MAGNESIA SCRUBBING APPLIED TO A COAL-FIRED POWER PLANT

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REVIEW NOTICE

MAGNESIA SCRUBBING

APPLIED TO

A COAL-FIRED POWER PLANT

by

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ABSTRACT

A full-size demonstration of the magnesia wet-scrubbing system for Flue Gas Desulfurization (FGD) was conducted on a coal fired utility boiler. The system was designed to de-sulfurize one-half the flue gas from a 190 MW rated capacity generating unit firing 3.5% sulfur coal. The FGD installation was equipped with a first-stage wet scrubber for particle emissions control followed by the magnesia unit.

Twenty-eight hundred hours of operation were logged at the generating station, and the FGD system's ability to re-move 90% of the inlet SO_2 was shown. The particle control capability of the unit was also demonstrated by reducing particle emissions to less than 0.01 gr / SCF when the unit was operated in series with an electrostatic precipitator. In a test program using only the wet scrubbing unit for par-ticle emissions control a collection efficiency of 99.6% was achieved.

Magnesia was regenerated and recycled successfully. The SO_2 produced during regeneration was used to manu-facture commercial grade sulfuric acid which was marketed. Correlations were developed to determine SO_2 removal for varying boiler loads and fuel sulfur content, and to control regeneration of acceptable alkali. Several other studies of the process technology and process chemistry were undertaken as part of the work.

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1.0 EXECUTIVE SUMMARY

The*Chemico-Basic magnesia slurry SO_2 recovery process for control of sulfur oxides emissions from fossil fuel fired utility boilers has been demonstrated on an oil fired boiler (The Magnesia Scrubbing Process As Applied To An Oil Fired Boiler, EPA 600/2-75-057). This process, with some modifications developed during early operations in New England, was next installed on a coal fired boiler at Potomac Electric Power Company's Dickerson Generating Station as a system to control both particle and sulfur dioxide emissions from the plant. The regeneration and SO_2 recovery steps of the process continued to be carried out at the Environmental Protection Agency's calcination facility at Essex Chemicals' Rumford Acid Plant in Rhode Island, which had originally been constructed for the New England SO_2 Control Project.

Major distinctions between these two FGD units are divided into process design variation and process chemistry differences. In the former category the principal variations between the design of the previously reported oil fired application and this coal fired boiler system were:

A) The addition of a first stage venturi scrubber for particle control only (no alkali is added to this stage). Flue gas exiting this first stage is lowered in temperature to near the adiabatic saturation point through the normal transport mechanisms.

B) Magnesia alkali added to the second stage for SO_2 control is slurried with centrate returned from the centrifuge instead of process water. Since gas entering the second stage is saturated with water vapor little or no evaporation takes

*Wherever the term "Chemico" is referred to in this report, the term "Chemico Air Pollution Control Company" shall be substituted therefore.

place; thus it is possible to eliminate
fresh water inputs to this stage.

C) The use of a co-current, rather than a
counter current dryer to dry the centri-
fuge cake. This design eliminates at least
one problem encountered with the counter-
current design used in oil fired application.
Dust exiting with the dryer off-gas can be
separated and fed directly to the dryer pro-
duct discharge without adding the pneumatic
conveying equipment necessary with counter-
current units.

D) The use of "wet" fan after the two-stage
scrubber unit to provide the induced draft
for the venturies instead of a hot, forced
draft type. An important element of the pro-
gram was the taking of flue gas containing coal
fly ash directly from the boiler, use of the
"wet" fan eliminated the erosion problem associated
with dry fans handling dirty flue gas and took
advantage of the lowered temperature and volume
handled after the scrubbers.

The major difference in process chemistry between the
two plants was the production of the magnesium sulfite hexa-
hydrate in this coal fired boiler application rather than
the magnesium sulfite trihydrate produced during operations
at the oil fired generating plant. Processing of the hexa-
hydrate proved similar in many cases, to the experiences
encountered when processing the trihydrate.

Another process chemistry difference was the evidence
that magnesium oxysulfates were formed, sometimes in large
quantities, during the slaking of MgO with centrate. This
resulted in a subsequent reduction in SO_2 removal efficiency.

Because of an overlap with the operations of the oil fired station the regeneration plant was not available to the Dickerson facility when the FGD system was ready for its inaugural operation. The lack of a regeneration facility plus problems discovered during the start up period limited the initial PEPCO operations to less than 1000 hours in the nine months period between September 1973 and June 1974.

On July 1, 1974 when the Rumford facility became available, an operating and development program was initiated at PEPCO's Dickerson Station. In the next six months another 1790 hours of operation were achieved despite a number of new problems. All major objectives were completed during the period:

1) Operations were initiated using regenerated MgO.
2) Particle removal efficiency of 99%+ was verified.
3) SO_2 removal efficiency was measured, improved and verified at 90%.
4) Operating conditions for continuous running were established, with emphasis on MgO slurry mixing, control and makeup.
5) MgO loss points were discovered and corrected.
6) An operations evaluation program was established.
7) Material balance measurements were made.
8) The SO_2 removal correlation developed in the previous study was improved to include the effect of regenerated MgO properties.
9) Preliminary correlations were developed to define operating variable influence on dryer and centrifuge system performance.

10) Laboratory investigations of fundamental
system properties were continued.

Some important objectives were only partially attained
because of a number of shut-downs in the latter period which
limited the time available for operation. Thus, a long dura-
tion run was not realized. The longest uninterrupted runs
were a twelve day continuous period in October and another
of eleven days in December. Despite these limited operations
two recycles of the magnesium oxide inventory were achieved
during the program.

While a number of causes contributed to the interrup-
tions the major "shut-down" problems was deterioration of
the piping in the first and second stage recycle loops of
the FGD plant. In the second stage extensive corrosion had
occurred in the unprotected steel pipe at some time during
the preliminary operations. In the first stage recycle pipe,
which was rubber lined, a number of failures occurred which
were attributed to the supply of off-specification pipe
and fittings during construction.

After a piping replacement program and other repairs
to the FGD plant had been completed in preparation for a
demonstration run, the project was terminated when a rou-
tine overhaul of the power plant's generator system in
January 1975 revealed a defect in the turbine case. The
resultant five month outage required for repair of the tur-
bine extended past the close-out date of the E.P.A. con-
tract for access to the acid plant and operation of the re-
generation facility, thus forcing the end of the project.

Despite the limited operations and lack of extended
operating data a number of conclusions concerning the oper-
ability at the plant can be gathered from the information
that was obtained.

1.1 OPERATIONAL EFFECT OF DESIGN VARIATION FROM THE
OIL FIRED CASE

A) Particle removal efficiency for both the case
in which gas was first cleaned in an electro-
static precipitator and the case where dirty
flue gas was taken directly from the boiler
exceeded process guarantees. With the elec-
trostatic precipitator in the circuit an aver-
age outlet loading of 0.002 gr/ACF was attained
with the unit handling its full rated capacity.
When treating dirty flue gas an average removal
efficiency of 99.6% was obtained at full load
operation. The outlet loading from the scrub-
ber system for this case was 0.011 gr/ACF.

B) Slurrying magnesia feed with centrate posed some
problems. It appears that part of the MgO feed
is complexed as a magnesium oxysulfate. This
resulted in the formation of lumps and gels which
plugged feed lines in the early operations. This
problem was solved by:

1) Providing an intensive mixer between the
MgO feeder and slurry tank.

2) Slurrying the MgO feed with the entire
recycle centrate stream to reduce concen-
tration.

3) Adding a steam sparger to the slurry tank
to heat the slurry to 180°F.

These fixes diminished the problems to a level
that allowed more routine system operation.
A reduction in SO_2 removal efficiency was also
noted over a period of time during which virgin
MgO was the major part of the feed. Continued

operations showed a recovery in efficiency when using regenerated MgO.

Performance tests for SO_2 removal run on recycled MgO gave an average 90% and 93.9% SO_2 removal efficiency with the scrubber operating at full rated capacity with SO_2 inlet concentrates of 771 PPM and 1418 PPM, respectively.

An explanation of the reduced efficiency when using virgin MgO is the more rapid formation of the complex, magnesium oxysulfate, with this more reactive material.

C) The co-current dryer system used in the PEPCO operation had a higher efficiency than the unit used in the oil-fired case. Extensive modifications of the counter-current dryer, to prevent material sticking to the walls, included elimination of most of the internal lifters. This would account for the higher co-current efficiency.

A number of instances were encountered during the PEPCO operations in which centrifuge cake feed was reported as sticking to the dryer walls. This was corrected several times "on the run" by reducing load. There were some cases where large deposits in the dryer resulted in a temporary shut-down.

It should be noted that the dryer had been designed to accept a set of chains, but these had not been installed pending the outcome of the development test work. Because of the unanticipated shut-down of the entire operation this potential was not demonstrated.

Dryer product from the PEPCO operation also proved more difficult to handle in this regeneration step, and resulted in a forced cut-back in calciner feed rate to one half that obtained on the oil fired application. The reduced feed rate was correlated with a higher percentage of fines in the PEPCO dryer product, with only 22% as + 25 mesh in the PEPCO dryer product versus 58% in the same mesh size for the Boston Edison dryer product.

D) The wet fan performance and service was excellent. There were no signs of deterioration, wear or corrosion after all operations completion in either E.S.P. treated or untreated flue gas modes.

1.2 EFFECT OF PROCESS CHEMISTRY VARIATIONS ON SYSTEM PERFORMANCE

A) Production of magnesium sulfite hexahydrate rather than magnesium sulfite trihydrate resulted in little or no relief from the problems of "wet" centrifuge cake encountered in the oil fired application.

In normal operations, after attaining equilibrium, the centrifuge cake contained a mix of 82% as hexahydrate, 18% as trihydrate for its magnesium sulfite component. Materials handling problems were solved, as in the oil fired case, by designing the system to take any consistency of the centrifuge cake.

Improvements were made in redesigning the centrifuge discharge chute with a vertical wall on the solids discharge side of the machine and by lining

the chute with plastic to overcome the sticking
tendency of the cake.

B) Processing problems resulting from the formation
of the complex SO_4Mg MgO H_2O have been described
in A-2 above. Laboratory experiments indicate
that this material is formed more readily when
slaking a highly reactive magnesia (as virgin
MgO grade used in this operation). Performance
improves when the feed is composed of a high per-
centage of recycled MgO. It appears that the
complex formation occurs during the step

$$MgO_{(s)} + H_2O \text{ (1)} \longrightarrow Mg(OH)_2 \text{ (s)}$$
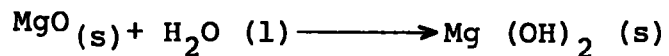
as subsequent laboratory tests showed no oxy-
sulfate formation when the starting material was
magnesium hydroxide.

C) Other Findings

Explanations were developed for the contradictions
in the findings of various researchers on the
thermographic analysis of the magnsium sulfite tri-
and hexa-hydrates. It was shown that the dehydra-
tion can be characterized as one-step in an open,
non-equilibrium process whereas in a closed, equi-
librium process it proceeds at the expected two
step dehydration. No evidence was found for the
existance of any lower hydrate.

This work led to a simple and accurate method of
analysis for the ratio of the two hydrates using
thermogravemetric analysis (T.G.A.) techniques.

2.0   INTRODUCTION AND BACKGROUND

The Chemico-Basic magnesia slurry process for SO_2 control had been developed in laboratory and pilot plant studies over a number of years. The first prototype plant employing this system was intalled on an oil fired boiler at Boston Edison Co.'s Mystic Station on a program (New England SO_2 Control Project) that spanned four years from the signing of the contract to the completion of the test work in July 1974.

Concurrently with the development of the "New England Project" Chemico pursued other potential applications for this efficient flue gas desulfurization method.

Applications were investigated that would further demonstrate the broad range of its use, particularly the advantages in those areas where a regenerable, non sludge-producing sulfur oxides control method was mandated.

Simultaneously, forward thinking utilities, such as Potomac Electric Power Company, were also investigating a number of process schemes that would provide a means of control of their sulfur oxides emissions in order to satisfy the new limitations being imposed by municipal, state and Federal governments. A principal criterion in selection of the process for control of the recognized pollutants was the economics associated with the alternate of a low sulfur content fuel supply.

In late 1970 Chemico submitted a proposal to PEPCO for a prototype demonstration plant using the Chemico-Basic process. The prototype location was set for PEPCO's Dickerson generating station site approximately 35 miles northwest of Washington, D.C. in Montgomery County, Maryland.

This site consists of 1000 acres in a rural area (but with suburban expansion from Washington developing within a few miles of the plant) bordered on the west by the Potomac River and the Chesapeake and Ohio Canal National Historic Park. The site had also been planned by PEPCO as the location of a 1700 MW expansion of generating capacity which was to be coal fired in accordance with company considerations for a balance of fuel types. PEPCO had successfully developed methods for adequate disposal of its fly ash from the Dickerson Station; therefore, a major consideration for future planning was the selection of a process for sulfur oxides control which would be acceptable at this environmentally sensitive site. Regenerable processes were a major candidate because of the complexity that would be added to operation of the power plant by the requirement to dispose of the larger volume of residue that would be produced in the throw-away processes. The Chemico-Basic magnesia F.G.D. system was eventually selected by PEPCO and engineering for the plant to be built at Dickerson Station commenced in July 1971. Construction of the plant started in July 1972 and was completed in August 1973.

A limited test program had been planned for the PEPCO operation as it was hoped that the major operating problems would have been developed and corrected in operation at the first prototype in Boston by the time the Dickerson plant was in operation. However, a series of events including delayed start up of both the Boston Edison and the PEPCO project, unanticipated problems found on starting up the processes, and the lack of a regeneration facility for PEPCO's early runs resulted in a restriction on the operation of the plant. Those operations that were conducted evidenced areas requiring additional, intensive investigation and development.

Some of these were:

1) Identification of the cause and remedy of agglomerates in the MgO slurry system.

2) Determination of losses and loss points as discrepancies in production and consumption calculations pointed to leaks of large magnitude in the magnesia system.

3) Determination of the extent and rate of corrosion as samples obtained from rail cars of $MgSO_3$ shipped to Rumford showed much higher levels of iron contamination than any experienced in the Boston Edison Operation.

4) Establishing actual SO_2 and particle removal efficiencies.

In order to provide information and solutions to these problems, a more comprehensive development and test program was prepared by Chemico and accepted by PEPCO in June 1974.

A major factor in planning of the new program was the extension of the data gathering and interpretation methods that had been used for the successful operations at Mystic station to operations of Dickerson. This immediately made the large data and correlation file which had been developed during the previous program accessible for extension and comparison with data generated from the coal fired application.

The program was divided into a series of tasks and phases in order to assure that the development proceeded in a fashion that would establish priorities first, attaining the fundamental requirements, and second leading to demonstration of the system reliability, if time permitted.

The first phase of the program was to determine control parameters that would allow sustained plant operations under conditions that established system equilibrium. Complica-

tions were encountered during this period because of need to continue shake-down operations with new and modified equipment.

The tasks slated for completion during this first phase were:

1) Evaluation of changes to the MgO slurry system.

2) Determination of the complete material balance at the plant.

3) Measurement of system pH throughout the plant.

4) Preliminary measurements of SO_2 removal.

5) Preliminary operation with regenerated MgO from the calcining facility.

6) Evaluation of equilibrium conditions in the fly ash system with the precipitator in operation.

7) Coordination of operations during the preliminary system testing (conducted by an outside testing service) in order to provide initial SO_2, SO_3 and particle control data.

The second phase in the program had as its goal the optimization of operation of the system at the Dickerson site and determination of the process conditions at the regeneration facility necessary to provide an alkali suitable for reuse after several cycles. Some differences between the oil and coal fired applications could be expected resulting from coal ash and/or first stage particle removal. These differences would affect the:

1) Efficiency of SO_2 removal.

2) Degree and rate of oxidation of the
   salts formed.
3) Efficiency of regeneration of MgO.
4) Activity of the regenerated MgO.

Evaluation of these areas required an investigation of the degree of contamination of MgO slurry with unremoved particulate matter and assessment of the SO_2 removal efficiency of each stage for various cases. This was to be done concurrently with the determination of the effect of fly ash contamination on the regenerated MgO and acid plant in long term operations.

In order to achieve these results in the shortest term possible, extensive use was made of the data file complied from the operating and analytical information logged during the Boston Edison operations. Using data processing methods, conditions at the Dickerson plant could be quickly analyzed and compared with information in the file. In this way trends indicating potential operating or process difficulties could be rapidly identified and the necessary corrective action taken so that maximum utilization of the intergrated plants would be achieved. The plan involved investigation of several parameters, such as system pH, pressure drop, recycle and gas flow and the resultant ash concentrations and solids levels in the various streams, dryer temperature, and liquid flow rates.

Most variable excursions would occur as a natural effect of process deviations. With data recording, sampling and chemical analysis on a routine schedule, they would be measured and their effects evaluated. Some of the variables such as gas flow and recycle rates were to be artifically varied in order to reduce the danger of gross contamination of the absorbent before the influence of the build-up of inerts on

the process could be assessed.

In order to determine the effect of changes in these parameters a factorial experimental program was to be used where possible.

It can be anticipated that the widest excursions in operating conditions would occur during the earliest part of the program as the operators gain skill in running the plant and as deliberate changes in conditions are made to overcome process and mechanical problems. As operations continue, these variations diminish or disappear as greater control is gained over the system so that steady conditions will be experienced during the latter part of this period.

Phase three of the program was to be a time extension so that continuous operations under the optimized conditions developed during Part II could be achieved. The duration of this phase would be contingent upon the time required to achieve three additional cycles of the inventory. Overlap with the previous period would result in a total of five regenerations of the magnesia and replacement of 1/2 of the inventory. This phase was never implemented.

Program Schedule

Phase I of the program, the conclusion of the shakedown operations and the preliminary operational testing, was estimated to require a one to two month period for completion. System feasibility as well as the suitability of the installed equipment was to be demonstrated in this Phase I. With this information plant design and equipment selection could be undertaken for any similar installation.

The second phase of the program, investigation of varying operating conditions on performance for system optimization and the determination of the quality of regenerated magnesia to obtain the required levels of SO_2 control

was estimated to require an additional four months. At the conclusion of the testing program the detailed information on operating values were to be used to fix control parameters for the final phase.

Phase three, a continuous operating period of three to four months' duration was to conclude the program.

A measure of the success of the program that was achieved stems from the reorientation of the program from the limited process guarantee tests to the more expansive one described in the preceding sections. In order to accomplish those goals, however, it was necessary to expand the socpe of work that was being undertaken at the Dickerson site. Provision had to be made for a staff of chemists and technicians to provide the analytical and testing support, technicians and operating engineers were necessary to provide supervision and advisory services for the plant operations and an overall organization had to be created to direct the project, assimilate the data, implement the changes necessary to solve the system problems and to coordinate the operations being conducted at both Dickerson and Rumford.

This was accomplished through a joint agreement between PEPCO, Chemico and the Environmental Protection Agency in which PEPCO provided the funding for the bulk of the operations at both plants, Chemico provided the project management function and EPA funded the analytical program and its support. EPA also provided funding for other emissions testing programs conducted to determine the effect of transient conditions.

3.0 PROCESS DESCRIPTION

The pollution abatement system installed at PEPCO's coal burning Dickerson Station on the Number 3 boiler is composed of a particle control scrubber and an SO_2 control absorber, both contained in a single, two stage unit (Fig 1). Particle control is effected by use of a Chemico designed variable throat venturi as a first stage followed by a venturi absorber using the Chemico-Basic Magnesium Oxide System for Flue Gas Desulfurization (FGD) as the second stage. The particle control stage, including the recycle and slurry streams and fly ash thickening units are independent and separate from the SO_2 control stage, thus preventing fly ash contamination of the magnesia used as the absorbent in that stage. Both the particle control streams and the F.G.D. streams are operated in a closed loop mode.

The original system concept was to provide a prototype demonstration unit designed to process one-half of the flue gas from the Unit 3 boiler, as shown in Fig. 2. In one configuration the flue gas to be treated is diverted from the stack after the electrostatic precipitator by using the venturi scrubber induced draft fan. A second configuration allows the ESP to be bypassed through new ductwork so that tests could be conducted with the full particle loading from the coal fired boiler treated in the wet scrubber unit. In either case, the flue gas cleaned in the first stage was processed for SO_2 removal in the second stage.

In the Chemico-Basic process for sulfur dioxide removal from flue gas the SO_2 is absorbed in a slurry containing
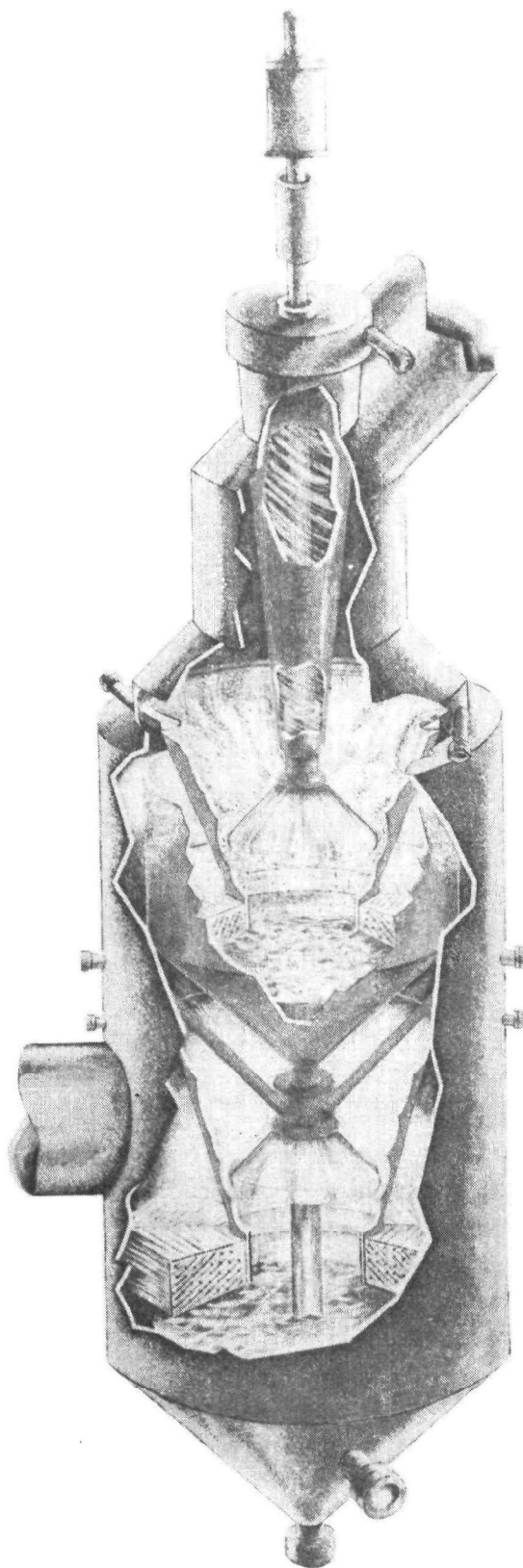
FIGURE 1
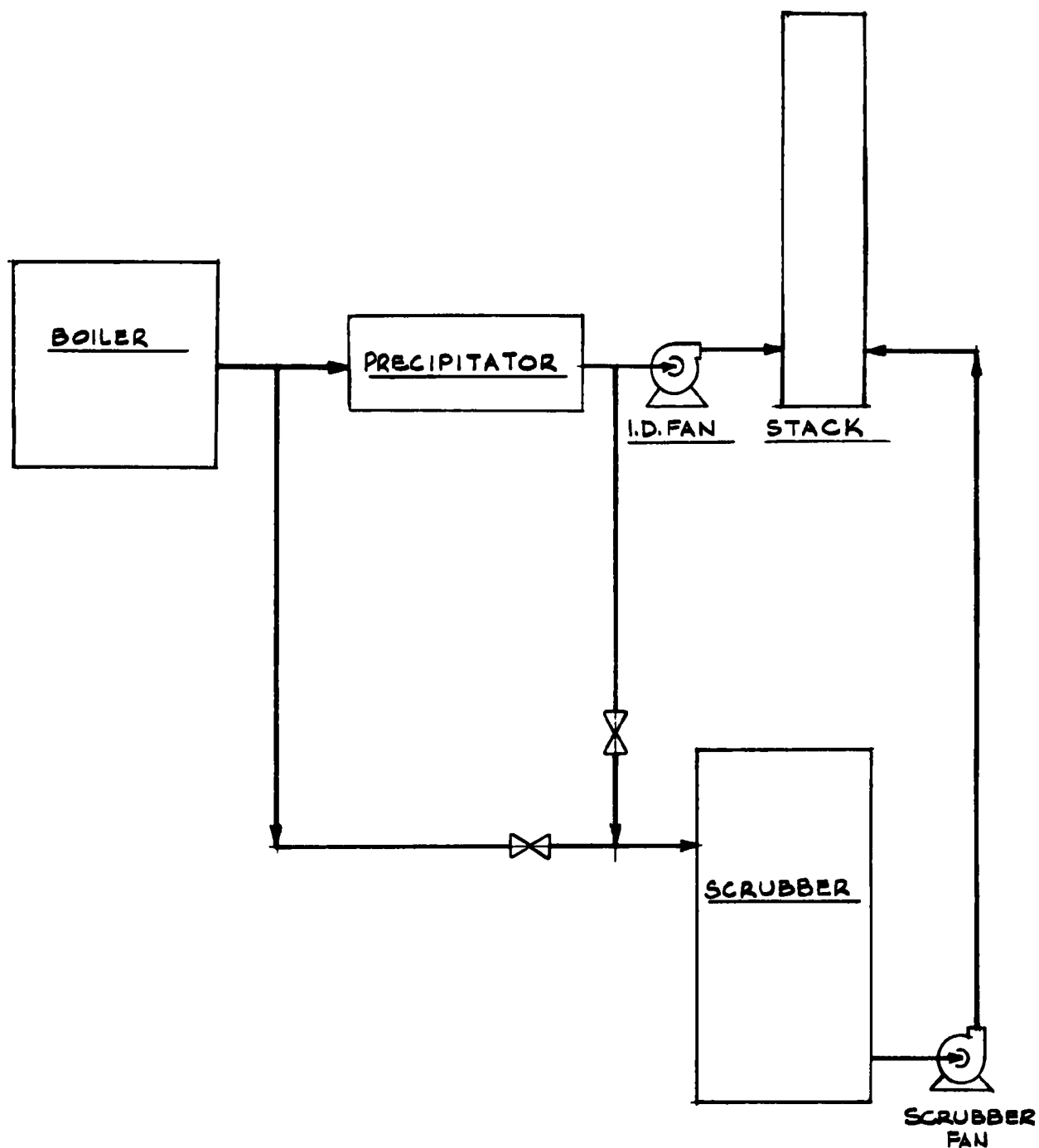
FIGURE 2
FGD GAS FLOW SCHEMATIC
DICKERSON № 3 - PEPCO

magnesia, precipitating the solid magnesium sulfite. The magnesium sulfite, after appropriate steps to reduce its moisture content, is then processed at a separate installation to regenerate the magnesia and recover the SO_2 for use in chemical manufacture. In this case the regeneration was accomplished at the E.P.A. facility at Essex Chemicals' Rumford Acid Plant in Rhode Island which had been built for the New England SO_2 Control Project, with the recovered SO_2 used in the manufacture of sulfuric acid.

3.0.1   Facility Description

Dickerson Station is located on the Potomac River outside the town of Dickerson, Maryland. The plant is situated in a rural, non industrialized area about 35 miles northwest of Washington, D.C. Coal is delivered to the plant by rail.

The station has three electric generators each rated at 190 MW. A fourth generator, rated at 800 MW is scheduled for installation nearby on the plant site by 1982. The installed 95 MW FGD system is sized to handle approximately one-half the exhaust gas flow from Unit No. 3. Pertinent data on this Unit are given in Table 1. Unit No. 3 has a dry-bottom coal-fired boiler that was designed by Combustion Engineering and installed in 1962.

The coal presently burned has an average gross heating value of 11,700 BTU/lb. Average ash and sulfur contents are 14 percent and 2 percent, respectively.

The boiler is fitted with an electrostatic precipitator (ESP) designed and installed by Research-Cottrell in 1962. Particle collection efficiency was estimated to be 94 percent. The FGD system is installed so that it can receive exhaust gas either from the outlet or breeching ahead of the ESP.

TABLE 1

PERTINENT DATA ON PLANT DESIGN, OPERATION
AND ATMOSPHERIC EMISSIONS

Boiler data - Dickerson No. 3 - PEPCO

Rated Generating Capacity MW	190
Average Capacity Factor (1974), %	81
Boiler Manufacturer	Combustion Engineering
Year Placed In Service	1962
Unit Heat Rate, BTU/kwh	9180
Maximum Coal Consumption, Ton/Hr.	74.5
Maximum Heat Input, BTU/hr.	1744×10^6
Stack Height Above Grade, Ft.	400
Flue Gas: Design Rate, ACFM	450,000
Maximum Rate, ACFM	650,000
Flue Gas Temperature, °F	245
Emission Controls:	
Particulate Matter	ESP with a venturi scrubber on half of gas flow.
SO_2	Venturi absorber on half of the gas flow.
Particle Emission Rate:	
Allowable, g/scf dry	0.03
SO_2 Emission Rates:	
Allowable, lb/Million BTU	1.6[1]

[1] 1% sulfur coal equivalent

3.0.2 Pollution Abatement System Description

A schematic representation of the pollution abatement process installed at the power plant is shown in Fig. 3. The principal element of the system is the two stage venturi scrubber/absorber which combines in a single vessel both particle removal and SO_2 control. Each of the two functions are separated in the unit with the flue gas being treated sequentially, first to remove fly ash then to reduce its SO_2 content to acceptable levels. Besides providing the means of cleaning the flue gas, this sequence assures that a negligible amount of fly ash will be captured in the magnesia slurry used for SO_2 removal in the second stage. This is necessary in order to prevent a buildup of coal fly ash which would result in the contamination of the regenerated MgO. A further advantage of this design is the ability to use the particle removal stage independently should it be desirable to continue the unit in operation without SO_2 control.

The Chemico/Basic's Magnesium Oxide System for the recovery of sulfur dioxide from plant flue gases utilizes the sulfur dioxide absorption characteristics of an aqueous slurry of magnesium sulfite, magnesium sulfate, and magnesium oxide. The process is accomplished in several steps:

> Absorption
> Dewatering & Drying
> Materials Handling
> Calcination

with the regeneration/recovery step (calcination) performed at a remote site.

