USE OF LIMESTONE - WET SCRUBBING FOR REDUCTION OF SULFUR OXIDE EMISSION FROM POWER PLANTS- FACILITIES AND PROGRAM FOR PROTOTYPE-SCALE TESTING

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Increasing worldwide concern about the quality of our environment has spurred research and development activity on all phases of pollution control. Much interest has been generated in improving the quality of air by reducing the amount of dust and objectionable gases emitted from industries that discharge gaseous effluents and particulates. The utility industry is one of the major areas where attention to the problem is being accelerated.

At present, most of the electricity generated in this country is based on combustion of fossil fuels. Power production in hydro plants is ideal from an air quality point of view, but, unfortunately, the available sites for this type plant have been nearly exhausted. Production of power from nuclear generation plants seems likely to increase at a rapid rate in the immediate future. However, the increasing demand for electricity will require continued use of fossil coal-and oil-fired plants for the foreseeable future.

In the natural process that converts organic matter into materials suitable for use as fuel, sulfur-bearing compounds are formed along with the carbonaceous material. Combustion of the fuel results in formation of sulfur oxides; reduction of sulfur oxide emission from combustion sources is one of the major objectives of the pollution control effort. Removal of sulfur prior to combustion would be ideal because the fuel could be processed in high volume before distribution. However, with the exception of natural gas, which can be desulfurized by prov n methods, reduction of sulfur in fuels to acceptable levels does not appear to be economically feasible at present. Development of technology for removal of sulfur from stack gases seems to be the most expedient approach to control of sulfur dioxide emission.

Many different processes for recovery of sulfur dioxide have been proposed and development work is being carried out on a variety of types. The process that has attracted the greatest interest, because of its relative simplicity, is absorption by limestone in a slurry scrubbing process. This process does not depend on marketing a byproduct; the low-value absorbent can be discarded.

Limestone - wet scrubbing can be used in two ways, either by injecting limestone into the power plant boiler and collecting the calcined lime in the scrubber or by introducing limestone directly into the scrubber circuit. In an EPA-funded project, TVA is carrying out full-scale studies of dry sulfur dioxide sorption by limestone injection into a coal-fired 140-mw unit at the Shawnee station. This program is being expanded to include a study of the wet scrubbing method.

The Bechtel Corporation prepared a preliminary engineering study of a test facility for lime-limestone scrubbing under a contract with EPA. As a continuation of this effort, Bechtel is participating in the program to fully characterize the limestone - wet scrubbing process. EPA is funding the project and providing technical and administrative direction, Bechtel has primary technical responsibility for design of the facility and the test program, and TVA is constructing and will operate the test facility. The test program will be directed by a technical team comprised of representatives from each group.

Design is complete and construction is scheduled for completion by January 1972. The overall project cost will approach $10 million.

Program Goals

The purpose of the project is to evaluate the feasibility, effectiveness, and economics of limestone - wet scrubbing. The test program has as its primary objective the development and demonstration of a closed-loop limestone scrubbing process. Both injection into the boiler and addition directly to the scrubber circuit will be evaluated. Following are the major goals of the study:

1. Investigate process chemistry and kinetics. The test program will be developed and conducted to provide for determination of the chemistry and kinetics of the various process steps. This is needed to both explain and solve operating problems and to allow safe extrapolation of process behavior beyond actual test conditions. Differences in process chemistry due to changes such as variations in operating conditions and reactant composition will be investigated.

2. Develop information for process optimization and scale-up. The test program will provide for development of reliable process models which describe the form and magnitude of responses to all important variables. This model should predict optimum process designs for different process sizes, modes of operation, and site restraints.

3. Investigate and solve mechanical design and operating problems. Scaling, gas distribution, corrosion, erosion, and other factors that are related to mechanical design will be evaluated.

4. Study waste disposal. The quantity and quality of liquid and solid wastes produced by the process will be determined. Treatment or disposal methods to avoid excessive water pollution will be identified.

5. Determine plume reheat requirement. The required degree of plume reheat to ensure localized air quality will be studied.

6. Define economics. The test program will provide suitable operating cost data and estimates of capital requirement to quantify economics for various size and site restraints.

7. Conduct long-term operation. The reliability of the process will be demonstrated by a period of long-term operation under normal operating conditions.

