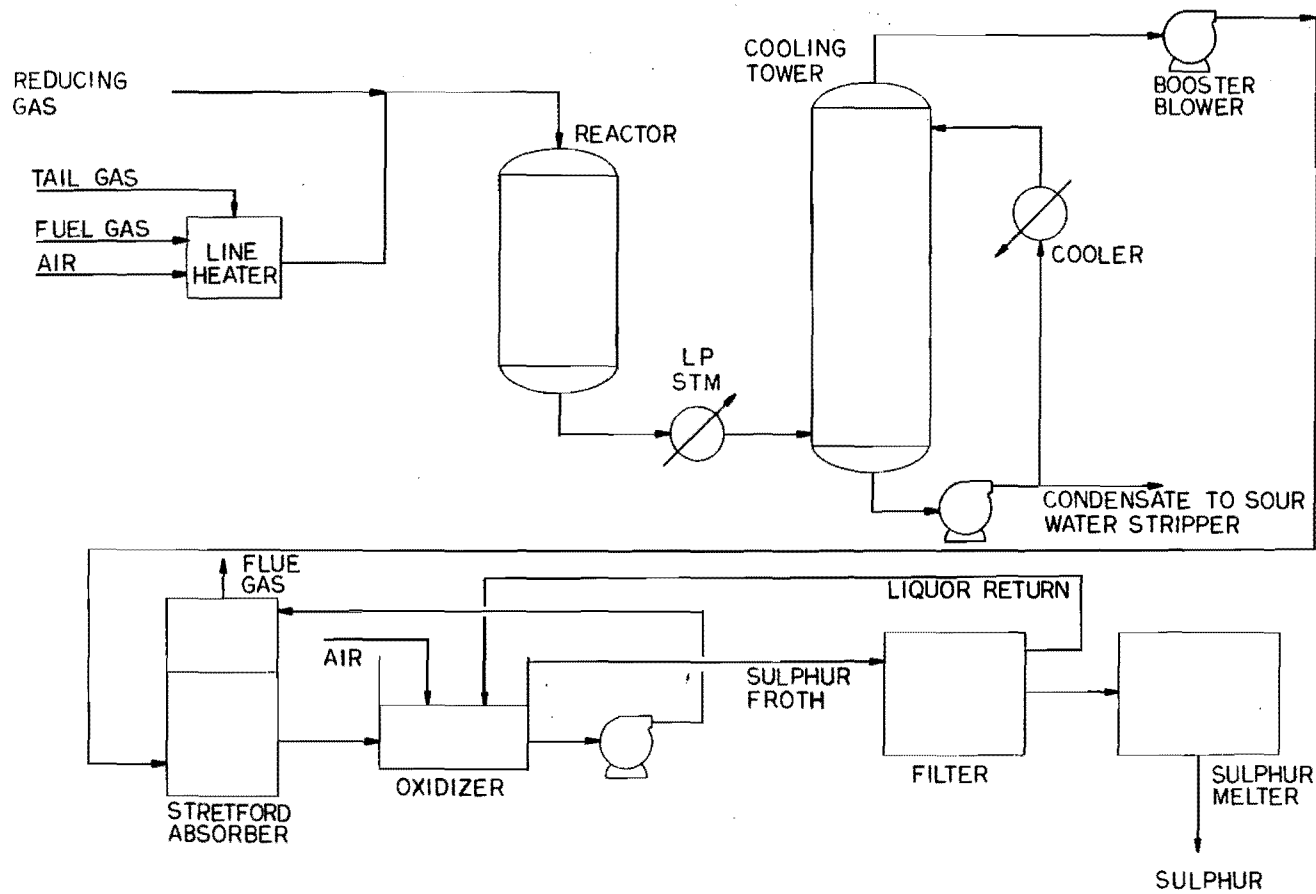
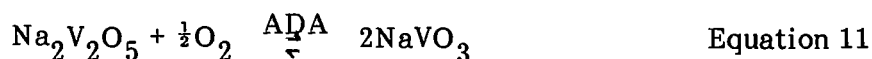
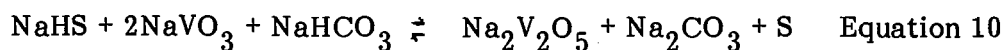
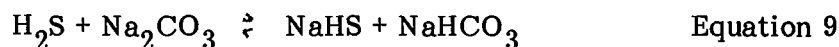


Figure 11. Beavon sulphur recovery process.

mixed with reducing gas generated by the partial oxidation of fuel gas. This stream is fed to the catalytic reactor where all sulphur compounds are hydrogenated/hydrolyzed to H_2S . The reactor effluent is then cooled in a water quench tower. The quench tower water is recirculated with a small purge stream being treated by a sour water stripper.

In the second phase of the process, the cooled gas is sent to a Stretford plant. H_2S is absorbed in a column by an aqueous solution of sodium carbonate and sodium meta vanadate/anthraquinone disulphonic acid. The H_2S rich solution is sent to the oxidizer into which air is sparged. Particles of sulphur are formed and collected as a froth at the top of the oxidizer tower. The froth is processed through filters or centrifuges and then washed, dried, melted and added to the main sulphur block. The regenerated carbonate solution is recycled back to the absorber. The clean tail gas from the top of the absorber is vented straight to atmosphere. The concentration of sulphur residual compounds in the clean tail gas is less than 0.1×10^{-3} volume fraction (with less than 10×10^{-6} volume fraction H_2S). There are several slight variations of this process, one of which is the use of the Japanese Takahax process (Tokyo Gas Co. Ltd.) instead of the Stretford process. The Takahax process is essentially the same as the Stretford process except Takahax uses a slightly different absorbent solution; sodium carbonate, 1-4 naphthoquinone and 2-sulphonate solution (Goar 1975). Another replacement for the Stretford Process is the Unisulf Process (Union Oil Co of California) which is described in more detail in Section 5.3.2.3. Recently, the Sulfint Process (Integral Engineering Vienna, Austria) has been developed which can also replace the Stretford Process. This process is described in detail by MacKinger, Rossati and Schmidt (1982).

5.3.2.2 Principal chemical reactions. The hydrogenation/hydrolysis reactions are shown in section 5.3.1.2. The Stretford reactions are as follows.



ADA = anthraquinone disulphonic acid

5.3.2.3 Design considerations and operability. The Stretford solution is very corrosive and must be properly handled. Carbon steel is used throughout for construction. However, to prevent corrosion, a coal tar derived epoxy resin can be successfully used as a lining for the vessels and piping (Interoffice Memorandum, 1981, J.O. No. 13793, Dynawest Process File 5.0301). One type of absorber used is a tray tower that typically uses redwood trays; however, fibreglass trays have been installed in some units (Kresse, Lindsey, and Wadleigh 1981). Problems with sulphur plugging these trays has been reported. The solution eventually becomes deactivated by contamination with sodium thiosulphates. Other designs use a venturi followed by a packed tower.

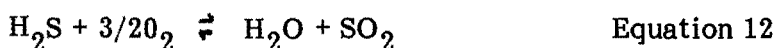
The Unisulf process has basically the same process configuration as the Stretford process. The chemicals used, however, are different. The Unisulf chemicals are not nearly as subject to chemical degradation as the Stretford solution. There is less sulphate formation and less of a vanadium problem. The growth of bacteria in the solution is not expected to occur as it does in the Stretford solution (telephone conversation May 11, 1982 with B.G. Goar, Perry/Goar Sulphur Systems, Texas). The Unisulf process has been extensively tested in pilot operations and is now being demonstrated commercially in a Rectisol offgas treatment unit. The process is expected to be ready for licensing within the year (telephone conversation May 13, 1982 with M. Peterson, Union Oil Co. of California).

The complexity of the BSRP, when compared to the Claus extension process, contributes significantly to operational troubles. Problems have occurred with operation of the oxidizer and foaming has occurred throughout the unit (in the Stretford section). Another problem, assuming the most probable location of an oil sands plant to be in northern Alberta, is the difficulty of winterization of the process. Most major items of equipment must be placed in a building, the most notable exception being the absorber (telephone conversation April 26, 1982 with A. Goelzer, SWEC, Houston).

5.3.3 Beavon Sulphur Recovery(BSR)/Selectox Process (Union Oil Co. of California)

5.3.3.1 Process description. This process, like the BSRP, has two phases (Figure 12). The first phase is essentially the same as the BSRP. In the second phase, the cooled gas is passed over BSR/Selectox I catalyst to selectively oxidize the H_2S to elemental sulphur. The sulphur is removed by condensation. Clean tail gas is then incinerated and vented to atmosphere. The concentration of SO_2 in the vent gas is as low as 0.5×10^{-3} volume fraction.

5.3.3.2 Principal chemical reactions. The hydrogenation/hydrolysis reactions are shown in section 5.3.1.2. The H_2S oxidation reactions are as follows:



With the Selectox catalyst, formation of SO_3 and oxidation of either hydrogen or saturated hydrocarbons is practically non-existent. The catalyst achieves 80% conversion of H_2S . It has proven to be highly active and stable over a long period of time without regeneration.

5.3.3.3 Design considerations and operability. Operation of this process is simple enough that operator attention is limited to a few hours per day. This simplicity of operation readily lends itself to the concept of skid mounted fully self-contained packaged units, easily transportable to any location.

The performance of the process has been proven by operation of a unit in West Germany that has consistently achieved an overall sulphur recovery of 99 percent or higher. The unit is reported to be reliable and easy to operate (Hass et al 1981).

5.3.4 Trentham Trencor-M Process

5.3.4.1 Process description. The Trencor-M process (Figure 13) is very similar to the SCOT process. Claus tail gas is heated and reacted

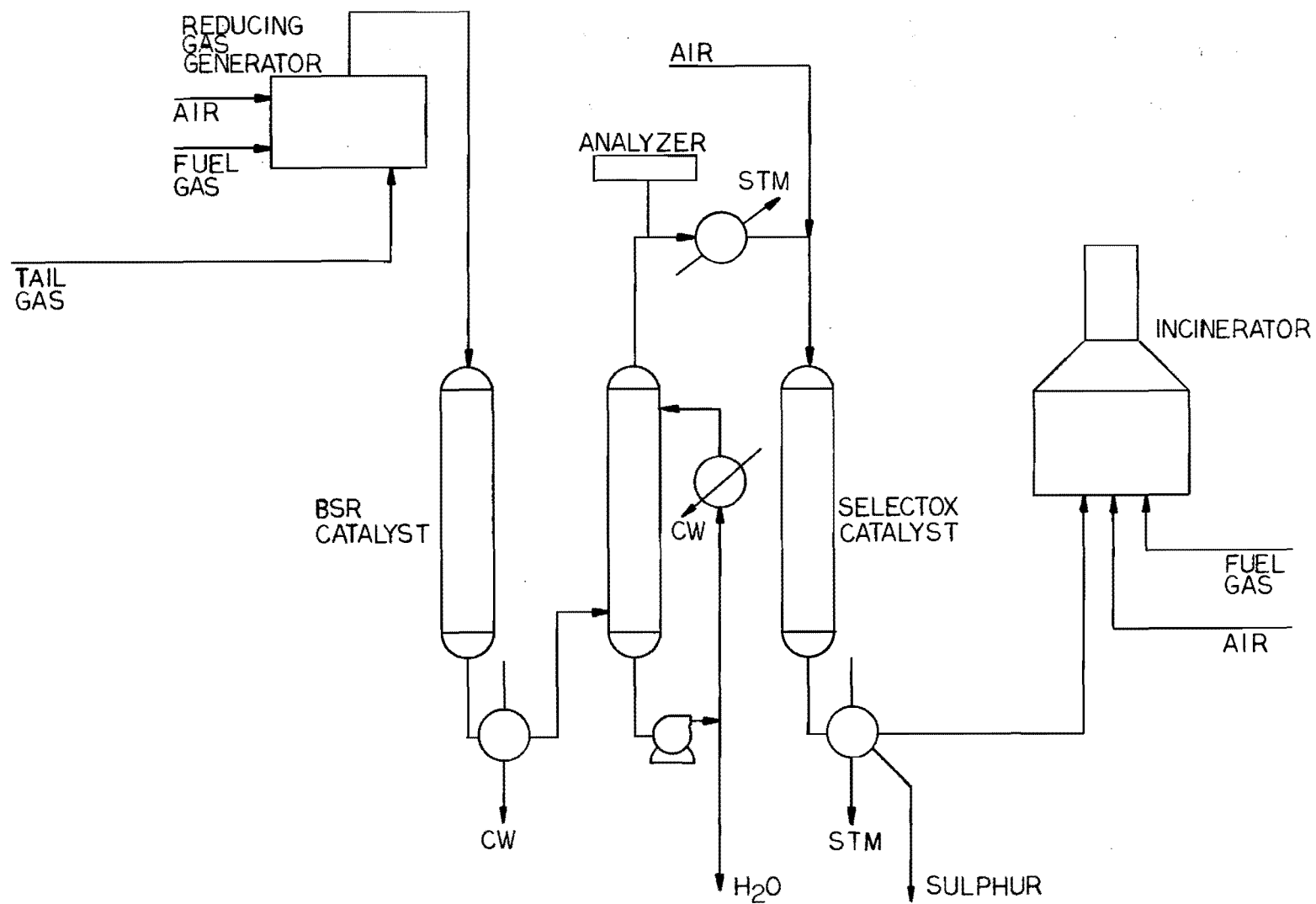


Figure 12. BSR/Selectox process.

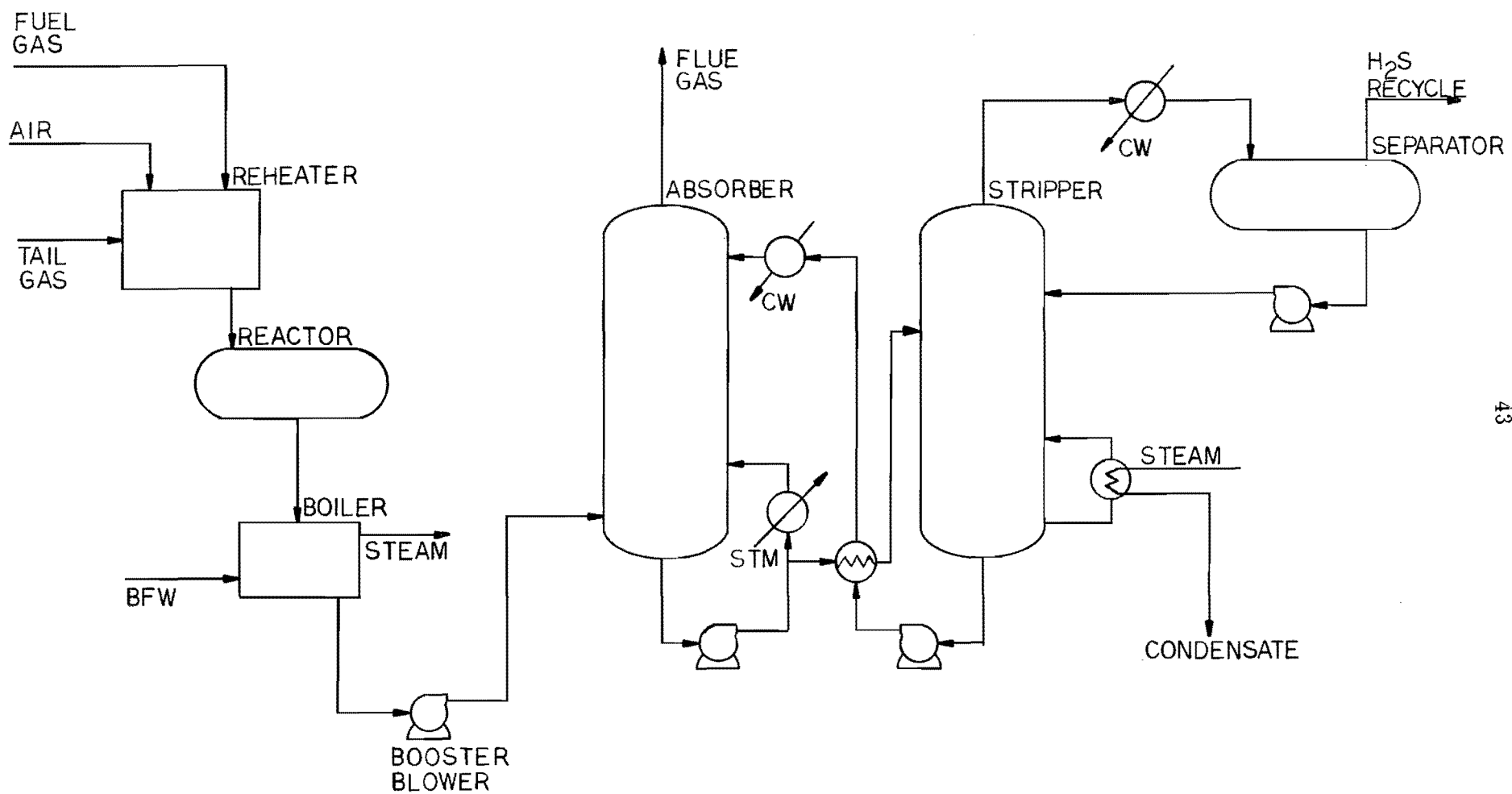


Figure 13. Trentham trencor-M process.

with hydrogen over a noble-metal catalyst to hydrogenate/hydrolyze all sulphur compounds to H_2S . The gas is then cooled and quenched before being sent to an amine absorber. An aqueous solution of methyldiethanolamine (MDEA) containing small amounts of inorganic salts is used (Goar 1975). The amine is regenerated in the conventional manner with the H_2S rich gas being recycled back to the front end of the Claus plant. The SO_2 concentration of the tail gas stream is less than 0.2×10^{-3} volume fraction. The principal chemical reactions, design considerations and comments on operability are essentially the same as for the SCOT process. Refer to sections 5.3.1.2 and 5.3.1.3.

5.3.5 Cleanair Process (Pritchard Corp.)

5.3.5.1 Process description. The Cleanair process is similar to the BSRP in that it uses the Stretford process as the final treatment step (Figure 14). The Claus plant tail gas is water quenched to allow the basic Claus reaction to continue and to hydrolyze the COS and CS_2 . This stream is then fed to the Stretford unit which is described in section 5.3.2.1. The clean tail gas has less than 50×10^{-6} volume fraction SO_2 equivalent. The principal chemical reactions, design considerations and comments on operability are essentially the same as for the BSRP. Refer to sections 5.3.2.2 and 5.3.2.3.

The process has been extensively piloted and has been scaled up to production size by Pritchard Corp. One commercial plant was in operation and two plants were under construction as of April 1979 (Hydrocarbon Processing 1979).

5.4 SULPHUR DIOXIDE REMOVAL PROCESSES

5.4.1 Ammonium Thiosulphate Process (ATS) (Pritchard Corp.)

5.4.1.1 Process description. The Ammonium Thiosulphate (ATS) Process removes residual sulphur compounds in Claus plant tail gas to produce a commercial form of aqueous ammonium thiosulphate solution which is sold as fertilizer (Figure 15). The tail gas is incinerated to produce a hot SO_2 rich stream. The gas is cooled, quenched and sent to a packed absorber where the SO_2 is absorbed by a weak aqueous ammonia solution. Ammonium sulphite and

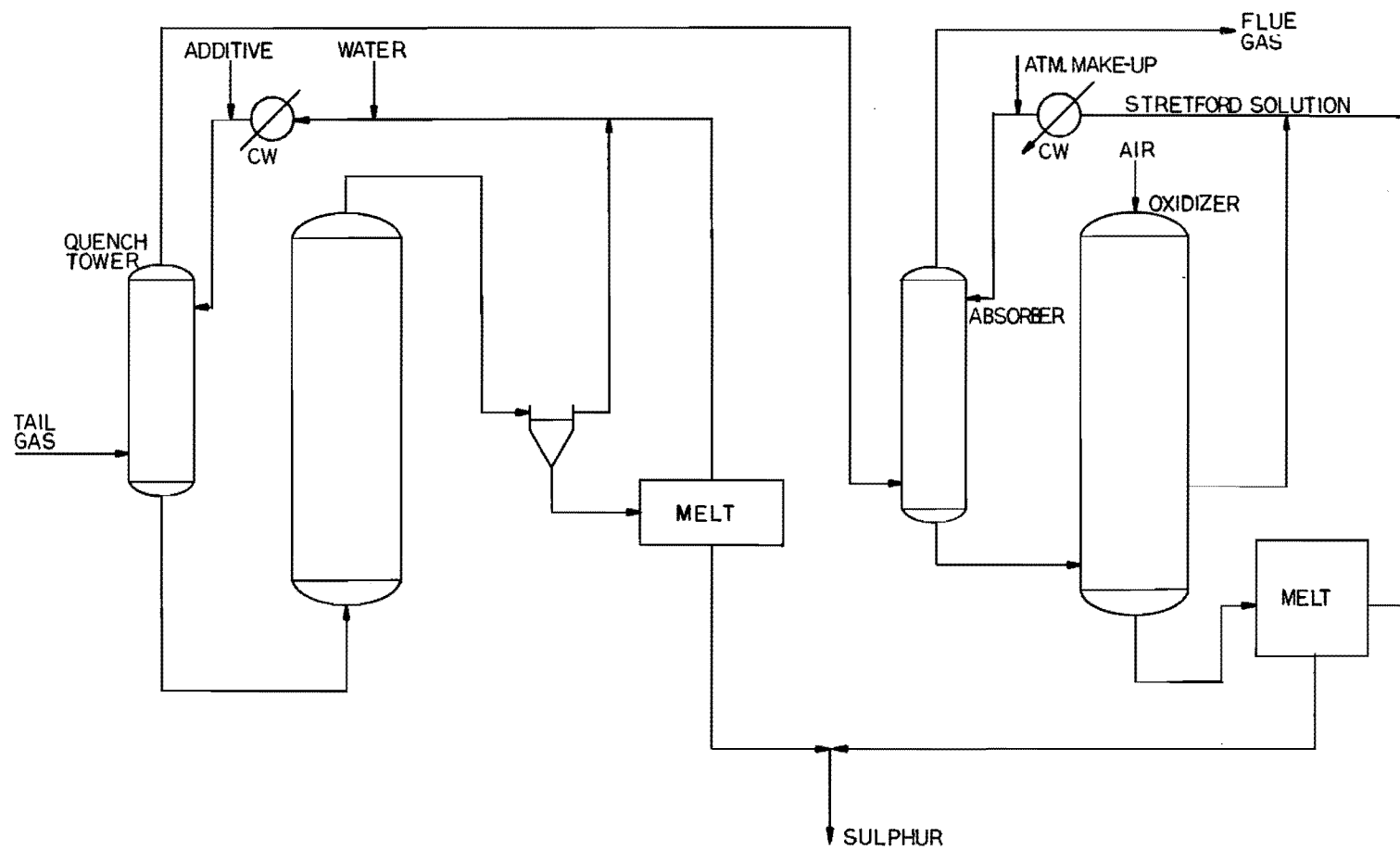


Figure 14. Cleanair process.

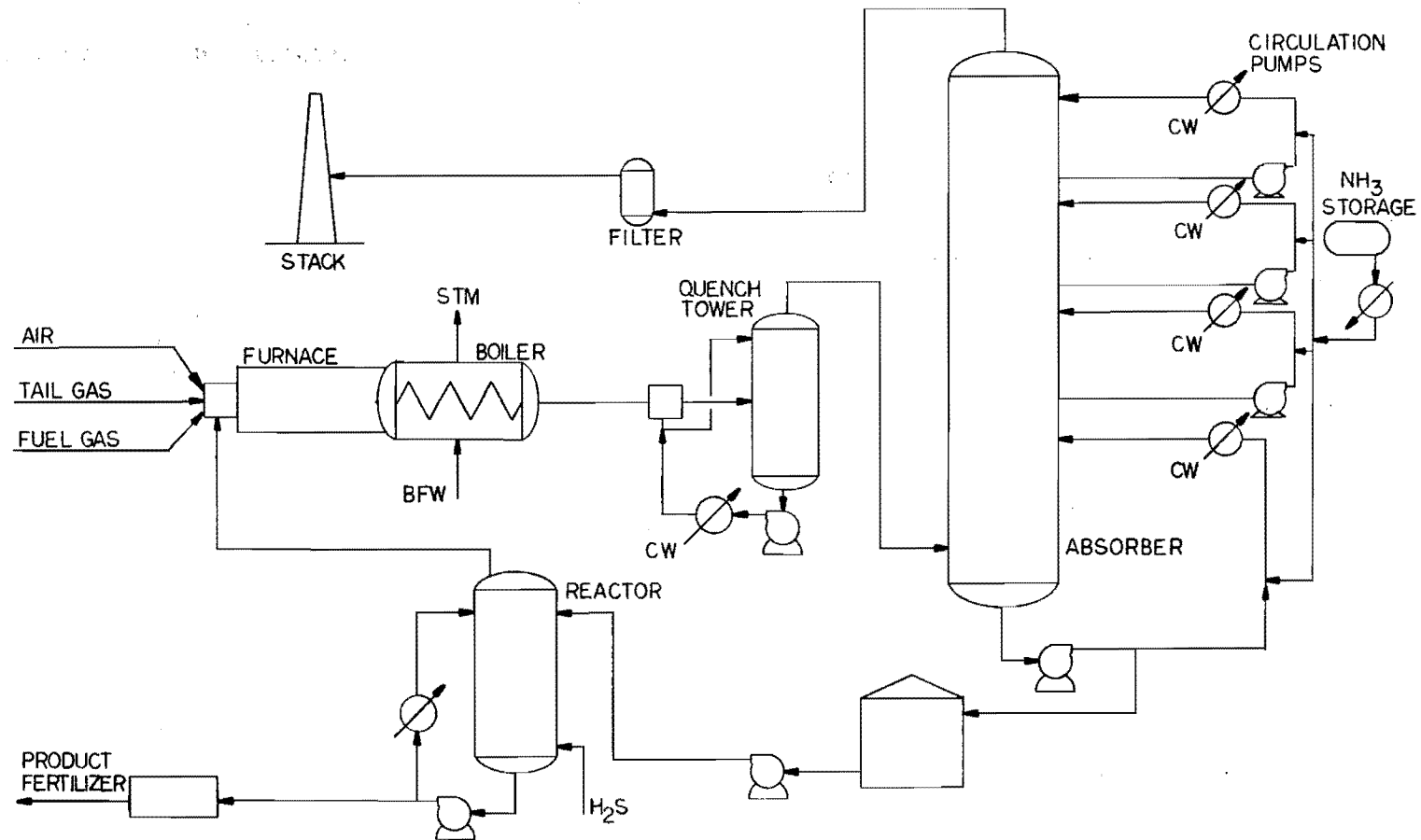
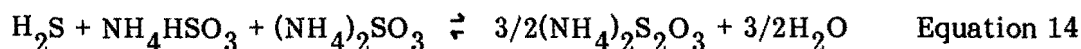


Figure 15. Ammonium thiosulphate process.

ammonium bisulphite are formed in the column. Clean tail gas is vented to the atmosphere. The ammonium sulphite/bisulphite solution is fed to the ATS reactor where ammonium thiosulphate is formed. The H_2S needed for the reaction is sparged into the bottom of the reactor. The product is then concentrated in a falling film evaporator to produce a fertilizer that is 0.6 mass fraction dissolved solids, 0.26 mass fraction sulphur and 0.12 mass fraction nitrogen (Berry 1980). The SO_2 concentration in the clean tail gas is less than 0.9×10^{-3} volume fraction.

5.4.1.2 Principal chemical reactions. Ammonium thiosulphate is formed by the following reaction:



5.4.1.3 Design considerations and operability. The main advantage of this process is the fact that it produces a salable fertilizer product. If the market exists, this fertilizer may be sold at a profit, even considering the cost of the added anhydrous ammonia (Berry 1980). However, if no market exists, then the product fertilizer becomes a disadvantage as some other means of disposal must be found.

The first ATS process was installed at the Colorado Interstate Gas Co., Table Rock, Wyoming facility in 1980.

5.4.2 Mineral and Chemical Resources Company Limestone Slurry Sulphur Recovery (Delta Engineering Corp. and Mineral and Chemical Resources Co.)

5.4.2.1 Process description. The Mineral and Chemical Resources Company (MCRC) process contacts incinerated (SO_2 rich) Claus tail gas with a limestone slurry (Figure 16). A typical plant consists of slurry contactors, a mist eliminator, a ball mill, a central sump and a filter. The product is a non-hazardous calcium sulphite/sulphate mixture. The process reduces the level of SO_2 to less than 50×10^{-6} volume fraction.

One plant in the United States has been operating successfully with this process since 1976.

5.4.3 Aquaclaus (Stauffer Chemical Co.)

5.4.3.1 Process description. Tail gas is first incinerated to convert all residual sulphur compounds to SO_2 and then cooled (Figure 17). The gas is then scrubbed with an aqueous solution of sodium phosphate which removes the SO_2 , principally as sulphite and bisulphite. The rich solution is fed to a reactor where sulphite and bisulphite are converted to elemental sulphur by direct reaction with a 25% stoichiometric excess of H_2S . The slurry of sulphur formed is concentrated and separated by melting, and the regenerated liquor is recycled to the absorber. Sodium sulphate is formed by the oxidation of bisulphate and by absorption of SO_3 (which is present due to excess oxygen in the incinerator). Because of this problem a purge stream is required (Goar 1975). The clean tail gas typically has less than $50 \text{ to } 100 \times 10^{-6}$ volume fraction SO_2 .

Although the process has been extensively tested in the pilot plant stage, a commercial installation has yet to be constructed.

5.4.4 United States Bureau of Mines (USBM) Citrate Process

5.4.4.1 Process description. The concept of this process (Figure 18) is very similar to that of the Aquaclaus process. The absorption liquid is an aqueous solution of citric acid and other carboxylates. Sulphur is formed in the reactor and then concentrated by air floatation in a floatation vessel. The process is capable of achieving less than 0.1×10^{-3} volume fraction SO_2 in the clean tail gas. Since the absorbing solution is clear, the process is free of scaling and other plugging problems (Madenbury and Seesee 1980).

The process is being incorporated in a heavy oil upgrading plant under construction in Texas (Johnson and Sliger 1982).

5.4.5 Wellman-Lord Process (Davey McKee)

5.4.5.1 Process description. Claus tail gas is incinerated and then cooled in a waste heat boiler (Figure 19). Final cooling is accomplished by water quench. The cooled gas is scrubbed in an absorber by sodium sulphite solution. Sodium bisulphite is produced which is then decomposed by evaporation, releasing SO_2 and H_2O . The SO_2 is separated to a purity of 0.95 mass fraction and recycled

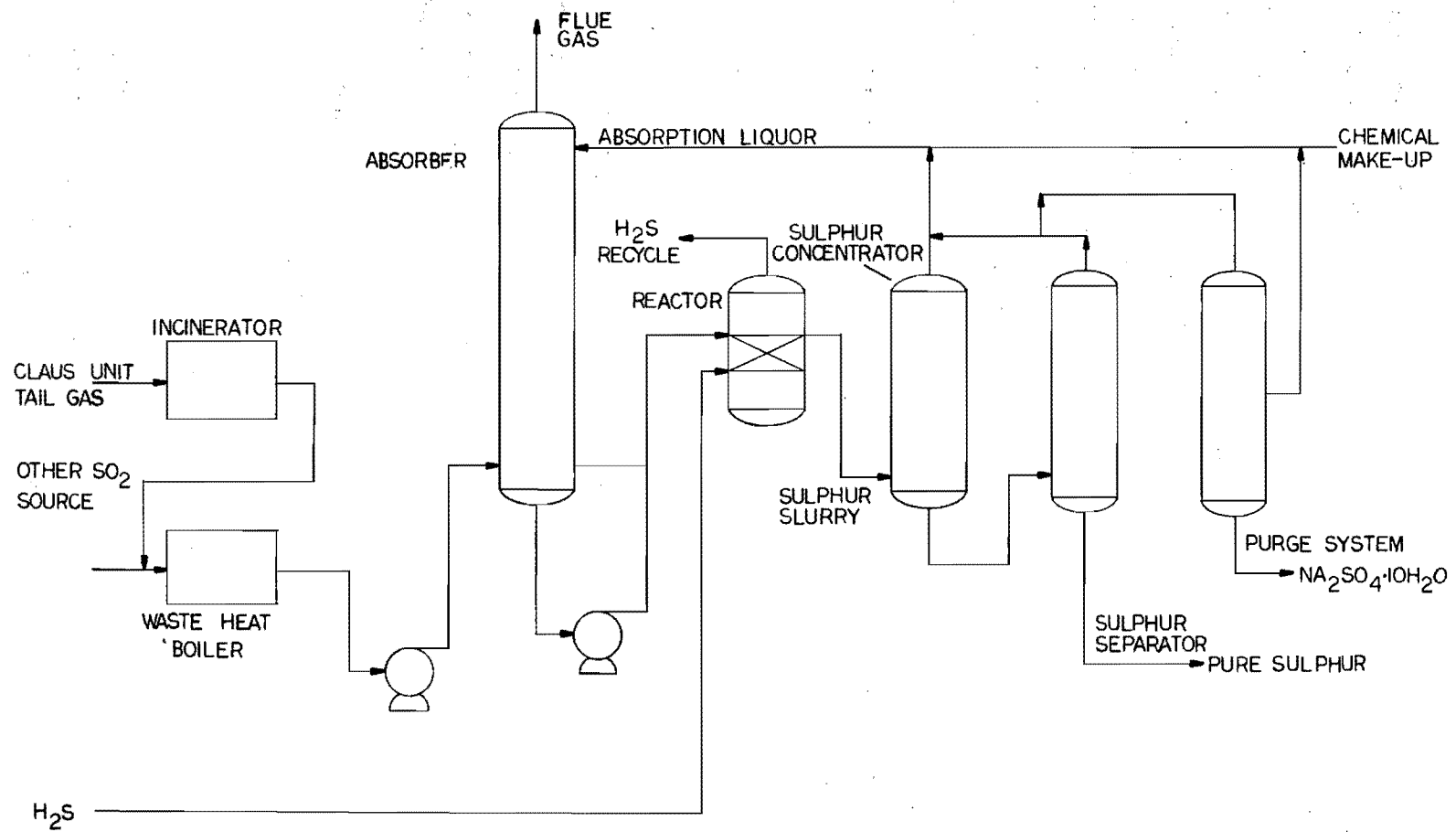


Figure 17. Aqua Claus process.

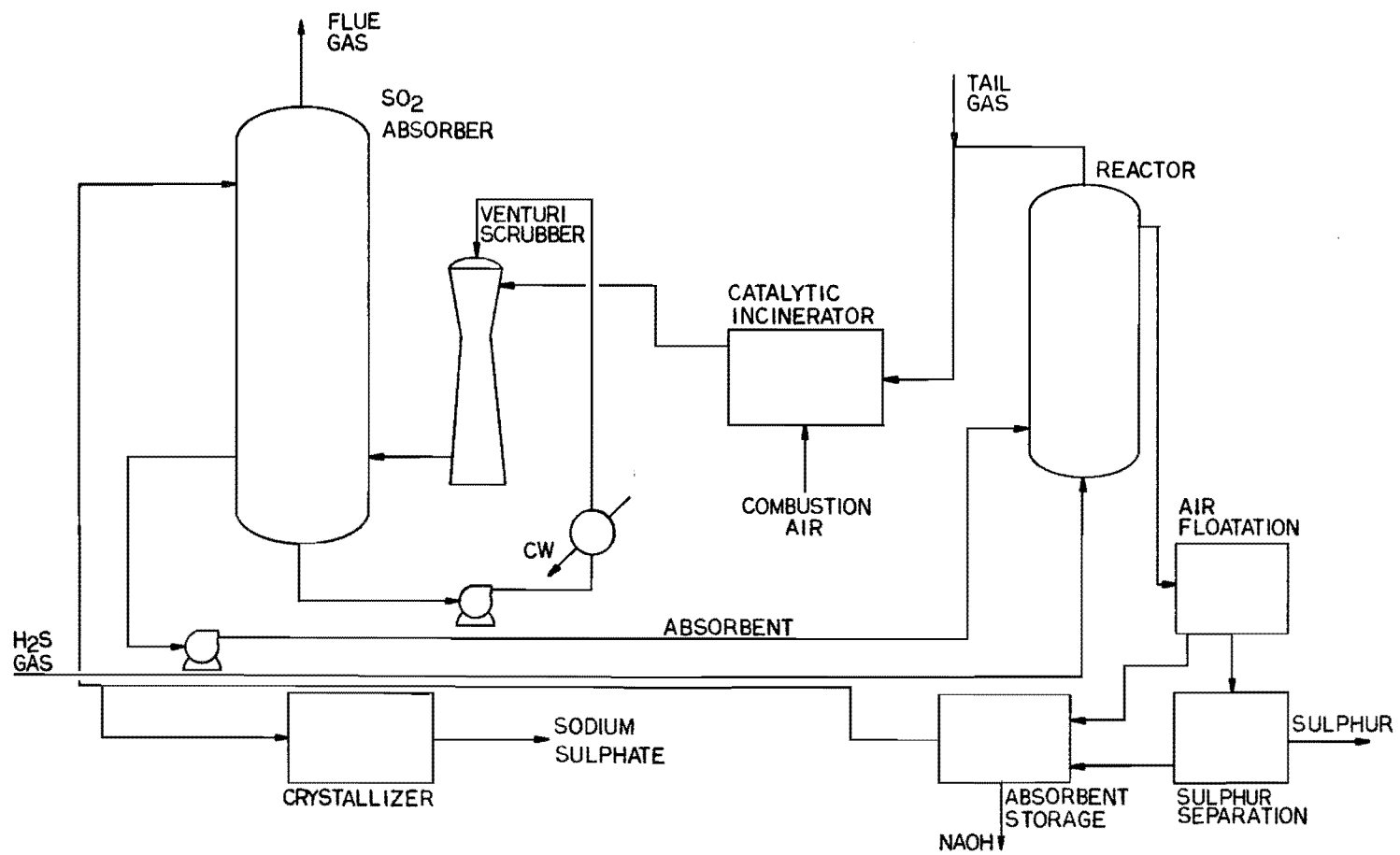


Figure 18. USBM citrate process.

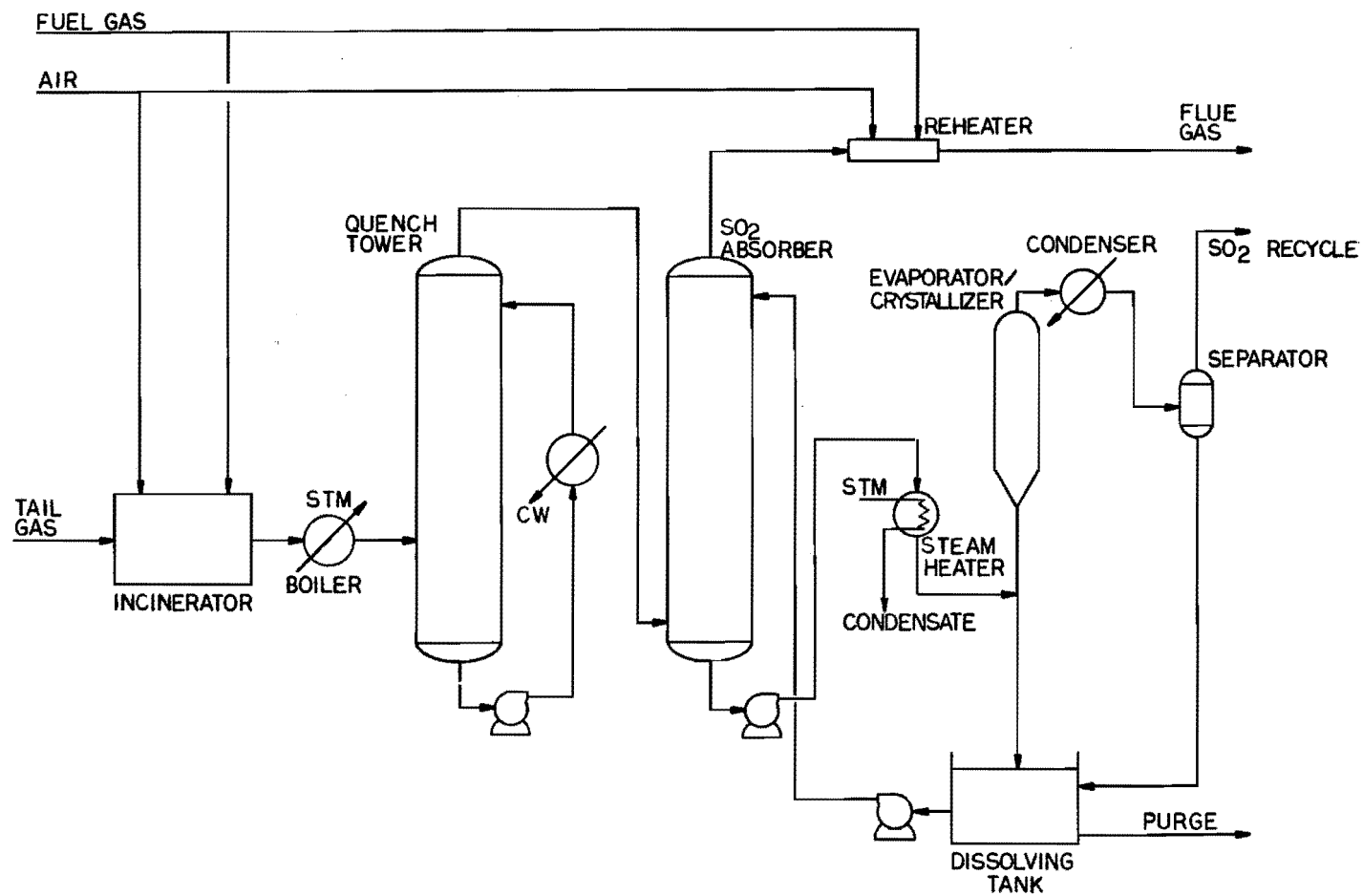
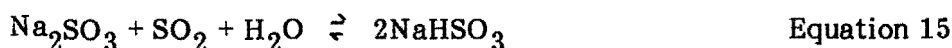


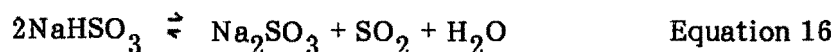
Figure 19. Wellman-Lord process (for tail gas treatment).

back to the Claus plant. The solution purge produces a dry salt product. The SO_2 concentration in the clean tail gas is less than 0.2×10^{-3} volume fraction.

5.4.5.2 Principal chemical reactions. SO_2 is absorbed by sodium sulphite via the following reaction:



The SO_2 is released in the evaporator-crystallizer via the following reaction:



5.4.5.3 Design considerations and operability. The Wellman-Lord process is particularly good for streams with a high CO_2 content since it does not create a CO_2 recycle problem. The unfamiliarity of many refinery operators with the process chemistry and the chemical-plant type equipment employed have caused many operators to be non-receptive to this process. The process is recommended only for large Claus plants because of the relative expense and complexity (Goar 1975).

Presently, there are seven commercial plants operating as tail gas treatment units for Claus plants. Many other units are used for flue gas desulphurization as described in Chapter 6.

5.4.6 Societe Nationale des Petroles d'Aquitaine (SNPA)/Haldor Topsoe Process

5.4.6.1 Process description. Tail gas is incinerated, cooled, and passed over a vanadium pentoxide catalyst which converts 95% of the SO_2 to SO_3 . Sulphuric acid (94%) is formed by mixing H_2O and SO_3 in a concentrator and absorber. There is 0.5×10^{-3} volume fraction SO_2 in the clean tail gas. The only commercial plant installed to date is at Lacq, France.

5.4.7 UCAP Process (Union Carbide Corp.)

5.4.7.1 Process description. Tail gas is incinerated, cooled and quenched (Figure 20). The cooled gas is then scrubbed in an absorber with a solution of 0.8 mass fraction triethanolamine. The SO_2 is thermally stripped from the solution in a vacuum stripper. The SO_2 , saturated with water, is recycled back to the catalytic Claus reactor. The amine solution has a special characteristic in that it absorbs virtually no CO_2 (Yon, Atwood and Swain 1979). Thus, CO_2 is not recycled back to the Claus plant. The clean tail gas contains less than 0.25×10^{-3} volume fraction SO_2 . In the Integrated-UCAP system, the Claus furnace is not required.

Gulf Oil Co. have built a commercial prototype to treat acid gas from their refinery in Venice, L.A.

5.4.8 Westvaco Process

5.4.8.1 Process description. This process uses a continuous, countercurrent, multi-stage fluidized bed absorber with carbon activated adsorption particles flowing downward and tail gas flowing upward (Goar 1975). The SO_2 is released from the carbon in the regenerator and recycled back to the Claus plant. The process is not believed to have developed beyond the pilot plant stage.

5.4.9 Lurgi LUCAS Process

5.4.9.1 Process description. Tail gas is first incinerated and then cooled from 580°C to 380°C . This stream is treated with hot coke and followed by further cooling and absorption of SO_2 from the cooled gas stream with a solution of aqueous alkali phosphate. The absorbed SO_2 is stripped from the solution in a regeneration tower and recycled to the front end of the Claus unit. The treated tail gas is reported to contain less than 0.35×10^{-3} volume fraction sulphur residuals (H_2S , SO_2 , COS , CS_2). Lurgi claims an overall sulphur recovery efficiency of 99.9 percent for a modified Claus/LUCAS facility (Goar and Sames 1982).

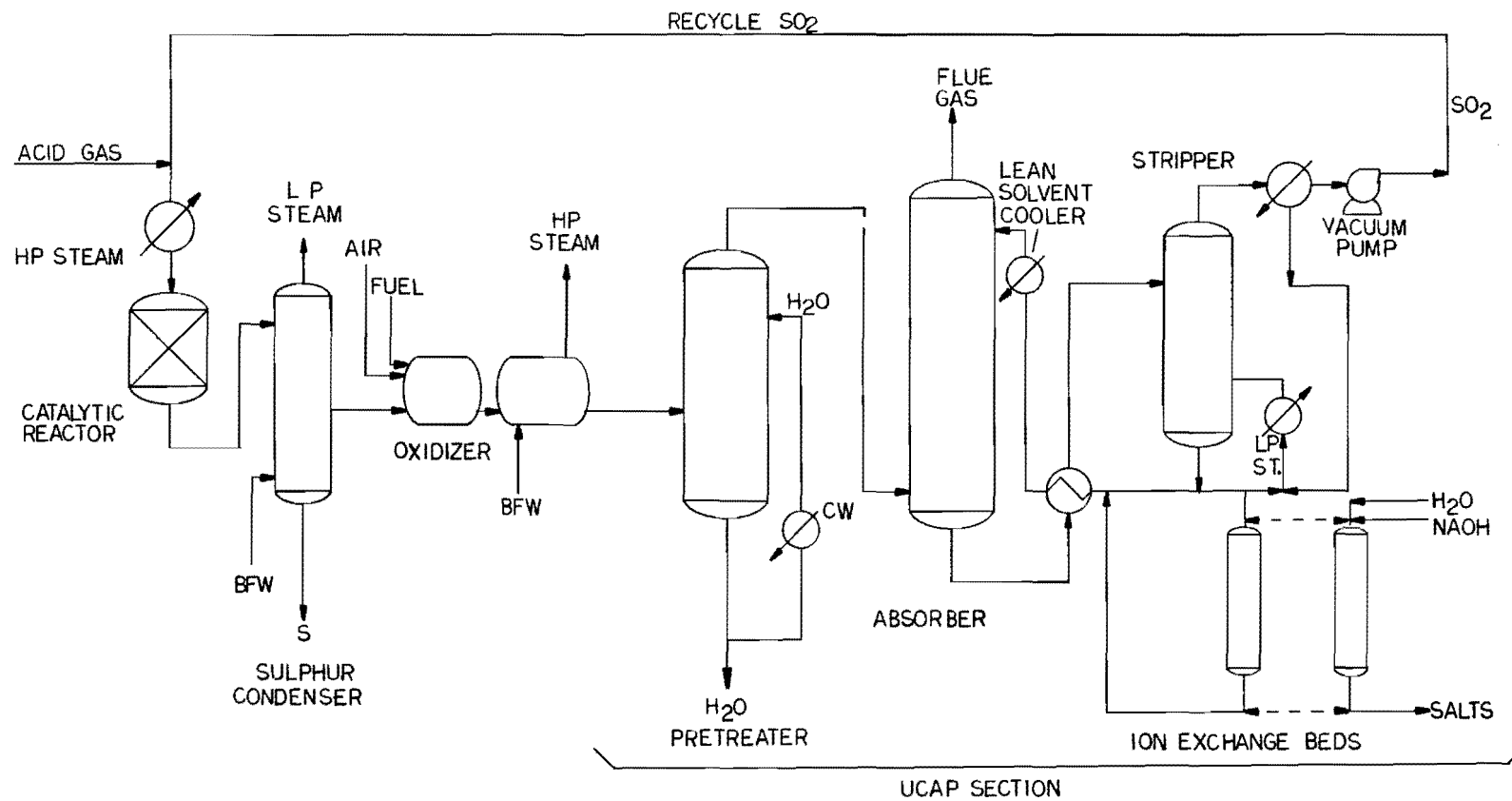


Figure 20. UCAP process.

5.4.10 Chiyoda Thoroughbred 121 Process (Chiyoda International Corp.)

5.4.10.1 Process description. The Chiyoda Thoroughbred 121 Process is a limestone based scrubbing process that produces gypsum as a byproduct. It is a more advanced and sophisticated version of the Chiyoda Thoroughbred 101 Process. Since it is used more often as a flue gas desulphurization operation, the reader is referred to Section 6.2.6 for a complete process description and discussion.

5.5 PROCESS ECONOMICS

The capital and operating costs for each process are shown in Table 4. Costs are developed from published information and expressed in mid 1982 Canadian dollars for a Fort McMurray location. These costs are based on a tail gas treatment plant that could process the tail gas from a 912 t/d modified Claus sulphur plant.

For some processes (noted in Table 4) minimal cost data is published. This minimal data has, however, allowed us to rank these processes in terms of cost. Reliable published cost data do not exist for several processes, namely: Townsend; CBA; MCRC; Lurgi Lucas; ATS; Chiyoda; and MCRC limestone slurry processes. Similarities exist between some of these processes and other costed processes. The Townsend Process is very similar to the IFP Clauspol 1500 Process and is expected to have similar costs. The CBA and MCRC subdewpoint processes are much like the Sulfreen Process and are also expected to have similar costs. The rest of these uncoded processes are sufficiently unique that they cannot be assumed as similar to another process in order to estimate costs.

In general, it can be noted that the Claus extension processes (Sulfreen, IFP Clauspol 1500) have the lowest capital cost as well as the lowest operating cost. This is to be expected as these processes are the simplest in concept and do not have the front end H_2S treatment section (hydrogenation/hydrolysis reactor or oxidizer). Operating costs are lower, most likely, because these processes do not burn gas in an oxidizer or reducing gas generator. Unlike some other types of processes, they do not use expensive chemicals.

Table 4. Tail gas treatment process costs.^a

Process	Installed Capital Costs	Annual Operating Costs
Sulfreen	12.0	0.9
IFP Clauspol 1500	15.0	0.9
SCOT	19.0	3.6
BSRP	19.0	3.6
BSR/Selectox ^b	12.0	2.3
Cleanair	19.0	3.6
Trentham Trencor-M	19.0	3.6
Wellman Lord	53.0	9.0
SNPA Haldor Topsoe ^b	36.0	6.0
Westvaco ^b	53.0	7.0
USBM Citrate	17.0	2.4
Aquaclaus	17.0	2.4
Integrated UCAP ^b	49.0	6.0

^a Costs in millions of mid 1982 Canadian dollars for a plant handling the tail gas from a 912 t/d Claus unit.

^b Denotes unreliable information. Shown for ranking purposes only.

The costs for the Integrated UCAP Process includes the one converter parent Claus plant. These costs were for a lean feed plant and are, therefore, used for ranking purposes only.

5.6 RETROFITTING

5.6.1 General Considerations

One of the most obvious problems with retrofitting a tail gas treatment plant concerns the requirements of space and plant location. The preferred location of the plant is as close to the Claus plant as possible. This location is preferred as it facilitates control of the plant, since the Claus plant operator would most likely operate the tail gas plant, as well as saving on piping costs. If the tail gas plant is located too far from the Claus plant, additional booster fans may also be needed. Line plugging would also be a problem as the sulphur in the gas would solidify in low, cool spots. Even with the use of steam tracing, this problem can occur. The plot area required for a tail gas treatment facility varies with the process selected and the size of the plant. For this report, an inlet of 1000 t/d sulphur with the bitumen has been defined. This corresponds to a tail gas treatment plant of approximately 36 t/d sulphur. The BSR/Selectox process appears to be of an average plot size when considering the number of columns, pumps, etc. The plot size required for a 36 t/d BSR/Selectox plant is approximately 11.6 to 14.5 m² (telephone conversation April 14, 1982 with M. Peterson, Union Oil Company of California).

The addition of a tail gas treatment unit would cause an increase in operating pressure in the Claus plant. This increase is normally in the range of 20 to 25 kPa. The furnace air blowers should be evaluated to ensure that they can handle the added pressure. The air blowers must also be able to deal with the increased flow capacity due to the tail gas unit's air requirements. Usually separate blowers are required. The liquid seal depth in the sulphur seal pots increases as a result of the higher Claus operating pressure. This increase can be as much as 1.52 m (corresponds to 25 kPa pressure drop).

5.6.2 Claus Extension Processes

The Claus Extension processes generally present no special problems for a retrofit. The CBA Process is the most difficult to retrofit as it is integrated into the Claus plant.

As a result of the low temperature operation of the processes, more fuel gas is needed for the downstream incinerator than for normal Claus offgas incineration.

5.6.3 Catalytic Hydrogenation/Hydrolysis Processes

Some of these processes (i.e. SCOT and Trencor-M) recycle H_2S back to the Claus plant. This recycle can increase the loading on the Claus plant by up to 10%. The concentration of H_2S and CO_2 in the recycle stream can have an effect on the Claus plant efficiency which in turn affects the efficiency of the tail gas treatment plant.

During retrofit, if the process has H_2S recycle, the Claus plant would have to be shut down longer than if the process was non-recycle. This is because some work would be necessary to modify the front end of the Claus plant to accept the recycle.

The incinerator fuel gas requirement for these processes is slightly higher than for standard offgas incineration.

5.6.4 Sulphur Dioxide Removal Processes

The processes involving SO_2 recycle (e.g. UCAP) cause less of a penalty in terms of the Claus plant loading because the volume of air which is fed to the Claus furnace may be reduced.

The effect on the Claus plant loading for each process is indicated in Table 5.

Sulphur dioxide removal processes have two incinerators that consume fuel gas. The first converts the sulphur compounds to SO_2 and the second reheats the clean tail gas so it can travel up the stack and create an acceptable plume. As a result, incinerator fuel gas consumption is nearly double that of a standard Claus tail gas incinerator.

5.7 START-UP AND SHUTDOWN

Start-up and shutdown of the tail gas treatment plant is basically controlled by the operation of the Claus plant. A planned shutdown should not cause a rise in the residual sulphur level in the tail gas. However, in practice, an emission violation is more the rule than the exception for refineries and oil sands plants since it is very difficult to match the turndown rate of the hydrocarbon processing units to that of the sulphur plant. In the event of an

Table 5. The effect of tail gas treatment processes on modified-Claus plant loading.

Process	Claus Loading Effect
IFP Clauspol 1500	no effect
Sulfreen	no effect
CBA	no effect
Townsend	no effect
SCOT	increase
BSRP	no effect
BST/Selectox	no effect
Trencor-M	increase
Cleanair	no effect
ATS	decrease
MCRC	no effect
Aquaclaus	decrease
USBM Citrate	decrease
Wellman-Lord	increase
Haldor-Topsoe	no effect
UCAP	increase
Westvaco	increase
Lurgi LUCAS	increase

emergency shutdown and subsequent bleeddown, sulphur laden gas will be flared.

The Sulfreen, CBA and MCRC processes can be started up at the same time as the Claus plant although, in practice, many are started up afterwards. The same precautions must be taken because the tail gas unit converters are the same as the Claus converters with the same type of catalyst considerations. The H_2S/SO_2 ratio is very important and must be carefully controlled in order to keep the recovery efficiency high.

For any of the other processes, the tail gas is initially bypassed around the tail gas treatment unit. The reason for this is that the TGT units would have trouble handling the gas from a Claus plant that is operating at a low recovery ($\sim 90\%$ during start-up). Another reason for bypassing is that it may take more men than are normally available to simultaneously start-up both the Claus plant and the tail gas unit. (Telephone conversation May 31, 1982 with John Sames, Western Research, Calgary).

5.8 APPLICABILITY OF TAIL GAS TREATMENT PROCESSES TO OIL SANDS PLANTS

Every process described in the Tail Gas Treatment Section is a technically feasible candidate for Claus tail gas treatment in an oil sands plant. There are, however, major differences between the processes in terms of overall sulphur recovery, operability and cost.

5.8.1 Claus Extension Processes

These processes are the easiest to operate and the least expensive in terms of both capital and operating costs. However, COS and CS_2 are not recovered. Since COS and CS_2 are likely to be present in the tail gas, the acceptability of one of these processes will be dependant upon the specified overall plant sulphur recovery. The technology is well proven for the Clauspol, Sulfreen and CBA Processes.

5.8.2 Catalytic Hydrogenation/Hydrolysis Processes

The ability to recover COS and CS_2 make these processes attractive for an oil sands plant application. They also are more expensive than the Claus extension processes.

The processes involving Stretford or Stretford type units might be too complex for an oil sands plant in terms of sulphur recovery versus operability problems. They have been proven technically and operated successfully throughout the world. However, the amine processes appear to be somewhat more desirable. The amine processes handle variations in Claus tail gas feed and composition very well (oil sands plant tail gas is expected to be highly variable), treats COS and CS₂ and have the characteristic that the amine regeneration facilities may be incorporated with the upstream amine plant regeneration unit. Alsands had proposed using one of these processes (the SCOT Process) in their oil sands plant application.

5.8.3 Sulphur Dioxide Removal Processes

Like the catalytic hydrogenation/hydrolysis processes described in the preceding section, the SO₂ removal processes recover COS and CS₂. In general, these processes are more complex than any of the other types of tail gas processes. Many of these processes are adaptations of flue-gas desulphurization processes such as the Chiyoda Thoroughbred 121 and Wellman-Lord Processes. While the technology has been proven, this group of processes is not as suitable for an oil sands plant tail gas clean-up application as are the catalytic hydrogenation/hydrolysis processes. Another important factor is the high cost of building and operating the SO₂ removal processes.

Some processes such as the ATS Process, Wellman-Lord Process, and the SNPA Haldor/Topsoe Process produce byproducts that could not be used by an oil sands plant. They would cause a disposal problem in the absence of a firm market for these byproducts.

6. FLUE GAS DESULPHURIZATION

6.1 INTRODUCTION

Flue gas desulphurization (FGD) processes that remove SO_2 from burner flue gases have become increasingly common in North American utility installations.

There are two areas of potential application in an oil sands plant. The first is on the CO boiler flue gas, the second is on the flue gas from a utility boiler burning residues from the primary upgrading process.

FGD processes in which the flue gas is cooled and saturated with the absorber product in liquid form are classified as "wet". Processes in which the flue gas is not saturated and which produce a dry product are classified as "dry". Within these classifications, processes that convert the flue gas SO_2 to an upgraded sulphur product (ie. sulphuric acid, elemental sulphur or more concentrated SO_2) and which reclaim the absorbent are classed as regenerable. Processes which combine the SO_2 with the absorbent to produce a product for disposal or sale are classed as nonregenerable (or throwaway).

Table 6 lists and classifies all processes described in this report. Table 7 details operational FGD installations at USA utilities. Tables 8 and 9 summarize planned FGD installations at utilities in the USA. Table 10 summarizes operational byproduct disposal practices in the USA. Table 11 illustrates the dominance of limestone and lime based systems (particularly the former) in both operational and planned USA applications. Figure 21 shows the growth of FGD capacity in the USA (with a projection to 1996).

As far as we have been able to ascertain (Memorandum 1981, letter dated March 10, 1982 from Environment Canada), there are no major FGD installations operating in Canada. The one installation at an advanced planning stage is a retrofit unit for two 500 MW coal fired boilers at an Ontario Hydro plant, most likely at Lambton (Ontario Hydro 1981). This would employ conventional limestone scrubbing with forced oxidation of the sludge to produce gypsum. The decision to produce gypsum was influenced by the environmental acceptability of the waste and the space required to store it. The possibility of byproduct sales was a minor consideration.

It should be noted that the situation in Ontario is quite different to that prevailing at FGD installations in the USA (or potentially in Alberta) in

Table 6. Flue gas desulphurization processes described in this report.