Absorption

In the absorption step the process chemistry which describes the removal of SO_2 from the flue gas can be most

THE DICKERSON REGENERATIVE WET SCRUBBING SYSTEM
POTOMAC ELECTRIC POWER CO. PROTOTYPE
PRECIPITATOR/SCRUBBER - ABSORBER
MgO ADDITIVE SYSTEM FOR SO$_2$ RECOVERY

SCHEMATIC PROCESS FLOW SHEET
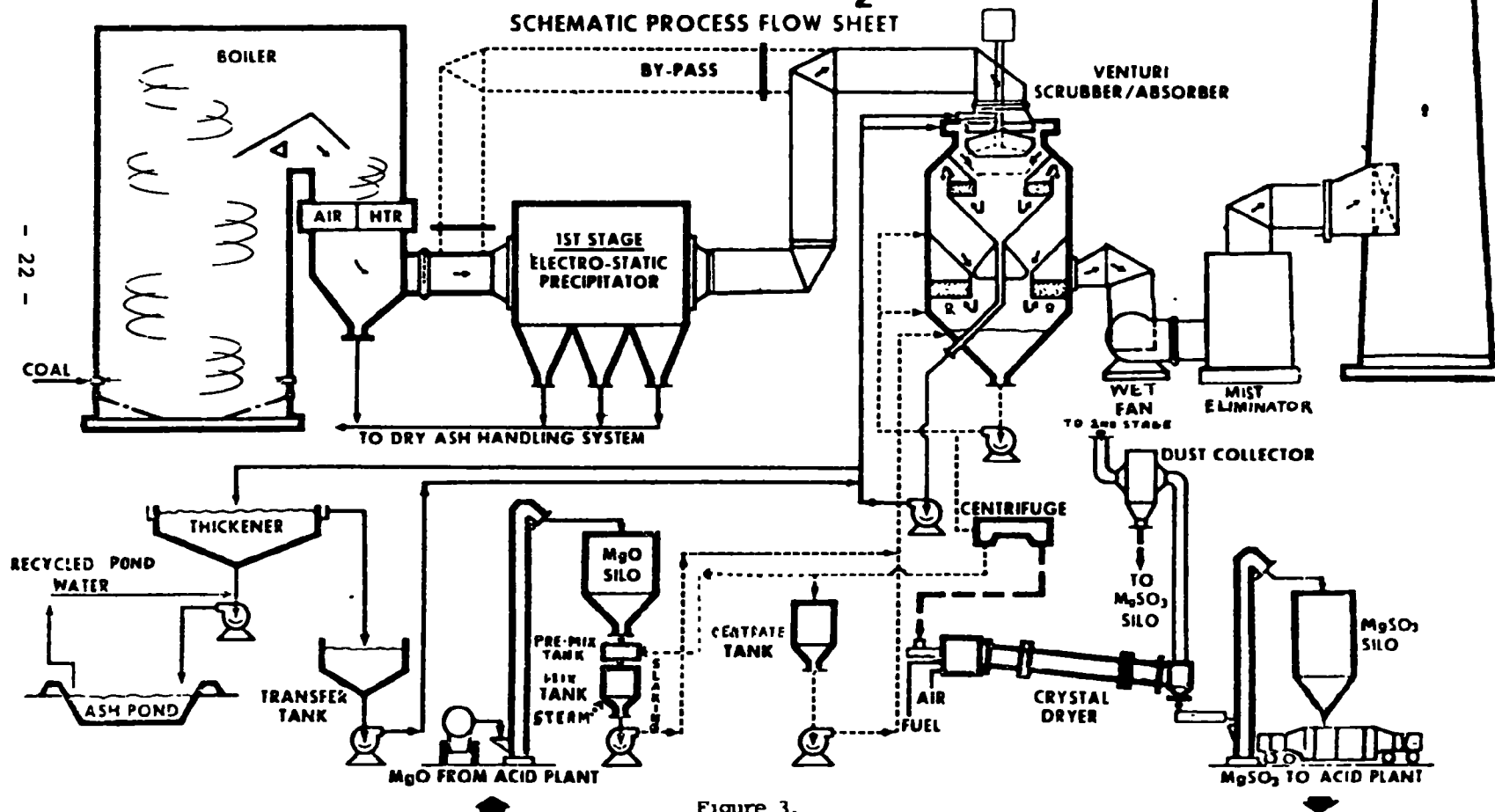
Figure 3.

simply explained as the diffusion of SO_2 through the flue gas to a liquid surface, then absorption of the SO_2 with the hydrated form of MgO, i.e.

$$MgO_{(aq)} + SO_2 \longrightarrow MgSO_3 \quad (3-1)$$
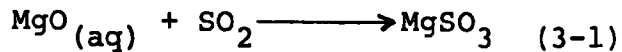
The $MgSO_3$ produced has a low solubility and can be separated from the absorbing slurry as a solid.

In the process, the flue gas containing sulfur oxides enters a venturi absorber of special design, and contacts the absorbing media which is an aqueous slurry of magnesium oxide, magnesium sulfite, magnesium sulfate, and a small percentage of other components. The process of SO_2 removal that occurs is explained by conventional mass transfer principles.

The venturi absorber can be considered as similar to a co-current, packed vessel. In the venturi the liquid slurry is introduced and flows downward on a surface over which passes an accelerating gas stream. The high velocity gas stream flowing over the liquid causes wave motion on the fluid surface, the waves increase in amplitude and finally disperse as fine droplets. Thus, the whole mass of liquid can be distributed in the form of atomized droplets in the gas stream.

There are several advantages in using the venturi as an absorber. The absorption surface is dispersed into and flows with the gas stream during the time absorption is occuring, thus eliminating the problems of plugging associated with conventional packed towers (the surface area per unit volume is approximately equivalent to dumped 3 inch rachig rings). Due to system dynamics, this surface area relation is relatively invariant over wide turn-down ratios, and high removal efficiencies can be maintained over the normal operating range of the power plant's boiler.

Dewatering & Drying

A stream from the absorption system enters a centrifuge where the solids which were formed by the absorption reaction in the slurry are separated. This bleed stream is controlled in order to maintain a constant solids content in the recycle slurry by removal of product magnesium sulfite and unreacted magnesium oxide and any precipitated magnesium sulfate. The system is operated so that the absorbed SO_2 is removed as an equivalent amount of the magnesium sulfur compounds.

The wet centrifuge cake containing hydrated magnesium sulfite, magnesium oxide and magnesium sulfate plus other solids removed in the venturi absorber-centrifuge system is passed to a rotary dryer to remove both unbound water and most of the water of crystallization. The dry product is easy to store, and the removal of water reduces shipping costs.

Materials Handling

The anhydrous magnesium sulfite and magnesium sulfate produced in the dryer is conveyed to a storage silo for transportation by rail or truck to the recovery acid plant. The same transport is used to return regnerated magnesia to the magnesium oxide silo at the power plant on the return trip.

Calcination System

Calcination is the process used for regeneration. The magnesium sulfite which has been separated and dried is thermally decomposed as represented by the following reaction:

$$MgSO_3 \longrightarrow MgO + SO_2 \quad (3-2)$$

The recovered SO_2 is used in the production of sulfuric acid and the regenerated MgO returned to the process for reuse. The dry product transported to the regeneration acid plant from the power plant is received, weighed and pneumatically

conveyed to a storage silo. It is fed to a direct-fired rotary kiln at a metered rate, and calcined to both generate sulfur dioxide gas and regenerate magnesium oxide. Coke can be added to provide a reducing atmosphere, as necessary, to reduce the residual magnesium sulfate to the oxide and sulfur dioxide. The hot flue gas containing sulfur dioxide and dust enters a cyclone where essentially all the dust is removed and returned to the calciner. The flue gas then enters a venturi scrubber for final dust cleaning. At the same time, the gas is cooled and adiabatically saturated.

The saturated flue gas is further cooled in a direct contact packed tower to meet the requirements of the acid plant water balance. The cleaned flue gas then enters the drying tower of an existing 50 T/D acid plant. At the Essex Chemicals' installation, the resultant product made from the recovery of the sulfur dioxide is 98% sulfuric acid.

The regenerated magnesia is cooled, conveyed to the magnesia storage silo, and recycled back to the power plant.

3.1 DETAILED PROCESS DESCRIPTION

The process flow sheet for the facility installed at Dickerson is shown in Fig. 4, material balances are given in Table 2 with the description of each item given in the Equipment List, Table 3.

3.1.1 Particle Removal

The first stage of the system uses a Chemico variable throat venturi. In this design, a 60° tapered plug is suspended by a height adjustment mechanism in a 60° converging section of the scrubber. By stroking the mechanism through its entire adjustment the throat opening can be varied allowing up to a two foot maximum spacing. In normal operation, with standard liquor circulation rates, the throat width has been adjusted to maintain an eleven inch pressure difference across the particle removal stage.
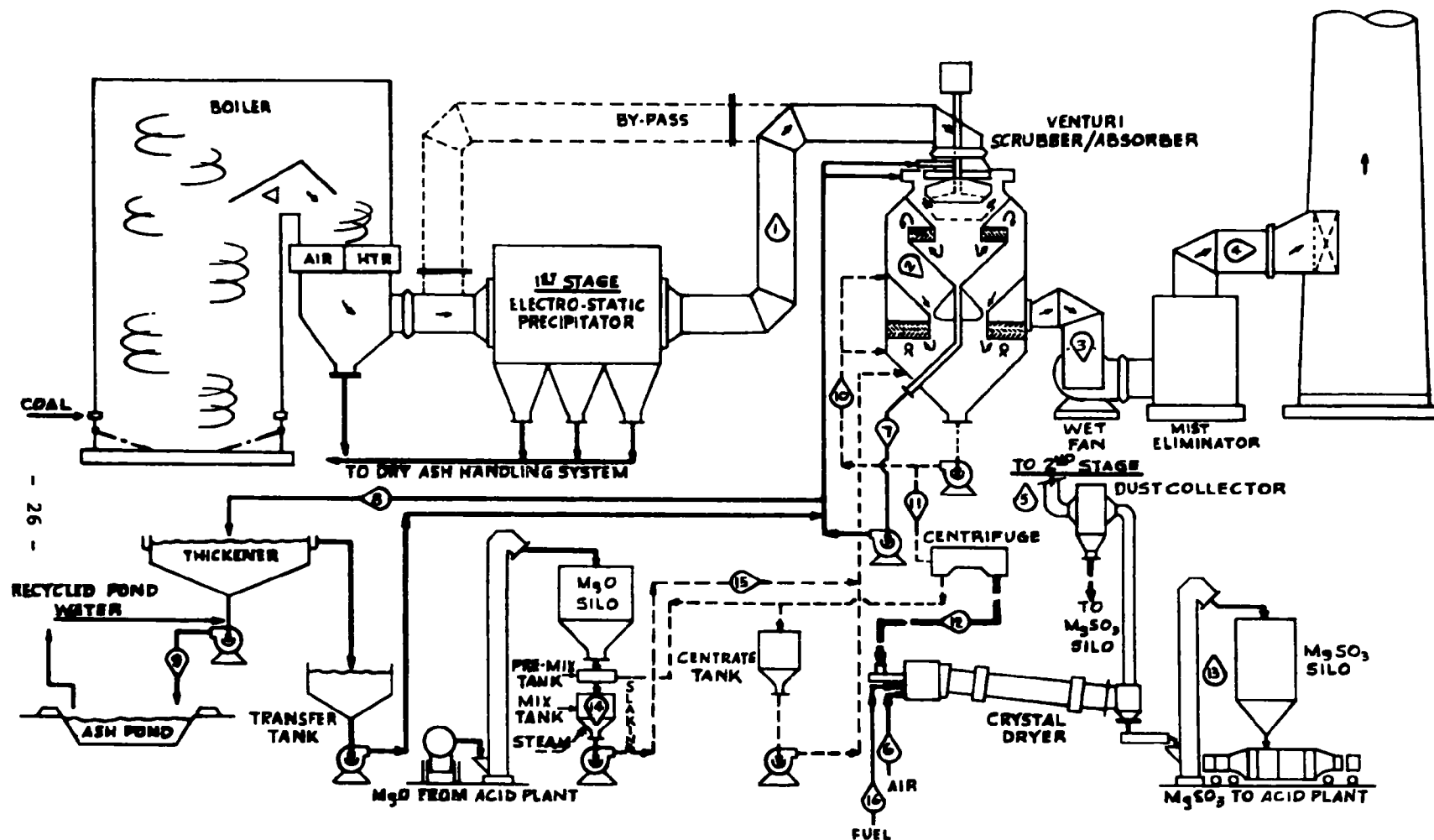
FIGURE 4
PEPCO REGENERATIVE
WET SCRUBBING SYSTEM

TABLE 1

STREAM PROPERTIES AND COMPOSITION

SO2 AND FLY ASH REMOVAL SYSTEM

STREAM NUMBERS		7	8	9	10	11	12	13	14	15	16
				LIQUID AND SOLID STREAMS							
Temp.	°F	117	117							38.1	
Flow	GPM	5,165	980	140	10,621	170				13.7	
Solids Content,%		2.0	2.0	13.2	13.3	13.2					
H2O	Lb/Min	42,870	8,166	1,102	82,850	1,322	10.4			300	
MgSO3	Lb/Min							86.3			
MgSO4	Lb/Min							4.9			
MgSO3·6H2O	Lb/Min					178	178	2.0			
MgSO4·7H2O	Lb/Min					9.9	9.9				
MgO	Lb/Min					9.9	9.9	9.9	45.3	45.3	
Inerts	Lb/Min					2.4	2.4	2.4	2.4	2.4	
Fly Ash	Lb/Min	875	166	166		0	0	0			
Total	Lb/Min	43,745	8,332	1,268	95,520	1,522	210.6	105.5	47.7	347.7	
Fuel	Btu/Hr										16.6 x 10^6

STREAM NUMBERS		1	2	3	4	5	6
				GAS STREAMS			
Temp.	°F	259	117	121	121	450	70
Pressure	In. W.G.	-11	-26	-36	0	-5.5	-0.6
Flow	ACFM	295,000	263,000	286,000	260,000	21,600	10,200
SO2	Lb/Min	62.5	62.5	6.25	6.25		
H2O	Lb/Min	581	1,209	1,420	1,420		
Dry Gas	Lb/Min	15,820	15,820	16,457	16,457		
Particulate	Lb/Min	166.6	0.85	0.89	0.89	0.22	

TABLE 3

EQUIPMENT LIST

Item Description	Code No.	Quantity	Motor Horsepower (HP)
MgO Make-Up Tank	G-101	1	
Dust Collector-MgO Silo	G-102	1	
Thickener	G-201 A,B	2	
Transfer Tank	G-202	1	
Distribution Box	G-203	1	
Sump Tank	G-204	1	
Mother Liquor Tank	G-301	1	
Dust Collector-Dryer	G-401	1	
MgO Storage Silo	I-101	1	
$MgSO_3$ Silo	I-401	1	
MgO Feed Pump	J-101 A,B	2	10
First Stage Recycle Pump	J-201 A,B	2	350
Second Stage Recycle Pump	J-202 A,B,C	3	250
Underflow Pump	J-203 A,B,C,D	4	
Transfer Pump	J-204 A,B	2	125
Sump Pump	J-205	1	30
Mother Liquor Pump	J-301 A,B	2	20
Induced Draft Fan	K-201	1	3500
MgO Agitator	M-101	1	5
Mother Liquor Agitator	M-301	1	3
MgO Weigh Feeder	O-101	1	
Dryer Feed Conveyor	O-401	1	1
Dryer Discharge Conveyor	O-402	1	2
Dryer Discharge Elevator	O-403	1	2
$MgSO_3$ Conveyor	O-404	1	2
$MgSO_3$ Weigh Feeder	O-405	1	
Two-Stage Venturi Scrubber	R-201	1	
Mist Eliminator	R-202	1	
Variable Speed Coupling	R-203	1	

TABLE 3 (Cont'd)

EQUIPMENT LIST

Item Description	Code No.	Quantity	Motor Horsepower (HP)
Centrifuge	R-301	1	200
Rotary Dryer	R-401	1	40
Dryer I.D. Fan	K-402	1	100
Instrument Air Dryer	V-101	1	

Liquor is circulated in this particle removal stage by recycle pumps, J-201 A & B (one operating, one spare, each with a design capacity of 5700 GPM and driven by a 350 HP motor) through rubber lined distribution piping to the upper level of the scrubber R-201. The recycle flow is split into two streams before reentering the scrubber. The flow in each stream is adjusted and set by pinch valves to provide uniform irrigation of the converging surfaces. The outer converging section is supplied by ten 4" tangential nozzles while the adjustable cone is supplied by three 6" lines feeding a single bull nozzle.

Flue gas enters the vessel and passes downwards through the irrigated converging section. As the gas is accelerated through the throat the liquid film is atomized and distributed through the gas stream. Particle collection occurs on the dispersed droplets through the mechanisms of impaction, diffusion and attraction. The flue gas and dispersed liquor continue through the central down-comer to the basin area of the first stage where the gas turns 180° upwards to pass through the first stage mist eliminators. The liquid droplets are first disengaged in the turning zone and fall into the first stage liquor pool, droplets small enough to be carried with the gas stream are captured by the slot type mist eliminator. The cleaned gas continues out of the first stage through the annular space between the outer shell and the wall of the first stage reservoir.

A bleed stream, about 15% of the total flow from the recycle pumps, is sent to a distribution box and thence to one of two thickeners, G-201 A & B, each of these is 40' in diameter with a rake mechanism feeding a central underflow discharge. The thickened underflow, approximately 20 GPM at 40 percent solids, is discharged to a distribution tank where water from the lower pond is added and the mixture is

pumped to the upper settling pond. The pond overflow cascades through a total of four settling ponds in series and the clear water from the lowest is again returned to the dilution tank.

The thickener overflow drops into a transfer tank and is returned to the first stage recycle loop by transfer pumps J-204 A & B, (one operating, one spare, each designed for 1190 GPM and driven by a 125 HP motor) so that closed loop operation is maintained.

It should be noted that the mechanisms for collection of particulate matter or sulfur dioxide both depend on the formation of droplets dispersed in the flowing gas. In the Chemico venturi the mechanism of atomizing the liquid by the accelerated gas stream is the same for either stage. However, the mode of operation of the stages is different. In the case of particle collection a specific droplet size distribution will be found to provide the maximum collection efficiency and the size distribution is directly related to a gas velocity flowing over the liquid surfaces. In the case of gas adsorption it is necessary to maintain a uniform specific surface area (i.e. area of droplet surface per volume of gas) which in the venturi, is self regulating, after initial adjustment, over a range of gas flows. Thus, first stage efficiency is maintained by operation at a fixed pressure drop to keep the best droplet size distribution while second stage efficiency is controlled by operation at fixed liquor recycle rates to maintain a uniform surface area of the dispersed droplets.

3.1.2   Detailed Process Description - SO_2 Removal

In this system magnesia, both regenerated and make-up material, is transferred from pneumatic discharge hopper trucks to the elevated MgO storage bin through a 4 in. pneumatic unloading system. The MgO bin, I-101, is 25 ft.

in diameter and 46.5 ft high. Magnesia is fed from the
silo, which is equipped with a vibrating hopper bottom,
O-103, to a 3760 gallon capacity MgO make-up tank G-101 by
an adjustable weigh feeder, O-101, with mother liquor to
make the desired MgO slurry composition. A small pre-mix
tank is interposed between the weighing system and the
steam heated make-up tank to insure dispersion of the MgO
powder and to act as a vapor seal. Heated magnesia slurry
is added to the recycle stream by the MgO make-up pump,
J-101 A, B. The magnesia slurry addition rate is controlled
by the operator to maintain the pH of the absorbing slurry
at the desired value.

The recycle stream for the absorber is circulated at
a rate of 10,767 GPM by pumps, J-202 A, B and C, (the capa-
city of each of these 250 HP pumps is half the design flow
of the recycle stream) to provide a slurry dispersion within
the vessel sufficient for the desired SO_2 removal.

The recycle stream itself is split into two streams
for distribution before reentering the venturi absorber.
The flow in each stream is adjusted and set by plug valves
to provide a uniform irrigation to the converging surfaces.
Distribution of absorbing slurry is made by ten, six inch
tangential nozzles supplying the outer converging section
while the inner cone is supplied by a single central nozzle.

The slurry enters the upper part of the absorber stage
with the flue gas which is pulled through the system by the
I.D. fan K-201 driven by an 3500 HP motor, designed to handle
286,000 ACFM at a discharge head of -26 in. water. The gas
and slurry mixture passes through the throat area into a di-
verging section, then into a central downcomer. To exit the
vessel the flow of the cleaned flue gas turns one hundred
eighty degrees upwards. In this step most of the larger
liquid droplets are disengaged from the flowing gas stream
and fall to the slurry pool in the conical base of the absor-

ber. The treated flue gas continues upwards through a slot-
type mist eliminator to further remove any entrained liquid
before the gas exits to wet fan K-201. The fan wheel of
K-201, driven through a variable speed drive, is continuously
sprayed with water to prevent solids build up on the blades.
Entrained liquid in the gas stream leaving the fan is removed
in Mist Eliminator vessel R-202 before passing the stack.

A stream of slurry, approximately 1.6% of the total
recycle, is taken from the discharge of the recycle pumps
to the centrifuge, R-301. This is a 36 in. x 72 in. horizontal,
solid bowl unit driven by a 200 HP motor, and in normal
operations it removes 50% of the solids in the liquid stream
going to it.

The solids separated in the centrifuge contain an
amount of SO_2 (as $MgSO_3$ or $MgSO_4$) equivalent to the amount
removed in the absorber. The centrate is discharged directly
to an agitated tank, G-301 of 1375 gallon capacity which
serves as a pump tank for this system, and then is returned
to the MgO slurrying system by pumps J-301 A & B. The basin
of the absorber is the reservoir for the system and contains
approximately 20,000 gallons of slurry. The other sources
of water entering the system are small amounts added as pump
seal water and an additional quantity used as a mist elimina-
tor wash; the latter is an intermittent addition.

The centrifuge cake separated in the centrifuge is fed
to a dryer by screw conveyor O-401, a 35 ft. long unit with
a 12 in. diameter ribbon flight. The dryer is a rotary unit
8 ft. in diameter by 50 ft. long. Heat is supplied from an
integral 18 ft. long oil fired combustion chamber at a maxi-
mum heat release rate of 26.3×10^6 BTU/hr.

The dryer off-gas exits in to a cyclone, G-401, designed
for 97% removal of the solids entering with the gas. From
the cyclone dust collector, the gas discharges via a booster

fan, K-402, to the venturi absorber where, mixed with the entering flue gas, it is cleaned of its remaining particle load. The separated fines collected by the cyclone returns directly to the dry product pneumatic conveying system discharging to the product silo.

The dryer product is discharged to the dryer discharge conveyor, D-402, 21.75 feet long unit with a 9 inch diameter solid flight screw. It then exits into a $MgSO_3$ weigh feeder O-405 at the boot of the $MgSO_3$ discharge elevator, O-403, which is designed to handle 5 tons/hour of dried magnesium sulfite. The product then travels through another conveyor, O-404, located on top of the $MgSO_3$ storage silo. The storage silo is 66.5 feet high and 25 feet in diameter, and is equipped with a vibrating discharge hopper, O-406.

The product $MgSO_3$ is finally gravity loaded into a waiting hopper truck for shipment to the MgO regeneration plant.

3.2   DETAILED PROCESS DESCRIPTION - MAGNESIA REGENERATION SYSTEM

Magnesium sulfite from the absorption system is received at the regeneration facility. The regeneration section flow sheet is shown in Fig 5 . Material balances are given in Table 4. The salt is unloaded from hopper trucks to the sulfite silo I-401 through a 4 in. pneumatic conveying system similar to that used for MgO at the power station. The sulfite silo was an existing tile structure, 25 ft. in diameter x 45 ft. high, which was water-proofed before this use. Sulfite is unlaoded from this silo through a pair of inclined screw conveyors, $MgSO_3$ conveyors 1 and 2, O-509 and O-510, equipped with 12 in. diameter helicoid flights, which carry the material from the below grade discharge spout to the boot of the $MgSO_3$ elevator.

This elevator, O-511, a continuous discharge unit 54 ft. high, is designed to handle 9 TPH of $MgSO_3$. It discharges
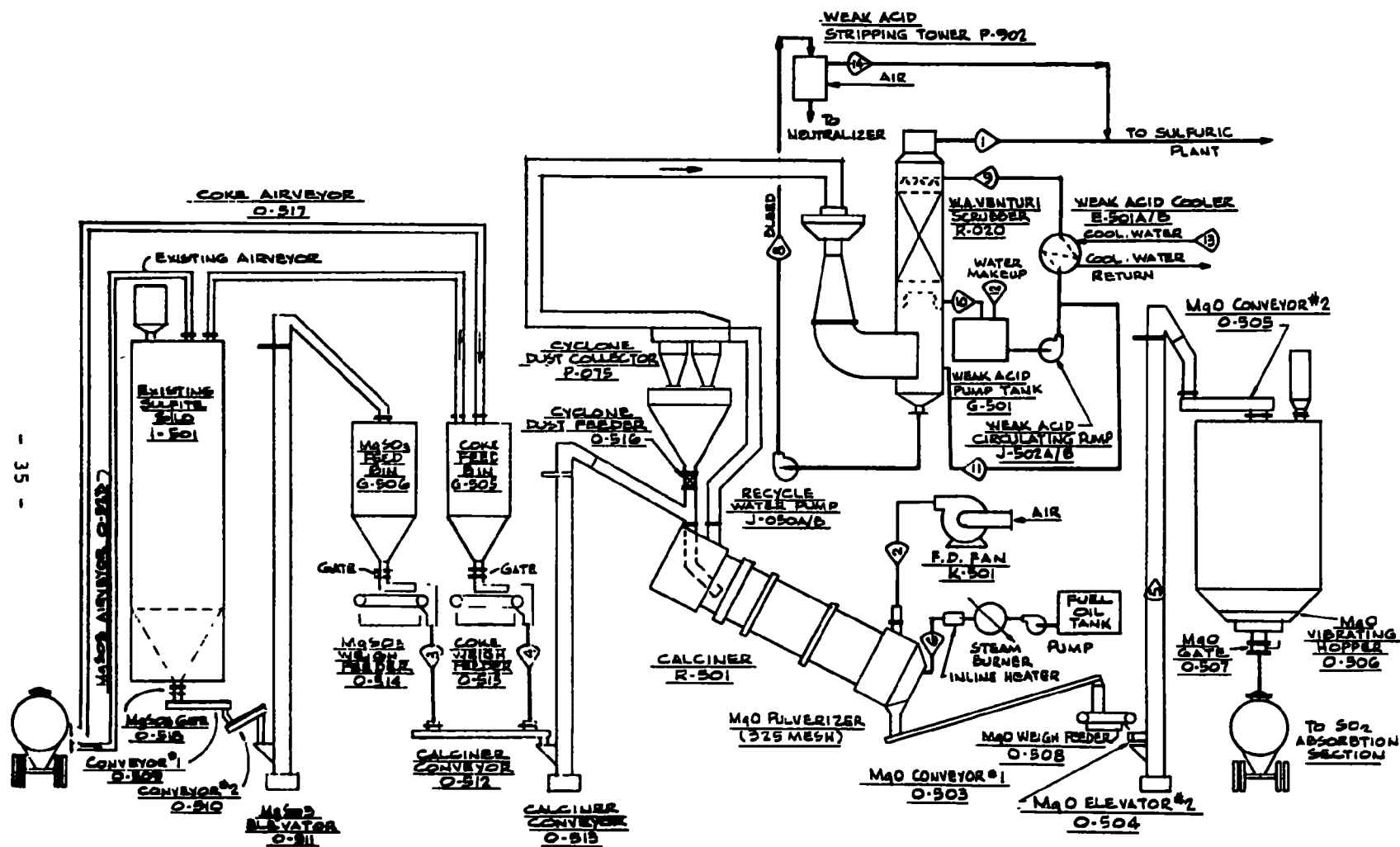
FIGURE 5

MgO REGENERATION SYSTEM

TABLE 4

STREAM PROPERTIES AND COMPOSITION
MgO REGENERATION SYSTEM

STREAM NUMBERS		3	4	5	6	7	8	9	10	11	12	13
				LIQUID & SOLID STREAMS								
Temp	°F			300	250	160	160 ·	90	150	150	Amb.	80
Pressure	PSIG											
Flow	GPM				1.5	91	2	119	125.5	80	1.5	205
$Mg(HSO_3)_2$	lb/Min						0.88					
MgO	lb/Min	8.24		38.35								
$MgSO_3$	lb/Min	72.50										
$MgSO_4$	lb/Min	4.12					1.5					
Inerts	lb/Min	1.89		1.81			0.1					
Fly Ash	lb/Min	0.25		0.25								
Total Solids	lb/Min	87.0	2	40.41			0.1					
H_2O	lb/Min						13.4					
Total Flow	lb/Min	87.0	2	40.41		760	15.88	99.2	1045	65	12	1708
Fuel Oil	lb/Min				12							

STREAM NUMBERS		1	2	14
		GAS STREAMS		
Temp.	°F	100	70	100
Pressure	In. W.C.	-45	0	-45
Flow	ACFM	2,980	2,140	640
Flow	SCFM	2,460	2,100	529
Total Dry Gas	lb/Min	206.2	161	39.0
H_2O Vapor	lb/Min	9.0		0.8
Total Wet Gas	lb/Min	215.2		39.8
SO_2	lb/Min	44.7		
O_2	lb/Min	1.8		
Dry Gas MW		34.4	29	29

to the $MgSO_3$ feed bin, G-506, a 6 ft. diameter by 11 ft. high vessel equipped with a vibrating bottom, which also serves as a surge bin for the weigh feeder O-514. This weigh feeder is continuously variable to a maximum capacity of 3.6 TPH and discharges to the calciner conveyor O-512, a 33 ft. long horizontal unit equipped with a 9 in. diameter helicoid screw. Coke is also discharged to this screw which serves to mix the two components as calciner feed prior to processing.

The coke is pneumatically conveyed to the coke feed bin G-505 9 ft. diameter x 19 ft. high, which also serves as the storage bin for this material. It is metered to the calciner conveyor by a weigh feeder which is also continuously variable up to a maximum capacity of 2.5 pounds per minute. The two streams (3 and 4 of Fig. 5) enter at points 9 feet apart and mix in the remaining 22 ft. section of the conveyor before reaching the calciner elevator O-513, a 43 ft. high centrifugal discharge unit. This elevator feeds directly to the calciner R-501.

The calciner is a refractory lined, oil fired, rotary kiln, 7 ft. 6 in. ID and 120 ft. long. Rotational speed is variable between 1.5 and 2 RPM using a variable diameter pulley drive, and the kiln has a slope of 3/8 in. per foot. The calciner product empties into four tube coolers attached to the shell and equipped with internal flights to contact the existing hot regenerated magnesia with incoming air which serves a secondary combustion air in the calciner, thus cooling the calciner product before it empties to the MgO conveyor #1, O-503.

This is a 9 in. diameter helicoid screw conveyor, 54½ ft. long, which elevates the product from the calciner tube cooler discharge seventeen feet to an enclosure housing the MgO processing equipment. The regenerated MgO is dis-

charged from O-503 to a magnetic pulley for tramp iron separation. The MgO then passes through a 1 in. mesh vibrating screen and enters a high speed pulverizer which reduces it to the finished grind shown in Table 5.

The cleaned, cooled, and pulverized regenerated magnesia flows by gravity to the MgO elevator O-504, a continuous discharge design, 89 ft. high, which brings the material to the top of the MgO storage silo where it is loaded by means of a horizontal screw conveyor (MgO Conveyor #2) O-505 equipped with a 9 in. helicoid screw.

The MgO silo, I-502, 25 ft. in diameter and 45 ft. high is equipped with vibrating hopper bottom, O-506, and elevated on a structural steel support for direct gravity loading of the returning trucks.

The gas from the calciner, containing SO_2 and products of combustion, as well as a small percentage of excess air, is first partially cleaned of particles in the cyclone dust collectors P-075. This is a dual cyclone array, designed for a 1 in. pressure drop. The collected solids are returned to the calciner with the feed to the unit.

The partially cleaned calciner gas containing 8-10% SO_2 is further cleaned in a venturi scrubber of Chemico's special design, operated at a pressure drop of approximately 25 in. of H_2O where it is also adiabatically saturated. Next the gas enters the separator tower section, which is an integral part of the venturi equipment. The lower section of this 4½ ft. diameter vessel serves a cyclonic liquid separator and the upper section, containing eight feet of 3½ in pall rings is irrigated with cooled weak acid to further reduce the temperature of the gas to 100^OF in order to maintain the acid plant's water balance. A slip stream of cooling liquor is stripped of dissolved SO_2 in the weak acid

TABLE 5

DRY SCREEN ANALYSIS

Screen Size (Tyler)	Unpulverized Calciner Product	Pulverized Calciner Product
+50	30.3 %	5.3 %
+100	18.1	9.5
+200	9.4	8.8
+325	13.1	49.8
-325	29.1	26.6

stripping tower P-502, a small (15 in. diameter x 14 ft. high) packed contactor.

The stripped SO_2 joins the main gas stream and is ducted to the acid plant in 18 in. diameter, FRP pipe.

3.3 ACID PLANT

The regeneration system was installed at the Rumford acid plant of Essex Chemical Company located in Rumford, RI. The Rumford plant is located 55 miles from the installation at Mystic Station and haulage of the dryer and calciner products between these two sites was done by truck. Both plants were equipped to load their respective products from elevated silos and receive their feed by pneumatic unloading.

The plant has been producing sulfuric acid since 1929 when it was built by Chemical Construction Corporation and for the past several years all acid produced was sold in the merchant market with no captive use. Markets for the acid made at this plant are manufactured of detergents, dyestuffs, pharmaceuticals, aluminum sulfate, tanning chemical, steel pickling, boiler water treatment, lead-acid batteries, galvanization, etc. Sales in this market were at the full published price, at the time of this program, approximately $46 per ton based on 100% H_2SO_4. No change in use or pricing was imposed when marketing the acid produced from MgO regeneration.

The plant is a contact sulfuric acid plant which uses sulfur as raw material. In the Chemico process the molten sulfur is injected into the furnace using a spray burner, with the process air first dried in a tower against 93% sulfuric acid. The catalyst is vanadium pentoxide.