Process Description

TVA, under an agreement with EPA, conducted a conceptual design study of the limestone scrubbing process; the report of this work (1) summarized the status of process developments.

The use of limestone or lime as an absorbent for sulfur oxides has been studied over an extended period. Most of the work has been small-scale, but some pilot plant and plant tests have been made. Introduction of the absorbent directly into the scrubber system dates back to the early 1930's when research programs were carried out in England; a closed-loop system utilizing lime or chalk as the reactant was operated commercially. The two steps of the injection-scrubbing method were first studied in a combined process by Combustion Engineering, Inc. This work led to installation of scrubbing systems on two full-scale generating units. The conclusion indicated by the prior work is that limestone scrubbing is a feasible method for controlling sulfur dioxide emission from power plants. However, several major process and operating problems were identified that must be resolved to establish efficiency and reliability.

In the Shawnee program, three parallel scrubbers will be tested simultaneously to expedite evaluation of various scrubber types. A flowsheet for one of the systems is shown in Figure 1. Gas will be withdrawn from the boiler ahead of the particulate removal equipment so that the entrained dust, including lime during injection-scrubbing tests, can be introduced into the scrubber. Analysis of the gas for sulfur dioxide, oxygen, and carbon dioxide will be made continuously by instrumental methods. Dust loading will be determined intermittently. Gas flow rate to each scrubber will be measured by venturi flow tubes and controlled by dampers on induced-draft fans. The concentration of sulfur dioxide in the outlet gas will be determined continuously. The efficiency of the process for removal of nitrogen oxides also will be determined by periodic checks of inlet and outlet concentration.

Quench sprays will be installed at the inlet of each scrubber to cool the gas prior to contact with the scrubbing slurry. Soot blowers will be installed to minimize solids deposition at each scrubber inlet. Experimental work by TVA has indicated that gas cooling may be necessary to prevent stripping of absorbed but unreacted sulfur dioxide from the slurry.

Variables that affect the rate of gas-liquid mass transfer and particulate removal efficiency in the scrubber will be studied so that optimization of the dual function can be established. The efficient removal of sulfur dioxide at a practical recirculation rate depends on an adequate limestone dissolution rate in the scrubber; factors that effect dissolution (slurry holdup, limestone particle size, stoichiometry, slurry solids content) will be evaluated. Mist elimination to prevent excessive solids carryover by slurry entrainment will be studied. Also, the reheat requirement is affected by water entrainment.

The system will be equipped with oil-fired reheaters to increase the temperature of the exit gas. In the scrubber, the gas will be cooled to its wet-bulb temperature and reheat therefore will be necessary to restore plume buoyancy for good dispersion. The Air Quality Branch (Division of Environmental Research and Development) of TVA, which has done extensive work in plume dispersion modeling (2), will assist with evaluation of the extent of reheat required. The exhaust gas from each scrubber system will be discharged through a separate stack.

Although limestone scrubbing is a relatively simple process, the process chemistry is complicated by soluble compounds from the coal ash, by low solubility of the absorbent and reaction products, and by supersaturation tendency of the calcium-sulfur compounds. The Radian Corporation has developed a computer program to preduct the composition of liquid and solid phases in the system at equilibrium conditions; this work has been useful in predicting boundary conditions. However, the actual steady-state conditions depend on rates, and kinetic data are scarce. Experimental results have shown that the slurry discharged from the scrubber has not reached equilibrium. Therefore, it is necessary to provide residence time outside the scrubber in order for absorbed sulfur dioxide to react with calcium, which must be brought into solution, and to precipitate supersaturated calcium salts formed in the scrubber. The system is highly sensitive to pH and the method of absorbent addition is important. A hold tank will be provided in which the residence time can be varied. A major portion of the slurry will be recirculated to provide a source of calcium for reaction in the scrubber and to furnish seed crystals for dissipation of supersaturation. A heat exchanger will be provided in the slurry system so that the effect of slurry temperature on sulfur dioxide absorption efficiency can be studied; river water will be the cooling medium. A sidestream will be withdrawn for separation of reaction products.