Process	Primary Reagent	Operational Mode	Regenerable	Form of Principal Waste Product	Development Status ^a	Upper Limit on SO ₂ in Flue Gas
Limestone	Limestone	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Lime	Lime	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Alkaline Flyash	Lime/Flyash	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Double Alkali	Soda Ash/Lime	Wet	No	H ₂ O/CaSO ₃ /CaSO ₄	I	No
Sodium Carbonate	Soda Ash	Wet	No	H ₂ O/Na ₂ SO ₃ /CaSO ₄	I	No
CT-121	Limestone	Wet	No	H ₂ O/CaSO ₄	I	No
Aqueous Ammonia	Ammonium Hydroxide	Wet	No	H ₂ O/NH ₄ HSO ₃ /(NH ₄) ₂ SO ₄	D/I	Yes
Wellman-Lord	Soda Ash	Wet	Yes	SO ₂	I	No
Magnesium Oxide	Magnesia	Wet	Yes	SO ₂	D	No
Citrate	Citric Acid	Wet	Yes	Sulphur	D	No
Dry Lime	Lime	Dry	No	CaO/CaSO ₃ /CaSO ₄ /Flyash	I	Yes
Copper Oxide	Copper Oxide	Dry	Yes	SO ₂	B	No
Melamine	Melamine	Wet	Yes	SO ₂	B	No

^a B = Benchscale; D = Demonstration unit; I = Industrial unit.

Table 7. Operational FGD installations at USA utilities (to June 1981).^a

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit		Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
				Rating MW					
Alabama Electric Tombigbee	2	Leroy, Alabama	9/78	179		Limestone	Peabody Process Systems	New	59.5
Alabama Electric Tombigbee	3	Leroy, Alabama	6/79	179		Limestone	Peabody Process Systems	New	59.5
Arizona Electric Power Apache	2	Cochise, Arizona	8/78	98		Limestone	Research-Cottrell	New	42.5
Arizona Electric Power Apache	3	Cochise, Arizona	6/79	98		Limestone	Research-Cottrell	New	42.5
Arizona Public Service Cholla	1	Joseph City, Arizona	10/73	119		Limestone	Research-Cottrell	Retrofit	58.5
Arizona Public Service Cholla	2	Joseph City, Arizona	4/78	264		Limestone	Research-Cottrell	New	75.0
Arizona Public Service Cholla	4	Joseph City, Arizona	3/81	126		Limestone	Research-Cottrell	New	95.0
Arizona Public Service Four Corners	1	Farmington, New Mexico	11/79	175		Lime/Alkaline Flyash	General Electric Environmental Service	Retrofit	80.0
Arizona Public Service Four Corners	2	Farmington, New Mexico	11/79	175		Lime/Alkaline Flyash	General Electric Environmental Service	Retrofit	80.0
Arizona Public Service Four Corners	3	Farmington, New Mexico	11/79	229		Lime/Alkaline Flyash	General Electric Environmental Service	Retrofit	80.0
Basin Electric Power Laramie River	1	Wheatland, Wyoming	7/80	570		Limestone	Research-Cottrell	New	90.0

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit Rating MW	Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
Big Rivers Electric Green	1	Sebree, Kentucky	11/80	242	Lime	American Air Filter	New	90.0
Big Rivers Electric Green	2	Sebree, Kentucky	11/80	242	Lime	American Air Filter	New	90.0
Central Illinois Light Duck Creek	1	Canton, Illinois	7/76	416	Limestone	Environeering, Riley Stoker	New	85.0
Central Illinois Public Service, Newton	1	Newton, Illinois	9/79	617	Dual Alkali	General Electric Environmental Service	New	90.0
Cincinnati Gas & Elect. East Bend	2	Rabbithas, Kentucky	3/81	650	Lime	Babcock & Wilcox	New	87.0
Colorado UTE Electric Craig	1	Craig, Colorado	10/80	410	Limestone	Peabody Process Systems	New	85.0
Colorado UTE Electric Craig	2	Craig, Colorado	12/79	410	Limestone	Peabody Process Systems	New	85.0
Columbus & Southern Ohio Elect. Conesville	5	Coneville, Ohio	1/77	411	Lime	Air Correction Division, UOP	New	89.5
Columbus & Southern Ohio Elect. Conesville	6	Coneville, Ohio	6/78	411	Lime	Air Correction Division, UOP	New	89.3
Commonwealth Edison Powerrton	31	Pekin, Illinois	4/80	430	Limestone	Air Correction Division, UOP	Retrofit	75.5
Cooperative Power Assoc. Coal Creek	1	Underwood, North Dakota	7/79	327	Lime/Alkaline Flyash	Combustion Engineering	New	54.0

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit		Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
				Rating	MW				
Cooperative Power Assoc. Coal Creek	2	Underwood, North Dakota	7/80	327	Lime/Alkaline Flyash	Combustion Engineering	New		54.0
Delmarva Power & Light Delaware City	1	Delaware City, Delaware	5/80	60	Wellman-Lord	Davy McKee	Retrofit		90.0
Delmarva Power & Light Delaware City	2	Delaware City, Delaware	5/80	60	Wellman-Lord	Davy McKee	Retrofit		90.0
Delmarva Power & Light Delaware City	3	Delaware City, Delaware	5/80	60	Wellman-Lord	Davy McKee	Retrofit		90.0
Duquesne Light Elrama	1 - 4	Elrama, Pennsylvania	10/75	310	Lime	General Electric Environmental Service	Retrofit		83.0
Duquesne Light Phillips	1 - 6	South Height, Pennsylvania	7/73	408	Lime	General Electric Environmental Service	Retrofit		83.0
Indianapolis Power & Light, Petersburg	3	Petersburg, Indiana	12/77	532	Limestone	Air Correction Division, UOP	New		85.0
Kansas City Power & Light, Hawthorn	3	Kansas City, Missouri	11/72	90	Lime	Combustion Engineering	Retrofit		790.0
Kansas City Power & Light, Hawthorn	4	Kansas City, Missouri	8/72	90	Lime	Combustion Engineering	Retrofit		70.0
Kansas City Power & Light, La Cygne	1	La Cygne, Kansas	2/73	820	Limestone	Babcock & Wilcox	New		80.0
Kansas City Power & Light, Jeffery	1	Wamego, Kansas	8/78	540	Limestone	Combustion Engineering	New		60.0

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit		Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
				Rating	MW				
Kansas City Power & Light, Jeffrey	2	Wamego, Kansas	1/80	490	Limestone	Combustion Engineering	New		60.0
Kansas City Power & Light, Lawrence	4	Lawrence, Kansas	1/77	125	Limestone	Combustion Engineering	Retrofit		73.0
Kansas City Power & Light, Lawrence	5	Lawrence, Kansas	4/78	420	Limestone	Combustion Engineering	Retrofit		52.0
Kentucky Utilities Green River	1 - 3	Central City, Kentucky	9/75	64	Lime	American Air Filter	Retrofit		80.0
Louisville Gas & Elect. Cane Run	4	Louisville, Kentucky	8/76	188	Lime	American Air Filter	Retrofit		85.0
Louisville Gas & Elect. Cane Run	5	Louisville, Kentucky	12/77	200	Lime	American Air Filter	Retrofit		85.0
Louisville Gas & Elect. Cane Run	6	Louisville, Kentucky	4/79	299	Dual Alkali	Thyssen/CEA	Retrofit		95.0
Louisville Gas & Elect. Mill Creek	1	Louisville, Kentucky	12/80	358	Limestone	Combustion Engineering	Retrofit		85.0
Louisville Gas & Elect. Mill Creek	3	Louisville, Kentucky	8/73	427	Lime	American Air Filter	New		85.0
Louisville Gas & Elect. Paody's Run	6	Louisville, Kentucky	4/73	72	Lime	Combustion Engineering	Retrofit		90.0
Minnesota Power & Light, Clay Boswell	4	Cohasset, Minnesota	4/80	475	Lime/Alkaline Flyash	Peabody Process Systems	New		84.3

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit Rating MW	Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
Minakota Power Milton R. Young	2	Center, North Dakota	9/77	135	Lime/Alkaline Flyash	Thyssen/CEA	New	36.1
Monongahela Power Pleasants	1	Willow Island, West Virginia	3/79	618	Lime	Babcock & Wilcox	New	90.0
Monogahela Power Pleasants	2	Willow Island, West Virginia	10/80	618	Lime	Babcock & Wilcox	New	90.0
Montana Power Colstrip	1	Solstrip, Montana	9/75	360	Lime/Alkaline Flyash	Thyssen/CEA	New	60.0
Montana Power Colstrip	2	Solstrip, Montana	5/76	360	Lime/Alkaline Flyash	Thyssen/CEA	New	60.0
Montana-Dakota Util. Coyote	1	Beulah, North Dakota	4/81	440	Sodium Carbonate/ Spray Drying	Wheelabrator- Prye/R.I.	New	70.0
Nevada Power Reid Gardner	1	Moapa, Nevada	3/74	125	Sodium Carbonate	Thyssen/CEA	Retrofit	90.0
Nevada Power Reid Gardner	2	Moapa, Nevada	4/74	125	Sodium Carbonate	Thyssen/CEA	Retrofit	90.0
Nevada Power Reid Gardner	3	Moapa, Nevada	6/76	125	Sodium Carbonate	Thyssen/CEA	New	85.0
Northern Indiana Public Service, Dean H. Mitchell	11	Gary, Indiana	7/76	115	Wellman-Lord	Davy McKee	Retrofit	90.0
Northern States Power Riverside	6 - 7	Minneapolis, Minnesota	11/80	110	Lime/Spray Drying	Joy MFG/Niro Atomizer	Retrofit	90.0

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit Rating MW	Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
Northern States Power Sherburne	1	Becker, Minnesota	3/76	740	Limestone/Alkaline Flyash	Combustion Engineering	New	50.0
Northern States Power Sherburne	2	Becker, Minnesota	3/77	740	Limestone/Alkaline Flyash	Combustion Engineering	New	50.0
Pacific Power & Light Jim Bridger	4	Rocksprings, Wyoming	9/79	550	Sodium Carbonate	Air Correction Division, UOP	New	91.0
Pennsylvania Power Bruce Mansfield	1	Shippingbort, Pennsylvania	12/75	917	Lime	General Electric Environmental Service	New	92.1
Pennsylvania Power Bruce Mansfield	2	Shippingbort, Pennsylvania	7/77	917	Lime	General Electric Environmental Service	New	92.1
Pennsylvania Power Bruce Mansfield	3	Shippingbort, Pennsylvania	6/80	917	Lime	Pullman Kellogg	New	92.2
Public Service of New Mexico, San Juan	1	Waterflow, New Mexico	4/78	361	Wellman-Lord	Davy McKee	Retrofit	90.0
Public Service of New Mexico, San Juan	2	Waterflow, New Mexico	8/78	350	Wellman-Lord	Davy McKee	Retrofit	90.0
Public Service of New Mexico, San Juan	3	Waterflow, New Mexico	12/79	534	Wellman-Lord	Davy McKee	New	90.0
Salt River Project Coronado	1	St. Johns, Arizona	11/79	280	Limestone	Pullman Kellogg	New	66.0
Salt River Project Coronado	2	St. Johns, Arizona	7/80	280	Limestone	Pullman Kellogg	New	66.0

Continued...

Table 7. Continued.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit		Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
				Rating	MW				
Sikeston BRD of Mun. Util., Sikeston	1	Sikeston, Missouri	6/81	235	Limestone	Babcock & Wilcox	New	80.0	
South Carolina Public Service, Winyah	2	Georgetown, South Carolina	7/77	140	Limestone	Babcock & Wilcox	New	45.0	
South Carolina Public Service, Winyah	3	Georgetown, South Carolina	5/80	280	Limestone	Babcock & Wilcox	New	90.0	
South Mississippi Elec. Power, R.D. Morrow Sr.	1	Hattiesburg, Mississippi	8/78	124	Limestone	Envroneering Riley Stoker	New	52.7	
South Mississippi Elec. Power, R.D. Morrow Sr.	2	Hattiesburg, Mississippi	6/79	124	Limestone	Envroneering Riley Stoker	New	52.7	
Southern Illinois Power Marion	4	Marion, Illinois	5/79	173	Limestone	Babcock & Wilcox	New	89.4	
Southern Indiana Gas & Elec., A.B. Brown	1	West Franklin, Indiana	3/79	265	Dual Alkali	FMC	New	85.0	
Springfield City Util. Southwest	1	Springfield, Missouri	4/77	194	Limestone	Air Correction Division, UOP	New	80.0	
Springfield Water, Light & Power, Oallman	3	Springfield, Illinois	12/80	185	Limestone	Research - Cottre	New	95.0	
St. Joe Zinc G.F. Weaton	1	Monaca, Pennsylvania	11/79	60	Citrate	Morrison * Knugsen/ U.S.B.M.	Retrofit	90.0	
Tennessee Valley Auth. Shawnee	10A	Paoucah, Kentucky	4/72	10	Lime/ Limestone	Air Correction Division, UOP	Retrofit	90.0	

Continued...

Table 7. Concluded.

Company Name/ Unit Name	Unit No.	Location	Start-up Date	Nominal Unit Rating MW	Process	Vendor	New or Retrofit	SO ₂ Design Removal Efficiency(%)
Tennessee Valley Auth. Shawnee	10B	Paoucah, Kentucky	4/72	10	Lime/ Limestone	General Electric Environment Service	Retrofit	90.0
Tennessee Valley Auth. Widows Creek	7	Bridgeport, Alabama	3/81	575	Limestone	Combustion Engineering	Retrofit	80.0
Tennessee Valley Auth. Widows Creek	8	Bridgeport, Alabama	3/77	550	Limestone	Tennessee Valley Authority	Retrofit	70.0
Texas Power & Light Sandow	4	Rockdale, Texas	12/80	382	Limestone	Combustion Engineering	New	75.0
Texas Utilities Martin Lake	1	Tatum, Texas	4/77	595	Limestone	Research-Cottrell	New	71.0
Texas Utilities Martin Lake	2	Tatum, Texas	5/78	595	Limestone	Research-Cottrell	New	71.0
Texas Utilities Martin Lake	3	Tatum, Texas	2/79	595	Limestone	Research-Cottrell	New	71.0
Texas Utilities Monticello	3	Mt. Pleasant, Texas	5/78	800	Limestone	General Electric Environmental Service	New	74.0
Utah Power & Light Hunter	1	Castle Dale, Utah	3/79	360	Lime	General Electric Environmental Service	New	80.0
Utah Power & Light Hunter	2	Castle Dale, Utah	6/80	360	Lime	General Electric Environmental Service	New	80.0
Utah Power & Light Hunter	1	Price, Utah	5/78	366	Lime	General Electric Environmental Service	New	80.0

Adapted from original tables in PEDCO (1981).

Table 8. Summary of FGD systems under construction in the USA (in June 1981).^a

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
Associated Electric Thomas Hill	3	New	670.	Limestone Pullman Kellogg	1/82
Basin Electric Power Antelope Valley	1	New	440.	Lime/Spray Drying Joy Mfg/Niro Atomizer	4/83
Basin Electric Power Laramie River	2	New	570.	Limestone Research-Cottrell	7/81
Basin Electric Power Laramie River	3	New	570.	Lime/Spray Drying Babcock & Wilcox	6/83
Big Rivers Electric D.G. Wilson	1	New	440.	Limestone Pullman Kellogg	7/84
Colorado Ute Electric Craig	3	New	447.	Lime/Spray Drying Babcock & Wilcox	4/83
Deseret Gen. & Trans. Moon Lake	1	New	410.	Limestone Combustion Engineering	9/84
East Kentucky Power Spurlock	2	New	500.	Lime Thyssen/CEA	0/82
Grand Haven Brd of Light & Power, J.S. Sims	3	New	65.	Lime Babcock & Wilcox	6/83
Hooster Energy Meron	1	New	441.	Limestone Mitsubishi Heavy Ind.	5/82
Hooster Energy Meron	2	New	441.	Limestone Mitsubishi Heavy Ind.	9/81
Houston Lighting & Power W.A. Parish	8	New	492.	Limestone General Elec. Environ. Serv.	11/82

Continued...

Table 8. Continued.

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
Indianapolis Power & Light Petersburg	4	New	530.	Limestone Research-Cottrell	10/84
Lakeland Utilities McIntosh	3	New	364.	Limestone Babcock & Wilcox	10/81
Louisville Gas & Electric Mill Creek	2	Retrofit	350.	Lime Combustion Engineering	12/81
Louisville Gas & Electric Mill Creek	4	New	495.	Lime Combustion Engineering	6/82
Morquette Brd of Light & Power Shiras	3	New	44.	Lime/Spray Drying General Elec. Environ. Serv.	10/82
Michigan SO Central FWR Agen. Project	1	New	55.	Limestone Babcock & Wilcox	6/82
Montana Power Colstrip	3	New	700.	Lime/Alkaline Flyash Thyssen/CEA	10/83
Montana Power Colstrip	4	New	700.	Lime/Alkaline Flyash Thyssen/CEA	0/84
Muscatine Power & Water Muscatine	9	New	166.	Limestone Research-Cottrell	9/82
Niagara Mohawk Power Charles R. Huntley	66	Retrofit	100.	Aqueous Carbonate/Spray Drying Rockwell International	4/82
Northern Indiana Pub. Service Schaffer	27	New	421.	Dual Alkaline FMC	6/83
Pacific Power & Light JIM Bridger	2A	Retrofit	100.	Lime/Sodium Carbonate Flakt	1/82

Continued...

Table 8. Continued.

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
Philadelphia Electric Cromby	1	Retrofit	150.	Magnesium Oxide United Engineering	5/83
Philadelphia Electric Eddystone	1	Retrofit	240.	Magnesium Oxide United Engineers	12/82
Philadelphia Electric Eddystone	2	Retrofit	334.	Magnesium Oxide United Engineers	12/82
Public Service Indiana Gibson	5	New	650.	Limestone Pullman Kellogg	0/82
Public Service of New Mexico San Juan	4	New	534.	Wellman-Lord Davy McKee	6/82
San Miguel Electric San Miguel	1	New	400.	Limestone Babcock & Wilcox	5/81
South Carolina Public Service Cross	2	New	500.	Limestone Peabody Process Systems	1/84
South Carolina Public Service Wynch	4	New	280.	Limestone American Air Filter	7/81
Tennessee Valley Authority Paradise	1	Retrofit	704.	Limestone General Elec. Environ. Serv.	3/82
Tennessee Valley Authority Paradise	1	Retrofit	704.	Limestone General. Elec. Environ. Serv.	6/82
Texas Municipal Power Agency Gibsons Creek	1	New	400.	Limestone Combustion Engineering	1/82
United Power Association Stanton	1A	New	50.	Lime/Spray Drying Research-Cottrell	6/82

Continued...

Table 8. Concluded.

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
Utah Power & Light Hunter	3	New	400.	Limestone General Elec. Environ. Serv.	6/83
Utah Power & Light Hunter	4	New	400.	Limestone General Elec. Environ. Serv.	6/85
Utah Power & Light Naughton	3	Retrofit	330.	Sodium Carbonate Air Correction Div. UOP	8/81
West Penn Power Mitchell	33	Retrofit	300.	Lime General Elec. Environ. Serv.	3/82
TOTAL			15887.		

^a Source: Pedco (1981)

Table 9. Summary of contract awarded FGD systems in the USA (at June 1981).^a

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
Arizona Public Service Four Corners	4	Retrofit	755.	Lime United Engineers	0/82
Arizona Public Service Four Corners	5	Retrofit	755.	Lime United Engineers	0/82
Basin Electric Power Antelope Valley	2	New	440.	Lime/Spray Drying Joy Mfg/Niro Atomizer	10/85
Big Rivers Electric D.B. Wilson	2	New	440.	Limestone Pullman Kellogg	1/86
Houston Lighting & Power Limestone	1	New	750.	Limestone Combustion Engineering	12/87
Houston Lighting & Power Limestone	2	New	750.	Limestone Combustion Engineering	12/87
Northern Indiana Public Service Schahfer	1B	New	421.	Dual Alkali FMC	6/85
Plains Electric G & T Plains Escalante	1	New	233.	Limestone Combustion Engineering	12/83
Platte River Power Authority Rawhide	1	New	279.	Lime/Spray Drying Joy Mfg/Niro Atomizer	12/83
Seminole Electric Seminole	1	New	620.	Limestone Peabody Process Systems	3/83
Seminole Electric Seminole	2	New	620.	Limestone Peabody Process Systems	1/85

Continued...

Table 9. Concluded.

Company Name/ Unit Name	Unit No.	New or Retrofit	Capacity MW	Process/ System Supplier	Start-up Date
South Carolina Public Service Cross	1	New	500.	Limestone Peabody Process Systems	5/88
Southwestern Electric Power Dolet Hills	1	New	720.	Limestone Air Correction Div. UOP	3/86
Southwestern Electric Power Henry W. Pirkey	1	New	720.	Limestone Air Correction Div. UOP	12/84
Sunflower Electric Holcomb	1	New	347.	Lime/Spray Drying Joy Mfg/Niro Atomizer	9/83
Tampa Electric Big Bend	4	New	475.	Lime/Limestone Research-Cottrell	3/85
Texas Power & Light Twin Oaks	1	New	750.	Limestone General Elec. Environ. Serv.	5/86
Texas Power & Light Twin Oaks	2	New	750.	Limestone General Elec. Environ. Serv.	8/88
Texas Utilities Martin Lake	4	New	750.	Limestone Research-Cottrell	0/87
Tucson Electric Power Springerville	1	New	370.	Lime/Spray Drying Joy Mfg/Niro Atomizer	2/85
Tucson Electric Power Springerville	2	New	370.	Lime/Spray Drying Joy Mfg/Niro Atomizer	3/87
TOTAL			11815.		

^a Source: Pedco (1981)

Table 10. Summary of end-product disposal practices for operational FGD systems^a.

Process/ Unit Name	Unit No.	Throwaway	Byproduct Type	Disposition
<u>Citrate</u>				
G.F. Weaton	1		Elemental Sulphur	
<u>Dual Alkali</u>				
A.B. Brown	1	Landfill		
Newton	1	Landfill		
Cane Run	6	Landfill		
<u>Lime</u>				
Conesville	5	Landfill		
Conesville	6	Landfill		
Cane Run	4	Landfill		
Green	1	Landfill		
Green	2	Landfill		
Green River	1 - 5	Pond		
Mill Creek	3	Pond	None	
East Bend	2	Landfill		
Pleasants	1	Pond	None	
Pleasants	2	Pond	None	
Cane Run	5	Landfill		
Hawthorn	3	Pond		
Hawthorn	4	Pond		
Paddy's Run	6	Pond		
Bruce Mansfield	1	Pond		
Bruce Mansfield	2	Pond		
Elrama	1 - 4	Landfill		
Hunter	1	Landfill		
Hunter	2	Landfill		
Huntington	1	Landfill		

Continued...

Table 10. Continued.

Process/ Unit Name	Unit No.	Throwaway	Byproduct	
			Type	Disposition
Phillips	1 - 6	Landfill		
Bruce Mansfield	3	Landfill		
<u>Limestone</u>				
Petersburg	3	Landfill		
Powerton	51	Pond		
Southwest	1	Landfill		
La Cygne	1	Pond		
Marion	4	Landfill		
Sikeston	1	Pond		
Winyah	2	Pond		
Winyah	3	Pond		
Jeffrey	1	Pond		
Jeffrey	2	Pond		
Lawrence	4	Pond		
Lawrence	5	Pond		
Mill Creek	1	Landfill	None	
Sadow	4	Pond		
Widows Creek	7	Pond		
Duck Creek	1	Pond		
R.D. Morrow, Sr.	1	Landfill		
R.D. Morrow, Sr.	2	Landfill		
Monticello	3	Landfill		
Craig	1	Pond		
Craig	2	Pond		
Tombigbee	2	Pond		
Tombigbee	3	Pond		
Coronado	1	Pond		

Continued...

Table 10. Continued.

Process/ Unit Name	Unit No.	Throwaway	Byproduct	
			Type	Disposition
Coronado	2	Pond		
Apache	2	Pond		
Apache	3	Pond		
Cholla	1	Pond		
Cholla	2	Pond		
Cholla	4	Pond		
Dallman	3	Landfill	None	
Laramie River	1	Landfill		
Martin Lake	1	Landfill		
Martin Lake	2	Landfill		
Martin Lake	3	Landfill		
Widows Creek	8	Pond		
<u>Limestone/Alkaline Flyash</u>				
Sherburne	1	Pond		
Bherburne	2	Pond		
<u>Lime/Alkaline Flyash</u>				
Coal Creek	1	Pond		
Coal Creek	2	Pond		
Four Corners	1			
Four Corners	2			
Four Corners	3			
Clay Boswell	4	Pond		
Colstrip	1	Pond		
Colstrip	2	Pond		
Milton R. Young	2	Landfill		

Continued...

Table 10. Concluded.

Process/ Unit Name	Unit No.	Throwaway	Byproduct	
			Type	Disposition
<u>Lime/Limestone</u>				
Shawnee	10A	Landfill		
Shawnee	10B	Landfill		
<u>Lime/Spray Drying</u>				
Riverside	6 - 7	Landfill		
<u>Sodium Carbonate</u>				
Jim Bridger	4	Pond		
Reid Gardner	1	Pond		
Reid Gardner	2	Pond		
Reid Gardner	3	Pond		
<u>Sodium Carbonate/Spray Drying</u>				
Coyote	1	Landfill		
<u>Wellman-Lord</u>				
Dean. H. Mitchell	11		Elemental Sulphur	
Delaware City	1	Pond	Sulphuric Acid	Marketed
Delaware City	2	Pond	Sulphuric Acid	Marketed
Delaware City	3	Pond	Sulphuric Acid	Marketed
San Juan	1		Elemental Sulphur	Marketed
San Juan	2		Elemental Sulphur	Marketed
San Juan	3		Sulphuric Acid	Marketed

^a Adapted from original table in Pedco (1981)

Table 11. Summary of FGD systems by process^a.

		Percent of total MW	
		June	December
		1981	1999
<u>Throwaway product process</u>			
Wet systems			
Lime		38.5	21.3
Limestone		47.6	36.1
Dual alkali		3.9	1.9
Sodium carbonate		3.0	3.0
NA ^b		-	5.2
Dry systems			
Lime		0.4	3.3
Lime/Sodium carbonate		-	0.1
Sodium carbonate		1.4	0.4
<u>Salable product process</u>			
Process	Byproduct		
Aqueous carbonate/ spray drying	Elemental sulphur	-	0.1
Citrate	Elemental sulphur	0.2	0.1
Lime	Gypsum	-	0.1
Limestone	Gypsum	-	0.2
Lime/Limestone	Gypsum	-	0.5
Magnesium oxide	Sulphuric Acid	-	0.7
Wellman Lord	Sulphuric Acid	2.3	1.2
Wellman Lord	Elemental Sulphur	2.7	0.8
<u>Process undecided</u>		-	25.0
Total		100.0	100.0

^a Source: Pedco (1981).

^b NA - Not available (these systems are committed to a throwaway product process; however, the actual process is unknown at this time).

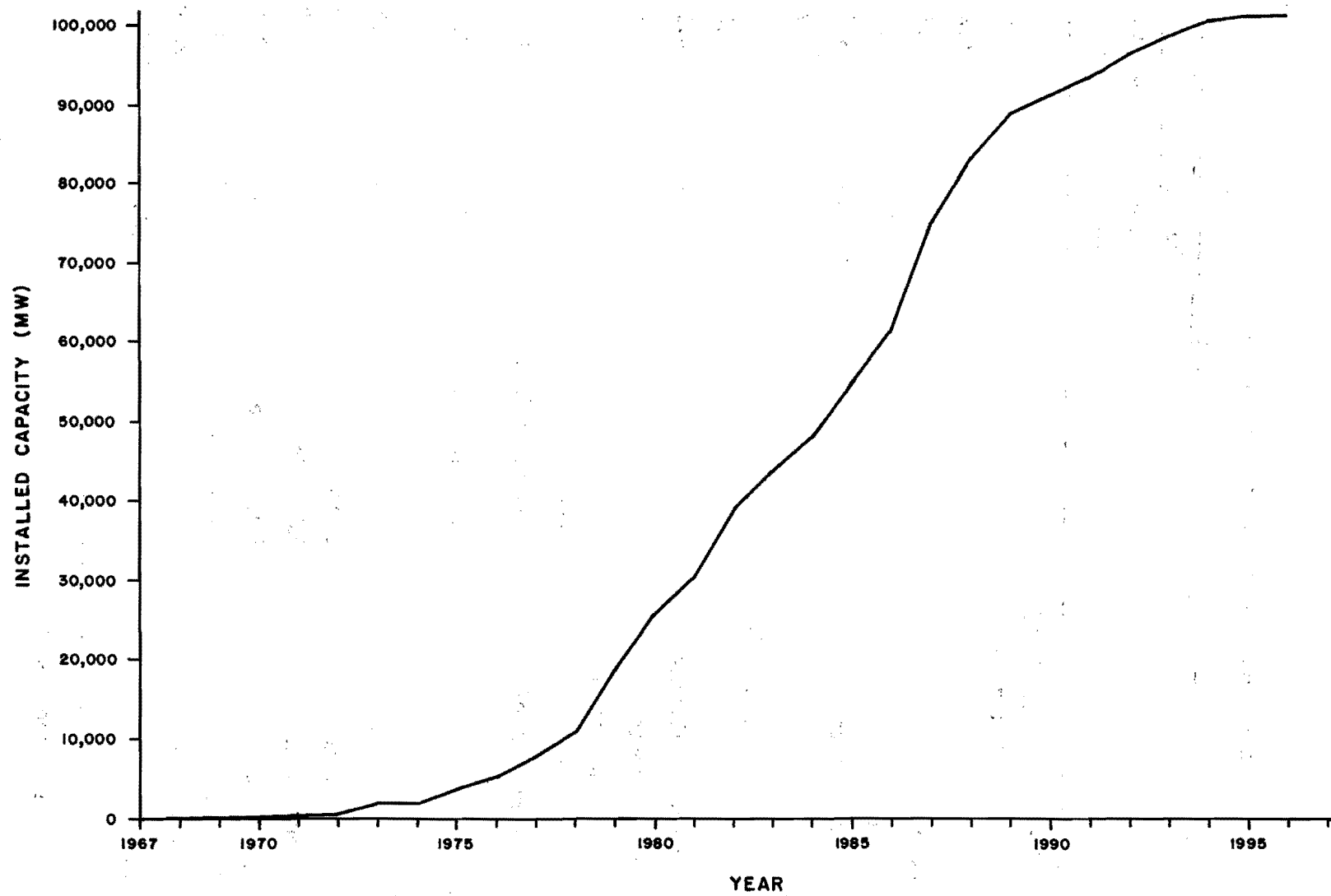


Figure 21. Growth of FGD capacity in the USA.

that the Ontario coal fired units are used for peak load only rather than base load power production. Based on power generation forecasts, which show a commitment to nuclear and hydro-electric installations this difference is likely to remain.

Ontario Hydro's SO_2 and NO_x emissions in 1982 will be about 600 000 t. By 1986 these will be reduced to less than 300 000 t. During this period electricity generation will increase by 40%. Most of the emission reduction will result from new nuclear units replacing coal. The scrubbers will contribute a 74 000 t/a reduction in SO_2 .

There is a small aqueous ammonia FGD unit installed at the Cominco smelter in Trail, British Columbia.

Apart from the USA, the other major concentration of FGD installations is in Japan. Although Western Europe, particularly West Germany, has a number of isolated FGD installations, the practice of most utilities, typified by the CEGB in Great Britain, is to rely on tall stacks for the dispersion of SO_2 . There is no European initiative to tackle the overall problem of SO_2 emissions (Anon 1979a).

6.2 FLUE GAS DESULPHURIZATION PROCESSES

6.2.1 Limestone FGD Process

6.2.1.1 Process description. The process (Figure 22) employs a limestone slurry to absorb SO_2 . The flue gas that has already passed through an electrostatic precipitator to remove fly ash is fed to the FGD system. In a retrofit booster fans will normally be required. On new units the main boiler ID fan may be sized to overcome the FGD system pressure drop. The gas enters the first, quencher section of the absorber near the base and spirals upwards. It is quenched to its saturation temperature by slurry sprays. The quencher provides further fly ash removal to augment the electrostatic precipitators and in particular to protect the rest of the absorber from fly ash excursions.

The partially cleaned gas then passes upwards through a liquid/gas separator that straightens the flow from a helical to a vertical pattern. The gas is counter-currently sprayed by further levels of sprays in the second stage of the SO_2 absorption process. The slurry from these upper sprays is prevented

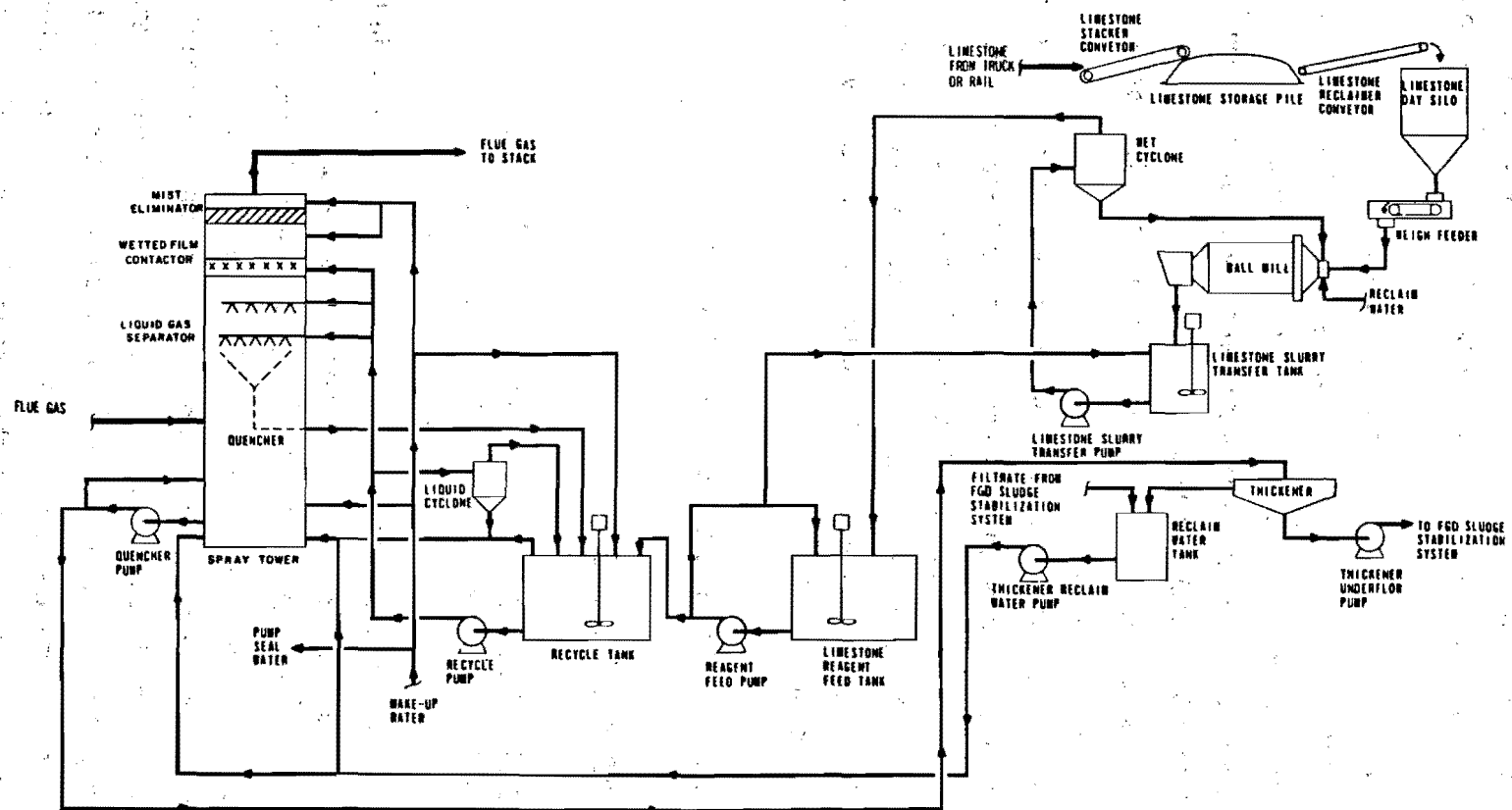


Figure 22. Limestone FGD process.

from entering the quencher section by the liquid gas separator, thus permitting independent operation of the two slurry circuits.

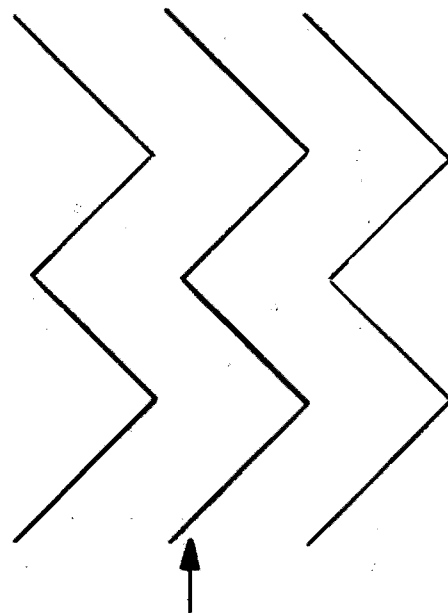
The gas now passes up through further sprays or through the wetted film contactor in the third and final stage of SO_2 absorption. The wetted film contactor (specific to Research Cottrell) provides liquid/gas interfacial area and allows both a high normal liquid gas ratio and a high turndown ratio. The contactor also enhances the performance of the mist eliminators by minimizing fine droplet formation and distributing the gas evenly across the tower area.

The cleaned gas then passes through a two stage mist elimination system. These are, typically, Chevron or open louvre devices (Figure 23). The mist eliminators have to be flushed regularly with clean water to prevent blockage. The most efficient method of cleaning is to use short bursts of high velocity water. To avoid problems of continually varying slurry concentration in the rest of the absorber, the mist eliminators are divided into segments which are sequentially washed. The water flow to an individual segment can not exceed the total water make up requirement for the unit. Washing is concentrated on the undersides of the mist eliminators which are more prone to blockage than the tops.

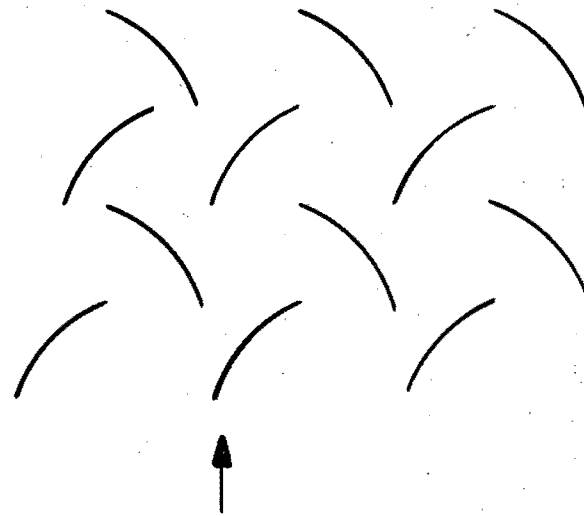
The cleaned gas still contains sufficient SO_2 and SO_3 to be extremely corrosive at its dew point. This together with other considerations (e.g., plume buoyancy) frequently require that the gas be reheated before passing to atmosphere via a stack.

Limestone delivery to any oil sands plant will be by truck since there are no rail facilities beyond Fort McMurray. The limestone is dumped into hoppers which feed conveyors that transfer it to a sheltered storage pile. The pile should be sufficient for one month's operation. Sheltered storage is necessary to protect the limestone from rain and snow. From the storage pile the limestone is conveyed to feed silos (one day's capacity). The feed silos supply weigh feeders which deliver limestone to the ball mills. The mills prepare the slurry, normally using reclaim water from the downstream sludge thickening process. The slurry is fed to a hydrocyclone which recycles oversize back to the mill before passing to the limestone feed tanks (one shift's capacity).

From the feed tanks the slurry is fed to the recycle tanks. The transfer rate is controlled by either the mass of SO_2 fed to the system



GAS FLOW
CHEVRON DESIGN



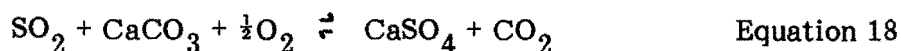
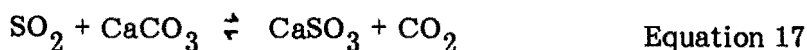
GAS FLOW
OPEN LOUVRE DESIGN

Figure 23. Mist eliminators.

(determined by combining the signals from an SO₂ analyzer on the flue gas inlet and a flow meter on the absorber gas outlet) or by slurry pH. The recirculating slurry in the upper zone can be passed through a hydrocyclone to reject oversize particles to the quencher section thus reducing the chance of nozzle blockage.

From the recycle tank the slurry is circulated to the spray section and wetted film contactor of the absorber. The recycle tank overflows to the quencher sump. The slurry in the sump is circulated to the quencher sprays. The slurry density increases as reaction products are formed. Make up water has to be added to the sump to maintain a reasonably mobile slurry. The make up water also helps to reduce erosion, and increases SO₂ absorption in the quench. The sump is purged to a thickener. The sump purge and water make up are controlled by density and level, respectively. As density increases, the purge valve opens causing the level to fall. This fall brings in make up water which reduces the density shutting off the purge. The purged slurry will normally contain 0.10 to 0.15 mass fraction solids. The thickener underflow will contain up to 0.35 mass fraction solids. The overflow is recycled to the FGD process.

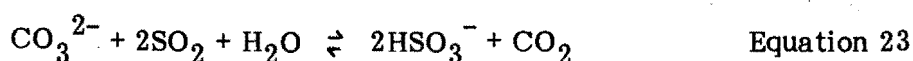
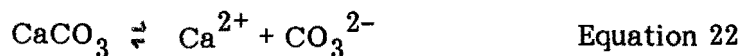
6.2.1.2 Principal chemical reactions. The overall removal of SO₂ can be represented by the simple equations:



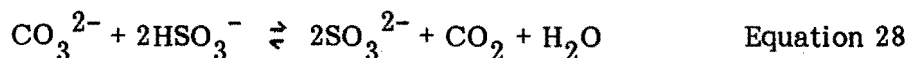
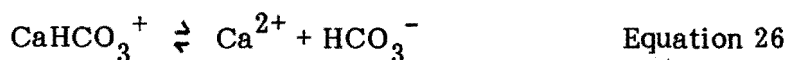
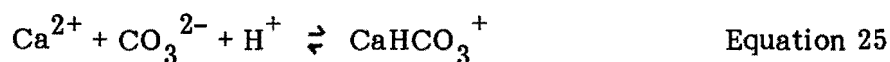
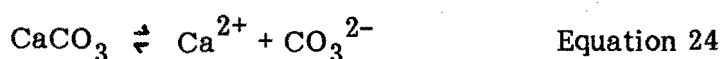
In practice as might be expected, the situation is considerably more complex. The removal process can, however, be broadly split between the physical absorption of SO₂ by water in the absorber and the chemical reaction between this dissolved SO₂ and limestone in the recycle tank. The key reactions are detailed below:

Absorber Reactions:





Recycle Tank Reactions:



The insoluble waste calcium products are actually hydrated as $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

6.2.1.3 Sludge stabilization. The sludge stabilization system described below would be used for any of the lime based systems producing a calcium sulphite/sulphate sludge (i.e., Limestone, Lime or Double Alkali Processes).

The scheme described in this section (Figure 24) produces a stabilized sludge suitable for disposal in a landfill site (e.g., the mined out area of an oil sand facility). It is possible to simply take the thickener sludge and dispose of it in lined or unlined ponds. Since this approach is clearly far from the best available technology, we have assumed that a sludge stabilization facility would be included at any oil sands plant.

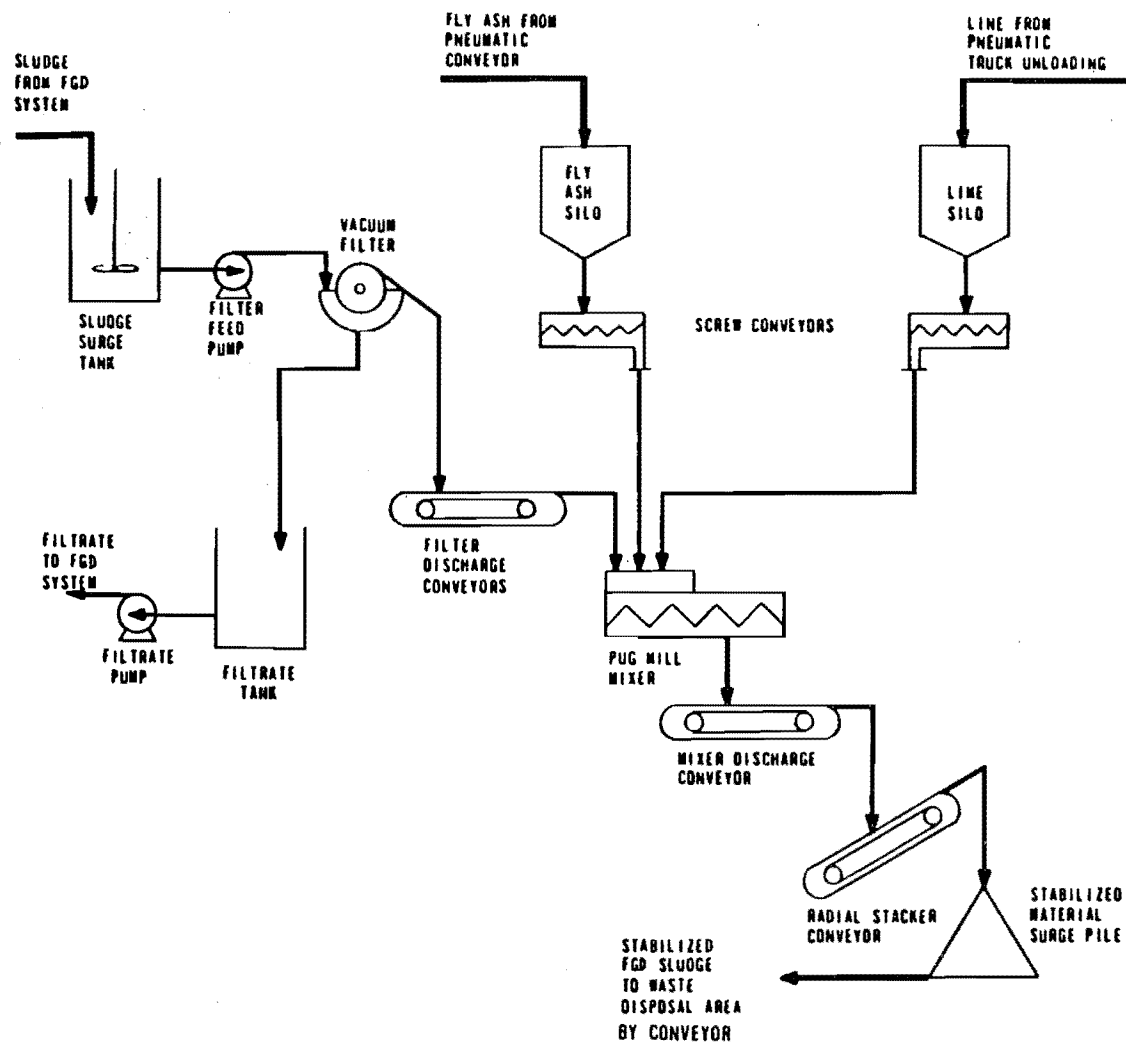


Figure 24. FGD sludge stabilization process.

The underflow from the FGD system thickeners passes forward via an agitated surge tank to a secondary dewatering system. The vacuum filter shown is normally used although solid bowl centrifuges have been used in a few systems.

The product (now up to 0.6 mass fraction hydrated solids) from the vacuum filter is fed to a pug mill where it is combined with fly ash from the electrostatic precipitators and lime. Both the fly ash and the lime are screw fed from storage silos. Where the FGD system is treating a residual oil or coke fired boiler there will also be a bottom ash product that can be fed to the pug mill. In the case of a CO boiler, there is unlikely to be very much bottom ash.

The product mix from the pug mill is conveyed to a radial stacker where it is accumulated in a surge pile. The fresh mill product is often too wet to handle, and may require three to six days before it starts to set and attain a consistency that can be handled with conventional earth moving equipment. If left for too long the pile may become quite hard and fracture in large pieces, making handling extremely difficult. The unstabilized sludge and the stabilized sludge prior to setting can be thixotropic; that is, a near solid that turns to liquid under stress (such as mechanical handling). Tracked equipment has been shown to be superior to rubber tired equipment in this operation.

The partially set material obtained after the first few days can be transported to a disposal area using any conventional equipment (e.g., trucks or conveyor belt). The setting process will continue at the disposal site. Material fixed in this manner has been used as landfill and road base material (Midkiff 1979b). The relative impermeability of the stabilized sludge in combination with a landfill technique that involves laying down successive thin layers (thus limiting the access of rain or surface water to each) produces a total mass with a low leach rate of trace elements. A description of the geophysical properties of stabilized FGD waste sludge is provided by Ruggiano and Paulson (1980).

The amount of sludge produced by the process varies somewhat with, for example, the reagent utilization in the absorption process. Typically, however, each tonne of SO_2 removed produces 4.5 t of stabilized sludge. The bulk density of the compacted material is approximately 1000 kg/m^3 and it is disposed of in thin layers (0.5 m) to a theoretically unlimited height. The deepest disposal bed achieved in practice is 30 m. Thus an FGD unit treating flue gas from the CO boiler on a plant of the scale defined for this study would

produce about 200 000 t/a of sludge requiring about 6700 m² for disposal. (Additional space is required to allow for site access and a three to one slope at the edge of the pile). By comparison, the tailings pond associated with this scale of plant occupies 20 000 000 m².

The description above is specific to the process offered by Conversion Systems Inc. (previously known as International Utilities Conversion Systems, IUCS), which is the most widely used stabilization process. Dravo offers a process in which the flyash and lime are replaced by Calcilox proprietary agent. In this process the stabilized sludge is sufficiently mobile to be pumped to the disposal site, where it settles. Supernatant water can then be recycled to the FGD process, although recycle is not always achieved in practice. The Chemfix process which uses a reagent containing silicates and cement has received very limited application.

It should be noted that none of these processes has ever been tested using the fly ash from any part of the oil sands process. While there is no compelling reason to doubt their efficiency, a reasonable test program prior to any final process selection would be a sensible precaution. Preliminary tests conducted by Conversion Systems Inc. on samples of Suncor and Syncrude flyash obtained by Alberta Environment have shown promising results (letter dated 26 July 1982 from J.L. Parke Conversion Systems Inc. Horsham PA.).

An alternative approach to stabilization is to use forced oxidation to convert all the sulphite to sulphate. If this approach is taken then the Chiyoda process (see Section 6.2.6 below) which incorporates the oxidation step in the absorber should be considered.

Whichever approach is taken, careful consideration should be given to the possible effects of extreme winter temperatures. For example, the initial sludge stabilization will almost certainly need to be performed indoors to prevent the whole mass from freezing solid.

6.2.1.4 Design considerations. Although in essence the limestone FGD operation described above is very simple, some of the earlier installations suffered from poor performance and low process availability. These problems generally resulted from two factors:

1. Insufficient attention to design details.
2. Lack of motivation to tackle obvious problems.

Current legislation has provided most operators with the motivation to operate their environmental protection units with as much care as the main production units. Experience with earlier units has highlighted areas critical to successful design. The three key areas to be considered in a limestone system are:

1. Slurry handling: design must avoid blocking and erosion.
2. Chemical scaling: design must minimize complicated internals.
3. Materials of construction: all wetted areas are subject to corrosion.

Some of the more general aspects of these areas are discussed below. For more detailed descriptions of design considerations and operating problems, Johnson and Hutchison 1980, Biedell and Stevens 1979 and Saleem 1980 can be consulted.

Once the slurry has been produced it is vitally important to keep it moving to avoid blockages. Therefore all slurry tanks are agitated and all pumped non-continuous slurry transfer operations are designed with a continuous recycle to the pump suction tank to minimize the amount of stationary slurry in the system. Particular care has to be taken to avoid sharp bends in pipework, which can lead to accelerated local erosion and/or blockage, and any dead ends (eg. at sampling or maintenance valves).

The control of slurry flows is achieved where possible without the use of control valves. Thus the purge from the upper spray recycle system to the quencher sump is by gravity overflow. This technique depends on adequate agitation in the recycle tank to avoid alternative problems. The recycle rates to sprays are controlled by switching pumps on and off rather than by conventional flow control. The slurry make up from the feed tank to the recycle tank is controlled by an on-off control valve rather than a modulating control valve since the latter tend to block at low velocities and erode at high velocities. Further discussion of control details for the system are given by Gruenberg (1979).

The low solubility of calcium sulphate necessitates certain design practices to avoid scaling. Scaling can be promoted either by local supersaturation causing rapid precipitation, or by long residence times given normal crystallization. Local supersaturation in the absorber can be avoided by operating at high liquid to gas ratios.

A reasonable residence time is required to crystallize the calcium salts this is provided in the recycle tank. Failure to provide sufficient recycle tank capacity will result in the return of supersaturated liquid to the absorber and, inevitably, scaling will occur.

To encourage precipitation as crystals rather than scale, it is advisable to maintain a reasonable solids concentration (at least 0.08 mass fraction) in the circulating slurry. These solids then provide seed sites for preferential precipitation.

The mist eliminator is often the area where scaling is first observed, hence the necessity for a carefully considered washing facility as described above. The quality of the water used in the washing operation is of major importance. Reclaim water that is saturated with calcium sulphate will almost certainly cause severe scaling of the mist eliminator. Scaling can be reduced by incorporating magnesium sulphate in the scrubbing slurry. The optimum magnesium concentration is reported as 2×10^{-3} to 3×10^{-3} mass fraction (Anon 1979b). With magnesium addition pH has to be carefully monitored since at high pH values a magnesium hydroxide gel, which will adversely affect the waste slurry treatment system, can form. Karlsson and Rosenberg (1980) give a more complete discussion of scaling in limestone and lime systems.

All wetted parts of the absorption system are subject to corrosion. The spray absorption sections are also subject to erosion as the slurry spray impinges on the absorber wall. The normal material selected is lined carbon steel, the lining being rubber or one of the glass reinforced plastics. Whichever lining is selected, strict attention to design detail and quality control during fabrication and installation is essential. A common failing with early installations was separation of the lining because the metal surface was not prepared properly prior to application. Tower internals can be either solid plastic or lined carbon steel. The spray nozzles are cast from silicon carbide refractory. They are designed with a hollow interior and a typical minimum opening of 25 mm to avoid plugging (Figure 25). The hot flue gas inlet to the quencher section has to be lined with an acid proof refractory for corrosion and temperature protection. Alloys such as 316L stainless steel or better can be used in place of linings. One of the risks is that operational transients can lead to extremely rapid local corrosion.

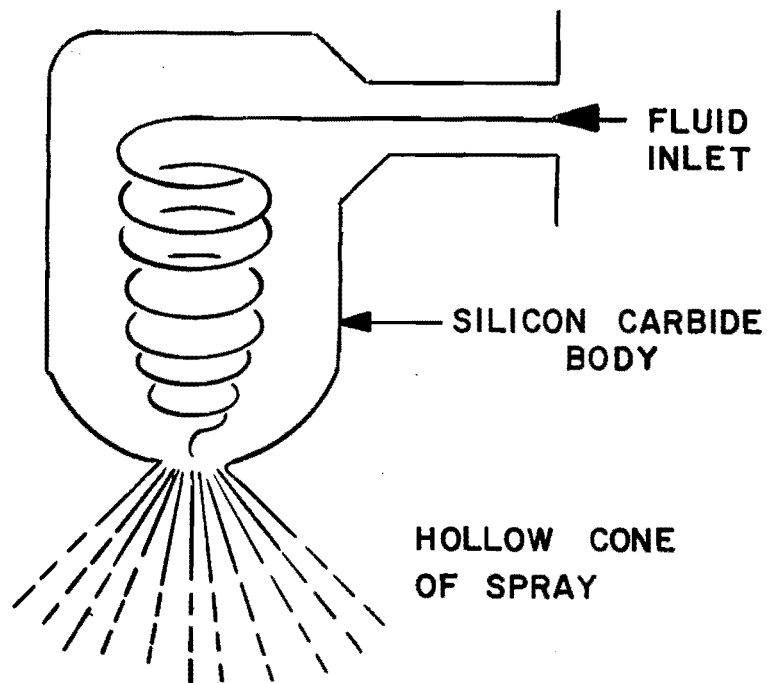


Figure 25. Hollow cone spray nozzle.

The use of plastic and/or rubber linings makes the absorber very susceptible to temperature excursions, which can arise in at least three ways. Loss of slurry circulation in the quencher section will immediately expose the whole of that section to inlet flue gas temperature. Loss of slurry circulation in the upper absorber section will eventually expose the whole tower to inlet flue gas temperature since the overall quenching action depends on a fresh supply of cold slurry. The flue gas feed to the unit will normally have been heat exchanged with combustion air fed to the boiler. If that heat exchanger is not functioning properly then the flue gas feed will be hotter than anticipated in the design and this will lead to a temperature excursion in the absorber. In order to protect the absorber from temperature excursions, an emergency bypass which is activated by any one of a number of thermocouples, is installed.

6.2.1.5 Transient conditions. Under normal start up conditions a boiler flue gas will contain more excess air than usual and therefore a lower SO_2 concentration. The total fuel consumption at start up is lower so that the absolute flue gas rate, and therefore SO_2 removal efficiency is likely to be lower than under steady state conditions. The SO_2 discharge to atmosphere will also be lower.

During turndown, a number of approaches can be taken. The normal policy is to switch off one or more of the slurry circulating pumps. With a multi tower absorption system it is also possible to shutdown one or more units if the remaining units have sufficient capacity to handle all of the flue gas. This combination of pump and tower turndown offers an extremely flexible approach and generally enables the FGD system to follow down to 15 to 40% of normal throughput, depending on the precise combination of towers and pump circuits installed. A more detailed discussion of possible turndown operating strategies is given by Johnson (1978).

One of the key variables controlling the efficient removal of SO_2 is the correct slurry circulation rate. Any reduction in the rate due to blocking or scaling would result in an increased SO_2 emission if no remedial action were taken. However, since in many cases flow reduction for these reasons is gradual rather than sudden, a properly monitored plant should be able to schedule a shutdown or transfer operation to a spare module before a serious SO_2 excursion results. A greater problem in terms of SO_2 emission excursions

is the potential variation of the SO_2 concentration in the flue gas feed to the unit. Such variation can arise either from changes in the sulphur content of the oil sand feed to the complex or from transient conditions in one of the upstream operations (particularly the fluid coker). Fluctuations of this nature are much harder to handle. Their very detection relies on an SO_2 analyzer which may not be reliable (particularly outside the 'normal' range). However, the impact of these fluctuations on the system is mitigated by the large inventory of slurry in the recycle tanks.

6.2.1.6 Efficiency and reliability. Limestone systems are generally not designed for more than 90% SO_2 removal with approximately 80% reagent utilization (Jahnig and Shaw 1981). To some extent SO_2 removal efficiency can be improved by increased reagent addition.

One limiting feature of the system is the low reactivity of the limestone. This can be countered, to some extent, by the use of additives. Magnesium oxide which has already been mentioned for scaling reduction has a positive effect on SO_2 removal. Adipic acid has also been used and demonstrated to increase limestone utilization to almost 100% while reducing capital cost as a result of the smaller reagent and waste handling equipment required. Mobley and Chang (1981) give a more complete discussion of adipic acid and several other potential organic additives.

Reliability as discussed in Appendix A, is difficult to define for a given technology depending as it does on many non-technical factors. However, for a typical modern unit, a reliability of 90% to 95% for an individual absorber system seems reasonable (Johnson and Hutchison 1980). In the context of an oil sands complex even the 95% figure is almost certainly too low if the operation of the complex is subject to successful FGD unit operation. This implies that some spare capacity has to be installed. Typically the limestone FGD system would require several parallel units (e.g. three or four) for 100% capacity. Therefore by providing one extra unit an acceptable overall reliability can be obtained at considerably less than 100% spare installed capacity. Other methods of designing redundancy into the system include spare pump circuits and additional levels of sprays.

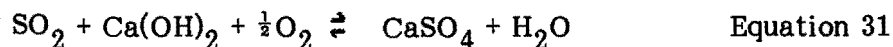
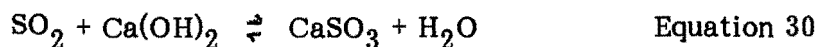
6.2.1.7 Limestone regeneration. All current and proposed limestone FGD installations produce a calcium sulphite/sulphate sludge for treatment and disposal. Ontario Hydro (Mozes 1978) has demonstrated, at the bench scale, that regeneration of most of the limestone is possible. The process studied involves roasting the sludge to produce calcium sulphide and then carbonating a slurry of the sulphide to produce limestone for recycle and hydrogen sulphide for feeding to a Claus plant. The high energy demand and potentially poor economics of the process prevented further development.

6.2.2 Lime FGD Process

6.2.2.1 Process description. The process (Figure 26) employs a lime slurry to absorb SO_2 . The flue gas that has already been through electrostatic precipitators is fed to the system. The gas path through the process is essentially similar to that described in the limestone process (Section 6.2.1.1 above), although the wetted film contactor is less likely to be installed.

