FLUOR ENGINEERS AND CONSTRUCTORS, INC. Contract 835504

10.0 FLUE GAS DESULFURIZATION

10.1 PROCESS DESCRIPTION

There are various processes available to remove sulfur dioxide (SO₂) from coal fired boiler flue gas. In broad sense Flue Gas Desulfurization (FGD) systems can be classified in two general categories, industrial applications and utility applications. The main difference between these two is the size of the unit, industrial systems being much smaller in size than utility systems. The Tri-State FGD unit falls into the utility application category.

There are two types of FGD processes available: throwaway and regenerable. In throwaway systems sulfur dioxide from the flue gas is scrubbed using an alkaline solution, such as lime, limestone or caustic. The sulfur compounds thus made, e.g. $CaSO_3$, $CaSO_4$, Na_2SO_4 , etc. have no commercial value and are extremely difficult to sell in the U.S. market. They are generally disposed of in a landfill after fixation. As a scrubbing agent is used only once, the raw material requirements and waste production ar large quantities.

The basis of Case 13 design and estimate was the FMC Double Alkali System.

The FMC Double Alkali FGD System removes sulfur dioxide from the boiler flue gas and ultimately converts it to a filter cake material consisting primarily of calcium sulfite. The system can be broken down into two subsystems, the sulfur dioxide absorption system and the sodium regeneration system.

Sulfur Dioxide Absorption Section - In the absorption section, the sulfur dioxide is absorbed in a solution of sodium compounds. The sulfur dioxide reacts with sodium sulfite in the process liquor to form sodium bisulfite. A bleed stream proportional to the amount of SO₂ collected is sent to the regeneration section.

Sodium Regeneration Section - In the regeneration section, the bleed stream from the absorption section is mixed with a slurry of calcium hydroxide. The calcium hydroxide reacts with sodium bisulfite to form calcium sulfite, a solid, and regenerate sodium sulfite. The solids are thickened and filtered to a clay-like filter cake and the regenerated solution is recycled to the absorption section for further SO, removal.

A total of six (6) absorption sections, one (1) per boiler, are provided. The bleed streams from the absorption sections are combined and subsequently split between two (2) identical regeneration trains.

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TRI-STATE SYNFUELS COMPANY Indirect Coal Liquefaction Plant Western Kentucky

10.2 FLOW SHEETS

Flow Sheets for the Flue Gas Desulfurization area are proprietary with the licensors involved. Details of the processes cannot be revealed until a licensing agreement is signed.

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TRI-STATE SYNFUELS COMPANY Indirect Coal Liquefaction Plant Western Kentucky

10.3 UNIT MATERIAL BALANCES

Refer to Section 10.6 for individual FGD licensor battery limit material balance and utility requirements. Individual FGD licensors include FMC's Double Alkali Process, Chiyoda's thoroughbred 121 process (CT-121), Davy McKee's Wellman-Lord Process, and finally, Peabody's Citrex Process. A process material balance from FMC is included in Section 10.2.

10.4 ACCOMPLISHMENTS AND DECISIONS MADE AND FINALIZED

After detailed evaluation of the technical and economic aspects of each process, we conclude that:

- 1. The FMC Double Alkali and Chiyoda CT-121 processes are equally acceptable from a process stand point and comparable economically.
- 2. The Davy McKee Wellman-Lord Process maybe unacceptable because of the extremely high capital cost.
- 3. The Peabody Citrex Process appears to be unacceptable because of a high capital cost and because it is not proven commercially for large capacity units.

The current recommendation is to further evaluate FMC's and Chiyoda's licensed process. Early bid/quote evaluation packages received from the four (4) licensors were based upon using the feasibility study steam requirements and the analysis of seven (7) candidate coals. The bid/quote specifications for 'FGD' should be revised to reflect the steam requirements based on the final process configuration, Case 13, and the design coal analysis.

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10.5 CURRENT STATUS

Evaluation packages were received from FMC, Chiyoda, Davy McKee, and Peabody. Included in Section 10.6 is a summary of capital cost, plot requirements, technical data, and commercial experience. The licensor evaluation package was based upon using the feasibility study steam requirements and analysis of seven (7) candidate coals. This package needs updating to reflect the steam requirements based on the final process configuration (Methanol/MTG Case) and the design coal analysis.

Before making a final licensor selection, the revised operating specification should be sent to FMC and Chiyoda for then to revise their commercial proposals: licensing and engineering fees, etc. A comparative capital cost estimate should be made comparing FMC and Chiyoda price to an independent 400 account equipment factored estimate.

10.6 LICENSORS AND EVALUATIONS

The following four licensors were contacted for proposals on a flue gas desulfurization (FGD) unit: FMC, Chiyoda, Davy McKee, and Peabody. The flue gas desulfurization unit duty specifications used for the preparation at proposals was based upon feasibility study steam requirements. Since, at that time, a coal selection had not been made, two cases were considered:

- A. Maximum sulfur in the flue gas (maximum sulfur case) resulting from the use of coal PB-19 (Peabody, seam-1L6, Randolph County). This coal was chosen for having the highest sulfur content of all coals considered (4.72%).
- B. Use of a fictitious coal having a sulfur content represented by an average of the seven candidate coals (average sulfur case). The fictitious coal had a sulfur content of 4.15%.

In the FMC Double Alkali process sulfur dioxide is converted to a solid disposable material by first absorbing it in a highly reactive sodium scrubbing solution and then using calcium to form the solids and recover sodium for reuse.