The method for separating product solids from the recirculating slurry in large-scale application of the process will depend largely on the real estate available and proximity of disposal areas to the power plant. The test facility will be provided with thickeners to concentrate the solids either for further dewatering in a filter or centrifuge or for transport to the pond. A filter and a centrifuge will be installed to study solids-liquid separation problems. In some potential applications of the process, solids disposal may have to be accomplished by transport of dewatered solids to relatively remote locations by truck, rail, or barge shipment. As an alternative, the solids may be discarded by discharge of the sidestream from the slurry effluent hold tank directly to a pond where settling will occur (hopefully). Pilot plant studies by TVA have indicated that settling may be hindered by formation of plate-like crystals of calcium sulfite.

In all modes, the liquid phase will be returned to the scrubber so that closed-loop operation will be effected. The solids content of the scrubber recycle stream will be controlled by blending of process streams; a radiation-type density measuring device will be utilized.

The quality of water associated with solids discharged to the pond will be evaluated to assess potential degradation in water quality as a result of seepage or overflow.

Equipment Selection

The existing facilities installed to study the dry injection method include:

1. Limestone-receiving hopper.
2. Belt conveyor and surge tank.
3. Oil-fired rotary dryer.
4. Dry ball mill.
5. Mechanical classifier.
6. Pulverized-stone storage silo.
7. Feed tank on load cells.
8. Pneumatic transfer and injection system.

This equipment will be used during tests of injection-scrubbing. The receiving and grinding facilities will be used to supply pulverized absorbent for direct addition to the scrubber circuit.

The equipment selected for wet scrubbing was sized for minimum cost consistent with ability to extrapolate results to commercial units; 30,000 acf per scrubber train was judged to meet these requirements.

The equipment arrangement for the test facility is shown in Figure 2. For resistance to corrosion, particularly during upset conditions, it was decided that equipment should be rubber-lined mild steel. In the following disucssion, it may be assumed that rubber lining is used except where noted.

The selection of scrubbers to be tested was one of the basic criteria for demonstration of the process; these devices should remove both particulates and sulfur dioxide with high efficiency. Particulate removal should be on the order of +99% (it is assumed that particulate must be removed to a level of 0.02 grain/ft^3 or lower to give a clear stack) and sulfur dioxide removal should be better than 85%. The scrubber should also effectively dissolve calcium oxide or calcium carbonate. Basic scrubber characteristics were considered in selection of types, but lack of available experimental data prevented a quantitative evaluation of predicted performance. One of the primary functions of the test program will be the development of such data. Expected mechanical performance of the scrubbers was also a factor in the choice; two major areas of concern are the buildup of solids on surfaces where hot gas first contacts the scrubbing solution and the plugging of gas-liquid contact zones. Other factors considered were pressure drop, turndown capability, ability to operate with slurry, ease of control estimated maintenance requirement, and compactness of design. A comparison of the various types considered is shown in Table I. It was concluded that the following scrubbers are the best candidates:

1. Venturi followed by an absorption section.

2. Turbulent-contact scrubber (mobile ping pong ball type).

3. Flooded-bed scrubber (marble bed type).

Gas ducts (40 in. diameter) between the boiler takeoff and the scrubber are mild steel, insulated to prevent condensation. Flue gas analysis, except for sulfur dioxide, will be made with gas chromatographs; an ultraviolet photometric analyzer will be used to monitor sulfur dioxide before and after each scrubber. Provision is made for addition of sulfur dioxide during selected tests to control the sulfur dioxide concentration. Methods for measuring particulates and nitrogen oxides are presently being evaluated. The venturi flow tubes (20-in. throat diameter by 9 ft high) are constructed of stainless steel and are mounted in a vertical run of straight duct in accordance with good engineering practice.

The venturi scrubber (Chemico) has a variable throat section fabricated from stainless steel. The overall dimensions are 6 ft 4 in. diameter and 11 ft high with a 3-ft-diameter throat. The gas velocity through the throat is controlled by a mechanically actuated conical plug.

Gas flow is downward through the scrubber and exits through a side outlet near the bottom into a companion absorber. The venturi should give good performance on particulate removal but the gas residence time may be too short for good absorption. Therefore, an absorption section was added in series. The absorber shell (8-ft diameter by 38 ft high) is designed to accommodate either packed or sieve tray internals.

The turbulent contact absorber (UOP) is designed for two scrubbing stages with provision for a liquid trapout tray or a third scrubbing stage. The vessel is 5 ft 7 in. square by 38 ft 8 in. high; internals are stainless steel.