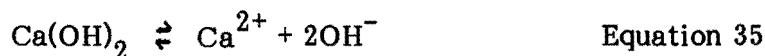
Delivery of lime to the site is by truck. Lime is routinely unloaded pneumatically. Because of its immediate exothermic reactivity with any moisture, the lime has to be stored in dry silos. Silo capacity should provide one month's storage. From the storage silos the lime is conveyed, again pneumatically, to feed silos (one day's capacity). The feed silos supply weigh feeders which deliver lime to slakers where a slurry is prepared using reclaim and makeup water. The slurry is transferred to feed tanks (one shift's capacity) from where it is fed forward to the recycle tank. The feed forward to the recycle tank is proportional to the SO_2 feed rate to the unit. Because of the higher reactivity of lime (relative to limestone) the single loop slurry system, described here, is more likely to be used than the double loop system described for the limestone case. The slurry is recirculated to the spray headers. Overflow from the recycle tank is to a waste slurry tank. From this point on through the dewatering and sludge stabilization areas the process is identical to that outlined for the limestone system.

6.2.2.2 Principal chemical reactions. The overall removal of SO_2 can be represented by the simple reactions:

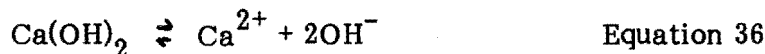


As with the limestone system, the process can be broadly split between physical absorption in the absorber and chemical reaction in the recycle tanks. The key reactions are detailed below:

Absorber Reactions:



Recycle Tank Reactions:



The insoluble waste calcium products are actually hydrated as $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

6.2.2.3 Design considerations. Many of the factors that have to be considered in a limestone unit are also relevant to a lime unit. Indeed many authors simply refer to limestone/lime units. There are, however, some obvious differences which are noted below:

1. Lime forms a slurry with a smaller particle size and is, therefore, slightly less prone to blockage than limestone.

2. The greater solubility of lime leads to less liquid phase resistance and generally gives better reagent utilization. This means that lime-based absorbers can employ a slightly simpler design, as noted above.
3. Lime is more soluble than limestone. This results in the system being less buffered and exhibiting a greater pH variation as a result of process changes.
4. Lime is more caustic than limestone and the overall plant design should ensure that sufficient washing down points etc. are provided. In general terms a more rigorous approach to slurry containment needs to be applied in a lime based plant.
5. The lime based sludge does not dewater as easily as the limestone equivalent and therefore requires larger thickeners.

6.2.2.4 Transient conditions. The same items that were discussed for the limestone system apply. The greater solubility of lime is thought to lead to slightly smoother operation during load changes.

6.2.2.5 Efficiency and reliability. Lime based systems can be designed for more efficient SO₂ removal and reagent utilization than limestone systems (e.g. 95% compared with 90% and 90% compared with 80% (Jahnig and Shaw 1981). Again, a trade off between the two is possible. In particular, it is easier to design a lime system for high SO₂ removal combined with high reagent utilization.

Reliability is likely to be the same overall as for a limestone system (i.e. 90% to 95% per module). Slightly greater availability in the slurry circulation system can be offset against a reduction in the solid lime pneumatic handling area.

6.2.3 Alkaline Flyash FGD Process

This process is essentially similar to the lime FGD process described in the previous section. The lime is supplemented by alkaline flyash from the boiler, thereby reducing the quantity of lime required in the process. The process can only be considered feasible when coupled with a boiler fuel producing an alkaline flyash. Its most general application to date has been in coal burning stations in the western states of the USA. Since the main

components of flyash in an oil sands plant are clay based silicates, the process is not practical for this application.

6.2.4 Double Alkali FGD Process

6.2.4.1 Process description. Like the two previous processes, the double alkali process produces an overall effect in which SO_2 is combined with calcium to produce a calcium sulphite/sulphate sludge. Rather than the direct reaction between calcium compounds and SO_2 previously described, the absorption is achieved by a sodium based solution which is then regenerated using lime (Figure 27).

The flue gas that has already passed through electrostatic precipitators to remove flyash is fed to the FGD system. The gas enters the quencher section where it is cooled and saturated by downcoming liquid before passing up to the absorber. In the absorber the flue gas is countercurrently sprayed with a solution of sodium compounds (carbonate, bisulphite, hydroxide and sulphite). After SO_2 removal the flue gas passes through a mist eliminator prior to atmospheric discharge via a stack.

The process requires a make up of sodium carbonate to replace sodium losses in the waste sludge (see below). The soda ash is truck delivered to the site and unloaded into storage tanks where water is added to form a concentrated solution. This solution is fed forward to the reagent recycle tank to maintain a 6 to 7 pH value of the circulating solution. Reclaimed reagent from the downstream thickener is added to the recycle tank to maintain the correct level.

Delivery of lime to the site is by truck. Lime is routinely unloaded pneumatically. Because of its immediate exothermic reactivity with any moisture, the lime has to be stored in dry silos. Silo capacity should provide one month's storage. From the storage silos the lime is conveyed, again pneumatically, to feed silos (one day's capacity). The feed silos supply weigh feeders which deliver lime to slakers where a slurry is prepared using makeup water. The lime slurry is transferred to feed tanks (one shift's capacity) from which it is fed forward to the lime reaction tank (to maintain a pH of 8.5 in the thickener overflow). In the reaction tank the lime is mixed with a purge stream from the recirculating reagent solution. Calcium sulphite and sulphate are

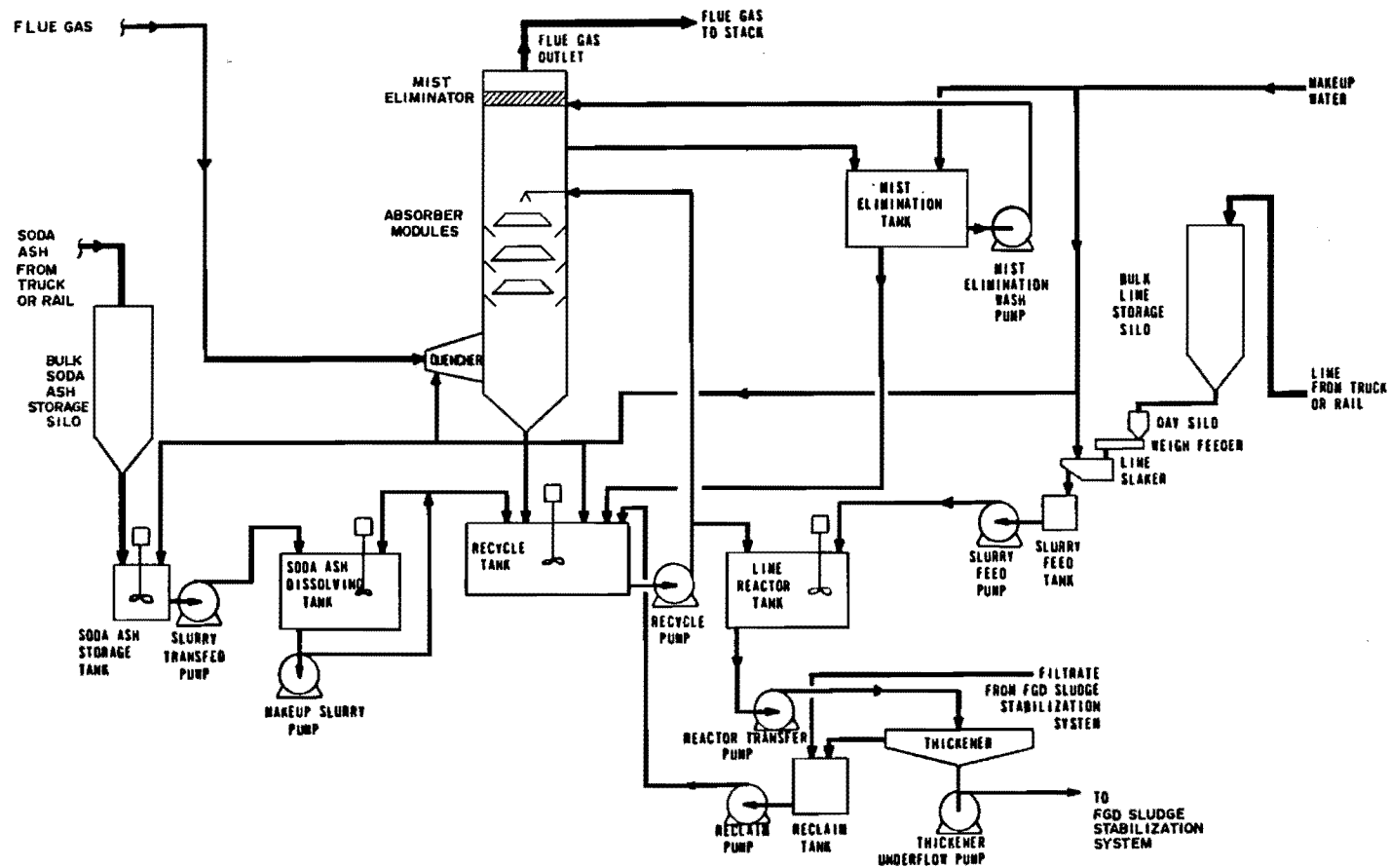
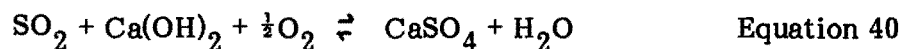
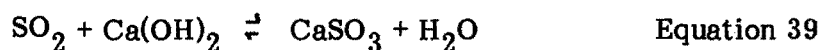


Figure 27. Double alkali FGD process.

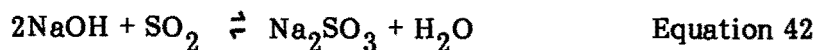
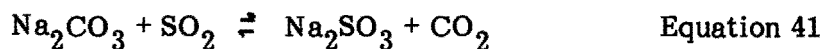
precipitated; sodium hydroxide is regenerated for recycle. The calcium sulphite/sulphate slurry is passed to a thickener. The overflow from the thickener is recycled to the reagent recycle tank. The underflow, containing about 0.35 mass fraction of hydrated solids passes forward to a sludge treatment unit identical to that described in Section 6.2.1.3 above.

6.2.4.2 Principal chemical reactions. The overall removal of SO_2 can be represented by the simple equations:

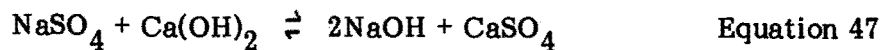
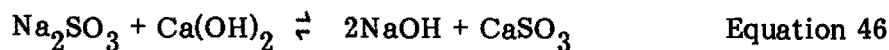
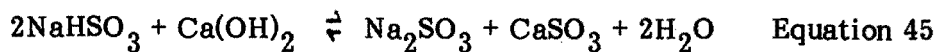


The process can be split between the absorption and regeneration sections.

Absorption Reactions:



Regeneration Reactions:



The insoluble waste products are actually hydrated as $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

6.2.4.3 Design considerations. The major difference between the double alkali system and the lime/limestone systems is the elimination of insoluble calcium compounds from the absorber circuit. This eliminates the two main problem areas, i.e., scaling and blocking, from this part of the process. The clean solution enables the use of more conventional control systems than are possible with slurries. Normal modulating control valves can be employed. Make up soda ash is controlled by pH rather than the more indirect SO_2 mass flow. This is not possible in the lime/limestone systems where the scaling conditions make the operation of reliable pH systems far more problematic. For the same reason packed or tray towers can be used instead of spray towers, this approach can lead to improved absorption efficiency at the expense of additional pressure drop (and, hence, power consumption).

In order to gain the full benefit of the system, it is essential that the thickener is designed so as to minimize solids in the overflow that would be recycled directly to the absorber.

The problems relating to slurry handling still occur in the regeneration area but equipment here is much simpler than in the absorber. The sludge produced by direct precipitation in the reaction tank is somewhat easier to dewater than that produced in an absorber (Anon. 1979). While all wetted areas of the absorber are subject to corrosion, the abrasion found in slurry fed absorbers is not a problem.

6.2.4.4 Transient conditions. Behaviour under typical start up conditions should be generally similar to that of a slurry based system.

While the system, like any other, is vulnerable to excursions in the feed concentration of SO_2 , it is likely to be able to make a better response since there is more chance of the extra reagent that would be injected under these conditions actually being utilized, because there is chemical as well as physical absorption in the tower. The use of trays or packing in place of a simple spray tower will limit the turndown that can be achieved on a single unit.

6.2.4.5 Efficiency and reliability. SO_2 can be removed with 95% efficiency. Reagent utilization approaching 100% for each chemical (lime and soda-ash) is reported. A simple appraisal of the process suggests that the absorber operating with a clear solution should be more reliable than a slurry based system. The reagent preparation system and sludge stabilization are common to both types of process. The double alkali process has the additional regeneration area. A reasonable supposition reinforced by experience on some of the US systems is that the potential reliability is greater than that of a slurry based process.

6.2.5 The Sodium Carbonate FGD Process

This process is essentially similar to the double alkali process described in the previous section but without the regeneration step. This means that the only reagent consumed is expensive sodium carbonate (approximately five times the stoichiometric equivalent cost of lime) and that the waste product is a solution of sodium salts that requires ponding, rather than a solid byproduct that can be stabilized.

The main application of this process is in small industrial units where the reagent cost and byproduct problem are relatively insignificant. Both counts make the process unsuitable in an oil sands environment.

6.2.6 The Chiyoda Thoroughbred 121 Process

The Chiyoda Thoroughbred 121 (CT 121) process is a development of the well established CT 101 process. The process is designed specifically to produce a gypsum product. The CT 101 process has been installed at 12 utilities in Japan, the largest being a 350 MW single module unit (Chiyoda 1982). The CT 121 process has yet to be commercially operated in North America.

6.2.6.1 Process description. The process (Figure 28) employs a jet bubbling reactor to absorb SO_2 . The flue gas which has been treated in electrostatic precipitators is fed to a prescrubber. The gas is scrubbed with water to further reduce the solids content and cool it to saturation temperature before passing to the main absorber. In the main absorber (Figure 29) the flue gas is sparged into the limestone slurry absorbant together with an additional supply of ambient air. The sparging action creates a jet bubbling froth layer (Figure 30)

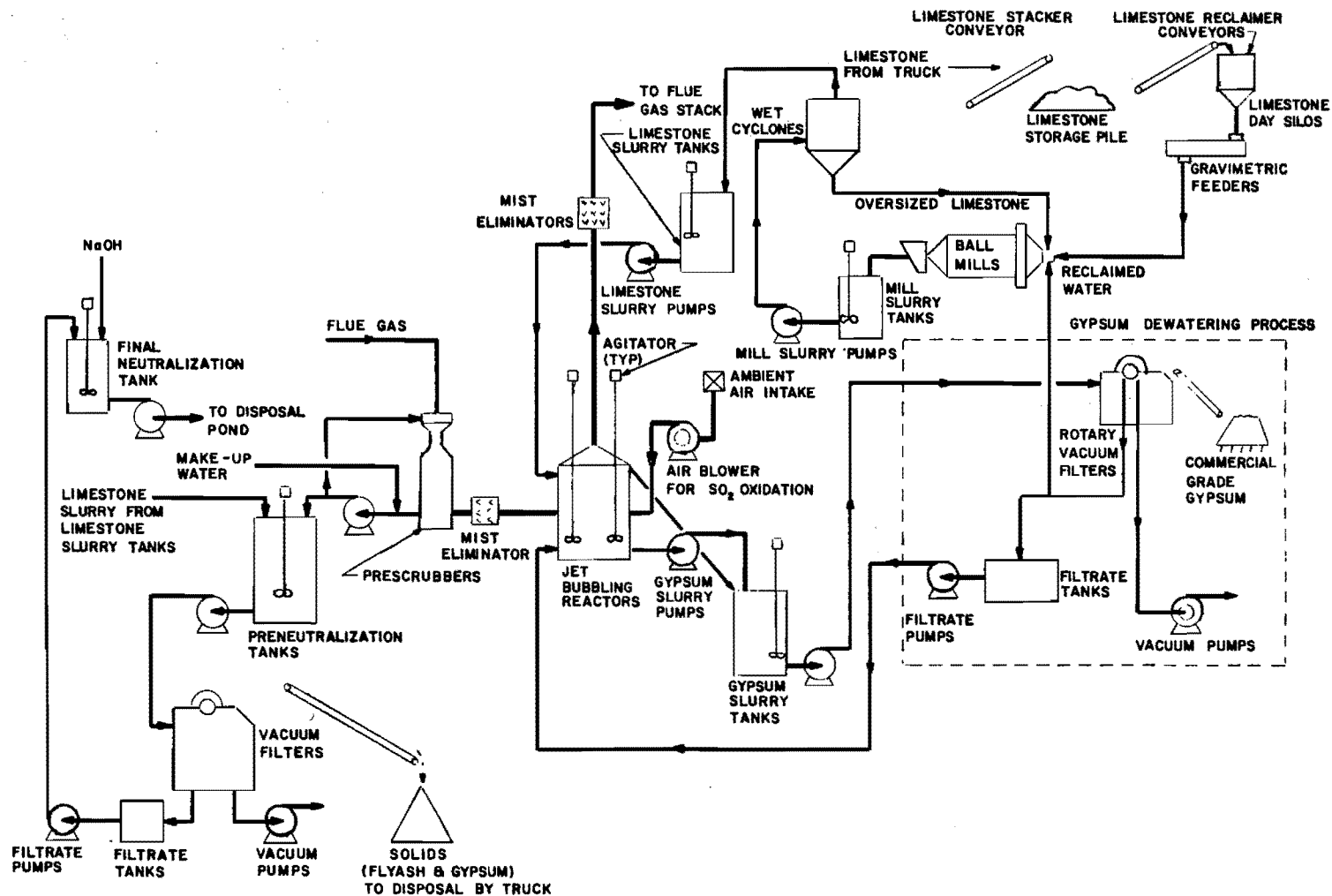


Figure 28. CT 121 process.

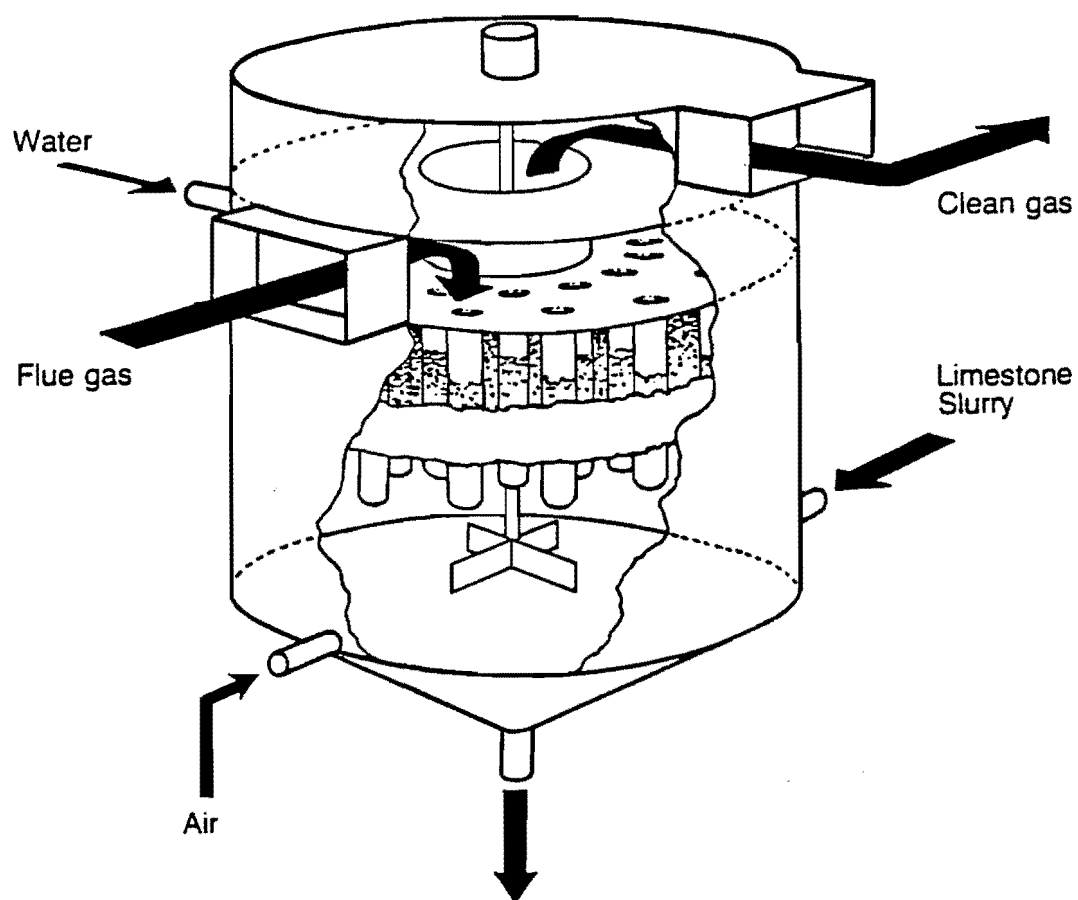


Figure 29. CT 121 jet bubbling reactor.

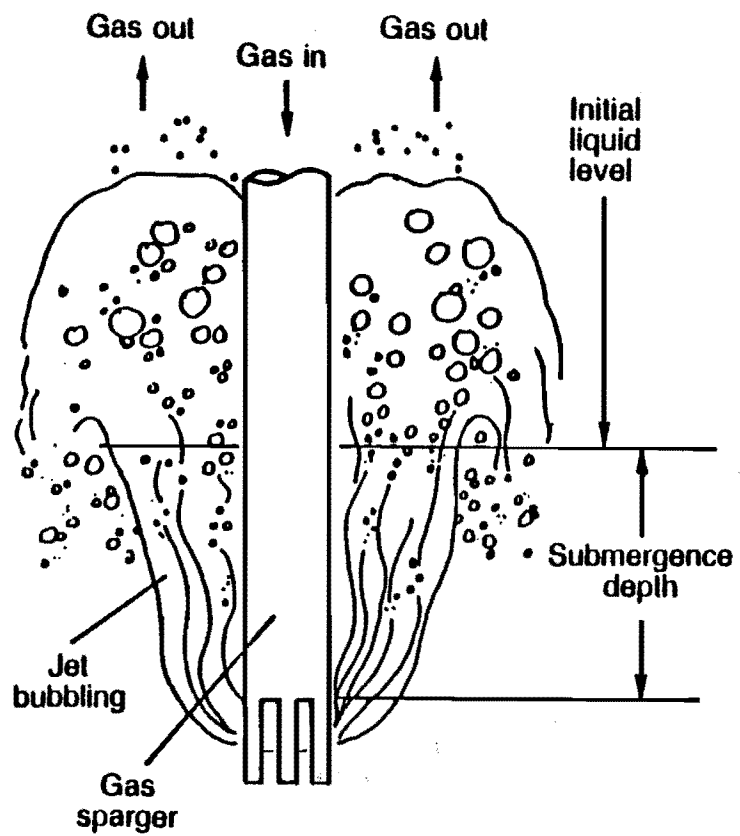


Figure 31. CT 121 absorber flow patterns.

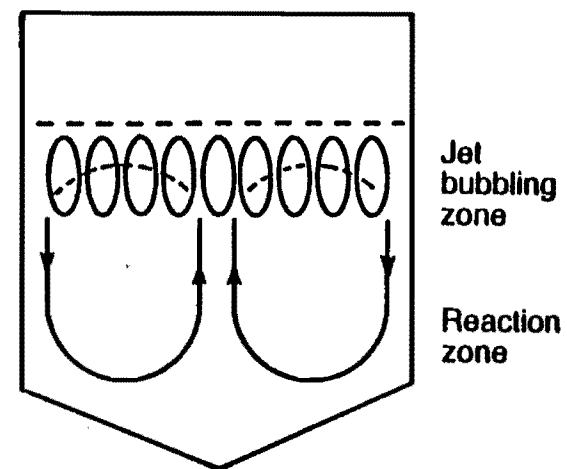


Figure 30. CT 121 sparger action.

in which the SO_2 is absorbed and oxidized to calcium sulphate (gypsum). Flow patterns in the jet bubbling reactor are shown on Figure 31. The stripped gas then passes through mist eliminators prior to atmospheric discharge via a stack.

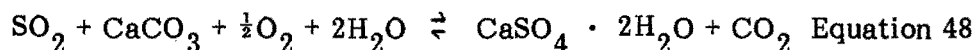
Limestone is unloaded from trucks into hoppers which feed conveyors that transfer it to a sheltered storage pile. The pile should be sufficient for one month's operation. Sheltered storage is necessary to protect the limestone from rain and snow. From the storage pile the limestone is conveyed to feed silos (one day's capacity). The feed silos supply weigh feeders which deliver limestone to the ball mills. The mills prepare the slurry, normally using reclaim water from the downstream dewatering process. The slurry is fed to a hydrocyclone which recycles oversize back to the mill before passing to the limestone feed tanks (one shift's capacity).

From the feed tanks the slurry is fed to either the absorber or the pre-neutralization tank (see below).

The acidic prescrubber effluent is neutralized in a two stage process using limestone and caustic soda as shown (Figure 28). A solid gypsum/flyash byproduct only suitable for disposal is produced together with a small stream of sodium sulphate solution.

Gypsum is pumped from the absorber via a surge tank to rotary vacuum filters. The gypsum product is of commercial grade and can be sold if the market exists. The filtrate is recycled to the ball mills and the absorber.

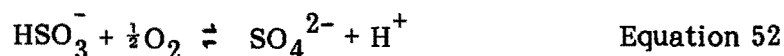
6.2.6.2 Principal chemical reactions. The one stage process can be represented by the following reactions:



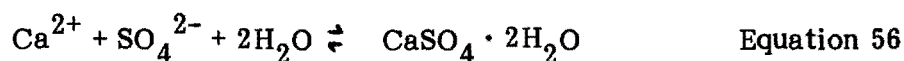
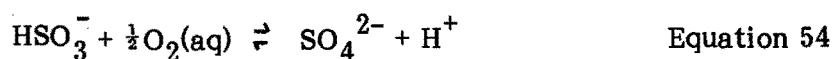
As illustrated in Figure 31, the Jet Bubbling Reactor can be divided into two zones which are both liquid-phase continuous.

Reaction equations in the jet bubbling zone:





Reaction equations in the reaction zone:



The controlling steps for the jet bubbling zone are gas-phase mass transfer of SO_2 and oxidation of HSO_3^- . For the reaction zone, liquid-phase mass transfer of O_2 and gypsum crystal growth are the controlling steps.

6.2.6.3 Design considerations. While the ancilliary unit operations (slurry preparation, product dewatering, etc.) are similar to those in previously described processes, the absorber itself is not.

Gas liquid contacting is by sparging into a liquid layer rather than by counter current flow against a slurry spray. The slurry is fed to the process on a once through basis, eliminating the need for a recirculating system. By their nature the sparge pipes are totally immersed in the absorbent slurry. Therefore, attention has to be given to ensuring that they never block, particularly during turndown and shutdown conditions.

For a given SO_2 concentration in the flue gas, removal efficiency is largely dictated by the pressure drop through the absorber. This in turn is set by the height of liquid above the sparger. Removal efficiencies of 90% to 95% have been observed on a $95\,000\text{ m}^3/\text{h}$ (st) prototype with pressure drops ranging

from 2.7 to 3.4 kPa (275 to 350 mm H₂O). On the same prototype magnesium sulphate was found to increase removal efficiency by up to 5% while adipic acid, which is generally considered to improve the conventional limestone process, was not found to be particularly effective (Noguchi and Idemura 1981).

6.2.6.4 Transient conditions. Turndown to 40% of maximum throughput would be guaranteed on a single module (telephone conversation, Don Clasen, Chiyoda International Corporation, April 29, 1982). This turndown, together with the option of shutting of one or more parallel absorbers, should cover any normal operating requirement.

6.2.6.5 Efficiency and reliability. As discussed above, removal efficiencies of 95% can be obtained at the expense of pressure drop (hence power consumption) in the system. Utilization of up to 98% of the limestone has been obtained although further testing on large scale units would be required to claim this figure with confidence. Both figures, however, are indicative of removal and utilization efficiencies comparable to either the limestone or lime based slurry system.

While high reliability is reported from the prototype, it is probable that this unit benefitted from closer attention than would necessarily be the case in a normal industrial unit. Overall the process has a slurry preparation system similar to all those discussed so far. The spray absorber is replaced by the bubbling absorber. There is no sludge stabilization system but there is a pre-scrubber with associated effluent treatment. There is no compelling reason to suppose that the long term reliability of the process will differ significantly from those described already, that is, 90% to 95% for an individual module.

6.2.7 Aqueous Ammonia FGD Process

This process (Figure 32) has the unusual attraction of potentially utilizing one waste stream (the aqueous ammonia from the sour water stripping system) to clean up another, the flue gas. The ammonia can alternatively be provided by the direct absorption of ammonia in water; however, this has a significant effect on the process operating costs. The process has been commercially operated in Canada at the Cominco smelter in Trail, British Columbia. This is a relatively small unit and further piloting would be required

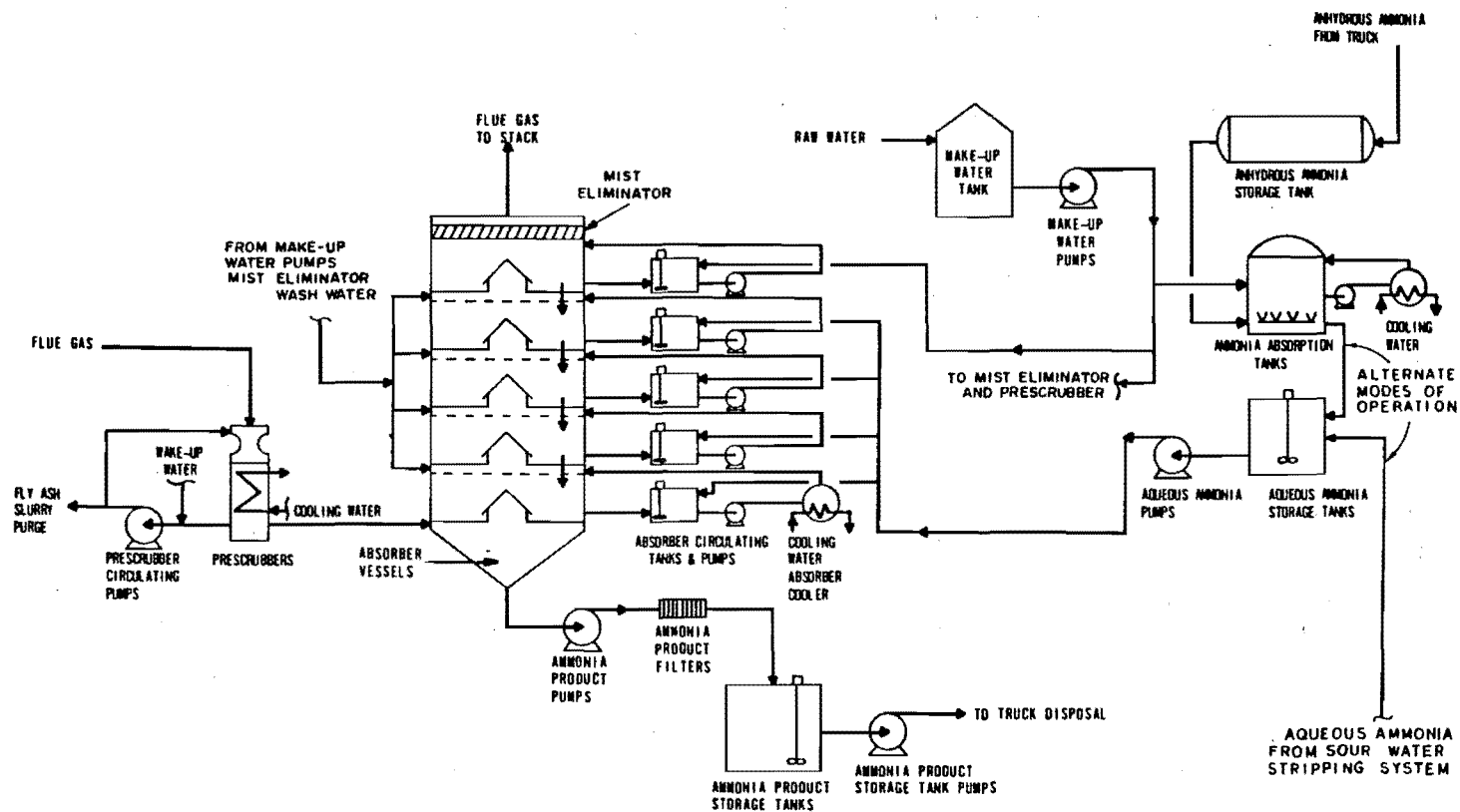


Figure 32. Aqueous ammonia FGD process.

before the process could be installed on a large industrial unit. To date the process has not been demonstrated at SO_2 concentrations above 2.5×10^{-3} volume fraction which limits its potential application.

6.2.7.1 Process description. The flue gas which has been treated in electrostatic precipitators is fed to a prescrubber. The gas is scrubbed with water to further reduce the solids content; it then passes over in line coolers to further reduce the temperature before passing to the main absorber.

The flue gas has to be cooled below the adiabatic saturation temperature (typically 65°C) to about 48°C to ensure that SO_2 is absorbed in the absorber. This additional cooling produces a larger purge than would be the case if solids removal were the only criteria.

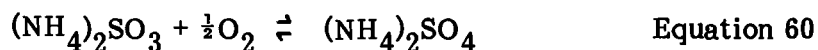
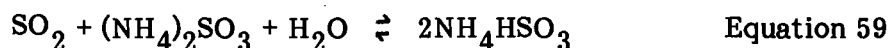
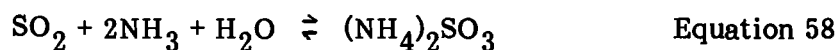
In the main absorber, which essentially comprises four valve trays each with liquid recycle loops which contain an agitation system to ensure good mixing and minimum unreacted liquid bypass to lower trays, the flue gas is contacted with a scrubbing solution of ammonium sulphite-bisulphite. The flue gas passes through a mist eliminator prior to reheat and atmospheric discharge.

Make up ammonium hydroxide is added to each stage and controlled so that the concentrations of both SO_2 and ammonia decrease on higher stages. This is necessary to avoid both ammonia emissions and blue fumes (see below). Each tray is followed by a water washed mist eliminator.

Ammonium hydroxide solution, assumed to be available from on site sour water strippers, is stored in surge tanks (typically one day's capacity) and then pumped via feed tanks to the individual absorption stages. Addition to each stage is pH controlled. The bottom tray product is an aqueous solution containing as main components, approximately 0.17 mass fraction NH_4HSO_3 , 0.07 mass fraction $(\text{NH}_4)_2\text{SO}_4$. The balance is water and minor components. This stream is suitable for use as a fertilizer and should be relatively easy to market in Alberta. A reasonable product storage volume, say a month, should be provided since there is no alternative outlet for the absorber product.

If the absorber product cannot be marketed, then deep well injection can be used to dispose of it. This will, however, substantially increase the operating costs of the process.

6.2.7.2 Principal chemical reactions. SO_2 is absorbed by contact with fresh ammonium hydroxide and ammonium sulphite in the scrubbing solution. Some sulphite is oxidized to sulphate.



6.2.7.3 Design considerations. The process uses relatively sophisticated tower internals in the form of valve trays. This has two ramifications in relation to the simpler spray processes. Firstly, the design of the pre-scrubbing system is more important. Secondly, the tolerances required in tray manufacture dictate that they must be made of metal.

Conditions within the tower necessitate an alloy such as stainless steel or Hastelloy. The most severe conditions are on the top tray where very little ammonia is present and the liquid can have a pH value as low as 2. Hastelloy is required here but lower trays where the liquid has a pH value around 6 could be installed as stainless steel. A decision to install lower stages in a cheaper material could only be justified if there was reasonable confidence in the overall control system and ammonium hydroxide supply. It may well be prudent to construct all trays of Hastelloy.

One problem that has been noted with ammonia based scrubbers is the appearance of a blue haze in the stack effluent. It has been concluded (TVA 1970) that "proper operation" of the process will avoid this problem. Proper operation in this context means designing and operating the system so that at all points in the absorber the product of the ammonia, SO_2 and water vapour partial pressures is less than a critical k value above which solid ammonium bisulphite is formed. The critical k value is itself a function of temperature. The relationship showing fume free and fume forming zones is illustrated on Figure 33. U.S. Patent 3 843 789 gives a detailed description of the calculation procedure required to conform to the k value criteria.

If operation in the fume free regions can not be guaranteed, then a downstream fume eliminator, either a Brinks filter or a wet electrostatic precipitator will be required.

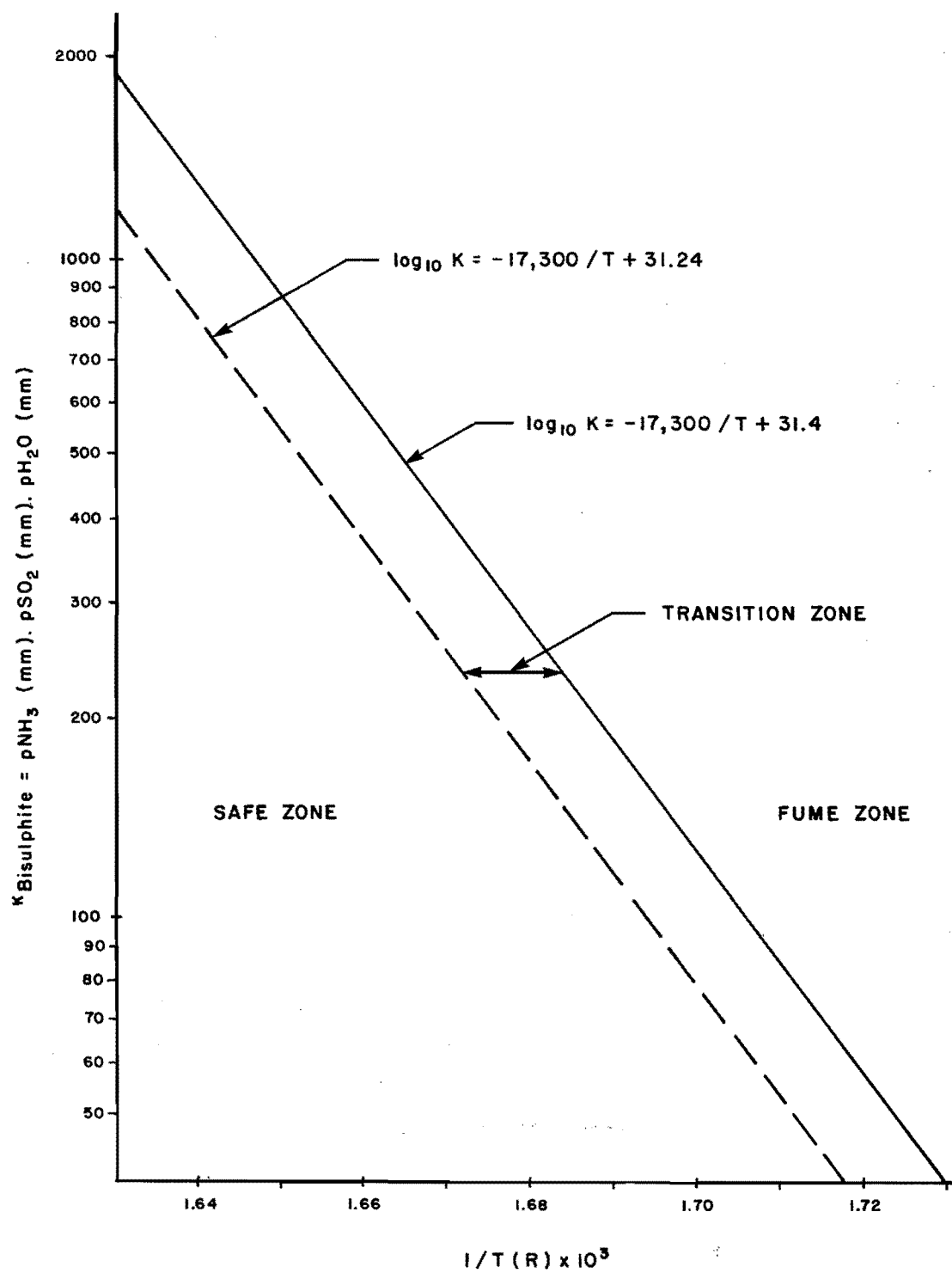


Figure 33. Aqueous ammonia process. Fume criteria.

The ammonium hydroxide source for the process can be the plant sour water system. At an early stage of any design a complete analysis of this stream should be obtained to confirm that it does not contain any impurities that will have an adverse effect on either the process or the downstream use of the byproduct as fertilizer.

6.2.7.4 Transient conditions. The independent control and reagent supply to each stage provides a reasonable operating flexibility under normal transient conditions (i.e. start up and turndown catered for in the process design). Performance under unexpected transient conditions (e.g. high SO₂ content in flue gas) should be as satisfactory as any other process from an SO₂ removal standpoint but it may be difficult to maintain the process in the fume free region.

6.2.7.5 Efficiency and reliability. The process can achieve SO₂ removal efficiencies of 90%. The high degree of stagewise control gives good reagent utilization. There is very little unreacted ammonia in the liquid byproduct although some will be lost in the flue gas. Utilization should exceed 90%. Insufficient data on reliability is available from full scale installations to form an accurate assessment. A simple overview of the process which has no solids or slurry handling suggests that it should probably be more reliable than the slurry based systems (i.e. 90% to 95% or better).

6.2.8 The Wellman Lord FGD Process

The Wellman Lord process (Figure 34) is a regenerable process in which the SO₂ from the flue gas is recovered in a concentrated stream suitable for subsequent conversion to either sulphur or sulphuric acid. In an oil sands context it is virtually certain that the SO₂ byproduct from the process would be fed to the Claus plant for the recovery of elemental sulphur.

6.2.8.1 Process description. The flue gas which has been treated in electrostatic precipitators is fed to a prescrubber by booster fans. The gas is scrubbed with water to further reduce the solids content and cool it to saturation temperature before passing to the main absorber.

In the main absorber, which essentially comprises three valve trays each with liquid recycle, the flue gas is countercurrently contacted with a scrubbing solution of sodium sulphite-bisulphite. The flue gas passes through a mist eliminator prior to atmospheric discharge via a stack.

The principal absorption reaction is the combination of SO_2 with sodium sulphite to form sodium bisulphite. However, some of the sulphite is oxidized to sulphate by oxygen in the flue gas.

The regeneration area, therefore, has two functions. The first is to regenerate SO_2 from the bisulphite formed in the absorber, the second is to purge byproduct sulphate and replace the lost sodium as soda-ash.

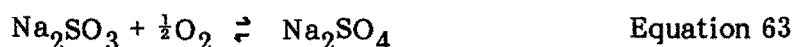
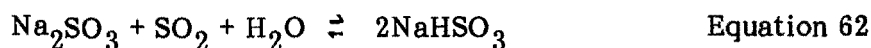
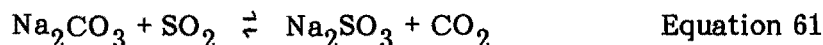
Absorber bottoms solution purge stream is fed to a forced circulation crystallizer. The concentrated slurry product is fed to a dewatering system, typically a centrifuge, from which the mother liquor is recycled to the evaporation system. The sulphate crystals are dried and stored in silos for subsequent disposal or sale. Vent gas from the drier is scrubbed prior to a atmospheric discharge.

Most of the absorber solution together with the crystallization system mother liquor recycle is fed to the evaporator. A double effect evaporation system is used to reduce total steam consumption. Overhead vapours from the crystallizer and first effect of the evaporator are condensed in the heater of the second effect. Subatmospheric flash steam from the boiler condensate is combined with the overhead vapour from the second effect. The vapours are condensed to remove water and the resultant SO_2 (typically 0.95 mass fraction SO_2) is compressed and transferred to a Claus plant. Condensate from these condensers together with that from the second effect heater is steam stripped to remove residual SO_2 .

The slurry from the first evaporator is passed through a separator to purge some of the mother liquor to the sulphate drier. As shown in Figure 34, the remainder of the stream, together with slurry from the second effect and stripped condensate, flows into a dissolving tank where the sulphite crystals are dissolved and make up soda ash solution is added. A stream from this tank is circulated to the vent scrubber.

Fresh absorber solution is pumped from the dissolving tank to an absorber feed tank and from there to the absorber.

6.2.8.2 Principal chemical reactions. The principal reactions in the absorber are between SO_2 , soda ash and sodium sulphite, with some byproduct sulphate formation.



The regeneration is simply the reverse of the bisulphite formation.

6.2.8.3 Design considerations. The prescrubber that is required for solids removal to protect the trays can be separate from the main absorber or incorporated into it, as shown in Figure 34, depending on the reagent to be used for neutralization. Separation allows the use of cheaper limestone whereas incorporation dictates that additional soda ash is used.

One of the key design areas is the evaporation and crystallization area. The slurry rate through the heaters has to be large enough to avoid a large temperature rise and thereby excessive scaling. Conditions in the crystallizer have to be designed to produce sulphate (by maintaining a low solids concentration). However, for downstream sulphate dewatering and drying a high solids content is preferable. Therefore, the crystallizer normally incorporates a solid liquid separation device.

6.2.8.4 Transient conditions. The turndown of the absorber is dictated by the design of the trays. A typical operational turndown to 40% of design should be possible. There is, however, the probability of lower removal efficiency at these rates (because of liquid weeping through the trays).

6.2.8.5 Efficiency and reliability. Removal efficiencies of 90% have been reported (Wood 1979) on large industrial units. As the process is regenerable, the only reagent consumption is for prescrubber effluent neutralization and make up to compensate for byproduct sulphate formation. Since both will vary widely with individual installations, typical reagent utilization cannot be quoted.

The availability of the process has been reported as 60% to 85% (Pruce 1981c). Much of the low availability is attributed to the evaporation and crystallization areas, and to poor performance of the SO_2 recovery unit. The complexity of the process and its dependence on another major unit (i.e., the Claus plant) certainly make it likely that the availability of the process will be lower than that of the simpler non-regenerative processes.

6.2.9 Magnesium Oxide FGD Process

The magnesium oxide process (Figure 35) is a regenerative process in which the SO_2 from the flue gas is concentrated to produce a feedstream suitable for subsequent conversion to either sulphur or sulphuric acid. In an oil sands context, the SO_2 byproduct would almost certainly be fed to the Claus plant for the recovery of elemental sulphur.

6.2.9.1 Process description. The flue gas which has been treated in electrostatic precipitators is fed to a prescrubber. The gas is scrubbed with water to further reduce the solids content and cool it to saturation temperature before passing to the main absorber. In the main absorber the flue gas is countercurrently contacted with a spray of magnesium sulphite/bisulphite slurry. The SO_2 free gas then passes through mist eliminators prior to atmospheric discharge.

A purge from the absorber slurry recirculation stream is fed to centrifuges. The liquid cenrate is recycled to the slurry preparation system, the wet cake is fed forward by screw conveyers to a rotary drier operating at 200°C where moisture and water of crystallization are removed. The dry magnesium sulphite passes to an intermediate storage silo prior to regeneration of the magnesium oxide. The drier vent gases are vented to atmosphere via a cyclone.

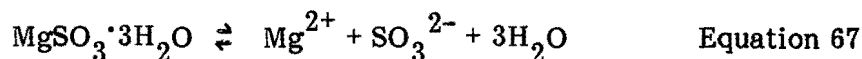
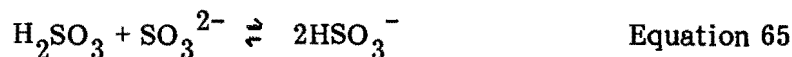
The dry solids are calcined in a fluid bed drier at about 820°C where the sulphite and most of the sulphate decompose to give magnesium oxide and SO_2 . The hot vent gas is treated to recover heat and solids, the option shown on Figure 35 is one of a number of alternatives. The cooled treated gas, containing about 0.15 volume fraction SO_2 , is transferred to a Claus plant via booster fans.

Solids are purged from the fluid bed to maintain the inventory, then ground and combined with the recovered overhead solids and recycled to the slurry preparation system. Inerts and magnesium sulphate which accumulate in the bed have to be purged from the process for disposal.

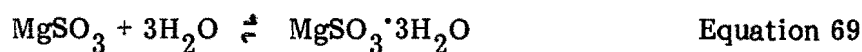
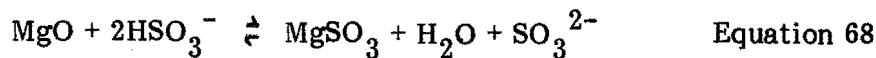
Fresh magnesium hydroxide is prepared in a slurry vessel using recycle solids with reclaim and make up water. Additional magnesium oxide is added to compensate for the purge from the calciner and any other losses. The fresh slurry is pumped back to the absorber recycle tank at a rate controlled by the pH of the recirculating slurry.

6.2.9.2 Principal chemical reactions. The absorption itself is broadly split between physical absorption in the spray tower and chemical reaction in the recycle tank. The key reactions are detailed below:

Absorber reactions:



Recycle tank reactions:



The regeneration is split between the simple drying and the fluid bed calciner.

Calciner reactions:

6.2.9.3 Design considerations. As with the limestone process much of the chemical reaction occurs in the absorber recycle tank which therefore has to be sized with adequate retention time. The regeneration process contains two separate vent gas treatment systems (for the dryer and the calciner) both of which must be designed for high solids recovery if unacceptable magnesium losses are to be avoided.

The successful operation of the regeneration process relies on three unit operations (dewatering, drying and calcining) each of which by FGD standards is relatively sophisticated. Good design in these areas with reasonable intermediate storage between units is essential. Poor design could easily lead to a domino effect in the process, whereby insufficient dewatering overloads the drier which then produces a wet product. The wet product would be impossible to convey to the calciner, giving the option of either a process shutdown or continuation with excessive make up reagent.

6.2.9.4 Transient conditions. The behaviour of the absorber itself under transient conditions is unlikely to be very different from that of a typical slurry system. Turndown to 40% on an individual module coupled with a multistream design should provide sufficient flexibility for any reasonable operating situation.

The recycle nature of the process common to all regenerative processes obviously makes it far more susceptible to unplanned transients (such as increased SO_2 concentration in the flue gas) than the once through throwaway processes.

6.2.9.5 Efficiency and reliability. Upto 95% removal of SO_2 can be achieved (Jahnig and Shaw 1981) although until further experience is obtained

this should probably be regarded as an upper limit with 90% being a more reasonable expectation.

The limited data on availability that has been reported (Pruce 1981c) indicates that the 60% to 85% obtained for the equally complex Wellman-Lord process is a more reasonable estimate than the 90% to 95% obtained with simpler processes.

6.2.10 USBM Citrate FGD Process

This process is at a relatively early stage of development with only a 60 MW demonstration unit operated to date and is, therefore, unlikely to be considered sufficiently proven for an oil sands environment for some years. The process is described and discussed in section 5.4.4 of this report.

6.2.11 Dry Lime Scrubbing FGD Process

6.2.11.1 Process description. Flue gas that has not been treated for solids removal enters the spray drier absorber. In the absorber the flue gas is co-currently contacted with a finely dispersed or atomized spray of lime slurry. The hot flue gas evaporates the slurry. The treated flue gas containing a particulate mixture of reaction products, unreacted lime and the original flyash leaves the absorber slightly above the saturation temperature. The treated flue gas then passes through a solids recovery system, either an electrostatic precipitator as shown or a bag filter, and is discharged to atmosphere via a stack. Because the process (Figure 36) maintains the gas above the saturation temperature reheat, to combat further heat loss at winter temperatures is either unnecessary or minimal.

Delivery of lime to the site is by truck. Lime is routinely unloaded pneumatically. Because of its immediate exothermic reactivity with any moisture the lime has to be stored in dry silos. Silo capacity should provide one month's storage. From the storage silos the lime is conveyed, again pneumatically, to feed silos (one day's capacity). The feed silos supply weigh feeders which deliver lime to slakers where a slurry is prepared using makeup water. The slurry is transferred to feed tanks (one shift's capacity) from which it is fed forward to the absorber. Additional makeup water is also fed to the absorber. The lime feedrate is controlled by the total SO_2 feed to the system.

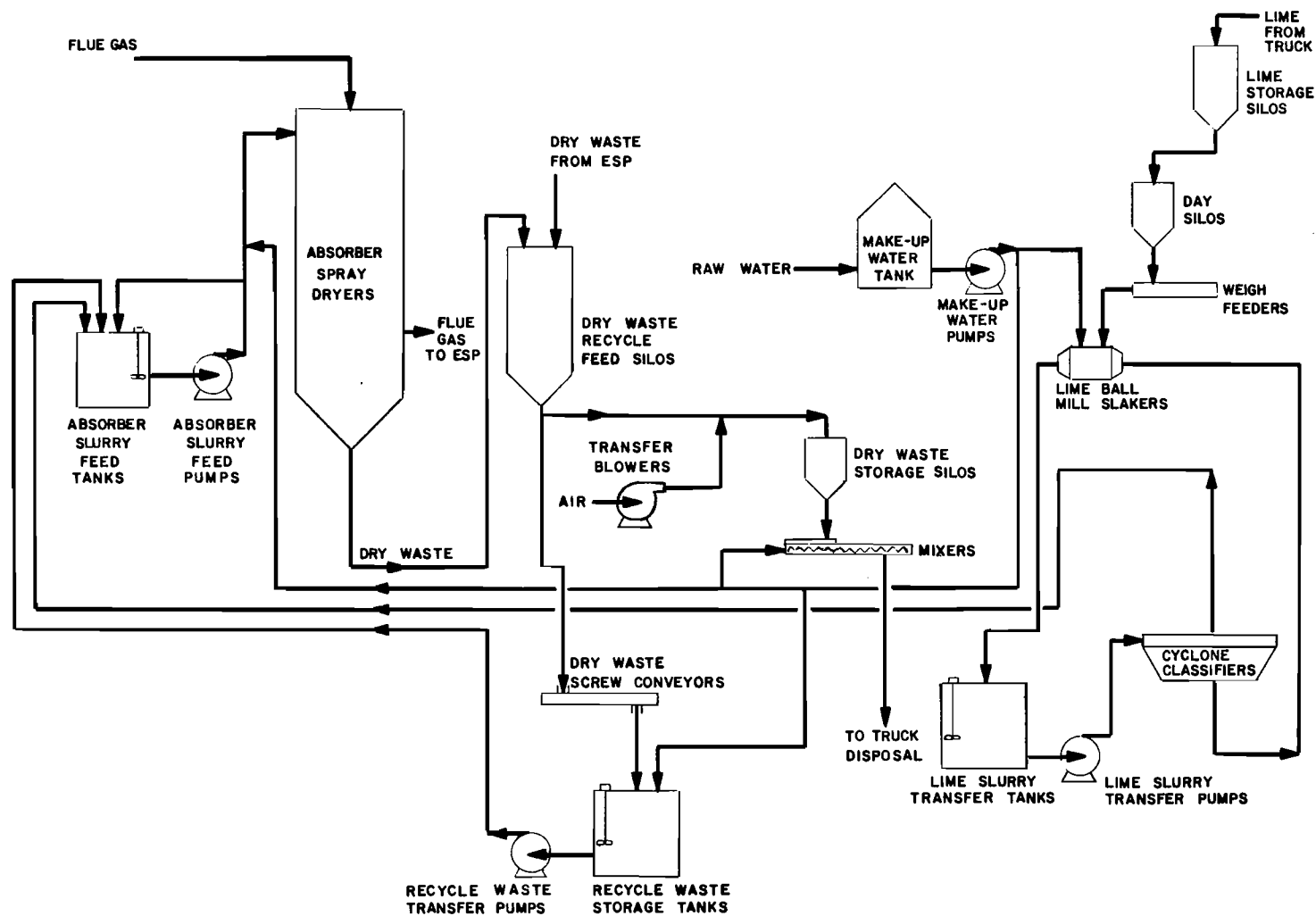
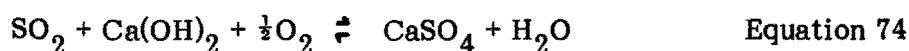
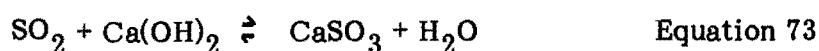


Figure 36. Dry lime FGD process.

The water feedrate is controlled by the temperature at the absorber exit which has to be maintained above saturation for the process to remain dry. Recovered solids are stored in intermediate silos. They are stabilized by the addition of water in mixers. The stabilized waste is essentially similar to that obtained from any of the wet lime based processes and can be disposed of in the same manner (see Section 6.2.1.3 above).

6.2.11.2 Principal chemical reactions. The SO_2 is absorbed to form calcium sulphite and calcium sulphate. The overall equations being:



The calcium products are hydrated as $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The detailed chemistry is identical to that described for the lime process (Section 6.2.2).

6.2.11.3 Design considerations. The once through nature of the process gives a distinct trade off between SO_2 recovery and lime utilization. At a stoichiometrically equivalent feed rate the two are equal. Absorption efficiency is also closely related to the approach to saturation. The closer the approach (i.e. the cooler the absorber outlet gas) the longer the droplets take to dry, and since absorption is more rapid in the liquid phase than the solid, the more efficient the absorption. Conversely, however, the closer the approach to saturation, the higher the risk of an operational upset producing a wet rather than a dry product with the consequent downtime that would be required to unblock the absorber and, more importantly, the baghouse or ESP. A 25°C approach is typical. Lane (1979) gives a detailed discussion of the design parameters for a spray drier absorber system. Figure 37 shows the typical variation of SO_2 removal and reagent utilization as a function of stoichiometric ratio. In some cases the recycle of a portion of the solid drier product will economically increase reagent utilization.

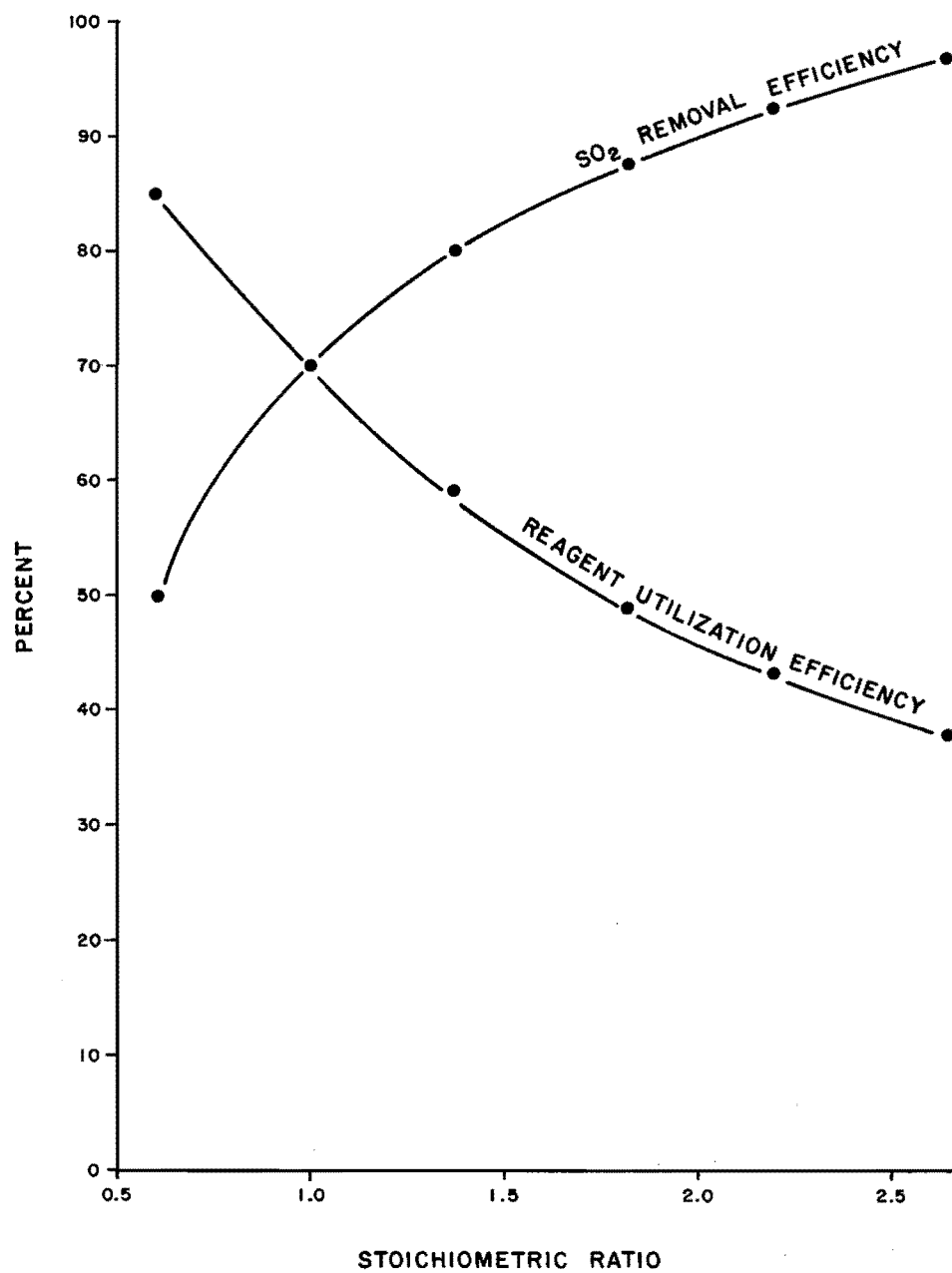


Figure 37. Dry lime process. Lime utilization and SO₂ removal efficiency.