The Chiyoda Thoroughbred-121 Process (CT-121) bubbles the flue gas through a jet-bubbling reactor, removing sulfur oxides from the flue gas and producing a stable gypsum sludge. Limestone is the raw material used to absorb sulfur dioxide.

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10.6 LICENSORS AND EVALUATIONS (Continued)

The Wellman-Lord Process uses sodium sulfite solution to absorb sulfur dioxide. The resulting solution is regenerated to release a concentrated sulfurdioxide stream and reconstituted absorbing solution. The concentrated sulfur dioxide is further reacted with natural gas (Allied Chemical Reduction Process) to give the by-product, sulfur.

Peabody's Citrex Process uses sodium citrate solution to absorb sulfur dioxide, the rich solution (sulfur dioxide) is further reacted with hydrogen sulfide to give sodium citrate solution and the by-product sulfur.

Battery limit material balances for all four processes are given in Attachment 3.

We have evaluated the proposals in detail and presented the major results on the attached comparison sheets (Attachment 1). All four licensors met our technical specifications with the exception of Chiyoda, whose process characteristics do not allow a pressure drop as low as our specified maximum, therefore, Chiyoda provided a booster fan. After examining the economic and technical aspects of the proposals, we eliminated the Davy McKee and the Peabody process from further consideration. Our decision was based on the following:

- 1. The Davy McKee (Wellman-Lord FGD and Allied Sulfur) Process capital cost is 175 million dollars, which is very high when compared to the other three processes.
- a. Peabody's Citrex Process capital cost is 90 to 95 million dollars, roughly 1.5 times the FMC and Chiyoda capital costs.
 - b. Peabody does not have extensive experience in operating FGD units. Their largest operating unit has a capacity of 60MW.

After elimination of the McKee and Peabody process, an analysis of the capital required for FGD support f: .lities was conducted for the FMC and Chiyoda Process(s (Attachment 2). In this analysis the rough capital installed cost for peripheral material handling equipment (raw materials and waste) was estimated by Fluor.

The following table gives an estimate of the total capital cost required for the FMC and Chiyoda processes (including support facilities) as well as operating costs for the two processes (without support facilities).

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TRI-STATE SYNFUELS COMPANY Indirect Coal Liquefaction Plant

FLUOR ENGINEERS AND CONSTRUCTORS, INC. Contract 835504

Western Kentucky

(Continued) LICENSORS AND EVALUATIONS 10.6

			Chiyoda International Corporation	FMC, Corporation
1.	TOT	AL COST (5 in millions)		
	Ά.	Installed Cost, Per proposal	55.00	57.70
	в.	Engineering and Licensing Fees	2.06	5.10
	c.	Installed Support Facilities, Esti by Fluor (See Attachment 2)	mates _7.06	7.70
		Total FGD Capital Requirements	64.15	70.50
2.	OPE	CRATING COST* (\$ in millions)		
	А. В.	Fixed Operating, La and Maintenance Variable Operating	bor 1.51 Cost <u>24.72**</u>	1.99 21.78
		Total***	26.23	23.77

- * Based on Current cost of chemicals and utilities, see Attachment 4.
- ** Gypsum disposed of in landfill.
- *** Does not include support facilities operating cost.

FMC has designed and built FGD units of similar size to that which would be required for the Tri-State project. The FMC Double Alkali Process is commercially proven. As shown above, operating costs for the FMC process are less than that for Chiyoda. The FMC process does, however, produce and unstable and difficult to handle sludge.

Chiyoda's CT-121 process has successfully passed through the 23MW demonstration coal fired plant. It is claimed that CT-101 (an older, commercially proven process) is basically the same process as CT-121, except for replacement of the spray tower with a jet bubbling reactor. There are thirteen CT-101 commercial operating FGD units for oil fired boilers worldwide. Attachment 5 contains process evaluation "parameters" for all processes considered.

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Western Kentucky

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10.6 LICENSORS AND EVALUATIONS (Continued)

Note: All information contained in the following Attachment is relevant only to the feasibility study plant. (Full size F.T. plant with coal data from that time frame.) The FGD quotations contained in Section 10 are also based on the feasibility study case.