When first built in 1928 the Rumford plant was an indoor plant typical of its time and had a capacity of about

20 tons per day of 100% sulfuric acid. Substantial modifications were made to the plant in 1948 by Chemico to increase its capacity to 50 tons per day. The modifications included improved converters, a converter heat exchanger, waste heat boiler and economizer all installed outdoors. In addition, the cast iron cooling section was enlarged and moved outside.

This was the plant that was modified in 1971 to accept the calciner off-gas essentially converting it to a metallurgical (roaster) gas plant; however, in the modification the capability to continue to burn sulfur and augment the SO_2 from the regeneration plant was retained.

Typical feed gas analyses to the acid unit are shown in Table 6.

The regeneration of magnesia, described in the previous section, produces an off-gas from the calciner approximately 100 fold richer in SO_2 than the power plant combustion gases treated in the SO_2 Absorption System. The calciner gas is of sufficient strength to be used as a feed for the manufacture of sulfuric acid.

The small, sulfur burning acid plant (Fig. 6) required some modifications to enable it to accept the calciner gas. Provisions were also made during these modifications allowing the plant to burn sulfur as an alternative source of SO_2 or to operate on a combined feed from both combustion of sulfur and gas from the regeneration plant.

3.3.1   Acid Plant Modifications

The principal element replaced in the acid plant was Main SO_2 Blower, K-901. The original blower handled only air required for the conversion of SO_2 to SO_3 and was not designed to be gas tight (as required when feeding the acid plant with gas containing SO_2), or capable of the required

TABLE 6
SULFURIC ACID UNIT FEED GAS
COMPOSITION, MOLE %

Source Of Gas	N_2	CO_2	O_2	H_2O	SO_2
Regeneration Section	73	6	5	7	9
Sulfur Burning	79		12		9

FIG. 6

SULFURIC ACID PLANT — PROCESS FLOW DIAGRAM

AT ESSEX CHEMICAL CO RUMFORD, R I

- 43 -

control of suction pressure for operation of the re-
generation plant. The replacement blower is an axial flow
compressor of 5,240 CFM capacity driven by a 200 HP motor.
It is capable of a suction pressure of up to 44 in. H_2O for
the venturi pressure drop, duct and equipment losses, and
calciner draft at the regeneration plant, and a 75 in. H_2O
discharge pressure for the acid plant. The unit was de-
signed to handle either air or a typical feed gas as shown
below:

ACID PLANT FEED GAS

SO_2	6.8%
O_2	9.4%
N_2	74.7%
CO_2	8.1%
CO	0.9%

The blower was equipped with an adjustable recycle
control in order to accommodate the variable feed rate of
the regeneration plant.

Another important element added to the acid plant was
the Cold Heat Exchanger E-901. This piece of equipment
supplies the heat to the incoming cold calciner gas equiva-
lent to that available in the gas when burning sulfur in the
sulfur furnace. This is necessary to ensure that the gas
entering the first mass of the primary converter is hot
enough to sustain the reaction. The exchanger, E-901, is
a vertical shell and tube unit 3 ft. diameter x 9 ft. high
containing 1700 sq. ft. of surface. Hot gas exiting the
secondary converter enters the tube side on E-901 and heats
the calciner gas passing through the shell side to 540°F.

3.3.2   Acid Production

In the acid plant, calciner gas enters (Stream 1 on
Fig. 6) and is diluted with sufficient air through the air
filter for conversion and passes to the acid plant's drying

tower where it is contacted with 93% sulfuric acid to re-
move the water from the gas. Entrained liquid is removed
in F-901A, the Dry Tower. Any SO_2 absorbed by the 93% acid
is stripped in the new Tower (F-903), a 30 in. diameter x 15 ft. high
ceramic tower containing a 10 ft. bed of $1\frac{1}{2}$ in. saddles,
and returned to the main gas stream. The small amount of
additional air is used for trim of the oxygen concentration.
The gas is pressurized by the SO_2 blower and enters the Cold
Heat Exchanger, passes to the Converter Heat Exchanger, E-902
and finally enters the converters H-901 A & B. The heat
balance for the conversion step is maintained by using the
gas from the second mass of the Primary Converter, H-901A,
to heat the gas from the Cold Exchanger, and the gas leaving
the fourth mass of the secondary converter, to heat the
incoming feed.

Next, the stream containing 6.7% SO_3 is contacted with
98% H_2SO_4 in the Absorption Tower F-902 A & B. The gas
streams from these towers are first demisted in R-902 A & B,
then the remaining SO_2 is removed in the Tail Gas Scrubbing
section shown in Fig. 7 and Table 7 to reduce the concentra-
tion of SO_2 leaving the plant to allowable levels.

The absorbant used in the Tail Gas Scrubbing section
is NaOH solution.

In order to allow a rapid change to sulfur burning,
when the plant is operated on 100% calciner gas, the sulfur
furnace was equipped for oil firing. The combustion products
from this operation are vented to the atmosphere through a
short stack which could be bypassed. In normal operation,
however, sulfur was burned concurrently because of a low
$MgSO_3$ feed rate. This procedure had the advantage of allow-
ing a rapid change should the calciner gas flow be interrupted.
This alternative was possible because of the several dampers
which had been incorporated in the ductwork.
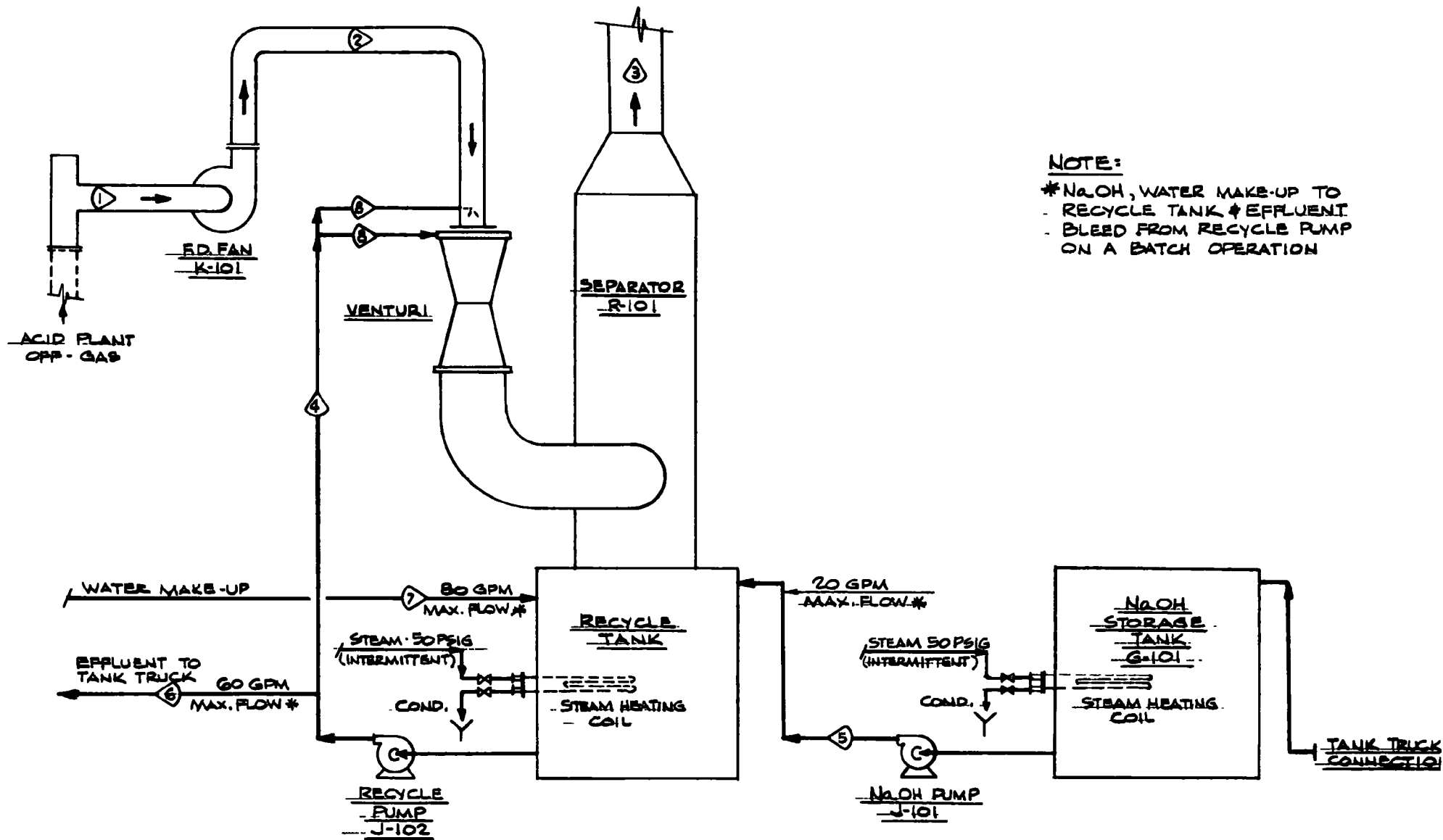
NOTE:
* NaOH, WATER MAKE-UP TO RECYCLE TANK & EFFLUENT BLEED FROM RECYCLE PUMP ON A BATCH OPERATION

ACID PLANT OFF-GAS

F.D. FAN
K-101

VENTURI

SEPARATOR
R-101

WATER MAKE-UP

80 GPM
MAX. FLOW *

20 GPM
MAX. FLOW *

NaOH
STORAGE
TANK
G-101

RECYCLE
TANK

STEAM 50 PSIG
(INTERMITTENT)

COND.

STEAM HEATING
COIL

STEAM 50 PSIG
(INTERMITTENT)

COND.

STEAM HEATING
COIL

EFFLUENT TO
TANK TRUCK

60 GPM
MAX. FLOW *

RECYCLE
PUMP
J-102

NaOH PUMP
J-101

TANK TRUCK
CONNECTION

FIGURE 7

TAIL GAS SCRUBBING SYSTEM

TABLE 7
STREAM PROPERTIES AND COMPOSITION

TAIL GAS SCRUBBER SYSTEM

STREAM NUMBERS		1	2	3	STREAM NUMBERS		4	5	6	7	8
Temperature	°F	160	165	77	Temperature	°F	77	Amb.	77	Amb.	77
Pressure	IN WC	0	14	0	Flow	GPM	152	0.6	3.0	3.0	76 •
Flow	ACFM	4,250	4140	5600							
					NaOH	lb/Min		3.75			
Dry Gas	lb/Min	279	279	276.3	Na_2SO_3	lb/Min	299		5.9		149.5
H_2O	lb/Min	0	0	5.6							
Wet Gas	lb/Min	279	279	281.9							
SO_2 (Design)	lb/Min	3.0	3.0	0.3	H_2O Liquid	lb/Min	1266	3.75	23.6	24.6	133
SO_2	PPM Dry By Volume	5000	5000	500	Total Solution	lb/Min	1565	7.5	29.5	24.6	782.5

4.0 POLLUTION ABATEMENT SYSTEM PERFORMANCE

Construction and check out of the system at Dickerson was completed by September of 1973 and gas was first passed to the unit on September 14th. In the following three month period 600 hours of operation were logged in the initial operation and debugging of the system. Most operating periods were of short duration, from 10 to 24 hours, before a system problem would force a halt. The major problem area encountered in the earliest runs was the MgO feed system, where plugging occurred in both the mix tank and slurry lines. The plugging was partially remedied by two modifications: the installation of a premix tank before the slaking tank to assure complete wetting of the MgO powder with recycle liquor, and addition of a steam sparging system to the tank. Both these remedies have also been found necessary to correct similar problems in the oil-fired application.

Other shut-downs in this period were caused by leaks that developed in the venturi scrubber internal piping between first and second stages. The leaks occurred in expansion joints where sections of the recycle lines left the first stage reservoir. Testing showed the joints supplied were off-specification stainless steel that was not resistant to this acidic stream.

Despite these problems two sequential six-day runs interrupted by a 24 hour boiler outage, were attained in the preliminary operations. While these runs did show the operability of the entire system their usefulness in assessing chemical stability was limited because of high entrainment losses from the venturi which prevented equilibrium conditions from being attained in the recycle streams. A low SO_2 removal efficiency was also noted in the preliminary testing.

An inspection of the scrubber in January 1974 showed that off-specification material, unresistant to the acidic environment of the first stage, had also been used in bolts, nuts, hanger rods, spray nozzles and some piping in the vessel. A major shut-down extending over the next six months was taken to replace corroded parts and repair damaged areas. A policy was also adopted to test each replacement item to ensure that it was of the specified type 316 stainless steel. A brief verification run was made at the beginning of May and the new problems which it uncovered were corrected in the following weeks, prior to starting regular operations.

During this initial operating period MgO regeneration was not available to the Dickerson plant. The EPA unit located at Rumford, Rhode Island was being used exclusively for regeneration of the MgO from the oil-fired system prototype. The regeneration plant was not scheduled to be available for Dickerson Station till July 1, 1974, when PEPCO would then have exclusive use of the facility. In anticipation of this use, PEPCO sent three rail cars of $MgSO_3$ from its operations to the Rumford facility for preliminary testing of magnesium sulfite derived from coal fired operation.

Before operations with regenerated MgO were started at the power plant some additional test work was conducted in June 1974. The low SO_2 removal efficiency, first noted in the debugging runs, was confirmed by these test runs and attributed to a low (1" to 3" $\triangle$P) second stage pressure drop. A restrictor, to reduce the second stage throat area by 40%, was designed in order to increase the pressure drop to design value.

The test runs exhausted the initial supply of MgO which had been delivered for start up operations. The abatement

system was idle for another six week period, awaiting a new shipment of MgO, the return of regenerated magnesia from Rhode Island and installation of the throat restrictor.

4.1 DEVELOPMENT TEST PROGRAM

The silos at the regeneration plant were completely emptied of all Boston Edison $MgSO_3$ in July 1974 and filled with PEPCO material from the rail cars. (The lack of any size reduction or lump breaking equipment in the path between the Dickerson dryer and regeneration plant calciner caused unloading problems then, and throughout the entire program). The operation, after a brief one-day adjustment period, produced a calciner product which tests showed to be of acceptable quality for recycle.

When the PEPCO $MgSO_3$ was processed in the calcining facility, it was found necessary to add carbon to the feed to effect the reduction of magnesium sulfate. The oil derived calciner feed had contained sufficient carbon to satisfy the reduction reaction needs as the absorber, in the oil-fired application, treated the gas directly from the boiler. This "scrubbed" out the soot and uncombusted fuel associated with oil-fired applications which not only reduced the power plants particle emissions but also provided the 0.5 to 1% carbon required in the process for reduction of $MgSO_4$.

Because of the necessity to prevent fly ash contamination of the recycled magnesia in the coal-fired application, the incoming flue gas at PEPCO was precleaned (by ESP and/or scrubber) to remove the fly ash. This also removed any carbon sources from the flue gas before it entered the second stage.

A supply of petroleum coke was located and added in the required proportions with the calciner feed. This was continued throughout the integrated operations at the acid plant with Dickerson Station.

These initial operations at the regeneration plant also saw the return of the "slide" problem which had been encountered and partially solved for the oil-fired application. (A "slide" was a description of a rapid emptying of a part of the calciner charge before decomposition of all the $MgSO_3$ in it). The slides caused overloading of the materials handling equipment on the kiln discharge, when they occurred, which forced a reduction in the kiln feed rate. Analysis of the product after a slide showed several percent of undecomposed $MgSO_3$. The frequency of occurrence of slides was eventually related to the size distribution of the entering feed. It was shown that a high percentage of fines in the feed triggered them. By adjusting the methods of operation of the dryer to reduce the amount of fines in the dried $MgSO_3$ during the oil-fired application calciner feed rates up to 80 lb/min were able to be achieved.

A different type dryer than the one used in the oil-fired boiler application had been designed for the PEPCO operation. (A counter-current design dryer had been installed at Boston Edison Company's Mystic Station while a co-current design dryer was installed at Dickerson Station). This difference in dryer types was one of the major equipment differences between the oil-fired boiler and coal-fired boiler applications in the MgO slurry dewatering process.

Analysis of the product from the PEPCO dryer showed that a higher percentage of fines were produced from the co-current dryer and that the fines could not be controlled by the tech-

niques used at Mystic Station. The slide problem limited
calciner feed rates to 40 lb/min rather than the 106 lb/min
design rate. Because of the interrupted operations of the
plant a dryer investigation could not be undertaken during
the program, and calciner feed rates were held at 40 lb/min.
However, this rate was sufficient to keep the FGD operation
supplied with recycle MgO.

At Dickerson Station a shipment of virgin MgO was received
July 29th and the first regenerated MgO was returned August
16th. With this inventory of material the performance test-
ing phase was started to provide preliminary reliability data
and optimization information.

Tests conducted over the following two weeks checked SO_2
removal efficiency prior to installation of the throat re-
strictor and tested a new configuration for MgO pre-mixing
using an eductor mixer. (The mixing test was inconclusive
because the unit obtained was too small and plugged). The
MgO slurrying system was returned to the original configura-
tion, an agitated pre-mix tank. The throat restrictor was
also installed in preparation for the series of performance
tests which were to follow.

The first six series of performance tests were started during
the last week of August and the test program continued through
the months of September with 400 hours of operation logged.
Test series conditions included full to half boiler load
with full to half design flow to the scrubber/absorber, and
inlet gas taken after the precipitators or with no pre-clean-
ing. Series designations are shown in Table 8 . A descrip-
tion of these tests and the results are presented in another
section of this report. Also incorporated into the foregoing
investigation was an analysis program of the first stage re-
cycle liquor, thickener and pond and river discharge flows

TABLE 8

PERFORMANCE TEST DESIGNATIONS

Test Series	Boiler Load (% of Design)	Scrubber Gas (% of Design)	Scrubbed Gas Pretreated
5A	100	100	E.S.P.
5B	50	50	E.S.P.
6	100	50	E.S.P.
7	100	100	NONE
8	100	50	NONE

for a number of chemical species of environmental significance.

Following these tests the plant was readied for the balance of the optimization program. Emphasis was placed on the assessment of the effect of coal fly ash on the regeneration and utilization of the recycled magnesia. A regular sampling and analysis program was initiated for flue gas monitoring and chemical determination of all major stream compositions. Over the next four months, system operations totaling 1350 hours provided much information on the effect of regeneration operations on the absorption of sulfur dioxide, operation of the centrifuge and dryer and the conditions of scrubber/absorber operation.

Attainment of the major goals of the project, multiple recycles of magnesia and conclusive demonstration of system reliability were thwarted by the deteriorated condition of the piping which evidenced itself almost immediately after entering this phase of the demonstration program. As the performance testing was completed the first of many failures in the rubber lined, first stage recycle piping occurred forcing a shut-down of the system. During the rest of the operations first and second stage pipe failure was the most common shut-down cause. A summary of operations during this period is given in Table 9 .

Some improvements were obtained when several sections of the second stage recycle pipe were replaced but leaks in the other sections and the unrectified first stage problem limited operating periods to days rather than weeks. The longest continuous run during this period was eleven days from December 13th through December 23rd. Operations resumed on December 27th and continued into January 1975 with tests of first stage operation alone. These tests also

TABLE 9

SUMMARY OF OPERATIONS FGD SYSTEM
PERFORMANCE TEST PHASE

Week Ending	Goal	Problem Areas	Number Of Interruptions	Avg. Load	Hours Of Scrubber Operation
11/01	System Repair				0
11/08	Repair				0
11/15	Operate at design load	Centrate Pump	1	60-80%	88
11/22	Establish dependable & continuous operation	Bucket Elevator[1] & Piping Leaks	2	60-70%	84
11/29	Continuous Operation	Dryer Fan Drive	1	70-80%	123
12/06	Continuous Operation	Piping Leaks	1	75-80%	77½
12/13	Continuous Operation	Piping Leaks & valve failure	2	60-80%	114½
12/20	Continuous Operation	Piping Leaks	1	60-85%	159½
12/27	Continuous Operation	Piping leaks & valve failure	2	60-90%	83½
01/03	Continuous Operation	Piping leaks	1	80-90%	53
01/10	Operate 1st Stage only			90-100%	78
01/17	Continuous Operation	MgO inventory depleted	1	60-70%	75
01/24	Continuous Operation	Piping Leaks & Conveyor Jam	1	50-60%	30
01/31	Continous Operation	Piping Leaks	1	50-60%	37½
					1003.5

1) Marginal bucket elevator capacity limited operation to average 70% of design

OVERALL AVAILABILITY 46.1%

provided data on first stage SO_2 removal capacity. A final series tested recycle liquor flow effect on SO_2 removal efficiency.

Operation of the regeneration plant during this period was sporadic because of the outages at Dickerson and the resultant interruptions in feed to be calcined. The major mechanical problem encountered at the regeneration plant was a failure of the pinion gear in the main drive on the calciner (due to misalignment and lack of lubrication). A replacement was locally fabricated and the unit was only out of service for two weeks during December. A summary of operations at the regeneration facilities is given in Table 10.

During the program approximately 2247 tons of $MgSO_3$ were processed to MgO at the acid plant.

During January 1975 plans were made for major overhaul of the PEPCO FGD system including replacement of all "thin" second stage pipe and repair of several sections of first stage rubber lined pipe. This work was scheduled in conjunction with PEPCO's planned 12 week overhaul of its No. 3 boiler and turbine. Repair of the FGD system was for the most part, completed by April. PEPCO, however, discovered a major defect in the No. 3 turbine during their boiler overhaul which necessitated a number of extensions of their boiler outage. Eventually the outage extended to the end of July 1975. The outage extensions created secondary problems in the financing of the project and the program was terminated.

TABLE 10

SUMMARY OF OPERATIONS CALCINER SYSTEM
PERFORMANCE TEST PHASE

Week Ending		Operated For Hours
11/01/74	Maintenance on Bucket Elevator	0
11/08/74	Routine Maintenance	0
11/15/74	Routine Maintenance - Accumulate $MgSO_3$ Inventory	0
11/22/74	Routine Maintenance - Accumulate $MgSO_3$ Inventory	58
	START-UP	
11/29/74	MgO Production for PEPCO	47
12/06/74	MgO Production for PEPCO	87.4
12/13/74	MgO Production for PEPCO	24
12/20/74	Maintenance on Calciner Main Drive and MgO Production for PEPCO	8.9
12/27/74	Complete Repairs on Calciner Main Drive and MgO Production for PEOCO	0
01/10/75	Run Test on Boston Edison $MgSO_3$ without Coke Addition	100.9
01/17/75	Test PEPCO $MgSO_3$ without Coke Addition	44.2
01/24/75	MgO Production for PEPCO	4.5
01/31/75	MgO Production for PEPCO	7.9

4.1.1 October 1974 - Details

Regular operation of the FGD system at Dickerson was resumed after the performance test work on September 30. This first operation was stopped after three days when problems with the MgO premix tank forced an outage. The system was restarted at 1 p.m. on the 3rd and ran continuously for the next 12 days at approximately 50 to 80% of design load. A failure of a 14" rubber lined pipe elbow in the first stage recycle loop forced another outage at 4 p.m. on the 14th.

The analytical program was fully implemented by October 16, 1974. The scrubber ran from a start up at 12:00 a.m., October 16 to 9:00 a.m., October 18. A planned shutdown was taken to repair several leaks in the first stage recycle lines and to attempt to increase the flows in MgO slurry feed system. The scheduled repair was completed by noon, October 18, however, after operations resumed low flow of MgO slurry resulted in loss of pH control in the second stage. Leaks in the MgO magnetic flow meters also caused delays. Flue gas treatment resumed at 3 a.m. October 23, 1974.

During the night of the 24th problems again occurred in the MgO slurry system with line plugging reducing pH in the second stage to 6.6; however, the situation was corrected and the system ran till 9 a.m. on the 25th when the unit was shut down for a boiler tube leak. The boiler was repaired by October 28, but the scrubber system was waiting for maintenance and was not returned to service.

4.1.2 November 1974 - Details

During the 30 day period, November 1 to November 30, 1974, the scrubber operated 318.9 hours out of a possible 720 hours for a 44.3% availability. During the period of operation the unit ran at 50% to 100% of design gas load

resulting in a total average available capacity for the month of November of 34%. Because of scheduled outage in the earlier portion of the month for leak repair and overall maintenance, most running time was logged in the latter portion of the month.

Scrubber Operation and Comments

The scrubber was brought on-line at 2 a.m., November 10, at 80% of design flow. Attempts to increase the gas flow to full load were hindered, as problems in the MgO-slurry feed system prevented pH control at increased loads. The system operated steadily, adjusting the scrubber gas flow to maintain a pH of 5.7, till 2:20 a.m. on the 11th, when the scrubber was taken off-line due to a leak at the inlet of the second stage bleed line.

Repairs were completed at 8:00 p.m. on the 13th. The system was returned to operation and the scrubber load was varied between 60 and 80% to compensate for station load changes during this period. On November 15, at 10 a.m., a reduction to 1/2 load was made to repair a leak in the centrifuge. When the centrifuge was diverted, the solids in the second stage recycle slurry reached a high level and the low load was maintained until the solids level was centrifuged down. At this time it was noted that the flow to the centrifuge had dropped to 55 gallons per minute, which prevented operating the unit at design gas loading. This was corrected by operating with both the main and spare pump. The plant continued in operation with the scrubber load gradually increased to 100%, holding pH in the 7.0 to 7.3 range. (Normal operating practice was to control pH by maintaining a steady MgO feed, adjusting the gas flow to maintain the pH set point affected by variations in the coals sulfur content).

A leak developed in a first stage recycle control
valve and the unit was taken off the line to make repairs
on the 16th. Operations resumed on the 19th and continued
through the 21st when the belt drive failed on the dryer
I.D. fan.

The fan repairs were completed and gas was put back
into the scrubber at 3:15 p.m. on November 23, but by 11 p.m.
the No. 3 boiler developed a tube leak, forcing a shutdown.
This was repaired and operations resumed by 2:40 a.m. on the
24th, six hours later another interruption was needed to re-
pair a bearing on the dryer product screw conveyor. The
system was returned to operation 2:45 that afternoon and
operated continuously through the end of the month. Operat-
ing adjustment had to be made during this period to accommo-
date generating station coal feeder problems.

During this final fifteen day period the scrubber
operated a total of 241.6 hours out of a possible 360 hours
for a 67.1% availability (51.7% average available capacity
based on a 77% of design gas flow).

4.1.3   December 1974 - Details

During the 31 day period, December 1, 1974 to
December 31, 1974, the scrubber operated 430.8 hours of a
possible 744 hours, an availability of 57.9%.

During the month of December various new studies were
initiated and the wet chemical method for the specific deter-
mination of $MgSO_3 \cdot 6H_2O$ and $MgSO_3 \cdot 3H_2O$ in the mixture was
used to determine the hydrate ratio in the centrifuge cake
samples. Previously, the ratio of $MgSO_3 \cdot 6H_2O/MgSO_3 \cdot 3H_2O$
had been approximately determined on the basis of percent
combined water (water of crystallization) as determined on an
OHAUS moisture balance.

Chloride in the system was also measured as a function
of operating time.

Scrubber/Absorber Operation and Comments

The run which had started on November 24 had to be aborted on December 1 after a leak developed in the rubber-lined bleed line to the thickener area. Operations were again resumed on December 5 and continued till 4:30 a.m. on the 11th when leaks in the first stage bleed line again forced an outage. During this period adjustments in operating conditions were used to control problems of MgO feed, station coal handling and centrifuge cake buildup in the discharge hopper.

Operations were resumed at 6 p.m. on the 13th and this run continued till the 23rd when leaks in both the first and second stage discharge headers forced a shutdown.

The system was restarted on the 27th but the run was aborted on the 29th after 64 hours of operation with another recycle pipe failure.

4.1.4 January 1975 - Details

Measurements of the pipe wall thickness and observations of the pipe involved in the numerous failures which had been encountered showed that a major system overhaul and pipe replacement program was necessary if any sustained operations were to be achieved. PEPCO has rescheduled an overhaul of the No. 3 generating unit to 1975. This was a five year inspection and overhaul of the generator originally due in 1973. Plans were made to recondition the scrubber system during the boiler outage scheduled to start in January 1975. Some additional test work was conducted with the pollution abatement system during January while waiting for the planned boiler shutdown.

These tests included four days of operation with first stage (particle control) only, and another series of tests to determine the effect of variation of recycle flow rate on SO_2 removal efficiency.

4.2 UTILITIES CONSUMPTION

Electric power consumption (in MW/Day) of the particle control and flue gas desulfurization system installed at Dickerson Station is given in Table 11 for the major operating periods of the test program.

Also included in the table are data on average fuel consumption for the dryer used in the FGD system along with an approximate gas flow processed during the period. While there is some effect caused by the variation in fuel sulfur content on the amount of centrifuge cake produced it appears that a significant factor in dryer fuel oil consumption is the weather. Fuel consumption is seen to increase during the winter months and decrease during the summer months while the gas flow processed through the system remained the same.

4.3 MgO CONSUMPTION

Magnesia consumption during the fifteen month period of operation of the plant was high. It is evident that the loss rate during the period of initial operations was higher than the loss rate during the latter planned operations phase.

MgO shipments to the plant were made corresponding to these two periods. An initial inventory of 357 tons of MgO was shipped to Dickerson between August and December of 1973 for the start-up operation. An additional 281.3 tons of virgin magnesia were added as make-up between July and November 1974 for the planned operations phase. The addition of make-up MgO at Dickerson between July and November is given in Table 12.

TABLE 11
UTILITIES CONSUMPTION
FGD SYSTEM

Major Operating Periods	Approximate Gas Flow % of Design	Average Electric Power Consumption MWH/Day	Average Dryer Fuel Consumption GPM
April 25-30, 1974		38.6	0.57
June 13-16, 1974		39.8	0.39
Aug. 13-17, 1974		34.8	0.33
Sept. 3-11, 1974		27.7	0.38
Oct. 16-18, 1974	66%	41.8	0.72
Nov. 24 - Dec. 1, 1974	75%	53.3	0.93
Dec. 6-10, 1974	70%	49.0	0.95
Dec. 14-23, 1974	67%	45.5	0.91
Dec. 27-29, 1974	80%	57.5	0.96
Jan. 12-14, 1975	70%	50.0	0.93
Aug. 12-14, 1975	70%	50.0	0.54
Aug. 22-26, 1975		33.8	0.32

TABLE 12

MgO MAKE UP

FGD SYSTEM

Date	Quantity Of Virgin MgO Received
7/29/74	67.6 Tons
9/1/74	73.4 Tons
10/24/74	67.4 Tons
11/4/74	72.9 Tons
	281.3 Tons

4.3.1 Losses - Preliminary Operations

Estimation of dryer product generated at Dickerson Station based on shipping records showed 485 tons of $MgSO_3$ were produced from the initial charge of 357 tons of MgO. This accounts for only 55% of the dryer product that should have been produced based on the design material balance.

An inventory evaluation also showed that 144 tons of MgO equivalent were lost during the same period giving a loss rate of 40.4% of the material fed. Since no magnesia regeneration was being performed during the early period the losses were essentially confined to the FGD system site. Part of the loss can be attributed to a number of unmeasured spills and discharges during this period, some of these were:

1) Material discarded when cleaning out the MgO slurry system after a plug.

2) Material lost when draining the scrubber for repair work.

3) Spills of dryer product due to material handling equipment overloads.

Another major loss point was entrainment and overflow from the second stage of the scrubber. The few chemical analyses of recirculating slurry taken during the early period showed a maximum of 8% magnesium sulfate in this stream. Since a concentration of 15% to 18% $MgSO_4$ is expected in the equilibrium system the low concentration indicated a large bleed (or leak) from the magnesia recycle loop.

Chemical analysis of the fan sump discharge during the performance testing conducted in August and September 1974 showed high levels of magnesium salts and solids in this stream. Analysis showed $MgSO_4$ concentrations as high as

10% again indicative of excessive entrainment. The entrainment was probably the major loss point sustained during these preliminary operations.

4.3.2 Losses - Planned Operational Testing Period

Corrective action was taken to reduce the entrainment from the scrubber system by lowering the operating liquid level in the second stage reservoir from 80% to 40% to reduce gas velocity in that zone. Analysis of the fan sump pit discharge in early October 1973 showed much lower $MgSO_4$ concentration. Losses from this source were reduced to less than 0.5% (based on Mg^{++} content of the fan discharge) during the final three months.

4.4 MgO REGENERATION

MgO inventory recording was started at Dickerson in October 1974 and the weekly inventory records are summarized for the period of operation in Tables 13 and 14 .