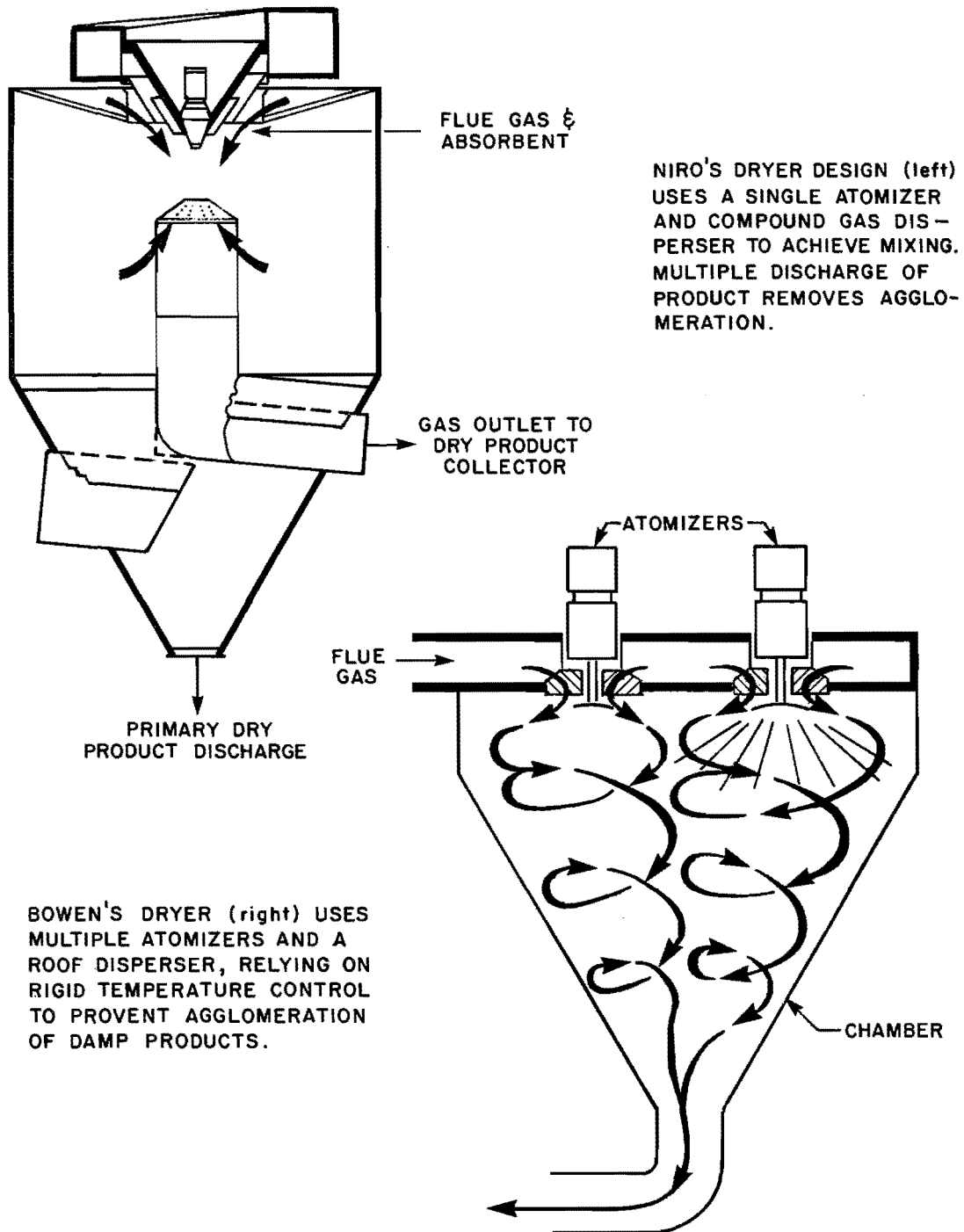
Quite obviously the need to maintain a dry absorber product coupled with a maximum possible reagent concentration in the feed (generally taken as 0.3 mass fraction of calcium hydroxide) means that there is an SO_2 feed concentration above which the process cannot work at the efficiencies quoted above. This limit corresponds to a fuel containing about 0.06 mass fraction sulphur which means that the process cannot be considered for the combustion of fluid coke in an oil sands complex but only for the treatment of CO boiler flue gas. (Fluid coke contains about 0.09 mass fraction sulphur and gives about 0.015 mass fraction SO_2 in the flue gas. The CO boiler flue gas typically contains 0.006 mass fraction SO_2 , less if the tail gas from the sulphur plant is fed to the boiler).

The key mechanical item in the absorber is the rotary atomizer or two phase nozzle that produces the slurry spray. Several proprietary designs are available; two are shown in Figure 38.

6.2.11.4 Transient conditions. The use of either single or multiple atomizers can achieve turndown to 20% of normal throughput on a single module if required (Midkiff 1979a).

The response of the system to an SO_2 excursion in the feed gas is limited by the necessity of maintaining a dry product as discussed above. Clearly the closer the normal design is to the upper SO_2 limit the more limited the ability to adequately respond to an SO_2 excursion in the feed.

6.2.11.5 Efficiency and reliability. Potential SO_2 removal efficiency and its interaction with reagent utilization has been discussed above. 90% removal is generally considered the upper limit making the process less suitable for critical duties than the wet processes. Reliability from full scale installations has not been reported. The system has many features in common with a wet system (e.g. lime storage and handling, slurry preparation, waste stabilization) but lacks the dewatering and recycle systems. The reliability of a proven industrial system could therefore be expected to be as good or better than that of a wet slurry system (i.e. in the 90% to 95% range).



DRYER DESIGN

Figure 38. Rotary atomizers.

6.2.12 Shell-Copper Oxide FGD Process

The flue gas is treated by an electrostatic precipitator before entering the FGD system. The absorber consists of a dry copper oxide acceptor which picks up SO_2 from hot flue gases. The chemical reaction produces copper sulphate. Multiple absorber vessels must be used in order that vessels can be taken out of service for regeneration. The copper oxide acceptors are regenerated by passing a hydrogen rich gas through the absorber vessel.

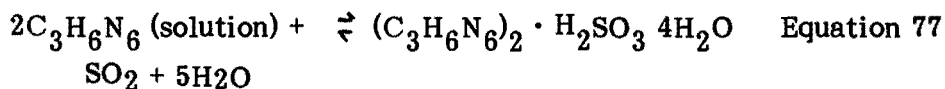
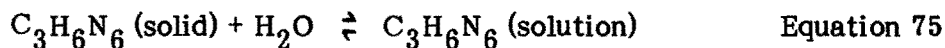
After leaving the absorber, the flue gas passes through an air preheater where process energy is recovered before the gases are discharged to the stack.

The SO_2 which is re-evolved during the regeneration step is processed through a water gathering system, a reduction reactor and finally a Claus Unit where it is converted to elemental sulphur.

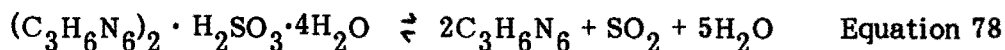
Problems have been experienced with poisoning of the copper oxide by trace impurities in the flue gas. Once poisoned the copper oxide is difficult to regenerate. As can be seen from Table 7 the process has not been installed at any utilities in the USA and is very unlikely to be considered for an oil sands plant.

6.2.13 The Melamine FGD Process

A wet regenerable process employing a melamine slurry to remove SO_2 from flue gas has been reported in the literature (Gautney et al 1982). The process employs melamine ($\text{C}_3\text{H}_6\text{N}_6$) to remove SO_2 according to the following equations:



Regeneration comprises reversing Equation 77 by thermal decomposition at 100 to 200°C.



As can be seen from Equation 78, the SO_2 byproduct is heavily diluted with water vapour. The low regeneration temperature is the main advantage claimed for the process, SO_2 removal of 95% is reported. As yet the process has only been demonstrated in the laboratory and extensive development would be required before implementation on an industrial scale.

6.3 PROCESS ECONOMICS

Capital and operating costs are presented in Table 12 for FGD plants treating 985 t/h ($1\,370\,000\text{ m}^3/\text{h}$) of flue gas containing 0.006 mass fraction SO_2 . This would be typical of the flue gas from a CO boiler utilizing the fluid coker burner gas on the size of plant specified for this study. To facilitate comparison with other published data for FGD systems, generally related to utilities, it should be noted that this is equivalent to a 250 MW unit.

Capital costs for regenerable processes only include the equipment described in the relevant section above. The cost of additional equipment that would be required to recover either sulphur or sulphuric acid from the SO_2 byproduct is excluded.

Data for all of the established processes (limestone, lime, double alkali, aqueous ammonia, Wellman-Lord, dry lime) are based on previous detailed estimates and expected to be $\pm 30\%$. Data for the other processes have been taken from Jahnig and Shaw (1981) with corrections for escalation and Fort McMurray conditions. For these processes which are less developed, accuracy can not be expected to be as high and potential process development to an industrial scale is likely to increase rather than decrease the cost.

All capital cost data refer to a new plant. Costs for a retrofit unit could be expected to be up to 60% higher for reasons displayed in Table 13.

Disposal costs are included for waste products (stabilized sludge, gypsum, and fly ash purge). Potential byproducts (ammonium salts, sodium sulphate, concentrated SO_2 streams) are neither charged nor credited since their value is highly dependent on market forces. It may reasonably be assumed, however, that a decision to proceed with a regenerable process would not be taken unless the additional cost associated with the treatment of the byproduct was more than offset by the potential revenue from it.

Tables 14 and 15 show the chemical demands and byproduct production rates of the processes.

Table 12. Capital and operating costs for FGD plants.

Process	Capital Cost ^a	Annual Operating Cost ^b				
		Labour	Utilities	Materials	Byproduct Disposal	Total
Limestone	85.0	1.8	2.7	3.1	2.4	10.0
Lime	80.0	2.1	2.5	6.1	2.1	12.8
Double Alkali	75.0	1.6	2.1	6.7	2.1	12.5
CT-121	65.0	1.8	2.7	2.5	1.5	8.5
Aqueous Ammonia ^c	65.0	1.4	11.4	0.6	3.4	17.0
Wellman-Lord	125.0	1.6	13.3	4.1	0.3	9.9
Magnesium Oxide	92.0	1.6	6.4	1.6	0.3	9.9
Citrate	82.0	1.5	4.8	3.4	0.3	10.0
Dry Lime	83.0	1.8	2.6	8.7	2.6	15.7
Copper Oxide	95.0	2.0	4.3	1.0	0.3	7.6

^a Total installed capital costs.

^b No byproduct credit included.

^c Aqueous ammonia assumed to be available at zero cost. (Commercial cost would add $\$3.7 \times 10^6/\text{a}$ to the materials cost).

^d All costs in millions of mid 1982 Canadian dollars.

Table 13. Typical capital cost variation with various retrofit requirements.

<u>Retrofit Requirements</u>	<u>Capital Cost increase %</u>
Long duct runs	4 to 7
Tight space	1 to 18
Delayed construction	5 to 15
New stack	6 to 20
Overall	1 to 60

^a Adapted from original table in Devitt et al (1976).

Table 14. Annual raw material demand for FGD processes.

FGD Process	Raw Material Demand ^{a,b}				
	Limestone t/a	Lime t/a	Soda-Ash t/a	Ammonia t/a	Other
Limestone	69 000	3 100	-	-	
Lime	-	42 000	-	-	
Double Alkali	-	38 000	3 250	-	
CT-121	58 200	-	-	-	
Aqueous Ammonia	-	-	-	12 750	
Wellman-Lord	-	-	5 150	-	
Magnesium Oxide					1 000 ^c
Citrate					3 600 ^d
Dry Lime					

^a Demands relate to 7 500 h/a operation.

^b All chemicals quoted at 100% purity.

^c Magnesium Oxide.

^d Sodium salts (thiosulphate, hydroxide, citrate).

Table 15. Annual byproduct production for FGD processes.

FGD Process	Byproduct Production Rate (t/a)						
	Wetted ESP Flyash	Prescrubber Purge	Sulphate Purge	SO ₂ ^a	Ammonium ^b Salts	Stabilized Sludge	Gypsum ^c
Limestone	-	-	-	-	-	200 000	-
Lime	-	-	-	-	-	175 000	-
Double Alkali	-	-	-	-	-	175 000	-
CT-121	17 000	15 000	-	-	-	-	100 000
Aqueous Ammonia	17 000	350 000	-	-	222 000	-	-
Wellman-Lord	17 000	15 000	8 500	33 250	-	-	-
Magnesium Oxide	17 000	15 000	-	33 250	-	-	-
Citrate	17 000	15 000	-	-	-	-	-
Dry Lime	-	-	-	-	-	215 000	-

^a Quoted as 100% SO₂.

^b 0.25 mass fraction aqueous solution.

^c Quoted as CaSO₄ · 2H₂O.

Generally, both capital and operating costs of all processes fall in a relatively narrow range. Exceptions are the Wellman-Lord process with a higher capital cost, the aqueous ammonia process with a high purge rate and cooling water demand and the dry lime process with its comparatively inefficient reagent utilization. While the regenerative processes do not require a large continuous reagent supply or generate byproducts requiring disposal, they do all have a large energy demand for the regeneration step which tends to offset this. It should also be noted that the only regenerative process that has been extensively operated, that is, the Wellman-Lord process, has significantly higher capital costs than the others. As noted above, the costs for the remaining regenerative processes must be considered somewhat more speculative until greater experience has been obtained.

6.4 RETROFITTING

6.4.1 Introduction

While many of the processes would pose similar problems in a retrofit situation, there are some significant differences. In all cases it should be noted that a retrofit that was envisaged at the time of the original plant design and planned for by, for example, the provision of adequate plot space and suitable break in connections, will be immensely easier than a "surprise" retrofit.

The limestone FGD system is described below in some detail. Other systems are only described in so far as they are notably different to the limestone system. As can be seen from Table 7, retrofit FGD units are extremely common in the USA.

6.4.2 Limestone FGD Process

In principal the retrofitting of a limestone FGD unit is a relatively simple operation involving the installation of the unit between an existing electrostatic precipitator and stack. Interaction with other process units is minimal.

In practice a number of problems can arise whose relative severity will vary at specific locations. Some of these are detailed below:

1. The FGD system will impose a new power demand on the site, effectively lowering the efficiency of the boiler to which it is attached. This in turn may upset the site power balance to the point where an extra demand is placed on the provincial grid.
2. The FGD system occupies a substantial plot area. Reagent storage, absorption equipment and sludge stabilization required for treatment of a typical oil sands CO boiler flue gas handling 1000 t/h would occupy a total of about 10 000 m². If no provision for this area was made in the original plant layout then considerable disruption to site operation will be caused by the retrofitting operation.
3. Should a unit have to be located further from the flue gas source than would be the case in a grass roots facility, additional booster fans with their associated power demand may well be required.
4. In many cases the tail gas from the sulphur plant is passed to a CO boiler for conversion of residual H₂S to SO₂ prior to atmospheric discharge. This practice, while convenient in the absence of an FGD unit, is far from optimal once one is to be installed. This is because by comparison with the boiler flue gas the sulphur plant tail gas has a low SO₂ content (e.g., 0.2×10^{-3} cf 2×10^{-3} volume fraction). Diluting the flue gas both increases the capital cost of the FGD unit and reduces the potential efficiency of the unit (by reducing the mass transfer driving force available). In such an instance it would be advisable to consider installing a separate sulphur plant tail gas incinerator.
5. A retrofitted limestone FGD unit will produce no more sludge than a grass roots facility. However, because the opportunity to consider the disposal of this sludge in the initial planning of the oil sands surface mining operation was probably missed, the incorporation at a later stage may well pose problems that could have been averted or minimized.

6.4.3 Lime FGD Process

The same general considerations that apply in the limestone case are relevant. There is, however, one important difference. The smaller tonnage of lime required coupled with the need to store it in vertical silos rather than on the ground means that a smaller overall plot area is required for the process, typically only 60% of that needed for the limestone process. This has obvious merit in the typical retrofit situation where space is at a premium.

6.4.4 Double Alkali FGD Process

The process can be considered in the same category as the lime based process.

6.4.5 Chiyoda Thoroughbred FGD Process

The process can be considered in the same category as the limestone FGD process.

6.4.6 Aqueous Ammonia FGD Process

The use of valve trays rather than a spray tower imparts a slightly higher power consumption to the process, the impact of which would have to be considered.

The potential use of available sour water eliminates the requirement for a large raw material storage area, and the direct disposal of the absorber product eliminates the need for any regeneration equipment. The process, therefore, has an obvious attraction in a retrofit situation where space is at a premium.

Because the only effluent produced by the process is the small fly ash purge stream from the pre-scrubber, the integration of the disposal system into an existing mine is considerably easier than with any of the lime based processes.

6.4.7 Wellman-Lord FGD Process

Any regenerative process is likely to be more complicated and have higher utility demands than a simple throwaway process. This is reflected in the capital and operating costs and also in the potential impact of a retrofitted plant.

By comparison with processes described earlier the Wellman-Lord process does not require such a large plot area because there are virtually no raw materials to store. Power consumption is comparable and the process has a large steam demand unlike any of the throwaway processes. Additionally the process, again unlike the throwaway processes, places a new demand on the downstream Claus plant, whose capacity may have to increase by between 10% and 30% depending on which flue gas stream is treated.

The process produces a concentrated SO_2 byproduct which has to be transferred to the Claus plant. In a retrofit situation the route that this line will have to follow could be far from optimal from both an economic and a safety standpoint.

On balance, therefore, the problems of retrofitting the Wellman-Lord process are more severe than those of a throwaway process and this can be considered as the price of regaining the sulphur in a useful form.

6.4.8 Magnesium Oxide FGD Process

The complication associated with any regenerative process retrofit will be applicable in this case. By comparison with the Wellman-Lord process the relatively weak SO_2 byproduct stream will be even harder to integrate into an existing plant.

6.4.9 Dry Lime FGD Process

By comparison with the wet systems there are three major differences to be considered:

1. The impact on the existing plant utility system will be lower.
2. The loading on the solids removal system will be higher after retrofitting and will probably necessitate an increase in its capacity.
3. The process is installed between the flue gas source and the solids removal system. This will almost certainly generate more complications for the break-in piping design than would be the case in a wet system which is downstream of both.

6.5 APPLICABILITY OF FGD PROCESSES TO OIL SANDS PLANTS

Only two of the processes described (aqueous ammonia and dry lime) have technical limitations on the maximum SO_2 content of the flue gas that would limit their application in an oil sands complex. Specifically they could not be considered for the treatment of the flue gas resulting from the combustion of high sulphur residues.

Regenerable processes are technically feasible but will only justify the additional investment and operating complexity entailed if either the market for sulphur byproducts improves considerably or the waste byproducts from the throwaway processes become an unacceptable environmental concern.

In the case of a surface mined oil sands plant where the mine area available for disposal will always greatly exceed that required to contain the sludge there is no immediate reason to suppose that this will be the case.

Historically oil sands plants have endeavoured to rely on proven technology where possible. Reference to Table 11 shows that a continuation of this policy would result in one of the lime based throwaway processes being the most likely candidate. The greater installed capacity of the limestone process may be offset by the slightly higher removal efficiencies of the other processes. In a retrofit situation the large plot area required for limestone storage may also become an offsetting factor.

In conclusion, it can be stated that experience at utilities in the USA has demonstrated that flue gas desulphurization can now be regarded as proven technology. This was certainly not the case when the two existing oil sands plants were built. The decision as to whether to install FGD units on future oil sands will be dictated by the sulphur balance and environmental cost benefit analysis associated with the specific project.

7. RESIDUE GASIFICATION

7.1 INTRODUCTION

With dwindling supplies and rising prices of petroleum and natural gas, coal has increasingly been looked upon as a source of energy as well as a feedstock for chemical products. The need to utilize coal in an environmentally acceptable manner (i.e., with minimal emission of particulates and combustion products, such as SO_x and NO_x) as an alternate source of energy has been recognized for a number of years. Gasification of high sulphur residues and solid fuels such as petroleum coke and coal followed by appropriate purification of the gasified products is an environmentally acceptable means of utilizing these normally polluting fuels. The coal gasification process routes used to utilize coal and produce a fuel gas or synthesis gas are shown in Figure 39.

Bitumen extraction and subsequent upgrading of bitumen form two major operations in the production of synthetic crude oil from oil sands. Most bitumen upgrading processes produce residue byproducts containing a significant amount of carbon (more than 0.7 mass fraction) and fines. Depending upon the upgrading process employed, this residue may be fluid or delayed coke; H-Oil, Eureka, or CANMET pitches; or others. This residue may amount to about 10 to 14% of the crude oil produced in a bitumen upgrading facility. Two commercial upgrading plants employing the delayed coking and fluid coking processes are in operation in Fort McMurray, Alberta. Although the byproduct coke has a higher heating value of around 33 MJ/kg (Antony, Desai and Friedrich 1981), the high sulphur content of about 0.05 to 0.09 mass fraction makes the coke difficult to utilize in a conventional manner, i.e., direct combustion. Despite this, the delayed coke from the Suncor plant at Fort McMurray is being utilized as boiler fuel for direct fired furnaces. This has proved to be troublesome in terms of environmental impact, and inefficient for heat recovery and carbon conversion. This inefficiency coupled with more stringent government regulations for sulphur emissions precludes this option for future facilities.

However, due to the high costs associated with the other methods of utilization of these residues and the potential for future improvements in

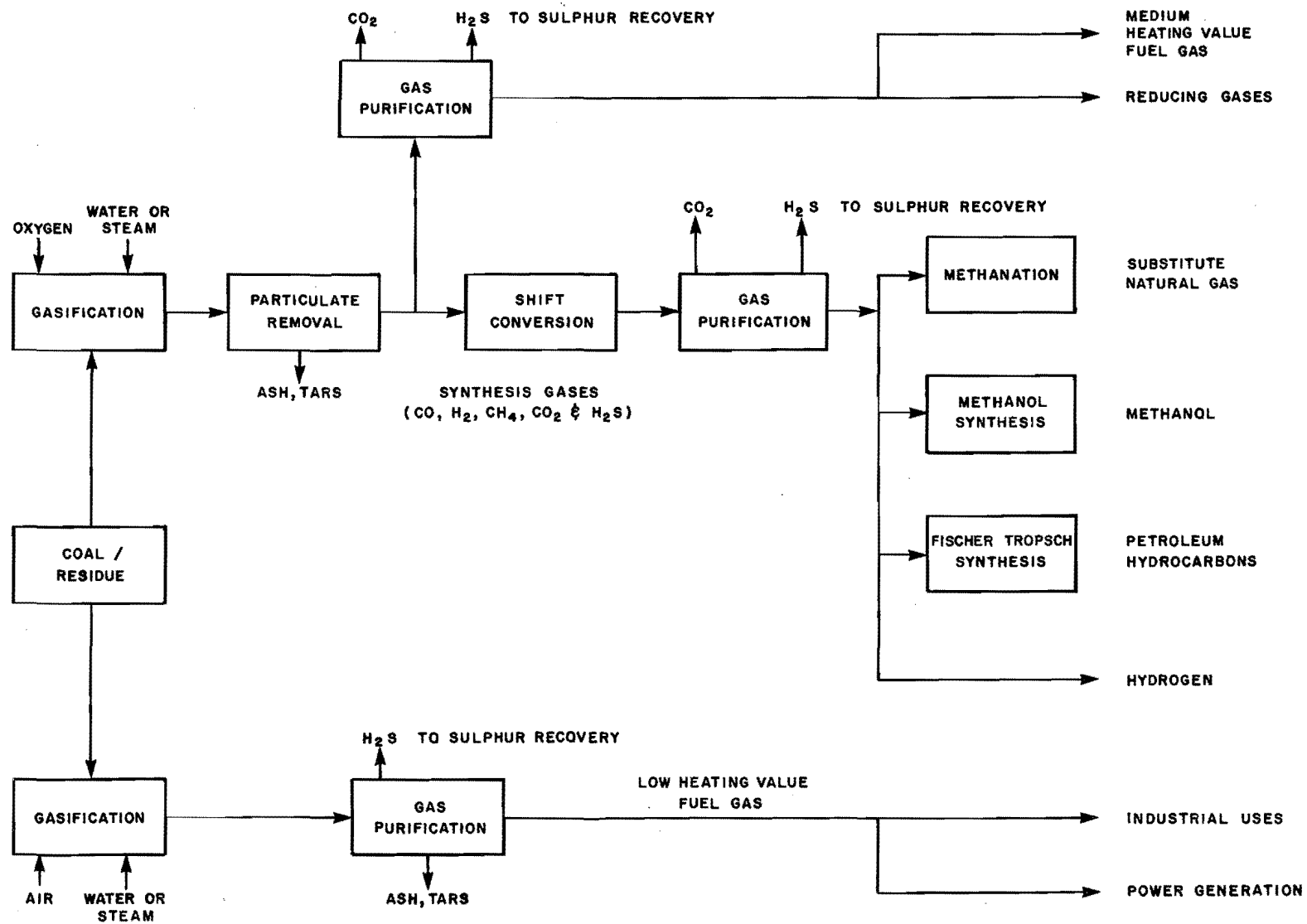


Figure 39. Coal/residue gasification process routes.

utilization technology, the fluid coke produced at Syncrude's Mildred Lake is presently being stockpiled. This coke amounts to 1 million cubic metres per year. An area of 5 km² will be required for stockpiling over the 25 year projected life of the project. This represents an incomplete utilization of the resource and an additional environmental consideration.

The need to utilize these byproducts has been emphasized by both the Energy Resources Conservation Board and the various companies associated with oil sands development. Three potential means of utilizing this residue are envisaged. These are discussed below.

7.1.1 Direct Combustion

In spite of the high sulphur content of these residues, direct combustion means are being sought and various technologies to cope with this sulphur are being developed. A brief discussion of one such alternative, fluidized-bed combustion, is presented in Section 8. of this report.

7.1.2 Residue Gasification

The phenomena of converting the solid carbon content of coke or pitch or coal to a gaseous product in the presence of steam and air or oxygen is termed gasification. Gasification of the residue from an overall environmental standpoint is superior to direct combustion. It utilizes residue with no new sources of sulphur emissions, no additional land surface disturbances and minimal stockpile requirements.

The process involves the following major chemical reactions:





The sulphur in the residue reacts with the produced hydrogen to form hydrogen sulphide.



The synthesis gas ($\text{CO} + \text{H}_2$) thus produced can be utilized in various ways in petrochemical processes and industry.

A major oil sands project will have large requirements for electric power, steam, and hydrogen for oil sands excavation, primary and secondary upgrading processes, and for general utility purposes. The gasification of residues can effectively be employed to provide any of these requirements. However, detailed discussion of the application of coke gasification in an oil sands project is considered to be outside the scope of this study. A brief discussion is presented below.

7.1.2.1 Utilization as medium heating value fuel gas. The combustion characteristics of the medium heating value (mhv) fuel gas produced are close to those of natural gas. The mhv gas can be substituted for natural gas and combusted with minimal modifications to burners and furnaces. The production of mhv gas requires air or oxygen plus steam feeds to the gasifier (Figure 40). The hot, raw gas from the gasifier is cooled in a waste heat boiler. Solids and hydrogen sulphide are removed before the gas is made available to the burners and furnaces.

Presently, residue gasification to produce medium heating value fuel gas for an oil sands project does not appear to be promising since natural gas is available at low cost. However, this may become attractive in the event of future increases in natural gas prices, improvement in gasification technology, or in-plant usage of the mhv product gas (Ambrose and Flynn 1977).

7.1.2.2 Utilization for generation of power by combined cycle. The potential application of coal gasification in Canada appears to be as a medium or low heating value fuel gas in specialized applications such as combined cycle power generation (Figure 41). The stringent sulphur emission laws will en-

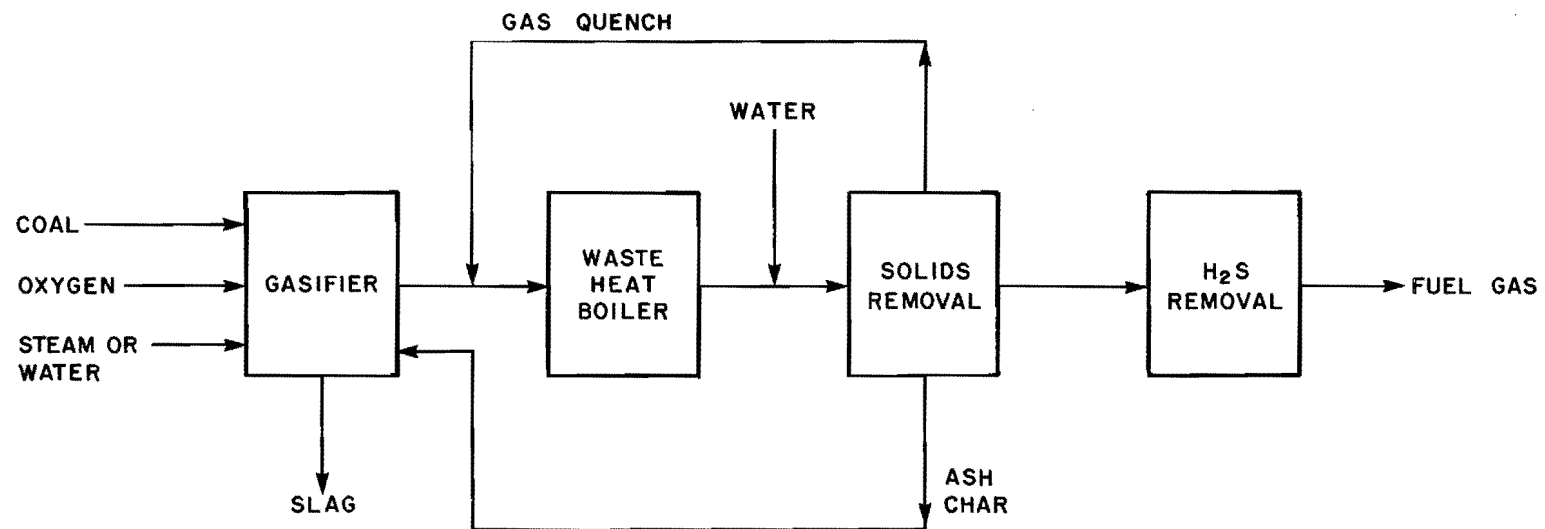


Figure 40. Typical configuration for gasifier based fuel gas production.

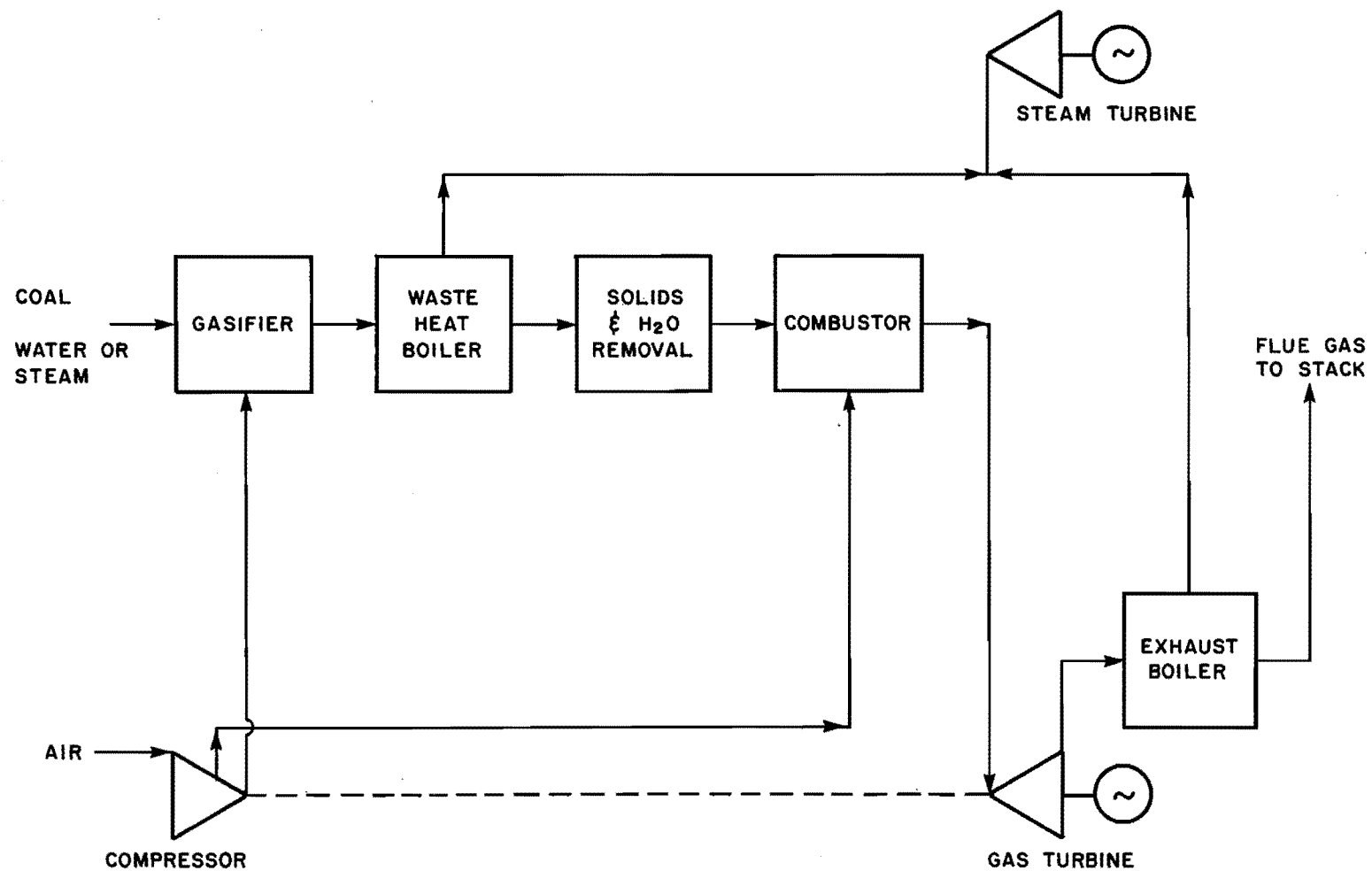


Figure 41. Typical configuration for gasifier based combined cycle power generation.

courage gasification in the power industry since combined cycle power generation has environmental and efficiency advantages over the conventional pulverized coal fired power generation followed by flue gas desulphurization. For the present, power generation by direct combustion of coal is limited to coals with low polluting properties. A promising method of utilization of coals with high sulphur and metals content is to gasify the coals, remove the harmful contaminants, and burn the resulting clean gas in a conventional combustion turbine to generate power. This method results in minimal environmental impact and makes possible the use of high sulphur coals and residue from oil sands. Fluidized bed combustion technology (discussed in Section 8) may also be suited for this purpose.

In the case of oil sands, direct power generation from residue is economically unattractive when compared to coal fired alternatives. The poor combustion properties of the coke require recycling of unburned carbon, support fuel, and flue gas desulphurization. The location of the plant, distant from the load center, will further increase the cost of deliverable power attainable from residue coke.

7.1.2.3 Utilization for chemical production. The raw gas can be utilized to produce hydrogen (Figure 42). The hydrogen thus generated can be employed in various upgrading processes in an oil sands complex.

Currently, the production of hydrogen by natural gas reforming has economic advantages over gasification. If the oil sands complex were to require a high degree of flexibility in other areas such as the location of potential steam flooding or carbon dioxide injection sources, then supplementation of the plant with steam for the turbines, fuel gas for firing, and/or hydrogen for refinery operations, all produced as a result of residue gasification, may be an attractive proposition. The high sulphur in the residue produces hydrogen sulphide which is subsequently removed by a cleanup process and oxidized in the Claus plant to form elemental sulphur. The heat recovered as steam may be employed in the various purification, extraction, and utility sections of the project.

The gasification of residue to produce a syngas of carbon monoxide and hydrogen can be used to provide the feedstock for numerous chemical

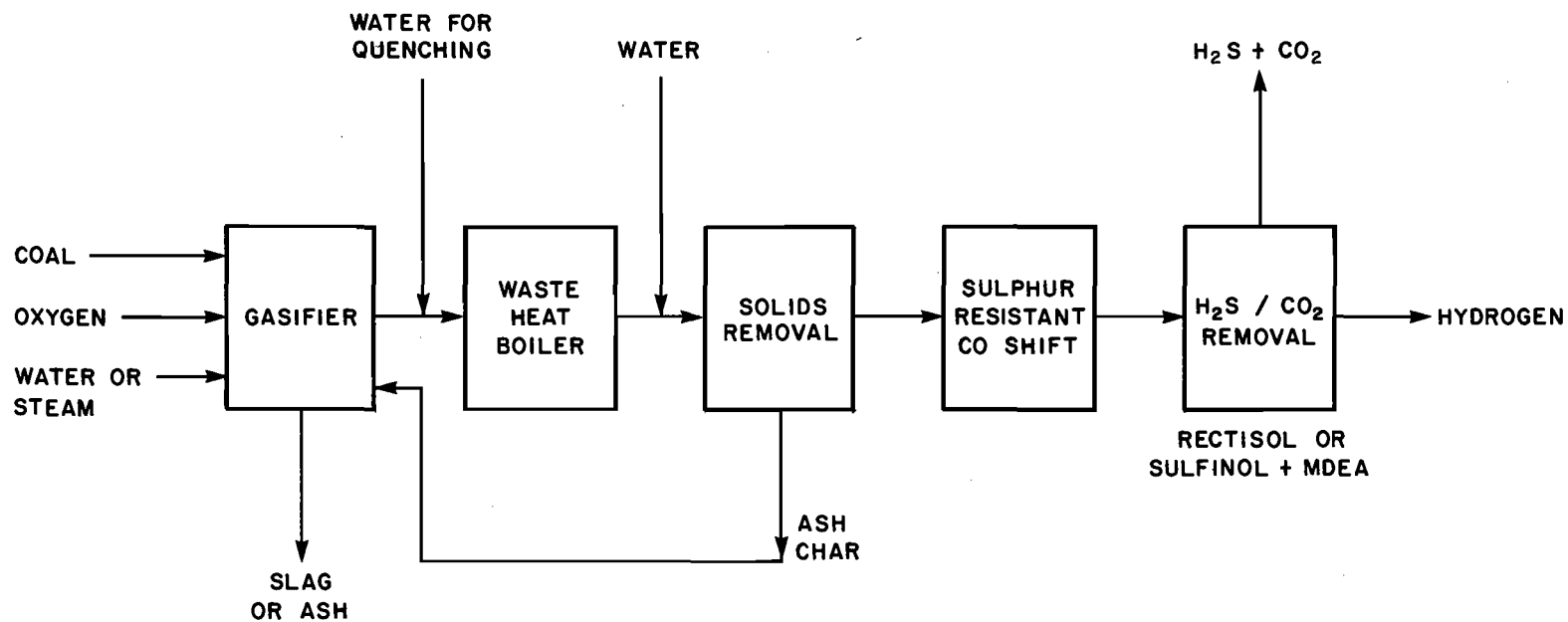


Figure 42. Typical configuration for gasifier based.

manufacturing processes, e.g., the production of methanol, acetic acid, ammonia, etc. (Figure 43).

The numerous applications for syngas produced via coal gasification have not been extensively commercialized by the modern petrochemical industry. This is primarily due to the fact that the gasification processes represent a high investment cost for technologies (processes) that most petrochemical companies feel unfamiliar with, and the overall conservatism of the petrochemical industry, in general.

The existing commercial gasifier units being proposed, and also under construction, are capable of processing 800 to 1000 t/d of coal. They are used to produce low or medium heating value gas.

7.1.3 Speciality Markets

The speciality uses of residue seem to be limited to usage for making bricks, solid building materials, road construction, etc. The use of coke, for example, in manufacture of electrodes and metallurgical coke is prevented by its high sulphur and metal contents (Ambrose and Flynn 1977).

7.2 **APPLICABILITY OF RESIDUE GASIFICATION TO OIL SANDS PLANTS**

The potential uses of residue gasification in Canada focus on a direct route using air or oxygen blown processes. As yet a firm commitment has not been made. Revisions to ongoing development programs would necessitate review to achieve a viable integration. The Alsands Group planned to implement fluid coke gasification in their project and to phase in gasification technology for the production of hydrogen. This is believed to represent the soundest approach for achievement of reliable economic operation while maximizing the utilization of byproduct coke.

Prior to utilization of the fuel gas for power generation or hydrogen production, the raw syngas must be stripped of undesirable byproducts. The byproduct formation depends on the coal composition and the gasification process employed. The syngas primarily consists of carbon monoxide, hydrogen, methane, carbon dioxide, nitrogen, hydrogen sulphide, and small quantities of other hydrocarbons.

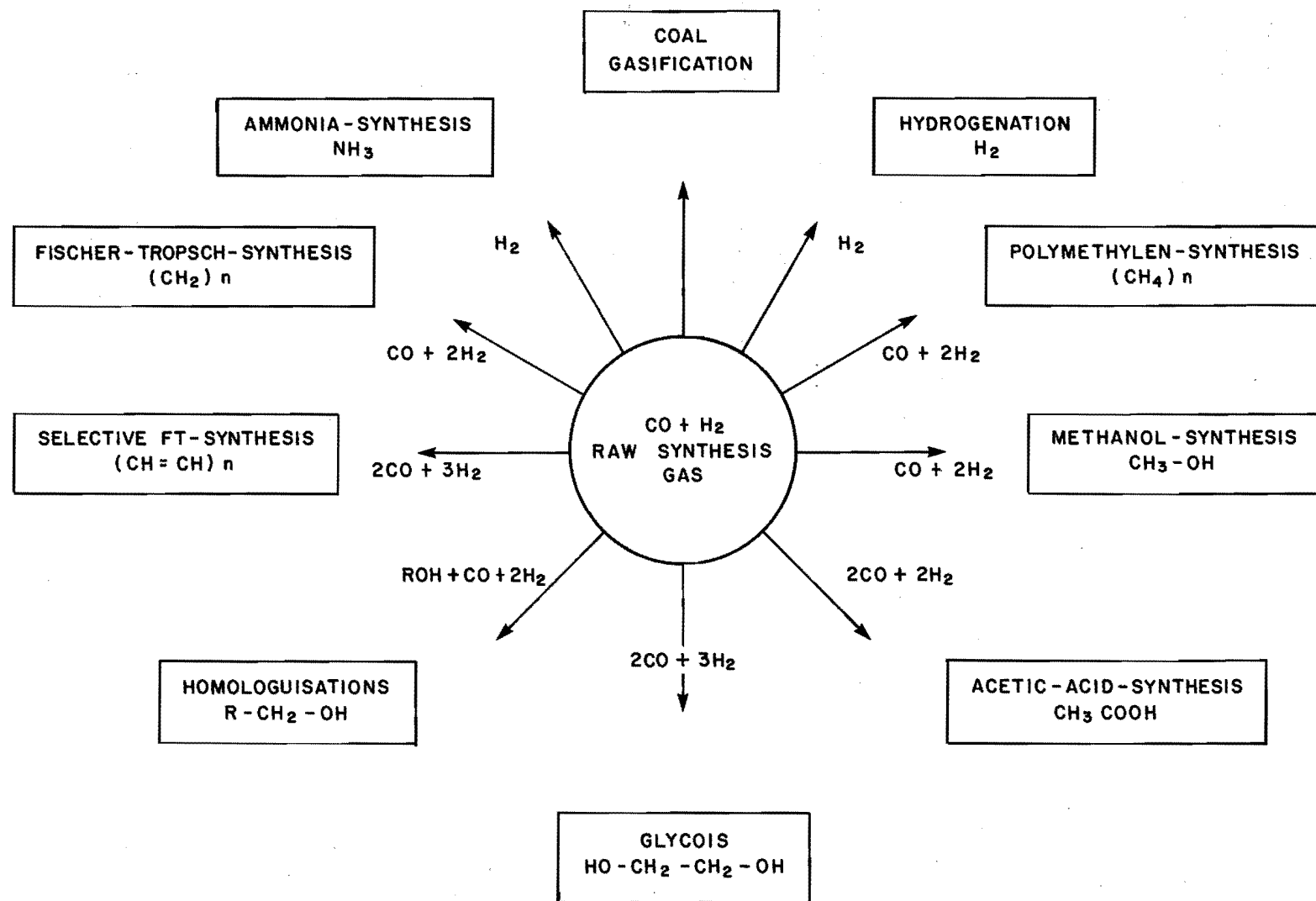


Figure 43. Hydrogen/carbon monoxide based chemical processes.

Depending on the end product desired, the downstream processes include various physical and chemical separation processes. A detailed description of these processes is beyond the scope of this study.

The selection of the process most applicable to either coke or residue gasification from the various alternatives available, as shown in Table 16, requires considerable understanding of the gasification technology and its implications. Since coke gasification is one of the major operations in an oil sands project, a careful energy integration is also required.

A number of factors influence the selection of a gasifier most suitable for a particular application. In the case of oil sands, some of these factors are:

1. Ability to process residue from potential bitumen upgrading processes, i.e., fluid coke, H-Oil pitch, Eureka pitch, or CANMET pitch.
2. Utilization of raw gas.
3. Suitability for high capacity and throughput.
4. Ability to process coke with a sulphur content as high as 0.09 mass fraction.
5. High thermal efficiency.
6. High quality product - minimal byproducts and entrained material.
7. Compatability with upstream and downstream processes.
8. Minimal environmental impact.
9. Operating flexibility.
10. Minimal operating problems.
11. Commercial history or proven ability.
12. Economics of the project.

In addition, the location of a gasifier in the northern parts of Alberta may require additional consideration because of climatic conditions.

The characteristics of the residue are dependant on the upstream upgrading process. They affect the selection of a gasifier and the corresponding downstream gasification processes. To avoid an unacceptable risk to the overall oil sands project economics, candidates for the primary

Table 16. Coal gasification processes.^a

No.	Gasification Process	Type of Reactor Bed	Operating Pressure, kPa
1	Lurgi	Fixed	600 to 3500
2	Lurgi/BGC Slagger	Fixed	600 to 3500
3	Lurgi-Ruhrgas	-	Atms
4	Kopper-Totzek	Entrained	100 to 200
5	Winkler	Fluidized	100 to 200
6	High Temperature Winkler	Fluidized	1 000
7	WD/IGI	Fixed	100 to 200
8	Williputte	Fixed	100 to 200
9	ATGAS	Molten Iron Bath	100 to 200
10	CO ₂ Acceptor	Fluidized	600 to 3500
11	Molten Salt	Molten Salt Bath	6500
12	Synthane	Fluidized	6500
13	U-Gas	Fluidized	600 to 3500
14	Agglomerating Ash	Fluidized	600 to 3500
15	Westinghouse	Fluidized	600 to 3500
16	Riley Morgen	Fixed	100 to 200
17	General Electric	Fixed	600 to 3500
18	Combustion Engineering	Entrained	100 to 200
19	Bi-Gas	Entrained	6500
20	Texaco	Entrained	2050 to 8270
21	Hydrane	Fluidized	600 to 3500
22	Hygas	Fluidized	6500
23	Stone & Webster/ General Atomic	-	-
24	Multiple Catalyst Process	-	-
25	Deco Process	-	100 to 200
26	COED-COGAS Multistage	Fluidized	-
27	Coaleon	Hydrocarbonization	-
28	Garrett	-	Continued...

Table 16. Concluded.

No.	Gasification Process	Type of Reactor	Operating Pressure, kPa
29	TOSCO	Fluidized	101 to 2170
30	Exxon Catalytic Process	Fluidized	3500
31	Fast Fluidized Bed Process	Fluidized	-
32	Shell Coal Gasification	Entrained	3500
33	CRG Series (A)	-	1000
34	FW-Stoic 2 Stage Gasifier	-	100
35	GE Two Stage	-	-
36	Saarberg/Otto	Entrained	100 to 2600
37	Wellman-Galusha	Fixed	100

^a Adapted from Hydrocarbon Processing, April, 1982 and Verma (1976).

upgrading process will be confined to those which are proven reliable, are commercially viable, and offer demonstrated potential for operability on Athabasca bitumen. The fluid coking process has been commercially demonstrated at Syncrude's facility. However, for future oil sands projects, residues from other upgrading processes such as the H-Oil pitch, the Eureka pitch, and CANMET pitch may also be potential alternative gasifier feeds. The selected gasifier must be able to process one of these potential feeds, with little or no complications.

Production of a medium heating value syngas with reduced quantities of entrained material lowers the downstream conditioning and scrubbing requirements and has, therefore, added economic and operability advantages. High thermal efficiency with high conversion of residue will tend to reduce byproduct formation and minimize the environmental impact.

The utilization of the clean gas from the gasifier will influence the downstream processes. Reliability and operability of all the processes required by gasification are important considerations.

The residue fluid coke produced at Syncrude's facility, is primarily very high in sulphur and metal contents (Table 17) and low in volatility. This coke has not yet been commercially gasified. The Texaco Development Corporation, however, has demonstrated gasification of the fluid coke. Their results still remain unpublished. Thus, in this report, coal gasification technology has been reviewed for adaption to residue from oil sands bitumen upgrading processes with emphasis on the fluid coke which is presently produced at Fort McMurray. The following section briefly describes some of the gasification processes.

7.3 GASIFICATION PROCESSES

Coal gasification processes can be divided into three major categories by the type of gasifier employed (Schlinger 1979). The three categories are:

1. Fixed (or slowly moving) bed.
2. The fluidized bed.
3. The entrained bed.

Table 17. Fusion characteristics and metal content of ash from Suncor coke.^a

<u>Ash fusion temperatures, °C</u>	<u>Oxidizing</u>	<u>Reducing</u>
Initial deformation	1140+	1410
Spherical softening	1480+	1480+
Hemispherical softening	+	+
Fluid	+	+

Ash Analysis

Major constituents by x-ray fluorescence

Mass fraction, dry fuel basis

SiO ₂	0.4500	CaO	0.0126
Al ₂ O ₃	0.2890	MgO	0.0101
Fe ₂ O ₃	0.0755	SO ₃	0.0001
TiO ₂	0.0323	Na ₂ O	0.0050
P ₂ O ₅	0.0033	K ₂ O	0.0129

Minor constituents by atomic absorption

ppm, dry fuel basis

V	1 050.0	Cr	5.0
Ni	440.0	Cd	0.1
As	2.0	Mo	43.0
Se	0.7	Mn	20.0
Sb	0.1	Cu	2.0
Hg	0.1	Co	6.0
Pb	8.0	Be	0.1
Ba	2.0	Zn	4.0
Sr	2.0		

^a Adapted from original table in CANMET Report No. ERP/ERL 81-27 (TR)

The principle differences in the method of gasification are:

1. The mechanical design of the gasifier.
2. The material flows in the gasifier.
3. Suitability of the various feedstocks.
4. Composition of the gases produced.
5. Environmental impact.

The three categories of gasifiers with typical temperature profiles across each are shown in Figure 44. A brief description of gasifiers within each category is given in the following sections. The suitability of these gasifiers for an oil sands application is also discussed.

7.3.1 Fixed Bed Gasifier

The fixed bed gasifier generally operates in a countercurrent mode and includes both batch and continuous processes. The Lurgi and Lurgi/British Gas Corporation slagging gasifiers are typical fixed bed gasifiers.

The fixed bed is characterized by zones of different temperatures (Kirk-Othmer 1960):

1. Ash zone at the bottom of the gasifier.
2. Oxidation zone or region of heat supply.
3. Endothermic gasification zone, where steam is decomposed and carbon dioxide reduced.
4. Devolatilizing zone where the incoming coal is dried and heated by hot gases flowing upwards.

Two well established gasifiers in this category are described below.

7.3.1.1 Lurgi Dry-Bottom Gasifier. The Lurgi dry-bottom gasifier was first commercialized in the 1930's and has since been modified to improve its capacity and operating efficiency. Presently, there are a total of 16 plants (Hydrocarbon Processing 1979) with 65 gasifiers in operation, including the SASOL I complex in South Africa. The recently completed SASOL II and the proposed SASOL III are also based on these gasifiers. These South African coal conversion plants produce a variety of products including ammonia and Fischer-Tropsch¹ derived gasoline.

¹ Fischer Tropsch: process of producing gasoline from natural gas.

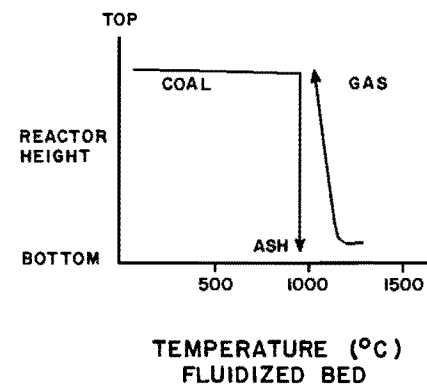
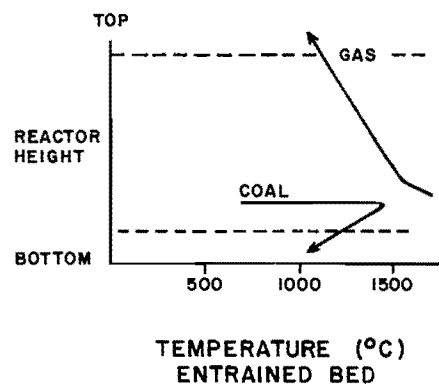
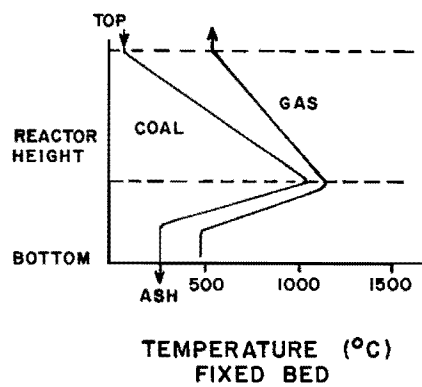
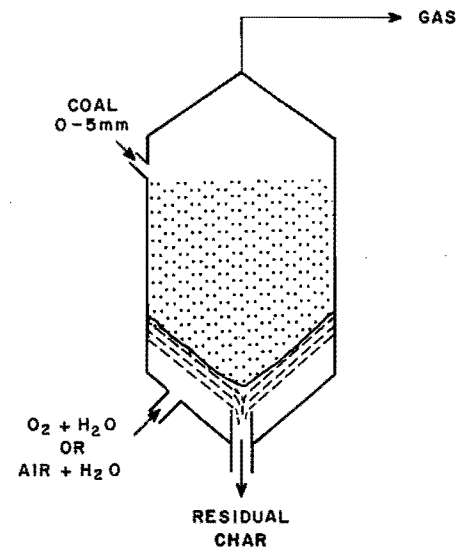
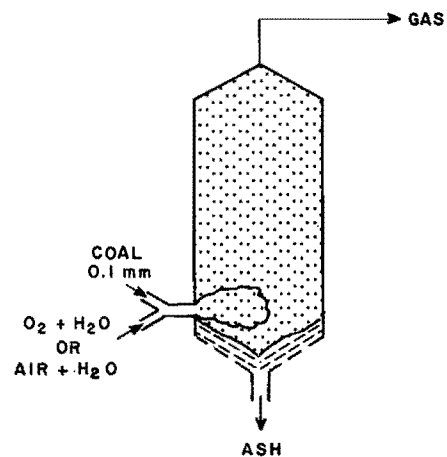
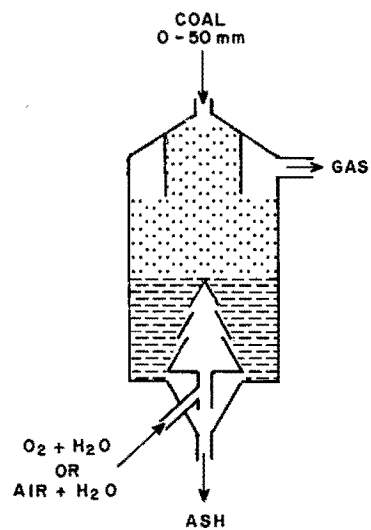


Figure 44. Gasifier classification.

The modern Lurgi gasifier (Figure 45) incorporates a jacketed pressure vessel capable of operating at 3100 kPa. Coal crushed and sized to about 50 mm (Brown 1981) is fed from a pressurized lockhopper to the top of the gasifier. A rotating distributor maintains an even surface at the top of the bed. When caking coals are used the gasifier has a continuous "in bed" agitation mechanism to minimize agglomeration effects.

A wide range of coals are currently being gasified using both air-steam and oxygen-steam. These gasification media are introduced into the gasifier bottom through a revolving grate. Dry ash drops through the grate into an ash lock chamber and is discharged periodically.

Part of the steam generated (about 20%) in the gasifier jacket is used for gasification and the rest (about 80%) is used as either process or utility steam within the complex.

The raw gas leaving the gasifier between 400 and 600°C consists of carbon monoxide, hydrogen, methane, carbon dioxide, and smaller quantities of ammonia, tar oil, naphtha, phenols, and nitrogen. Small amounts of coal dust are also contained in the raw gas. The gas is water scrubbed to remove ammonia, phenols, and particulates. The gas is cooled to condense tar and oil fractions. The phenols are removed from the water using the Lurgi Phenolsolvan process. Ammonia is removed in a final cleanup step.

The relatively high concentration (about 0.12 volume fraction) of methane in the raw gas makes it ideal for either substitute natural gas (SNG) or gasoline production. However, if hydrogen production is desired the methane acts as an inert impurity, unless the gas is passed through a steam reformer.

The Lurgi gasifier has a reported cold gas efficiency¹ of 85% (Papic 1976) for coal to synthesis gas production, converting nearly all the carbon. The oxygen consumption required for gasification is relatively low (0.2 to 0.5 t/t of dry feed). The raw gas effluent from the gasifier will contain a small amount of entrained solids. These advantages make the gasifier a viable candidate for commercial coal conversion facilities, particularly for SNG production.

¹ Cold gas efficiency - $\frac{\text{HHV of product gas}}{\text{HHV of residue}} \times 100$

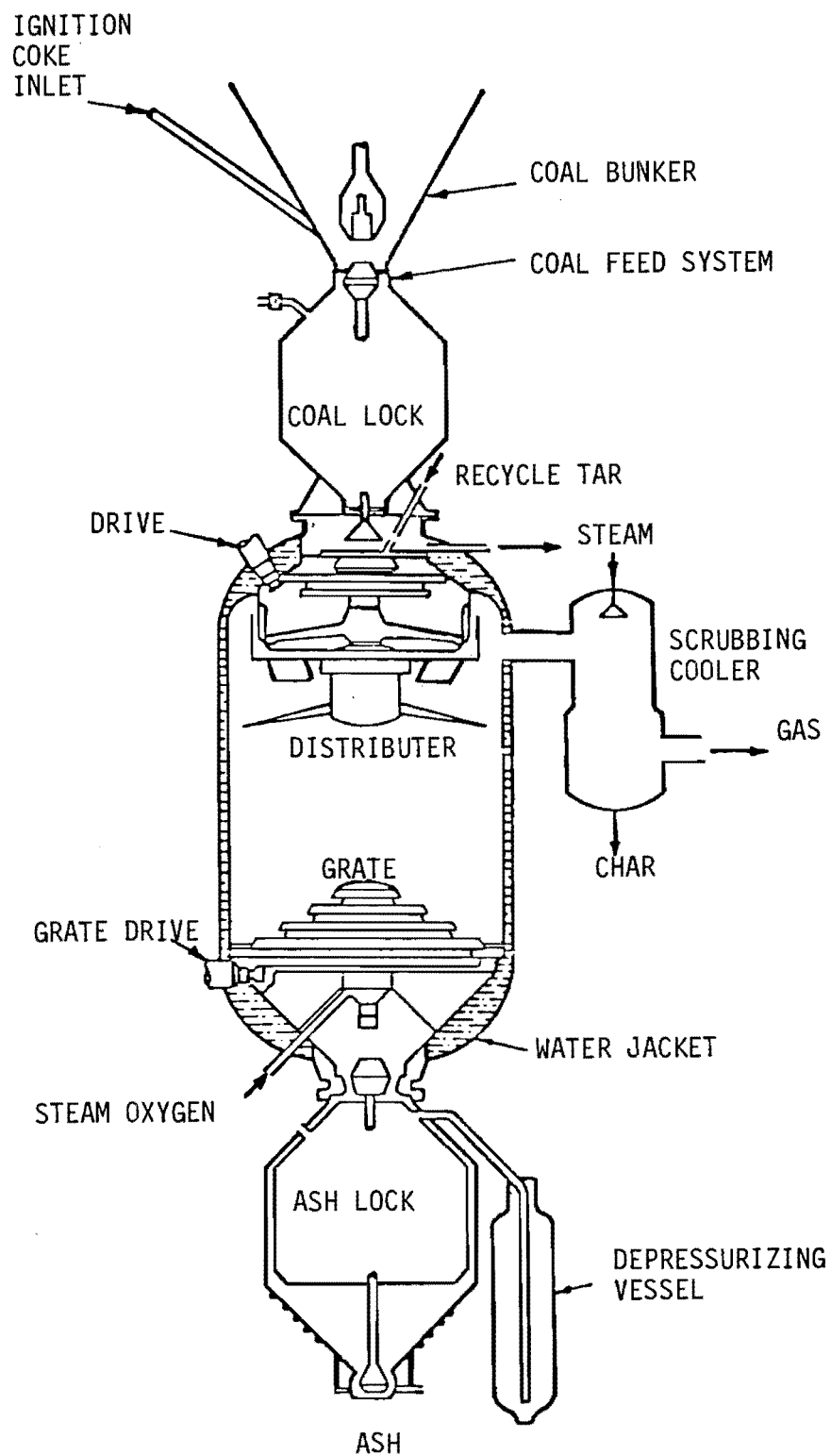


Figure 45. Lurgi dry-bottom gasifier.