The flooded-bed scrubber (Combustion Engineering) has a single stage of marble mobile packing. The vessel is 7 ft square and 17 ft 6 in. high. All of the scrubbers will accommodate either a chevron or fixed vane-type mist eliminator.

The reheater for each train is oil fired and has a maximum capacity of 5,800,000 Btu/hr. The induced-draft fans are constructed of stainless steel and are equipped with 400-hp motors.

All piping in the system is either rubber lined (2-1/2 inch and larger) or stainless steel (less than 2-1/2 in.). The scrubber hold tank for each scrubbing system is cylindrical (20-ft diameter and 21 ft high) with a flat bottom. They are sized for 1-hr retention time at 600 gpm; liquid levels will be adjustable so that residence time can be varied. The tanks are equipped with agitators and have overflow weirs to minimize loss of unreacted absorbent to the thickeners. Each system will have a thickener with rake and scraper discharge designed for 2 hr settling time. Two are 20 ft in diameter and 15 ft high. Because of higher recirculation rates in the TCA scrubber, the third thickener will be 30 ft in diameter.

Thickener underflow may be discharged to a pond area provided for waste solids disposal or to a further dewatering step. The pond is separate from the plant ash disposal area and is equipped with a reclaim sump for return of the clarified overflow; all scrubber systems will discharge to a common pond. However, compartmented areas are provided for storage of solids from markedly different reactants. The filter is a drum type with flexibility to operate with precoat. The centrifuge is a continuous type with a variable speed drive.

Control of the scrubbing systems will be carried out from a central graphic panelboard equipped with an electronic data acquisition system. The system is hard wired for data output in engineering units directly on magnetic tape. Onsite display of selected information will be available. Also, important process control variables will be continuously recorded and trend recorders will be provided for periodic

Test Program

The initial phase of testing will involve startup to check out equipment, piping, wiring, and controls, followed by a period of calibration and performance testing prior to start of planned experiments.

The first set of experiments will consist of screening tests designed to identify the principal independent variables that affect process performance or operating reliability. These tests will also establish the range of interest for the important variables. A statistical design of experiments will be used to obtain the required data at a reasonable significance level with a minimum number of runs. The correlation of effects will be based on process models which have been developed by Bechtel for each system. The models were derived through application of chemical engineering theory to produce a series of equations relating independent and dependent process variables. The variables are related by a series of coefficients; the numerical value of these coefficients will be determined from the experimental data by regression analysis.

Following the screening experiments, a set of primary experiments will be conducted to permit a detailed investigation of performance characteristics under optimized conditions. These data are required for application of the experimental results to design of commercial systems During this phase, periods of extended operation under uniform conditions are planned to provide information of operating reliability.

Mechanical design development will be carried out concurrently with the process-oriented tests. Many of the potential operational problems such as scaling, plugging, mist carryover, corrosion, erosion, and solids-liquid separation are directly influenced by process variables. It is important that feasible operating modes be established early in the program.

Systematic procedures for evaluating the effect of effluents on air and water quality are being developed.

In order to make maximum use of the facility, testing will be carried out on a continuous basis; the only planned delays between tests will be to allow the system to reach steady-state after a change in conditions. The analytical support required for the test program is formidable. It has been estimated that up to 420 chemical determinations per test will be needed. Instrumental procedures are being developed to minimize the cost of this work, Atomic absorption, X-ray diffraction, X-ray fluorescence, and conductivity methods are being evaluated.

The overall length of the test program has not been well defined. A test period of 2 yr has been assumed for budgeting purposes, but the actual time will depend on the many factors that tend to confound a comprehensive test program. The number of different types of limestone to be tested will have a major influence on the total program length. Also, it might be desirable to test improvements in the method that are likely to develop from pilot programs in progress around the world.