Test work at Dickerson in August had been carried out using regenerated MgO; however, the losses, which had occurred before the development program was initiated, necessitated re-plenishment of the inventory with virgin MgO. During September and October 141 tons of MgO were received and 109 tons of re-generated alkali were returned from Rumford for operation of the integrated system. During October the Dickerson system operated 420 hours of a possible 647 hours, consuming 80% of the alkali available and producing 482 tons of dryer product.

Thus, at the start of November, 141.4 tons of MgO and 100.6 tons of $MgSO_3$ were on hand at Dickerson. Of the MgO, approximately 65% had been regenerated at least twice. Be-fore operations were resumed at Dickerson 73 additional tons of virgin MgO was received and added to the silo. Inventory on November 8th, for the resumption of Phase II of the de-velopment program, was 213.3 tons of MgO and 100.6 tons of

TABLE 13

INVENTORY SUMMARY BY WEEK-FGD SYSTEM

Week Ending	MgSO₃ (Tons)		Closing (Tons)	
	Produced	Shipped	MgO	MgSO₃
11/1/74	0	19.5	110.4	56.6
11/8/74	0	0	182.3	56.5
11/15/74	32.8	20.9	150.5	68.4
11/22/74	98.4	35.4	105.2	131.4
11/29/74	142.5	141.2	110.1	123.3
12/6/74	54.0	141.4	131.0	14.0
12/13/74	116.8	35.1	68.2	95.9
12/20/74	157.9	108.6	26.9	145.1
12/27/74	83.6	114.6	73.9	96.2
1/3/75	65.0	0	48.9	161.2
1/10/75	0	0	48.9	161.2
1/17/75	85.9	88.5	54.8	158.5
1/24/75	8.0	76.3	118.3	90.2
1/31/75	---	43.2	105.1	71.5
		824.7		

Note: The table header shows "MgSO₃ (Tons)" spanning the Produced and Shipped columns.

TABLE 14

INVENTORY SUMMARY BY WEEK-REGENERATION SYSTEM

Week Ending	MgO (Tons) Produced	Shipped	Closing (Tons) MgO	$MgSO_3$
11/1/74	0	11.9	31	44
11/8/74	0	0	31	44
11/15/73	0	0	31	44
11/22/74	30	0	61	8
11/24/74	26.4	91.7	11.5	45.1
12/6/74	50.3	35.5	26.3	52.6
12/13/74	13.3	27.8	11.8	62.1
12/20/74	4.9	15.7	0	156
12/27/74	0	0	0	233.4
1/3/75	48.2	12.8	35.4	126.4
1/10/75	56.5	0	90.9	0
1/17/75	30.6	53.8	67.7	7.6
1/24/75	2.5	71.0	1.5	85.0
1/31/75	4.4	0	5.9	135.5

$MgSO_3$ (total MgO equivalent 250.6 tons). The approximate inventory on December 27th, after 730 hours of operation, was 73.9 tons of MgO and 329.6 tons of $MgSO_3$ (total MgO equivalent 196 tons). The inventory difference of 54.6 tons is attributed to process losses, approximately 150 lb/hr. This may be contrasted with 223.7 lb/hr. loss sustained in the final operational period of the New England SO_2 Control Project. As was the case in the oil-fired application, most of these losses occurred from uncontrolled spills and bleed streams at the regeneration plant; however, during this period, November to January the regeneration plant only operated a total of 226.3 hours accounting for the lower loss rate during the PEPCO project.

By the end of December the entire inventory had been processed through an additional cycle. Some limited runs were conducted in January with 142 hours of two stage operation at Dickerson which initiated a new cycle of regeneration.

At Rumford, 194 tons of $MgSO_3$ remaining from the New England SO_2 Control Project had been in storage since July 1974. The first rail car of this material (80 tons) was processed with dryer product from Dickerson during January 1975 in a rate check of the calciner feed capacity.[1]

An examination of the statistical summaries for the Dickerson operations reveals a trend of a gradual increase in unreacted MgO in the recycle liquor similar to that seen in operations at Boston Edison's Mystic Station.

Period	MgO in Recycle (Avg.)	Standard Deviation
11/10-11/29	3.81%	2.90
12/1-12/29	3.95%	3.10
1/11-1/27	5.79%	1.40

4.5 POST OPERATION FGD SYSTEM INSPECTION

In January 1975, before the FGD system overhaul, the

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[1] Due to lack of operations at PEPCO and eventual termination of the entire program the regenerated MgO never found use at Dickerson Station.

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major pieces of equipment in the plant were inspected to determine their condition. The scrubber vessel was found to be in good condition with only a few, small internal areas where its plastic lining had failed. The fan was found to be in excellent condition as was the secondary mist eliminator vessel. Most other equipment, vessels and pumps in the system were in good to satisfactory condition. Major failures and unsatisfactory conditions were noted for the first and second stage recycle piping. A report of the inspection is given in Appendix 1.

An operating history of the plant showing the number of runs started and their duration is given in Table 15.

Problems which had an adverse effect on operability of the FGD system were divided into several catagories which are described in the following sections.

4.5.1 1st Stage Piping

Problems with some portion of the 1st stage piping system were the most frequent cause of scrubber shutdowns and accounted for about one-third of the total. There are five separate, but interrelated causes of failure that have been recognized, as follows: (a) pulsation in the piping near the inlet to the scrubber, (b) high liquid velocities at some points in the system, (c) the presence of sharp objects in the system due to corrosion of stainless steel, (d) rubber lining thinner than specified, (e) poor adhesion of rubber lining to the steel pipe.

(a) Pulsation in the piping near the inlet to the scrubber caused several failures of the pinch valve liners. The valves were finally replaced with rubber lined spool pieces. The pulsation also contributed to the failure of the elbows just before the scrubber inlet in all three of the 6-inch lines to the center nozzle. The cause

TABLE 15

OPERATING HISTORY
FGD SYSTEM

Date	Number Of Runs Started	Duration Of Runs, Hours
1973:		
Sept.	2	46
Oct.	2	90
Nov.	4	142
Dec.	3	249
1974:		
Jan.	1	192
Feb.	0	0
Mar.	0	0
Apr.	5	174
May	1	100
June	0	0
July	0	0
Aug.	6	248
Sept.	6	326
Oct.	4	344
Nov.	5	318
Dec.	6	420
1975:		
Jan.	3	131
TOTALS	48	2,780

of the pulsation was eventually traced to the
hydraulic design of the piping system. The
pressure drop between the high point in the sys-
tem and the scrubber inlet was less than the
vertical distance, resulting in an alternate fill-
ing and emptying of the line. Corrective action
has been taken by the installation of restrictive
orifices in each of the inlet pipes, immediately
before entrance to the scrubber. Also, new tan-
gential nozzles have been designed for a higher
pressure drop--sufficient to compensate for the
head between the restrictive orifice plate and
the nozzle outlet.

(b)   Excessive liquid velocities caused failures in the
1st stage bleed control valve and in a 316 stain-
less steel pipe section immediately after the con-
trol valve. The corrective action taken (some-
time prior to August 1974) was the installation of
three eccentric orifice plates in horizontal piping
runs in order to increase the pressure at the down-
stream side of the control valve, thus permitting
the valve to operate in a more nearly open position
with reduced velocities through (and immediately
after) the valve. The eccentric orifice plates were
designed for velocities that would be adequately
low for normal conditions. However, with the actual
conditions, as will be discussed in (c), (d) and
(e), failures of the rubber lining occurred adjacent
to and downstream from the eccentric orifice plates.
The plates were removed, leading to a recurrence of
failures in and after the control valve. Correc-
tive action has now been taken by the installation
of a concentric orifice flange at the short, vertical,
discharge end of the line.

(c) Sharp pieces of metal were present in the liquid
     cycle on numerous occasions as a result of cor-
     rosion failures of stainless steel as will be
     described in a subsequent part of this section.
     The adverse effects were aggravated by conditions
     to be discussed in (d) and (e).

(d) The rubber lining as supplied was thinner than
     the 1/4" specified. This was substantiated in
     December 1974 by micrometer measurements of rub-
     ber samples from five locations, selected at ran-
     dom from pipe sections that failed.
     Readings, in inches, were as follows:

1	2	3	Avg.
0.167	0.150	0.161	0.159
0.160	0.155	0.160	0.158
0.156	0.153	0.154	0.154
0.160	0.160	0.150	0.157
0.139	0.133	0.133	0.135
		Average	0.153

In every instance the original "waffle" pattern
was still on the rubber and there was no evidence
of any erosion. Replacement pipe linings have
been a full 1/4-inch thickness and there have been
no failures of any of the replacement linings.

(e) Adhesion of rubber lining to the steel has been
     poor. This has not been measured quantitatively
     but has been judged qualitatively by pulling por-
     tions of the lining from pieces that have failed and
     also by inserting a knife or fingernail between steel
     and rubber flanges. The significance of poor adhe-
     sion is that it allows a small failure to grow rapidly
     into a large one that cannot be controlled with ex-
     ternal patches.

4.5.2 2nd Stage Piping

Failures of second stage piping became quite extensive in October 1974, and several replacements had to be made. Portions of the 16-inch and 20-inch piping that wore were repaired by applying a polyester or epoxy coating, reinforced with glass fabric to the thin area.

Failures are ascribed to a combination of erosion and corrosion. For long-term commercial use it is planned that rubber-lined piping will be specified.

An extensive series of piping thickness measurements were made in late December 1974, using an ultrasonic gauge, with the primary objective of establishing which portions of the piping system needed to be replaced (or covered) in order to provide for three months of additional operation.

4.5.3 Corrosion of Stainless Steel

During early operation of the scrubber there were a number of failures of stainless steel elements fabricated of type 304 or other types that are less corrosion resistant than type 316. Type 316 has performed with mixed results, depending on the specific environment encountered.

The first stage tangential inlet nozzles corroded and failed. It was concluded that the cause of failure in this case was the condensation of strong sulfuric acid from the flue gas onto the outer surface of the pipes--a mechanism similar to that which has been encountered in air heaters when flue gas is cooled to too low a temperature. Replacement nozzles were fabricated in both glass reinforced polyester plastic and stainless steel coated with glass reinforced polyester. Stress has been another cause of failure of type 316 stainless steel exposed to first stage liquid as evidenced by extensive attack where threads had been cut or cold bends had been made. This was particularly noticeable in the case of bolts in the south thickener and hanger rods supporting the first stage demister piping.

Replacements for the latter were heat treated after fabrication in order to prevent attack from this cause.

In the absence of either undue stress or conditions that permitted condensation of strong acid from flue gas, type 316 provided satisfactory performance. Examples are the hold-down straps for the mist eliminators, where there was general light pitting but no measurable loss of thickness and short sections of piping to the tangential nozzles, just before entrance to the scrubber, where thickness was very nearly equal to specifications and there was no visual evidence of corrosion.

5.0 PERFORMANCE TEST RESULTS

Performance tests of the particulate emissions and SO_2 control system installed at Dickerson Station were conducted by York Research Corporation. The testing period extended from August 26, 1974 through September 21, 1974 following a preliminary period in September for equipment set-up, familiarization, establishing gas velocity profiles and gas flow measurement.

The performance testing used methods detailed in the Federal Register, Vol. 36, No. 247, 1974 for:

    a)   Gas Analyses by Method 3
    b)   Particle Sampling Outlet by Method 5
    c) SO_2 Removal Efficiency by Method 6
    d) SO_3 Determination by Method 8

Particle sampling at the inlet was conducted in accordance with ASME PT6-27 (modified).

Sizing of the collected particle samples was done micro-scopically. This method is semi-quantitave as the actual de-minsions measured are the diameter or length of the particle. This gives a general indication of the particles size and a mathematical approximation of its mass.

The data have been abstracted from York Research Corporation's Report Y-8513 dated January 31, 1975.

5.1 PARTICLE EMISSIONS

Results of the particle emissions tests are summarized. in Table 16. Each result represents the average of four tests per series. Additional data are also provided on gas flow and composition.

TABLE 16
PARTICLE EMISSIONS TEST RESULTS
FGD SYSTEM

Test[1] Series	Boiler Load MW	ESP[2]	ΔP[3] in H_2O	Flue Gas Flow 10^3 ACFM		Temp. °F	CO_2 %	O_2 %	Gr/SCFD 12% CO_2	Gr/ACF
5A	183	Yes	10.2	299	Inlet	242	12.2	6.5	0.190	0.131
					Outlet	126			0.002	0.002
					Efficiency				99.0	98.5
5B	96	Yes	11.1	161	Inlet	241	11.9	6.7	0.101	0.070
					Outlet	116			0.005	0.004
					Efficiency				95.0	94.3
6	185	Yes	10.6	153	Inlet	240	12.3	6.4	0.120	0.085
					Outlet	136			0.007	0.007
					Efficiency				94.2	91.8
7	183	No	10.7	282	Inlet	245	11.9	6.5	3.654	2.474
					Outlet	118			0.014	0.011
					Efficiency				99.6	99.6
8	176	No	10.0	127	Inlet	232	11.6	7.1	3.276	2.212
					Outlet				0.017	0.014
					Efficiency				99.5	99.4

[1]Average of four (4) tests per test series

[2]Indicates whether the flue gas treated by the scrubber stage passed through the electrostatic precipitator (Yes) or not (No).

[3]First stage (scrubber) pressure drop.

As noted in Section 4.1 the conditions over which the tests were conducted were varied to provide data on a range of operational situations, taking gas either ahead of or after the precipitator.

These results show the low particle emissions attainable using the Chemico wet scrubber. In the tests taken after the precipitator outlet particle emissions were less than 0.01 gr/SCF for all cases despite the low inlet loading. For the full boiler load, full gas flow case (5A) fly ash emissions were less than 4 lb./hr. When the system was tested without the precipitator scrubber particle removal efficiencies of 99.5% plus were obtained.

As the installation was designed to process only one-half of the total gas flow from the boiler the results noted above do not represent the actual stack emissions as this consists of both the contribution from the scrubbed flue gas and the particle load remaining in the unscrubbed portion.

An estimate of precipitator efficiency can be obtained from the test results by using the inlet loading to the test series before and after the precipitator as a measure of the inlet and outlet condition of the precipitator. This estimate is shown in Table 17.

The improvement in the efficiency of precipitator operations, as shown in Table 17, as the amount of gas flow to it decreases was confirmed in a later series of tests which showed an increase to 99% efficiency in the ESP when the gas flow was divided equally between the scrubber and the precipitator.

5.2 SO_x EMISSIONS

Results of the sulfur oxides emissions tests are summarized in Table 18 and represent the average of four de-

TABLE 17

ESTIMATE OF

ELECTROSTATIC PRECIPITATOR EFFICIENCY

Boiler Avg. Load	Particle Load (Avg.) Inlet	Outlet	Efficiency (Based) On 3.6 GR/SCFD Inlet Load	Source (Test Series)
MW	Gr/SCFD	Gr/SCFD		
183	3.654			7
183		0.190	94.8%	5-A
96		0.101	97.2%	5-B

TABLE 18

SO_x EMISSIONS TEST RESULTS

FGD SYSTEM

Test Series	$P^{(1)}$ in H_2O	SO_2 (PPM) Inlet	SO_2 (PPM) Outlet	SO_2 Removal %	SO_3 (PPM) Inlet	SO_3 (PPM) Outlet
5A	15.1	779	78	90	34.6	3.56
5B	6.6	1373	157	88.7		
6	5.1	800	137	82.9	47.5	3.31
7	14.7	1418	88	93.9	2.9	0.64
8	5.2	1419	156	89.0	1.8	0.41

[1] Second stage (absorber) pressure drop.

*Test results abstracted from York Research Corporation, Final Report, Y-8513, Jan. 31, 1975.

terminations per series. Except for tests series 5A
most results for SO_2 removal were reasonably close to the
average, in test series 5A removal efficiencies measured
in the individual tests ranged from 83.5% to 96.8%.

In general, the trends noted by these results (reduced
efficiency at lower pressure drop and lower inlet SO_2 con-
centration) are similar to those seen in the oil fired appli-
cation of this prototype FGD method. The correlation de-
veloped from the New England SO_2 Control Project has been
used to analyze the data from this project.

SO_3 inlet and outlet concentrations were also deter-
mined during the performance test series and show a signi-
ficant reduction across the two stage scrubber for both gas
taken before the electrostatic precipitator and the gas
taken after the electrostatic precipitator cases.

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[1]Maryland State Department of Health and Mental
Hygiene 10.03.39 "Regulations Governing the Control of
Air Pollution in Area IV", maximum allowable emission
of particulate for all solid fuel burning installations
greater than 200 million BTU/hr. furnace are 0.03 GR/SCFD.

TABLE 19

REMOVAL EFFICIENCY FOR PARTICLE SIZE RANGES

Test Series	Removal Efficiency Above 5μM	1 to 5 μM	Below 1μM
5 - 1	99.0	97.5	94.6
5 - 2	99.8	99.2	99.0
5 - 3	99.0	99.9	98.6
5 - 4	98.8	97.5	97.0
Average	99.2	98.4	97.3

TABLE 20

COAL ANALYSES - COMPOSITE TO BUNKER #3

DATE From	1974 11-1	11-6	11-13	11-21	11-27	12-1	12-11
To	11-5	11-12	11-19	11-26	11-30	12-10	12-17
Total Moisture	6.03	5.93	8.67	7.50	7.95	9.66	10.69
Dry Volatile	22.58	22.31	21.58	21.14	22.44	23.36	25.18
Dry Ash	21.85	20.43	19.11	17.77	21.06	19.23	19.50
Dry S	2.36	2.36	2.15	2.15	2.25	2.13	2.17
Dry Btu	11,684	11,826	12,096	12,399	11,686	11,934	11,911
M&AF Btu	14,951	14,862	14.954	15,078	14,804	14,775	14,796

DATE From	12-18	12-25	1975 1-1	1-8	1-15	1-22	2-1	2-5
To	12-24	12-31	1-7	1-14	-121	1-31	2-4	2-11
Total Moisture	12.40	7.90	8.06	8.37	3.18	8.19	8.70	9.78
Dry Volatile	22.99	24.66	24.26	24.74	22.21	25.12	23.67	24.62
Dry Ash	17.53	15.51	17.05	15.34	13.09	17.80	16.68	16.09
Dry S	2.42	2.41	2.42	2.20	2.26	2.06	2.28	1.88
Dry Btu	12241	12711	12467	12809	13492	12477	12553	12514
M&AF Btu	14843	15044	15030	15130	15524	15142	15061	14914

Random Sample   Arsenic   13.6 ppm

Tellurium   1.4 ppm

Selenium   1.1 ppm

6.0 PROCESS CHEMISTRY

6.1 FIRST STAGE (PARTICLE CONTROL) OPERATION

While most attention was focused on the SO_2 removal
section of the system some work was done to determine the
composition of the various important streams in the first
stage liquor loop. Tests were conducted during the perfor-
mance test work carred out in August and September 1974.

These tests involved analysis for a number of chemical
species in the streams going to the first pond, the first
stage bleed, thickener underflow and overflow, and the sump
pump discharge. Components analyzed were calcium,
potassium, aluminum oxide, magnesium, chromium, cadmium,
titanium oxide, silica, sulfates, sulfites, and chlorine.
In addition, the pH and total dissolved solids were also
measured.

In order to complete the data and provide some standard
of comparision a series of baseline analyses was done for
both the inlet and outlet of the pond system and the various
system water supplies during a period of limited activity of
the FGD system, prior to the inauguration of the performance
test work.

The data for both the baseline period and the performance
test period have been abstracted for a number of streams and
are presented in Table 21. In these tests the baseline data
are given where available, while the compositions during the
testing period (samples were taken intermittently for the
period August 29 through September 21, 1974) are presented
as an average for all tests days for the first stage bleed,
the pond (Basin #1) inlet, and pond return (Make Up Water to
Dilution Tank).

TABLE 21

Chemical Composition at Various Streams in the
First Stage - Fly Ash Removal System

Sampling Point		Potassium ppm	Calcium ppm	Magnesium ppm	Iron ppm	Cadmium ppm	Copper ppm	Chromium ppm	Mercury ppb
First Stage Bleed	Avg. All Tests	24.6	7.8	562.0	87.4		.94	1.2	12.7
Inlet to Basin #1	Baseline	n.a.	11.4	78.1	38.0	.01	.23	0.6	2.0
	Avg. All Tests	12.9	8.8	755.7	41.3	.04		0.44	
Make Up Water to Dilution Tank	Baseline	16.4	10.1	83.7	69.2	.01	2.42	0.64	2.0
	Avg. All Tests	10.9	8.8	123.2	.4	.04	.08	.13	4.7
Service Water Supply	Baseline	n.a.	13.3	83.6		.07	.49	0.74	2.0

Table 21 (Cont'd)

Chemical Composition at Various Streams in the
First Stage - Fly Ash Removal System

Sampling Point		Sodium ppm	Flouride ppm	SO_4 ppm	Phosphate ppm	Cl ppm
First Stage Bleed	Avg. All Tests	17.0	1.4	4921.0	32.4	537.0
Inlet To Basin #1	Baseline Avg. All Tests	16.2	1.0 1.5	1.0 2024.4	2.1 18.0	224.0
Make Up Water To Dilution Tank	Baseline Avg. All Tests	21.8 10.0	1.0 1.9	408.1 597.8	16.3 7.8	64.2
Service Water Supply	Baseline	45.1	1.0	39.2	2.2	

6.2 PROCESS CHEMISTRY

In an aqueous environment the following series of reactions can be envisioned for SO_2 absorption by pulverized solid MgO:

1. Slaking of MgO

$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} \qquad (6-1)$$

$$Mg(OH)_{2(s)} \longrightarrow Mg(OH)_2 \text{ (Soln)} \qquad (6-2)$$

$$Mg(OH)_2 \text{ (Soln)} \longrightarrow Mg^{+2} + 2OH^- \qquad (6-3)$$

2. SO_2 Absorption

$$SO_{2(g)} \longrightarrow SO_2 \text{ (Soln)} \qquad (6-4)$$

$$SO_2 \text{ (Soln)} + H_2O \longrightarrow H_2SO_3 \qquad (6-5)$$

$$H_2SO_3 \longrightarrow H^+ + HSO_3^- \qquad (6-6)$$

$$HSO_3^- \longrightarrow H^+ + SO_3^{-2} \qquad (6-7)$$
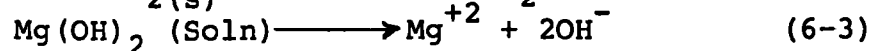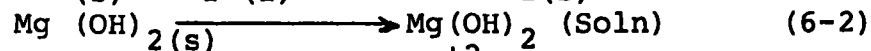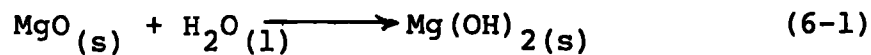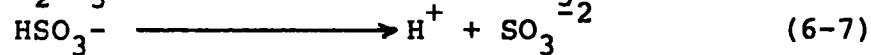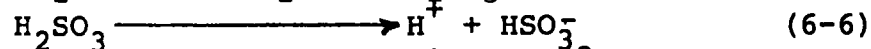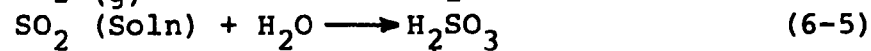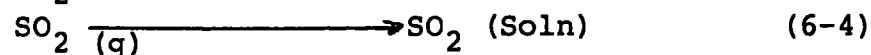
3. Formation of $MgSO_3$ and $Mg(HSO_3)_2$ \qquad (6-8)

$$Mg(OH)_2 \text{ (Soln)} + H_2SO_3 + (x-2)\, H_2O \longrightarrow$$
$$MgSO_3 \cdot XH_2O \qquad (6-8)$$
$$x = 3 \text{ or } 6$$

$$Mg(OH)_2 \text{(Soln)} + 2H_2SO_3 \longrightarrow Mg(HSO_3)_2 + 2\,H_2O \qquad (6-9)$$

$$MgSO_3 \cdot x\, H_2O \longrightarrow Mg^{+2} + SO_3^{-2} + x\, H_2O \qquad (6-10)$$

$$Mg(HSO_3)_2 \longrightarrow Mg^{+2} + 2HSO_3^- \qquad (6-11)$$

4. Other reactions (side):

$$CO_{2(g)} + H_2O \longrightarrow H_2CO_3 \text{ (Soln)} \qquad (6-12)$$

$$H_2CO_3 \text{ (Soln)} \longrightarrow H^+ + HCO_3^- \qquad (6-13)$$

$$HCO_3^- \longrightarrow H^+ + CO_3^{-2} \qquad (6-14)$$

$$2\, MgSO_3 \cdot x\, H_2O + O_2 \longrightarrow 2\, MgSO_4 + x\, H_2O \qquad (6-15)$$

$$Mg(OH)_2 \text{(Soln)} + H_2CO_3 + 3H_2 \longrightarrow MgCO_2 \cdot 5\, H_2O \qquad (6-16)$$

$$Mg(OH)_2 \text{(Soln)} + SO_3 \longrightarrow MgSO_4 + H_2O \qquad (6-17)$$

- 88 -
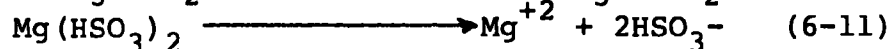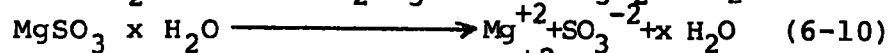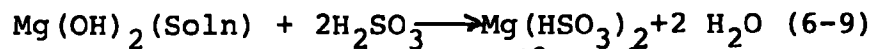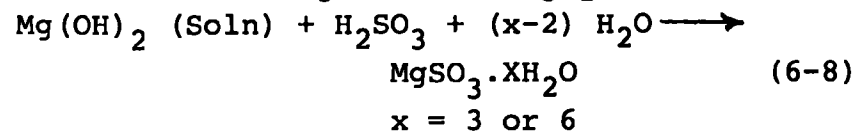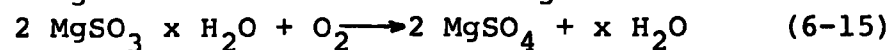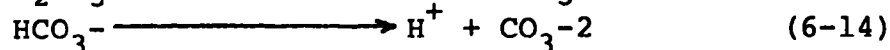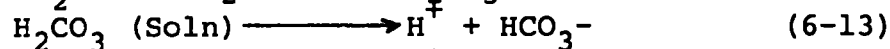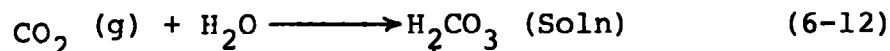
6.2.1 Absorber Reactions

In the system the main reaction in the second or SO_2 removal stage is the neutralization of H_2SO_3 by hydrated MgO to form insoluble hydrated $MgSO_3$. $MgSO_3$ crystallizes out with either three or six molecules of water. The nature of the hydrate, i.e., hexa- or tri- is partially dependent upon the temperature in the absorber. (Hexa-hydrate is stable at room temperature while the trihydrate is stable above 108^OF). The transition temperature of the two hydrates, according to the literature, is 42.5^OC (108.5^OF). During operations at PEPCO the temperature of the recycle slurry averaged about 110^OF. Since this temperature in the absorber is higher than the transition temperature it was expected that the trihydrate of magnesium sulfite would be the main product as was the case during the work on the Boston Edison Project. However, in actual operation, at Dickerson Station the centrifuge cake analysis showed almost 95% $MgSO_3 \cdot 6H_2O$.

6.2.2 Formation of Oxysulfates

At PEPCO feed MgO was digested in mother liquor that has as its main consitutent magnesium sulfate in solution (approximately 15% dissolved $MgSO_4$).

It is known that MgO may react with $MgSO_4$ solution to form a jell like substance. This jell consists mainly of basic magnesium sulfate, represented as: $xMgSO_4$ $yMg(OH)_2$ zH_2O. The values of x, y, and z are dependent upon the concentration of reactants and temperature.

During early operations at PEPCO, when virgin MgO was used in the unheated mixing tank considerable jell and lump formations occurred. X-ray and chemical analysis of these products showed the presence of $3Mg(OH)_2MgSO_48H_2O$ (i.e., oxysulfate in varying amounts admixed with quantities of unreacted $Mg(OH)_2$.

Laboratory studies, which were initiated to investigate this problem concluded that:

1) The problem appeared to be confined to operation with virgin MgO particularly at high $MgSO_4$ concentrations (15% $MgSO_4$ or more) in the centrate. The problem is further aggravated when the MgO-$MgSO_4$ mixture is allowed to stand for a time with insufficient agitation.

2) When calcined MgO (regnerated) of bulk density above 20 lb/ft^3 is used in the reaction no major problem was observed as long as proper agitation and temperature of digestion of virgin MgO were maintained.

Because of lack of operating time the laboratory observations with regnerated MgO could not be completely confirmed in the plant.

6.3 MAGNESIUM SULFITE CHEMISTRY

Fundamental questions in the Chemico Basic Magnesia Slurry Process are the chemistry of the formation and dehydration of the hexa and tri-hydrate forms of magnesium sulfite, and the mechanism of $MgSO_3$-$MgSO_4$ thermal decomposition in the presence of carbon and a reducing atmosphere.

Understanding of the first would allow control of the production of the hydrate type formed in the absorption system thereby affecting economies in the separation and drying of these materials.

Knowledge of the second might lead to process improvements for production of richer SO_2 off-gas, with more reactive MgO, or direct conversion to elemental sulfur.

Because of the complexity of these questions research work in the three areas was divided between the Chemico laboratory facilities at the Rumford, R.I., plant and the New Jersey Institute of Technology, (N.J.I.T.) Department of Chemical Engineering and Chemistry. Most of the instrument studies, i.e., Mass Spectroscopy, I.R. Spectroscopy, Differential Thermal Analysis, Thermogravimetric Analysis, etc. were performed at N.J.I.T. The results of these studies are given in the Appendicies.

The following section is a summary of the principal findings resulting from the work.

6.3.1 Conditions Governing the Formation of Magnesium Sulfite Hydrates

A literature survey showed the existence of only two hydrates of magnesium sulfite: $MgSO_3 \cdot 6H_2O$ and $MgSO_3 \cdot 3H_2O$. The hexahydrate is more stable at ambient conditions. The hydration energy of the two are as follows:

$$MgSO_3 + 6H_2O \longrightarrow MgSO_3 \cdot 6H_2O \ -13.38 \ K \ Cal.$$
$$MgSO_3 + 3H_2O \longrightarrow MgSO_3 \cdot 3H_2O \ -11 \ k \ Cal.$$
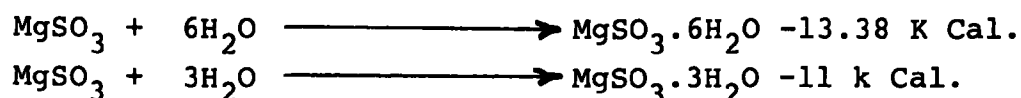
The N.J.I.T. study of the reaction of SO_2 (at $320^\circ F$) with MgO slurry at 120°, 135°, 149° and $176^\circ F$ showed that at 120° and $135^\circ F$ the major product was $MgSO_3 \cdot 6H_2O$ while the trihydrate, $MgSO_3 \cdot 3H_2O$ was the dominant product at 149° and $176^\circ F$. Presence of $MgSO_4$ in solution (up to 18%) and passage of excess air did not have any significant influence on the nature of the hydrate formed.

At Rumford, the reactions of SO_2 (at $300^\circ F$) with MgO (virgin and regenerated) were studied at 135°, $140-145^\circ$ and $150^\circ F$. The pH was maintained at 6.8-7.20. Samples were collected periodically and the filtrates were returned to the reactor. The results of the study agreed with the conclusions noted above.

At $135^\circ F$ the major product was the hexahydrate and trihydrate was the predominant one at $150^\circ F$. The study at $140-145^\circ F$ was interesting--it showed the gradual change from hexahydrate (original product) to trihydrate (final product). The complete transormation of the hexahydrate to trihydrate took place in 4-5 hours of run. The study ($140-145^\circ F$) also showed that the transition of hexahydrate to trihydrate is accompanied by a reduction of crystal size (from 200 to 50 micrometers).

Analysis of centrifuge cakes from PEPCO and Boston support the validity of the contention that (a) the ratio of the two hydrates at any temperature is controlled by the equilibrium value at that temperature, (b) hexahydrate persists even above the transition temperature and (c) the rate of transition is slow (cf. Kovachev Ts. et al., Khimiya i Industriya. Sofia 42 (5) (1970) 209-211. Transition temperature of the hydrates, $40^\circ C$ or $104^\circ F$).