In order to prevent ash from melting or slagging, the Lurgi gasifier is limited to relatively low temperature gasification, producing oil, naphtha, tars, phenol, etc. as by-products (at higher gasification temperatures these byproducts are decomposed into carbon monoxide and hydrogen). The gasifier is unable to process coal fines and high caking coals. The gasifier is mechanically complicated and is specially designed for a given type of coal (Papic 1976).

7.3.1.2 British Gas Corporation (BGC)/Lurgi Slagging Gasifier. (Bowden and Sudbury 1977; Tart and Rampling 1981.) A series of experiments carried out by British Gas Corporation on a commercial Lurgi gasifier at Westfield, Scotland have demonstrated the ability of a modified Lurgi system to be operated in a slagging mode (Brown 1981). These tests have also included sustained runs supplying synthetic natural gas to the British Gas pipeline system. Over 4000 operating hours have been logged with gasification of more than 50 000 tons of coal. A demonstration plant is being planned for Southeast Ohio by a consortium headed by Conoco Coal Development Company.

The gasifier (Figure 46) is a refractory lined pressure vessel, cooled by steam generation in a water jacket much like the original Lurgi gasifier. The principal modification of the Lurgi dry bottom gasifier is replacement of the revolving grate with a slagging hearth system and tuyeres¹ for oxygen and steam addition. Minimum quantities of injection steam (approximately 20% more than the stoichiometry of the gasification reaction) are used, while oxygen consumption is slightly higher than for the dry ash Lurgi unit. Operation in the slagging mode increases operating temperatures and hence reaction rates. Solid material leaves the slagging gasifier as a slag rather than a dry ash.

Gasification occurs at approximately 3100 kPa and about 1260°C. Due to the high operating temperature, byproduct tars and oils can be recycled and then injected through the tuyeres into the slagging area. Recycled dusty tar and coke/coal fines can be fed at the top of the gasifier.

The comparative gas compositions from the Lurgi dry-bottom and BGC/Lurgi slagging gasifier modes of operation are shown in Table 18 (Brown

¹ Tuyeres: nozzles through which oxygen and steam blast is delivered to a blast furnace.

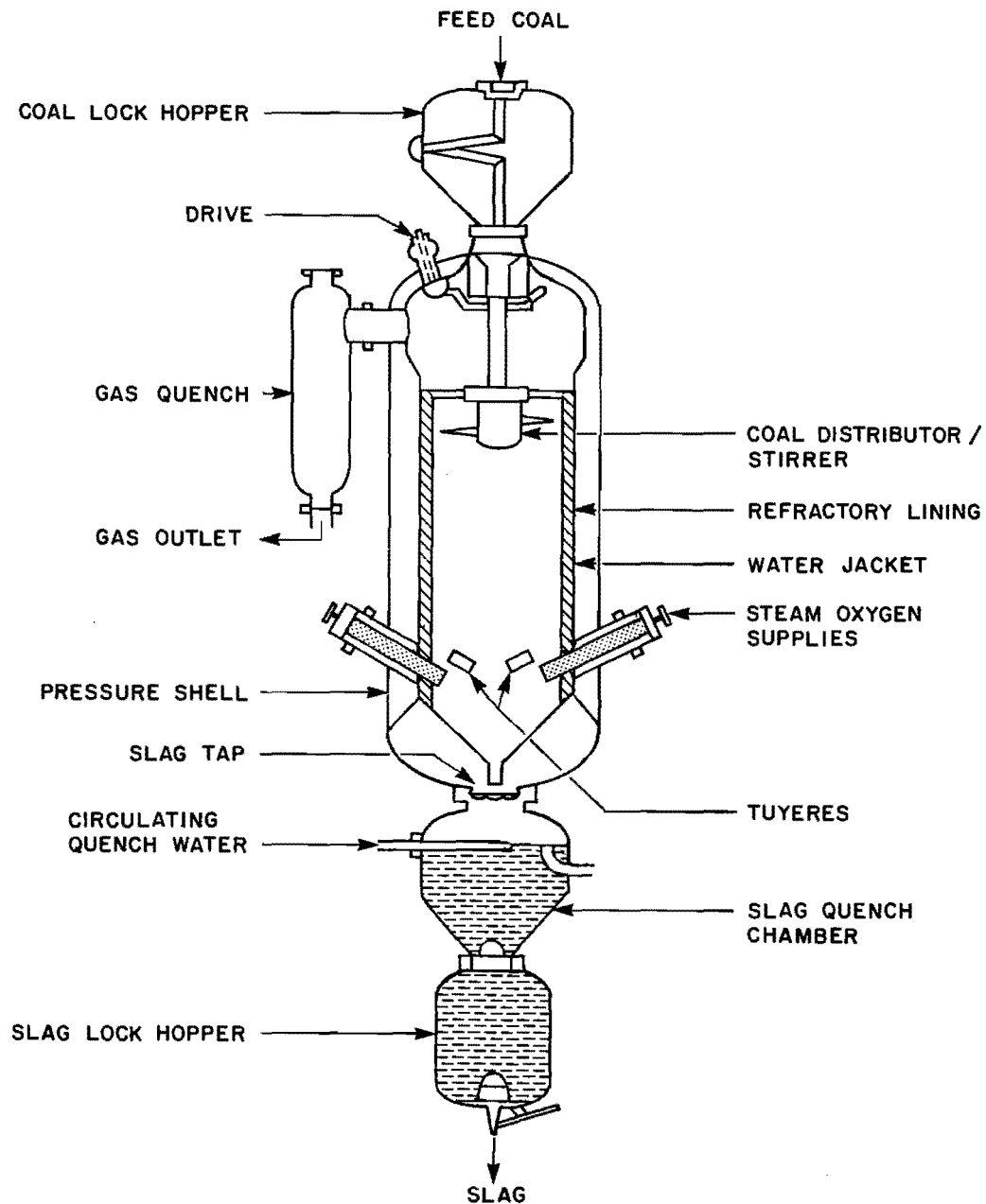


Figure 46. BGC/Lurgi slagging gasifier.

1981). As can be seen from the table, the reduced injection steam requirement of the slagging Lurgi gasifier will result in the production of less carbon dioxide and more carbon monoxide, which will increase the heating value of the crude gas.

The BGC/Lurgi slagger is capable of handling most types of coals at four to six times the capacity of an identically sized dry bottom unit. Coals whose ash content exceeds 15% or whose moisture content exceeds 35% are considered to be not suitable for the Lurgi slagger. Coal feeds containing up to 25% fines can be processed, in contrast to the Lurgi dry-bottom unit which cannot process fines at all. A 92% overall efficiency¹ of synthesis gas production is reported. The reduced byproduct yield (tars, phenols, etc.) relative to the Lurgi dry-bottom unit is an added advantage of the slagger.

Despite these restrictions and the relatively high cost of a standard gasifier (reactor) - approximately \$2 million in 1974 - Lurgi gasifiers continue to gain increasing acceptance. However, the reactors are more attractive as fuel gas (medium or low heating value gas) generators.

7.3.1.3 Summary and Conclusion. The fixed bed gasifier systems are characterized by large coal inventories, long coal residence times, low exit gas temperatures, high carbon conversion and high tar content of the raw syngas product.

The gasifiers are not suitable for caking coals, liquid or wet solids feeds. Difficulties can be experienced when using coals with low ash fusion temperatures, which require excessive steam to lower the operating temperature in order to control slag formation.

The removal of byproducts, such as tars, phenols, cresols, and other organic compounds, involves scrubbing operations which contribute to additional environmental and operational expenses. The process requires an extensive wastewater treatment facility.

The relative hardness and low volatile content of the residue coke from bitumen upgrading make the fixed bed gasifier system unattractive for the processing of coke from oil sands. Further, where a synthesis gas is to be used

¹ Overall efficiency:

$$\frac{(\text{Higher heat value of gas} + \text{Heat recovered as steam}) \times 100}{\text{Higher heat value of residue}}$$

Table 18. Product composition from dry and slagging Lurgi gasifiers^a.

Cr de Gas Component	Lurgi Dry Vol. Fractions	Lurgi Slagging Vol. Fractions
CO ₂	0.245	0.026
CO	0.245	0.606
H ₂	0.397	0.278
CH ₄	0.086	0.076
C _n H _m	0.016	0.004
N ₂	0.011	0.01
CV (MJ/N _m ³)	12.4	14.8

^a Adapted from Brown (1981)

as a petrochemical feedstock (as likely in oil sands project) rather than converted into SNG, or where the cost rather than heating value of a synthetic feed gas is the overriding consideration, the fixed bed gasifier hold few inherent advantages. In such cases, it may be preferable to consider other gasifiers.

7.3.2 Fluidized Bed Gasifier

The fluidized bed concept was first used in the Winkler gasifier in the 1920's (Bailey and Goodman 1977).

Unlike the fixed bed gasifiers, the fluidized bed gasifiers operate with a closely sized crushed coal of 1.5 mm diameter. Within the gasifier, the coal is suspended by an upflow of steam, oxygen or air, plus gasified products from the coal. The bed exhibits good mixing uniformity. Good gas-solid contact resulting in efficient temperature control and high heat transfer rates. Preheating or pretreatment (drying or oxidation) of caking coals may be necessary to avoid defluidization.

The gasifier is normally operated at a low temperature, below the softening or initial deformation temperature of coal ash, typically well below 1100°C (Schlinger and Richler 1980). Higher temperature operation in order to control the rate of ash agglomeration is possible with certain coals. The agglomerated ash is selectively removed from the bottom of the gasifier and quenched. Some of the gasifiers based on this fluidized technology are discussed below.

7.3.2.1 Winkler Gasifier. The Winkler gasifier is the only commercially available coal gasification system based on fluidized bed reactor technology. Forty-one gasifiers have been built since 1926, four of which are still operating today (although none have been built in the past 20 years). A feasibility study for a 7500 t/d methanol plant employing four Winkler gasifiers is currently being carried out by Cook Inlet Region Inc. and Placer Amex Inc. (Synthetic Fuels Report 1982).

The Winkler gasifier (Figure 47) is 20 m high and 5 m in diameter. If the fluidized coal charge were allowed to settle, it would form a 3 m thick bed in the gasifier. Closely crushed coal (5 to 10 mm) is continuously supplied from a pressurized hopper and fluidized by a primary injection of oxygen and

steam immediately above the grate. A secondary injection above the fuel bed serves to gasify unreacted coal entrained in the raw gas. The reaction to form synthesis gas usually takes place at 800 to 1000°C depending on the nature of coal (Papic 1976). The normal operating pressure is atmospheric. A significant quantity of fly ash and tar associated with the raw gas is removed by a series of cyclones, wet scrubbers, and a water quench. Ash that does not leave with the gas is withdrawn from the bottom of the gasifier by means of a rotating scraper.

The gasifier exhibits a lower carbon conversion rate and consumes more oxygen than the two Lurgi processes. It has a low cold gas efficiency of about 75%. Finally, because of the atmospheric operation of the gasifier, utilization of the raw syngas for synthesis or combined cycle application will require costly compression downstream of the gasifier.

7.3.2.2 High Temperature Winkler Gasifier. Since 1965, development work has been carried out on a High Temperature Winkler (HTW) gasifier at Wesseling, West Germany (Franke 1979 and Adlhoch and Theis 1980). Since 1978, a HTW pilot plant has been in operation at Frechen, West Germany, processing up to 13 t/h of dry lignite. A demonstration plant is planned, the gasifier and gas preparation units processing 25 t/h of coal are scheduled for completion in 1983/84.

The HTW gasifier (Figure 48) is designed to operate at pressures up to 1000 kPa and temperatures of 1100°C. The high temperature and pressure are expected to increase gasification rates with a resultant increase in capacity. The gas quality is improved by having higher carbon monoxide and hydrogen contents than the Winkler. Compression of the raw gas is eliminated and carbon-containing flue dust is recycled to the gasifier to increase carbon conversion¹ to 95%.

The gasifier has drawbacks similar to those of the Winkler. The high temperature involves the risk of ash fusion which may interfere with the smooth operation of the gasifier. Limestone, lime, or dolomite addition may

¹ Carbon conversion:
$$\frac{\text{Total carbon feed} - \text{carbon disposal in ash}}{\text{Total carbon feed to gasifier}} \times 100$$

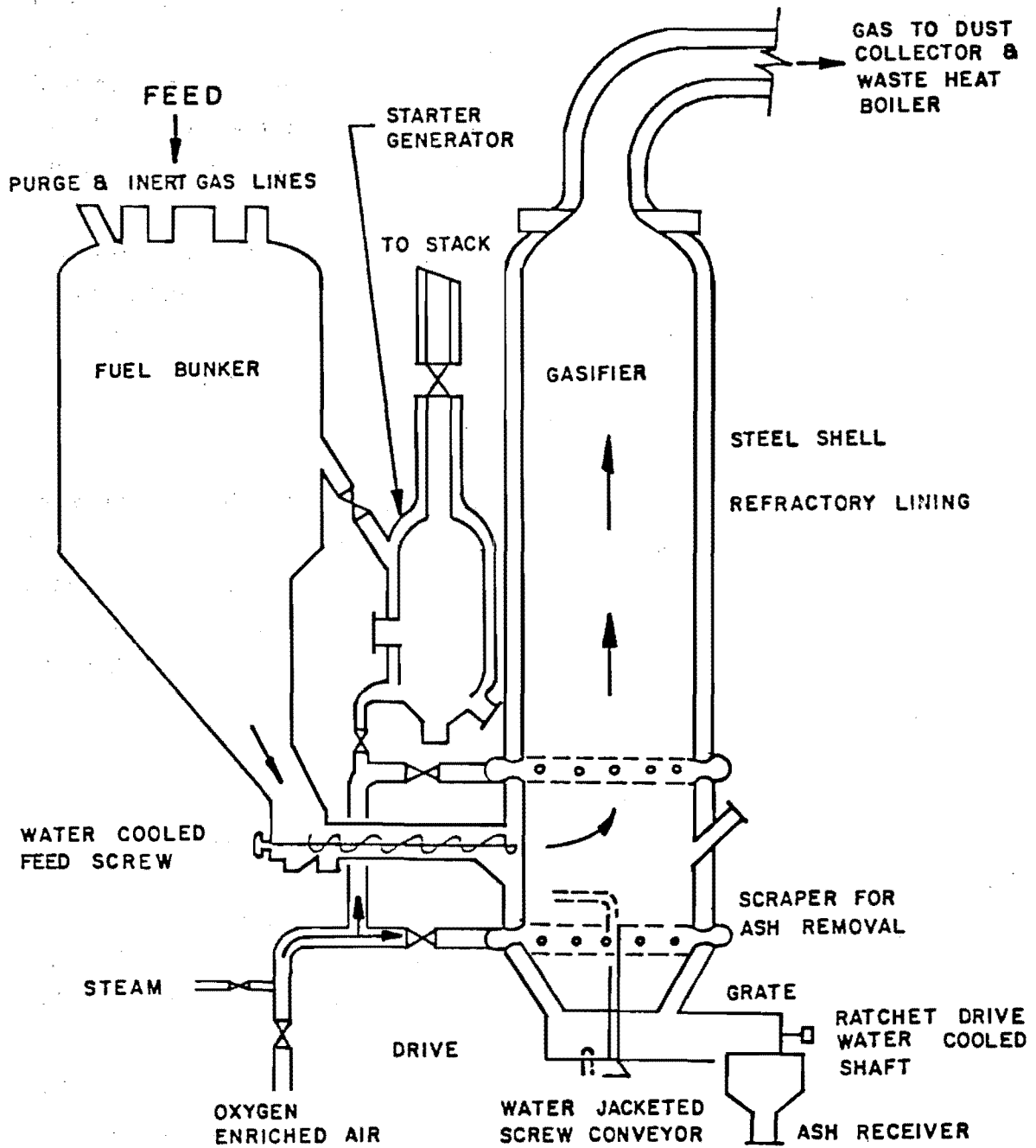


Figure 47. Winkler gasifier.

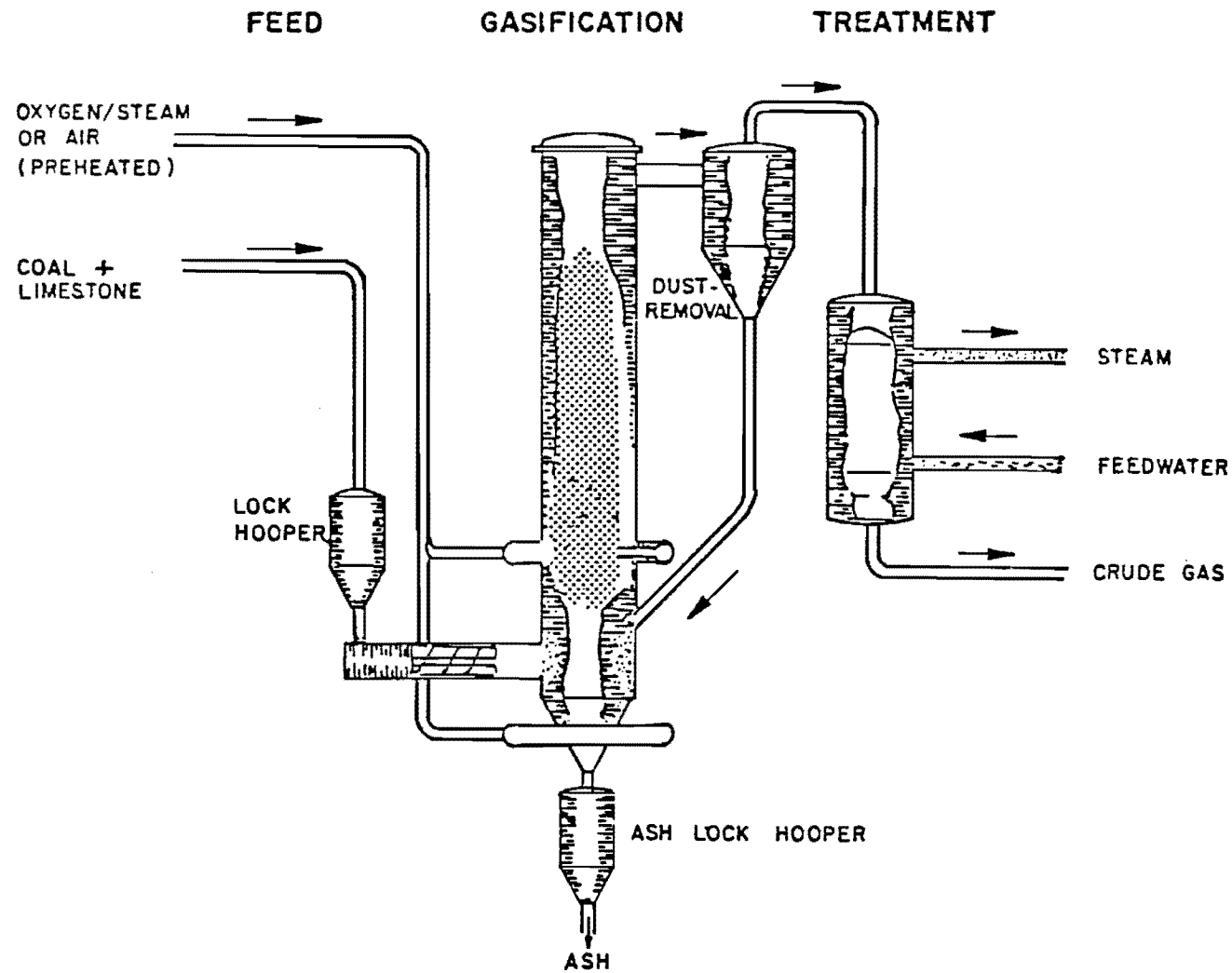


Figure 48. High temperature Winkler gasifier.

help to overcome this problem. These disadvantages of the gasifier are presently under review. The gasifier has not yet been commercialized. American Hoechst Corporation plans to build an HTW plant near Cologne to convert 2.2 million t/a of coal.

7.3.2.3 Westinghouse Gasifier. Westinghouse Advanced Coal Conversion Department, in 1972 aided by funding from the U.S. Department of Energy (DOE), developed the Westinghouse Fluidized Bed gasifier (Figure 49). The technical feasibility of the gasifier process has been demonstrated in their 35 t/d process development unit in Waltz Mill, Pennsylvania. Over 7000 hours of testing have been completed since 1975 using both air and oxygen. Westinghouse has announced plans to build a full scale commercial gasifier at SASOL II by 1983.

Crushed coal is dried in a fluidized bed and then transported to a devolatilizer-desulphurizer unit. Here devolatilization, desulphurization, and partial hydrogasification reactions occur in a single recirculating fluidized bed operating at 800° to 1000°C and 1000 to 2000 kPa. Desulphurization is carried out by using dolomite sorbent in the devolatilizer section. Spent dolomite is regenerated and recycled.

The char from the devolatilizer-desulphurizer is fed into the bottom of the gasifier through a central jet. Steam and oxygen are fed to the bottom of the gasifier such that the bed of char circulates around the jet. The carbon in the char is consumed by combustion and gasification, producing particles rich in ash. These particles agglomerate, forming larger and denser particles in the bed. The particles migrate to the annulus around the feed tube where a rotary valve and lock hopper continuously remove this collected ash.

The raw product gas contains approximately 0.08 mass fraction methane and has no tars or other hydrocarbon byproducts. The entrained char particles are separated in the cyclone and reinjected into the gasifier.

The gasifier has a turndown capability to 25% and also a low steam and water usage. Efficiencies as high as 80% cold gas and 94% overall have been recorded, with carbon conversion as high as 95%.

Drawbacks of the gasifier include: a large amount of char is entrained with the raw gas; the flexibility in operating parameters is limited; and; agglomerating properties which may restrict the temperature of operation.

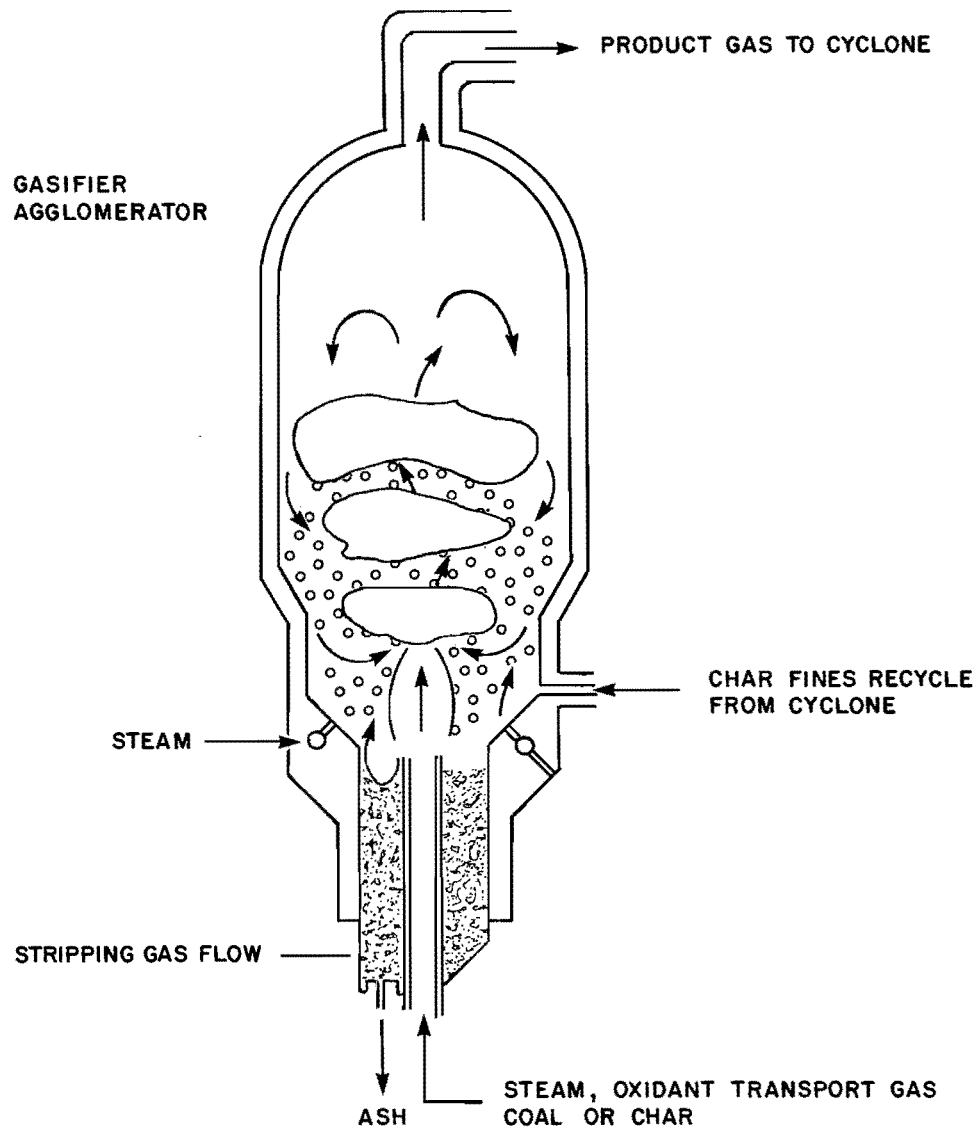


Figure 49. Westinghouse gasifier.

7.3.2.4 U-Gas Gasifier. This process was initiated by the Institute of Gas Technology (IGT) in 1945. Since 1974, a 22 t/d unit has been operating combining this fluidized bed technology with ash agglomeration techniques. Based on encouraging results, the DOE and Memphis Light, Gas, and Water Division plan to build and operate a 3110 t/d demonstration plant. The plant will employ four coal gasifiers operating at 620 kPa producing 4.70 million m³/d of gas.

In the U-Gas process (Figure 50) crushed coal (6 mm) is fed via lockhoppers to a pretreater to destroy caking properties. The pretreater is operated in a fluidized bed mode at the gasifier pressure and 400°C. This treatment forms an oxidized outer layer on coal particles, preventing agglomeration and possible blockage of the gasifier.

From the pretreater the coal is fed directly to the fluidized bed gasifier operating at 2400 kPa and about 1100°C. Air (or oxygen) and steam are introduced to the bottom of the gasifier.

Agglomerated low carbon content ash is removed from the bottom of the gasifier. The design of the system maintains a bed of approximately 70% carbon and 30% ash. The temperature of the jet is maintained near the softening point of the ash particles for the specific coal being gasified. Ash particles agglomerate and grow until heavy enough to fall out of the fluidized bed.

Fines elutriated from the fluidized bed are separated by one internal and two external cyclones arranged in series. Fines removed by the cyclones are returned to the bed. Fines from the external cyclones are recycled with the incoming air/steam stream. The entrained fines are thus exposed to the high temperature of the jet for complete extinction. The raw gas contains no tars or oils but is comparatively rich in methane. The gasifier has a reported cold gas efficiency of 79% converting as much as 98% of the feed carbon to product gas. No liquid feed has been attempted. The unit has also exhibited a potential turndown to 30%.

Disruption in the coal feed causes problems and careful monitoring of the steam/oxidant ratio is critical for proper agglomeration. The process suffers from fines separation problems, as much as one third of the treated carbon is carried over and requires recycle. The unique technique of ash agglomeration to remove low carbon ash selectively is a significant advantage

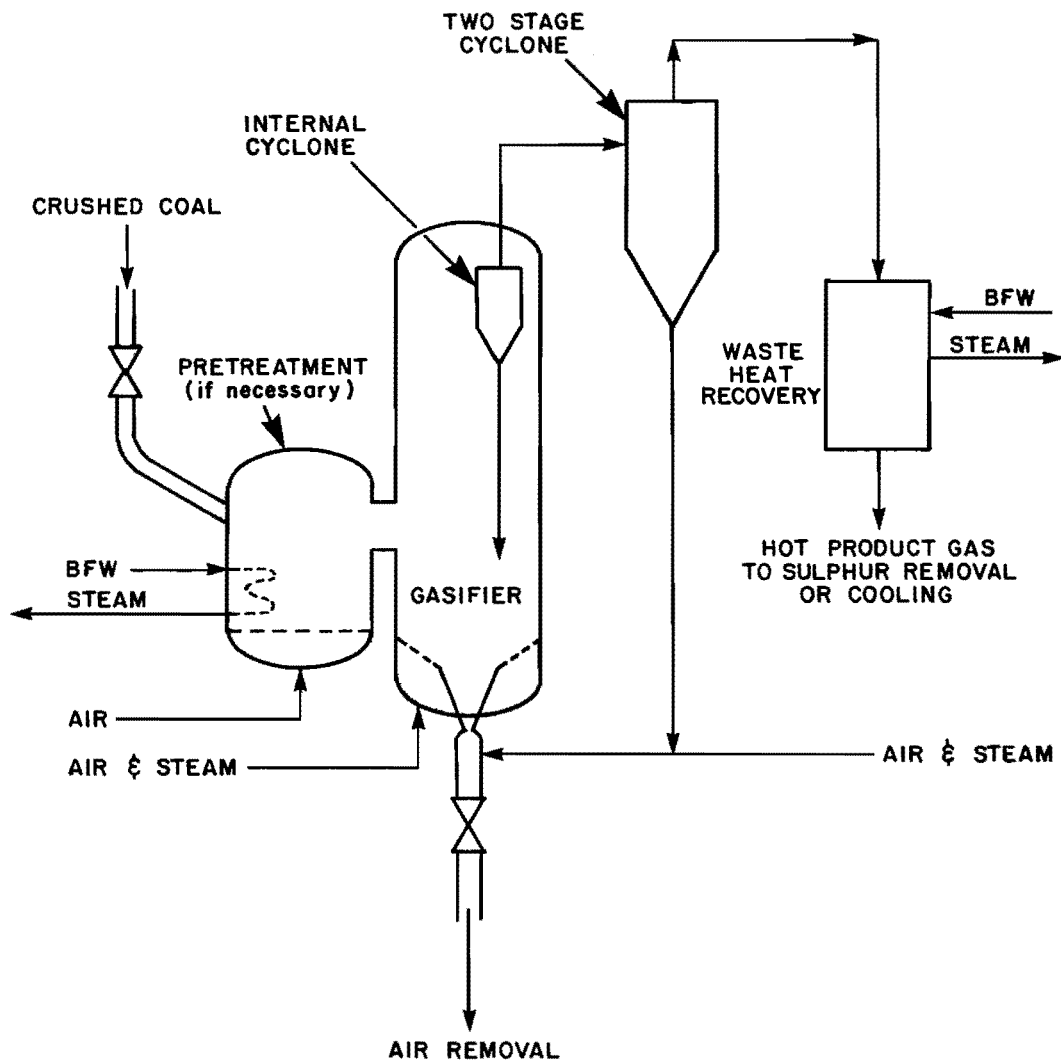


Figure 50. U-gas gasifier.

over other fluidized bed processes. The ash, however, may contain 0.05 to 0.1 mass fraction carbon, thus affecting the 98% carbon conversion.

7.3.2.5 Exxon Catalytic Gasifier. The Exxon Catalytic gasifier has been under study by Exxon Research and Engineering Company since the late 1960's and is one of the newest of the fluidized bed gasifiers (Figure 51). In June 1980, Esso Netherlands revealed details of a 90 t/d coal gasification plant to process a variety of feedstocks. This plant is scheduled to go on stream in 1984.

The Exxon Coal Gasification Process is based on the use of basic and weak acid potassium salts as catalyst for the breakdown of coal. The benefits of such a catalyzed reaction are as follows:

1. The rate of gasification is increased, allowing reduced gasification temperature.
2. The tendency for swelling and caking of coals is reduced.
3. The methanation reaction is promoted.

The Exxon fluidized bed process has some advantages over other methods. The slagging problem is eliminated, since oxygen or air is not injected. Ash is removed with the catalyst. This process will operate on a wide variety of coals without the pretreatment often needed for other fluidized bed designs. Yet, the advantages of the fluidized bed are maintained and include absence of tars and higher hydrocarbons in the product; moderate temperatures of reaction; and stable, easy to control operation with high turndown.

The process is still in the development stage and requires improvement in the catalyst regeneration section and cryogenic methane separation. These factors are important to make this process cost effective.

However, as noted, the system is primarily designed to produce methane which may not be the prime objective of coke gasification in the oil sands project.

The process, once proven and operated on large scale, may become an attractive proposition for SNG production.

7.3.2.6 Summary and Conclusions. As noted, most of the fluidized bed gasifiers are still undergoing various stages of development. Also, some have

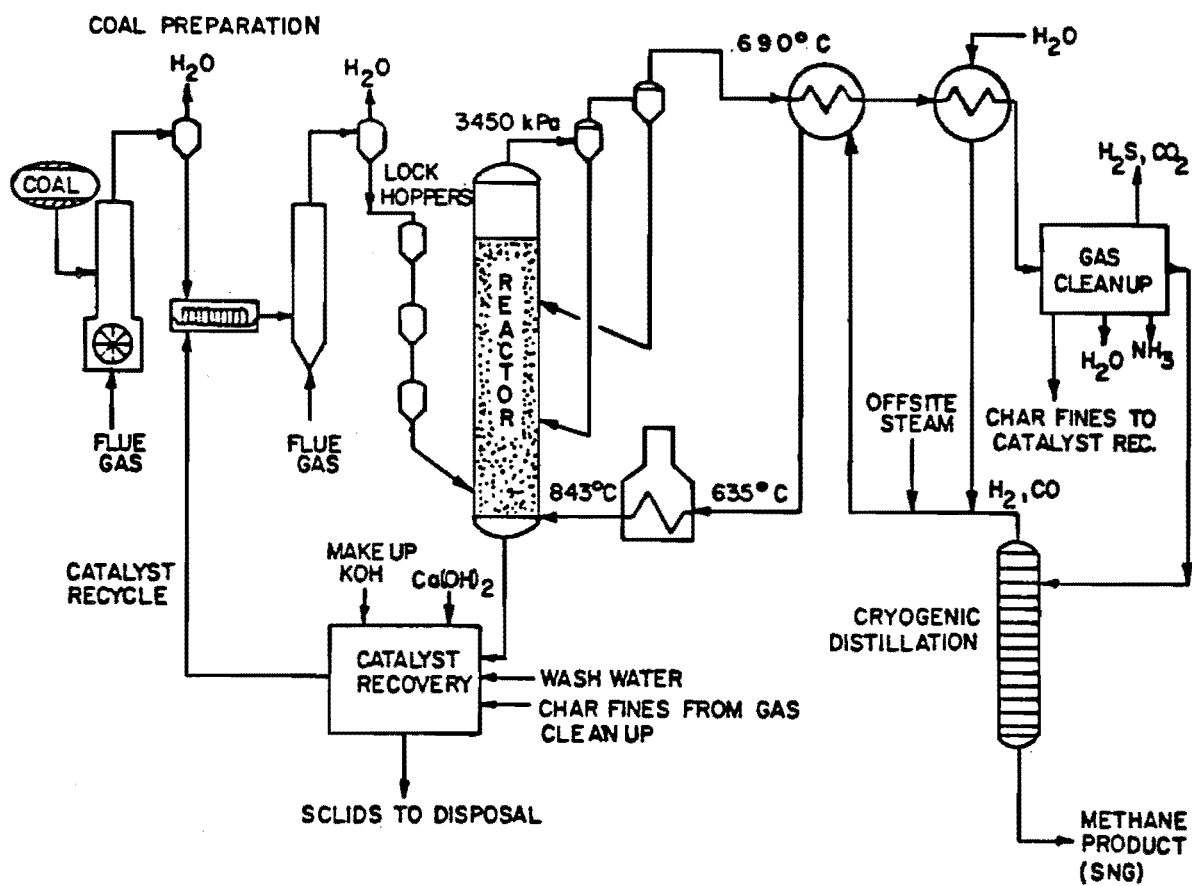


Figure 51. Exxon catalytic gasification process.

specific application to SNG production. The gasifiers lack feed versatility, i.e., they are not suitable for hard residues, liquid feeds, large particle size (greater than 10 mm), etc. Further, the feed must be reactive and have a high ash fusion temperature. The atmospheric pressure operation of some of the gasifiers requires gas compression for hydrogen production.

The gasifiers produce high dust loading in the raw syngas. The formation of byproduct tars and partially oxidized material is lower than in the case of fixed bed systems. Nevertheless, removal and disposal of the byproducts pose a number of operational and environmental problems. The gasifiers tend to be of relatively low capacity and suited to reactive feeds of low ash content.

7.3.3 Entrained Bed Gasifier

The entrained bed (flow) gasifier, dating back to the 1950's (Schlinger, Falbe and Specks 1979), is the most recent development and is distinguished by the fact that the oxygen and coal feeds are co-current as opposed to the counter-current mode of the previous two systems. The entrained flow gasifier is similar to pulverized coal-fired boilers.

Entrained flow gasification has the highest potential of applicability for residue gasification due to a number of inherent advantages:

1. Suitability for the largest range of available solid or liquid feeds.
2. Minimal undesirable byproducts produced.
3. Environmental impact is minimized.
4. Extremely clean gas is produced.

The coal fines (less than 0.1 mm diameter), oxygen, and steam are introduced to the reactor where near complete gasification of coal takes place.

The entrained flow gasifier is normally operated at temperatures above the melting point of the coal ash. At these temperatures, generally at or above 1250°C, gasification reactions are much faster and coal residence time is shorter (two to three seconds). The high operating temperature and pressure of the gasification process results in zero tar production. The injection steam requirement is low, while throughput and single pass conversion of the coal are high. This type of gasifier produces a raw syngas which requires cyclones or water scrubbing to remove particulate matter entrained in the raw syngas.

In the case of an Alberta oil sands project, residue inventory is expected to be large and of relatively constant composition. The fluid coke from the present Syncrude plant, as shown in Table 19, is of good homogeneous composition and particle size distribution.

The high throughput and high flexibility of the entrained flow gasifiers with minimal undesirable byproducts make these gasifiers good potential candidates for large oil sands projects.

Gasifiers based on entrained flow technology are currently in commercial operation for processing heavy residue oils from refineries. Some of these gasifiers are being developed for coal gasification in demonstration and pilot plants.

When the gasification takes place at high pressure, the feeding of residue from an atmospheric chamber into a pressurized reactor can be achieved by:

1. dry feeding (mechanically, via pressurized vessels);
2. wet feeding (hydraulically, in the form of a coal/coke slurry).

The dry feeding system causes considerable wear on the conveyance and sealing equipment during the charging of the pressure chamber. This in turn can cause potential health hazards or even explosions from escaping synthesis gas. Handling problems may also be experienced in the conveying system. The need to dry the coke recovered in the downstream gas scrubbing system is a further disadvantage.

The wet feeding system, on the other hand, requires additional oxygen. The water in the slurry feed is vapourized and then superheated to a high reaction temperature (about 1250°C). Due to the high water requirement of the slurry, the process may not be suitable for geologically young coals.

7.3.3.1 Koppers-Totzek gasifier. (McGurl and Farnsworth 1976, Michaels and Kamody 1976.) The Koppers-Totzek gasification process became commercial in the early 1950's and has since been used in 22 plants with 55 gasifiers.

Table 19. Estimated Properties of Fluid Coke.^a

		<u>Wt. Fraction</u>	
Composition:	C	0.813	
	H	0.019	
	N	0.017	
	O	0.005	
	S	0.087	
	Ash	0.059	
	Ni	810	mg/kg
	V	2560	mg/kg
Heating Value:	Lower	29.8	MJ/kg
	Higher	30.2	MJ/kg
Properties:	Hardgrove Index	15 to 20	
	Surface Area	10	m ² /g
	Bulk Density	0.88 to 1.04	kg/dm ³
	Volatility	2%	
Particle Size:	<u>Micron</u>	<u>Cumulative Wt. Fraction less than</u>	
	100	0.00 to 0.19	
	200	0.36 to 0.62	
	400	0.78 to 0.94	
	1 000	0.86 to 0.98	

^a Adapted from original table in Ambrose and Flynn 1977.

The Koppers-Totzek unit (Figure 52) is an entrained flow gasifier consisting of a refractory-lined, water-jacketed, carbon steel vessel. Coal dust with 90% of particles below 0.09 mm is dried to a moisture content of less than 0.01 mass fraction and is then fed to screw conveyors with mixing heads. These heads pass the dust into nozzles where it is mixed with oxygen and steam at about 130°C. The homogeneous mixture is then fed via horizontally opposed water-cooled heads to the gasifier.

Gasification is nearly instantaneous and complete at temperatures of about 1500°C and near atmospheric pressure. Carbon conversion of more than 98% can be obtained.

The fusion characteristics of the ash can be adjusted by flue gas addition. About 80% of the ash is removed in liquid form and flows through a water sealed shaft into a water quench where it is granulated and removed by an extractor. The remainder of the ash, along with unreacted carbon, is entrained with the raw gas. The gas is quenched to 900°C, at which point the molten ash will solidify before entering a waste heat boiler, where high pressure steam is produced. The solids are then removed either by water scrubbing or by a sequence of cyclones and electrostatic precipitators.

A raw medium heating value fuel gas is produced, comprised predominantly of carbon monoxide and hydrogen. Neither methane nor other hydrocarbons are present in the gas.

The Koppers-Totzek is a simple, versatile, and reliable process. Operation at atmospheric pressure will tend to reduce mechanical maintenance problems. The gasifier is capable of processing a wide variety of feeds without caking restrictions. High carbon conversion rate and high capacity are other features of the process. The overall gas efficiency is approximately 90%, which includes the sensible heat of the process.

One major disadvantage of the Koppers-Totzek process is the relatively high oxygen consumption and the extensive solids cleanup of the product gas. As in the Winkler process, the low pressure raw gas needs to be compressed for most chemical synthesis or combined cycle applications.

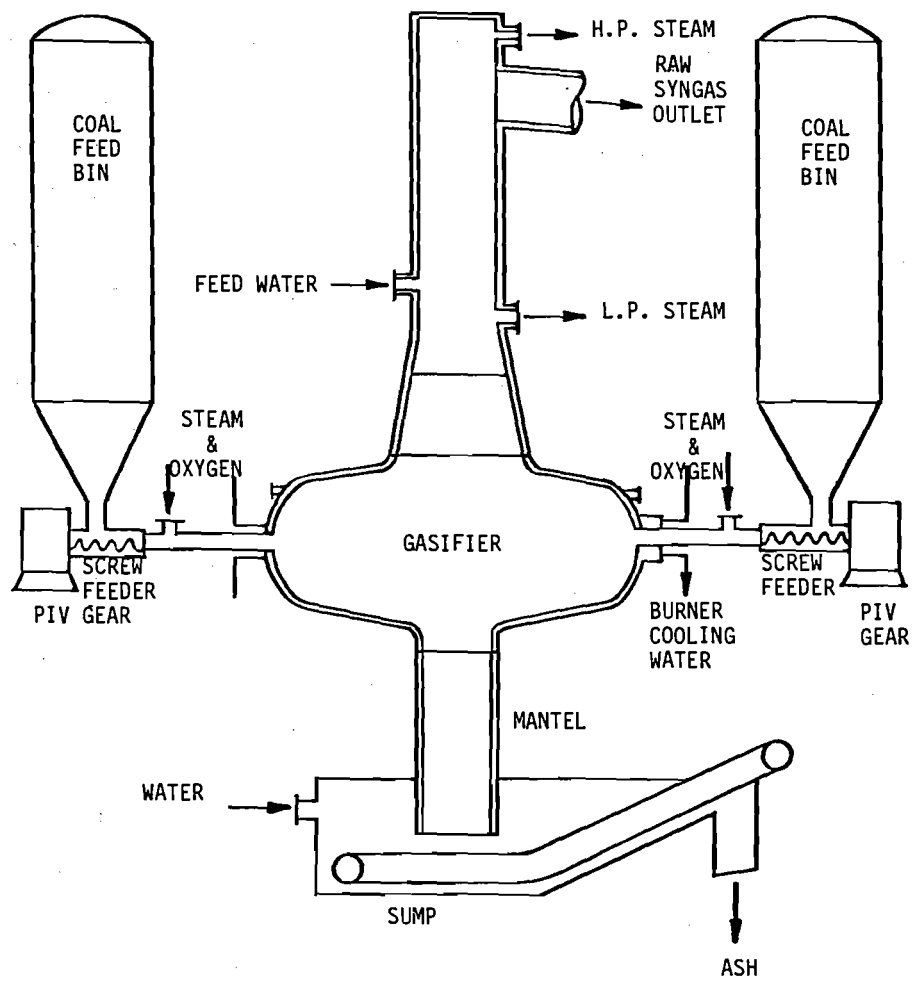


Figure 52. Koppers-Totzek gasifier.

7.3.3.2 Shell-Koppers Gasifier. Shell International Petroleum (experienced in high pressure partial oxidation of residual oil) and Krupp Koppers GmbH, Essen, Germany (experienced in coal gasification) jointly developed the Shell-Koppers gasifier Vogt and van der Burgt (1980). Since 1976, a pilot plant has been in operation at Shell's Amsterdam laboratory. Successful operation of the unit led to a 150 t/d demonstration plant which started operation in 1978 at the Deutsche Shell AG Harburg refinery. To date the plant has completed 2500 operational hours on coal. Preliminary engineering of a full size commercial unit (1000 t/d) is in progress.

Although the Shell-Koppers gasification process has been through the initial stages of development, the recent (1982) dissolution of the partnership between Shell International and Krupp Koppers GmbH of Germany, may present a degree of uncertainty to future development. The process has now been renamed Shell coal gasification. Shell International Petroleum Maatschappi BV and Shell Oil Company will be involved in its future development. Future plans for this program are not known at this time.

If the high capacity, heat transfer rates, efficiency, feed conversion, and various advantages of the Shell-Koppers gasifier are maintained in the development of the Shell coal gasification system, the process may be a prospective candidate for residue gasification in an oil sands project.

7.3.3.3 Texaco Gasifier. Texaco gasification technology has been utilized in 75 plants with 160 gasifiers in 22 countries since 1953. These partial oxidation units operated primarily on liquid residues and tars. To extend this technology to coal gasification, two demonstration plants are being operated; one by Ruhrchemie A.G. in Oberhausen-Holtien, Germany, and the other in Muscle Shoals, Alabama with capacities of 165 t/d and 180 t/d, respectively. The former has logged over 10 000 hours of operation since 1978 at pressures ranging from 2400 to 4100 kPa, with a longest sustained run of 30 days. The latter, the Muscle Shoals site, should be considered to be a commercial sized pilot plant. Since initiation in October 1980, the entire plant has now logged 700 hours of operation with the longest continuous run, achieved in June 1982, of 225 hours. Recently, Texaco Inc., Ruhrkohle A.G., and Ruhrchemie A.G., have signed a research and development agreement in anticipation of bringing

the Texaco coal gasifier closer to commercialization. Also, the Southern California Edison Project (Cool Water) is planning to use a 1000 t/d entrained bed Texaco gasifier.

The Texaco gasification process is capable of operating on a wide variety of feedstocks. These feedstocks include various types of coals and lignites, coke, residues and chars from coal liquefaction and other gasification processes, wastes with lower heating value, liquid fuels, and solid waste materials.

The process incorporates a pressurized, entrained bed slagging gasifier with a unique slurry feeding system. The gasifier is a refractory lined vessel and can operate at pressures from 2050 to 8270 kPa (Figure 53).

High slurry concentration is vital for achieving high throughput and overall efficiency. Hence, to ensure maximum slurry concentration, the crushed coal is combined with water and wet ground. The slurry, after being pumped to a feed tank, is heated and metered with oxygen to the reactor. The coal is rapidly oxidized to a synthesis gas rich in carbon monoxide and hydrogen, at reaction temperatures of 1200 to 1300°C.

Slagged ash flows from the bottom of the gasifier into a quench section. The granulated slag is then removed via a water-flooded lockhopper. Depending on the end products desired, the raw syngas is either water quenched or first passed through a waste heat boiler and then on to a water scrubber. Most of the quench water obtained is recycled and only a small portion sent to a treatment plant.

The clean syngas is primarily carbon monoxide, hydrogen, and carbon dioxide. A wide variety of feeds can be processed by the gasifier. Some feeds, such as lignite, are not desirable and may require extensive pretreatment. A cold gas efficiency of up to 76% with overall gasifier efficiency of 92% and carbon conversion up to 98% have been reported (Konkol, Ruprecht, Cornils, Durrfeld, and Langoff 1982).

The process, at present, is being modified to reduce maintenance requirements. The highly erosive nature of the slag requires special valves and a suitable switching sequence for the lock control. The refractory material is effected by corrosive attack of both the gas and the slag.

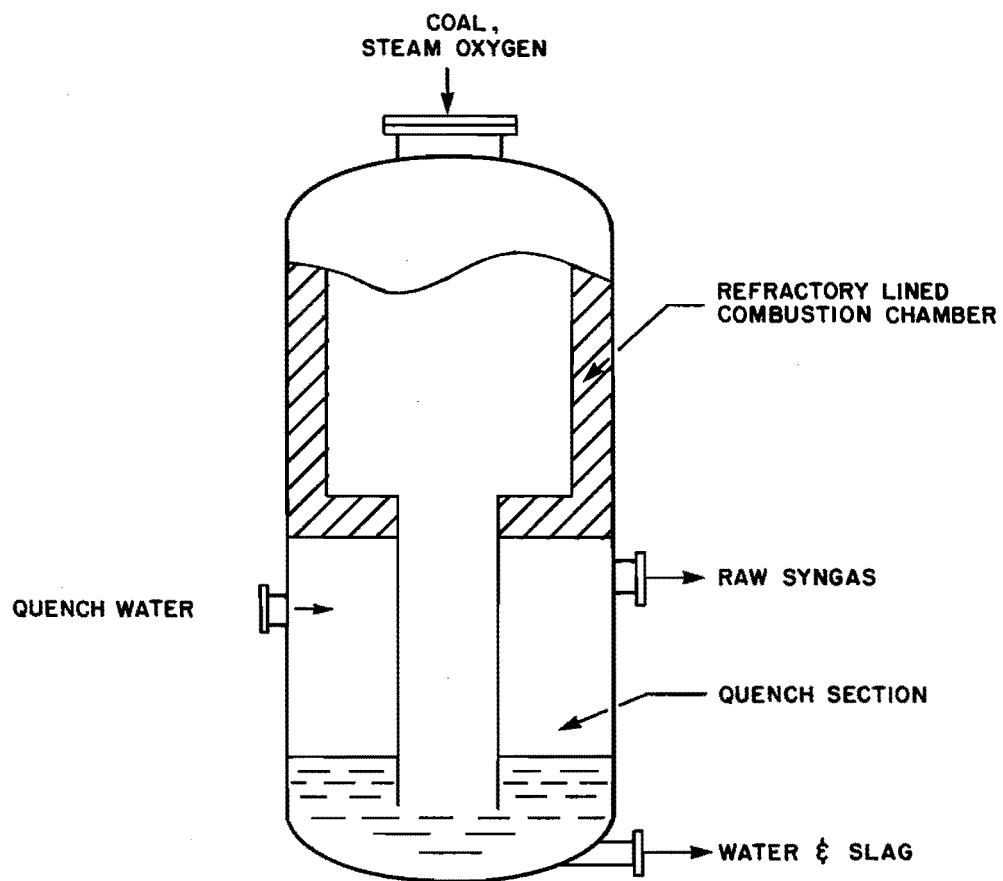


Figure 53. Texaco gasifier.

Due to the high (0.6 mass fraction) concentration of water required for soft coals, the wet feeding operation is only suitable for hard coals, which require 0.4 mass fraction water (Hermann 1982). In addition to various environmental and economic factors, the application of the gasifier to the oil sands project will primarily be determined by the slurry properties of the residue or the ability of the gasifier to process solid feed. The sulphur content (as high as 0.09 mass fraction) of the residue may have an added influence on the process applicability.

The Texaco gasifier is the only gasifier to have operated on fluid coke derived from oil sands bitumen. The tests performed at the Montebello Research Laboratory have proven satisfactory (letter dated June 2/82 from W.B. Crouch, Texaco Development Corporation, 2000 Westchester Avenue, White Plains, New York 10650). Following this work, the Texaco Development Corporation licensed the gasifier to the Alsands consortium to produce hydrogen.

In addition, over one-half of the coal gasification proposals submitted to the U.S. Synfuels Corporation in 1981 have specified the use of the Texaco Coal Gasification Process.

7.3.3.4 Combustion Engineering Gasifier. Work on the Combustion Engineering gasifier was initiated in 1972. A test facility has been operating at Windsor, Connecticut to assess the applicability of the entrained gasifier for electric power generation. A 150 MW plant, a scaleup of 150%, is currently being designed for Gulf States Utilities Nelson Steam Plant in West Lake, Louisiana.

The Combustion Engineering process (Figure 54) is designed to operate at atmospheric pressure and temperatures of up to 1800°C. Pulverized coal and recycle char are fed through tangentially oriented combustion nozzles within the combustion section of the gasifier. More pulverized coal is injected tangentially through the reducing nozzles into the gasifier above the combustion zone. The volatiles are cracked in the lower, high temperature section of the gasifier.

The molten slag is removed from the bottom of the combustion section and quenched. Apart from being a gasifying medium, the steam is used to control the combustion temperature within the gasifier.

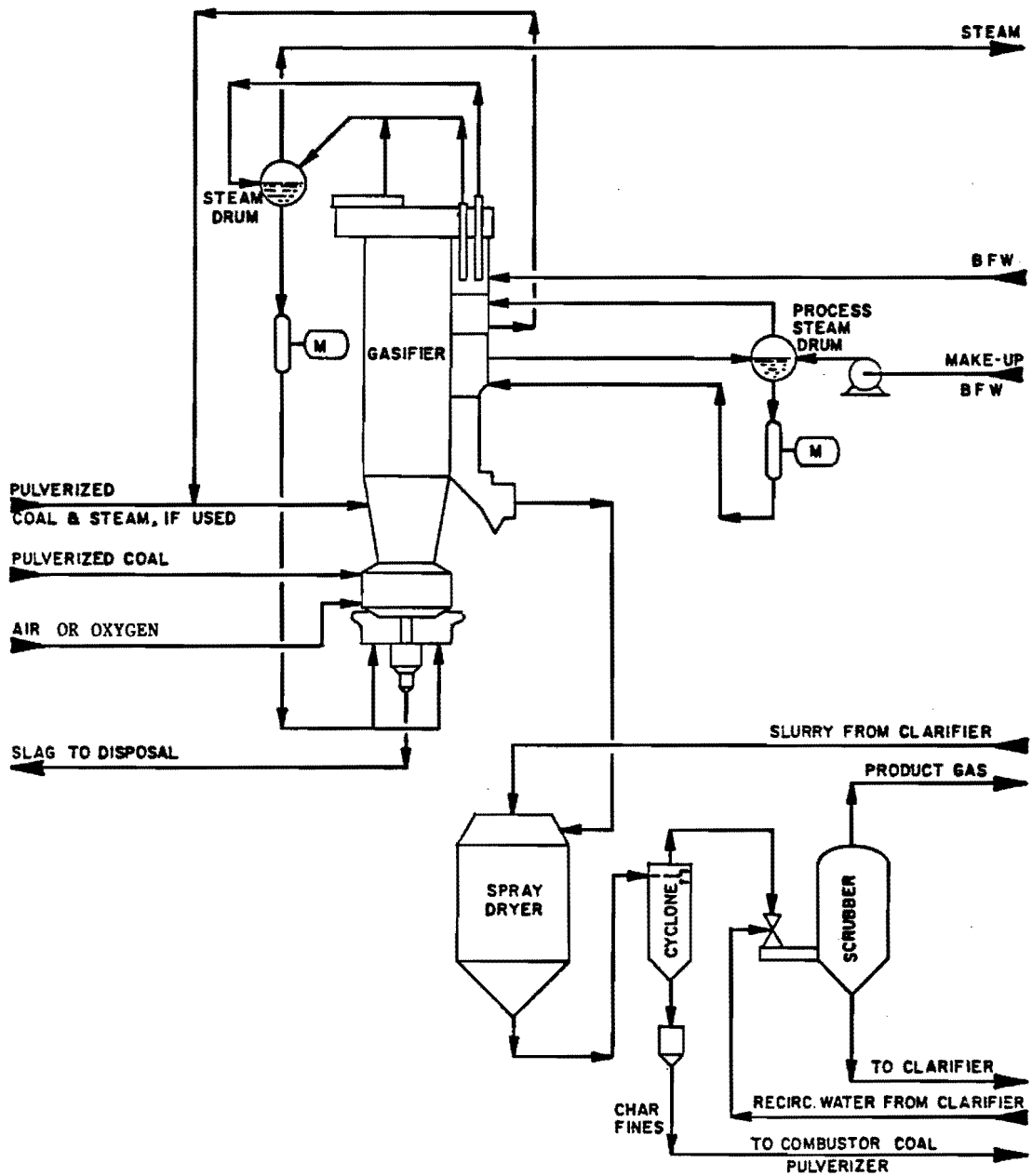


Figure 54. Combustion engineering gasifier.

The use of oxygen instead of air will generate m_hv gas but will require the addition of an oxygen plant. Various types of coals can be gasified. No liquid feeds have yet been attempted. Near complete conversion of carbon with a cold gas efficiency of 77% has been reported (Patterson and Darling 1980). The gasifier is primarily suited to generation of power and low or medium heating value gas. Due to the atmospheric operation, the gasifier has a lower capacity, lower heat transfer coefficient, and a longer residence time than the Texaco gasifier. The absence of steam injection in the process requires a close control of the fuel/oxygen ratio to maintain operating conditions, since high temperature and high ash fusion temperature feedstocks may cause destruction of the gasifier refractory wall. Char recycle is significant and represents a process inefficiency.

7.4 GASIFIER SELECTION

This section reviews the advantages and disadvantages of the three categories of gasifiers and the selection of the most preferable gasifier for oil sands application. The various aspects of the processes described in Section 7.3 are summarized in Table 20.

The fixed bed gasification processes are restricted to dry coal of a specific grade with the lowest possible proportion of fines with caking properties. Operational problems would be anticipated with the fixed bed gasifier because the residue fluid coke from bitumen upgrading contains a significant amount of fines and the H-Oil, Eureka, and CANMET pitches would be wet. Further, the unavoidable formation of byproducts due to the relatively low gasification temperature presents additional operational problems, as well as added capital cost in the gas and water cleanup and purification.

The fluidized bed process, using noncaking coal as feedstock, has the disadvantages of a relatively low specific throughput and a limited reaction temperature that is below the melting point of ash. The vast amount (2000 t/d) of residue produced obviously requires a high capacity gasification plant.

Both the fixed and fluidized bed gasifiers are undergoing further refinements. However, at the present time it is believed that the entrained bed gasifier, because of higher throughput, higher capacity, less byproduct formation, near complete carbon utilization, and greater feed flexibility, is the preferable choice for an oil sands requirement. A number of entrained flow

Table 20. Gasification processes summary.

Gasifier Name	Lurgi	BGC/ Lurgi	Winkler
Reported Cold Gas Thermal Efficiency (HHV)	85% ^a	92% ^a 92% ^b	75%
Operating Temperature, °C	480	1260	800 to 1 000
Operating Pressure, kPa	2410/3100	3100	137
O ₂ , t/t Dry Feed	0.2 to 0.5	0.46 to 0.56	0.35 to 0.6
Steam, t/t Dry Feed	1.0 to 2.6	0.3 to 0.4	0.15
Maximum Commercial Gasifier Capacity, t/d	-	-	263
Expected Date of Commercialization	Commercial	1982	Commercial
No. of Commercial Installations	Several	none	24
No. of Commercial Gasifiers	165	none	70
Scale of Development Unit, t/d	-	350	-
Development Unit start-up	-	1974	-
Type of Gasifier	Fixed Bed	Fixed Bed	Fluidized
Feed Stocks to date	coal/coke	coal/coke	coal/coke
Ash removal	dry ash	liquid slag	hot granulated
Features	<ul style="list-style-type: none"> - cannot process liquids - fluid coke must be sized - cannot process fines - high methane produced - phenol/tar production with reactive feeds 	<ul style="list-style-type: none"> - cannot process liquids - fluid coke must be sized - high methane produced - phenol/tar production with reactive feeds 	<ul style="list-style-type: none"> - low carbon conversion - not tested with liquid feeds - reactive solid feeds required - atmospheric pressure operation

Continued...

Table 20. Continued.