References

1. Tennessee Valley Authority. "Sulfur Oxide Removal from Power Plant Stack Gas: Use of Limestone in Wet-Scrubbing Process" (1969). Report No. PB 183-908, Clearinghouse for Scientific and Technical Information, 5285 Port Royal Road, Springfield, Virginia 22151

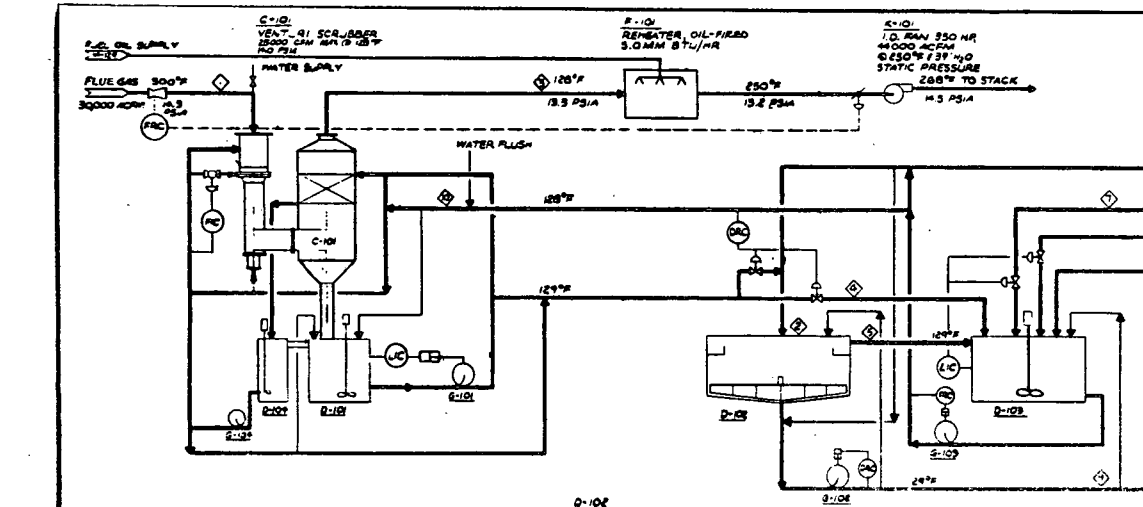
2. Thomas, F. W., Carpenter, S.B., and Colbaugh, W. C. J. Air Pollut. Contr. Assn. 20 (3), 170-177 (March 1970).

TABLE I

SCRUBBER PERFORMANCE SUMMARY

Type of Scrubber	Estimated SO_2 Removal Efficiency (%)	Estimated Particulate Removal Efficiency, N_{tp}	Est. Scrub. Liq. Req. gal/1000 ft^3 of inlet gas	Pressure Drop* (Inches H_2O)	Resistance to Solids Plugging in Contact Area	Compactness	Normal Gas Velocity ft/min	Turndown*** Capability (%)
Venturi	85+ (with absorption section)	4.0+	11 - 17**	6 - 15	good	good	10000 - 15000 (throat)	50+
Flooded Bed	90+	4.0+	8 - 11	6 - 10	good	good	500 (shell)	35
Turbulent Contact (2 stages)	85+	4.0+	15 - 30	6 - 10	good	good	850+ (shell)	25 - 35
Impingement Plate (2 stages)	85+	4.0	8 - 20	7 - 9	good if proper design is used	good	500 (shell)	30
Cyclone	70	2+	4 - 10	2 - 5	poor because of nozzle plugging	poor	2000 - 4000 (inlet)	15
Packed Bed	90+	3.5+	15 - 30	3+	poor	fair	200 - 450 (shell)	30
Nozzle	70	4.0	--	6+	good	good	--	15
Spray Tower	60	1.7	2 - 5	2+	poor because of nozzle plugging	poor	200 (shell)	15
Cross Flow	80	2.0+	6 - 12	4+	poor	good	200 (shell)	15

* From scrubber inlet to mist eliminator outlet
** Includes absorption section
*** For a single unit with no partitions



G-104 RECIRCULATION PUMP 630 GPM

D-102 RECIRCULATION TANK 5'-0 ø x 21'-0"

D-101 SCRUBBER EFFLUENT HOLD TANK 20'-0 ø x 21'-0"