• тr1-state	SYNFUELS COHPANY	ATTACH	HENT I ((COMPARISON SHEET)	ት ELNOR	:2/18/81
	FLUE GAS DESULPURIZATION (FGD)				
1	ITEM	FMC - DOUBLE ALKALI	CILLYODA CT-121	DAVY MCKEE WELLMAN-LORD FGD, ALLTPD SULFUR	PEADODY CITREX
1. VALIDIT	Y OF PROPOSAL	UNTIL 12/2/81	URTIL 1/2/82	LINT11- 12/31/81	
2. CAPITAL	Costs				
A UNI	T INSTALLED COSTS BASIS	\$57,703,000 (Nov 1981 Dollars)	\$55,000,000 (Late 1981 Dollars)		
B. ENG	INEERING FEES	\$298,000	\$60,000	\$300,000	\$75,000
	TERHS	PROGRESS BILLINGS	30% ON AWARD, MONTHLY PAYHEITS		
1	PHASE II	\$2,000,000	\$1,200,000	\$6,000,000	J. J TIMES BASE SALARY
•	TERMS	PROGRESS BILLINGS	HORTHLY DILLINGS		
TOT	AL ENGINEERING FEES	\$3,178,000	ş1,260,000	\$6,320,000	
	NATES AND LIGENCE PEPS	\$1,918,000	\$100,000		
• C. ROY •	TERMS	1/3 AFTER PUASE I 2/3 AFTER PUASE II	501 AFTER LICENSE AGREEHENT 401 AFTER DESIGN PACKAGE		-
1			10% AFTER SUCCESSFUL ACCEPTANCE		
3			SPECIFIC DATE		
	NAL UNIT COST	\$62,800,000	\$57,060,000	\$175,000,000	590,000.00B
4	EXCLUSIONS	SITE PREPARATION, BUILDINGS,	FOUNDATIONS, BUILDINGS,		· · ·
!}		TRANSFER, SLUDGE DISPOSM	AND PRIMARY CRUSHING - GYPSUN		
			TRANSFER AND DISFOSAL		
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		CHEVODA CT-121	DAVY MCKEE	PEABODY CITREX
17EH	PMC - DOUBLE ALKALI		WELLMAN-LOND PLD, ACLIED SOLLON	
ANNUAL OPERATING COSTS				
FIXED (Labor, Maintenance) VARIABLE (Chemical, Utilities)	\$1,986,000 \$21,787,000 \$23,773,000	\$1,510,000 \$24,723,000 \$26,233,000	\$3,705,000 \$30,724,000 \$33,929,000	\$1,699,000 \$38,198,000 \$39,897,000
BY-PRODUCT INCOME	\$0	\$0	\$14,450,000	\$20,074,000
NET OPERATING COST Basis of Operating Costs	\$23,088,000 Average 502 Casu	\$24,234,000 • AVERIGE SO2 CASE	\$19,479,000 Average 50 ₂ case	\$19,823,000 Maximum so ₂ case
. PLOT REQUIREMENTS EXCLUSIONS	163,000 50. PT. Waste disposal	103,400 SQ. FT. LIMESTONS AND GYPSUM STORAGE	204,100 50. FT. None	105,000 SQ. FT. Chemical Storage, water treating
. TECHNICAL			938	928
A. ANNUAL ON-STREAM FACTOR	933	90% (maximum sulfur case)	90% (maximum sulfur case)	901 (maximum sulfur case)
B. SO2 REHOVAL EFFICIENCY	15 in. H20	18.5 in. H20	15 in. H ₂ 0	15 in. H20
D. QUANTITY OF BY-PRODUCT To Disposal	142 TPH (43.7% H20)	122.5 TPII Gypsum (2011120)].] TPH SODIUM SULFATE 17.7 TPH SULFUR	7.7 TPH GLAUBER'S SALT 24.6 TPH SULFUR
to Sales Basis	AVERAGE 502 CASE	AVERAGE 502 CASE	AVERAGE SO2 CASE	AVERAGE 502 CASE
. COMMERCIAL EXPERIENCE	FOUR OPERATING Commercial installations	THO 23mm DEMONSTRATION FACILITIES	SEVERAL OPERATING COMMER- CIAL FACILITIES	LARGEST UNIT CAPACITY Approximately 60mm
			war ei is sudi notice p	OSOCITSWAL OF REITHI OASA CT 10 THE AFSINCTION ON THE RE AFTHE FROM OF THIS REPORT

PROPOSAL EVALUATION (COMPARISON SHEET)

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PROPOSAL EVALUATION (COMPARISON SHEET)

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ITEN	FMC - DOUBLE ALKALI	CHIYODA CT-121	DAVY HOKEE WELLMAN-LORD FGD, ALLIED SULFUR	LEABODY CITRE
7. DOCUMENTATION	EVALUATION PACKAGE FROM FMC,	TROPOSAL TO FLUOR ENGINEERS AND CONSTRUCTORS FOR CHIYODA	MELIHAN-LORD FGD SYSTEM/ALLED SULFUR SYSTEM, VOL. 1 & VOL.11	PEADODY EVALUATION PACK ON CITREX PROCESS
	HUVENER 4, 1301	THOROUGHBRED 121 FLUE GAS	a) HOVEHBER 1981 #2013/0	
	THE REFETING NOTES	DESULFURIZATION SYSTEM. NOV.	b) NOVERBER 1981 42813/1 Rev.1	
	HOVENBER 11, 1981	4, 1901		
	LETTER FROM FHC, NOV. 11, 1901	CHIYODA KEETING NOTES, NOV. 17, 1901	DAVY MCKEE MEETING NOTES, November 11, 1901	
	LETTER FROM FHC, NOV. 20, 1901			
		D CLASEN (CILLYODA), DEC.		
	TELEPHONE DISCESSION WITH	0, 1901	[}
	T. BROAD (FRC), DECI TOT TOT			}
	LETTER FROH FMC, DEC. 15, 1981	LETTER FROM CHIYODA, DEC. 14,		
		1981		
	LETTER FROM H.C. PATTEN & CO.			
	INC. DEC. 21, 1981	}		
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ATTACEMENT 2-1

ROUGH ESTIMATED INSTALLED COST FOR FGD SUPPORT FACILITIES

I. THC CORP. (Double Alkali Process)

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SLUDGE DISPOSAL	
1. Pug Mill @ 75 H.P.	\$ 40,000
2. Filter cake transfer conveyor 165 T/HR, 1500'	435,000
3. Fly ash conveyor 1000', 100 T/HR	120,000
4. Sludge conveyor 2 MI, 280 T/HR	3,062,400

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\$3,657,400

210,000

3,832,000

\$7,699,400

\$3,062,400

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E. SODA ASH HANDLING SYSTEM

C. <u>LIME CONVEYING</u> 1. Conveying by barge 2.5 miles and 500 T/HR \$3,828,000 includes loading and unloading

2. Weigh Scale

Total

II. CHIYODA INTERNATIONAL CORP. (CT-121 Process)

A. <u>GYPSUM DISPOSAL</u>
 1. Gypsum Disposal
 Loading, Unloading, and Conveying,
 2 MI, 200 T/HR

B. LIMESTONE 1. Conveying, loading and unloading \$3,957,000 Total 5000', 500 T/HR 2. Limestone crusher 67,000 3. Weigh Scale 4,000

> \$4,028,000 \$7,090,400

Total*

* Does not include fraction of coal conveyor capital cost.