Centrifuge Cake From Boston (135°F) 2-20-74 to 2-21-74		Centrifuge Cake From PEPCO (120°F) 12-10-73 to 2-15-73	
Hours	Ratio of $\frac{3H_2O}{6H_2O}$	Hours	Ratio of $\frac{3H_2O}{6H_2O}$
0	0/100	24	16/84
4	12.5/87.5	48	9/91
12	30/70	74	11/89
16	37/63	97	18/82
20	49/51	130	7.5/92.5
24	55/45		
28	58/42		
32	70/30		

The variation in PEPCO samples was probably due to temperature fluctuations in the system (the PEPCO system did not stablize at the time. However, analysis of centrifuge cakes at later dates always showed a preponderance of hexahydrate in PEPCO cakes).

6.3.2 Dehydration of Magnesium Sulfite Hydrates

DTA, TGA and DSC studies with the two hydrates of magnesium sulfite, $MgSO_3$ $6H_2O$ and $MgSO_3$ $3H_2O$ showed that the path of dehydration and temperature of dehydration are dependent on the manner of heating, i.e., whether dehydration took place in an enclosed vessel or open or flow-through vessel. (Appendix 2).

For example:

<div align="center">CONDITIONS</div>

DTA Study	CLOSED	OPEN
$MgSO_3$ $6H_2O$	Two endotherms observed (at 107° and 205°C)	One endotherm only (at 90°C)

CONDITIONS

DTA Study	CLOSED	OPEN
$MgSO_3 \cdot 3H_2O$	One endotherm only (at 205°C)	One endotherm (at 160°C)

TGA study also showed similar behavior of the two hydrates:

CONDITIONS OF STUDY

TGA Study	CLOSED	OPEN
$MgSO_3 \cdot 6H_2O$	Two endotherms (at 125° and 220°C)	One endotherm only (at 70°C)
$MgSO_3 \cdot 3H_2O$	One endotherm (at 200°C)	One endotherm (at 100°C)

This study also showed that TGA (enclosed environment) can be used to determine quantitatively the amounts of the two hydrates in a mixture of the two. Presence of inerts (any substance which does not change weight between 175° and 400°C) does not interfere with the determination. The only potential interferring element relevant to magnesia process is $MgSO_4 \cdot 7H_2O$ ($-7H_2O$ at 200°C). The interference by $MgSO_4 \cdot 7H_2O$ can be easily avoided by washing the sample with absolute ethyl alcohol (only $MgSO_4 \cdot 7H_2O$ dissolves). The amounts of the two hydrates, in a mixture, are calculated as follows:

$$\%MgSO_3 \cdot 6H_2O = \frac{\% \text{ wt. loss at } 175°C \times 2 \times 100}{50.9}$$

$$\%MgSO_3 \cdot 3H_2O = \frac{100 \times (\% \text{ wt. loss at } 400°C - \text{wt. } \% \text{ loss at} 175°C)}{34.10}$$

Additional dehydration studies were carried out in the laboratory.

The two hydrates were heated in a vacuum oven (12 inches of mercury) at $80^{\circ}C$ ($176^{\circ}F$), $120^{\circ}C$ ($248^{\circ}F$) and $150^{\circ}C$ ($302^{\circ}F$) for extended periods of time. Samples were withdrawn at intervals and chemically analyzed.

At $176^{\circ}F$ and $248^{\circ}F$ little or no change was observed with $MgSO_3$ $3H_2O$ even after 25 days. At $176^{\circ}F$ the hexahydrate changed to trihydrate after 2 days (confirmed by chemical and x-ray analysis). At $248^{\circ}F$ the hexahydrate dehydrated to yield a hydrate of apparent composition $MgSO_3 2H_2O$ after 21 days.

At $302^{\circ}F$ the hexahydrate changes to trihydrate within two hours. Holding the compound at this temperature results in a continuous, gradual loss of water. After 200 hours at $302^{\circ}F$ the starting hexahydrate had an apparent composition of $MgSO_3 \frac{1}{2}H_2O$. When starting with the trihydrate it appears to be stable up to 48 hours at the $302^{\circ}F$ temperature. Then it looses water rapidly to give the apparent hydrate $MgSO_3 \frac{1}{2}H_2O$.

The rates of dehydration of the two hydrates at $330^{\circ}F$ are also different the hexahydrate loosing water more rapidly than the trihydrate. The rates of dehydration at $330^{\circ}F$ were studies using Ohaus moisture balance. To form the anhydrous salt, $MgSO_3$, containing 10% moisture at $330^{\circ}F$ following retention periods were necessary:

for $MgSO_3 6H_2O$ 10 minutes

     $MgSO_3 3H_2O$ 25 minutes

The dehydration study indicates that the water molecules are more strongly bound in the trihydrate than in hexahydrate.

6.3.3 Mass Spectroscopy of the Two Hydrates of Magnesium
       Sulfite vs. Temperature

The two hydrates were heated from 35° to $400^{\circ}C$ in a

Finnigan Quadrupole 1015 mass spectrometer. No other
species except SO_2 and H_2O were observed. The plot of
$\log \left(\dfrac{SO_2}{H_2O}\right)$ vs. temperature showed that the two hydrates
decomposed in a similar manner (under vacuum conditions).
(Appendix 3).

6.4 PULVERIZATION

The SO_2 removal capability of MgO in the Chemico
magnesia system is dependent on both intensive and exten-
sive properties of the regenerated material.

Of the extensive properties, the size range of the
MgO particles returned for slaking is very important. Ex-
perimental data indicate that grinding the calcined magnesia
increases its reactivity. However, there is a limit to which
that reactivity can be increased.

Laboratory data now indicate that a size range of -100
to +200 mesh (between 75 and 150 micrometers) is satisfactory
for recycled, regenerated magnesia. This is shown in the
attached graph (Figure 8). The greatest increase in MgO
activity occurs when +50 mesh size particles are reduced to
-50 to +100 mesh, additional improvement in SO_2 removal is
obtained when size is reduced to -100 to +200 mesh. Reduc-
tion to finer size has only a slight affect on activity in-
crease.

The properties of regenerated MgO (shown in Table 22)
are determined by both calcining conditions and contaminent
level.

FIGURE 8

EFFECT OF PULVERIZATION ON SO$_2$ EFFICIENCY
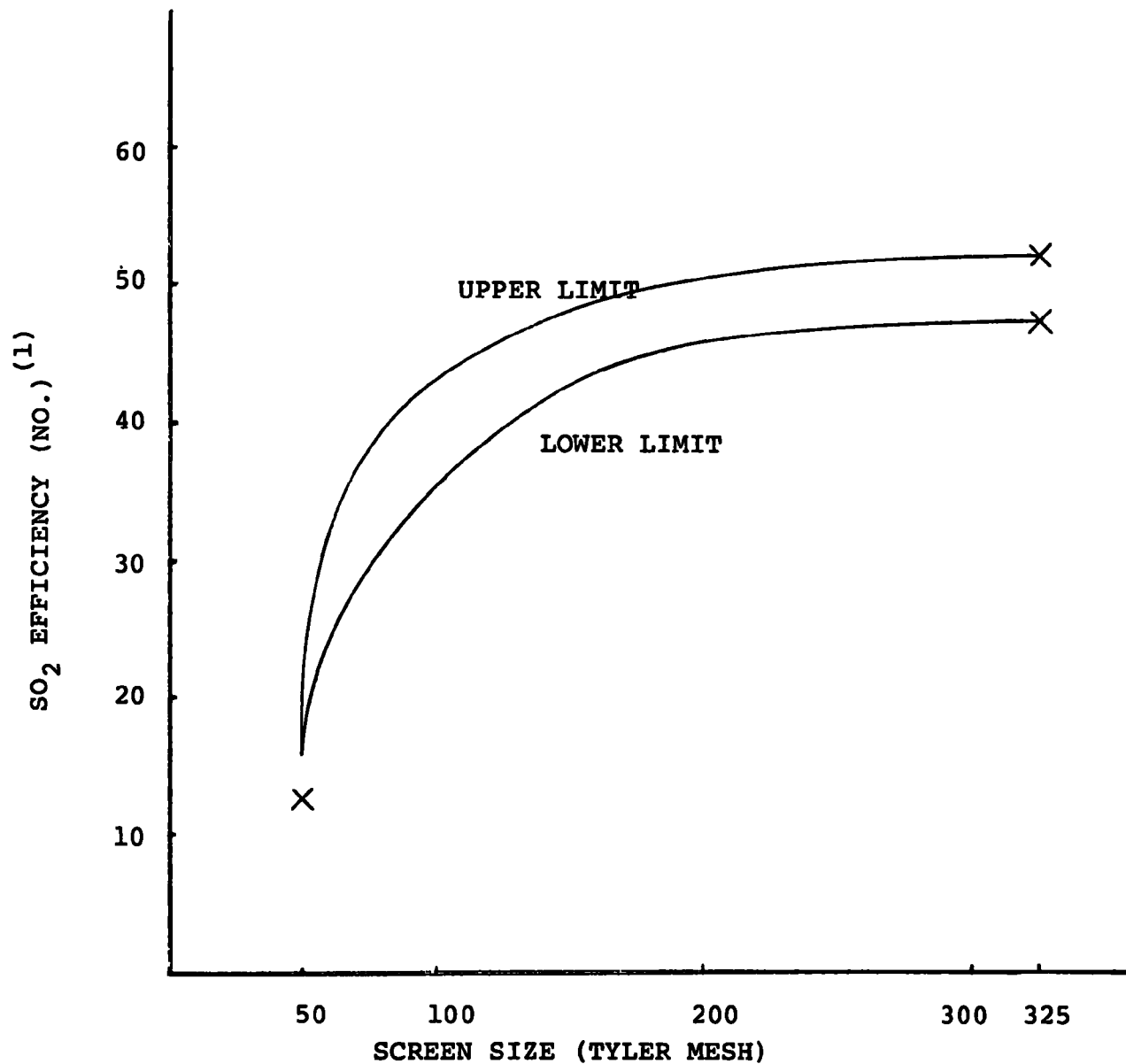
(1) Measure of uptake of SO$_2$ by measured quantity of regenerated MgO by the method described in "The Magnesia Scrubbing Process as Applied to an Oil Fired Power Plant" EPA 600/2-75-057 pg. 253 ff.

TABLE 22

PROPERTIES OF DIFFERENT FRACTION REGENERATED MgO

(SAMPLE NO. PR-289)

Analysis	+50 Mesh Fraction	-50 to +100 Mesh Fraction	-100 to +200 Mesh Fraction	-200 to -325 Mesh Fraction	Ground +50* Mesh Fraction to (-100 to +200) Mesh
%MgO	89.96	89.46	90.52	91.73	
%MgSO$_4$	1.73	2.43	2.60	2.35	
%MgSO$_3$	0.50	1.42	1.33	0.98	
SO$_2$ Eff.	13	37	47	48	48

7.0 CORRELATION OF PROCESS DATA

With the initiation of the planned operations program
process data were collected and recorded regularly. In order
to assimilate, store, analyze and deseminate this information
efficiently, a computerized method of handling the data was
employed. As a result, it was possible to effect a real-time
feedback to the process or correlated and trend results at the
time they are most useful, along with accumulating the infor-
mation in a permanent data bank available for analysis and
retrieval. The statistical computer program package utilized,
permits the use of the same format data file as input to a
wide range of sub-programs, including regression calculations,
x-y plotting, file listings, trend plots, etc. This flexibility
reduced the number of files that needed to be maintained, and
provided speed advantages.

Figure 9 illustrates the flow of information between
scrubber and calciner operating systems and the computer data
bank. Operating conditions and analyses are entered on punch
cards on a daily basis for primary storage and transferred to
computer disk files for futher processing. At monthly inter-
vals the following statistics were generated for all variables:
average, maximum, minimum, standard deviation, and a percent
change relative to a base period. The final stage in the data
flow was the integration of the operating log and analysis
files, plus the inclusion of appropriate time lags for the
scrubber and regeneration facilities to form single disk files
suitable for input to correlation and plotter computer programs.
The process data bank becomes the source of retrieval of pro-
cess information for continued analysis and for comparison with
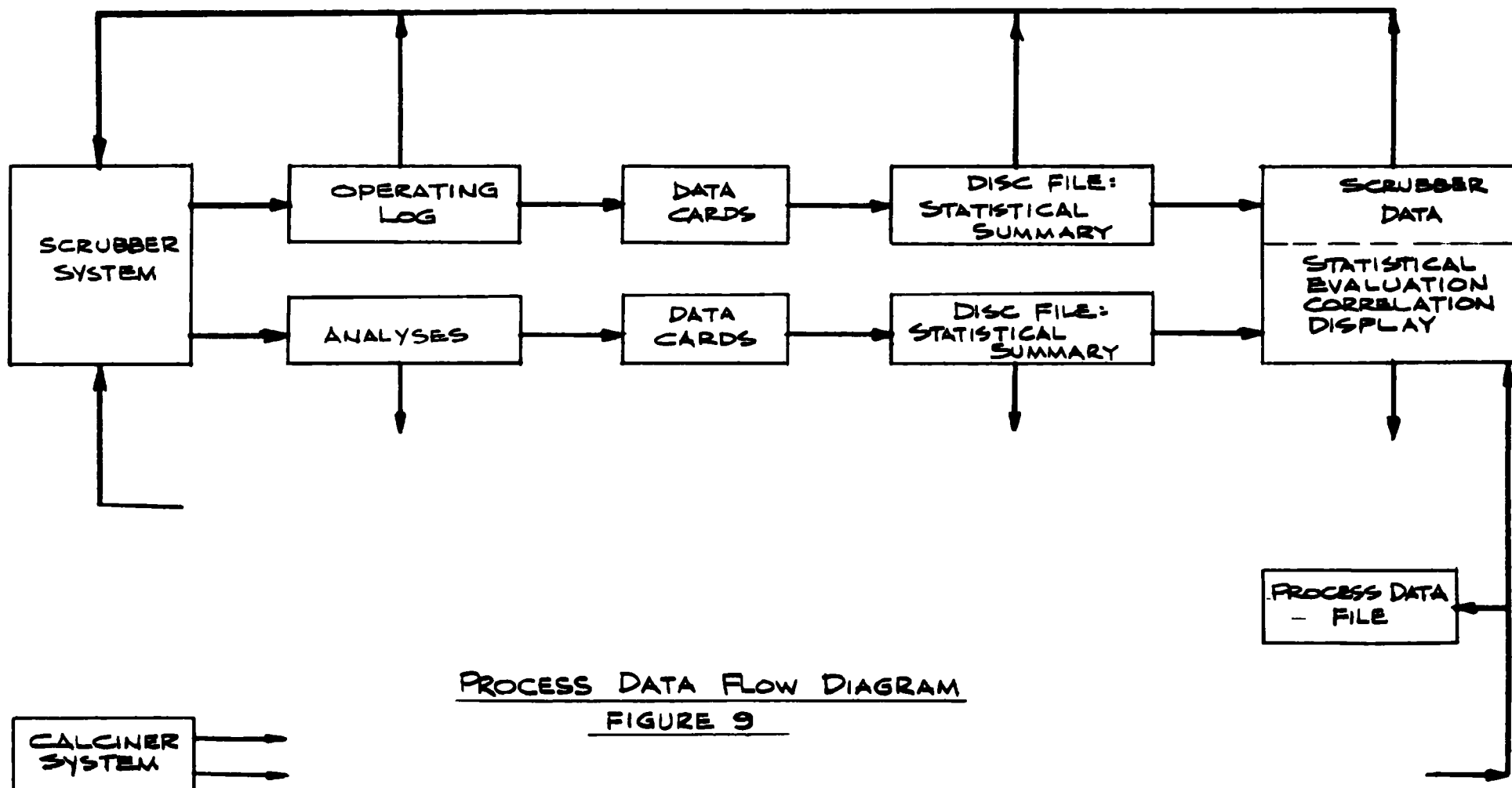
PROCESS DATA FLOW DIAGRAM
FIGURE 9

results from other installations.

The process correlations developed in the previous "New England SO_2 Control Project", EPA Ref. CPA 70-114, were developed primarily using the data bank as input to a stepwise multiple linear regression program. This approach minimizes the number of computer runs required to determine equations that are statistically significant, prior to their evaluation for consistency with observed data. F ratio tests are employed to establish significance levels for testing of equation variables, and coefficients are calculated by least squares techniques. With respect to the SO_2 removal efficiency correlation, log transformations were required by the regression program. Continued investigation of mass transfer coefficient in this program may lead to the use of non-linear programs.

Normal excursions in the process variables are sufficient to satisfy the required scope of the test program variation in levels of operating data to fulfill the requirements of this method of operations data analysis.

7.1 SO_2 REMOVAL

A correlation relating SO_2 removal efficiency, pressure drop and SO_2 inlet concentration had been developed during the previous operation of the MgO system prototype on the oil fired boiler. Included in the formulation of the correlation were data points from the performance testing of Dickerson. The data accumulated during the additional operation of this project was used to improve the correlation based on the variations of SO_2 removal efficiency and other operating factors which were observed.

7.1.1 First Stage SO_2 Absorption

A series of tests were performed with the scrubber to assess the SO_2 removal capability of the first (particle removal) stage of the system. Results of these tests are given

in Table 23. These tests showed an average removal efficiency for the first stage of 6.7%.

7.1.2 Effect of Pulverization of Regenerated MgO

During the period of scrubber operation at PEPCO from November 1974 to January 1975, the observed SO_2 removal efficiency varied more than could be expected from normal changes in operating conditions, i.e., pressure drop, SO_2 inlet concentration, etc. Efficiency decreased approximately 10% in November before recovering in December and January. The efficiencies were adjusted to constant operating conditions and plotted to show that a significant variation in SO_2 removal remained after adjustment of pH and pressure drop which was assumed to be related to other process variables. Figure 10 is plot of removal efficiency vs. time illustrating this phenomenon. The scale of the plot is expanded to show the effect more clearly.

Laboratory studies indicated that a critical particle size range was required to maintain activity of the regenerated magnesia. In order to determine whether any relationship existed between MgO particle size distribution and SO_2 removal activity in the FGD system, a series of MgO samples were taken from the weigh feeder at Dickerson for screen sizing and activity measurements. Results of this analysis are shown in Table 24 along with corresponding scrubber operating conditions for the time frame over which the samples were taken.

This information was analyzed by linear regression techniques and showed a significant particle size correlation with SO_2 removal efficiency in the -50 to +100 mesh range. The correlation is given in equation 7-1.

$$R = -7.68 - 0.0338 \ (P_{100})^2 \qquad (7-1)$$

$$R = \% \text{ reduction in } SO_2 \text{ removal efficiency}$$

$$\text{Where } P_{100} = \% \ (-50 \text{ to } +100 \text{ mesh}) \text{ material in MgO Feed}$$

TABLE 23

SO$_2$ REMOVAL IN FIRST STAGE

| Date | Time | SO$_2$[1] | | Efficiency % |
		Inlet ppm	Outlet ppm	
1/8/74	1700	1300	1220	6.2%
	1900	1300	1290	0.8
	2100	1390	1200	13.7
	2300	1430	1340	6.3
1/9/74	2100	1300	1300	0.0
	0300	1390	1360	2.2
	0500	1500	1380	8.0
	0700	1300	1300	0.0
	0900	1070	990	7.5
	1100	1080	900	16.7
	1300	980	900	8.2
	1500	900	800	11.1

Average Removal Efficiency 6.7%

[1] Abstracted from the continuous emissions monitoring data obtained using a Flourescent SO$_2$ analyzer.

FIGURE 10
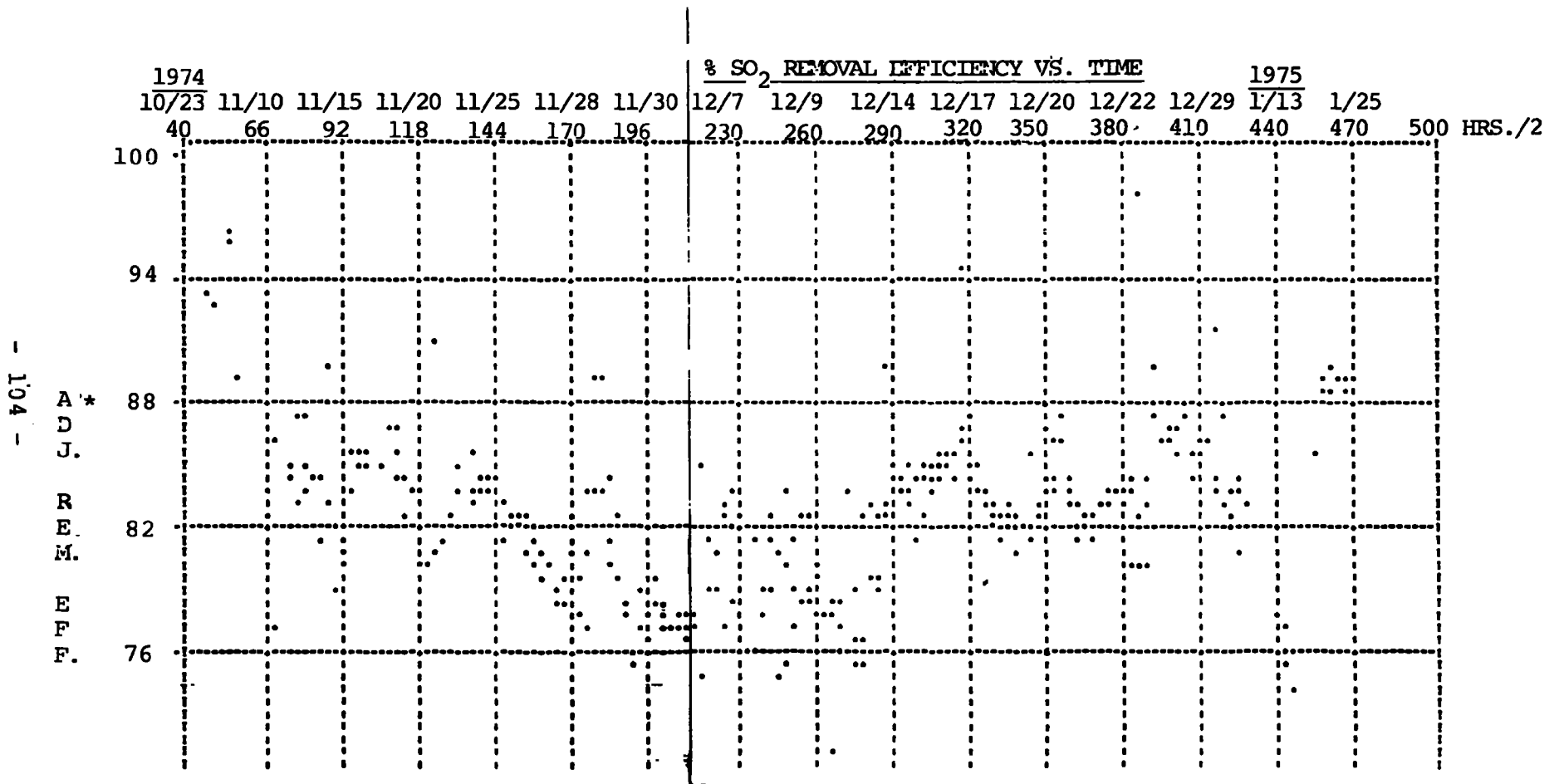
*Observed SO$_2$ rem. eff. adjusted to common basis of 9"Δ P, 7 pH
1900 PPM Inlet SO$_2$.

TABLE 24

WET SCREEN ANALYSIS OF MgO BELT SAMPLES

Date (1974)	11/20	11/21	11/24	11/25	12/1	12/9	12/18	12/20	12/23	12/27
Time	——	———	———	———	——	0800	2000	1200	0400	1200
Tyler Screen Mesh Size - %										
+50	1.0	0.8	0.5	0.3	4.6	5.2	3.6	6.6	0.7	1.8
-50,+100	0.8	0.5	0.6	0.8	14.5	5.4	5.7	6.8	1.9	2.5
-100,+200	2.6	1.5	1.3	1.7	8.2	12.2	10.3	13.3	7.7	3.6
-200,+325	4.1	2.2	2.7	3.3	6.9	11.8	13.8	10.1	13.6	2.5
-325	91.5	95.0	94.9	93.9	65.8	65.4	66.6	63.2	76.1	89.6
Operating Conditions										
P, In. H_2O	(1) 9.5	(1) 9.3	(1) 8.9	(1) 8.2	(1) 6.4	4.2	8.4	3.6	8.5	5.9
SO_2 Removal Eff.,%	85.1	86.2	83.8	84.1	76.0	79.0	82.0	80.6	83.6	83.0
SO_2 Inlet Conc., PPM	1210.	1240.	910.	920.	1080.	1170.	1200.	960.	840.	900.
Predicted[2] SO_2 Removal Eff. - %	85.0	85.0	84.9	84.6	76.4	79.5	83.5	77.0	84.6	82.9
(Actual-Predicted) Efficiency, %	0.1	1.2	-1.1	-0.5	-0.4	-0.5	-1.5	3.6	-1.0	0.1

[1] Average Conditions For Day

[2] From Equation 7-1

After determining the pulverized MgO particle size the resultant correction can be subtracted from the efficiency obtained from the correlation developed from the previous operations. This basic correlation is given in equation 7-2.

$$SO_2 \text{ Removal} = 1-Exp\ ((2.666\ (\Delta P)^A\ (SO_{2I})^B (10)^C\ -3))\quad 7-2$$
Efficiency (Base)

Where A = -1.014

B = -3.75 + 0.271 ln SO_{2I}

C = 6 - 0.031 pH

SO_{2I} = SO_2 inlet concentration (ppm)

ΔP = pressure drop, inches H_2O

Figure 11 is a plot of the predicted effect of the concentration of -50, +100 mesh size in the MgO on SO_2 removal using equation 7-1 at constant process conditions. Results show that SO_2 removal decreases with increasing concentration of this size range, which is consistent with laboratory observations. Figure 12 is a plot of observed vs. predicted efficiency during the subject time period.

7.1.3 Reduction in Activity of Magnesia

Equation 7-1, showing particle size effect also predicts a 7.68% offset from removal efficiency calculated from 7-2, a correlation based on ΔP, pH, and inlet SO_2 concentration.

An analysis of inventory records during the period covered by the testing program revealed that the magnesia feed consisted of a mix of virgin and regenerated MgO. The beginning inventory on October 18th at Dickerson was 46 tons of regenerated MgO in the following week 140 tons of virgin MgO were added as makeup to the silo. About 22 tons of regenerated MgO were returned to Dickerson in the period from October 18th through November 29th while about 120 tons of MgO were consumed in the operations there. Thus during the period of reduced efficiency virgin material was the principal feed to the system. A comparison of the manufacturer's analysis, Table 25,

FIGURE 11

EFFECT OF MgO PARTICLE SIZE ON SO_2 REMOVAL EFFICIENCY

BASIS: PEPCO Operation Nov.-Dec. 1974

Adjusted to 7" Δ P, 7 pH, 1000 PPM SO_2 Inlet

FIGURE 12

OBSERVED VS. PREDICTED SO$_2$ REMOVAL EFFICIENCY
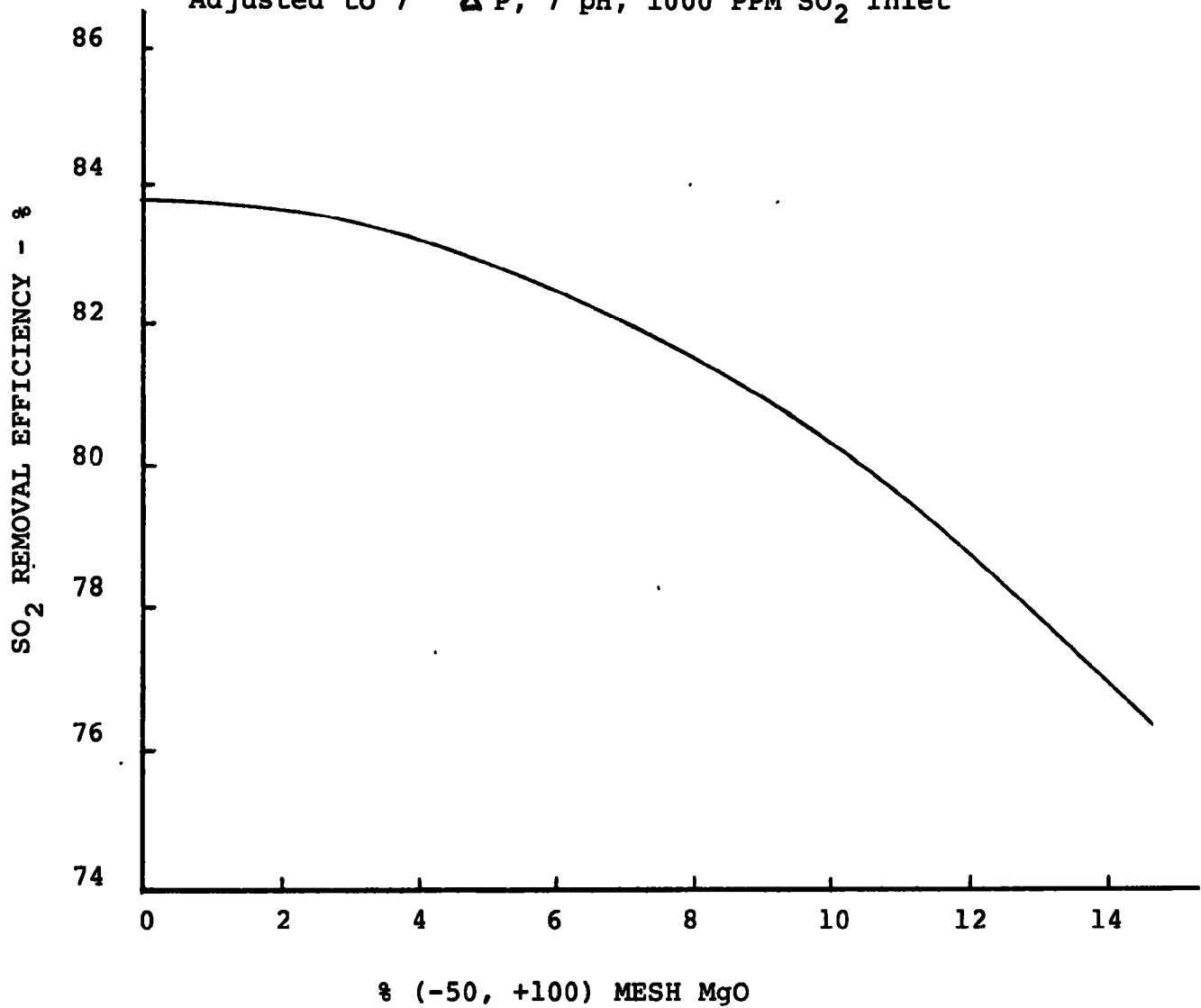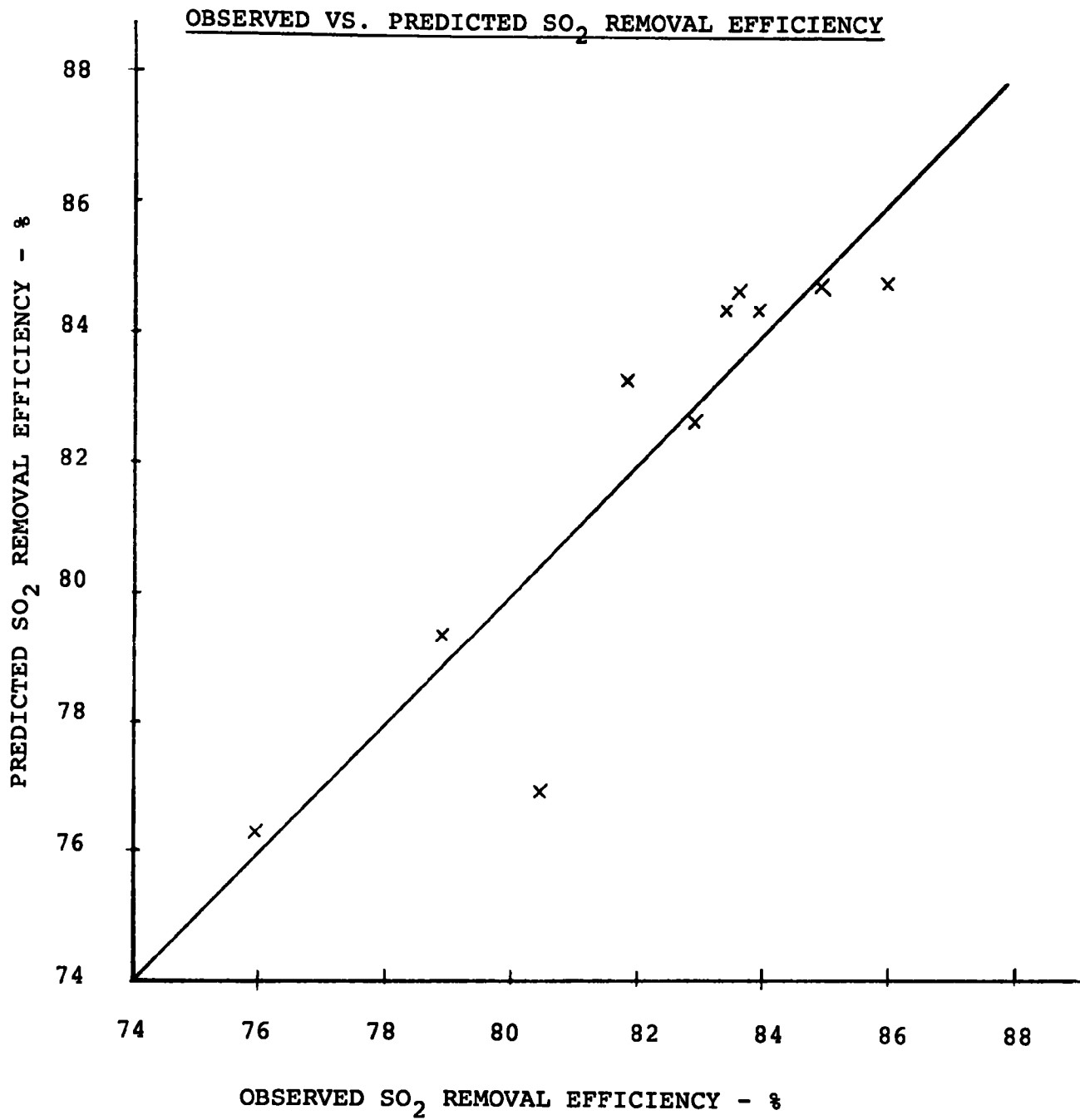
TABLE 25
MANUFACTURERS ANALYSIS OF MAGNESIA
SHIPPED TO DICKERSON STATION

	7/12/74 L&N200196	8/20/74 L&N200487	10/7/74 L&N200257	10/25/74 L&N200304
CaO	1.62	1.78	1.94	1.96
SiO_2	0.7	0.60	0.61	0.62
R_2O_3	0.51	0.54	0.43	0.70
Cl	0.18	0.26	0.12	0.19
SO_3	0.69	0.78	0.67	0.64
-325 M	99.75	99.09	98.71	99.61
LOI	6.22	5.46	4.33	4.57
S.A.	66.7	52.4	79.3	94.7

Where R_2O_3 = Iron and aluminum oxides
  -325 M = Percent less than 325 mesh
    LOI = Loss on ignition
    S.A. = Surface area

for the virgin MgO supplied during the period of the program showed little deviation from that supplied at the beginning of the Development Program.