G-101 SCRUBBER EFFLUENT PUMP 630 GPM

G-102 THICKENER UNDERFLOW PUMP 50 GPM

G-103 SCRUBBER PROCESS WATER RECIRC. PUMP 630 GPM

COMPONENT	M.W.	1 FLUE GAS TO SCRUBBER MPH	LB/HR	2 THICKENER FEED MPH	LB/HR	3 FLUE GAS TO STACK MPH	LB/HR	4 SLURRY TO PROC. WATER TANK MPH	LB/HR	5 THICKENER OVERFLOW MPH	LB/HR	6 FILTRATE-CENTRATE MPH	LB/HR	7 MAKE-UP WATER MPH	LB/HR	8 SOLIDS DISPOSAL MPH	LB/HR	9 THICKENER UNDERFLOW MPH	LB/HR	10 LIQUOR TO SCRUBBER MPH	LB/HR
SO_2	64.06	7.6	487	—	—	0.8	49	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CO_2	44.01	411.8	18121	—	—	411.4	18106	—	—	—	—	—	—	—	—	—	—	—	—	—	—
N_2	28.01	2314.7	64858	—	—	2314.7	64858	—	—	—	—	—	—	—	—	—	—	—	—	—	—
O_2	32.00	28.4	1135	—	—	28.4	1135	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CO	28.01	142.4	4955	—	—	140.6	4900	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H_2O	18.02	258.9	4665	4220.2	76048	943.4	9792	9548.1	172,056	3843.7	69264	304.0	5478	360.2	6490	72.4	[illegible]	3364	60664	[illegible]	[illegible]
SO_3	80.06	0.0	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$CaCO_3(S)$	100.08	3.8	218	—	—	0.0	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$CaSO_4(S)$	136.15	1.0	133	—	—	0.0	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$MgCO_3(S)$	84.32	3.8	153	—	—	0.0	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$MgSO_4(S)$	120.38	1.0	118	—	—	0.0	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
FLYASH	—	**	735	**	725	**	7	**	1641	**	0	—	—	—	—	**	25	**	725	**	1641
INERTS	—	**	46	**	46	**	0	**	103	**	0	—	—	—	—	**	46	**	46	**	103
$CaSO_3 \cdot 2H_2O$	156.16	—	—	1.7	266	—	—	3.9	602	0.0	0	—	—	—	—	1.7	266	—	266	3.9	602
$CaSO_4 \cdot 2H_2O$	172.18	—	—	3.6	619	—	—	6.0	1032	0.0	0	—	—	—	—	3.6	619	2.4	412	4.0	688
$MgSO_3 \cdot 3H_2O$	158.42	—	—	1.6	256	—	—	3.7	579	0.0	0	—	—	—	—	1.6	256	1.6	256	3.1	494
$CaCO_3$	100.09	—	—	0.5	54	—	—	0.8	77	0.0	0	—	—	—	—	0.5	54	0.5	54	0.8	77
$MgCO_3(S)$	84.32	—	—	0.3	20	—	—	0.8	66	0.0	0	—	—	—	—	0.3	20	0.3	20	0.8	66
Ca^{++}	—	—	—	**	41	—	—	**	93	**	37	**	3	—	—	**	[illegible]	**	[illegible]	**	[illegible]
Mg^{++}	—	—	—	**	3454	—	—	**	6099	**	2419	**	191	—	—	**	1277	**	1277	**	[illegible]
$SO_4^{=}$	—	—	—	139.1	13396	—	—	235.4	22615	94.8	9104	7.5	720	—	—	1.6	153	4.4	423	337.8	[illegible]
Cl^-	—	—	—	5.2	494	—	—	14.0	1117	5.6	440	0.4	36	—	—	0.1	8	0.4	44	22.5	1447
TOTAL		3173.3	95,310	4337.1	91,324	3439.4	98,484	9812.5	205,458	3944.1	81,234	311.9	6428	360.2	6490	81.0	[illegible]	392.1	9753	[illegible]	[illegible]

** = NOT INCLUDED IN TOTALS

NOTES:

1. MATERIAL BALANCE IS BASED ON 0% REGENS DOLOMITE.
2. PUMP GPM ARE AT DESIGN CONDITION.

* 3 SOLIDS TO DISPOSAL VALUES REPRESENT SOLIDS OUTPUT FROM CENTRIFUGE OR VACUUM FILTER; SEE FLOW DIAGRAM M-16.

4. SOLIDS DISPOSAL AND REMOVAL SYSTEMS FOR FILTRATE AREA SHOWN ON DWG. M-16

TEXACO CORPORATION
SAN FRANCISCO

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
FLUE GAS SCRUBBING TEST FACILITY
T.V.A. SHAWNEE POWER PLANT, PADUCAH, KY.