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ATTACHMENT 3-2

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UNIT 46: FGD UNIT LICENSOR: DAVY MCKEE

BATTERY LIMIT MATERIAL BALANCE

AND UTILITIY REQUIREMENTS

(AVERAGE CASE)



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ATTACHMENT J-4

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UNIT 46: FGD UNIT LICENSOR: PEABODY

BATTERY LIMIT MATERIAL BALANCE

AND UTILITIES

(MAXIMUN SULFUR CASE)



ATTACHMENT 4

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OPERATING COST ESTIMATION BASIS*

Operating costs estimated for the FGD Units is based on following data: A. Labor Cost, Operating and maintenance = (\$10 x 2) per hour Administrative = $(\$20 \times 2)$ per hour B. Electricity = \$0.055/KWH = \$ 2.45/1000 LB. C. Steam: L.F. (150 Psig or less) H.P. (@ 600 Psig) = \$ 3.25/1000 LB. D. Water: Cooling = \$ 0.053/1000 Gallon Circulated Boiler feed = \$ 0.98/1000 Gallon Make-up = \$ 0.50/1000 Gallon E. Fuel: Gas/Natural gas = \$ 5.0/MMBTU = \$ 5.0/MMBTU Oil F. Raw Materials: Soda Ash = \$92.0/Short Ton = \$31.5/Short Ton Lime = \$20.0/Short Ten Limestone Citric Acid = \$ 0.71/Pound Anti-oxidant = \$ 1.35/Pound G. Waste Disposal: Sludge or Gypsum = \$ 6.0/Short Ton = \$100/Short Ton H. Others: Sulfur Operating hours = 8160/Year

*Chemical prices are obtained from 'Chemical Marketing Reporter'

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ATTACHMENT 5-1

Note: This Attachment is for information only - Basis is the feasibility study plant.

1.0 PROCESS SELECTION PARAMETERS:

The selection of an FGD system depends on the capital and operating costs of the process, but there are other parameters which also give weightage for the selection or the rejection of a process. Such major factors are:

- o Material handling raw material and waste.
- Raw material cost, consumption and availability.
- o By-product recovery and marketability.
- o System availability and reliability.

2.0 PROCESS SELECTION DESIGN BASIS:

It is intended that any of the seven coals shall be fired to the boiler. Raw materials and waste production of FGD system can be estimated using the following basis:

- Sulfur content of coal = 4.15% wt. (average of seven coals).
- 2. Higher heating value of coal = 10,115 Btu/lb (average of 7 coals). Calculated lower heating value of coal = 9540 Btu/lb.
- 3. Coal burning rate = 9.63 x 10⁵ lb/hr. (In U.S. higher heating value is used for boiler calculations).

 $\frac{(1381 \text{ Btu/lb}) \times (6 \times 10^6 \text{ lb/hr})}{(10,115 \text{ Btu/lb}) (0,85 \text{ eff.})} = 9.63 \times 10^5 \text{ lb/hr}.$

Steam production: 6 x 10⁶lb/hr, 1500 psig, 900°F superheated. Total quantity of sulfur burned = 39,975 lb/hr.

- 4. Plant operates for 8160 hours per year and plant life is 30 years.
- 5. For new source, EPA allowable SO, emission (NSPS) = 1.2 lb/million Btu of heat input.

i.e., 11,690 lb/hr (max.) of SO₂ can be vented.

2.0 (Continued)

It is anticipated that there will be some SO₂ emission from other units, e.g., incinerator, etc., so, SO₂ emission from FGD should be less than 11,690 lb/hr, say 7200 lb/hr (based on 90% SO₂ removal efficiency).

Assuming 90 percent of the total sulfur in the coal is reported as SO_2 in flue gas, i.e., no SO_3 and 10 percent sulfur goes out with ash. (Range is 70 to 90 percent of sulfur as SO_2 in flue gas, given by chemical engineer's handbook, J.H. Perry p. 94 fourth edition).

 $o^{\circ}o$ Total SO₂ in flue gas = 39,975 x 0.90 x 2 = 71,955 lb/hr.

SO, to be removed by FGD = 71,955 - 7200 = 64,755 lb/hr.

 $0^{\circ}0$ 50₂ removal efficiency = $\frac{64,755}{71,955}$ = 90% (required)

The main FGD processes used by the U.S. utility industry or under construction are listed below:

- A. Throwaway processes:
 - 1. Lime

X

- 2. Limestone
- 3. Double Alkali
- B. Regenerable processes:
 - 1. Citrate process Foster-Wheeler reduction (Resox)
 - 2. Wellman-Lord Allied Chemical process
 - 3. Magnesia process
 - 4. Aqueous carbonate/spray drying

Some of these processes are used by various licensors and each supplier has their own alterations and modifications to overcome operational difficulties and obtain economic advantages.