It has been noted (Sec. 6.3.4) that analysis of materials from the MgO slurrying system in the earliest phase of the project showed that the highly reactive virgin MgO exhibited a stronger tendency to form magnesium oxysulfates, which would hinder the SO_2 absorption efficiency of the magnesia slurry. It is thought that the deviation noted here is a measure of the additional reduction in efficiency resulting from the formation of the complex when a feed of virgin MgO is admixed with centrate.

7.2 CENTRIFUGE OPERATION

Centrifuge operations at both PEPCO and Boston Edison were compared and analyzed with regard to process optimization. The effect of centrifuge feed rate on efficiency and solids removal rate was determined by regression analysis of the operating data. Since the two centrifuges are mechanically identical, it would be expected that similar operating characteristics would be observed, and this was confirmed by analysis. The following results were obtained:

1. Centrifuge efficiency, i.e., pounds solids removed in centrifuge cake per pound solids in centrifuge feed, was shown to be a function of centrifuge feed rate with efficiency declining with increasing throughput.

2. Solids removed from the system was shown to pass through a maximum value as total feed rate to the centrifuge is increased.

Figures 13 and 14 show these results for centrifuge operation with average recycle compositions, normal rotational speed and standard weir height.

FIGURE 13

EFFECT OF CENTRIFUGE FEED RATE ON SEPARATIONAL EFFICIENCY

BOSTON

PEPCO

SEPARATIONAL EFFICIENCY, %

CENTRIFUGE FEED RATE GPM

- 111 -
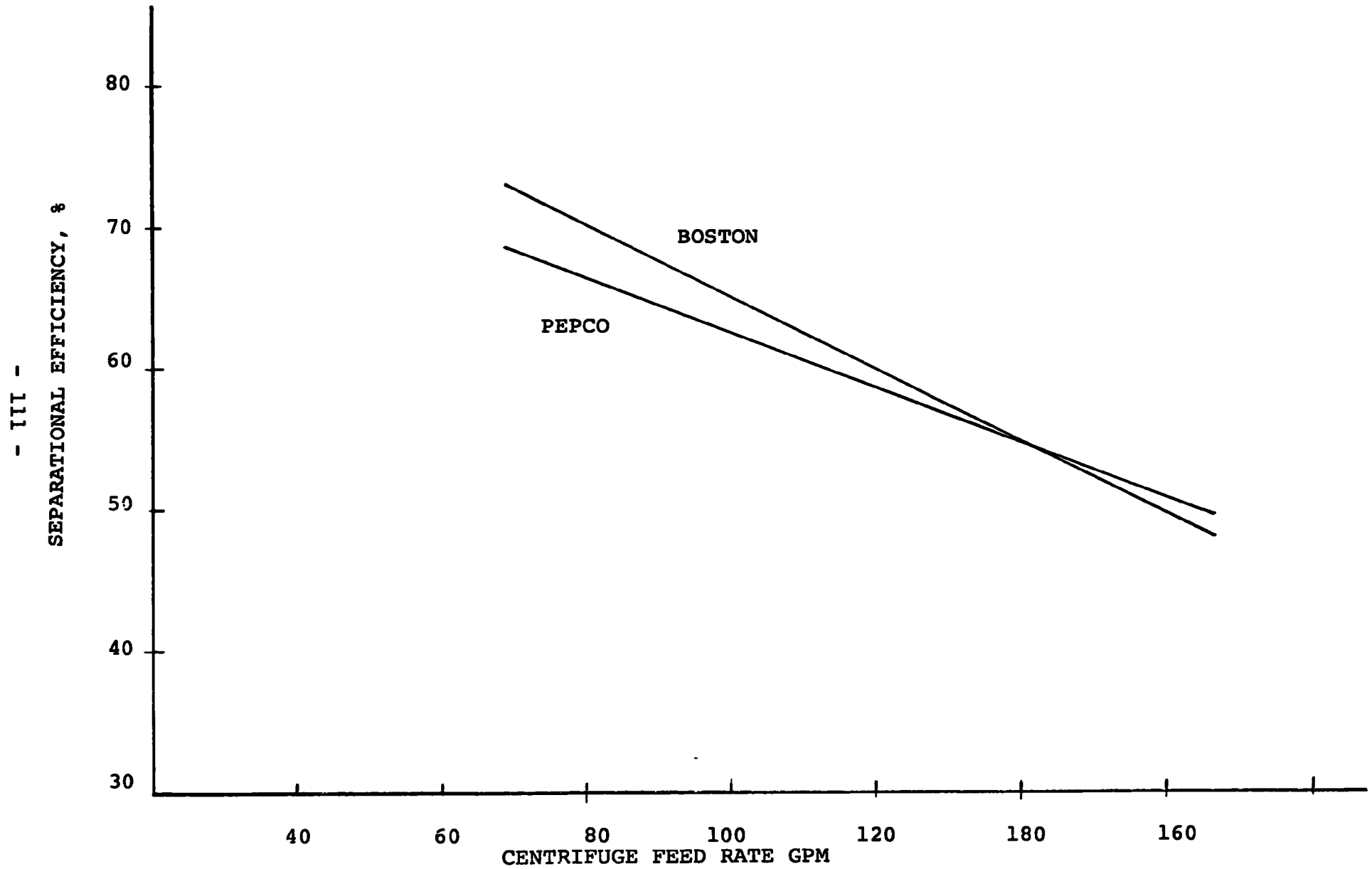
FIGURE 14

CENTRIFUGE OPERATION

LB./MIN. SOLIDS SEPARATED VS. FEED RATE
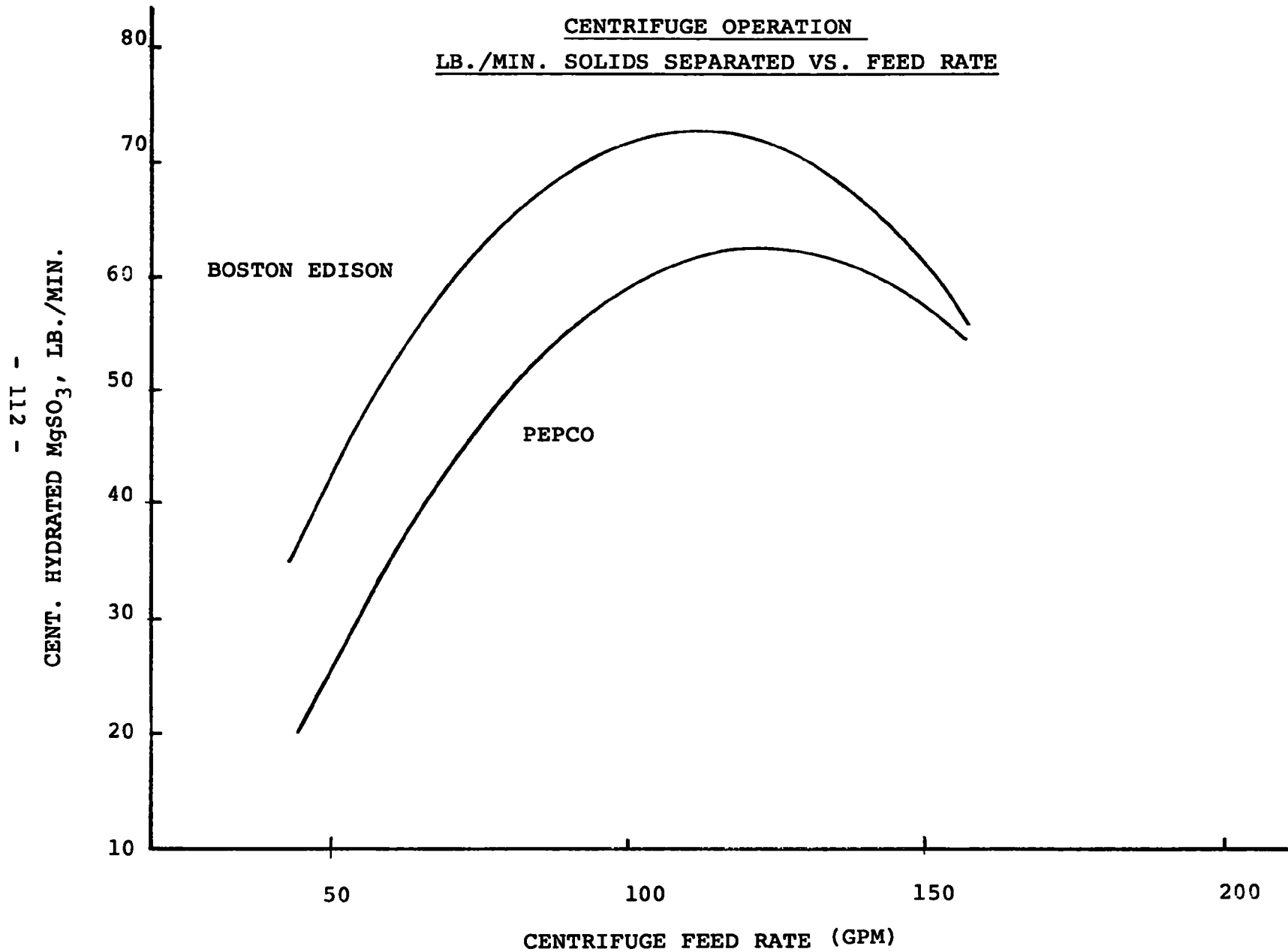
7.3 DRYER OPERATION

Data from the operations at PEPCO were analyzed to determine the influence of dryer operation conditions on dryer efficiency. A scatter plot of dryer solids vs. product temperature is shown in Fig. 15. In addition, the data collected during the Boston Edison operation were analyzed and compared. The results of preliminary review of the effect of dryer product and dryer outlet gas temperature on product moisture content is shown in Fig. 16. Variations in the performance of the dryers is attributed to the use of a counter-current unit at Boston and a co-current unit at PEPCO. A statistical analysis of this data shows a minor interaction between dryer product and dryer outlet gas temperature.

An analysis of the change in the ratio of $MgSO_4$ to $MgSO_3$ in the dryer feed and product streams, an indication of oxidation accurring in the dryer, showed a slight decrease in the $MgSO_4$ concentration for PEPCO operations as compared to the oil fired boiler application for the average range of system operations. This is shown in Figure 17.

7.4 CALCINER FEED RATE

A limitation on reliable operation of the integrated plants was reduced calciner feed rate. A low (40 lb/min.) feed rate was necessary to control slides and unprocessed $MgSO_3$ in the calcined product, Fig. 18. Initial investigations during the work at Mystic Station indicated a relation between particle size of the dryer product and frequency of slides. Further investigation showed that variation in size distribution of the dryer product was associated with variation in moisture content of the product. During the final phases of the program at Boston the dryer was operated to produce a product with a moisture content of approximately

FIGURE 15

COMPARISON OF PEPCO AND BOSTON EDISON DRYER OPERATION

(FOR RANGES OF DRYER GAS OUTLET TEMPERATURE)

FIGURE 16

DRYER OPERATION

PEPCO DATA
3/31/75

OUTLET GAS TEMPERATURE °F
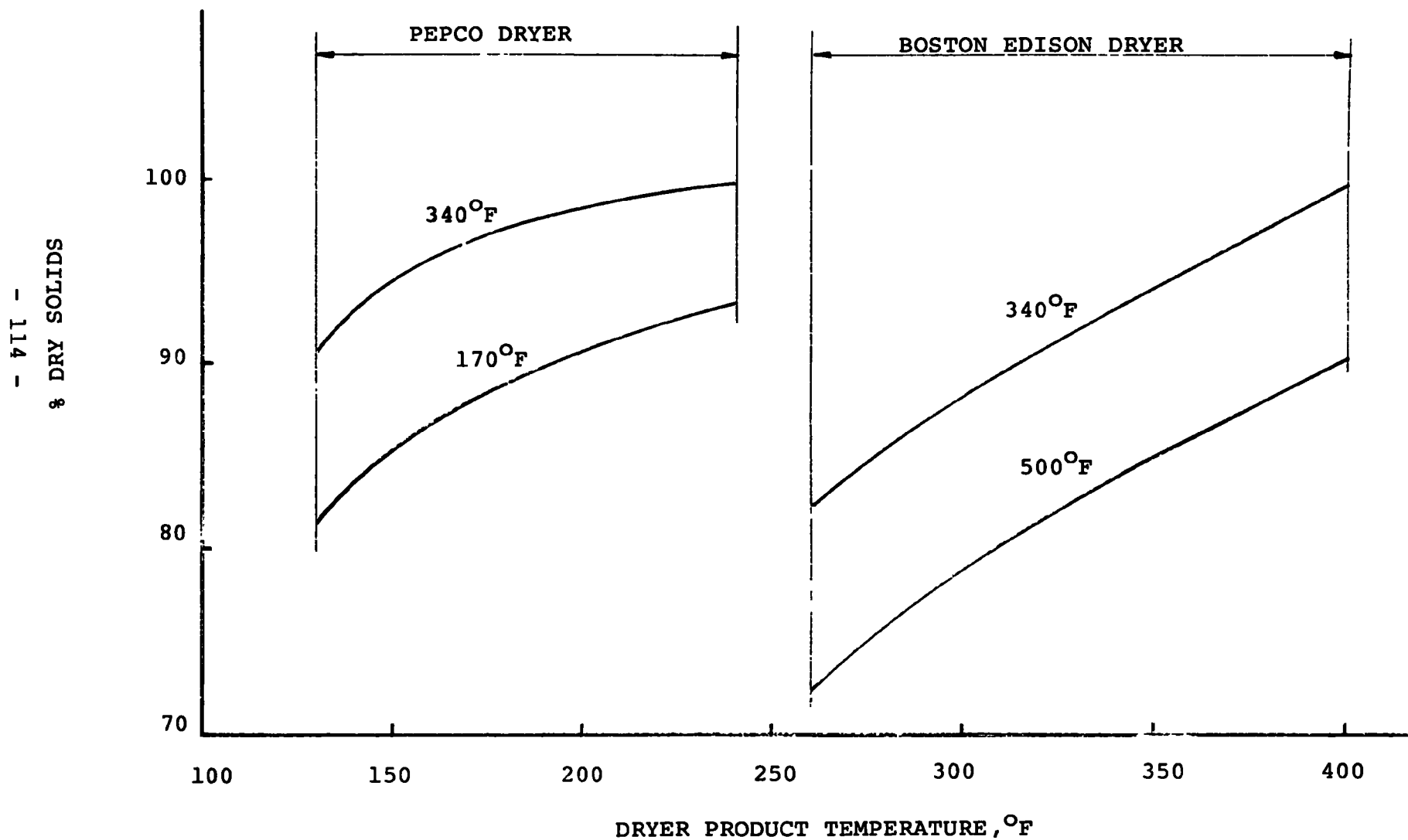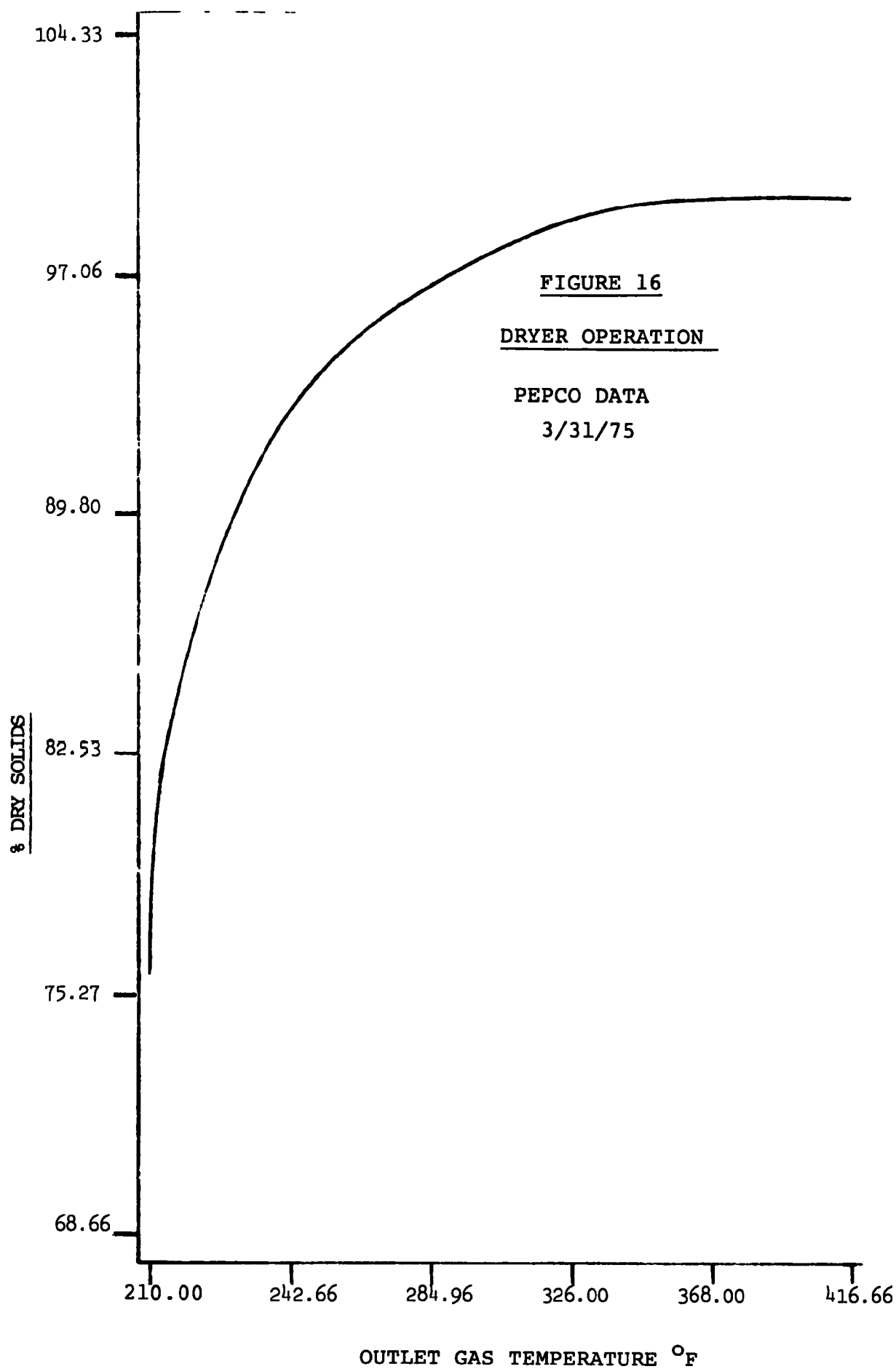
FIGURE 17

COMPARISON OF MgSO₃ OXIDATION IN DRYER
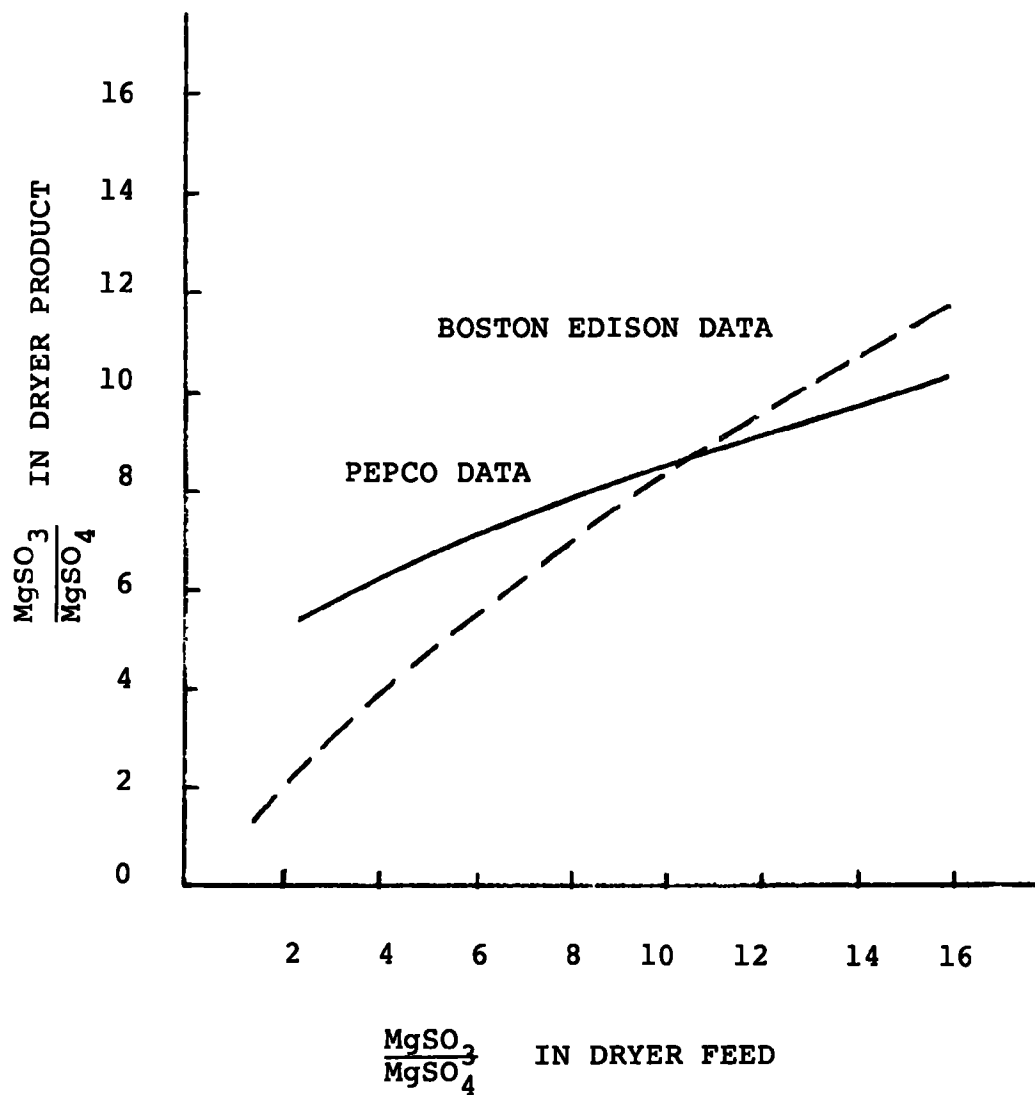
FIGURE 18

CALCINER OPERATIONS ON PEPCO MgSO$_3$
EFFECT OF FEED RATE ON MgSO$_3$ IN PRODUCT
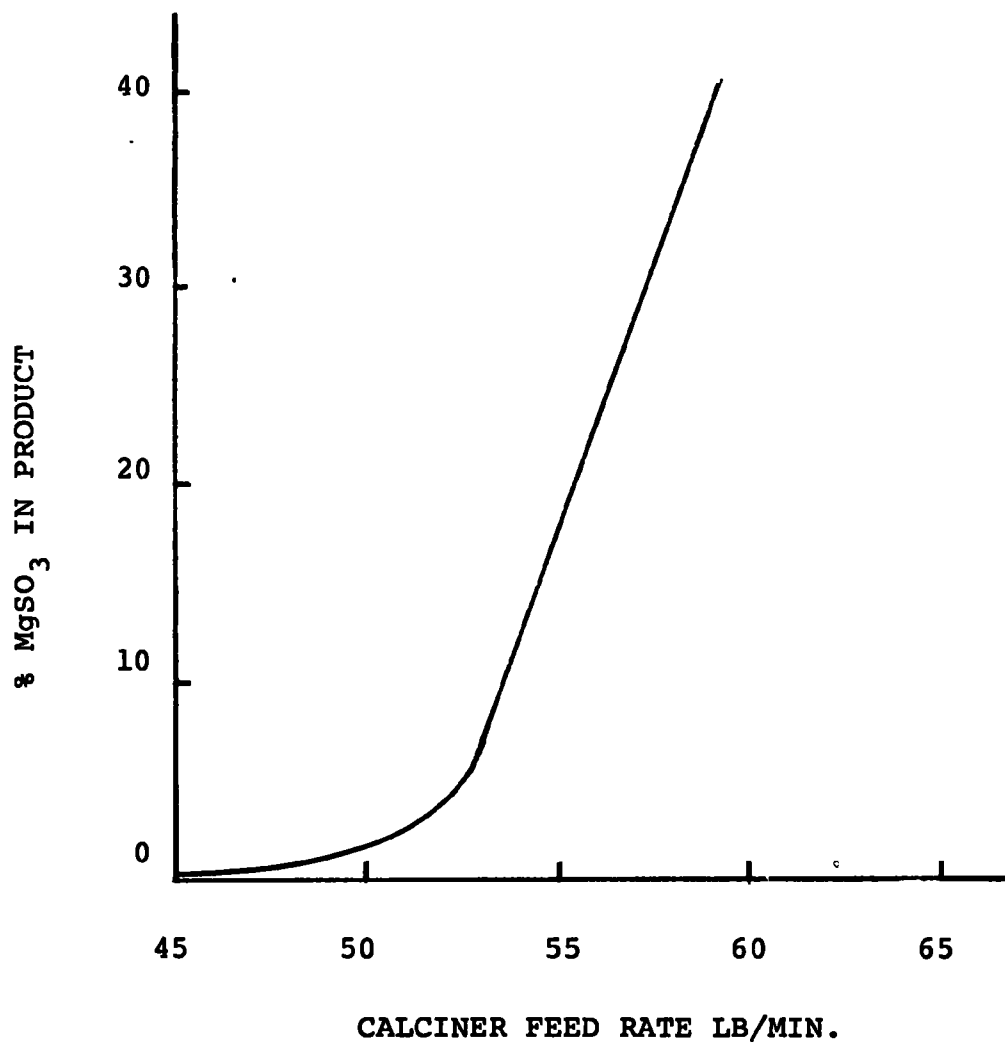
16% which eliminated the slides in the calcination step. The investigations at Dickerson showed there was a significant difference in the size distribution of the product produced from its dryer compared to material produced at Boston as shown in Tables 26 and 27.

Table 26 shows the average values and standard deviations for 25 Boston dryer samples and 22 PEPCO dryer samples covering the following mesh size ranges: +25, -25, to +50 -50 to +100 and -100 to +200. Table 25 presents a statistical analysis of these results.

TABLE 26

SIZE DISTRIBUTION OF DRYER PRODUCTS

Mesh Size Range	BOSTON 25 Samples		PEPCO 22 Samples	
	Average	Std. Deviation	Average	Std. Deviation
+25	58.1	10.2	22.3	11.4
-25, +50	14.9	4.5	29.5	8.5
-50, +100	9.4	4.4	23.5	8.4
-100, +200	4.7	2.0	11.1	4.0

TABLE 27

COMPARISON OF

BOSTON AND PEPCO SIZE RANGE AVERAGES

Mesh Size Range	Significance Level	Difference (Boston-PEPCO)	99% Confidence Limits
+25	99% +	35.8	27.2-44.5
-25, +50	99% +	14.6	9.2-19.9
-50, +100	99% +	14.1	8.8-19.4
-100, +200	99% +	6.4	3.9-8.9

8.0 DATA

8.1 MONTHLY AVERAGE OPERATING CONDITIONS

Operating data are summarized as montly averages for the planned operational testing period. Included in this information are:

Table 28 Operating Conditions for the FGD System

Table 29 Stream Compositions for the FGD System

Table 30 Operating Conditions for the Regeneration Unit

Table 31 Stream Composition for the Regeneration Unit

8.2 DATA LISTING

Data recorded from the PEPCO operations for the period October 15, 1974 through the end of the program in January 1975 are given in Table 32 . Data were recorded at two hour intervals, which is the interval between successive listing in the table for extended runs.