Gasifier Name	High Temperature		
	Winkler	U-Gas	Westinghouse
Reported Cold Gas Thermal Efficiency (HHV)	90% ^b	79%	80%
Operating Temperature, °C	1100	1010/1065	930/1020
Operating Pressure, kPa	1000	70/2450	1500
O ₂ , t/t Dry Feed	0.5	0.55 to 0.68	2.2 to 2.8 (air)
Steam, t/t Dry Feed	0.7	0.2 to 0.6	0.25 to 0.3
Maximum Commercial Gasifier Capacity, t/d	-	-	-
Expected Date of Commercialization	1984	1985	1988
No. of Commercial Installations	none	none	none
No. of Commercial Gasifiers	none	none	none
Scale of Development Unit, t/d	13	22	32
Development Unit start-up	1978	1974	1975
Type of Gasifier	Fluidized	Fluidized	Fluidized
Feed Stocks to date	coal/coke	coal/coke	coal/coke
Ash removal	hot granulated	agglomerated	agglomerated
Features	<ul style="list-style-type: none"> - low pressure operation - low carbon conversion - reactive solid feeds required - not commercially proven 	<ul style="list-style-type: none"> - no liquid feed experience - not commercially proven - fines recovery not yet proven 	<ul style="list-style-type: none"> - not commercially proven - no liquid feed experience - high methane production

Continued...

Table 20. Continued.

Gasifier Name	Exxon Catalytic	Koppers- Totzek
Reported Cold Gas Thermal Efficiency (HHV)	90% ^b	75%
Operating Temperature, °C	700	1500
Operating Pressure, kPa	3500	115
O ₂ , t/t Dry Feed	none	0.6 to 1.1
Steam, t/t Dry Feed	1.6	0.0 to 0.5
Maximum Commercial Gasifier Capacity, t/d	-	772
Expected Date of Commercialization	1990	Commercial
No. of Commercial Installations	none	22
No. of Commercial Gasifiers	none	55
Scale of Development Unit, t/d	6	-
Development Unit start-up	1975	-
Type of Gasifier	Fluidized	Entrained Flow
Feed Stocks to date	coal/coke	coal, coke residual oil
Ash removal	hot granulated	quenched slag
Features	<ul style="list-style-type: none"> - not commercially proven - many novel process steps - high methane production 	<ul style="list-style-type: none"> - well proven process - has processed both liquid and solid feeds - can process unreactive solids - high carbon conversion

Continued...

Table 20. Concluded.

	Shell-Koppers ^c	Texaco	Combustion Engineering
Reported Cold Gas Thermal Efficiency (HHV)	77 to 83%	77%	77%
Operating Temperature, °C	1500	1300 to 1550	1760/950
Operating Pressure, kPa	3500	2000 to 8370	115
O ₂ , t/t Dry Feed	0.6 to 1.1	0.6 to 1.1	4.37 (air)
Steam, t/t Dry Feed	0.0 to 0.5	0.3 to 0.5 ^d	none
Maximum Commercial Gasifier Capacity, t/d	-	910	-
Expected Date of Commercialization	-	commercial for liquids ^e	1984
No. of Commercial Installations	none	75	none
No. of Commercial Gasifiers	none	160	none
Scale of Development Unit, t/d	150	130/180	110
Development Unit start-up	1978	1978	1978
Type of Gasifier	Entrained Flow	Entrained Flow	Entrained Flow
Feed Stocks to date	coal/coke	coal, coke, pitch residual oil	coal/coke
Ash removal	quenched slag	quenched slag	quenched slag
Features	<ul style="list-style-type: none"> - liquid feed experience as Shell process - operates at elevated pressure while maintaining K-T process advantages 	<ul style="list-style-type: none"> - liquid feed experience - high pressure operation - tolerance for wide variety of feeds - high carbon conversion 	<ul style="list-style-type: none"> - not commercially proven - no liquid feeds tested - atmospheric pressure operation - high temperature may cause refractory problems

^a Including liquid by-products.

^b Carbon conversion efficiency.

^c Since April 1982 called Shell coal gasifier. Future development trends unknown.

^d For solid feeds, slurry water replaces steam.

^e 1983 commercialization expected for coal feeds, large number of projects considered.

gasifiers are undergoing tests in large pilot plants operating at high pressure. The most advanced gasifiers have been mentioned in the previous section.

However, due to the lack of experience and technical expertise required for hydrogen production by the residue gasification route, the selection of a gasification process will be based on the logical development of the process judged most attractive after extensive research.

The actual commercialization steps will involve:

1. Successful demonstration of plant operation on residue coke or pitch from bitumen upgrading.
2. Development of design basis specifications for a commercial scale unit.
3. Construction of a prototype facility in the upgrading plant.
4. Successful operation of the prototype unit.
5. Completion of the design, engineering, and construction of the full size facility.

Various entrained bed gasification processes are on the verge of commercialization. It is anticipated that some of these processes will be sufficiently proven in time for the development of the next oil sands project.

The single-stage, oxygen-blown, atmospheric Koppers-Totzek gasifier is presently the only commercially proven entrained bed gasifier. However, the atmospheric pressure level of the gasifier may place it at an economic disadvantage since raw gas produced from the gasifier will require compression for hydrogen production. In the case of pressurized gasifiers, the amount of compressed oxygen required is approximately one third of the amount of synthesis gas produced, resulting in potentially lower compression costs.

The high pressure entrained flow gasifiers, with their ability to process either coke or pitch, seem to be best suited to oil sands application. Since Texaco has done pilot work on coke and has published a great deal of coal and pitch data, their process can most easily be evaluated quantitatively. The process utilizes the experience and technological expertise of the Texaco Development Corporation, which has commercialized the gasifier for heavy residue oils. This experience, backed up by further modifications to the Texaco

gasifier, has led to the construction of two U.S. coal gasification plants based on Texaco coal gasification technology. In addition, extensive successful feasibility tests were also performed on fluid coke by the Texaco Development Corporation at Montebello, California.

The advantages of using entrained flow gasification with a wet feeding system will be further discussed in the following sections.

7.5 DESIGN BASIS

7.5.1 Feedstocks

The residue which forms the feed to the gasifier depends on the upstream bitumen upgrading process. Accordingly, fluid coke, H-Oil pitch, Eureka pitch, and CANMET pitch may be used as feeds for gasification. However, the only upgrading process so far employed in an oil sands project is the proven coking process with subsequent release of fluid coke or delayed coke.

The fluid coke contains very little hydrogen and is thus quite unreactive. Cokes and chars which also contain small quantities of hydrogen have been tested in gasification demonstration plants.

The ratio of carbon to hydrogen for H-Oil and CANMET are similar to liquid hydrocarbon feeds processed by Texaco gasifiers. Eureka pitch resembles the coal liquefaction bottoms which Texaco has gasified in a pilot scale unit at the Montebello, California laboratory.

The estimated properties of oil sands fluid coke are given in Table 19.

When compared to coal, the bitumen derived feeds contain more sulphur and less ash. In addition, the fluid coke contains a high concentration of heavy metals (Table 17). Such concentration may cause both corrosion and wastewater treatment problems in gasification.

7.5.2 Determination of Feedrate

The heavy bitumen from oil sands extraction consists of approximately 0.05 mass fraction sulphur. In primary bitumen upgrading, 17.6% of this sulphur is rejected into the residue coke by the fluid coking route. Consequently, the mass fraction of sulphur in the coke is approximately 0.086

(which is considerably higher than those observed in most coals). The design capacity, as defined by Alberta Environment for this study, is based on 1 000 t/d of sulphur in bitumen. This gives 176 t/d of sulphur in the residue coke. Thus the capacity of the gasifier required would be equivalent to a coke feed rate of 2050 t/d.

7.5.3 Raw Gas

A typical composition of raw synthesis gas produced by gasification of an eastern U.S. coal using the Texaco process is given in Table 21.

The raw gas from a fluid coke gasifier may, however, be different in composition, primarily due to the hydrogen and sulphur content of the coke.

In the gasifier, the bulk of the sulphur (98.8%) in fluid coke is converted to hydrogen sulphide which is subsequently removed from the raw gas and converted to elemental sulphur in the Claus plant.

Immediately downstream of the gasifier, the raw gas is cooled and stripped of the entrained ash particles. The gas then undergoes carbon monoxide shift conversion before being cleaned in the solvent scrubbing train, with high quality hydrogen being the eventual product.

7.6 ENTRAINED FLOW GASIFICATION PROCESS

7.6.1 Process Description

The primary function of a gasifier in the oil sands application will probably be the production of hydrogen required for the upgrading of refinery processes within the complex.

A fully integrated gasification process for hydrogen production (Figure 55) consists of the following general processing steps:

1. Feed preparation.
2. Gasification.
3. Particulate removal.
4. Shift conversion.
5. Gas purification.

The process requires oxygen as a gasification media. Steam will also be required for pitch feed but steam for solid feeds will be internally

Table 21. Typical Composition of Raw Synthesis Gas.^a

Eastern U.S. Coal Composition		Raw Synthesis Gas Composition	
	Wt. Fraction		Wt. Fraction
C	0.676	H ₂	0.358
H	0.052	CO	0.448
S	0.033	CO ₂	0.181
N	0.010	CH ₄	0.001
O	0.111	CH ₄	0.001
Ash	<u>0.118</u>	H ₂ S + COS	<u>0.011</u>
Total	1.000	Total	1.000

^a Adapted from original table in Hydrocarbon Processing, April 1982.

generated from the slurry water. In order to maintain high purity of hydrogen (free from nitrogen, argon, etc.), oxygen is injected into the gasifier. The absence of nitrogen in the oxidant feed reduces the volumetric flow which results in lowered capital and operating costs. Steam is used both to control the gasification temperature and to supply hydrogen for the shift conversion reaction.

The cooling of the hot raw gas from the gasifier produces high and/or low pressure steam in the wasteheat boilers.

A flow diagram of the Texaco gasification process is shown in Figure 56 and a short description of the process is given in the following sections.

7.6.1.1 Feedstock preparation. The Texaco gasification process operates with an aqueous suspension of feed. This should be of special significance to the oil sands project, where fluid coke is also available as a slurry. The slurry is pumped to the gasifier section from storage tanks. Coal/coke is fed from the bunker to the grinder by means of a conveyor-type weigher. However, in the case of oil sands, very little grinding of the fluid coke may be required due to the fine homogeneous nature of the fluid coke. This slurry system eliminates the need for the expensive and hazardous process of drying the feed. By selecting a suitable type of grinding mill, it is possible to produce a highly concentrated coal slurry of the required fineness in one pass. Monitoring of solid content and grain size together with chemical additives help to maintain the viscosity of the slurry and to minimize any problems associated with the transport of the slurry. A homogenizing vessel, sited downstream from the grinding unit, also serves as a feed receptacle for the high pressure pumps. The pumps are similar to those already used in the chemical industry.

7.6.1.2 Gasification. The gasification reactor is a cylindrical, brick-lined vessel. The material used for the brick lining must be suited to the specific gasification conditions. The coal slurry is fed into the top of the reactor through a burner where simultaneous mixing of oxygen and gasification takes place. The temperature in the reaction chamber is above the melting point of

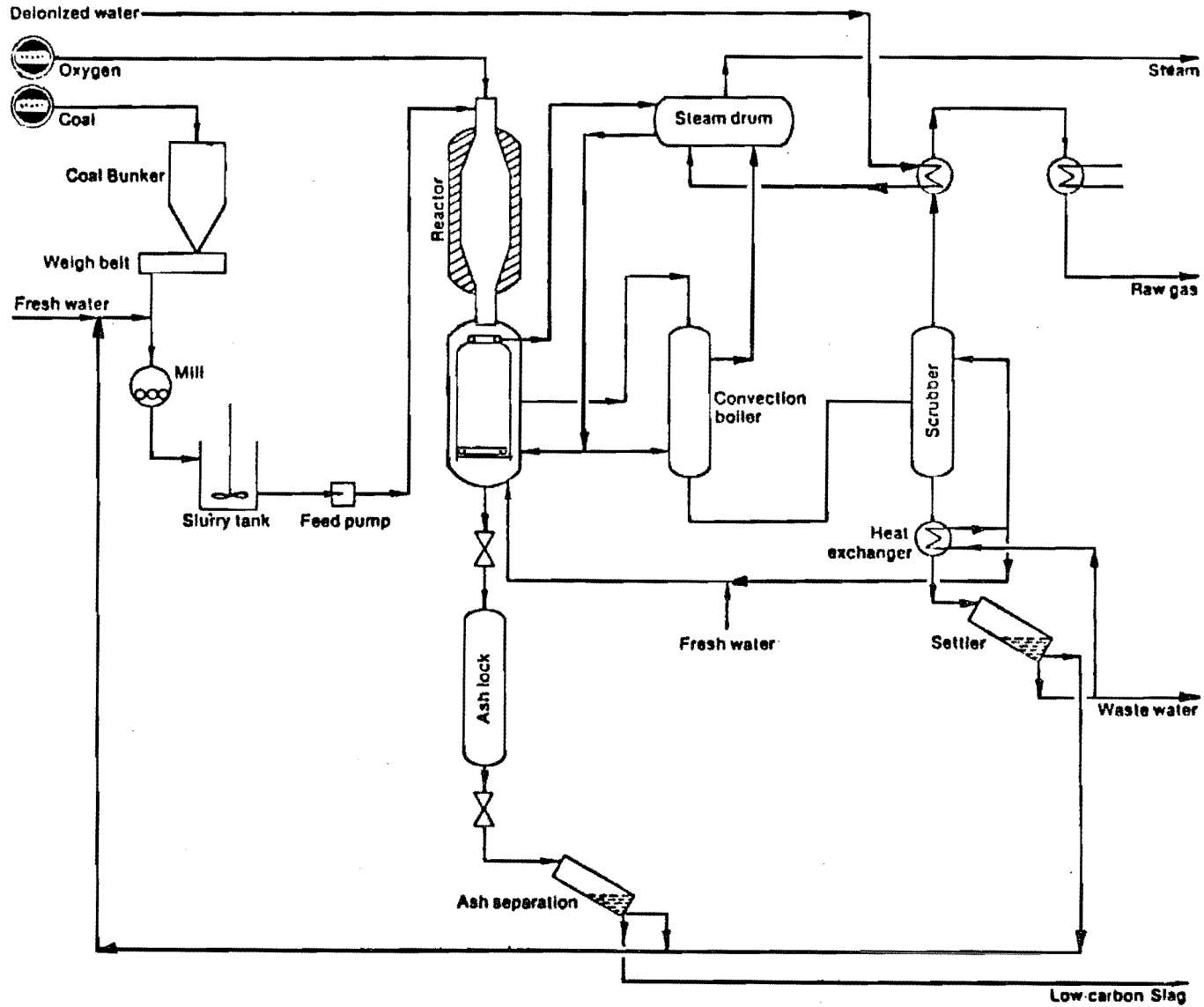


Figure 56. Texaco gasification process.

the ash. At this temperature, between 1200 and 1300°C, and an operating pressure between 3000 and 8270 kPa, the gasification reactions proceed very rapidly to achieve a high conversion of the coke in a few seconds. Typically two to three percent of the carbon is left in the ash.

7.6.1.3 Waste heat system. Depending upon the final product desired from gasification, the waste heat system can be operated in the following two modes:

1. Gas cooler with external steam generation.
2. Direct quench with internal steam generation.

In the gas cooler mode of operation, the radiant cooler, situated directly under the reaction chamber, serves to cool the gas to solidify the slag. The radiant chamber is constructed to prevent the contact between the slag and cooling surfaces and to permit good heat transfer conditions. The gas is then drawn off from the side of the lower part of the radiant cooler and is fed to the convection cooler. The small amount of solidified fine ash still present in the gas passes through the convection cooler. High pressure steam is produced from both the radiant and convection coolers. The steam is used in downstream process areas.

Prior to the carbon monoxide shift conversion unit, the cooled synthesis gas is sent to a carbon scrubber where the gas is water scrubbed and saturated to remove the final amounts of particulate matter. Since the hydrogen sulphide has not been removed from the synthesis gas, a sulphur resistant catalyst such as the cobalt-molybdenum catalyst developed by BASF may be used in the conversion.

7.6.1.4 Slag removal. The slag, collected in a water bath at the bottom of the radiant cooler, proceeds into a water-filled slag lockhopper. The vessel is emptied intermittently into a slag container. The slag is then either transported or disposed. In the case of residue coke from oil sands, the high concentration of titanium and vanadium (Table 17) which eventually will end up in the slag, economically may be worth recovering (Abdul Majd 1981) by further processing.

A series of valves operating on an automatic cycle in the slag discharge system must be constructed of special materials suitable for use with

highly abrasive solids. In addition to regulating the removal of slag, the valves must ensure that no gas leaks can occur during discharge.

Water from the slag container, consisting of solids and fine soot particles, is recycled to the slurry preparation.

In the gasification of coal, the high operating temperature of the Texaco gasifier produces a molten, glass-like, inert slag (Schlinger and Richler 1980). Inert slag is, potentially, a marketable product that can be used in various applications such as highway construction, sand blasting, etc. This slag may or may not be inert. If after leaching tests have been conducted and the slag were found to be capable of interacting with groundwater, it would require further processing and disposal site preparation.

7.6.1.5 Gas scrubbing. The cooled raw gas consisting of a small amount of fine dust is further cooled in a water scrubber to remove entrained matter. The quench water is recirculated. To avoid an excess of solids buildup in the water, a blowdown is continuously maintained. After solids separation, the water can either be recycled to the washing system or used in the coal slurry preparation. Depending on the amount of soluble constituents in the coal/coke, a small portion of the water is sent to wastewater treatment. This also prevents the salt content from rising to critical values, where corrosion may become a problem.

7.6.1.6 Carbon monoxide shift conversion. The scrubbed quenched gas saturated with steam is then passed through a train of carbon monoxide shift converters where sulphur resistant catalyst is employed. Almost complete conversion of carbon monoxide is achieved. Additional steam injection facilities are provided for the latter converters.

7.6.1.7 Gas purification. There are several commercially available acid gas removal systems. The selection of the most appropriate one depends upon the pressure, the levels of hydrogen sulphide and carbon dioxide in the raw synthesis gas, the specified levels of these impurities after cleanup, and the degree of removal of the hydrogen sulphide and carbon dioxide components.

In the case of oil sands, a hydrogen sulphide-free carbon dioxide stream pure enough to be vented to the atmosphere would be required. Another consideration would be the sulphur concentration in the offgas stream which could be sent to a Claus or Stretford unit for further processing. Both of these units can produce a marketable sulphur product.

7.6.2 Design Considerations

7.6.2.1 Feed System. The Texaco coal gasification process incorporates a slagging entrained flow pressurized gasifier. Whereas other entrained gasifiers employ a dry coal feed system, the Texaco gasifier utilizes a concentrated slurry of ground coal and water. This novel feed system is thus free from the difficulties associated with dry feed. Through the usage of stainless steel equipment and specially designed slurry pumps, the coal-water slurry can be conveyed and pressurized with minimal problems. The slurry can be compared in many ways to heavy oil, thus making coal gasification similar to oil gasification. The use of liquid feedstock also permits gasification of a wide range of carbon containing liquids.

7.6.2.2 Pressure. The high pressure operation ensures a high throughput in the gasifier. The product gas is available at high pressure for secondary synthesis processes. Additional compression of the gas is eliminated, resulting in significant utility savings.

7.6.2.3 Slag Removal. An aqueous phase suspension system has also proved suitable for the removal of slag from the gasifier. The slag entrained in the discharge water is finely grained and has good sedimental properties. The lockhopper system also has the ability to handle submicron slag particles which tend to flocculate in a water carrier.

7.6.2.4 Reaction Conditions. The high reaction temperature associated with a slagging entrained flow gasifier allows for a short residence time in the reactor, high coal conversions, and good hydrogen and carbon monoxide selectivities. This benefits both the synthesis gas yields and the gasifier efficiency.

7.6.2.5 Solids Separation. The gas/solids separation system downstream of the gasifier and the large amount of circulation water used does not prevent the occasional buildup of high ash loadings in the water stream, causing wear to the pumps and valves. This can be overcome by the proper selection of corrosion and erosion resistant materials. Two additional methods of alleviating these problems, a special treatment for streams with high erosion and corrosion potential, and the limitation of the line pressure in water streams that contain little or no solid matter, were investigated. In addition, the clarification of recycle water was improved by using flocculants, modification of settling basins, and by testing of various alternative separation techniques.

7.6.2.6 Efficiency. The performance efficiency of the Texaco gasification process relies on the optimization of several operating parameters. Some of these parameters are:

1. slurry concentration and coke reactivity;
2. oxygen requirement;
3. temperature and pressure of operation;
4. the type of scrubbing and, to a lesser degree, the purification system employed.

The slurry concentration has a significant effect on the gasification efficiency. High concentration of coke in the slurry gives higher throughput and results in increased carbon monoxide and decreased carbon dioxide concentration in the raw gas. The efficient utilization of coke energy has been the major issue in determining the economic viability of coke gasification.

The slurry concentration requires additional heating and vapourization of water within the gasifier. This results in an increased requirement of the oxygen feed to the gasifier.

The raw gas concentrations of carbon monoxide, carbon dioxide, and hydrogen are dependent on the water content of the slurry. A typical raw syngas composition obtained from coal slurry of 0.7 mass fraction solids is shown below:

<u>Component</u>	<u>Mass Fraction</u>
CO	0.54
H ₂	0.34

CO ₂	0.11
H ₂ S	0.003
N ₂ /Ar	0.006
CH ₄	0.0001

Slurry concentrations of more than 0.6 mass fraction solids are possible with fluid coke. Depending on the reactivity of coal and reaction temperature, carbon conversions of between 94 and 98% have been achieved through one pass. During test runs performed by Texaco with fluid coke, carbon conversion rates for the coke were found to be consistent with those for coal.

The consumption of oxygen in the gasification process is an important economic consideration. About 250 m³ of oxygen per 1000 m³ of synthesis gas is normally required with coal slurry concentration of 0.6 mass fraction.

The operating pressure and temperature of the gasifier has a direct effect on the carbon conversion and throughput of the process. Normal operating temperature is between 1300 and 1600°C, at an operating pressure of about 4 000 kPa.

An overall thermal efficiency of up to 94% has been reported with a cold gas efficiency of 76%, i.e., the gas contains 76% of the chemically-bound energy available from the coal. The remaining 18% of the overall thermal efficiency is contained in the high pressure steam produced in a waste heat boiler. Low pressure steam is generated by further cooling of the quenched gas, thus increasing the overall efficiency of the process.

7.6.2.7 Refractory. The reactor wall has to be lined with ceramic refractory as a protection against the reducing atmosphere in the gasifier, and the reactor is also subject to attack by the corrosive slag.

Erosion of the refractory within the gasifier is an important design consideration. The rate of the corrosive attack is mostly dependent on the operating temperature of the gasifier. Variations in the coal/coke rate, oxygen and steam rates, and operating pressure will also contribute to the refractory erosion. This corrosion is caused by penetration of the liquid slag into the pore-formation of the refractory material of the gasifier. The rate of the slag penetration increases with decreasing viscosity, i.e., increasing temperature.

The chemical reaction at the slag/refractory interface also increases with temperature.

Since efficient gasification requires high temperature operation, various means were developed for increasing the service life of the refractory lining. Development consisted of the following:

1. the use of better resistant materials to reduce chemical reaction rate;
2. decreasing the penetration rate of the slag by the use of fluxing material;
3. increasing the viscosity of the slag, sufficiently to reduce corrosive penetration but not high enough to cause operation problems.

Development based on these guidelines resulted in a predicted service life of the gasifier lining of more than one year, for various types of coal.

7.6.3 Environmental Considerations

Advances made in the Texaco gasification process with respect to the environmental aspects are of special importance:

1. The gas produced is practically free of undesirable byproducts such as aliphatic, olefinic and aromatic hydrocarbons, phenols, and tars. This considerably simplifies the expensive gas purification and water treatment required in other lower temperature gasification processes.
2. The molten glass-like slag from coal gasification is considered to be inert. Because of the anticipated high metal content, the slag from coke residue, however, may require leaching tests before being disposed of.

The safe disposal of the slag is a major consideration in an oil sands project, since more than 10% of the coke processed ends up as ash. This may amount to about 250 t/d of ash.

3. Due to the high temperature of gasification, the waste-water contains only traces of organic compounds. With the exception of naphthalene, toluene, and benzene, present at levels of parts per billion, no hazardous organics as included in the U.S.

Environment Protection Agency pollutant list could be detected (Schling and Richler 1980).

The waste can be treated in commercially available water treatment processes to meet present environmental regulations.

4. During the gasification process, the high sulphur content in the residue coke is converted to hydrogen sulphide. There are many downstream purification processes which employ solutions of varying types of solvents to selectively remove hydrogen sulphide from the stream containing carbon dioxide and hydrocarbons. The hydrogen sulphide-free carbon dioxide can be released directly to the atmosphere.

7.6.4 Adaptability

The Texaco gasifier is reported to have tested various types of coal, including fluid coke, from oil sands (Schlinger 1980). The hardness of coals tested at Oberhausen, West Germany falls between Hardgrove indices of 55 and 100. The estimated Hardgrove index for residue coke, however, is 15 to 20, which may make the coke difficult to grind. But as mentioned previously, grinding may not be required if the coker product is of acceptable quality for gasification.

The coals tested were also of low (0.008 to 0.039 mass fraction) sulphur content. The residue coke, however, has a much higher sulphur content (0.087 mass fraction). This may be an added concern as to the choice the refractory lining of the gasifier and also for the downstream scrubbing processes.

The higher C/H ratio of the residue coke than for the coal makes it less reactive. This may require modifications to the gasifier startup procedure. In addition, the amount of oxygen and steam requirements will differ from that for coal.

Further process development may possibly be required in the areas of waste heat recovery and slag removal if the Texaco gasification process is to be used for hydrogen production.

Clearly, there are specific process considerations to be resolved before any gasification process can be successfully integrated into an oil sands

complex. However, developmental studies already performed indicate that these are not considered to represent any technological barrier.

7.6.5 Economic Discussion

Coal gasification plants can be selected to best process the specific type of coal being considered. The coal preparation requirements of a gasification plant are influenced by the coal mining process. This may have a significant influence on the capital and operating costs of a gasification unit.

Since published reports were the primary source of data, corrections had to be made to arrive at the capital and operating costs for a Texaco oil sands gasification plant. These were due to:

1. The published costs are often based on a U.S. location, where the severe weather conditions experienced in Northern Alberta may not prevail. However, the additional capital charge associated with the winterization and certain special materials of construction is not expected to add more than 5 to 10% of the installed gasification equipment costs.
2. The gasification technology is based on coal rather than coke gasification. The coal will require different preparation facilities than the coke obtained from bitumen upgrading.
3. Most of the published data are either for fuel gas, methanol, or gasoline production facilities, rather than for hydrogen production.

The Texaco coal gasification process has been proposed and costed for various projects in the U.S. (Pace 1982). For example, the Cool Water Gasification project for 1000 t/d coal feed to produce 100 MW net power is estimated at U.S. \$300 million (1982 first quarter). Another proposed gasification plant producing $1.19 \times 10^9 \text{ m}^3/\text{d}$ medium heating value gas, 321 MW power, 635 t/d methanol, and 200 t/d sulphur is estimated at U.S. \$416 million (1982 first quarter).

A Central Coal Gasification plant by Northern Indiana Public Service Company employing a Texaco Coal Gasification process to utilize 6210 t/d of Indiana coal had an estimated total investment cost of U.S. \$880 million (1980 fourth quarter). The plant was designed to produce 1465 MW of low to

medium heating value gas (Cameron 1981) at an annual operating cost, excluding the cost of coal, of U.S. \$38 million.

Netzer (1980) and Tart and Rampling (1981) have also presented the economics of coal gasification processes.

The gasification processing steps for an oil sands project have been discussed in Section 7.6. Accordingly, the capital and operating costs were estimated for coke slurry preparation (including grinding), coke gasification, acid gas scrubbing and carbon dioxide removal, an oxygen plant, and carbon monoxide shift conversion. The capital cost for utility and steam and water treatment plants were also estimated.

An economic evaluation for gasification of 2200 t/d of fluid coke to produce mhv gas has been discussed by Flynn and Ambrose (1977). The clean mhv gas formed a replacement for a portion of the natural gas required by the Mildred Lake plant. As a result, an estimated savings in natural gas with a gross energy equivalent of 379 MW (8.3 million M³/day) was obtained.

On the basis of published information, the costs presented by Flynn and Ambrose, the total installed capital and operating costs for processing 2050 t/d of fluid coke at a location around Fort McMurray have been estimated and are summarized in Table 22.

The operating costs include operating and maintenance labour and raw material costs. Utility and coke costs are not included. The credits from natural gas savings and steam exported are not included in these costs.

A brief mass balance of inputs and outputs from the gasification unit is given in Table 23.

Assuming that the hydrogen produced by gasification process was previously obtained from natural gas partial oxidation or steam reforming, implementation of a coke gasification unit in an oil sands complex would save more than 750 t/d of process natural gas.

Steam generation from gasification can be used to drive the compressor in the air separation plant. The hydrogen sulphide is sent to the Claus plant and a clean carbon dioxide vent discharged to the atmosphere. The inert slag from the bottom of the gasifier can be sold if markets are available in the vicinity or can be disposed of along with mine tailings within the complex.

Table 22. Capital and annual operating costs
for Texaco gasification plant. ^{a,b}

Total installed capital cost	\$496 000 000
Total annual operating cost	\$26 000 000

^a Costs are presented in mid 1982 Canadian dollars.

^b Utility and coke costs and byproduct credits are not included.

Table 23. Gasification mass balance.

Inputs (t/d)		Outputs (t/d)	
Fluid coke	2050	Hydrogen	350
Oxygen	1850	Carbon Dioxide	5200
Water	2100	Slag	250
		Hydrogen Sulphide	200

7.7 RETROFITTING

As mentioned earlier, coke gasification can represent a major portion of an oil sands project. Initial planning of the project should consider accommodating energy integration, the hydrogen product, the hydrogen sulphide constituent of the raw gas, the oxygen supply, and other equipment associated with gasification within the rest of the complex.

Unlike the Flue Gas Desulphurization and Tail Gas Treatment units, the coke gasification unit is primarily a production facility with primary concern for the most effective utilization of the coke and improvement of the yield from the oil sands. Gasification, from an oil sands point of view, is an alternative to hydrogen production by partial oxidation or steam reforming of natural gas. An installation of coke gasification would thus replace several existing operations within an oil sands complex.

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Retrofitting of a gasification unit to an existing synthetic crude facility involves a number of complexities. Some of the essential considerations are discussed below:

1. A Texaco coke gasification plant involves slag and coke storage, an oxygen plant, grinding and slurring preparation, gasification, heat recovery, gas cleaning, and wastewater treatment. These units require a considerable plot area, for example, a 5000 t/d (2.5 times the capacity for this study) plant with all the above facilities requires a plot area of about 40 000 m².
2. Slurring involves large amounts of water, both fresh and recycled. Water treatment and cooling tower facilities must cope with these water demands. Import of makeup water and integration of the utility requirements for the complex are also required.

3. The oxygen plant is required to supply oxygen to the gasifier at pressures of 4000 to 5000 kPa. However, if an oxygen plant is already available, the capacity and the supply pressure of the existing oxygen unit must be considered.
4. The gasifier installation must consider steam export from the unit. Steam is generated from the gasifier quench area and also by cooling of the raw gas. Direct quenching of raw gas results in a lower steam requirement for the downstream shift conversion thus reducing the impact on the boiler feed water system and steam generation.
5. The removal of wastewater from the process requires a wastewater treatment facility. Recycle of process condensate to the gasifier minimizes the impact on water treatment. The slag, if found to be inert, is a marketable byproduct, and as such will represent an operating credit to the facility. If it is not inert, the slag will require an environmentally secure dump area for disposal.
6. The purification of the raw gas and conversion to hydrogen involves shift converters, hydrogen sulphide scrubbing, and carbon dioxide removal. Also, the hydrogen sulphide offgas stream sent to an existing Claus plant would necessitate an increase in capacity to handle the additional sulphur associated with the gasification of fluid coke.

In addition to all the above requirements, a control room with various safety and maintenance features would be required.

7.8 RESIDUE GASIFICATION IN OIL SANDS PLANTS

As described in this section, gasification provides a potential means of utilizing high sulphur residues in an environmentally acceptable manner. The gasification process can be designed as either a prime source of energy or as part of a hydrogen production facility, with incidental energy recovery.

The technology remains to be demonstrated on a commercial scale using oil sands residues. However, considerable progress to this objective has been made since the design and construction of the two existing oil sands plants.

8. FLUIDIZED BED COMBUSTION (FBC)

8.1 INTRODUCTION

The increased concern over world oil supplies and the desire for energy self sufficiency has had a significant influence on the processing industry which will rely on high sulphur feeds as main sources of energy. The heavy oils of western Canada and the coke derived from oil sands bitumen upgrading processes form a part of these fuels.

During the 1930's, the desire to increase steam output to supply large turbogenerators led to the development of pulverized coal firing. This has since become a conventional method for steam generation for large power plants. The pulverized coal combustion technology has been well documented elsewhere (Morrison 1978).

The need to utilize the high sulphur and/or low grade fuel and to meet the strict environmental standards contributed to the development of fluidized bed technology for steam generation. This system offers considerable advantages over the conventional pulverized coal fired systems (Smith 1977). The use of fluidized bed combustion to burn coal is an emerging technique and various aspects of this technology are being evaluated through a number of development projects.

This section of the report outlines the development trends of the techniques and discusses some of the problems and issues facing this development.

8.2 BACKGROUND

A fluidized bed consists of a bed of solid particles suspended by an upflowing stream of gas. As the gas flow rate is increased, the particles tend to separate and the bed begins to expand. Further increase in gas flow rate forms bubbles which rise through the bed causing a highly turbulent mixing of the particles. This gives the bed the appearance of boiling fluid hence the term bubbling bed is sometimes used for describing fluidized beds operating at moderate gas velocities.

FBC technology may be used to effect sulphur removal from flue gas through the burning of sulphur containing fuel in a bed of limestone or

dolomite that has been fluidized. This technology combines fuel combustion, heat transfer and desulphurization in a single combustor.

The origin of fluidized bed combustion (FBC) is generally traced back to the Winkler gas generator, developed during the early 1920's in Germany. Extensive FBC research and development work was conducted in England during the mid 1960's. The U.S. Government originally entered into the development of fluidized bed combustion because of the potential for lower-cost industrial size boilers. Later, about 1967, the advantages of lower NO_x and SO_2 emissions were observed. However, it was not until the U.S. Clean Air Act of 1970 that the impact of these findings was realized. The oil embargo of 1973 further promoted the development of FBC technology. Thus development of fluidized bed combustion technology became a prime mission of the U.S. Department of Energy and other oil importing countries.

The primary reason for the development of FBC technology is to reduce the use of oil and instead utilize low grade and/or high sulphur fuels in an environmentally acceptable manner for the production of heat. This heat may be in the form of steam, hot air or hot-process fluids.

There are three principal forms of FBC technology being developed: Atmospheric Fluidized Bed (AFB), Pressurized Fluidized Bed (PFB) and Circulating Fluidized Bed (CFB). AFB involves a relatively shallow bed operating at atmospheric pressure within the combustion zone. PFB involves a deeper bed operating at up to 10 atmospheres or higher within the combustion zone. CFB involves a bed, generally at atmospheric pressure, which is circulated outside the combustion zone for purpose of heat recovery and then returned to the combustion zone.

8.3 POTENTIAL OF FLUIDIZED BED COMBUSTORS

The inherent advantages of fluidized bed combustors make them ideal candidates for converting low grade fuel to a useful clean process energy. FBC has various advantages over pulverized coal combustion. FBC offers a means of overcoming the problems of high ash, low heating value and sulphur retention which have inhibited the use of these fuels in many applications with conventional combustion techniques. However, FBC technology is still in its development stages (although industrial boiler units are available commercially up to approximately 150 t/h steam generation rate) and is expected to be fully

commercialized by the end of the decade. The FBC systems are expected to be used in large power generating plants and in the process industry for utility steam, hot drying air or as cracking furnaces.

Some of the expected benefits of this technology are discussed below.

8.3.1 Fuel Flexibility

Unlike a conventional coal-fired boiler, fuel types, fuel quality and ash properties are not a significant factor in fluidized bed boilers. The combustion temperature is low and prevents ash from softening and melting. High, medium and low quality and low grade fuel, including petroleum coke, lignite, anthracite refuse, municipal waste, biomass and wood chip can be efficiently and economically burned, meeting clean air criteria, without the use of a stack gas cleanup system.

A principal objective of Atmospheric Fluidized Bed Combustion (AFBC) is the burning of low quality fuels such as anthracite fines, lignites and washery tailings that cannot be burned or do not burn well in other types of combustion systems. The fluid coke as mentioned in Section 7 is fairly hard and unreactive. When burned in conventional pulverized combustors, carbon burnout is incomplete and inefficient (Anthony, Desai and Friedrich 1981). The use of AFBC will overcome these problems.

8.3.2 Reduced Emissions

One of the prime incentives for development of the AFBC boiler is the promise of sulphur capture during the combustion process. High-sulphur fuels burned in the presence of a sorbent in the FBC eliminate the need for flue-gas treatment. This will result in lower investment and operating costs for the facility.

The combustion process occurs in the presence of limestone. The limestone reacts with the sulphur dioxide formed during combustion to produce calcium sulphate (gypsum), a dry solid material. The optimum sulphur capture depends on the combustion temperature calcium to sulphur ratio and the general operating condition (Zheng 1982). Sulphur dioxide retention in excess of 90% has been reported.

NO_x emissions from FBC are relatively low compared with emissions from conventional coal combustion methods. Pilot FBC boilers typically have NO_x emissions in the range of 0.15 to 0.2 kg/10⁶kJ. This is below the U.S. New Source Performance Standards (0.3 kg for bituminous coal and 0.25 kg/10⁶kJ for subbituminous coal). The low NO_x emission of FBC is believed to be primarily due to the low combustion temperature employed in the system.

Typical boiler emissions for two FBC systems are given in Table 24.

8.3.3 Low Combustion Temperatures

AFB Combustors typically operate at temperatures between 800 and 950°C. This range of combustion temperatures arises primarily from:

1. the need to operate below the temperature at which the ash fuses;
2. the range of maximum sulphur retention;
3. the desire to minimize the release of alkali metals from the ash.

The low operating temperature also has the desirable effect of releasing low levels of NO_x .

In Pressurized Fluidized Bed (PFB) applications higher temperatures than 950°C may be desirable for increased thermal efficiency.

Higher combustion temperatures are possible for fuels with high fusion temperatures. Residual coke from bitumen upgrading has fairly high ash fusion temperatures (Table 25). However, high temperature is detrimental to sulphur retention. This, in the case of coke, is further complicated by the high (0.05 to 0.09 mass fraction) sulphur content.

8.3.4 Reduced Heat Transfer Area, Small Boiler Volume

It has generally been assumed that the high heat transfer coefficients to surfaces in the bed will enable smaller, more compact boilers to be built. For small industrial boilers there may be a saving in size and cost over conventional coal firing equipment but not over oil or gas fired boilers. Compact, completely shop assembled units may be available for units smaller than 35 t/h of steam.

As only 40 to 60% of the heat released is removed from the bed, there is still the need for large convective passes.

Table 24. Typical boiler emissions for FBC systems.^a

Pollutant	SAIC ^b	Kauttua ^c	U.S.
	Boiler kg/10 ⁶ kJ	Boiler kg/10 ⁶ kJ	Standards kg/10 ⁶ kJ
Particulate	0.08	-	0.17
Sulphur dioxide	0.14	0.11	1.29
Nitrogen oxide	0.14	0.18	-
Carbon monoxide	-	0.03	-

^a Adapted from original tables in Leon and Choksey (1981) and Oakes (1982).

^b Shamokin Area Industrial Corporation, burning Anthracite culm in AFBC.

^c Burning Cumberland coal in Pyroflow CFBC.

Table 25. Fusion characteristics of ash from Suncor coke.^a

Ash fusion temperatures, °C	Oxidizing	Reducing
Initial deformation	1140+	1410
Spherical softening	1480+	1480+
Hemispherical softening	+	+
Fluid	+	+

^a Adapted from original table in CANMET Report ERP/ERL 81-27 (TR).

A definitive size advantage is obtained for the combustor in pressurized applications. However, this may require additional facilities to clean the gas sufficiently to be suitable for use in a gas turbine (see Section 8.6).

8.3.5 Feedstock Preparation and Ash Disposal

Within limits, FBC can handle variously sized fuel. Pulverizers are not required since it is not necessary to reduce the size of the feedstock below 60 mm. Stoker sized coal up to approximately 30 mm may generally be fed to units equipped with over-bed feeders whereas units with under-bed pneumatic feed generally require approximately 6 mm.

Since the normal operating temperature of the bed is below the fusion temperature of the coal ash, the ash does not fuse into clinker or slag. Thus, the ash can be removed as a granular product, easily handled by a conventional pneumatic solids transport system. Ash and spent bed material removed from the bed for bed inventory control is normally cooled prior to disposal whereas this is not normally necessary for particulates removed from the cooled flue gas. A safe disposal site may be required, normally consisting of a properly designed land fill wherein leaching to surrounding areas is controlled. However, extensive studies by others have concluded that AFBC residues are non-hazardous. For example, the residues may be useful for agricultural purposes or for stabilizing road making materials. Since the residue is essentially gypsum, it may also be useful in the wall board and other building material industries.

8.3.6 Economics and Efficiency

One of the objectives in burning residues is to produce a low-cost source of steam. Recent studies (Mesko 1980) show that the cost and size for power stations based on atmospheric fluidized combustion system will be comparable to power stations based on conventional coal fired system. This is reflected in Tables 26 and 27. Only when flue-gas desulphurization is required does a fluidized bed combustor show a significant cost advantage. The cost of

Table 26. Capital cost comparison for Georgetown FBC and a pulverized coal fired boiler facility for 45 t/h steam rate.^a

	Thousands of Dollars ^b	
	FBC Boiler Facility	Conventional Boiler Facility
Purchased Process Equipment such as Fans, Drives, Transformers, Switchgear, Stack, Dust Collection and Conveying Equipment	\$ 1068	\$ 1735
Boiler Installation including Controls and instrumentation	1482	1262
General Construction	1154	1654
Steel Fabrication and Erection	475	525
Mechanical Construction	917	796
Electrical Construction	275	290
Professional Services	<u>1100</u>	<u>1100</u>
TOTAL	\$ 6471	\$ 7362

^a Source: Mesko 1980.

^b Costs presented in 1978 US dollars.

Table 27. Detailed operating and owning costs for fluidized bed and conventional steam generators.^a

Item	Cost \$/tonne of steam boiler type ^b		
	Fluidized Bed		Conventional
	Culm	Coal	Coal
Materials			
coal or culm	0.40	3.86	3.80
limestone	0.22	0.48	-
chemicals	0.24	0.48	0.48
lime	-	-	0.66
soda ash	-	-	0.04
water	0.36	0.36	0.36
Labour and Utilities			
Electricity	2.00	1.92	1.72
Labour	0.84	0.26	0.52
Maintenance	0.60	0.52	0.58
Waste Handling	<u>0.20</u>	<u>0.06</u>	<u>0.22</u>
Direct Costs (Total)	4.30	7.94	8.38
Indirect Costs (Insurance, amortization and taxes)	<u>3.82</u>	<u>3.52</u>	<u>3.98</u>
TOTAL COST	9.12	11.46	12.36

^a Adapted from original tables in Leon and Choksey (1981).

^b Costs are presented in 1979 US dollars.

generating 10 t/h of 1400 kPa steam from culm¹ priced at \$1/t showed the culm-fueled boiler to have 30% cost advantage over a stoker fired boiler using a scrubber for SO₂ control. Similarly, the cost of an FBC plant burning commercial coal is expected to be less than that of a conventional coal-fired plant with scrubber. Studies of utility sized FBC installations have indicated potential savings of approximately 15% over conventional coal-fired plants with scrubbers.

8.3.7 Reduced Fireside Fouling, Corrosion and Erosion

This is a real advantage when dealing with high fouling feedstocks since the FBC technique offers greater operational reliability and lower maintenance costs. Normally, soot blowers are not required.

However, the National Coal Board in the U.K. has recently indicated the need for material development and understanding for applications where high temperature components (650°C) are exposed to beds containing sulphated limestone. Stringer (1982) has also emphasized the need for long term corrosion and erosion tests for fluidized bed combustors.

Nevertheless, FBC presents less problems than the pulverized combustion systems.

8.3.8 Firing Gas Turbines

To date there is no adequate demonstration that it is possible to fire a gas turbine with the exhaust gases from a fluidized combustor. The difficulty lies in cleaning the combustion gases sufficiently to enable them to pass through the turbine. Devices which have been used to clean the gas include

¹ Culm is a generic term for any nonsalable byproduct resulting from the production of marketable coal. It contains appreciable amounts of coal, and is essentially a low-cost, poor-quality fuel reserve. Over 1 billion t of anthracite culm have accumulated over the years, in the form of small mountains throughout northeastern Pennsylvania.

Similar piles of coal refuse (gob) are found in bituminous mining regions; for example, Illinois has the equivalent of an estimated 60 million t of coal in its bituminous refuse. These culm banks are eyesores, which can pollute air, land, and water as a result of spontaneous combustion and acid runoff.

multi-stage cyclone separators, hot electrostatic precipitators, ceramic filters and granular bed filters. Further development is taking place in this area as well as in the area of improved gas turbine materials. Once this problem is solved, the utilization of combustion gases in a turbine for power generation may become commercial. Other methods of gas turbine utilization being developed include heating air in the FBC unit and expanding the hot air or a mixture of flue gas and hot air through the turbine, thereby minimizing turbine erosion.

8.4 FLUIDIZED BED COMBUSTION DEVELOPMENT ACTIVITY

One might perhaps wonder why with such an impressive list of advantages fluidized combustion is taking some time to become commercially acceptable. This is partly because differing developmental problems from a diversity of possible applications tend to be lumped together. More importantly, the earlier promises are in practice difficult to fulfill completely. Industry is also reluctant to adopt new technology unless there is adequate demonstration or clear economic advantages. Economic conditions and high interest rates have tended to discourage new capital projects in general.

However, fluidized bed combustors are available commercially. These include incinerators, small (less than 75 t/h of steam) packaged boiler and hot gas generators and water-tube boilers up to 150 t/h. Not all the developments have operated successfully. Trouble free operation depends not only on the suitability of the application but also on the design skills and experience of the group marketing the equipment.

The two major applications of FBC are as industrial boilers and power generators. Development in other fields of application include marine applications either for steam turbines or as waste heat boilers, the disposal of coal mining wastes, crop drying, disposal of sewage, incineration of wastes such as wood chips, etc. A recent study of the fluidized bed combustion of anthracite wastes indicated the potential of the technique for exploiting these waste dumps from previous mining activity.

The development activities of FBC technology falls in three major categories.

1. Atmospheric Fluidized bed combustion (AFBC);
2. Pressurized Fluidized bed combustion (PFBC);

3. Circulating Fluidized bed combustion (CFBC).

The first two can broadly be termed as conventional at bubbling bed systems and the third a recently developed second generation fluidized bed system.

In current FBC applications at atmospheric pressure the heat released is generally used to raise steam in industrial boilers or to incinerate waste materials. At increased pressures it is proposed to recover the energy by passing the pressurized combustion gases through gas turbines in a combined cycle. This system would generally be restricted to the generation of electricity. The recent second generation CFBC system is currently used primarily for industrial boilers.

Many countries have nationally financed development programs on fluidized combustion. A number of developments which have reached the pilot plant or the demonstration stage are mentioned in the following sections.

The application of FBC to the Canadian energy situation was, however, somewhat problematic, as no Canadian boiler manufacturers were engaged in the development of FBC boilers. The Department of Energy Mines and Resources (EMR) subsequently initiated a program of five FBC demonstration projects (Lee 1980). These demonstration projects are either at the conceptual stage or undergoing techno-economic assessments (Taylor and Friedrich 1982).

8.5 ATMOSPHERIC FLUIDIZED BED COMBUSTION

A number of projects (Table 28) involving various types of AFBC are being developed for utilization of low grade and low quality fuels. The objectives of these projects are many fold. The development of an efficient, reliable and economic AFBC encompasses several considerations with particular emphasis on fuel adaptability and pollution control.

For more than a decade Great Britain has accumulated a considerable body of experience in the fluidized combustion of coal. The most popular conventional pulverized coal fired boiler in Britain is the horizontal shell boiler. Although the National Coal Board (NCB) is attempting to adapt this to fluidized bed firing, the preferred designs have:

1. vertical combustion chambers with vertical thermosyphon tubes to give water flow by natural circulation; or

Table 28. Atmospheric Fluidized Bed Combustion Projects.

Organization	Location	Description	Size MW(th)	Objective	Status
UNITS IN BRITAIN					
Universities, etc.	Various e.g., Cambridge, Sheffield, Aston, Imper- ial College	Laboratory scale fluidized beds	0.01 to 0.1	Fundamental studies	Operating
National Coal Board	Cheltenham	Fluidized combustion test rig	0.1	Feedstock testing facility	Operating
National Coal Board	Cheltenham	Materials testing facility	0.1	For corrosion/ erosion tests of boiler tubes and metallic components	Operating. Recently completed 2 x 1000 and 4 x 250 hours tests
Stone Platt Fluidfire	Netherton	Hot water boiler	0.3	Commercial prototype	Operating
National Coal Board	Cheltenham	Hot water boiler	0.6	To obtain design data	Commissioned 1974 still in operation
National Coal Board	Cheltenham	Fluidized bed coal washery tailings combustor, 1 tonne/h input	0.7	To demonstrate combustion of colliery tailings	Commissioned 1974 still in operation. No heat recovery facility
Heeman Environmental Systems Ltd/Combustion Systems Ltd	Caernarvon	Sewage sludge incin- erator	0.7	Commercial design	Operated since 1977
National Coal Board	Dudley	Conversion of horizon- tal shell boiler designed for conven- tional coal firing	1.2	To demonstrate the application of fluidized bed combustion to horizontal shell boilers	Commissioned 1975 still in operation
National Coal Board	Peterborough	Fluidized bed test rig	1.5	Obtaining design data for 30 MW (th) boiler	Commissioned 1977
National Coal Board	Bury	Vertical shell steam boiler	2.5	Field trial demonstration	Commissioned 1977
National Coal Board	Hereford	Vertical shell hot water boiler	3	Field trial demonstration	Commissioned 1977
National Coal Board	Cheltenham	Horizontal oil-fired shell boiler	3	Development for retrofit on gas or oil-fired boilers	Boiler has been installed but retrofit not completed
National Coal Board	Letherhead	Vertical shell boiler	3.3	Operation and test plant	Operating since 1969
National Coal Board G.P. Worsley & Co. Ltd.	Selby	Hot gas generator for crop drying	5	Commercial proto- type demonstration crop dryer	Commissioned 1976 in commercial use
National Coal Board/ G.P. Worsley & Co. Ltd.	Newark	Hot gas generator for crop drying	5	As above	Commissioned 1977 in commercial use
National Coal Board/ G.P. Worsley & Co. Ltd.	Okehampton Thetford Lincoln	Commercial furnaces	5	Commercial design	In commercial use

Continued...

Table 28. Continued.

Organization	Location	Description	Size MW(th)	Objective	Status
National Coal Board	Widnes	Hot gas generator for crop drying	6	Commercial phototype demonstration crop dryer	Commissioned 1975 in commercial use
National Coal Board	Newcastle-under-Lyme	Locomotive type steam boiler	10	Field trial demonstration	Commissioned 1978
Combustion Systems Ltd./Babcock & Wilcox (UK) Ltd.	Renfrew	Babcock cross type steam boiler	16	Retrofit of oil boiler. To obtain operating data on fluidized combustion firing	First operated 1977. Results of trials have been used for commercial scale designs
UNITS IN U.S.					
Universities	Various eg. MIT, Virginia	Laboratory scale/pilot scale test rigs	0.01 to 0.6	Fundamental studies	Operating
Virginia Polytech	Virginia	Stone Platt Fluidfire Hot water boiler	0.3	Demonstration of commercial design	Installed 1978
Department of Energy	Morgantown	Fluidized bed boiler 0.1 tonne/h input	0.3	To burn anthracite waste	Operating
FluiDyne	Minneapolis	Atmospheric pressure furnace	0.3	Test unit	Operating
Department of Energy	Oak Ridge	Atmospheric fluidized bed combustor heating air for closed cycle gas turbine (MIUS)	0.3 to 0.5	Test unit to provide information for the construction of commercial scale plant	Operation began in 1979
Department of Energy/Battelle Columbus	Columbus	Industrial fluidized bed boiler	1	Demonstration plant	Operation began in 1980
Department of Energy/FluiDyne/Owatonna Tool Co.	Owatonna	Industrial fluidized bed furnace	1.5	Demonstration plant	Operation began in 1979
Combustion Systems Ltd/Johnston Boilers	Ferrysburgh, Michigan	Locomotive type boiler	4	Commercial design	Operating since 1977
Department of Energy/Exxon Research and Engineering Co	Linden	Industrial fluidized bed boiler	4	Demonstration plant	Operation began in 1979
Department of Energy	Morgantown	Three cell fluidized bed combustor	4	Test unit to provide information for building industrial plants	Operation began in 1979
Electric Power Research Inst/Babcock & Wilcox Co.	Alliance	Fluidized bed test facility	7	To collect information	Operating
Department of Energy/Combustion Engineering Co.	Great Lakes Naval Training Centre	Two industrial fluidized bed boilers	16	Demonstration plant	Plant under construction Operation began in 1980

Continued...

Table 28. Continued.

Organization	Location	Description	Size MW(th)	Objective	Status
Ohio State Dept of Administrative Services/Babcock & Wilcox (UK) Ltd.	Columbus, Ohio	Atmospheric fluidized bed boiler, retrofit	18	Commercial plant for hospital services	Under construction, commissioned the end of 1979
Department of Energy/Georgetown University	Washington DC	Industrial fluidized bed boiler	33	Demonstration plant	Operation started in 1979
Department of Energy/Foster Wheeler/Pope Evans & Robbins	Rivesville	Multiple chamber fluidized bed	100	To collect information for the construction of a 200 MW (e) plant planned for 1980	Operating since 1977
Ohio State/Babcock Riley Stoke Co.	Ohio	Industrial fluidized bed boiler	6	Heating for Central Ohio Psychiatric Hospital	Started April 1980
D.O.E./Foster Wheeler	Wilkes Barre Pa.	Demonstrating saturated steam plant	60	District heating for downtown area	Operating
Tennessee Valley Authority/Babcock and Wilcox		Pilot plant	20	To collect information for operation of a 200 MW demonstration plant	Commission in May 1982
UNITS IN AUSTRALIA					
Universities of Adelaide, Melbourne, NSW, Sydney	Adelaide, Melbourne, Sydney	Laboratory scale test facilities	0.076 to ^a 0.15 dia.	Combustion studies	Operating
Australian Mineral Development Laboratories	Frewville, SA	Fluidized bed test facility	0.3 dia.	Incineration of chlorinated hydrocarbons	Operating
CSIRO Division of Process Technology	North Ryde NSW	Atmospheric fluidized bed pilot plant	0.3 x 0.3	Combustion and corrosion studies	Operating
State Electricity Commission of Vic	Richmond, Vic	Atmospheric fluidized bed pilot plant	0.35 x 0.35	Combustion and fouling studies on brown coals	Operating
Broken Hill Pty Ltd.	Shortland, NSW	Fluidized combustor (no heat recovery)	0.6 x 0.9	Test facility	Operating
Pyrecon Pty Ltd.	Spit Junction NSW	Incinerator test facility	1.1 dia.	Industrial waste incineration	Operating
Metropolitan Waste Disposal Authority	Castlereagh, NSW	Fluidized bed incinerator (Pyrecon Pty Ltd.)	1.1 dia.	Trial commercial installation for disposal of liquid wastes	
Flameless Incinerators Pty Ltd.	Brisbane, Qld	Fluidized bed incinerator	0.9 x 1.2	Trial commercial installation at a state-owned abattoir	Commissioned in 1979
Joint Coal Board/CSIRO Division of Process Technology	Camden, NSW	Demonstration plant for disposal of coal wastes	1.6 x 2.6	Demonstration of combustion of wastes for safe disposal and generation of power	Operating

Continued...

Table 28. Continued.

Organization	Location	Description	Size MW(th)	Objective	Status
UNITS IN THE FEDERAL REPUBLIC OF GERMANY					
Babcock-BSH	Essen	Tailings combustor, 0.1 t/h input	0.2	To demonstrate com- bustion of pre-dried tailings	Operating
Ruhrkohle AG	König Ludwig	Coal-fired power plant	5.8	Demonstration plant for district heating	Start of construction 1978
Lurgi-Gesellschaft für Chemis und Hutten- wesen GmbH	Frankfurt	"Turbulent layer" fluidized bed furnace	33	Combustion of low grade fuels	Operating
Ruhrkohle AG	Düsseldorf	Coal-fired power plant	35	Retrofit of existing plant for combined production of power and heat	Start of construction 1978
Ruhrkohle AG	Greiseman	Fluidized bed combus- tion plant for burning flotation tailings	35	Prototype plant	Construction started in 1977
Saarbergwerke	Volkingen/ Fenne	Fluidized bed combustor in power station with stack gas scrubbing	667	Large-scale demonstration plant	In the planning phase
UNITS IN INDIA AND SWEDEN					
Central Mechanical Engineering Inst	Durgapur India	Fluidized bed boiler test facility	0.3	Demonstration of combustion of coal washery rejects and coke breeze	Commissioned 1972
Central Fuel Research Institute	Dhanbad India	Scale down hot water boiler	0.8	Combustion studies	Operating
Fuel Research Institute	Jorhat India	Scale down hot water boiler	0.8	Sulphur removal studies	Operating
Bharat Heavy Electricals Ltd.	Bharat India	Atmospheric boiler	4	Demonstration	Operating
AB Enköpings Värmeverk	Enköping Sweden	Coal and oil at atmospheric pressure boiler	25	High pressure water for dist. heating scheme	Plant operation Feb., 1978
UNITS IN CANADA					
CANMET/Canadian Forces Base	Summerside, Prince Edward Island	Combustion performance with low grade coal and wood chip heating plant	20 t/h steam	Demonstrate AFBC Technology and provide exposure technology to Canada	To be commis- sioned in Nov., 1982
CANMET/CCRL ^b	NA ^c	Atmospheric boiler	100 t/h steam	Industrial Steam Plant	Operating
CANMET/Nova Scotia Power Commission	Nova Scotia	NA ^c	100 MW(e)	Commercial Thermal Power Plant	Design Phase
CANMET/Luscar Ltd.	NA ^c	Coal-dryer	NA ^c	Demonstration of drying coal washery rejects	NA ^c
R & D Programs In-house and Contract	CCRL Ottawa, etc.	Pilot and bench scale facilities	NA ^c	General combustion emission and metallurgy studies	Operating

^a Bed size in metres^b CCRL Canadian Combustion Research Laboratory^c Information not available

2. vertical combustion chambers with horizontal convective sections - a locomotive type boiler arrangement such as illustrated in Figure 57.

A technology overview and various aspects of AFBC projects in the U.S. have been well documented by DOE, Morgantown Energy Technology Center (1981). A summary of key AFBC projects in the U.S. are given in Table 29. Pioneering work in the 1960's by the consulting firm Pope, Evans and Robbins led to the construction of the world's largest (100 MW) atmospheric pressure plant at Rivesville, West Virginia. This pilot project featured a coal fired multi-cell fluidized-bed boiler (Figure 58). The plant was decommissioned following an extensive testing program. The Georgetown University central heating plant built by Pope, Evans and Robbins employs a Foster Wheeler boiler (Figure 59). A similar boiler installation at Canadian Forces Base, Summerside, Prince Edward Island, is scheduled for completion in December 1982 (Taylor and Friedrich 1982). The implementation of a large AFBC commercial plant has a number of technological uncertainties. Many of these are related to size and scale-up concerns and to long term operating characteristics. These have caused many organizations to build pilot and demonstration facilities (Table 28), for example, the Tennessee Valley Authority (TVA) has recently started up a large scale pilot unit (20 MW) to permit further process evaluation at utility steam conditions (Smith 1982). The information obtained from this pilot plant operation will be utilized to construct a 50 to 200 MW demonstration plant. A 1.83 m x 1.83 m unit commonly known as TVA 6' x 6' AFBC development facility located at Babcock & Wilcox's Alliance Research Centre, the 20 MW AFBC boiler and the envisaged 200 MW AFBC boiler are shown in Figures 60, 61 and 62.

Due to the large number of diversified development projects with various problems and objectives, a detailed development aspect is difficult to envisage for this study. Hence, the basic principals of the AFBC and major general problems associated with these projects are discussed.

A typical Fluidized Bed Steam Generator (Figure 63) consists of various subsystems which in themselves represent key technology areas that must be developed to a reliable and cost effective state to assure total system acceptability. A brief discussion of these systems is presented below.