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Figure 1: Throwaway and Regenerable Processos

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3.0 LIME SYSTEM

3.1 PROCESS

Flue gas is scrubbed with lime solution in vertical multistage contacting tower, forming calcium sulfite or sulfate. Calcium sulfate formation rate depends on available oxygen in the system. Sulfite/sulfate solution is dehydrated using thickener and filters for disposal as sludge. Figure 2 shows a typical lime scrubbing system. The main problem with this system is deposition of sulfate/sulfite scale. These deposits are mixtures of fly ash, sludge and sometimes soluble salts. This process needs large quantities of lime source or needs to make lime on site. The chemical reactions for this process are:

(i) $CaO + H_2O$ $Ca(OH)_2$ quicklime water slacked lime 56 18 74 (ii) $Ca(OH)_2 + SO_2$ $CaSO_3 + H_2O$ $CaSO_3, \frac{1}{2}H_2O + H_2O$ 74 64 120 18 129 9 (iii) $CaSO_3 + \frac{1}{2}O_2$ $CaSO_4$ 120 16 136

3.2 RAW MATERIAL REQUIREMENTS

Slacked lime requirements = $\frac{74}{64} \times 64,755 = 74,873$ lb/hr (100% pure) = 37.4 T/hr OR quicklime requirements = $\frac{56}{64} \times 64,755 = 56,660$ lb/hr (100% pure) = 28.3 T/hr Notes: a. commercial grade lime contains @ 90 to 98% alkali, and

b. actual lime requirements will be more than stochiometric

o^oo Estimated quicklime (CaO) requirements =

28.3 x
$$\frac{1}{0.94}$$
 x 1.10 = 33.12 T/hr

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TRI-STATE SYNFUELS COMPANY Indirect Coal Liquefaction Plant Western Kentucky

3.3 WASTE PRODUCTION

The byproduct generated by an FGD system depends on the adsorbent, the flue gas characteristics and the mode of operation of scrubber. The main constituents of the byproducts are calcium sulfate and calcium sulfite. The ratio of sulfite to sulfate depends on the extent of oxidation, which is in turn mainly a function of liquid slurry composition and the free oxygen content of flue gas. If the main constituent of the sludge is calcium sulfite, dewatering is extremely difficult.

Assuming 80% CaSO₃ and 20% CaSO₄ produced,

 $o^{0}o$ CaSO₄ produced = $\frac{136}{56}$ x 0.2 = 13.75 T/hr and CaSO₃ produced = $\frac{120}{56}$ x 0.8 = 48.51 T/hr

Unused lime = 33.12 - 28.30 = 4.82 T/hr

o^oo Total waste stream, solids = 48.51 + 13.75 + 4.82 + fly ash + fixation material = 67.08 T/hr + fly ash + fixation (approx. 20-80% wet basis)

Waste stream from rotary or vacuum filter @ 55% Sclids = 67.08/.55 = 122 ST/hr.

Assuming 30% fly ash addition (wet basis).

o^oo Total sludge needs to be transported = 158.6 ST/hr

(Containing, 67.08 ST/hr solids, 54.92 ST/hr water ar 36.6 ST/hr fly ash and fixation material).

Considering 8160 operating hours per year,

10% moisture at landfill conditions, in 30 years waste produced, = (103.68 x 1.1) x 8160 x 30 = $27.92 \times 10^6 \text{ ST}$

Assuming 85 lb/ft³ density and 10' high filling

 $o^{\circ}c$ Land requirements = $\frac{27.92 \times 10^{6} \times 2000}{85 \times 10}$ = 65.69 x 10⁶ sq. ft. - 1508 acres/30 years (1 acre = 43,560 sq. ft.)

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CLEAN GAS TO STACK FLUE GAS 8Y - PA 55 SCRUBBL R Co(OH)₂ BOOSTER F AN Co503 Ca504 FLUE GAS FROM ELECTROSTATIC -PRECIPITAT DE (ESP) THICKENER エ Ca503 Ca503 LIME SILO RECYCLE FILTER 502 + CalOH)2 - Co503 . 0.5H20 FILTRATE CaO Ca(OH); ---- WATT'R LIME SLAKER PUG STABILIZING MILL ADDITIVE REAGENT SURGE IANK DISPOSAL

Figure 2 : Lime Scrubbing System

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4.0 LIMESTONE SCRUBBING SYSTEM

4.1 PROCESS

Aqueous slurry of limestone is used to absorb and remove SO_2 from the flue gas. In a holding tank absorbent slurry is retained for a long enough time to allow adequate precipitation and settling of the calcium sulfite and sulfate formed in the absorber. The solids in the slurry slipstream are concentrated in a thickener. The underflow of slurry from the thickener, containing about 30-35% solids is filtered in a rotary vacuum filter to about 55% solids. Figure 3 shows typical limestone scrubbing system. The main problem for this process is scaling and corrosion/erosion.

The chemical reactions for this process are:

 $CaCO_3 + SO_2 + \frac{1}{2}H_2O$ $CaSO_3, \frac{1}{2}H_2O + CO_2$

100 64 9 129 44

Some oxidation also occurs:

 $SO_2 + CaCO_3 + \frac{1}{2}O_2 + 2H_2O$ $CaSO_4, 2H_2O + CO_2$ 64 100 16 36 172 44

4.2 RAW MATERIAL REQUIREMENTS

CaCO₃ requirements = $\frac{100}{64} \times 64,755 = 101,180$ lb/hr = 50.6 T/hr

Commercial grade limestone contains 90% CaCO, and 10% excess requirements.