TABLE 28

OPERATING CONDITIONS FOR THE FGD SYSTEM

MONTHLY DATA AVERAGES

VARIABLE	11/74	12/74	1/75
SO_2 (PPM)			
IN	1057.86	1061.95	1272.22
OUT	193.46	207.90	214.89
% REMOV	81.54	80.57	81.95
pH	7.04	7.06	7.11
POWER PLANT RATE (MW)	174.03	153.98	142.82
DIFF. PRESSURES (IN. H_2O)			
TOTAL	7.49	6.77	6.49
MIST	0.23	0.19	0.21
DRYER	0.76	0.69	0.80
TEMPERATURES (F)			
-ABSORBER INLET	109.26	110.88	108.54
MAGNESIA SLURRY	157.02	139.20	130.33
-DRYER GASOUT	274.65	311.03	254.11
PROD.	179.36	200.62	165.30
FLOWS (GPM)			
CIRC.	10152.78	10823.13	11546.30
CENTFD	72.74	83.09	154.61
CENTRIFUGE TORQ.	34.75	40.38	43.94

TABLE 29

STREAM COMPOSITIONS FOR THE FGD SYSTEMS

MONTHLY DATA AVERAGES

VARIABLE	11/74	12/74	1/75
DRYER			
% SOL.	93.63	96.94	91.30
% $MgSO_3$	68.06	68.12	66.45
% $MgSO_4$	8.28	9.08	7.70
% MgO	4.78	6.82	7.78
CENTRIFUGE			
% SOL.	88.86	88.33	88.45
% $MgSO_3$	41.78	42.81	42.19
% $MgSO_4$	4.44	4.86	4.02
% MgO	3.06	3.03	5.25
RECYCLE			
% SOL.	6.98	10.90	8.72
pH	7.17	7.30	7.22
-FILTRATE			
% $MgSO_4$	17.05	18.95	13.13
-CAKE			
% MgO	3.81	3.95	5.79
MOTHER LIQUOR			
% SOL.	2.46	4.80	2.20
-CAKE			
% MgO	6.14	5.68	9.73

TABLE 30

OPERATING CONDITIONS FOR THE REGENERATION UNIT

MONTHLY DATA AVERAGES

VARIABLE	10/74	11/74	12/74	1/75
CALCINER				
-TEMPERATURES (F)				
MDKILN	1260.59	1361.25	1451.97	1494.86
GASOUT	571.75	534.04	544.39	582.89
PRODEX	224.72	160.00	155.22	169.74
-SOLID FLOWS (PPM)				
$MgSO_3$	50.20	51.62	56.61	55.40
COKE	0.43	0.32	0.30	0.31
NEUT. pH LIQ.	5.25	5.83	6.01	6.40
ACID PLANT FEED GAS (%)				
02	5.76	7.34	7.57	7.40

TABLE 31

STREAM COMPOSITIONS FOR THE REGENERATION UNIT

MONTHLY DATA AVERAGES

VARIABLE	10/74	11/74	12/74	1/75
CALCINER FEED				
% H_2O	11.20	11.38	6.00	6.45
% $MgSO_3$	64.08	67.47	63.78	68.42
% $MgSO_4$	7.89	7.25	9.25	8.63
% MgO	5.80	4.94	7.69	6.28
% CARBON	2.66	1.35	1.76	1.32
CALCINER PRODUCT				
% $MgSO_3$	0.45	0.15	0.92	0.46
% $MgSO_4$	0.90	1.29	1.08	3.74
% MgO	89.78	94.62	93.57	93.41
BULK DENSTIY	27.61	22.73	22.41	21.31

TABLE 32

RUN DATES AND DATA LISTINGS

RUN DATES

STARTING	ENDING	CASE NO.'S
10/15/74	10/18/74	1-31
11/24/74	12/1/74	128-214
12/6/74	12/10/74	218-277
12/14/74	12/23/74	279-384
12/27/74	12/29/74	386-415
1/12/75	1/14/75	421-451

The following identifies the abbreviated words on Pages 126 - 133:

SO_2 IN PPM = Parts Per Million Of SO_2 Into Scrubber

% SO_2 REM = Percent SO_2 Removed In Scrubber

D GAS T = Dry Gas Temperature

D PROD T = Dry Product Temperature

CIRC GPM = Recycle GPM

FAN AMPS = Current required To Drive Fan

CASE NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
1	MISSING	MISSING	7.3000	4.0000	MISSING	MISSING	10000.0000	190.0000
2	MISSING	MISSING	7.2000	9.0000	MISSING	MISSING	9800.0000	250.0000
3	MISSING	MISSING	7.2000	8.6000	MISSING	MISSING	10000.0000	230.0000
4	MISSING	MISSING	7.0000	9.0000	MISSING	MISSING	9800.0000	230.0000
5	MISSING	MISSING	6.9000	6.0000	240.0000	150.0000	9800.0000	200.0000
6	MISSING	MISSING	7.0000	5.6000	300.0000	145.0000	10000.0000	200.0000
7	MISSING	MISSING	6.8000	5.5000	380.0000	160.0000	10000.0000	200.0000
8	MISSING	MISSING	6.9000	5.0000	330.0000	160.0000	10000.0000	200.0000
9	MISSING	MISSING	6.9000	5.5000	280.0000	170.0000	10000.0000	200.0000
10	MISSING	MISSING	6.9000	5.5000	270.0000	175.0000	10000.0000	200.0000
11	MISSING	MISSING	6.9000	5.5000	240.0000	175.0000	10050.0000	200.0000
12	MISSING	MISSING	6.8000	5.5000	240.0000	165.0000	9900.0000	190.0000
13	MISSING	MISSING	6.9000	5.5000	255.0000	165.0000	9900.0000	200.0000
14	MISSING	MISSING	6.9000	5.5000	220.0000	160.0000	9900.0000	200.0000
15	MISSING	MISSING	6.9000	6.0000	280.0000	170.0000	9900.0000	200.0000
16	MISSING	MISSING	7.1000	7.6000	320.0000	195.0000	9800.0000	200.0000
17	MISSING	MISSING	7.1000	5.5000	275.0000	180.0000	9800.0000	200.0000
18	MISSING	MISSING	6.9000	6.0000	280.0000	180.0000	9800.0000	200.0000
19	MISSING	MISSING	7.0000	5.2000	280.0000	175.0000	9900.0000	200.0000
20	MISSING	MISSING	7.0000	5.5000	280.0000	170.0000	MISSING	200.0000
21	MISSING	MISSING	7.1000	5.5000	360.0000	170.0000	MISSING	200.0000
22	MISSING	MISSING	7.0000	5.5000	250.0000	165.0000	MISSING	200.0000
23	MISSING	MISSING	6.8000	5.5000	260.0000	185.0000	MISSING	200.0000
24	MISSING	MISSING	6.7000	4.0000	220.0000	175.0000	MISSING	190.0000
25	MISSING	MISSING	6.9000	5.5000	230.0000	165.0000	MISSING	200.0000
26	MISSING	MISSING	6.7000	3.5000	225.0000	160.0000	MISSING	190.0000
27	MISSING	MISSING	6.9000	4.0000	225.0000	160.0000	MISSING	MISSING
28	MISSING	MISSING	6.8000	4.5000	225.0000	165.0000	MISSING	190.0000
29	MISSING	MISSING	7.1000	3.5000	235.0000	165.0000	MISSING	180.0000
30	MISSING	MISSING	7.1000	3.5000	235.0000	165.0000	MISSING	180.0000
31	MISSING	MISSING	7.0000	3.3000	220.0000	155.0000	MISSING	MISSING
32	MISSING	MISSING	6.8000	7.0000	MISSING	MISSING	MISSING	210.0000
33	MISSING	MISSING	6.3000	4.0000	MISSING	MISSING	MISSING	180.0000
34	MISSING	MISSING	6.9000	9.0000	210.0000	155.0000	MISSING	225.0000
35	MISSING	MISSING	6.9000	8.0000	220.0000	165.0000	MISSING	225.0000
36	MISSING	MISSING	6.7000	9.6000	250.0000	170.0000	MISSING	220.0000
37	MISSING	MISSING	6.9000	8.6000	240.0000	175.0000	MISSING	220.0000
38	MISSING	MISSING	6.9000	8.6000	235.0000	175.0000	MISSING	220.0000
39	MISSING	MISSING	6.9000	8.6000	235.0000	175.0000	MISSING	220.0000
40	MISSING	MISSING	7.0000	8.6000	220.0000	170.0000	MISSING	220.0000
41	MISSING	MISSING	6.8000	7.0000	210.0000	160.0000	MISSING	220.0000
42	MISSING	MISSING	6.9000	7.0000	210.0000	160.0000	MISSING	220.0000
43	MISSING	MISSING	7.3000	7.0000	210.0000	160.0000	MISSING	220.0000
44	MISSING	MISSING	7.3000	8.5000	225.0000	160.0000	MISSING	220.0000
45	MISSING	MISSING	7.3000	10.5000	225.0000	168.0000	MISSING	240.0000
46	1110.0000	94.5900	7.4000	13.4000	210.0000	177.0000	MISSING	280.0000
47	1760.0000	93.8100	7.3000	13.2000	260.0000	180.0000	MISSING	280.0000
48	1260.0000	93.9100	MISSING	MISSING	MISSING	MISSING	MISSING	150.0000
49	1260.0000	93.8100	MISSING	MISSING	MISSING	MISSING	MISSING	150.0000
50	MISSING	MISSING	7.2000	2.5000	265.0000	MISSING	MISSING	160.0000
51	MISSING	MISSING	6.6000	1.4000	220.0000	165.0000	MISSING	150.0000
52	MISSING	MISSING	7.1000	1.5000	270.0000	170.0000	MISSING	150.0000
53	1260.0000	95.2400	5.9000	3.0000	300.0000	185.0000	MISSING	165.0000
54	1200.0000	84.0000	5.9000	3.0000	300.0000	195.0000	MISSING	175.0000
55	1200.0000	84.0000	5.7000	4.8000	275.0000	190.0000	MISSING	190.0000
56	1260.0000	84.6700	6.8000	2.0000	290.0000	175.0000	MISSING	150.0000
57	MISSING	MISSING	6.3000	6.5000	MISSING	MISSING	12400.0000	220.0000

NO.	1 SO2INPF	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
58	MISSING	MISSING	6.6000	5.5000	MISSING	MISSING	12400.0000	200.0000
59	MISSING	MISSING	7.3000	6.2000	MISSING	MISSING	10000.0000	220.0000
60	MISSING	MISSING	7.3000	6.2000	MISSING	MISSING	10000.0000	200.0000
61	MISSING	MISSING	6.5000	1.000	260.0000	150.0000	11200.0000	150.0000
62	MISSING	MISSING	6.8000	3.5000	282.0000	162.0000	11400.0000	190.0000
63	MISSING	MISSING	6.8000	3.5000	282.0000	162.0000	11400.0000	180.0000
64	MISSING	MISSING	7.1000	4.0000	282.0000	180.0000	11700.0000	200.0000
65	1140.0000	77.8900	6.7000	2.5000	310.0000	175.0000	12000.0000	175.0000
66	1200.0000	79.0000	6.8000	4.2000	280.0000	175.0000	11700.0000	190.0000
67	1200.0000	79.5000	6.6000	5.0000	265.0000	165.0000	12000.0000	190.0000
68	870.0000	75.8600	8.0000	6.0000	MISSING	MISSING	7700.0000	220.0000
69	1080.0000	84.4400	7.2000	6.0000	MISSING	MISSING	7500.0000	220.0000
70	MISSING	MISSING	6.7000	4.0000	265.0000	150.0000	9500.0000	200.0000
71	MISSING	MISSING	7.6000	3.0000	280.0000	155.0000	9400.0000	170.0000
72	MISSING	MISSING	7.6000	3.0000	310.0000	155.0000	9100.0000	180.0000
73	MISSING	MISSING	7.5000	3.0000	310.0000	155.0000	9300.0000	210.0000
74	900.0000	83.3300	7.0000	6.5000	295.0000	160.0000	10000.0000	220.0000
75	900.0000	82.0000	7.1000	5.0000	290.0000	175.0000	9400.0000	200.0000
76	960.0000	80.6300	6.9000	5.2000	300.0000	185.0000	9400.0000	210.0000
77	960.0000	77.5000	6.9000	3.0000	270.0000	173.0000	9400.0000	175.0000
78	900.0000	86.6700	7.0000	7.0000	300.0000	170.0000	MISSING	220.0000
79	960.0000	83.1300	7.2000	7.0000	270.0000	170.0000	MISSING	220.0000
80	1020.0000	85.2900	7.3000	8.3000	310.0000	180.0000	MISSING	240.0000
81	1020.0000	84.1200	7.1000	8.0000	285.0000	182.0000	MISSING	230.0000
82	960.0000	80.0000	7.3000	MISSING	300.0000	185.0000	MISSING	200.0000
83	960.0000	84.3800	7.5000	8.0000	260.0000	185.0000	MISSING	235.0000
84	960.0000	81.2500	7.5000	8.0000	260.0000	185.0000	MISSING	230.0000
85	960.0000	81.2500	7.5000	8.0000	260.0000	185.0000	MISSING	230.0000
86	1140.0000	81.0500	7.1000	5.8000	340.0000	190.0000	MISSING	200.0000
87	1200.0000	78.5000	7.2000	3.0000	MISSING	MISSING	MISSING	170.0000
88	1260.0000	80.0000	7.0000	3.0000	315.0000	195.0000	MISSING	170.0000
89	900.0000	76.6700	7.0000	5.2000	315.0000	180.0000	MISSING	200.0000
90	960.0000	79.3800	7.0000	5.2000	290.0000	170.0000	MISSING	200.0000
91	900.0000	79.3300	6.9000	7.0000	300.0000	175.0000	MISSING	220.0000
92	940.0000	80.1200	7.1000	7.0000	310.0000	195.0000	MISSING	220.0000
93	1080.0000	80.5600	7.0000	7.0000	300.0000	190.0000	MISSING	MISSING
94	900.0000	84.0000	7.2000	9.4000	280.0000	188.0000	MISSING	250.0000
95	840.0000	86.4300	7.3000	12.0000	245.0000	182.0000	MISSING	280.0000
96	900.0000	86.6700	7.2000	13.0000	225.0000	186.0000	MISSING	300.0000
97	900.0000	86.6700	7.1000	12.5000	280.0000	200.0000	MISSING	300.0000
98	1080.0000	86.1100	6.8000	11.5000	270.0000	190.0000	MISSING	280.0000
99	1080.0000	86.1100	6.8000	11.5000	270.0000	190.0000	MISSING	280.0000
100	1080.0000	86.1100	7.1000	9.5000	250.0000	190.0000	MISSING	260.0000
101	1020.0000	79.4100	6.8000	MISSING	200.0000	160.0000	MISSING	240.0000
102	960.0000	79.3800	6.8000	5.0000	240.0000	150.0000	MISSING	180.0000
103	960.0000	75.0000	7.2000	1.2000	238.0000	155.0000	MISSING	160.0000
104	MISSING	MISSING	7.3000	7.0000	MISSING	MISSING	8500.0000	240.0000
105	780.0000	85.3800	7.1000	9.5000	MISSING	MISSING	8200.0000	260.0000
106	1560.0000	MISSING	6.8000	7.0000	250.0000	175.0000	8600.0000	240.0000
107	1380.0000	86.9600	7.1000	9.2000	255.0000	175.0000	8600.0000	260.0000
108	1380.0000	86.9600	7.1000	9.2000	MISSING	180.0000	8600.0000	260.0000
109	1380.0000	86.9600	7.1000	9.2000	MISSING	180.0000	8600.0000	260.0000
110	1320.0000	85.3600	7.2000	10.000	MISSING	180.0000	9500.0000	260.0000
111	1140.0000	84.7400	6.9000	10.000	240.0000	180.0000	11200.0000	260.0000
112	1140.0000	84.2100	7.1000	8.0000	250.0000	170.0000	11200.0000	230.0000
113	1150.0000	84.3500	7.1000	8.5000	300.0000	195.0000	11200.0000	230.0000
114	1080.0000	83.3300	7.1000	10.000	200.0000	190.0000	10400.0000	260.0000
115	1140.0000	84.2100	7.0000	10.000	200.0000	190.0000	10700.0000	260.0000
116	1140.0000	84.2100	7.0000	10.000	200.0000	150.0000	11100.0000	260.0000
117	1140.0000	MISSING	7.0000	10.000	200.0000	150.0000	11100.0000	260.0000
118	1140.0000	84.2100	7.2000	10.000	200.0000	160.0000	11300.0000	270.0000

E NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
119	1140.0000	79.4700	7.0000	7.2000	200.0000	155.0000	11400.0000	230.0000
120	1140.0000	79.4700	6.8000	7.2000	210.0000	160.0000	11800.0000	220.0000
121	MISSING	MISSING	7.1000	7.2000	210.0000	160.0000	11800.0000	220.0000
122	MISSING	MISSING	7.3000	8.9000	MISSING	158.0000	12300.0000	230.0000
123	900.0000	81.3300	7.2000	10.2000	212.0000	158.0000	10400.0000	260.0000
124	1200.0000	92.0000	7.1000	11.7000	212.0000	180.0000	10100.0000	280.0000
125	1680.0000	94.6400	7.0000	11.4000	225.0000	177.0000	10400.0000	280.0000
126	1680.0000	94.6400	7.1000	10.000	200.0000	130.0000	10400.0000	250.0000
127	960.0000	81.8800	7.0000	9.6000	220.0000	155.0000	10400.0000	250.0000
128	960.0000	81.8800	7.2000	7.0000	250.0000	130.0000	9200.0000	220.0000
129	900.0000	82.0000	7.1000	7.8000	245.0000	170.0000	9300.0000	230.0000
130	900.0000	85.3300	7.1000	9.7000	242.0000	175.0000	9300.0000	250.0000
131	900.0000	85.2200	7.1000	9.7000	261.0000	183.0000	9300.0000	250.0000
132	900.0000	84.4400	7.0000	10.5000	265.0000	180.0000	9300.0000	250.0000
133	MISSING	MISSING	7.5000	2.5000	MISSING	155.0000	9400.0000	170.0000
134	MISSING	MISSING	7.4000	5.5000	MISSING	160.0000	9500.0000	200.0000
135	900.0000	82.6700	7.0000	6.8000	215.0000	155.0000	9500.0000	220.0000
136	960.0000	82.5000	6.9000	6.8000	203.0000	155.0000	MISSING	220.0000
137	960.0000	85.6300	7.0000	8.6000	230.0000	165.0000	9600.0000	240.0000
138	900.0000	84.0000	MISSING	8.9000	228.0000	165.0000	9700.0000	240.0000
139	900.0000	84.0000	7.1000	8.8000	230.0000	172.0000	9700.0000	240.0000
140	900.0000	84.6700	7.1000	9.0000	220.0000	163.0000	10000.0000	240.0000
141	900.0000	84.6700	7.1000	9.0000	250.0000	172.0000	10100.0000	240.0000
142	900.0000	84.0000	7.0000	9.1000	265.0000	175.0000	10100.0000	240.0000
143	960.0000	84.3800	6.9000	9.1000	272.0000	173.0000	10000.0000	240.0000
144	960.0000	84.3800	7.0000	8.5000	240.0000	160.0000	10000.0000	240.0000
145	900.0000	82.0000	7.1000	8.5000	210.0000	160.0000	10500.0000	240.0000
146	900.0000	82.0000	7.1000	9.3000	220.0000	158.0000	10400.0000	240.0000
147	900.0000	83.3300	7.2000	8.7000	220.0000	153.0000	10100.0000	240.0000
148	960.0000	83.1300	7.3000	9.0000	220.0000	153.0000	10100.0000	240.0000
149	960.0000	82.5000	7.1000	9.0000	240.0000	159.0000	10000.0000	240.0000
150	1020.0000	82.3500	6.9000	9.0000	230.0000	170.0000	10200.0000	240.0000
151	1020.0000	82.3500	6.9000	9.0000	230.0000	170.0000	10200.0000	240.0000
152	1020.0000	82.9400	6.9000	9.0000	230.0000	170.0000	10200.0000	240.0000
153	1020.0000	82.9400	6.9000	9.0000	230.0000	170.0000	10200.0000	240.0000
154	1020.0000	82.9400	6.9000	9.0000	230.0000	170.0000	10200.0000	240.0000
155	1020.0000	81.1800	7.2000	9.1000	270.0000	180.0000	10200.0000	240.0000
156	960.0000	80.6300	7.0000	9.0000	290.0000	180.0000	MISSING	240.0000
157	1080.0000	82.2200	7.0000	8.5000	300.0000	180.0000	MISSING	240.0000
158	1020.0000	81.1800	7.1000	8.5000	280.0000	185.0000	MISSING	240.0000
159	1020.0000	81.1800	7.1000	9.0000	280.0000	190.0000	MISSING	240.0000
160	1020.0000	80.0000	7.0000	9.0000	220.0000	170.0000	MISSING	240.0000
161	1080.0000	80.5600	7.0000	9.0000	220.0000	170.0000	MISSING	240.0000
162	1140.0000	80.5300	7.0000	9.0000	230.0000	180.0000	MISSING	240.0000
163	1140.0000	80.5300	7.0000	9.0000	230.0000	180.0000	MISSING	240.0000
164	1140.0000	79.4700	7.2000	9.0000	225.0000	180.0000	MISSING	240.0000
165	1020.0000	79.2400	7.2000	8.6000	220.0000	190.0000	MISSING	240.0000
166	1380.0000	79.3300	6.9000	9.0000	220.0000	170.0000	MISSING	240.0000
167	1080.0000	79.3300	7.1000	9.7000	220.0000	170.0000	MISSING	240.0000
168	1020.0000	80.0000	7.1000	9.0000	225.0000	170.0000	MISSING	240.0000
169	1020.0000	82.9400	7.0000	9.0000	220.0000	170.0000	MISSING	240.0000
170	1020.0000	82.3500	7.0000	9.0000	220.0000	170.0000	MISSING	240.0000
171	960.0000	81.2500	7.1000	9.0000	220.0000	170.0000	MISSING	240.0000
172	960.0000	78.1300	7.2000	9.0000	220.0000	165.0000	MISSING	240.0000
173	1080.0000	80.0000	5.9000	9.3000	225.0000	175.0000	MISSING	240.0000
174	960.0000	77.2900	7.0000	8.5000	230.0000	170.0000	MISSING	230.0000
175	1140.0000	81.5800	6.9000	10.000	230.0000	170.0000	MISSING	240.0000
176	1200.0000	84.0000	6.9000	9.3000	240.0000	175.0000	MISSING	230.0000
177	1200.0000	84.0000	5.9000	9.3000	240.0000	175.0000	MISSING	220.0000
178	1200.0000	84.0000	6.9000	9.3000	240.0000	175.0000	MISSING	190.0000
179	1200.0000	84.0000	7.0000	4.0000	310.0000	180.0000	MISSING	190.0000

SE NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
180	1200.0000	84.0000	7.0000	4.0000	315.0000	180.0000	MISSING	190.0000
181	1080.0000	78.8900	6.9000	4.0000	300.0000	165.0000	MISSING	190.0000
182	1080.0000	78.8900	6.7000	5.1000	400.0000	205.0000	MISSING	180.0000
183	1080.0000	78.8900	6.9000	3.9000	345.0000	185.0000	MISSING	170.0000
184	1080.0000	79.3300	6.9000	6.0000	335.0000	185.0000	MISSING	210.0000
185	1140.0000	82.1100	7.0000	8.0000	325.0000	180.0000	MISSING	230.0000
186	1080.0000	77.7800	7.1000	5.8000	400.0000	195.0000	MISSING	200.0000
187	1080.0000	77.7800	6.9000	7.0000	340.0000	160.0000	MISSING	220.0000
188	1080.0000	77.7800	6.9000	7.0000	340.0000	160.0000	MISSING	190.0000
189	1140.0000	76.3200	6.7000	6.0000	280.0000	165.0000	MISSING	200.0000
190	1140.0000	73.6800	6.7000	6.0000	280.0000	155.0000	MISSING	200.0000
191	1140.0000	73.6800	7.0000	5.8000	365.0000	240.0000	MISSING	200.0000
192	1140.0000	73.6800	7.0000	5.1000	410.0000	240.0000	MISSING	200.0000
193	1080.0000	75.5600	7.0000	5.9000	420.0000	253.0000	MISSING	200.0000
194	1140.0000	77.8900	6.9000	6.2000	420.0000	251.0000	MISSING	200.0000
195	1080.0000	76.1100	7.0000	6.0000	435.0000	262.0000	MISSING	200.0000
196	1020.0000	74.7100	7.0000	5.5000	425.0000	256.0000	MISSING	200.0000
197	1020.0000	74.7100	7.1000	5.5000	450.0000	245.0000	MISSING	200.0000
198	1140.0000	77.8900	7.0000	6.0000	450.0000	245.0000	MISSING	210.0000
199	1140.0000	77.3700	7.0000	6.5000	450.0000	260.0000	MISSING	210.0000
200	1140.0000	76.3200	7.1000	6.4000	430.0000	260.0000	MISSING	210.0000
201	1140.0000	76.3200	7.0000	7.0000	410.0000	250.0000	MISSING	210.0000
202	1140.0000	77.3700	7.0000	6.8000	390.0000	240.0000	MISSING	210.0000
203	1140.0000	76.3200	7.0000	6.6000	365.0000	235.0000	MISSING	210.0000
204	1140.0000	74.7400	7.1000	MISSING	370.0000	235.0000	MISSING	210.0000
205	1140.0000	76.3200	7.0000	6.6000	360.0000	230.0000	MISSING	210.0000
206	1140.0000	76.3200	6.9000	6.5000	360.0000	230.0000	MISSING	210.0000
207	1140.0000	76.3200	7.0000	6.5000	350.0000	220.0000	MISSING	210.0000
208	1140.0000	76.3200	7.0000	6.5000	350.0000	210.0000	MISSING	210.0000
209	1080.0000	75.5600	7.0000	6.5000	350.0000	210.0000	MISSING	210.0000
210	1080.0000	76.6700	7.1000	6.5000	320.0000	190.0000	MISSING	210.0000
211	1080.0000	76.6700	7.1000	6.5000	350.0000	190.0000	MISSING	210.0000
212	1020.0000	76.4700	7.1000	6.6000	340.0000	200.0000	MISSING	210.0000
213	1020.0000	76.4700	7.1000	6.2000	350.0000	200.0000	MISSING	210.0000
214	960.0000	72.5000	7.1000	5.4000	375.0000	250.0000	MISSING	210.0000
215	960.0000	75.6300	7.3000	3.0000	MISSING	MISSING	MISSING	170.0000
216	960.0000	75.6300	7.3000	3.0000	MISSING	MISSING	MISSING	200.0000
217	1020.0000	79.4100	7.2000	5.5000	200.0000	MISSING	MISSING	200.0000
218	1020.0000	76.4700	7.0000	5.2000	250.0000	185.0000	MISSING	200.0000
219	1020.0000	76.4700	7.0000	5.2000	250.0000	185.0000	MISSING	200.0000
220	1020.0000	76.4700	7.0000	5.2000	250.0000	185.0000	MISSING	200.0000
221	1200.0000	MISSING	7.5000	6.6000	310.0000	195.0000	MISSING	210.0000
222	1020.0000	80.5900	7.1000	8.0000	225.0000	170.0000	MISSING	230.0000
223	1110.0000	83.7800	7.1000	9.5000	225.0000	180.0000	MISSING	240.0000
224	1080.0000	77.7800	7.1000	9.5000	225.0000	210.0000	MISSING	240.0000
225	1080.0000	82.7800	7.1000	9.0000	275.0000	210.0000	MISSING	240.0000
226	1080.0000	79.3300	7.0000	8.4000	280.0000	210.0000	MISSING	230.0000
227	1140.0000	83.6800	7.0000	8.4000	275.0000	205.0000	MISSING	240.0000
228	1080.0000	81.6700	7.1000	8.4000	270.0000	210.0000	MISSING	240.0000
229	1140.0000	82.6300	7.1000	8.5000	285.0000	210.0000	MISSING	240.0000
230	1140.0000	76.3200	7.0000	9.0000	270.0000	200.0000	MISSING	240.0000
231	1140.0000	74.3200	7.1000	9.0000	260.0000	190.0000	MISSING	240.0000
232	1140.0000	74.3200	7.1000	9.0000	260.0000	190.0000	MISSING	240.0000
233	1140.0000	74.3200	7.2000	9.0000	250.0000	190.0000	MISSING	240.0000
234	1140.0000	74.3200	7.2000	9.0000	250.0000	190.0000	MISSING	240.0000
235	1140.0000	74.3200	7.2000	9.0000	250.0000	190.0000	MISSING	240.0000
236	840.0000	75.0000	7.2000	7.0000	280.0000	195.0000	MISSING	240.0000
237	1080.0000	81.6700	7.1000	8.4000	310.0000	210.0000	MISSING	240.0000
238	1140.0000	79.9500	7.0000	8.5000	290.0000	190.0000	MISSING	240.0000
239	1140.0000	79.9500	7.1000	8.5000	275.0000	200.0000	MISSING	240.0000
240	1080.0000	77.7800	7.0000	8.5000	300.0000	210.0000	MISSING	240.0000

NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
241	1140.0000	82.6300	7.0000	8.5000	340.0000	240.0000	MISSING	240.0000
242	1140.0000	81.5800	6.8000	8.6000	305.0000	215.0000	MISSING	240.0000
243	1140.0000	78.9500	7.0000	8.5000	290.0000	205.0000	MISSING	240.0000
244	MISSING	MISSING	7.0000	8.5000	330.0000	215.0000	MISSING	240.0000
245	1380.0000	80.4300	6.7000	7.5000	320.0000	210.0000	MISSING	240.0000
246	1140.0000	74.7400	6.9000	8.4000	275.0000	205.0000	MISSING	230.0000
247	1140.0000	74.7400	6.9000	7.4000	250.0000	215.0000	MISSING	210.0000
248	1230.0000	78.7000	7.0000	6.2000	300.0000	210.0000	MISSING	200.0000
249	1230.0000	78.7000	7.0000	4.0000	400.0000	185.0000	MISSING	180.0000
250	1080.0000	72.2200	7.0000	4.0000	410.0000	200.0000	MISSING	180.0000
251	1140.0000	73.6800	7.0000	4.0000	400.0000	210.0000	MISSING	180.0000
252	1260.0000	76.1900	7.1000	4.0000	390.0000	225.0000	MISSING	180.0000
253	1140.0000	73.6800	7.1000	4.0000	450.0000	225.0000	MISSING	180.0000
254	1380.0000	78.2600	7.0000	4.4000	390.0000	225.0000	MISSING	180.0000
255	1380.0000	78.2600	7.0000	4.4000	300.0000	200.0000	MISSING	180.0000
256	1380.0000	78.2600	7.1000	4.4000	380.0000	175.0000	MISSING	180.0000
257	1170.0000	74.3600	7.1000	4.2000	350.0000	220.0000	MISSING	180.0000
258	1020.0000	75.8800	7.0000	5.0000	325.0000	200.0000	MISSING	180.0000
259	1020.0000	75.8800	6.9000	4.4000	325.0000	200.0000	MISSING	180.0000
260	1080.0000	77.2200	7.0000	5.0000	325.0000	200.0000	MISSING	180.0000
261	1020.0000	74.1200	7.1000	4.5000	320.0000	205.0000	MISSING	190.0000
262	1020.0000	74.1200	7.0000	4.5000	320.0000	205.0000	MISSING	190.0000
263	1140.0000	76.3200	6.9000	6.2000	320.0000	205.0000	MISSING	200.0000
264	1140.0000	76.3200	6.9000	6.2000	330.0000	205.0000	MISSING	200.0000
265	1200.0000	74.0000	7.1000	6.0000	320.0000	200.0000	MISSING	200.0000
266	1200.0000	77.0000	7.0000	6.4000	320.0000	210.0000	MISSING	200.0000
267	1020.0000	70.5900	6.9000	7.0000	320.0000	205.0000	MISSING	200.0000
268	1320.0000	77.2700	6.9000	7.0000	325.0000	218.0000	MISSING	205.0000
269	1140.0000	73.6800	7.1000	5.2000	325.0000	224.0000	MISSING	200.0000
270	1140.0000	73.6800	6.9000	4.7000	325.0000	215.0000	MISSING	190.0000
271	1140.0000	73.6800	7.2000	1.000	325.0000	215.0000	MISSING	160.0000
272	1140.0000	73.6800	7.3000	1.2000	325.0000	215.0000	MISSING	160.0000
273	1080.0000	72.7800	7.3000	2.8000	325.0000	192.0000	MISSING	170.0000
274	1080.0000	72.2200	6.9000	4.2000	335.0000	195.0000	MISSING	180.0000
275	1140.0000	73.6800	7.0000	4.0000	352.0000	210.0000	MISSING	180.0000
276	1140.0000	73.6800	7.0000	5.7000	352.0000	215.0000	MISSING	190.0000
277	1200.0000	75.0000	7.0000	7.2000	350.0000	220.0000	MISSING	200.0000
278	1200.0000	75.0000	7.0000	5.8000	350.0000	220.0000	MISSING	205.0000
279	1200.0000	80.0000	7.2000	5.0000	325.0000	210.0000	10200.0000	190.0000
280	1200.0000	80.5000	7.2000	5.0000	325.0000	210.0000	10200.0000	190.0000
281	1200.0000	80.5000	7.2000	5.0000	325.0000	210.0000	10200.0000	190.0000
282	1080.0000	77.7800	7.2000	5.5000	325.0000	205.0000	10200.0000	190.0000
283	1020.0000	76.4700	7.2000	4.8000	325.0000	215.0000	10200.0000	190.0000
284	1080.0000	81.6700	7.2000	6.2000	320.0000	220.0000	10200.0000	200.0000
285	1080.0000	77.7800	7.2000	6.2000	320.0000	215.0000	10200.0000	200.0000
286	960.0000	74.3800	7.1000	2.5000	318.0000	225.0000	10200.0000	150.0000
287	1020.0000	81.7600	6.9000	6.3000	280.0000	190.0000	10200.0000	200.0000
288	960.0000	81.2500	6.9000	6.0000	277.0000	197.0000	10200.0000	200.0000
289	1020.0000	84.7100	6.9000	8.0000	270.0000	195.0000	10200.0000	220.0000
290	1080.0000	83.8900	7.0000	7.0000	265.0000	210.0000	10200.0000	210.0000
291	1080.0000	83.8900	7.2000	7.0000	265.0000	200.0000	10200.0000	210.0000
292	1080.0000	83.8900	7.3000	7.0000	265.0000	200.0000	10200.0000	210.0000
293	1080.0000	83.3300	7.2000	7.0000	265.0000	200.0000	10200.0000	210.0000
294	1080.0000	83.6100	7.2000	6.5000	270.0000	215.0000	10200.0000	210.0000
295	1050.0000	84.0000	7.2000	6.7000	265.0000	200.0000	10200.0000	220.0000
296	1020.0000	82.6500	7.0000	6.7000	265.0000	195.0000	10200.0000	220.0000
297	1050.0000	92.0000	7.0000	6.7000	280.0000	195.0000	10200.0000	220.0000
298	1080.0000	80.5600	6.9000	6.5000	280.0000	195.0000	10200.0000	220.0000
299	1140.0000	84.2100	7.0000	8.2000	280.0000	205.0000	10200.0000	230.0000
300	1020.0000	82.6500	6.8000	6.0000	280.0000	205.0000	10200.0000	230.0000
301	1140.0000	83.6800	7.0000	7.0000	285.0000	205.0000	10200.0000	220.0000