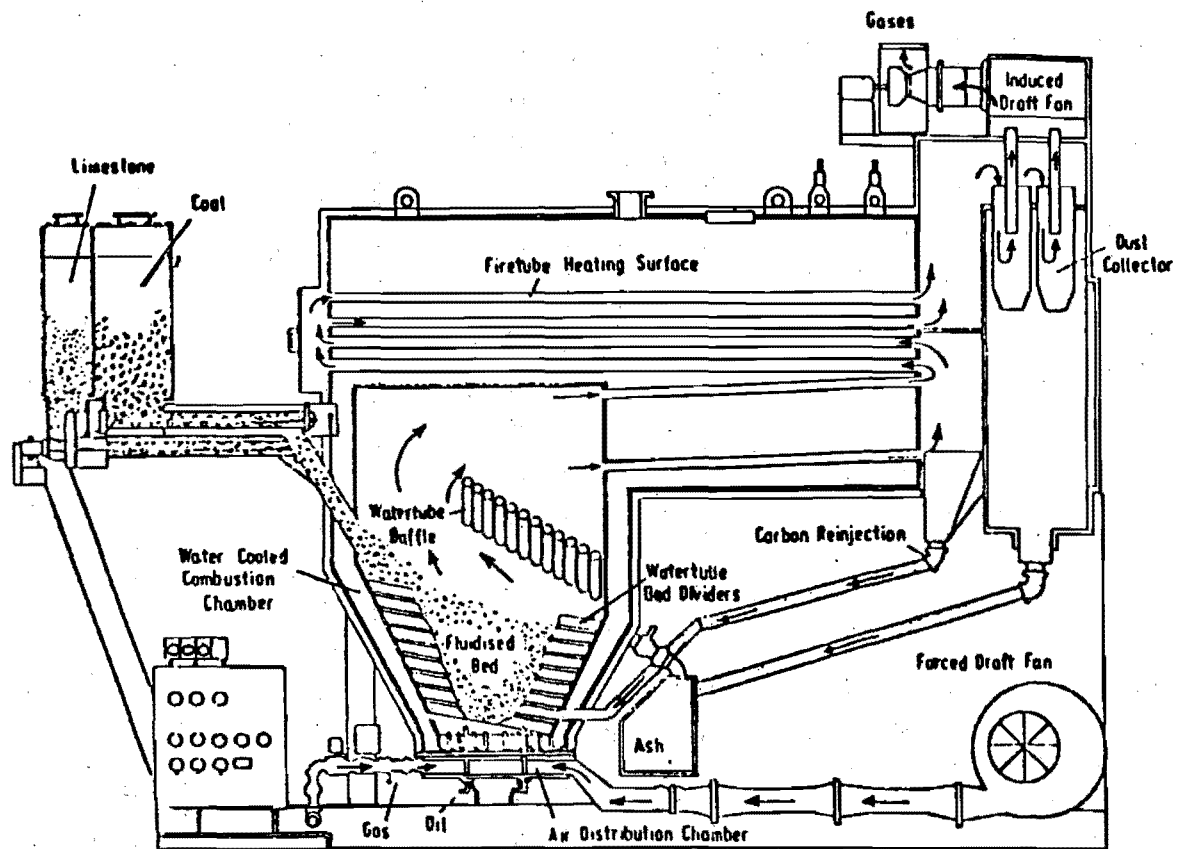


Figure 57. Locomotive type packaged fluidized bed boiler.

Table 29. Summary features of key AFBC projects in the US.^a

Project	Summary Features				
	Fly-Ash Recycle % of Fuel Feed	Fuel-Feed Technique	Limestone Feed Technique	Fly-Ash Feed Technique	Turndown Ratio, Controlled Variable
Alexandria		In-bed pneumatic combined coal and limestone	Combined with coal	In-bed pneumatic	
Rivesville	30	In-bed pneumatic combined coal and limestone	Combined with coal	In-bed pneumatic to Carbon Burning Cell (CBC)	
Georgetown	78 (Nominal)	Overbed stoker	Above-bed gravity	In-bed pneumatic	4:1, two-cell, bed- level temperature
CR/Great Lakes	0 - 90 (Exp. Var.)	Combined coal, limestone, fly ash in-bed pneumatic	Combined with coal, fly ash	Combined with coal, stone	3:1, segmented plenum, select slump
Fluidyne	40	In-bed pneumatic combined coal and limestone	Combined with coal	In-bed, pneumatic	3:1, bed level
Exxon	0	In-bed pneumatic combined coal and limestone	Combined with coal	In-bed gravity	
Wilkes-Barre	50	In-bed pneumatic	Above-bed gravity	In-bed gravity	4:1, two-cell
Shamokin		Above-bed gravity	Above-bed gravity	In-bed gravity	2½:1, T, Fl. vel., segmented plenum

Continued...

Table 29. Continued.

Project	Output	Status	Bed Size (ft)	Nominal Active Bed Height (ft)	Nominal Superficial Air Velocity (fps)	Freeboard Height (ft)
Alexandria		Present unit operating	3 x 3	2	6 to 12	16' 8" since 1978
Rivesville	30 MWe 1265 psig 950°F	Concluding test plan. Dismantle 1980.	A - 12 x 12 B - 12 x 12 C - 10 x 10 D - 6 x 12	2	8 to 12	A 3 B 3 C 3 D 10
Georgetown	100,000 lb/hr steam 275/625 psig-saturated	Operating since July 1979	5.5 x 19.3 x 2 beds	4.5	6 to 8	11
CE/Great Lakes	50,000 lb/hr steam - 365 psig, 560°F	Under construction, operation scheduled March 1981	8 x 17	3	7	9
Fluidyne	30 x 10 ⁶ Btu/hr - air 900°F	Inactive. Vertical slice work complete.	3 x 5	3.5	3.6	5
Exxon	15 x 10 ⁶ Btu/hr - oil	Pilot heat flux unit studies complete. Commercial unit design specification complete September 1980.	2 x 4	Exp. Var.	Exp. Var.	
Wilkies-Barre	100,000 lb/hr steam	Design.	11 x 12	5	8	
Shamokin	20,000 lb/hr steam 150 psig saturated	Under construction.	10 x 10	10,25 x 6	5.3	12

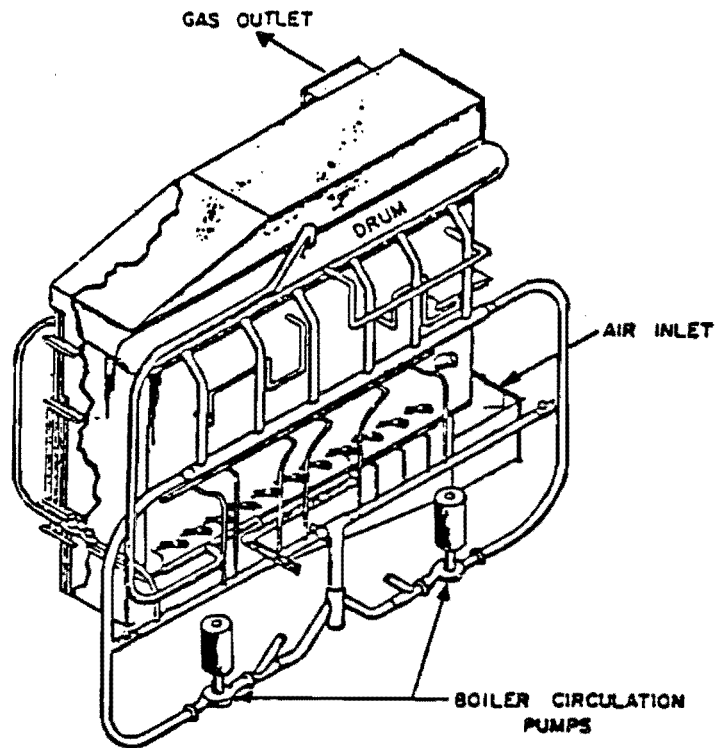
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Table 29. Concluded.

Project	Summary Features							
	Fuel				Sorbent			Ca/S Ratio
	Type	Sulphur	Size ^b (in)	Rate (lb/hr)	Type	Size	Rate (lb/hr)	
Alexandria	Various	Variable	1/4 x 0	Max. 1 000	Limestone	1/8 x 0	Max. 500	3:1
Rivesville	Eastern Bituminous		1/2 x 1/4	38 000	Limestone	1/8 x 0	12 000	3.5:1
Georgetown	Eastern Bituminous	3.29%	1 x 0	9 565	Limestone		3 133	3:1
CE/Great Lakes	Illinois No. 6 Freeman	3.5%	1/4 x 0	6 710	Limestone		3 260	4:1
FluiDyne	Illinois No. 6	3.6%		500	Dolomite		180	1:1
Exxon		3%		1 562	Limestone			
Wilkes-Barre	Anthracite Culm (5 000-7 500 Btu/lb)	.44% 53%-Ash	1/8 x 0	24 000	Limestone	1/4 x 0	Not necessary with design fuel	1:8
Shamokin	Anthracite Culm (4 012 Btu/lb)	0.55% 64.84%-Ash	4 mesh x 0	8 188	Limestone	1/4 x 0	983	5.8:1

^a Imperial units are used in this table to facilitate reference to the original data.

^b Coal size as fed to combustor.



Rivesville Multicell Fluidized-Bed Boiler
(MFBB) Isometric View

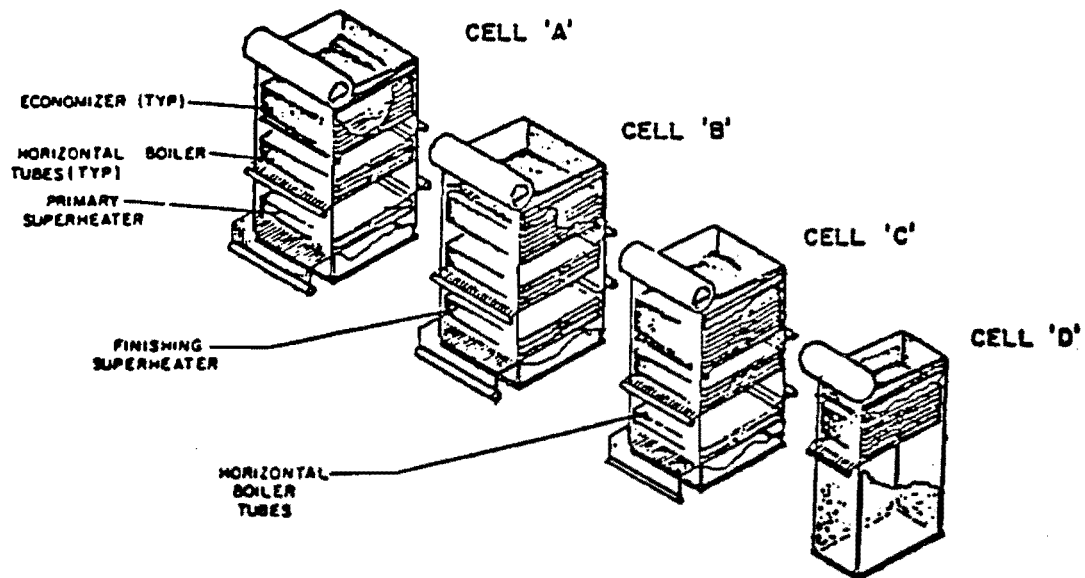


Figure 58. Multi-cell fluidized bed boiler.

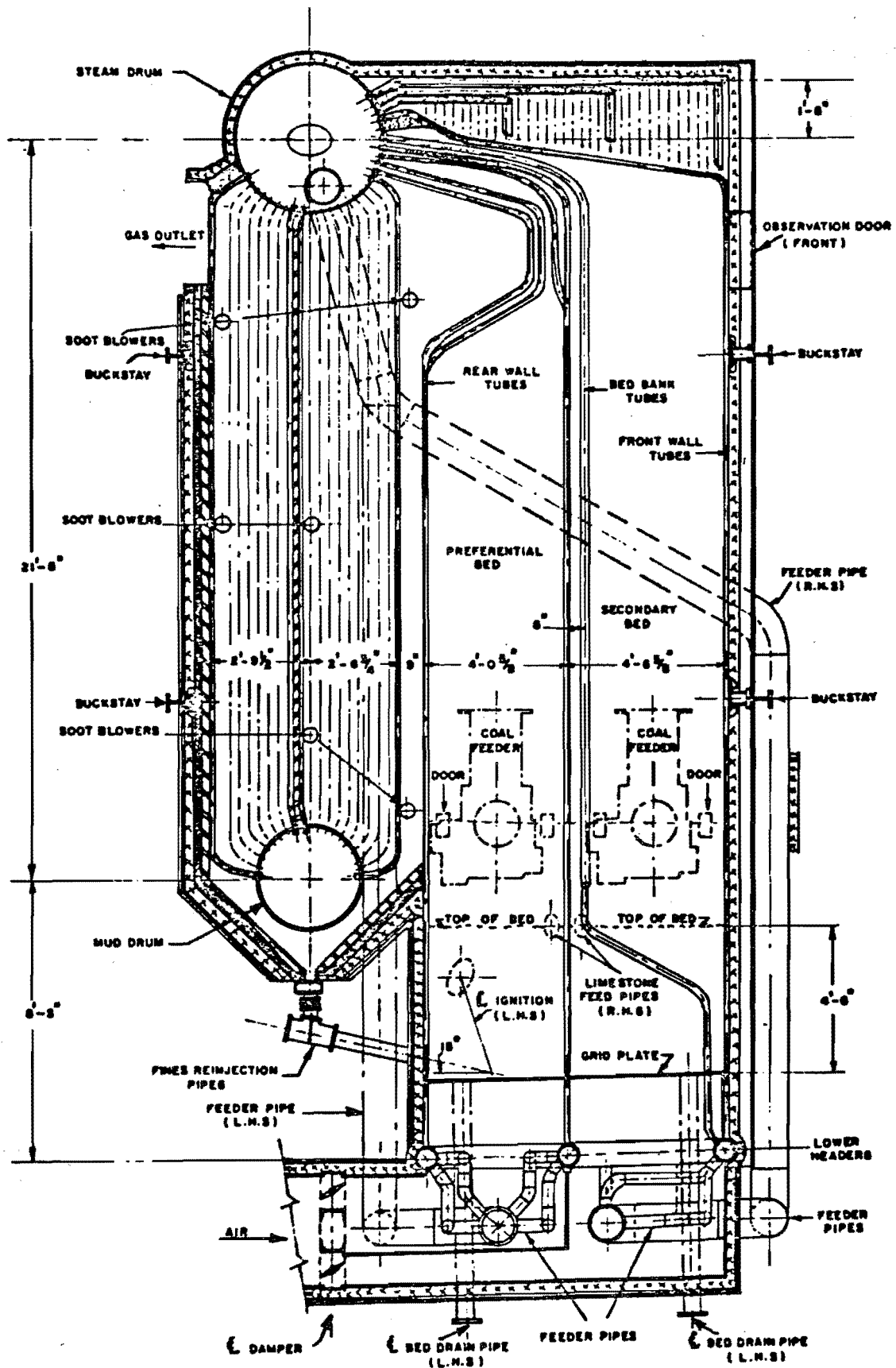


Figure 59. Foster Wheeler boiler.

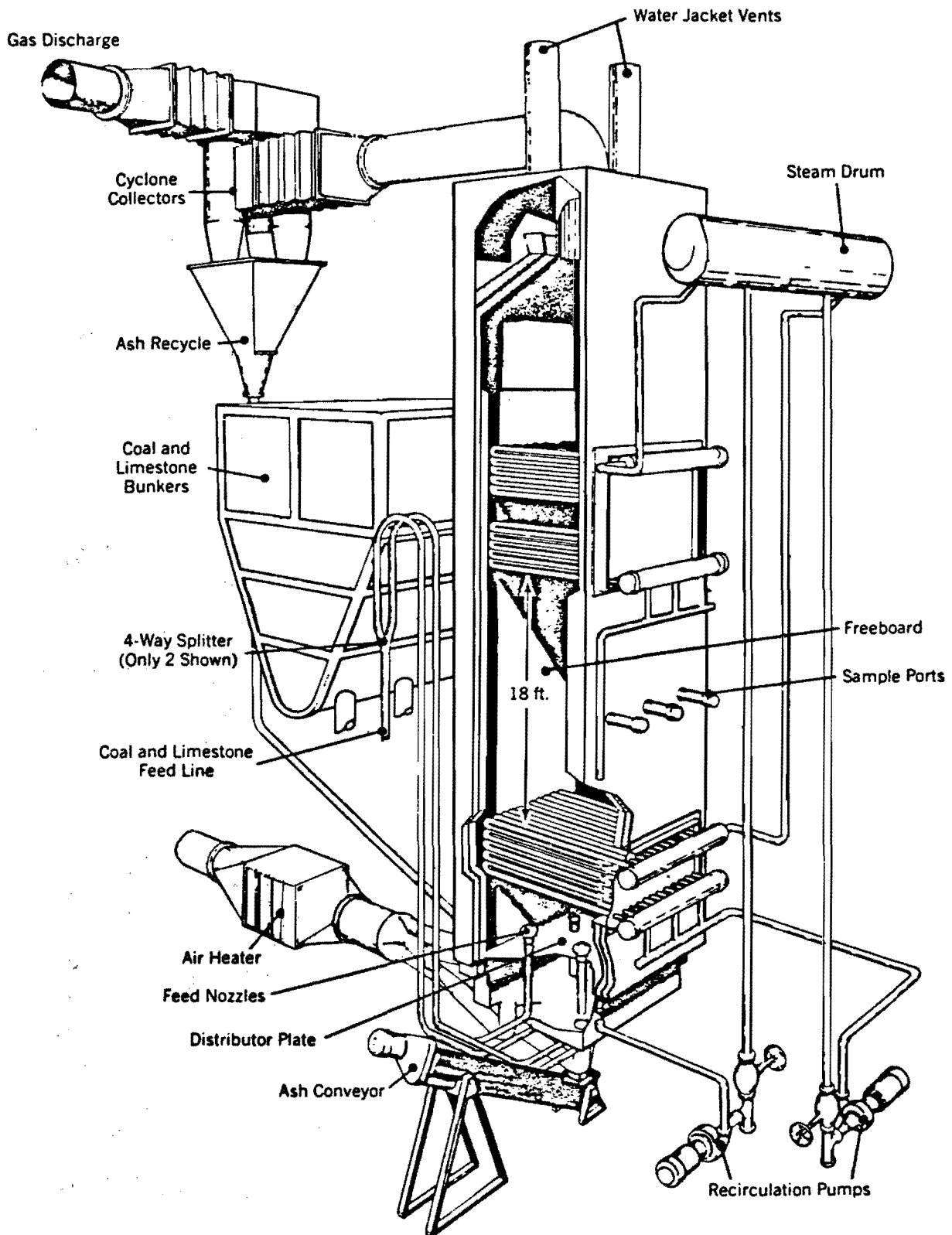


Figure 60. 6' x 6' AFBC development facility.

- 1 AFBC boiler
- 2 Coal silo
- 3 Limestone silo
- 4 Tandem coal/limestone feeder
- 5 Fuller-Kinyon pump
- 6 FD fan
- 7 Air heater
- 8 Secondary air supply duct
- 9 Overfire air supply duct
- 10 Steam drum
- 11 Circulation pump
- 12 In bed boiler surface
- 13 In bed superheater
- 14 Primary superheater
- 15 Economizer
- 16 Dust collectors
- 17 Recycle system
- 18 Bed ash coolers

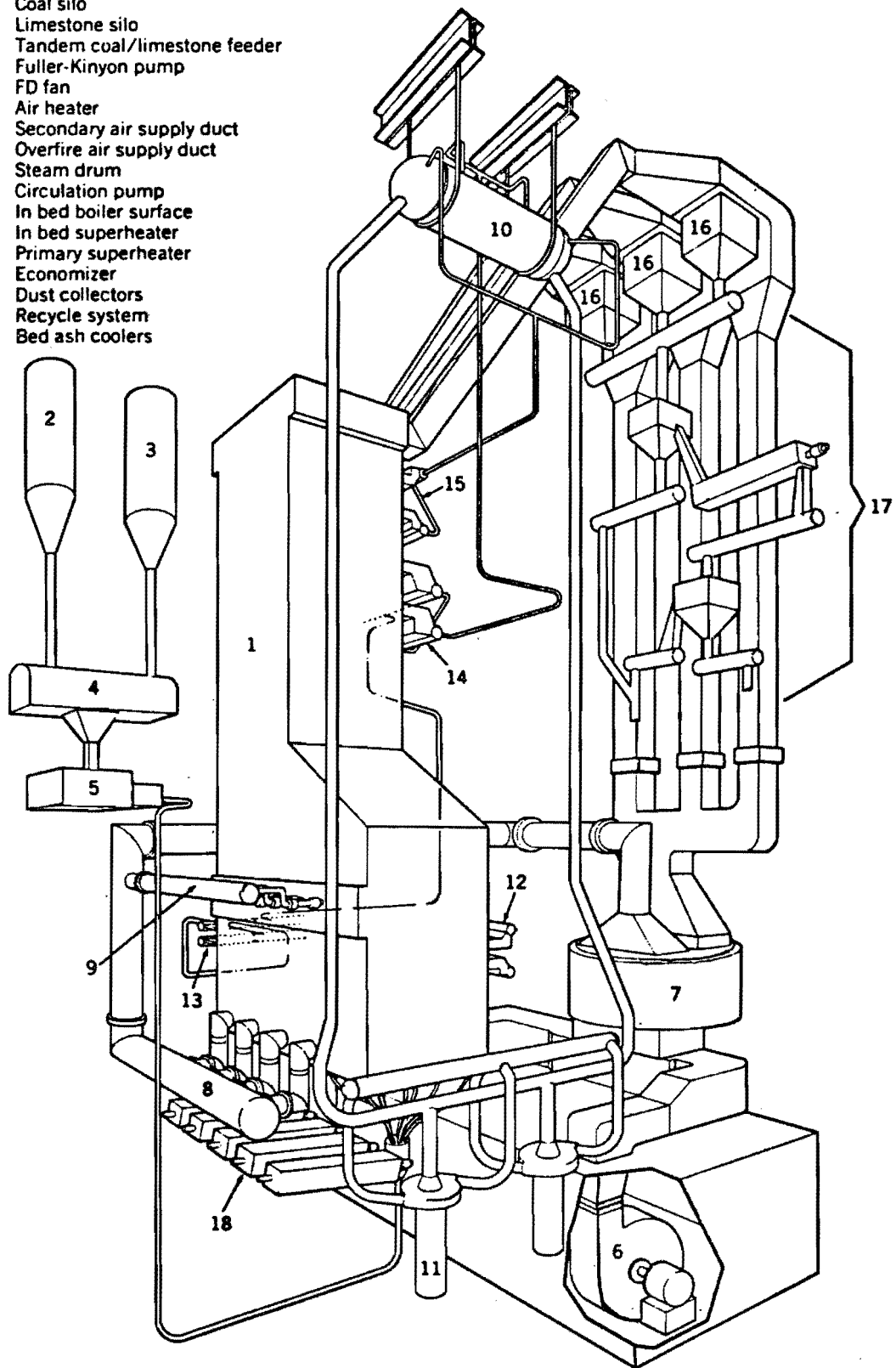


Figure 61. 20 MW pilot AFBC boiler.

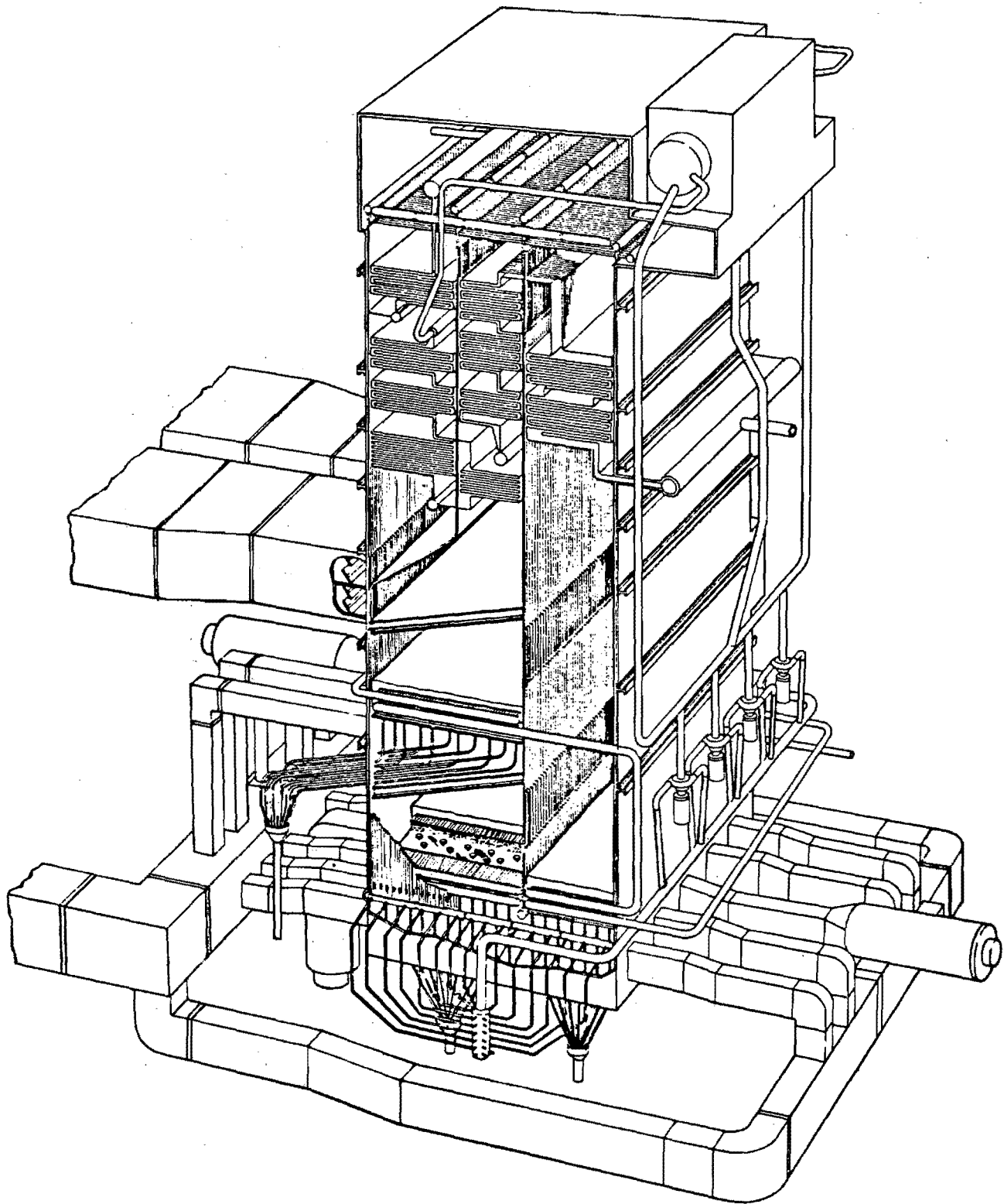


Figure 62. 200 MW AFBC boiler.

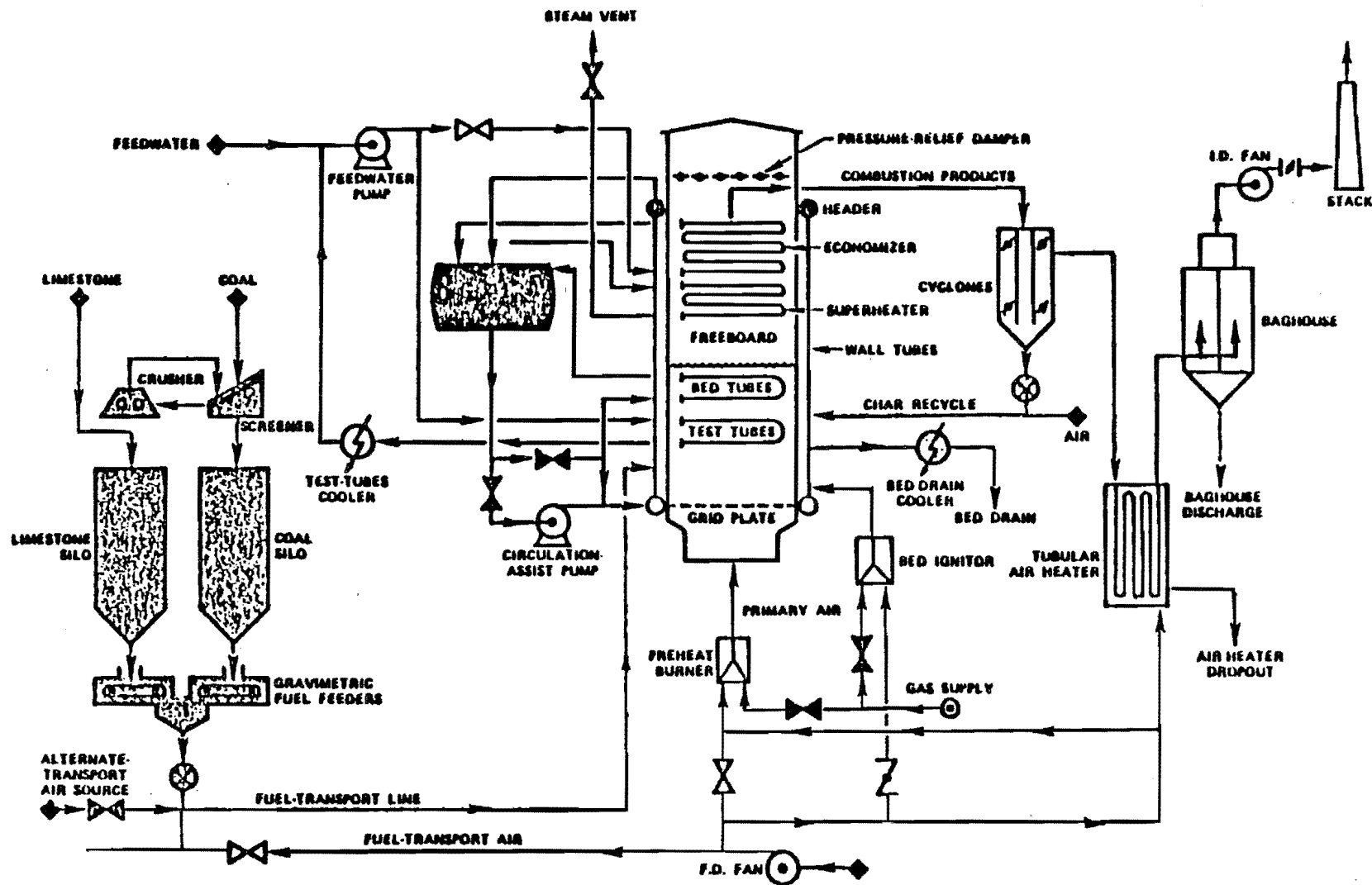


Figure 63. Typical FBC steam generator facility.

8.5.1 Fuel Feed System

Fuel feed system selection depends on the fuel properties of particle size and proximate analysis particularly moisture, ash and volatile matter. The solid fuel is fed to the AFBC by various techniques and devices, including pneumatic, screw, mechanical overbed stoker and mechanical overbed gravity feeding systems.

8.5.2 Heat Transfer

In order to realize the enhanced heat transfer of FBC, effective heat transfer surface must be placed in contact with the hot bed material. This has normally been accomplished in the case of AFBC and PFBC by placing tubes within the combustion bed. Selection of incorrect bed-to-tube design heat transfer rates has led to poor load control when bed-level adjustment is used to select the amount of tube surface in the bed (Golan 1979). However, CFBC units normally place heat transfer surface external to the combustion bed, thereby simplifying load control.

8.5.3 Air Distribution

The fluidized bed air-distributor plate serves a dual function of uniformly distributing air to the bed and supporting the weight of the defluidized or slumped bed. Problems which were experienced with the early grid designs include:

1. warpage and cracking due to excessive thermal stress;
2. seal leakage between grid segments and between the grid and its attachment to the combustor/boiler walls;
3. weeping of solids down through the grid holes and into the air plenum or windbox during bed defluidization. This problem has been virtually eliminated with current designs.

The grid normally has uniformly spaced and uniformly sized holes. In some designs pneumatic solids feed pipes pass through the grid into the bed where coal, limestone and recycle flyash are discharged.

8.5.4 Flyash Recycle

Unburned carbon from the fluidized bed is blown out of the bed (elutriated) with other fine-bed material and ash. The larger particles are

usually captured in boiler hoppers, moderate size particles are captured in cyclones and fines less than ten micron captured in fabric filters. This material or a portion of it may be reinjected at temperatures ranging from 190°C to 430°C into the 850°C bed in order to enhance combustion efficiency and limestone utilization. The effectiveness of recycle on combustion efficiency is affected by:

1. combustion characteristics of recycled material;
2. recycled-solids temperature and particle size;
3. bed temperature;
4. residence time in bed which is a function of superficial velocity and discharge location;
5. conveying air-to-solids ratio from pneumatic conveying systems,
6. volatility and reactivity of feed;
7. feed technique and location.

To consistently be able to design working reinjection systems, the combustion fundamentals of recycled FBC carbon (Massimilla, Miccio, Russo and Stecconi 1979) must be understood.

8.5.5 Ignition

The fluidized bed may be raised to the ignition temperature of the main fuel by directing the products of combustion of a gas or oil-fired burner:

1. directly into the fluidized bed from the side;
2. into the bed from above;
3. into the fluidizing air duct to preheat the air which then fluidizes the bed and heats the bed material.

The sizing and location of the burner depends on various factors:

1. size of bed or bed zone to be ignited;
2. main fuel-ignition temperature;
3. bed-material thermal properties, i.e. specific heat and conductance;
4. heat removal from the bed by fluidizing air and inbed heat exchangers;
5. air distributor grid and vessel material.

Two problems have been encountered during ignition. One is loss of heat to inbed heat transfer surface and to fluidizing air when attempts are made to distribute the heat. The other problem is fusion of ash and bed material or "clinkering". These potential problems may be overcome through proper design and operation.

8.5.6 Output Control

Control of FBC is required to match the steam or process-fluid generation rate to the load. Control may be achieved by regulating bed temperature and/or bed level. The range over which the bed temperature may be controlled is limited by the desired processes of SO_2 , capture NO_x production, and fuel combustion. For systems with in-bed tubes, bed-level control by various methods is the usual means of turndown. Lowering the bed height uncovers in-bed tubes thereby decreasing the heat transfer rate on the exposed tubes.

Bed level is usually regulated by varying the superficial air velocity. To maintain proper combustion and sulphur capture the coal, air and limestone flow rates must be adjusted with changes in bed level and superficial velocity.

8.5.7 Particulate Emission Control

Feedstock attrition combined with high fluidization velocities presents a high particulate emission potential from fluidized-bed combustors. To comply with the U.S. Environmental Protection Agency (EPA) particulate emissions regulations and to recover unburned carbon, FBC flue-gas systems are equipped with particulate removal devices such as drop-out collectors in boiler bank and economizers, cyclones, electrostatic precipitators and bag filters.

The selection of these devices depend upon the size distribution of collectable particles, operating temperature, collection efficiency and energy consumed by the device (pressure drop, electrical consumption).

Experience has shown that particulate properties may be widely variable and highly dependent on coal and limestone types as well as on FBC operating conditions such as flue gas temperature, percentage of full load operation, operating Ca/S ratio as compared to design, load stability and bed temperature. Selection of appropriate particulate filters for FBC application has been reasonably successful.

8.5.8 Sorbents

Utilization of sorbents has up to now largely consisted of a once-through then dispose policy. The continuation of this policy can be impractical for large-scale commercial application. In general, calcium to sulphur ratios of greater than 2.5 (molal) are expected to meet the SO₂ emission standards with feedstocks containing 0.03 to 0.04 mass fraction sulphur. The utilization policy and the high consumption rate result in lower plant efficiencies and higher operating and disposal costs.

Several techniques for reducing sorbent consumption are being evaluated. These are:

1. use of high recycle rates;
2. limestone hydration to enhance utilization;
3. limestone regeneration;
4. alternative once-through sorbents;
5. alternative regenerative sorbents;
6. limestone/catalyst combination to enhance sulphur capture.

8.6 PRESSURIZED FLUIDIZED BED COMBUSTION

As mentioned earlier, the primary application of PFBC is in electrical power generation. It is not possible to cover all the power generation projects in this study. Many of the studies (Table 30) consist of detailed conceptual designs and costings which are based on limited operating data. The PFBC technology is in its early development stage and has presented a number of operating problems for the various projects.

However, the increase in electrical power output per square metre of bed area with increasing system pressure (Figure 64) is undeniably a clear advantage of PFBC over the AFBC.

The use of PFBC further offers several other potential advantages over AFBC for baseload power generation. These include:

1. pressurization reduces combustor size and the number of fuel feed points compared to AFBC;
2. higher heat transfer and volumetric heat release rate relative to conventional boilers and AFBC;
3. higher overall plant efficiency from combined cycle operation;
4. higher combustion efficiency and improved sorbent utilization.

Table 30. Pressurized Fluidized Bed Combustion Products

Organization	Location	Description	Size MW (th)	Objective	Status
Rolls Royce	Ansty (Britain)	Pressurized fluidized bed operating with 0.1 MW(e) Rover gas turbine	0.3	To collect information on operation of pressurized combustor with no in-bed tubes	Plant in operation but not coupled to gas turbine
National Coal Board	Leatherhead (Britain)	Pressurized fluidized bed boiler	5	Tests on corrosion and erosion of turbine blades in fixed cascade	Operational since 1970
National Coal Board/ ME Boilers Ltd.	Sheffield (Britain)	High pressure steam unit using ME "coil" type boiler	30	Demonstration plant for commercial production of high pressure steam	Commissioned 1980
NCB (IEA) Services Ltd.(supported by UK, US, FRG govts)	Grimethorpe	Pressurized fluidized bed	85	To collect basic information for the operation and design of pressurized fluidized bed	Operation of test plant started 1979
Environmental Protection Agency/Exxon Research & Eng. Co.	Linden (U.S.)	Pressurized fluidized bed unit-"Miniplant"	1	Test rig for combustion heat transfer and acceptor regeneration	Operating
Curtiss-Wright	Wood-Ridge	Pressurized fluidized bed air heater, coupled to a Rover gas turbine	2.3	Technology development unit	Operating
Department of Energy/ Combustion Power Co.	Menlo Park (U.S.)	Pressurized fluidized bed combustion system	4	To test gas clean-up techniques and turbine blade erosion	Plant operated
Department of Energy/ Argonne National Laboratory	Argonne (U.S.)	Pressurized fluidized bed component test and integration unit	10	To collect information for operation on larger scale. Investigate gas cleaning techniques	Recently suspended
Department of Energy/ Curtiss-Wright	Wood-Ridge (U.S.)	Open cycle gas turbine plant with pressurized fluidized bed combustor	43	Information for construction of demonstration plant	Plant operation began 1977
Bergbau-Forschung GmbH/Vereinigte Kesselwerke AG	Bottrop	Pressurized fluidized bed air heater with 2MW(e) Sulzer gas turbine	22	To collect information for construction of a 100 MW(e) coal-fired power station	Plant construction began 1977
Bharat Heavy Electricals Ltd.	Vancouver (Canada)	Pressurized boiler, combined cycle	4	Demonstration	Construction stage 1977
British Columbia Hydro/Coal Processing Consultants	Vancouver (Canada)	Air heater cycle	200	Demonstration plant	Conceptual design stage completed

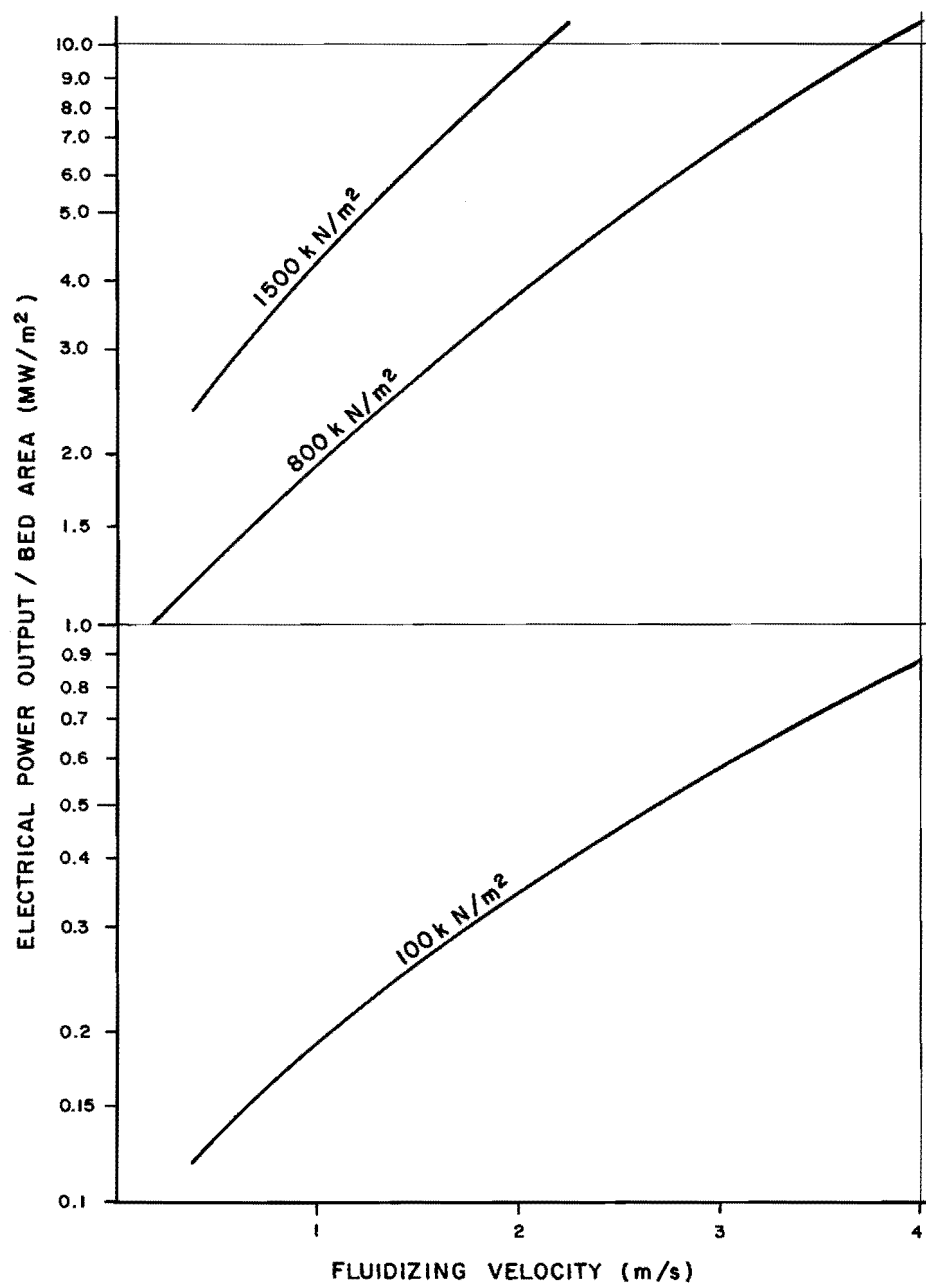


Figure 64. FBC specific power output.

The increased pressure operation results in lower combustion temperature, consequently further lowering the NO_x emission. The emission characteristics of PFBC are below the present U.S. environmental emission standards and the projected plant efficiency is in the vicinity of 40% (coal pile to power). Thus PFBC combined cycle offers an attractive alternative to conventional pulverized coal/wet scrubber power plants.

Power generation by PFBC can be achieved by two contrasting concepts (Figure 65):

1. air heater concept (air cycle);
2. steam boiler concept (steam cycle).

The development of power generation applications in the U.K. are largely confined to the NCB and Babcock Power (U.K.) Ltd (Nauze 1979). In Germany, most of the development work was concentrated in the development of PFBC due to their higher efficiencies than alternative power generating systems.

General Electric, a principle advocate of the steam cycle, conducted a plant design study (1975) and constructed two test facilities (Figure 66). In 1975, work began on the Grimethorpe Experimental Facility (Figure 67) for NCB-International Energy Agency. The design capacity of the plant is 80 MW (thermal) operating at 600 to 1200 kPa at 800 to 950°C. The facility was commissioned in 1979.

In the U.S., under contract to the DOE, a 13 MW (electrical) pressurized unit incorporating a gas turbine is being constructed by Curtiss-Wright at Wood Ridge, New Jersey (Figure 68). The design is based on air heating cycle in which a majority of the total air is heated in tubes passing through the bed. Recent NCB studies have shown severe corrosion of tube alloys at the high temperatures required for this cycle when limestone is present in the bed. These results should be considered in further development of this cycle. The development and operational aspects of some of the projects are well documented by DOE M.E.T. Centre (1980).

American Electric Power (AEP), in partnership with Stal Laval and Deutsche Babcock is planning to construct a 171 Mw(e) steam cooled combine cycle PFBC plant at AEP's Tidd station near Brilliant Ohio, in the mid 1980's. The plant will generate 110 Mw (e) by steam turbine and 67 Mw(e) by gas turbine.

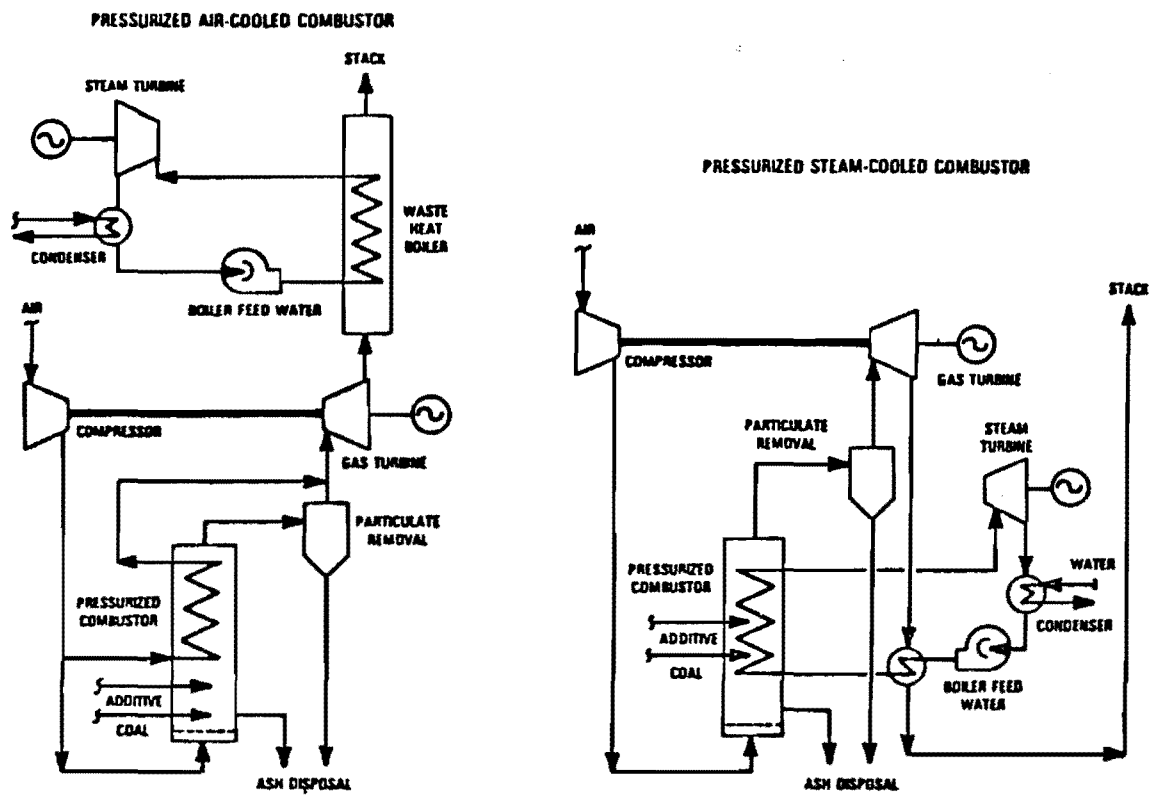


Figure 65. PFBC power generation.

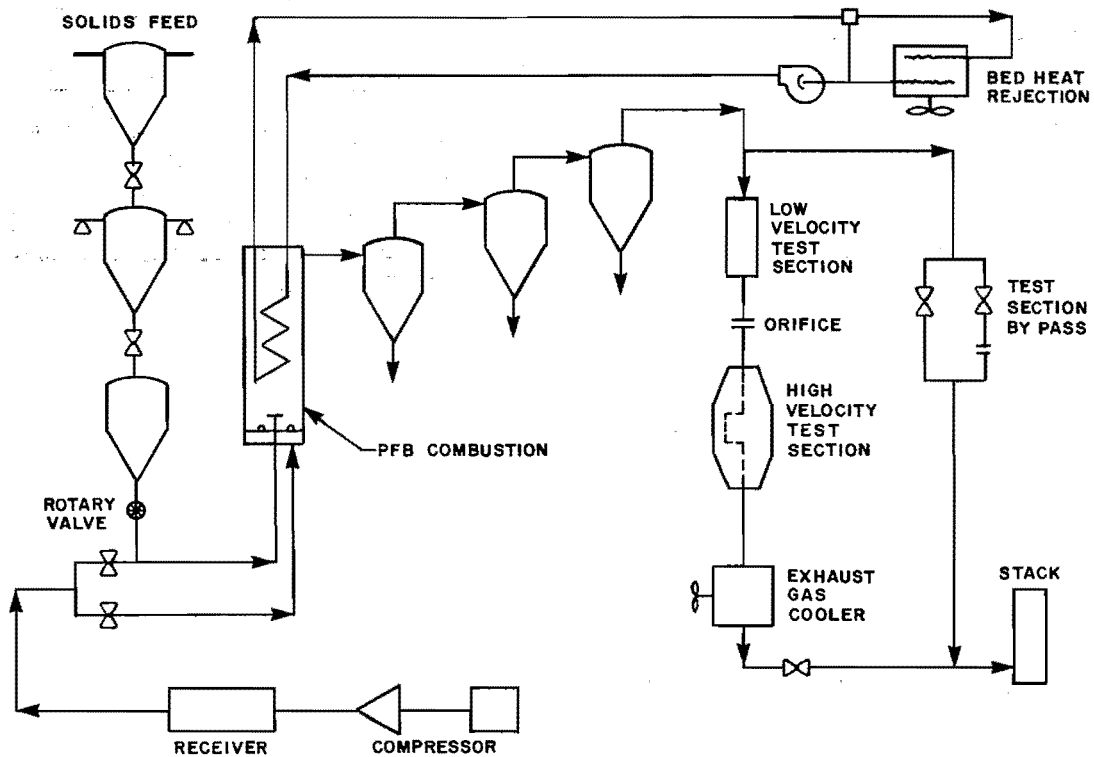
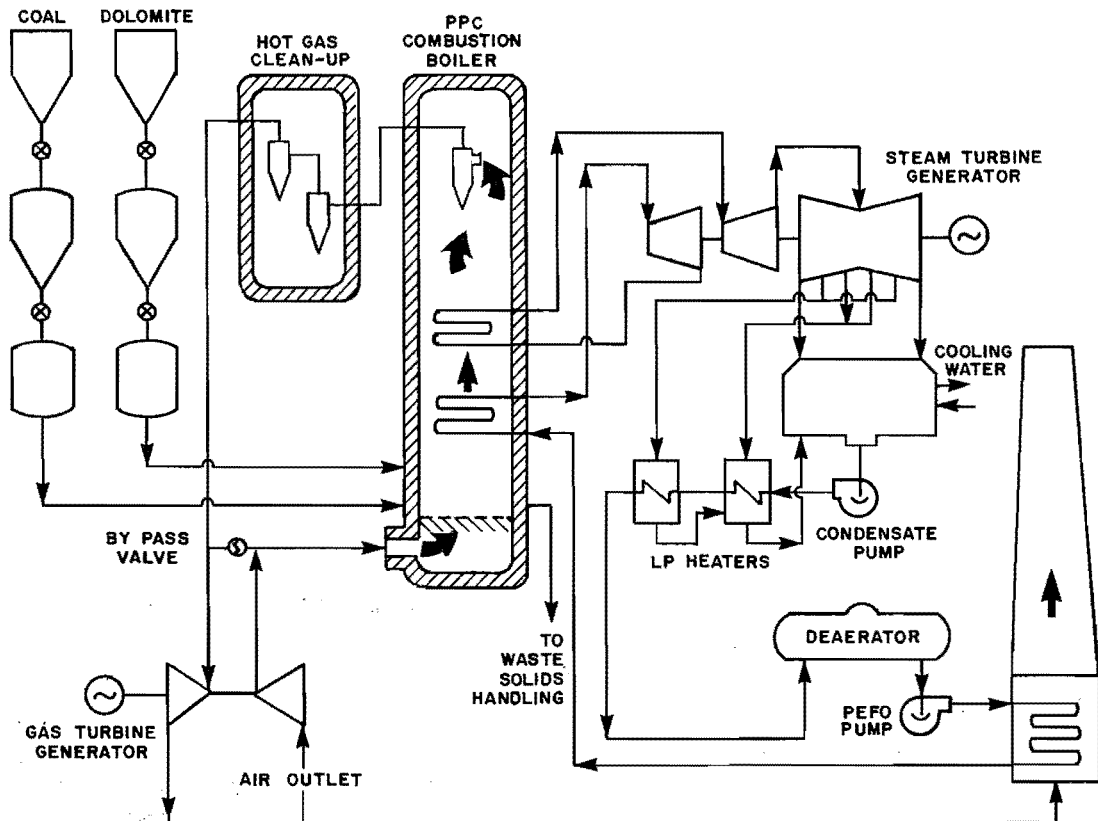


Figure 66. General electric test facilities.

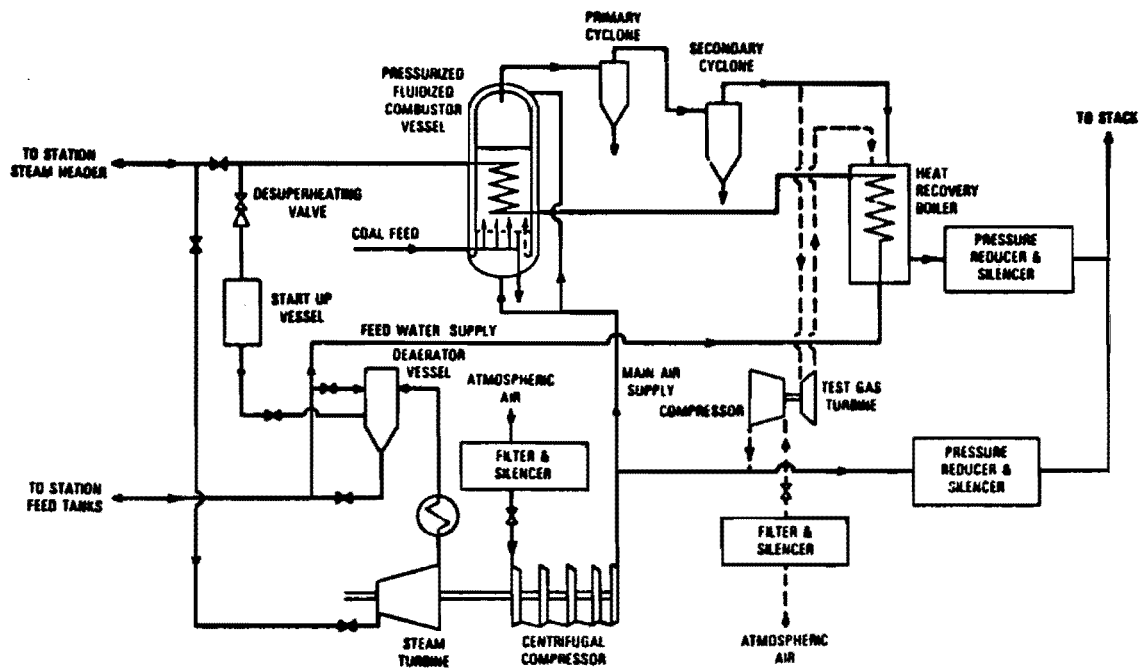


Figure 67. Grimethorpe experimental PFBC facility.

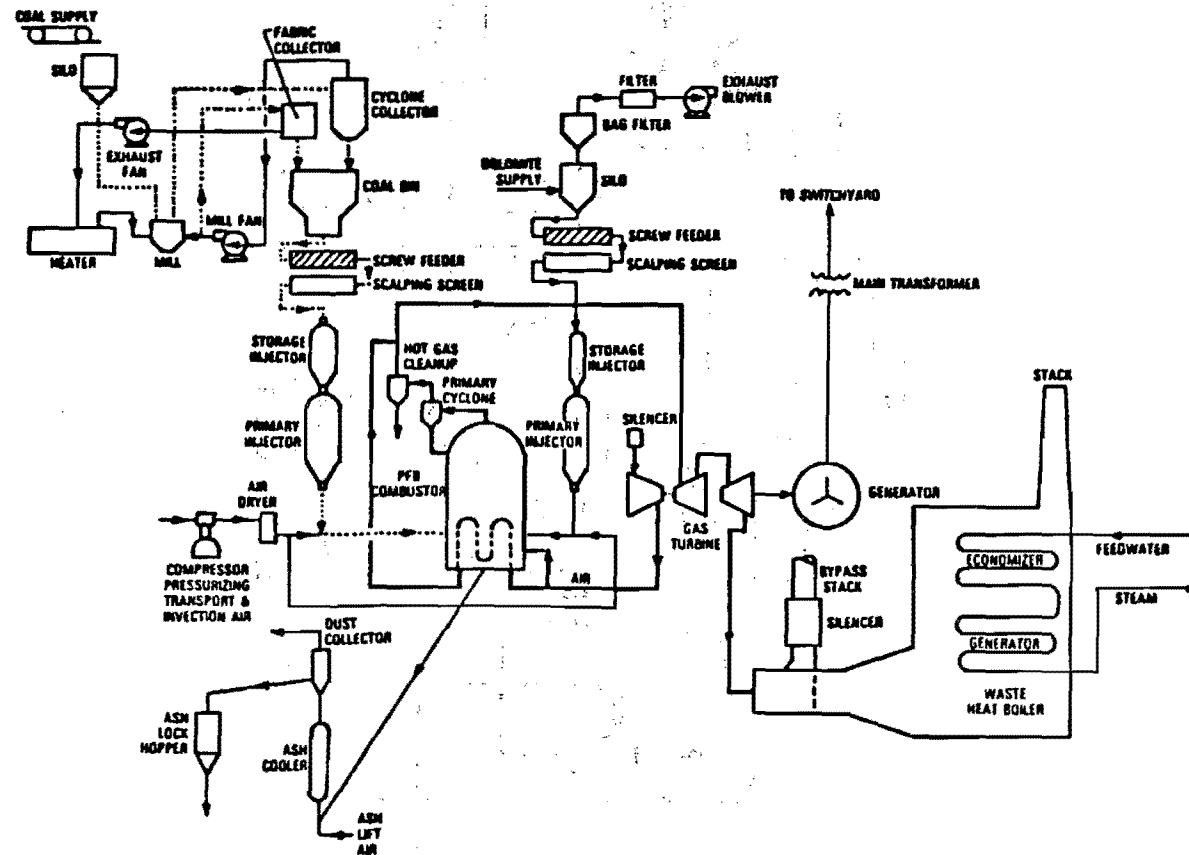


Figure 68. Curtiss-Wright PFBC power generator.

The NCB and Babcock Power (U.K.) Ltd. with the Swedish turbine manufacturer Stal Laval are designing a pressurized fluidized combustor system coupled to a 70 MW (electrical) gas turbine for the British Columbia Hydro Authority in Canada. The project is at present in its design stage and the construction of the demonstration plant is expected to be completed by 1988.

The IEA-Grimethorpe and Curtiss-Wright (Figures 67 and 68) facilities form the two main projects for the PFBC steam-cycle and air-cycle development program, respectively. Several key issues and problem areas in PFBC development have been identified that require a solution before PFBC can be commercialized. Some of the problems ranked more or less in terms of the degree of criticality are:

1. turbine tolerance (erosion and corrosion);
2. hot gas clean up (erosion and corrosion protection scheme);
3. hot gas intercept valve development;
4. scale up of pfbc configuration including geometry and solids feeding;
5. dynamic system controls configuration;
6. long-term heat exchanger exposure to PFBC operating conditions.

The first three problems are considered most critical (of a "make or break" nature) while the remaining tend to lower operating costs and/or increase efficiency.

8.6.1 Turbine Tolerance

Despite optimistic projection of the improvement in particulate removal state-of-the-art, gas turbine life/gas-cleanup tradeoff remains the principal technology issue preventing commercial application of the PFBC/combined cycle (CC) concept.

The three major phenomena responsible for this prevention are:

1. hot corrosion due to saturated alkali (sodium and potassium) vapour content in the PFBC exhaust gas;
2. mechanical erosion by solid particulate impact;
3. fouling by particulate deposition.

The first two phenomena result in deterioration of the turbine hardware and require improved materials and improved hot gas particulate and alkali removal devices for protection, the third acts to reduce gas flow, reduce performance and eventually cause compressor stall.

Although the exhaust gases from PFBC are much lower in the sodium-potassium alkali contamination than those from conventional pulverized coal burning plant, the gases together with sulphur and chlorine create a highly corrosive environment even for sulphidation resistant gas turbine alloys. The particulates in the exhaust contribute to turbine blade erosion.