 0° consumption = 50.6 x $\frac{1}{0.90}$ x 1.10 = 61.8 T/hr

4.3 WASTE PRODUCTION

Assume 80% CaSO₃ and 20% CaSO₄ produced: $o^{\circ}o$ CaSO₄ = $\frac{136}{100} \times 50.6 \times 0.20 = 13.76$ T/hr and, CaSO₃ = $\frac{120}{100} \times 50.6 \times 0.80 = 48.57$ T/hr unused limestone = 59.0 - 50.6 = 8.4 T/hr

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4.3 WASTE PRODUCTION (Continued)

 $o^{\circ}o$ Total waste stream (solids) = 13.76 + 48.57 + 8.4 + fly ash + fixation = 70.73 + fly ash + fixation

Waste stream from rotary or vacuum filter @ 55%

Solids = 70.73/.55 = 128.6 ST/hr.

Assuming 30% fly ash added (wet basis).

o^oo Total sludge needs to be transported = 167.2 ST/hr.

(Containing, 70.73 ST/hr solids, 57.87 ST/hr water and 38.6 ST/hr fly ash and fixation material.

Considering 8160 operating hours per year, 10% moisture in landfill conditions, landfill density of 85 $1b/ft_3$ and 10' filling height.

o^oo land requirements

$$= \frac{(109.33 \times 1.1) \times 8160 \times 30 \times 2000}{85 \times 10} = 69.3 \times 10^{6} \text{sq. ft.}$$

= 1590 acres/30 years

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Stabilizing Additive and Fly Ash Sludge ROTARY PUG NILL FILTER Stack Gas To Storage Reheat and Disposal TO STACK Filtrate FLUE GAS FRON ESP ABSORBER VENTURI SCRUBBER so³ Slipstream SURGE THICKENER Overflow Underflow Slurry KOLD TANK Recycle Liquor STORAGE, Limestone CRUSHING, SLURRYING

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5.0 DOUBLE ALKALI

5.1 PROCESS

SO, is absorbed using sodium sulfite (Na_2SO_3) solution, forming sodium bisulfite. Oxygen also reacts with Na_2SO_3 giving sodium sulfate. Sulfate ion is not active in absorbing sulfur dioxide. The pH of the scrubbing solution is controlled at 6.5 (gives equimolar solution of sodium sulfite and bisulfite). A bleed stream from the absorber recirculation loop is directed to the lime reactor, and the absorber reservoir is replenished with regenerated sodium sulfite, maintaining the pH at a desired value.

Calcium sulfite is precipitated by lime addition in a lime reactor to regenerate sodium sulfite for use in the absorber. The lime reactor overflows to a thickener tank. The regenerated liquor flows to a surge tank into the absorber as needed. Soda ash is added to the system to make up for any losses. Sludge from the thickener is concentrated to 50-60% solids using a rotary filter. The double alkali process has better reliability and availability. Figure 4 shows a double alkali process.

The chemical reactions are:

 $Na_2SO_3 + SO_2 + H_2O$ 2NaHSO₃ 126 64 18 208 also, $Na_2SO_3 + \frac{1}{2}O_2$ Na_2SO_4 126 16 142

Regeneration of sodium:

2	NaHSO3	+	$Ca(OH)_2$	CaSO ₃ ,	≵⊞₂0	+	Na_2SO_3	+	1½H20
	208		74	129			126		27

5.2 RAW MATERIAL REQUIREMENTS

Slacked lime requirements, $Ca(OH)_2 = \frac{74}{64} \times 64,755 = 74,873 \text{ lb/hr}$ = 37.4 T/hr

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5.2 RAW MATERIAL REQUIREMENTS (Continued) Commercial grade lime contains 90-98% alkali; $o^{\circ}o$ Actual Ca(OE)₂ requirements = $\frac{37.4}{.94}$ = 39.9 T/hr OR CaO requirements = 30.1 T/hr Soda ash consumption depends on factors like filter wash, chlorine content, and oxygen content of the flue gas, etc.; but for estimation purposes Na₂CO₃ consumption can be taken as 0.03 mole per mole of Ca(OH) consumption: 0° Na₂CO₃ consumption = .03 x (37.4) x $\frac{106}{74}$ = 1.60 T/hr 5.3 WASTE PRODUCTION Assume 80% CaSO₃ and 20% CaSO₄ = $\frac{120}{74} \times .8 + \frac{136}{74} \times .2 \times 37.4 = 62.2 \text{ T/hr}$ Waste stream from rotary or vacuum filter @ 55% Solids = 62.2/.55 = 113.1 ST/hr Assuming 30% fly ash added (wet basis). $o^{\circ}o$ Total sludge to be transported = 113.1 x 1.3 $= 147.0 \, \text{ST/hr}$ In landfill conditions, 10% moisture, density = 85 lb/ft³ 10' filling depth, 8160 hr/year operation for 30 years. $o^{\circ}o$ Area required = $\frac{(96.1 \times 1.1) \times 2000 \times 8160 \times 30}{10 \times 85}$ $= 60.8 \times 10^{6} \text{ sq.ft.}/30 \text{ years}$ = 1396 acres/30 years

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6.0 CITRATE PROCESS

6.1 PROCESS DESCRIPTION

It uses an aqueous solution of sodium citrate to absorb and remove SO, from flue gas. The main reaction is;

 $SO_{3} + H_{2}O = HSO_{3} + H^{+}$

The absorption and dissociation of SO₂ in water can be represented by above reaction. As SO₂ is absorbed in water, the concentration of hydrogen ions (H⁺) in solution increases. Eventually, the hydrogen ion concentration increases to the equilibrium point where no further absorption of SO₂ can occur. In order to reduce hydrogen ion concentration, it is reacted with "buffering agent" such as sodium citrate.