PROCESS FLOW DIAGRAM
[illegible] SCRUBBER
[illegible] REGENERATED DOLOMITE INJECTION

M-104

FIGURE 1

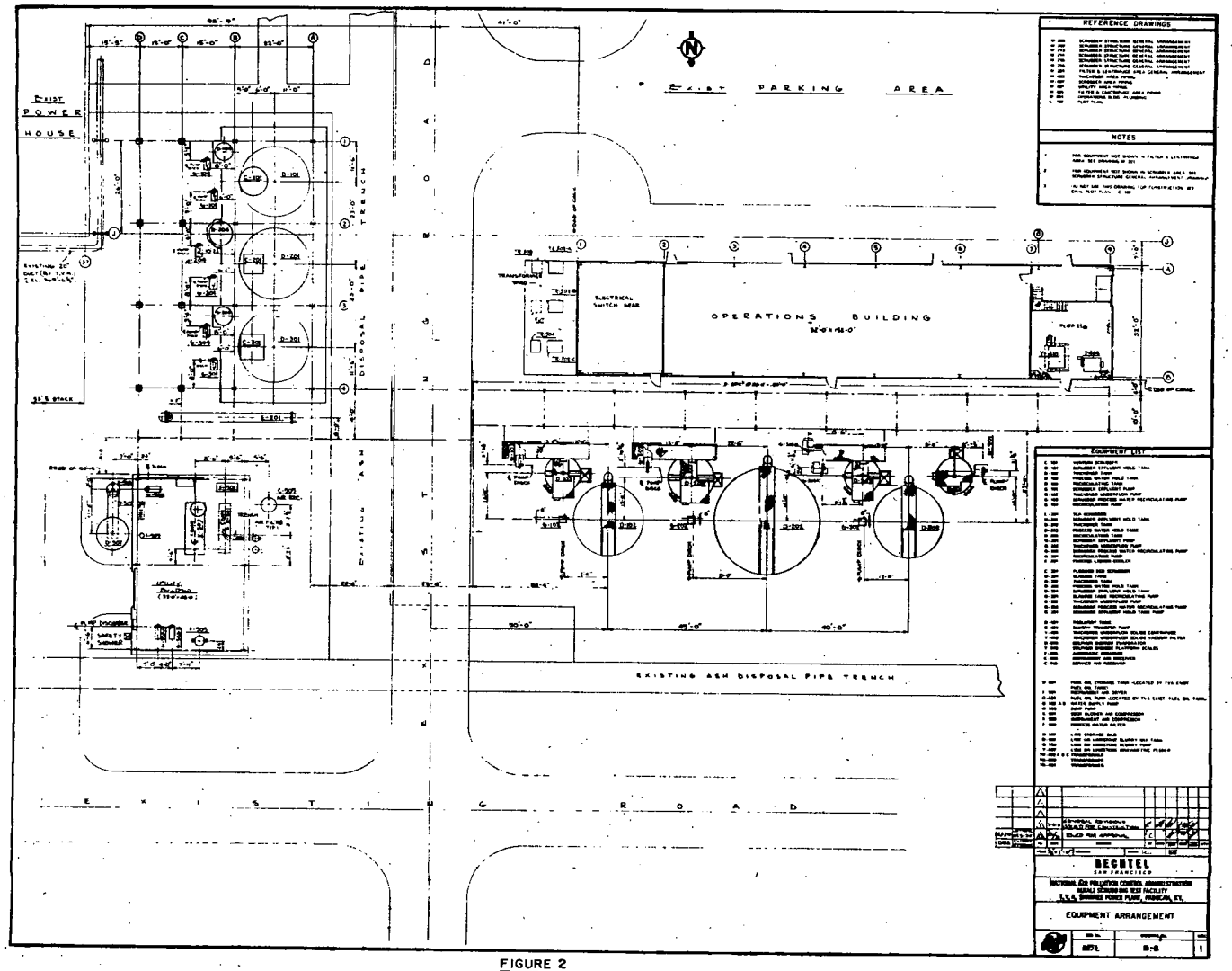

EXIST POWER HOUSE
EXIST PARKING AREA
OPERATIONS BUILDING
ELECTRICAL SWITCH GEAR
EXISTING ASH DISPOSAL PIPE TRENCH
EXISTING ROAD
REFERENCE DRAWINGS
NOTES
EQUIPMENT LIST
BECHTEL
SAN FRANCISCO
EQUIPMENT ARRANGEMENT

FIGURE 2