It is likely that a conservative turbine design using proper materials could withstand the erosive environment of PFBC; however, the corrosive atmosphere of PFBC exhaust gases compounds the problem.

Most development work in this area has focused on improved hot gas cleanup and fundamental understanding of the gas turbine particulate tolerance. The condensation from a saturated alkali-vapour system may be unavoidable. This assumption has led to significant activity in corrosion-resistant protection materials (alloys coatings).

Significant test programs are being conducted to overcome this problem.

8.6.2 Hot Gas Cleanup

The exhaust gases leaving the combustor contain significant quantities of particulate matter (dolomite sorbent, coal ash, and unburned carbon) as well as SO_2 and alkali vapours (sodium and potassium). The individual or combined effects of these impurities will promote turbine erosion, corrosion and deposition which will cause unacceptably short life and loss of aerodynamic efficiency of the turbine.

There is also an environmental question in terms of allowable emissions of stack particulates. The conventional gas-cleaning equipment (i.e. baghouses) could meet the restriction on environmental emission when operating at atmospheric pressure. At elevated pressure, however, they are not suitable.

Progress in hot gas clean up has been generally slow, although significant work has been accomplished at the bench and process development unit scale level. Several approaches have been proposed and are being

developed. The method most actively investigated is inertial separation (cyclones). Other methods include granular-bed filters, electrostatic precipitators fabric filters, metal or ceramic filters and molten bath scrubbers. These methods (except conventional cyclones) will require considerable development before they can be applied, while some methods are more advanced than others many questions such as ultimate efficiency, reliability, scale-up, equipment life and economics must be answered by both bench scale and pilot plant experiments.

1. Conventional cyclones have been the principal choice for high temperature particulate cleanup due to the relative insensitivity of performance with respect to temperature and because it is a state of the art technology. They have the advantage of high operational reliability, high capacity capable of operating at high temperature and pressure, and relatively low cost. The major disadvantage of cyclones is the low collection efficiency for small particles and at off-design gas flows. Tests by Curl, Exxon and Curtiss-Wright with staged cyclones have been encouraging and suggest that cyclones alone may be sufficient to prevent excessive turbine erosion. This method is being pursued at Grimethorpe, the Curtiss-Wright pilot plant and the Stal Laval pilot plant.
2. Advanced cyclones in the form of small cyclones (multiclones) are manifolded together in a parallel flow arrangement. These allow high efficiency with high gas flow. However, the tubes are prone to plugging in the lower cone body, this may limit the use of multicones in future PFBC application. High efficiency rotary flow cyclones which employ secondary counterflowing air have recently been introduced. Other advanced cyclones such as General Electric's Electrostatic Enhanced Cyclone and the University of Buffalo's Acoustically conditioned cyclone are in the early stages of development.
3. Granular-Bed Filters (GBF), a promising technique is under development by several companies for high-temperature and pressure gas cleanup. The GBF collects particulate matter

through two principal mechanisms, filter coke formation and impaction.

The GBF combines several important particulate collection features such as high operating temperature, moderate to high gas capacity per unit volume, potentially high collection efficiency for fine particles and potentially high reliability. The problems associated with GBF's are high pressure drop and the necessity for cleaning the bed.

4. Positive Filters such as fabric filters are widely used devices for removing dust and fumes from a gas stream. A baghouse is inherently highly efficient even for small particles. Unfortunately for PFBC, however, commercially available bag filters are limited to operating temperatures of about 290°C.

Current work is aimed at increasing the operating temperature for fabric filters.

5. A reliable fast acting Hot Gas Intercept trip valve must be developed to protect the gas turbine generator from overspeeding in the event of loss of load to the generator. This valve must function in the hot corrosive flue gas environment.

8.6.3 PFBC Configuration

The PFBC configuration involves combustor geometry and fuel feeding. Combustor geometry operating parameters and coal and sorbent properties have been varied to achieve improved operation. The bubbling-bed concept employs relatively low fluidizing velocity and typically uniform distributor plate and tube-bundle geometry. Although bench-scale and process development unit scale combustors of different configurations have been tested and have operated efficiently and reliably, combustor performance and scalability must be demonstrated in large facilities. This may be accomplished at Curtiss-Wright (cylindrical-shaped combustor) and at Grimthorpe (rectangular-shaped combustor).

The fuel feeding system, as with AFBC systems, requires consideration as to the number of feed points for an economical and operational incentive. In the case of PFBC reliable fuel and sorbent feeders must be

developed to operate at elevated pressures. In terms of hardware, the required spacing and detailed design of the feed injectors has yet to be optimized.

8.6.4 Dynamic Control and Stability

Dynamic response and control parameters have not been quantified to date. The two pilot plant facilities, Curtiss-Wright and Grimethorpe, will be available for dynamic control testing, but not until 1983 to 1984.

8.6.5 Heat Exchanger Materials

Proposals for PFBC units include designs with super-critical water-cooled tubes, boiling water/steam cooled tubes and gas cooled tubes of horizontal and vertical configuration. Materials to be used for in bed or above-bed heat exchangers will be selected based on long-term resistance to corrosion mechanical properties, cost and availability. For PFBC, it is envisaged that boiler tubes will be controlled in steam cooled heat exchangers to a metal temperature between 480 and 680°C, while materials for air-cooled applications will be required to operate in the range of 660 to 820°C.

The following conclusions may be drawn from published data:

1. Conflicting corrosion results have been indicated under the same apparent conditions. This suggests that the bed conditions, coal type, sorbent type and temperature all influence the corrosion process.
2. Corrosion conditions are generally more severe in the bed than above the bed. Reducing conditions can accelerate corrosion.
3. Corrosion in the bed is not linearly related to temperature. Maximum corrosion rates occur between 660 and 800°C.
4. High chromium low to intermediate nickel and austenitic stainless steels exhibit the best corrosion resistance in 660 to 800°C temperature range.
5. High nickel (0.4 mass fraction) alloys have low sulphidation resistance.
6. Coating or claddings applied to high strength nickel alloys show promise for extending service life.

Verification and scalability of these results will be determined in long-term testing of pilot plants.

8.7 CIRCULATING FLUIDIZED BED COMBUSTION (CFBC)

The technical limitations associated with conventional fluidized bed combustion technology have initiated, within the past few years, the development of new advanced circulating fluidized bed combustors.

The combustion of fuel and recovery of heat in a conventional fluidized bed was simultaneously performed in a single chamber where the majority of the heat transfer surface was immersed in the fluidized bed.

However, CFBC technology is principally characterized by the decoupling of the fuel combustion and heat removal zones of the boiler and the elimination of tubes in the combustion bed. The implementation of this phenomenon has resulted in a number of different techniques. Thus, the precise nature of operation of these CFBC combustors is largely dependent on the techniques utilized and the physical construction of the CFBC unit.

The CFBC systems offer several advantages over conventional FBC systems. These include:

1. Smaller combustor cross section and higher processing capacity due to higher gas velocity.
2. Reduced NO_x emission due to lower excess air and capability for staged combustion (i.e., secondary combustion air can be introduced above the combustion zone).
3. Potentially better load follow capability than conventional fluidized beds. This enables a controlled turnup and turndown of the system.
4. Simplified fuel and limestone feed system due to decoupled combustion and heat removal zones.
5. Higher carbon conversion improved sorbent utilization and lower excess air requirements have resulted due to improved gas/solids contact.
6. Higher sulphur retention due to improved gas/solids mixing.
7. Better fuel flexibility due to simplified feed system and improved gas/solids mixing.
8. Capability of retrofit by utilizing existing boiler as waste heat boiler.

Although CFBC systems offer the above advantages, some areas of concern have been identified. These may include, depending on the particular technology involved:

1. Higher auxiliary power than AFB may be required to maintain high velocity and circulation of solids.
2. The design and efficiency of hot cyclones (approximately 890°C) are certain. Several, but not all of the technologies use hot cyclones.
3. Erosion potential due to high velocities. This should not be a problem, however, with proper design.

Although CFBC units are still under development, a few industrial sized units are currently available on the market. The main contributors to the development of CFBC technology have been Lurgi, Battelle, Ahlstrom and Stone & Webster/Conoco Coal Development Company.

Lurgi has licensed its CFBC technology to Combustion Engineering in the U.S. and Deutsche Babcock in Europe. Battelle is licensed to Struthers and Foster Wheeler U.K. In the mid seventies, a test program was initiated in Finland at the Hans Ahlstrom laboratory, to burn high-sulphur feeds. Pyropower Corporation, a new corporation formed by General Atomic Company and Ahlstrom of Helsinki has been testing various coal in CFBC Combustion developed by Ahlstrom (Figure 69). The Ahlstrom unit is offered in the U.S. by Pyropower Corporation. In 1979, Stone & Webster and Conoco Coal Development Company joined to develop circulating bed technology in their Solid Circulation Fluidized Bed (SCFB) boiler (Figure 70).

This technology has been developed through the pilot plant phase. Stone & Webster is currently pursuing the commercialization of the technology and as a part of that effort the construction of a 22 to 45 t/hr stream plant firing coal or petroleum coke. Stone & Webster, the exclusive licensor of SCFB technology, has licensed the technology to Foster Wheeler Boiler Corporation and Babcock Power Ltd.

The principal features of some of the CFBC systems are discussed in the following four sections.

8.7.1 Lurgi/Combustion Engineering

The Lurgi unit utilizes a bed of ash and limestone and includes a waterwall lined combustor section operating at 6 to 9 m/s gas velocity. The combustor discharges flue gas and entrained bed material at approximately 840°C to a hot primary cyclone which recirculates the captured solids either

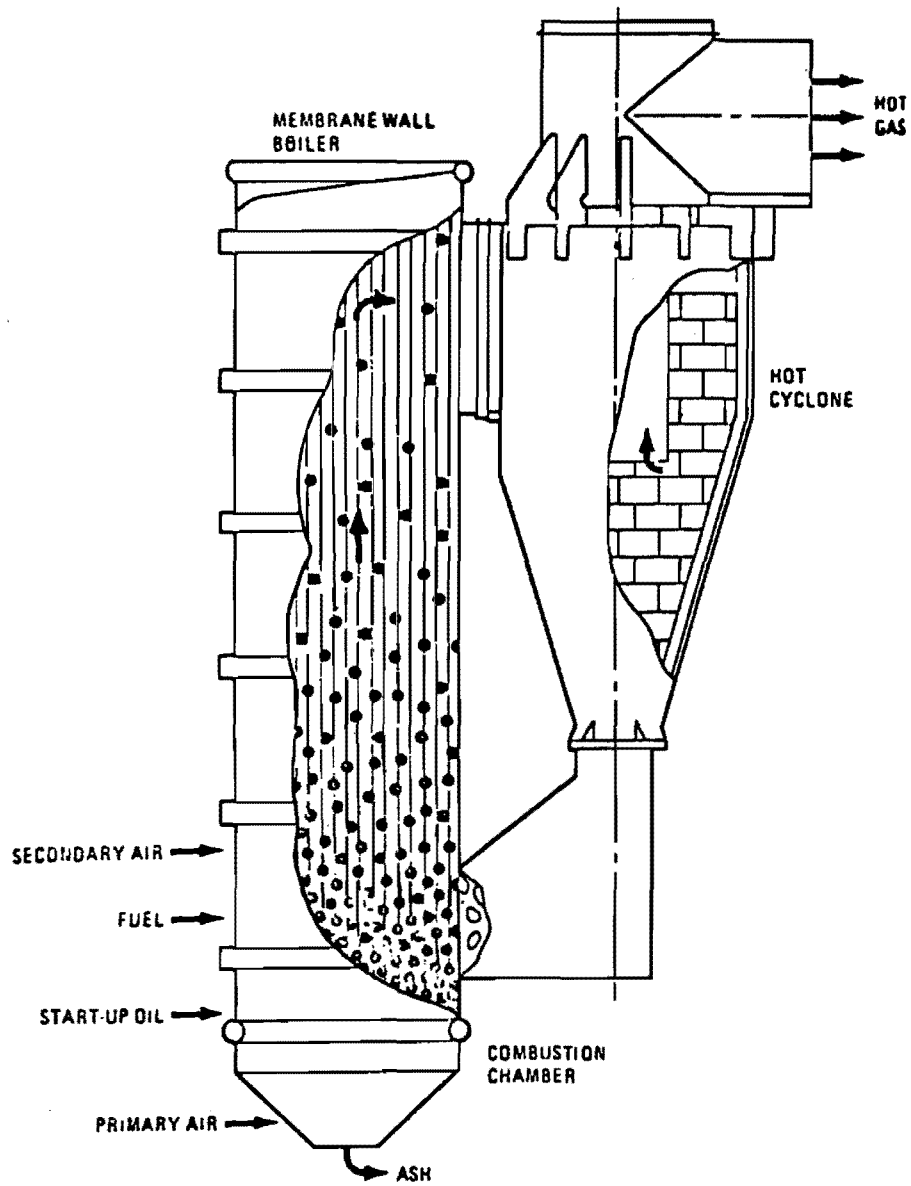


Figure 69. Pyropower CFBC system.

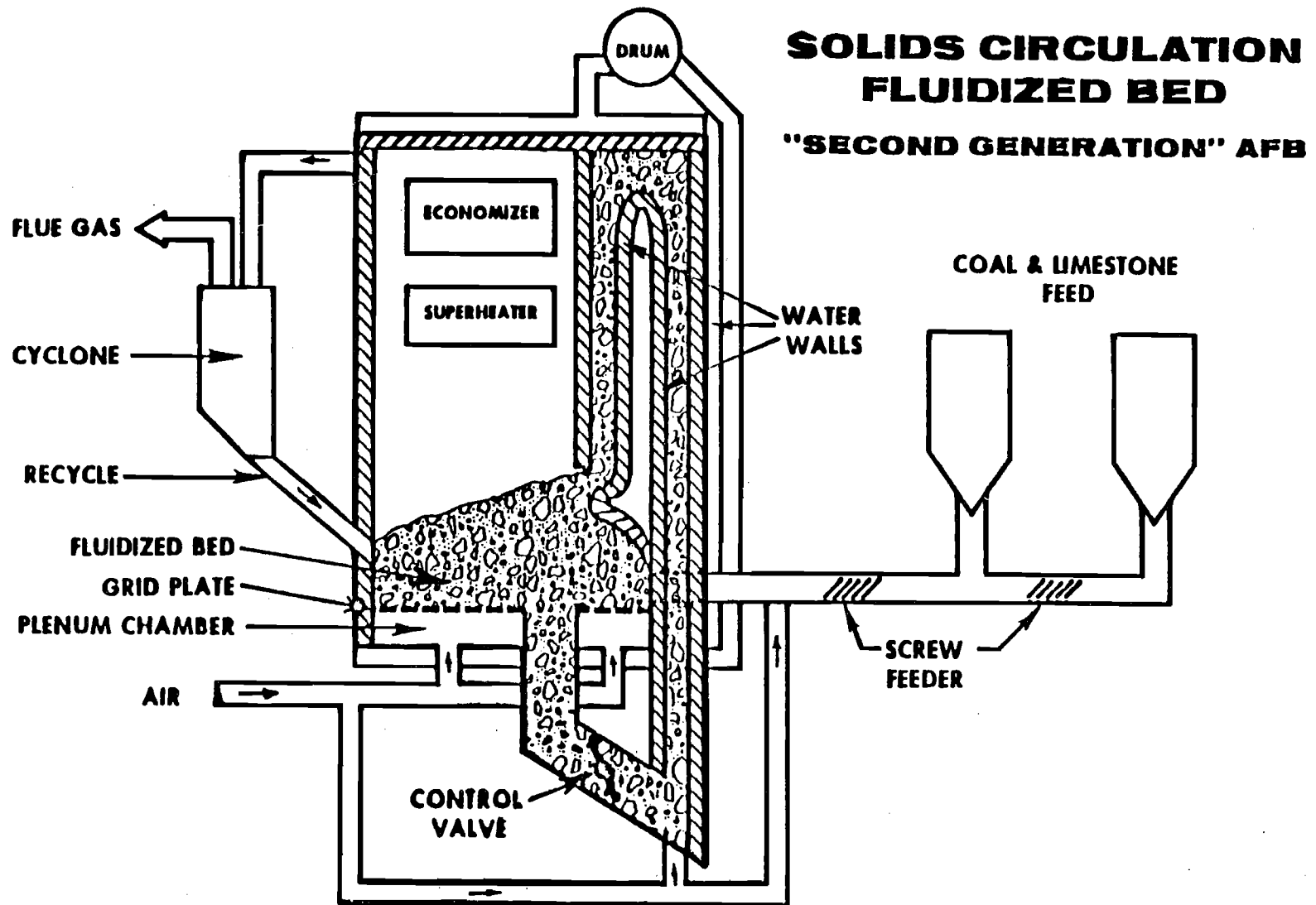


Figure 70. Solid circulating boiler.

directly back to the combustor bed or to an external fluidized dense bed cooler where additional heat is removed via in-bed tubes. The cooled solids exiting the cooler are then either returned to the combustor bed or sent to waste. Flue gas exiting the primary cyclone at 840°C then passes through a secondary hot cyclone to a waste heat boiler where it is cooled to about 300°C , passed through a hot electrostatic precipitator, further cooled in an air heater, and discharged to atmosphere. Combustor bed inventory is maintained either by draining hot bed material through an ash cooler to waste or purging the fluidized bed cooler discharge to waste.

8.7.2 Battelle/Struthers

The Battelle unit utilizes a bed of ash, limestone and inert high specific gravity material and includes a waterwall lined combustor section which superimposes an entrained bed operating at gas velocity over a fluidized dense bed fueled by up to 35 mm coal. The combustor includes a secondary air input above the dense bed and discharges flue gas and entrained bed material at approximately 840°C cyclone which recirculates the captured solids through an external fluidized dense bed cooler where heat is removed via in-bed tubes. The solids exit the fluidized bed cooler at approximately 593°C and return through an "L" valve to the combustor bed. Flue gas exiting the primary cyclone at 840°C then passes through a waste heat boiler where it is cooled to 204°C , hence through a secondary cyclone and baghouse prior to release to atmosphere. Waste material is purged from the secondary cyclone and baghouse.

8.7.3 Stone & Webster/Conoco Coal Development Company

An inert solid is fluidized at about 3 m/s in a dense phase mode (Figure 69). Solids are withdrawn from the bed, pass through a solids control valve and are lifted in dilute phase through a riser using about 15% of the stoichiometric air. The solids are returned to the bed via a downflow channel and "ski slope" which imparts a horizontal velocity casting them across the surface of the bed. In this fashion, the bed is continuously circulated at up to 100 times the typical coal feed rate imparting important lateral mixing of

solids. Coal and limestone are introduced into the bed where they are rapidly distributed throughout the bed by the swirling action of the solids.

Steam is generated by passing hot solids from the combustion zone through the water wall riser and downflow channels using secondary air as the lifting medium. Output steam rate is maintained at the desired rate by controlling the quantity of solids circulated through the channel.

The limestone used is finer than has been used in first generation systems. As such there is a greater area per unit volume and it tends to have a greater capacity for the absorption of SO_2 . Limestone, which has been sulphated, and coal ash, which has been ground by the bed action to a fine size, are carried overhead with the flue gas through the convection section where they are partially cooled.

The cooled flue gas and entrained solids pass through a stage of cyclones where the coarser particles are separated from the flue gas. The captured solids are returned to the combustion bed at up to five times the coal feed rate. Normally, additional evaporator surface or superheater tubes, or both, are located in the convection sections along with the economizer section of the system. As a result, the gases loading the cyclones are only at 370°C .

8.7.4 Ahlstrom/General Atomic (Pyropower)

The Ahlstrom unit (Figure 70) utilizes a bed of ash, limestone and sand and includes a water-wall lined combustor section which superimposes an entrained bed operating at approximately four m/s gas velocity over a dense fluidized bed fueled by up to 25 mm size coal. Secondary air is introduced at various levels. Flue gas and entrained bed material are discharged at approximately 840°C to a hot cyclone which recirculates captured solids through a nonmechanical seal back to the combustor bed. Flue gas exiting the cyclone at 840°C then passes through a waste heat boiler, air heater, and baghouse prior to release to atmosphere. Waste material is purged from the bed at 840°C and the baghouse at approximately 150°C .

The successful operation of the early CFBC systems has led to the acceptance of this advanced circulating fluidized bed technology in the U.K., Germany, Scandinavia (mainly for peat and wood water) and the U.S. By the end of 1981, six commercial CFBC systems by Pyropower were in operation and five under construction, including one in the U.S. for Gulf Exploration and

Production. This is the first unit in the U.S. for generating steam for heavy oil recovery by burning coal and is scheduled for start-up late this year. The application of the CFBC, however, is for small industrial size steam supply systems. A 25 t/h steam demonstration plant, using the Stone & Webster SEB technology is under construction and is scheduled for start-up in late 1983.

The CFBC technology is still new and very little information is available on its application for large electric power generating facility.

8.8 APPLICATION OF FBC TECHNOLOGY TO OIL SANDS PLANTS

The application of FBC technology in an oil sands complex can be envisaged for utilizing the abundance of residue expected from the primary upgrading processes for oil sands bitumen. Depending on the primary upgrading process, these residues, as mentioned in Section 7 of the report, could be fluid coke, H-Oil pitch, Eureka pitch or CANMET pitch.

However, the ability of FBC systems to process residue such as H-Oil pitch, Eureka pitch and CANMET pitch is not known to have been demonstrated specifically. Other pitches and pitch-like materials including No. 6 fuel have been successfully fired by Foster Wheeler, Esso (U.K.), Babcock Power Ltd., and Central Power & Light. The delayed coke (.0565 mass fraction sulphur) from Suncor Oil Sands extraction process has been burned in a pilot scale AFBC at Canadian Combustion Research Laboratory (CCRL) and by Pyropower.

Although both the delayed fluid coke have a high heating value when burned by means of conventional pulverized-fired technology special furnace designs are required to compensate for the low volatile matter content of coke. The high sulphur and metal content further represents an environmental pollution problem in terms of SO_2 emissions and ash disposal.

Both AFBC and PFBC thus appear to be a possible means of harnessing economical energy for an oil sands complex. The limestone required for sulphur capture is known to exist in the Fort McMurray area. However, nothing is known of its characteristics as a sulphur sorbent.

The results of the tests performed at CCRL have been published by CANMET (1981). The studies carried out at a bed temperature of 950°C (higher than those used for coal because of high fusion temperature, see Table 25) and superficial fluidizing velocities of less than 2 m/s indicated a carbon carryover

of 4% of input fuel. Concentration of NO_x in the flue gas was typically around 0.1×10^{-3} volume fraction. A limestone known to be a good sulphur sorbent was found to reduce SO_2 emissions by about 80%, when supplied at Ca/S ratio of 3:1.

On an industrial scale, combustion of residue coke in an FBC would appear to present the problem that high combustion efficiency requires bed temperatures of about 950°C , whereas sulphur neutralization by limestone is most efficient at bed temperatures of about 850°C . The high (as much as 0.09 mass fraction) sulphur and high metal content (Tables 17 and 20) will contribute to environmental corrosion and erosion problems. In addition, the SO_2 emissions and ash disposal will require further evaluation. A number of aspects outlined below, need resolving before a FBC technology can be employed in an oil sands complex.

All these factors are major considerations in commercialization of efficient, reliable and economically competitive FBC systems. In addition, the application of FBC in an oil sands complex may require the capability of processing the residue feeds such as H-Oil, CANMET and Eureka pitch.

8.8.1 Sulphur Dioxide Emissions with Reduced Limestone Utilization

A primary function of FBC is to burn high sulphur fuels with minimal SO_2 emissions. This is achieved by addition of limestone to the fluidized bed. However, a high Ca/S ratio of 3:1 has been required by AFBC technologies to retain 90% of sulphur from a coal containing 0.03 to 0.04 mass fraction sulphur. Residue from oil sands with much higher sulphur content may require even higher amounts of limestone.

A number of means are being investigated to reduce the limestone consumption:

1. increased recycle of fly ash and partially sulphated limestone (Yeager 1982);
2. physical activation of limestone (Chessell 1979);
3. chemical activation of limestone (Chessell 1979, and Shearer, Johnson and Turner 1979);
4. regeneration as in chemically active fluidized bed (CAFB) (McMillan and Zoldak 1977);

5. recirculating of fine limestone as in circulating fluidized bed combustion technology.

8.8.2 Emissions of NO_x

The low temperature operation of FBC results in reduced NO_x emission. However, combustion efficiency is favoured by high temperatures. The technique of overfire air (a portion of fluidizing air is diverted to above the fluidized bed) is known to reduce the NO_x emission. Also, increased recycle rates will improve combustion efficiency.

8.8.3 Turndown

The steam demand in an oil-sands complex fluctuates considerably. An effective turndown system thus may be the primary requirement. Most conceptual designs for utility scale FBC boilers achieve turndown by dividing the fluidized bed into multiple segments (Yeager 1982). However, these systems create several design and control problems.

A continuous reduction of air and fuel while maintaining the fluidized bed has been demonstrated at the 6' x 6' facility operated by Babcock and Wilcox Co. A 50% turndown was achieved.

The advanced CFBC's have, in general, a faster and simpler turn-down system than the conventional FBC's. The principle employed is reduction in fuel and air feed rates with reduction in circulating flow rate.

8.8.4 Feed System for Fuel and Limestone

The merits of the overbed and underbed feed with mechanical and pneumatic systems are being evaluated. The CFBC, however, presents a system with less problems. The introduction of recycle to the fluidized bed, the optimum size for reduced carry over, high combustion efficiency and sulphur retention is also being developed.

9. NO_x CONTROL

9.1 INTRODUCTION

NO₂ is most commonly known as the brown, smoggy haze overhanging most large cities in the world. The precursor to NO₂ is NO, which is produced as a result of fossil fuel combustion. NO is easily oxidized to NO₂, hence, the general term NO_x. The emission of these compounds has become subject to increasingly stringent control regulations.

9.2 NO_x CONTROL REGULATIONS

NO_x emissions are regulated because of medical and environmental considerations. NO₂ reacts with hydrocarbons and ozone in sunlight to produce smog and compounds that irritate eyes, aggravate certain respiratory diseases and injure plants (Pruce 1981a).

In the past, Alberta provincial regulations have set maximum NO_x concentration levels at 60 g/m³ (annual arithmetic mean), 200 g/m³ (24 hour concentration) and 400 g/m³ (1 hour concentration). However, effective May 1, 1981, all new construction approved by the Energy Resources Conservation Board must comply with the following NO_x emission standards for all combustion sources (pers. comm. J.A. Jaferi, Alberta Environment, June 3, 1982):

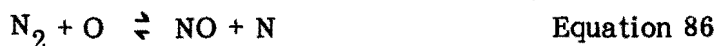
1. 0.26 kg/GJ (0.6 lbs/10⁶ Btu) for solid fuel (coal, coke, etc.)
2. 0.13 kg/GJ (0.3 lbs/10⁶ Btu) for liquid fuel
3. 0.086 kg/GJ (0.2 lbs/10⁶ Btu) for gaseous fuel

NO_x regulations in the United States are the same as the new Alberta standards. The U.S. Environmental Protection Agency (EPA) is presently pushing for more stringent emission standards - 0.086 to 0.13 kg/GJ (0.2 to 0.3 lbs/10⁶ Btu) for solid fuel by the mid 1980's (Pruce 1981a). The Japanese government imposes the world's most stringent NO_x standards and, as a result, a great deal of work originates in Japan.

9.3 NO_x FORMATION

In a combustion process NO_x is formed from two different sources of N₂. Thermal NO_x is produced from molecular N₂ in the air and fuel NO_x is produced from oxidation of N contained in the fuel. When coal is burned, fuel NO_x contributes 60 to 80% of the total NO_x emission.

The reactions that take place to form NO_x are elementary. However, the process itself is fairly complex, involving equilibrium and non-equilibrium mechanisms in the precombustion, combustion and post-flame areas. The reactions are as follows:



These reactions occur at a temperature in excess of 1760°C .

Many aspects of the combustion process affect the rate and quantity of NO_x formed. The O_2 concentration is important because the fuel and the N_2 compete with each other for O_2 . Thus, the formation of NO_x is highest when the fuel is burned with an excess of air. This statement is true more so for oils than for gas, because oil has more fuel nitrogen (Coe 1980).

The formation reactions are slow compared to the fuel residence time. Consequently, the formation of NO_x is proportional to residence time in the primary combustion zone (Coe 1980).

High flame temperature increases the potential for higher NO_x emissions. Furnace design becomes important in this aspect because of the possibility of hotspots forming.

9.4 CONTROL STRATEGIES

To be able to meet the NO_x emissions regulations, some type of control strategy must be adopted. These strategies may be divided into three general groups: operational aspects; equipment design and modification; and NO_x removal. Operational aspects deals with the way in which existing equipment may be used in order to minimize NO_x emissions. This is the least expensive method of NO_x reduction. In most cases burner and/or furnace design and/or modification is an effective method of NO_x control. These methods are more expensive than the operational methods. These two groups involve the actual burn characteristics, burn patterns, excess air considerations, etc. The last group differs from the first two in that it treats the flue gas. Several processes are commercially available for the reduction of NO_x . This

group is the most expensive and the most effective. These three groups are discussed in the sections that follow.

9.4.1 Operational Aspects

9.4.1.1 Low excess air. Operation with low excess air (LEA) is standard practice on many oil and gas fired burners. Although the flame temperature is at its highest at the stoichiometric air/fuel ratio, thus promoting NO_x formation, the concentration of NO_x is highest with an excess of air. This is because NO_x formation is a function of both temperature and oxygen partial pressure. Unfortunately, with LEA operation comes increase in other emissions such as CO and unburned hydrocarbon.

9.4.1.2 Staged combustion. Staged combustion can be described as operating a burner with LEA and then treating the CO rich mixture with a secondary stream of air in a separate combustion zone. This promotes fuel rich combustion (and, therefore, low NO_x production) in the primary combustion zone and complete combustion in the second zone. When operated in this manner, emissions from gas burners can be reduced 60 to 70% and for oil or coal fired burners, 40 to 50%.

There are basically two ways of achieving staged combustion. The first method is to operate certain burners fuel rich and others air rich in order to promote the staging effect. If possible, the top burners should be operated with 100% air. This type of operation involves no retrofitting.

The next step beyond operational changes involves a small degree of retrofitting. In some cases an extra row of overfire air ports is added above the top burner row. The lower burners are then operated fuel rich to achieve staged combustion. Burner modifications are covered in more detail in Section 9.4.2.1.

Unfortunately, staged combustion techniques may also present operating problems. Operation of the burners with varying fuel/air mixtures can cause the boiler to be derated. Staged combustion can result in longer flames in some boilers causing impingement of the flame on the furnace wall. This condition can lead to slagging and corrosion in the lower furnace region (Pruce 1981a).

Application of this technique to small industrial units may not be possible as many of these units have only a few burners and no room for overfire air ports.

9.4.1.3 Delayed fuel/air mixing. Delayed mixing is a method designed to control thermal NO_x . Since the formation of this NO_x is mainly a function of temperature, the easiest way to reduce it is by lowering this temperature. This is achieved by delaying the mixing of fuel and air. The configuration of burners may be altered as well as their number and spacing. Additional air ports may also be added.

Application of this method results in a longer burn time. Consequently, optimum operating conditions may call for a larger combustion zone, which would allow a greater heat transfer capability and, thus, help keep the temperature down.

If delayed mixing is taken to extremes, however, it can result in unburned fuel and a subsequent loss of efficiency.

This method is used by many utility companies and is largely responsible for their meeting today's emission standards (Whitaker 1982).

9.4.1.4 Flue gas recirculation. Flue gas recirculation (FGR) is another control method aimed at reducing production of thermal NO_x . Inert flue gas is recirculated back into the combustion zone in order to reduce the flame temperature. To be effective, the flue gas has to be mixed with combustion air in the windbox or at the throat of the burner. It has been found that reintroducing the gas into the furnace hopper has little or no effect on the emission of NO_x because the gas tends to hug the walls.

The ability of FGR to control NO_x emissions is dependent on the type of fuel used. Since the method controls only thermal NO_x , it is most useful for burning fuels such as natural gas which only produce small amounts of fuel NO_x in relation to thermal NO_x . The use of this method on coal fired burners has little effect. Reduction levels of 20 to 50% with 20 to 40% recirculation have been observed (Pruce 1981a).

The amount of flue gas recirculated is limited by flammability considerations. Too much inert gas can starve the flame of O_2 .

Installation of recirculation equipment is expensive although the system is very easy to operate. One special problem associated with the burning of coal or coke is that the recirculated flue gas must be cleaned of all particulate matter in an effort to avoid plugging and erosion of passages.

9.4.2 Equipment Design and Modifications

9.4.2.1 Burner design and modification. The burner governs the fuel/air mixing process and the injection pattern into the furnace.

Tangential firing is used in about half the boilers among U.S. utilities (Whitaker 1982). These boilers are primarily fired by coal. Combustion Engineering (CE) and Acurex Corp. have developed a slight variation of conventional tangential firing that is known as the fireball concept (Pruce 1981a, Whitaker 1982, Parkinson 1981). Fuel, primary combustion air and 20% of the secondary combustion air are injected from the four corners of a furnace (Figure 71). This creates a fuel rich fireball in the center of the furnace. The rest of the secondary air is injected parallel to the furnace walls thus creating a lean mixture in that area. The fuel rich combustion zone inhibits formation of both fuel and thermal NO_x . The wall air mixes into the vortex further up in the furnace thereby completing the combustion process. Combustion Engineering hope to reduce NO_x emissions to 0.13 to 0.15 kg/GJ (0.3 to 0.35 lbs/ 10^6 Btu). An additional benefit of this method is that since the walls of the furnace are blanketed by air, corrosion and slagging are greatly inhibited.

A distributed mixing burner (DMB) has been developed by Energy and Environmental Research Corp. (EER) which has been reported to have emissions of 0.086 kg/GJ (0.2 lbs/ 10^6 Btu) at the laboratory scale. Pulverized coal is the fuel used by this burner. The commercial viability of the burner has yet to be proven although it is now being used in a 450 MW Utah Power & Light Co. unit. It makes use of a tertiary air injection port. Parkinson (1981) gives a detailed description of its configuration. Retrofitting problems for the DMB include fitting of tertiary air ports and possible structural modifications to the furnace wall. The DMB is intended for use in wall fired furnaces.

Foster Wheeler has developed a wall-fired, coal-burning, split-flame burner. Emission rates of 0.17 kg/GJ (0.4 lbs/ 10^6 Btu) with no staging and 0.086 kg/GJ (0.2 lbs/ 10^6 Btu) when using overfire ports to achieve staging conditions,

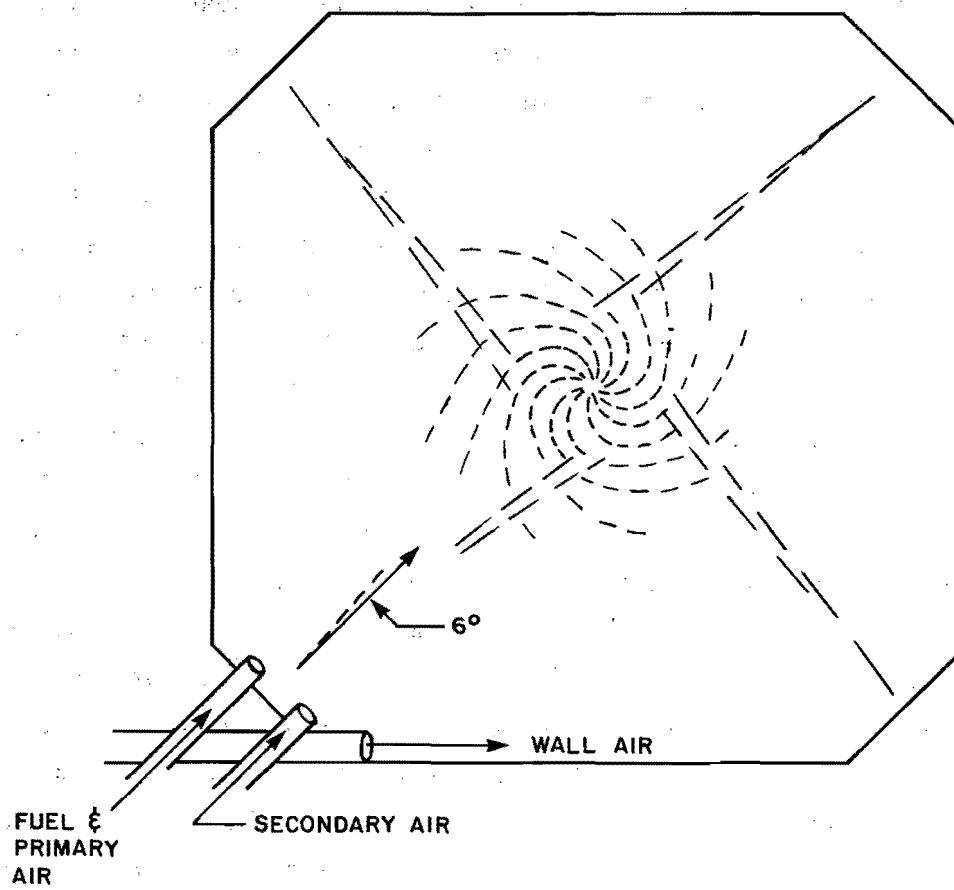


Figure 71. Tangential firing pattern.

have been reported. Pruce (1981a) and Parkinson (1981) both give details of the burner configuration and operation.

Babcock and Wilcox (U.S.A) (B & W) market a coal burner that utilizes the principle of delayed mixing. Coal is fed through a central pipe and primary and secondary air through two outer ports. B & W claim NO_x emissions of 0.065 kg/GJ (0.15 lbs/ 10^6 Btu) (Parkinson 1981).

All of the burners mentioned so far use coal as the fuel. However, the primary fuel for industrial burners is usually a liquid. These fuels are normally introduced into the furnace by one of the many different designs of atomizers. Widely varying characteristics of spray angle, drop size, etc. are exhibited due to the variety of atomizers.

The same principles of staging, delayed mixing and gas recirculation apply to gas and liquid fuel burners for NO_x reduction. A narrowing of the spray angle creates longer flames, thereby causing delayed mixing. This is done by either reducing the number of holes or repositioning them. Atomizer hole size is currently being tested with reference to creating fuel-rich and fuel-lean combustion zones.

A recently developed self-recirculation burner uses gas recirculation and two stage combustion. The key feature of this burner is the creation of a strong recirculation eddy in the large burner throat, which draws combustion products back into the fuel stream (Pruce 1981a).

Reduction in NO_x emissions from liquid fuels is often a tradeoff in terms of particulate emissions. These particulates consist of soot, cenospheres and coke. The local stoichiometry within the flame plays a dominant role in the formation of NO_x particulates. The Alberta provincial regulation for particulates emission limits emissions to 0.043 kg/GJ (0.1 lb/ 10^6 Btu).

9.4.2.2 Furnace design and modification. While burners govern the ratio and injection pattern of fuel and air, it is the design of the furnace that influences the overall thermal, kinetic and other combustion phenomena. Furnace design considerations are only applied to new units.

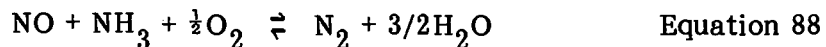
Babcock and Wilcox have designed a furnace that has the shape of an hourglass. Coal and air are injected and burned in the lower section of the furnace. The mixture then passes through a venturi section and is immediately contacted by staging air (staging air is injected just above the throat of the

venturi). This configuration is referred to as the primary combustion furnace (PCF). Pilot plant scale PCF's have been reported to have NO_x emissions of 0.086 kg/GJ (0.2 lbs/10⁶ Btu) (Whitaker 1982). Application of this type of combustion strategy to individual burners is described by Pruce (1981a).

Arch-fired furnaces (AFF) have been used for over 60 years by Wisconsin Electric Power Co. (WEPCO). Only recently, however, have the NO_x emissions from these furnaces been analyzed. KVB Inc. reports NO_x emissions approaching 0.13 kg/GJ (0.3 lbs/10⁶ Btu) for units ranging in size from 80 to 275 MW. AFF's have downward firing burners situated at the top of the furnace (the arch) with air being injected through the front wall, perpendicular to the flame jet (Figure 72). This creates a condition of slow mixing, thereby reducing NO_x emissions.

9.4.3 NO_x Removal

9.4.3.1 Thermal De NO_x . Thermal De NO_x (Exxon Research and Engineering Co., Linden, N.J., USA) is a selective non-catalytic reduction process. It is based on the fact that NH_3 will react with NO_x at certain temperatures rather than with other flue gas components. NH_3 is simply injected into the flue gas where the temperature is from 930 to 980°C. At these temperatures, the following reaction takes place:



If the temperature is too high, NH_3 and O_2 react to form NO . On the other hand, if the temperature is too low, no reaction occurs and NH_3 is emitted. This narrow temperature range is one of the major drawbacks of the process. The reaction temperatures may be lowered by the injection of H_2 , however, it does not broaden the range.

Application of this process to a flue gas stream results in slightly increased CO emissions as it inhibits the oxidation of CO to CO_2 . For normally operating oil and gas fired boilers, this situation presents no problem since the CO oxidation reaction is usually complete before the gases reach the NH_3 injection point.

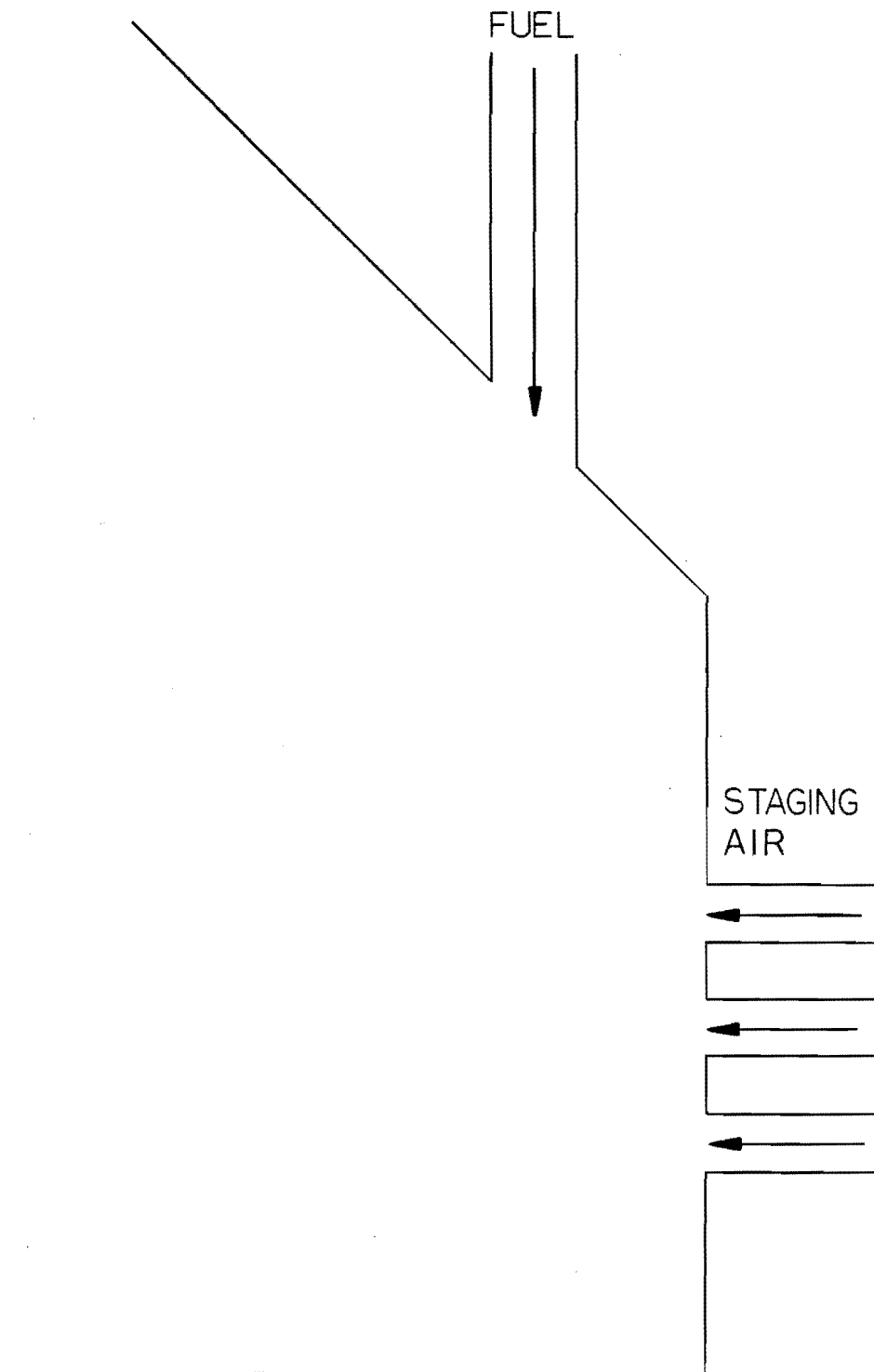


Figure 72. Arch fired furnace.

Other effects such as the possible formation of HCN, conversion of SO_2 to SO_3 , sulphate formation and fouling have all been found to be negligible (Lyon 1979).

Thermal DeNO_x has been found to be equally effective for oil, gas and coal fired boilers. While laboratory tests indicate the ability to reduce NO_x emissions by over 90%, in practice reductions of approximately 50 to 60% are achievable (Lyon 1979).

The commercial viability of this process has been proven in eleven units in Japan and one unit in the U.S.A. Economically, the process is more attractive than the Selective Catalytic Reduction (SCR) Process (described in Section 9.4.3.2) because it eliminates the need for costly catalyst.

9.4.3.2 Selective Catalytic Reduction (SCR). The SCR Process (this process is available from several different licensors) is based on the same chemistry as the Thermal NO_x Process. In this case a catalyst is used to lower the reaction temperature to a range of 204 to 343°C (Hill 1981).

NO_x reduction rates of over 90% have been reported at several installations in the U.S.A and Japan (Blair, Massey and Hill 1981; Hill 1981; Pruce 1981a). Unreacted NH_3 has been limited to 10×10^{-6} volume fraction.

A catalyst of vanadium oxide on a titanium oxide base is used almost universally because it is highly resistant to SO_3 poisoning. Catalyst lifetime is approximately one year for coal fired boilers. These claims are largely unsubstantiated for large-scale units (Pruce 1981a). The potential for reconditioning the catalyst and the possibility of catalyst disposal problems are subjects that have yet to be studied since no catalysts have been taken out of service to date.

Problems have arisen with the effect of ammonia on downstream equipment, especially the air preheater. Several new designs are currently being developed and tested in order to alleviate the problem. Continuous monitoring of the flue gas has also proven to be a problem, especially for fuels containing sulphur. Chemiluminescent, nondispersive infra-red and nondispersive ultraviolet analyzers can be used successfully only with streams containing low concentrations of SO_2 .

Treatment of a flue gas that contains a significant amount of particulate matter can be difficult to handle as the particles plug up the catalyst. This causes a pressure buildup across the bed. An intermittent moving bed reactor has been developed and proven successful in long run pilot plant tests. This reactor is described by Ostsuka et al (1979).

Although there are only a few SCR units operating in North America (there are more in Japan), the operating results gathered thus far indicate that the process is quite safe and reliable (Hill 1981). Blair, Massey and Hill (1981) discuss the operation of the newly installed SCR unit at the USA Petrochem refinery in Ventura, California.

9.4.4 Turbines and Compressors

Approximately 35% of all NO_x emissions in Alberta are from industrial gas compressors and gas turbines. There are two categories of control strategy: operational adjustments and hardware additions which prevent NO_x formation; and exhaust gas treatment. Reductions in emissions usually result in unburned fuel, higher CO emissions and increased fuel consumption.

Rich air to fuel ratios reduce NO_x emissions by 44% with a fuel penalty of 4%. Retardation of the spark timing reduces NO_x by 25% with a 5% fuel penalty (Zelensky and Colley 1982).

Hardware additions are becoming more and more common. Exhaust recirculation can reduce NO_x 36% with a fuel penalty of 2%. Turbocharging reduces NO_x by 25% and decreases fuel consumption by 5%. Redesigned combustion chambers reduce NO_x by 60%. Water injection reduces NO_x by 70% with a 1% fuel penalty (Zelensky and Colley 1982).

Catalytic combustion is a new technique that may provide cost effective NO_x control. Combustion of a lean fuel/air mixture over a platinum/nickel oxide catalyst occurs at a temperature of less than 1649°C , well below the temperature at which thermal NO_x is formed. Major technical problems still exist for this technique, however. Catalyst and substrate materials have not yet shown structural integrity and long life. Serious catalyst degradation has also occurred at high pressure (Pruce 1981b).

9.5 APPLICABILITY OF NO_x CONTROL TECHNOLOGY TO OIL SANDS PLANTS

Syncrude burns only a small fraction of its coke while Suncor burns most of theirs. Since coke has a relatively high nitrogen concentration, this fuel can be expected to protment. Reductions in emissions usually result in unburned fuel, higher CO emissions and increased fuel consumption.

Rich air to fuel ratios reduce NO_x emissions by 44% with a fuel penalty of 4%. Retardation of the spark timing reduces NO_x by 25% with a 5duce higher levels of NO_x than other types of fuels, such as natural gas. The main sources of NO_x emissions in an oil sands plant are much like those found in an oil refinery. The largest source is probably the process heaters.

Application of any of the previously discussed control strategies to the oil sands plant appears to be straightforward and without any special or unusual problems.

10. THE INCREMENTAL COST OF SULPHUR EMISSION CONTROL

The Alberta Government has established guidelines limiting the total emission of sulphur from an oil sands operation to 3.2 t per 1000 m³ of bitumen fed to the upgrading process (0.5 long tons per 1000 bbl).

The possible strategies available for conforming to these guidelines will be dictated by the configuration of the upgrading plant being considered. The process economics developed in this report relate to a plant employing the Syncrude/Alsands configuration, in which the Fluid Coker has the most important influence on the distribution of sulphur and, hence, potential SO₂ emissions. Table 31 summarizes the cost and benefit of employing the Claus plant and the two principle "add-on" technologies described in the report (i.e., tail gas plant, and FGD plant) in this context. The other technologies considered in this report (i.e., residue gasification and fluidized bed combustion) cannot be considered in the same way since they would be employed to recover energy from residues that would otherwise be stockpiled rather than "added-on" to reduce and otherwise inevitable emission. The costs presented in Table 31 have been obtained by averaging the costs for the candidate processes described in previous sections. Capital and operating costs have been levelized to a single capital figure by adding four times the annual operating cost to the capital cost. The final two columns of Table 31 demonstrate clearly how the law of diminishing returns applies in this area. Defining basic Claus recovery and cost as 100% it can be seen that by adding both tail gas treatment and flue gas desulphurization 111% removal is achieved at 372% cost.

The information contained in Table 31 is represented on Figure 73 to show how SO₂ emissions to atmosphere decrease with increasing investment in pollution control equipment.

The recovery of 64 t/d quoted for the FGD plant is based on 90% SO₂ removal which may be somewhat conservative. However, even a recovery of 100% (71 t/d) will not affect the conclusions demonstrated in the table.

Table 31. Relative cost of sulphur emission control technologies.^{a,c}

	Claus Plant	Tail Gas Treatment	Flue Gas Treatment
Capital Cost	39	17	85
Annual Operating Cost	4.4	3.0	10
Levelized Cost	56.6	29.0	125.0
Sulphur Removal: t/d	875	36	64 ^b
t/1000 m ³ Bitumen	43.16	1.78	3.16
Cumulative Removal %	100	104	111
Cumulative Cost %	100	151	272

^a Costs are shown in millions of mid 1982 Canadian dollars.

^b 90% removal assumed.

^c Plant capacities are defined by the flowsheet (Figure 5) on page 12 of this report.

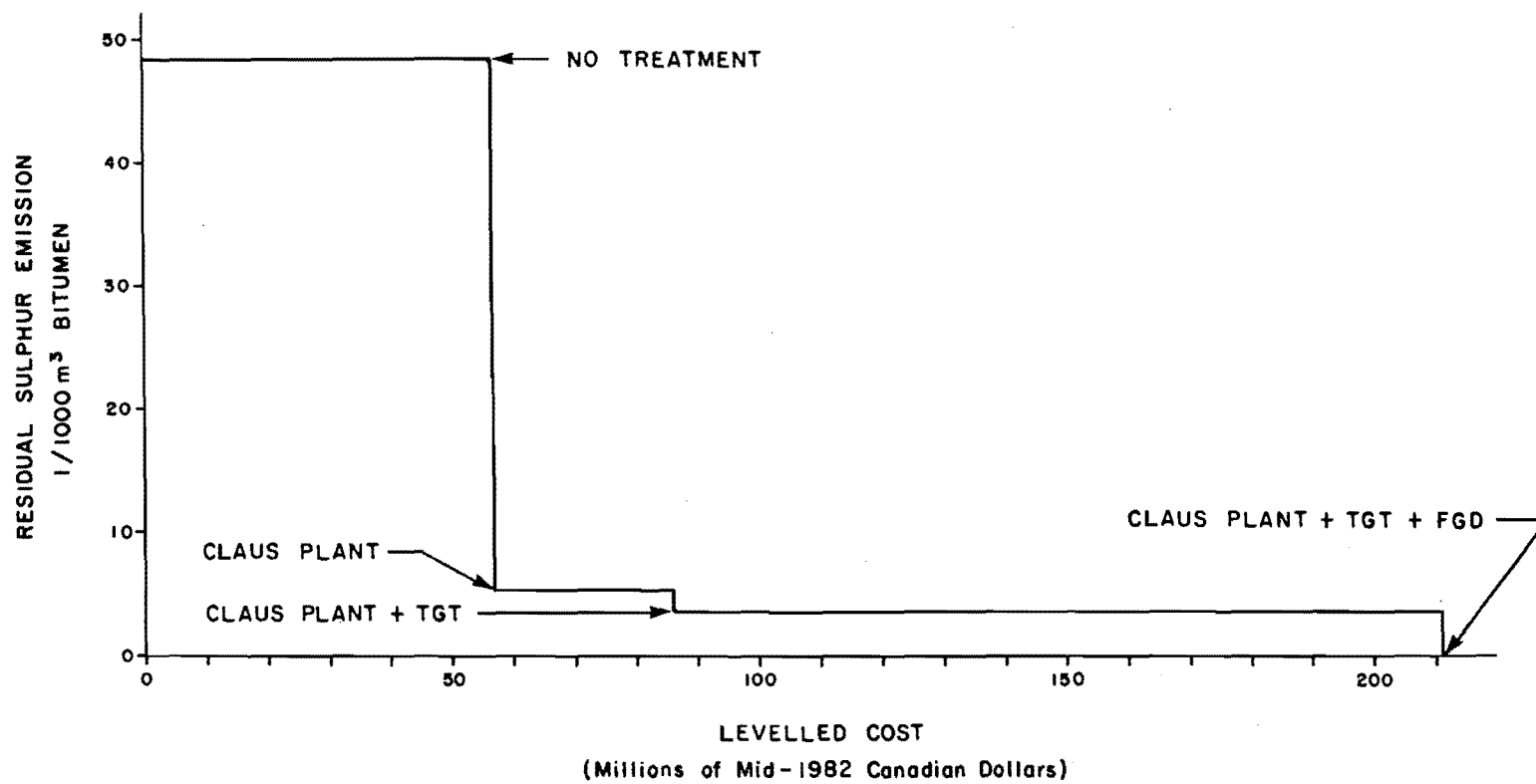


Figure 73. Incremental cost of sulphur emission control.

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12. APPENDIX

12.1 THE REPORTED AVAILABILITY OF CHEMICAL PROCESSES

The large investment associated with modern industrial equipment of all types, carries a correspondingly high penalty for downtime and, in particular, unscheduled and unprofitably used downtime. The prediction of plant availability has become increasingly important and sophisticated. Nevertheless, reported data must be treated with some care. Table 32 shows four alternative definitions of "availability". The last definition is particularly interesting, highlighting the two essential components of any availability figure, that is, the portion associated with equipment failure (the mean time to fail, MTF) and the portion associated with the management system designed to correct that failure (the mean time to repair). If it were possible to install two mechanically identical processes with the same MTF, the availability of those two processes could be vastly different if the MTR's are different. This could easily be the case if the management of one process decided to employ a continuously available shift maintenance team and the management of the identical process at a different location did not. (Table 33 gives a simple example). This appendix has been written to introduce the complexities of availability data. Kletz (1973) provides probably the best paper in the field.

12.2 THE ACCURACY OF PUBLISHED COST DATA

A report like this, essentially an overview of available technology which may be applied in a particular field, must rely on published cost data of a general nature in establishing relative economic rankings. Any attempt to become more accurate rapidly leads to the necessity of resolving questions specific to the site being considered.

The potential pitfalls of relying on published data to provide anything beyond a relative ranking have best been illustrated by a detailed survey of the costs of installed and operating FGD processes in the USA (Pedco 1981), instigated by the Environmental Protection Agency. Since the survey was based on achieved rather than estimated costs, it was anticipated that some consistency would emerge. This did not prove to be the case. The reasons for

the lack of consistency are partly site specific, partly a variance in factors included in the different reported costs and partly the different economic conditions pertaining at the time of each installation. However, even after adjustments have been applied to eliminate variance arising from the content of the reported costs, the resultant spread was significant. Table 34 summarizes both the reported and adjusted capital and annual costs of operational FGD systems in the USA. Of particular note is the difference in some cases between the reported and adjusted costs. This illustrates the importance of knowing precisely what is, and what is not, included in reported capital and operating cost data.

The variation in reported cost data for other technologies is similar. In the tail gas treatment area variations of 50% for some processes were found. For example, the reported costs for the IFP Clauspol 1500 process (when converted to 1982 Canadian dollars for a consistently sized plant) varied between \$10 million and \$15 million.

Table 32. Alternative definitions of availability.

1	Hours process operated / Total hours in period
2	Hours process operated / Hours process called on to operate
3	Hours process available / Total hours in period for operation (whether of not operated)
4	Mean time to fail / Mean time to fail + Mean time to repair (MTF) (MTF + MTR)

Table 33. Potential management impact on availability.

	MTF (h)	MTR (h)	Availability
Case 1 (Shift Maintenance Team)	60	2	0.97
Case 2 (Shift Maintenance Team)	60	8	0.88

Table 34. Reported and adjusted capital and annual costs for operational FGD systems.^{a,b}

	REPORTED						ADJUSTED					
	Capital			Annual			Capital			Annual		
	Range \$/kW	Average \$/kW	^c	Range mills/kWh	Average mills/kWh		Range \$/kW	Average \$/kW		Range mills/kW	Average mills/kWh	
All	23.7 to 24.30	79.1	45.4	0.05 to 13.02	2.64	3.14	35.1 to 258.9	113.5	54.6	1.69 to 18.67	7.21	3.82
New	23.7 to 243.0	77.5	47.2	0.05 to 5.52	1.84	1.84	35.1 to 242.1	103.8	43.3	1.69 to 12.83	6.31	2.68
Retrofit	29.4 to 157.4	81.2	41.4	0.46 to 13.02	4.54	4.64	57.5 to 258.9	132.3	69.4	4.21 to 18.67	9.12	4.99
Saleable	132.8 to 185.0	153.0	23.8	13.02 to 13.02	13.02	0.0	233.6 to 258.9	249.1	13.6	15.23 to 18.67	16.44	1.94
Throwaway	23.7 to 243.0	73.7	41.8	0.05 to 11.32	2.15	2.65	35.1 to 242.1	104.2	42.5	1.69 to 16.27	6.41	3.03
Alkaline Flyash/Lime	100.3 to 101.4	101.0	0.6	0.53 to 2.97	2.16	1.41	133.8 to 142.9	136.8	5.2	5.75 to 7.62	6.99	1.08
Alkaline Flyash/Limestone	49.3 to 49.3	49.3	0.0	0.75 to 0.75	0.75	0.0	94.4 to 94.4	94.4	0.0	4.99 to 4.99	4.99	0.00
Dual Alkali	47.2 to 174.8	97.8	67.7	1.30 to 1.30	1.30	0.0	80.6 to 242.1	134.6	93.1	4.59 to 12.83	7.79	4.41
Lime	29.4 to 243.0	80.1	50.6	0.92 to 11.32	3.65	3.02	57.5 to 192.7	105.1	19.1	3.70 to 16.27	7.79	3.63
Limestone	23.7 to 168.0	65.0	34.9	0.95 to 7.76	1.78	2.54	35.1 to 140.7	93.4	42.5	1.69 to 10.44	5.61	2.65
Sodium Carbonate	42.9 to 100.8	69.2	30.7	0.23 to 0.46	0.38	0.13	79.9 to 138.5	101.7	28.0	5.29 to 6.78	5.88	0.73
Wellman-Lord	132.8 to 185.0	153.1	23.8	13.02 to 13.02	13.02	0.00	233.6 to 258.9	249.1	13.6	15.23 to 18.67	16.44	1.94

^a Source: Pedco (1981)

^b In this table, which is designed to show cost variation, the data are presented in 1980 US dollars.

^c Standard deviation.

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