 SO_2 rich citrate solution is then steam stripped in a stripping tower where SO_2 is distilled out of the solution and solution is regenerated for further use. SO_2 and water vapor distilled overhead from the stripper is condensed at a pressure of about 60 psia. The condensate forms two immiscible liquid phases; water phase and wet SO_2 phase. The water phase is returned to the stripper and the wet SO_2 liquid is sent to intermediate storage. At this point:

- (i) SO, could be dried and be sent to acid manufacturing plant for the production of sulfuric acid, OR
- (ii) The wet SO₂ could be revaporized and further processed for conversion to elemental sulfur.
 (Resox process proprietary development of the Foster Wheeler Energy Corporation.) Sulfur making process is shown in Figure 5.

Crushed Anthracite coal and gaseous SO_2 are contacted in a vertical, countercurrent reactor at atmospheric pressure and a temperature within the range of 1100-1500°F. The carbon in the coal acts as a reducing agent to convert SO_2 to gaseous elemental sulfur as represented by:

C (s) + SO₂ (g) S (g) + SO₂ (g)

12 64 32 44

The reactor temperature is maintained and controlled by the injection of air and steam into the reactor. The sulfur in the reactor product gas is condensed and sent to the heated storage tank. The tail gas from the sulfur condenser

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6.1 PROCESS DESCRIPTION (Continued)

contains CO_2 , water vapor, and some SO_2 , which needs to be incinerated in boilers or separate thermal incinerators. A mixture of ash and unreacted coal is discharged from the bottom of the reactor and sent to storage. It can be used as boiler feed.

6.2 RAW MATERIAL REQUIREMENTS

Soda Ash	-	821 lb/hr
Lime	=	1443 lb/hr
Citric Acid	=	41.0 lb/hr
Anthracite Coal	=	15.00 T/hr

6.3 WASTE PRODUCTION

Small quantity of purge stream (Glober's Salt) produced which needs waste treating and disposal. Waste production rate is about 8.0 T/hr.

6.4 SULFUR PRODUCTION

Total SO_2 in the flue gas = 64.77 lb/hr, i.e., 32,387 lb/hr of sulfur. Sulfur production is estimated at 82.3%, i.e., 13.3 T/hr. Remaining sulfur is sent to waste disposal as Glober's Salt.



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TRI-STATE SYNFUELS COMPANY Indirect Coal Liquefaction Plant Western Kentucky

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7.0 WELLMAN LORD PROCESS

PROCESS DESCRIPTION 7.1

It uses an aqueous solution of sodium sulfite (Na₂SO₃) to absorb and remove SO₂ from the flue gas. Flue gas is first washed with water in a venturi scrubber to cool and saturate the gas along-with removal of chlorides, sulfur trioxide and residual flyash. The reaction in the absorber is:

208

 $SO_{2} + Na_{2}SO_{3} + H_{2}O$ 2NaHSO, 126 18

Some oxidation also occurs to form sodium sulfate

 $2Na_2SO_3 + O_2$ $2Na_2SO_4$ 252 32 284

Sodium sulfate is crystallized from the slipstream of spent absorbent solution. The sulfate is then centrifuged and dried in a steam-heated dryer.

The spent absorbent solution is thermally regenerated in forced circulation evaporators. In evaporators SO2 and water vapors are released, and sodium sulfite crystals precipitate from the solution.

 $2NaHSO_3$ heat $Na_2SO_3 + SO_2 + H_2O$ 126 64 18 208

Sodium sulfite slurry produced from the evaporators is dissolved in stripped condensate which is derived from the evaporator overhead vapors. Sodium carbonate makeup is added to the dissolving tank to replace the sodium lost in the purge streams. The sodium carbonate reacts with sodium bisulfite in the dissolving tank to form additional sodium sulfite.

 $Na_2CO_3 + 2NaHSO_3$ $2Na_2SO_3 + H_2O + CO_2$ 252 18 44 106 208

Concentrated stream of sulfur dioxide is reduced to elemental sulfur in two steps. In the first step, a portion of the SO2 in the feed gas is reduced with natural gas (methane) to yield elemental sulfur and hydrogen sulfide.

2CH ₄ +	3502	2H2S	+ S +	2C0 ₂ +	2H20	(Reduction Step)
32	192	68	32	88	36	

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7.1 PROCESS DESCRIPTION (Continued)

In the second step, H₂S reacts with unreacted SO₂ from the reduction step to form additional sulfur.

 $2H_2S + SO_2$ 3S + $2H_2O$ (Claus Step) 68 64 96 36

The overall reaction is:

 $CH_4 + 2SO_2 2S + 2H_2O + CO_2$

16 128 64 36 44

The molten sulfur product from the reduction and Claus step is sent to storage or sulfur pits. Sulfur is at 85% total sulfur in flue gas Figure 5 shows this process scheme.

7.2 RAW MATERIAL REQUIREMENTS

Soda Ash		5	3.15	T/F	nr	
Lime		=	1444	lb/	hr /	
Natural Gas	(reductant)	-	2.083	3 x	105	SCF/hr

7.3 WASTE PRODUCTION

A very small amount of waste is produced. Only purge streams will need waste treatment and disposal.

7.4 SULFUR PRODUCTION

Total sulfur production rate = 13.76 T/hr, with 85% sulfur recovery. Remaining sulfur is sent to disposal.

Fuel Oil Air CLAUS 502 + H25 Tall Gas INCINERATOR SULFUR REDUCTION RECOVERY Natural Gas Byproduct Sulfur 502 Vapor Stack Gas COMPRESSORS Reheat PURCE TO STACK L Sulfate BY-PASS Stream **CONDENSER** Wet SO₂ FLUE GAS Return Liquor AND purge FROM ESP STRIPPER Condensa te Alkali THERMAL Makeup REGENERATOR ABSORBER (EVAPORATORS) DISSOLVING TANK VENTURI SCRUBBER Slurry so2 Warer Regenerated SURGE Solution Purge To Ash Pond SURGE

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Figure 6: Wellman-Lord and Allid Chemical Reduction Process

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8.0 MAGNESIA PROCESS

8.1 PROCESS DESCRIPTION

Aqueous slurry of magnesium oxide is used to absorb and remove SO_2 from the flue gas. The resulting magnesium sulfite and magnesium sulfate slurry is dried and calcined to yield recycle magnesium oxide and SO_2 rich gas suitable for conversion to sulfuric acid. The slurry slipstream from the SO_2 absorption section is centrifuged to dewater the magnesium sulfite and sulfate solids. The liquor removed by the centrifuge is recycled to the mix tank where magnesium oxide is slurried to produce Mg(OH)₂ for use in the absorber.

The dewatered solids from the centrifuge pass through a fired, rotary kiln dryer to remove residual free water and water of hydration. The anhydrous magnesium sulfite and sulfate are then transported by a bucket elevator into a storage hopper. The dryer off-gases go through a cyclone for dust recovery before exiting to the stack.

In order to recover SO_2 and MgO from the anhydrous magnesium sulfite and sulfate solids, the solids are thermally decomposed by calcining at about 1600°F. Coke is used in the calciner as a source of heat and to provide reductant carbon required to decompose magnesium sulfate into SO_2 and MgO.

The recovered MgO is transported to a storage hopper to recycle to the slurry mix tank.

The SO_2 -rich offgas (@ 10-12% by volume) from the calciner goes through a cyclone and a water scrubber for residual MgO dust removal. The gas is then sent to an acid plant for conversion to sulfuric acid.

Chemical reactions are: SO₂ Absorption

(i)	MgO +	H20		Mo	J(CH)	2			
	40	18			58				
(ii)	Mg (OH)	2 +	so,	+	5H ₂ O		Mg	SO3.6H20	
	58		64		90			212	
(iii)	Mg (OH)	2 +	S0₂	+	6H20	+	50₂	MgSO ₄ .7H	20
	58		64		108		16	246	

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8.1	PROCESS DESCRIPTION	(Continued)

Regeneration:

(i)	$C + 2MgSO_4$			2MgSO ₃ + CO			CO2
	12	104			208		44
(ii)	MgS03		MgO	+	SC2		
	104		40		64		

8.2 RAW MATERIAL REQUIREMENTS

Magnesium	Oxide	=	1210	lb/hr
Coke		=	2000	lb/hr
Fuel Oil		=	3036	gal/hr

8.3 WASTE PRODUCTION

A small quantity of purge stream is produced which needs waste treating and disposal.

8.4 SULFURIC ACID PRODUCTION

The amount of sulfuric acid (98% con.) produced = 48.7 T/hr.

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9.0 AQUEOUS CARBONATE

9.1 PROCESS

Contacts hot flue gases with an aqueous sodium carbonate solution in a spray dryer. Sodium carbonate reacts with and removes SO_2 from the flue gases, and the solution is evaporated to dryness by the hot flue gases. The dry reaction products (a mixture of sodium sulfite, sulfate, and unreacted sodium carbonate) are removed from the flue gases by passage through cyclones and an electrostatic precipitator. The reaction products are further regenerated using crushed coal to give sodium carbonate and hydrogen sulfide gas. The hydrogen sulfide is converted to elemental sulfur as an end product.

Chemical meactions are: SO₂ absorption section

(i)	Na_2CO_3 -	+ SO ₂	$Na_2SO_3 +$	CO2
	106	64	126	44

(ii)
$$Na_2CO_3 + SO_2 + \frac{1}{2}O_2$$
 $Na_2SO_4 + CO_2$
106 64 16 142 44

(iii) SO₃ in the flue gas also reacts with Na₂CO₃ to yield Na₂SO₄

> $Na_2CO_3 + SO_3 Na_2SO_4 + CO_2$ 106 80 142 44

Regeneration:

(i)	$2C + Na_2SO_4$	$Na_2S +$	3/2 CO ₂
	10 142	78	88
(ii)	$3/2C + Na_2SO_3$	$= Na_2S +$	3/2 CO ₂
	18 126	78	66

9.2 RAW MATERIAL REQUIREMENTS

Sođa	Ash	=	4.7	' T/hr
Coal	Feedstock	=	34.0) T/hr
Fuel	Oil	=	950 G	al/hr

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9.3 WASTE PRODUCTION

There are no liquid purge streams from aqueous carbonate process. The discharge of ash and unreacted coal will require appropriate handling and disposal.

9.4 SULFUR PRODUCTION

The amount of sulfur production = 16.1 T/hr



Figure 8: Aqueous Carbonate Process

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