CASE NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DEL	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
302	1140.0000	81.5800	7.0000	6.7000	280.0000	200.0000	10200.0000	210.0000
303	1140.0000	83.6800	7.1000	6.5000	280.0000	MISSING	10200.0000	210.0000
304	1140.0000	82.1100	7.0000	6.0000	MISSING	MISSING	10200.0000	210.0000
305	1140.0000	82.6300	7.2000	5.5000	285.0000	195.0000	10200.0000	210.0000
306	930.0000	83.8700	7.3000	6.3000	280.0000	192.0000	MISSING	210.0000
307	960.0000	82.8100	7.3000	6.0000	280.0000	MISSING	10000.0000	MISSING
308	840.0000	82.1400	7.3000	4.7000	305.0000	185.0000	10500.0000	150.0000
309	900.0000	83.3300	7.1000	6.0000	310.0000	185.0000	10800.0000	200.0000
310	900.0000	85.3300	6.9000	8.2000	310.0000	190.0000	10800.0000	220.0000
311	900.0000	85.3300	7.0000	8.3000	310.0000	203.0000	10800.0000	220.0000
312	840.0000	84.2900	7.1000	7.5000	300.0000	205.0000	10400.0000	220.0000
313	840.0000	85.0000	7.1000	7.0000	300.0000	200.0000	10600.0000	220.0000
314	840.0000	85.0000	7.2000	7.0000	MISSING	MISSING	10600.0000	220.0000
315	840.0000	83.5700	7.2000	7.2000	300.0000	200.0000	10600.0000	220.0000
316	810.0000	77.0400	7.3000	2.3000	300.0000	190.0000	MISSING	160.0000
317	1080.0000	86.1100	7.1000	8.0000	310.0000	195.0000	11900.0000	180.0000
318	840.0000	85.0000	7.1000	6.0000	310.0000	205.0000	MISSING	200.0000
319	810.0000	87.7800	7.0000	9.0000	300.0000	210.0000	11600.0000	250.0000
320	840.0000	85.7100	7.1000	10.6000	280.0000	200.0000	11600.0000	250.0000
321	900.0000	85.3300	7.1000	10.4000	250.0000	185.0000	11600.0000	250.0000
322	960.0000	86.2500	7.0000	12.0000	260.0000	180.0000	11600.0000	250.0000
323	960.0000	85.6300	7.1000	10.000	260.0000	180.0000	11600.0000	250.0000
324	1020.0000	84.1200	7.0000	9.8000	260.0000	183.0000	10600.0000	250.0000
325	960.0000	83.7500	7.1000	10.000	265.0000	180.0000	10800.0000	250.0000
326	960.0000	83.7500	7.1000	9.8000	267.0000	175.0000	10800.0000	250.0000
327	1080.0000	84.4400	7.1000	10.000	272.0000	175.0000	10800.0000	250.0000
328	1100.0000	83.0900	7.0000	9.5000	300.0000	165.0000	10900.0000	230.0000
329	1140.0000	83.6800	7.0000	9.5000	300.0000	170.0000	10900.0000	230.0000
330	1140.0000	81.5800	7.1000	7.5000	350.0000	220.0000	11200.0000	210.0000
331	1140.0000	81.5800	7.1000	9.5000	350.0000	215.0000	11200.0000	230.0000
332	1200.0000	83.0000	7.0000	9.4000	300.0000	190.0000	11200.0000	230.0000
333	1200.0000	83.0000	7.0000	9.6000	320.0000	190.0000	11200.0000	230.0000
334	1200.0000	82.0000	7.0000	8.4000	330.0000	185.0000	11200.0000	210.0000
335	1140.0000	83.1600	7.0000	8.4000	320.0000	190.0000	11200.0000	210.0000
336	1140.0000	82.6300	7.0000	8.0000	320.0000	185.0000	10800.0000	220.0000
337	1080.0000	82.7800	7.0000	8.2000	325.0000	190.0000	11000.0000	220.0000
338	1080.0000	80.5600	7.0000	8.2000	325.0000	190.0000	11000.0000	220.0000
339	1080.0000	82.2200	7.0000	8.4000	335.0000	195.0000	11100.0000	220.0000
340	1080.0000	82.2200	7.0000	8.4000	335.0000	192.0000	11100.0000	220.0000
341	1200.0000	78.5000	7.0000	2.8000	MISSING	MISSING	11200.0000	170.0000
342	1260.0000	80.9500	7.1000	6.6000	350.0000	185.0000	11200.0000	200.0000
343	1320.0000	80.9100	7.1000	6.6000	370.0000	205.0000	11200.0000	200.0000
344	1380.0000	80.8700	7.0000	7.0000	370.0000	230.0000	11200.0000	200.0000
345	1200.0000	78.0000	7.0000	3.3000	370.0000	235.0000	10900.0000	160.0000
346	1140.0000	75.7900	7.1000	3.5000	370.0000	220.0000	10700.0000	160.0000
347	1140.0000	76.5800	7.0000	3.7000	385.0000	220.0000	10700.0000	160.0000
348	1110.0000	76.7500	7.1000	3.5000	385.0000	210.0000	10700.0000	160.0000
349	1140.0000	76.3200	7.0000	3.3000	380.0000	215.0000	11000.0000	160.0000
350	1080.0000	77.7800	7.0000	3.5000	380.0000	210.0000	11000.0000	160.0000
351	960.0000	80.6300	7.0000	3.6000	385.0000	160.0000	11000.0000	160.0000
352	900.0000	90.0000	7.1000	3.6000	380.0000	160.0000	11000.0000	160.0000
353	960.0000	78.1300	7.1000	3.6000	390.0000	220.0000	11000.0000	160.0000
354	1020.0000	78.2400	7.1000	3.8000	400.0000	220.0000	11000.0000	160.0000
355	1020.0000	76.4700	7.1000	3.7000	400.0000	215.0000	11000.0000	160.0000
356	1080.0000	77.7800	7.1000	3.7000	400.0000	210.0000	11000.0000	160.0000
357	960.0000	78.1300	7.1000	3.0000	400.0000	205.0000	10900.0000	160.0000
358	990.0000	80.3300	7.1000	-.2000	410.0000	230.0000	10900.0000	180.0000
359	990.0000	81.2100	7.0000	5.8000	410.0000	230.0000	10900.0000	200.0000
360	1050.0000	81.7100	7.1000	5.6000	410.0000	235.0000	10900.0000	200.0000
361	1080.0000	82.2200	7.0000	6.5000	400.0000	240.0000	10900.0000	200.0000
362	1080.0000	81.1100	7.0000	6.5000	340.0000	215.0000	10900.0000	200.0000

CASE NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DELTA P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
363	1140.0000	80.0000	6.9000	6.5000	335.0000	205.0000	10900.0000	200.0000
364	1140.0000	81.5800	6.8000	6.5000	335.0000	208.0000	10900.0000	200.0000
365	1140.0000	81.0500	7.0000	6.6000	330.0000	210.0000	11200.0000	200.0000
366	1140.0000	81.5800	7.1000	6.6000	330.0000	215.0000	11200.0000	200.0000
367	1140.0000	81.5800	7.1000	6.8000	330.0000	205.0000	11200.0000	200.0000
368	1140.0000	80.5300	7.0000	6.8000	330.0000	210.0000	11200.0000	200.0000
369	1140.0000	81.3200	7.2000	6.2000	330.0000	210.0000	11200.0000	200.0000
370	1110.0000	81.8900	7.1000	6.5000	335.0000	215.0000	11000.0000	200.0000
371	1110.0000	82.1600	7.2000	6.5000	335.0000	210.0000	11000.0000	200.0000
372	1080.0000	82.2200	7.1000	6.4000	335.0000	210.0000	11000.0000	200.0000
373	1080.0000	82.2200	7.0000	6.3000	335.0000	205.0000	11000.0000	200.0000
374	840.0000	82.8600	7.2000	6.3000	335.0000	180.0000	11000.0000	200.0000
375	900.0000	83.3300	7.1000	7.0000	365.0000	197.0000	11000.0000	210.0000
376	900.0000	83.3300	7.1000	7.0000	365.0000	197.0000	11000.0000	210.0000
377	900.0000	83.3300	7.1000	7.0000	365.0000	197.0000	11000.0000	210.0000
378	900.0000	83.3300	7.1000	7.0000	365.0000	197.0000	11000.0000	210.0000
379	900.0000	83.3300	7.1000	7.0000	365.0000	197.0000	11000.0000	210.0000
380	900.0000	83.3300	6.9000	8.0000	360.0000	210.0000	10900.0000	220.0000
381	900.0000	83.3300	6.9000	8.5000	350.0000	220.0000	10800.0000	220.0000
382	840.0000	83.5700	7.0000	8.5000	350.0000	230.0000	10800.0000	220.0000
383	840.0000	84.2900	7.0000	8.8000	340.0000	225.0000	10800.0000	220.0000
384	960.0000	80.0000	7.0000	8.5000	330.0000	210.0000	10800.0000	220.0000
385	1080.0000	77.2200	7.0000	4.0000	MISSING	MISSING	9900.0000	200.0000
386	1080.0000	77.2200	7.1000	2.2000	MISSING	MISSING	11000.0000	160.0000
387	780.0000	78.4600	7.2000	5.9000	MISSING	MISSING	10900.0000	200.0000
388	780.0000	78.4600	7.2000	5.9000	MISSING	MISSING	10900.0000	200.0000
389	900.0000	81.3300	7.2000	5.9000	260.0000	185.0000	10900.0000	200.0000
390	900.0000	82.6700	7.2000	5.9000	260.0000	185.0000	10900.0000	210.0000
391	900.0000	88.0000	7.2000	5.9000	260.0000	185.0000	10900.0000	220.0000
392	900.0000	88.0000	7.2000	8.5000	260.0000	185.0000	10900.0000	240.0000
393	960.0000	87.5000	7.1000	8.8000	265.0000	185.0000	11000.0000	240.0000
394	900.0000	86.6700	7.1000	9.2000	265.0000	185.0000	11000.0000	260.0000
395	900.0000	86.6700	7.1000	9.2000	260.0000	175.0000	11000.0000	260.0000
396	900.0000	86.6700	7.1000	9.2000	260.0000	175.0000	11000.0000	260.0000
397	1020.0000	88.2400	7.1000	9.2000	255.0000	180.0000	11000.0000	260.0000
398	900.0000	86.6700	7.1000	9.4000	280.0000	170.0000	10850.0000	260.0000
399	900.0000	87.3300	7.0000	10.3000	285.0000	192.0000	10850.0000	260.0000
400	900.0000	87.3300	7.0000	10.3000	285.0000	192.0000	10850.0000	260.0000
401	1000.0000	85.6000	7.0000	9.0000	285.0000	192.0000	10850.0000	260.0000
402	1140.0000	86.8400	7.0000	9.0000	210.0000	170.0000	10850.0000	260.0000
403	1020.0000	87.6500	7.0000	10.000	210.0000	170.0000	10850.0000	260.0000
404	1020.0000	88.2400	7.0000	10.000	210.0000	170.0000	10850.0000	260.0000
405	1020.0000	88.2400	7.1000	10.000	200.0000	170.0000	11200.0000	260.0000
406	960.0000	85.0000	7.1000	10.000	200.0000	170.0000	11200.0000	260.0000
407	960.0000	85.0000	7.1000	10.000	200.0000	170.0000	11200.0000	260.0000
408	960.0000	86.2500	7.2000	10.000	200.0000	170.0000	11200.0000	260.0000
409	1080.0000	85.1100	7.1000	10.2000	MISSING	175.0000	10700.0000	260.0000
410	1040.0000	85.7300	7.1000	10.000	275.0000	175.0000	11050.0000	260.0000
411	1080.0000	87.2200	7.0000	10.000	275.0000	200.0000	11050.0000	260.0000
412	1140.0000	87.3700	7.0000	10.000	275.0000	200.0000	11050.0000	260.0000
413	900.0000	86.6700	7.2000	10.000	275.0000	200.0000	11100.0000	260.0000
414	1380.0000	79.7000	7.0000	3.5000	250.0000	180.0000	11400.0000	180.0000
415	1500.0000	80.4000	7.0000	3.0000	260.0000	180.0000	11400.0000	180.0000
416	1060.0000	81.3200	7.0000	5.0000	MISSING	MISSING	11400.0000	220.0000
417	1020.0000	81.1800	7.0000	5.0000	MISSING	MISSING	11400.0000	220.0000
418	1440.0000	85.8300	7.0000	5.5000	MISSING	MISSING	MISSING	220.0000
419	1440.0000	85.8300	7.0000	6.0000	260.0000	170.0000	MISSING	230.0000
420	1200.0000	87.5000	7.1000	7.0000	260.0000	180.0000	MISSING	220.0000
421	1140.0000	81.5800	6.9000	7.0000	260.0000	180.0000	11200.0000	230.0000
422	1200.0000	83.5000	7.1000	7.4000	260.0000	180.0000	11700.0000	230.0000
	1140.0000	80.5300	7.2000	6.3000	? 0000	170.0000	11700.0000	210.0000

CASE NO.	1 SO2INPPM	2 %SO2 REM	3 PH	4 DEL P	5 D GAS T	6 D PROD T	7 CIRC GPM	8 FAN AMPS
424	1140.0000	79.4700	7.1000	6.5000	260.0000	170.0000	11900.0000	210.0000
425	1440.0000	82.0800	6.9000	6.2000	265.0000	170.0000	11600.0000	210.0000
426	1560.0000	82.3100	7.0000	6.1000	265.0000	190.0000	11600.0000	210.0000
427	1560.0000	81.5400	7.1000	6.0000	260.0000	195.0000	11500.0000	210.0000
428	1560.0000	MISSING	7.2000	6.0000	263.0000	198.0000	11300.0000	210.0000
429	1560.0000	MISSING	7.1000	6.0000	260.0000	190.0000	11400.0000	210.0000
430	1560.0000	MISSING	7.2000	6.0000	260.0000	188.0000	11400.0000	210.0000
431	1560.0000	MISSING	7.1000	6.0000	260.0000	187.0000	11400.0000	210.0000
432	1500.0000	MISSING	7.1000	6.2000	265.0000	190.0000	11400.0000	210.0000
433	1440.0000	MISSING	7.2000	6.2000	260.0000	192.0000	11300.0000	210.0000
434	1440.0000	MISSING	7.2000	6.2000	260.0000	190.0000	11300.0000	210.0000
435	1320.0000	MISSING	7.1000	6.4000	260.0000	190.0000	11300.0000	210.0000
436	1500.0000	MISSING	7.2000	6.0000	260.0000	190.0000	11600.0000	210.0000
437	870.0000	68.2800	7.2000	6.0000	260.0000	145.0000	11000.0000	210.0000
438	870.0000	68.2800	7.1000	6.3000	270.0000	180.0000	11400.0000	210.0000
439	1020.0000	76.4700	7.2000	6.3000	270.0000	180.0000	11400.0000	210.0000
440	1020.0000	77.0600	7.0000	6.8000	285.0000	165.0000	12000.0000	210.0000
441	1060.0000	76.7900	7.0000	6.8000	300.0000	175.0000	11800.0000	210.0000
442	1080.0000	76.6700	7.0000	6.9000	310.0000	170.0000	11800.0000	210.0000
443	1020.0000	74.7100	7.0000	6.9000	305.0000	170.0000	11800.0000	210.0000
444	1080.0000	75.0000	7.0000	6.9000	305.0000	170.0000	11800.0000	210.0000
445	1140.0000	75.2600	7.0000	6.9000	300.0000	170.0000	11800.0000	210.0000
446	1080.0000	73.3300	7.1000	7.0000	325.0000	165.0000	11800.0000	210.0000
447	1200.0000	MISSING	7.1000	6.9000	300.0000	174.0000	11800.0000	210.0000
448	1200.0000	MISSING	7.0000	7.0000	310.0000	175.0000	11800.0000	210.0000
449	1200.0000	MISSING	7.0000	7.0000	310.0000	175.0000	11800.0000	210.0000
450	1200.0000	MISSING	7.1500	6.5000	305.0000	175.0000	11500.0000	210.0000
451	MISSING	MISSING	7.2000	6.5000	305.0000	175.0000	11500.0000	210.0000
452	1560.0000	MISSING	7.1000	3.4000	MISSING	MISSING	11700.0000	190.0000
453	1560.0000	MISSING	7.1000	3.4000	MISSING	MISSING	11700.0000	170.0000
454	1050.0000	MISSING	6.9000	1.2000	MISSING	MISSING	11600.0000	160.0000
455	1050.0000	MISSING	6.9000	MISSING	MISSING	MISSING	11600.0000	170.0000
456	1500.0000	82.0000	7.4000	4.5000	MISSING	MISSING	11600.0000	200.0000
457	1500.0000	84.0000	7.2000	4.0000	200.0000	125.0000	11600.0000	200.0000
458	1500.0000	84.0000	7.1000	4.3000	200.0000	120.0000	11600.0000	200.0000
459	1500.0000	84.0000	7.1000	MISSING	200.0000	120.0000	11600.0000	200.0000
460	1500.0000	84.4000	7.1000	4.4000	200.0000	125.0000	11200.0000	200.0000
461	1380.0000	89.1300	7.2000	7.8000	200.0000	130.0000	11200.0000	250.0000
462	1140.0000	88.4200	6.9000	9.0000	210.0000	155.0000	11300.0000	250.0000
463	MISSING	MISSING	7.1000	7.5000	200.0000	MISSING	11300.0000	240.0000
464	1140.0000	89.4700	7.2000	9.0000	210.0000	150.0000	11700.0000	260.0000
465	1080.0000	89.4400	7.1000	9.2000	200.0000	150.0000	MISSING	250.0000
466	1060.0000	89.0600	MISSING	9.3000	170.0000	145.0000	MISSING	MISSING
467	1320.0000	88.6400	7.2000	9.4000	200.0000	135.0000	11700.0000	240.0000
468	1320.0000	89.0900	7.1000	9.0000	200.0000	140.0000	11700.0000	260.0000
469	1320.0000	89.5500	7.1000	9.0000	200.0000	135.0000	11700.0000	260.0000
470	1260.0000	89.5200	7.1000	8.8000	200.0000	140.0000	11700.0000	260.0000
471	MISSING	MISSING	7.5000	1.2000	MISSING	MISSING	11400.0000	160.0000
472	1140.0000	MISSING	7.4000	10.8000	MISSING	MISSING	11400.0000	240.0000
473	MISSING	MISSING	7.4000	8.0000	MISSING	115.0000	11400.0000	240.0000

NUMBER OF CASES READ. 473

VARIABLE NO. NAME	MEAN	STANDARD DEVIATION	TOTAL FREQUENCY
1 SO2INPPM	1092.036	163.471	403
2 %SO2 REM	81.224	4.444	382
3 PH	7.050	0.166	469
4 DELTA P	6.873	2.290	466
5 D GAS T	287.215	57.256	429
6 D PROD T	186.475	24.718	432
7 CIRC GPM	10725.461	911.543	278
8 FAN AMPS	215.052	28.681	468
9 C TORQUE	37.770	8.549	437

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19) Koehler, G. Report of Operation of a Magnesia FGD System on an Oil Fired Boiler. AIChE Symposium Series, No. 148, (July 1975).

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10.0 CONVERSION FROM ENGLISH TO METRIC UNITS

TO CONVERT FROM	TO	MULTIPLY BY
Atmosphere (normal)	Bar	1.01325
Atmosphere (normal)	Pascal	101,325
Barrel (42 US gallons)	Meter^3	0.15899
British thermal unit (BTU)	Joule	1055.1
BTU/Hour	Watt	0.29307
BTU/pound mass	Joules/gram	2.32600
BTU/pound mass - $^\circ$F	Joules/gram - $^\circ$K	4.18680
Foot	Meter	0.30480
Foot^2	Meter^2	0.09290
Foot^3	Meter^3	0.02832
Foot^3/minute	Meter^3/minute	0.02832
Foot-pound force	Joule	1.35582
Gallon (US)	Meter^3	0.00379
Gallon (US)/minute	Meter^3/hour	0.22712
Grain	Milligram	64.7989
Horsepower	Kilowatt	0.74570
Inch	Centimeter	2.5400
Inch H_2O (60°F)	Kilopascal	0.24884
Pound Force	Newton	4.44822
Pound mass av	Kilogram	0.45359
Pound mass av	Metric ton (tonne)	0.0004536
Pound force/inch^2	Kilopascal	6.89476
Pound mass/foot^3	Kilograms/meter^3	16.0185
$^\circ$Rankine	$^\circ$Kelvin	0.55556
Ton mass (US short)	Kilogram	907.185
Ton mass (US long)	Kilogram	1016.05

APPENDIX I

POST OPERATION INSPECTION REPORT
DATE OF INSPECTION - Jan. 17-24, 1975

(NOTE: Refer to Figure I-1, where numbers refer to following sections)

Plumb Bob Control Mechanism

Operation has been satisfactory.

Upper Section of 1st Stage (5)

(a) The polyester coating was gone from the stem and the top 8" of sloping sides of the plumb bob. The metal is type 316L stainless steel at this point and measurements indicated no loss of thickness.

(b) The coating was also gone from most of the 316 stainless steel lip projecting from the sloping wall just above the throat.

(c) In the throat area there were about 10 spots ranging in size from 12 square inches to 30 square inches where the entire coating had been removed from the metal. The metal is 316L stainless steel at this point. It is possible that these coating failures were caused, by debris from the 4 inch stainless steel nozzles which had failed.

(d) Above the projecting lip on the sloping outer wall, there were a number of holes in the lining where the carbon steel had been attacked so that only the lining on the other side of the steel plate prevented a hole in the vessel. The figure is typical of this type of failure.

EL. 362'-0"

EL. 333'-0"

EL. 311'-0"

EL. 296'-0"
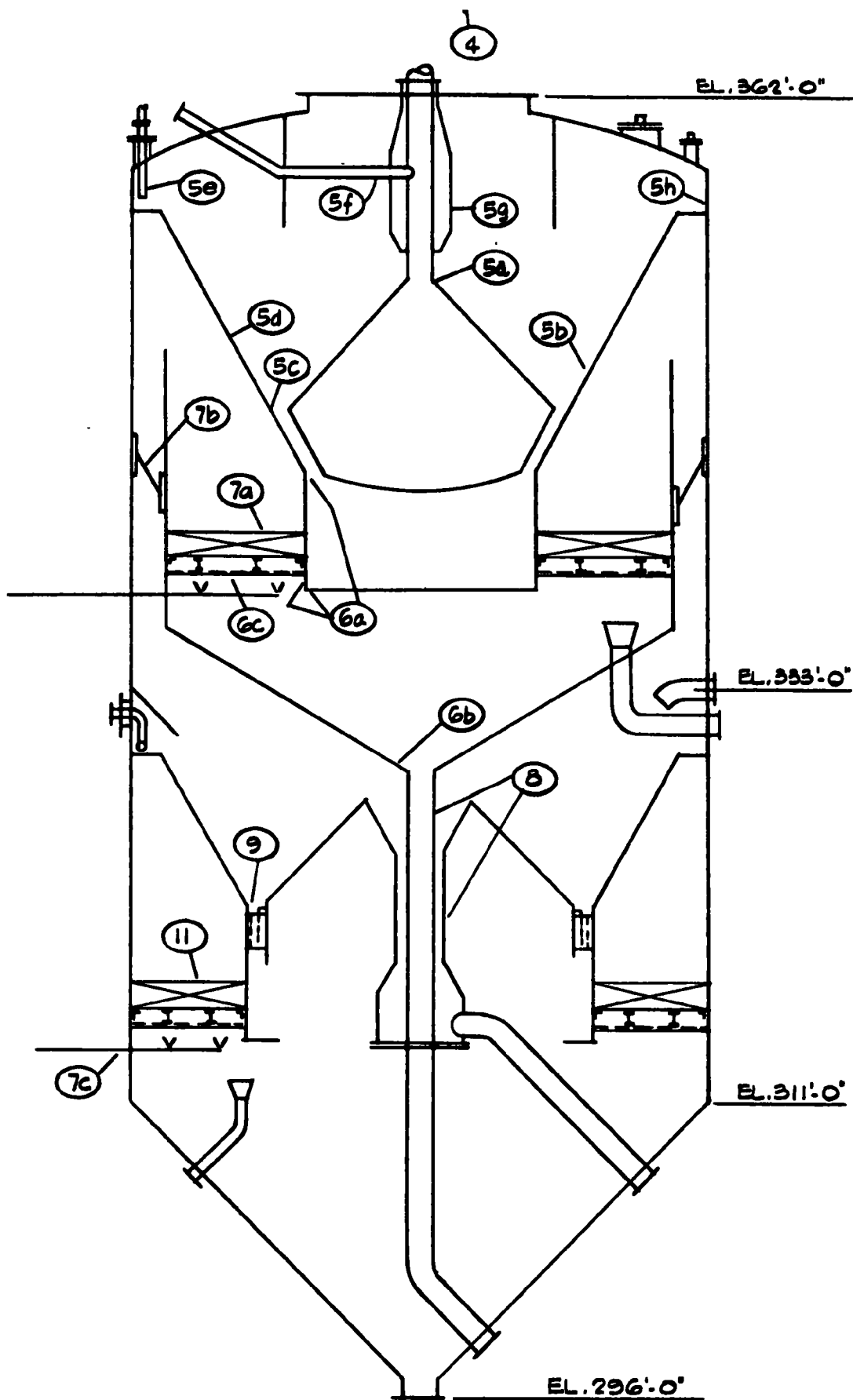
SCRUBBER OUTLINE

FIGURE I-1

(e) As was discussed previously in the section on corro-sion of stainless steel all of the 4-inch tangential nozzles were subjected to extensive failure. Two were still in place, but were in shreds.

(f) The three six-inch stainless steel lines that feed the center manifold were subjected to the same type of attack as the four-inch tangential nozzles and pipes. There was less severity because of the protective coating of brick cast which had been applied over these pipes. Repairs have been carried out by removing the brick cast and coating these six-inch pipes with glass reinforced polyester plastic.

(g) The center manifold was in good condition both inter-nally and externally.

(h) There were two holes through the external wall of the vessel adjacent to tangential inlet nozzles. It is not known the extent to which these were caused by nor-mal erosion or by impaction by partially failed inlet nozzles. Except for these two failures the coating at this portion of the vessel was in good condition.

Lower Section of 1st Stage (6)

(a) The polyester lining was in fair condition, with re-pairs needed at several points in the throat section, at the bottom of the skirt and on the outer surface of the inner skirt.

(b) There was one small (3/8 inch diameter) hole in the bottom of the cone near the vortex breaker where a repair had been made.

(c) There was considerable loss of metal by corrosion of
     type 316 stainless steel from the hanger rods, clips,
     clamps and bolts. As indicated previously, corrosion
     was most severe in areas which had been stressed and
     the replacement pieces have been stress-relieved before
     installation.

1st Stage Mist Eliminator Section (7)

(a) The mist eliminators were clean and in excellent con-
     dition. However, all of the J hooks and clips used
     as hold-downs had failed and most were completely mis-
     sing. These are among the sources of metal that have
     contributed to failures of rubber-lined pipe. The 2
     inch x 0.2 inch straps used as auxiliary hold-downs
     for the mist eliminators have performed their function
     well. There is evidence of slight pitting, but no loss
     of thickness.

(b) The new clevis type 1st stage cone support hangers
     showed slight signs of pitting, but are structurally
     in excellent condition. These were of 316 stainless
     steel and were installed in July 1974. The Inconel
     625 pins installed with them were in excellent condi-
     tion and showed no sign of attack.

(c) The 1st stage mist eliminator wash system has operated
     satisfactorily.

Upper Section of 2nd Stage (8)

This portion of the scrubber was found to be in generally
good condition. There was a small hole (possibly 1/16
inch in diameter) in the stainless steel pipe just below the
base.

Inspection Report (Information of two-stage scrubber
absorber and the recycle pipe have been presented in
the previous report).

2nd Stage Throat Area   (9)

Failure of the coating in the area of the 2nd stage throat
was very extensive as illustrated in photographs 10-7 and
10-10. Assurance of adequate structural integrity was pro-
vided by a series of thickness measurements.

The throat restrictor provided substantial protection for
the inner surface of the throat except where there apparently
were gaps between the restrictor and the inner surface.
Planned repairs and changes include division into an inner
and outer ring, a reduction in the total width (to decrease
pressure drop), and caulking between the restrictor plates
and walls to eliminate flow and erosion at these points.

Gas Systems

(1) Fan

The fan has given excellent service throughout the
entire history of the scrubber. Inspection indicated
that the rotor, which is of high alloy stainless steel
is in a condition apparently as good as new. The
rubber lining of the fan housing is also in a condition
as good as new. The only problem was a failure in one
of the pipes which feeds water to the fan rotor. This
pipe had failed presumably as a result of continued
vibration. Repairs were effected by welding.

(2) Secondary Mist Eliminator

The secondary mist eliminator was clean and in excel-
lent condition except for some evidences of corrosion
of the various 316 stainless steel hanger rods, etc.
This was similar to the corrosion observed in the 1st
stage of the scrubber although substantially less in
extent.

(3) Ducts and Dampers

There was a fair amount of build-up of fly ash in the ducts as would be expected, but the ducts were otherwise in good condition. The major problem with the dampers has been leakage during shut down, permitting a flow of gas backwards through the ducts and scrubber and a progressive increase in fly ash build-up and decrease in damper effectiveness. At the conclusion of operations in late January, whenever the scrubber was shut down there was a very high flow of gas backwards through the scrubber.

A seal ring has now been installed on the outlet damper, with the expectation of drastically reducing (and possibly eliminating) this problem. It is also expected that better continuity of operation will be obtained and this in itself will permit better performance of the dampers on the few occasions when shut downs are expected to be necessary.

Liquid Systems

(1) 1st Stage Recycle Pumps

These have performed excellently at all times. Inspection through the suction piping indicates an appearance "like new."

(2) Thickeners

These have performed satisfactorily. The south thickener had a number of failures in the coating which were repaired. The north thickener, in contrast, had no coating failures. The bolts that hold the arms of the thickener rakes were corroded excessively in the south thickener, but little or no corrosion was observed in the similar bolts in the north thickener.

(3) Thickener Underflow System

This system has performed satisfactorily and inspection did not indicate any defects.

(4) Thickener Overflow Return System

This system has performed satisfactorily from a mechanical standpoint and inspection did not indicate any defects.

(5) 2nd Stage Recycle Pumps

These pumps have given generally satisfactory performance. The impeller on each of the three pumps has been replaced once. In a commercial installation it is expected that rubber covered impellers would be specified and that impeller replacement would not be necessary. At the conclusion of the operating period in late January 1975, performance curves were obtained on the three pumps as indicated in Figure I-2.

(6) Mother Liquor Tank

This tank has given satisfactory performance. The gears on the agitator were replaced on one occasion. Presumably their failure was due to a build up of solids in the bottom of the tank leading to excessive side thrusts on the agitator.

(7) Mother Liquor Pumps

Operation has been satisfactory.

(8) MgO Premix Tank

Operation of this tank has been satisfactory since the changes were made in the summer of 1974.

FIGURE I-2

PERFORMANCE CURVES
2nd STAGE RECYCLE PUMPS

Scrubber Level 24%
January 1975

$\underline{GPM}$

-O- "A" Pump

-□- "B" Pump

-△- "C" Pump

PSI
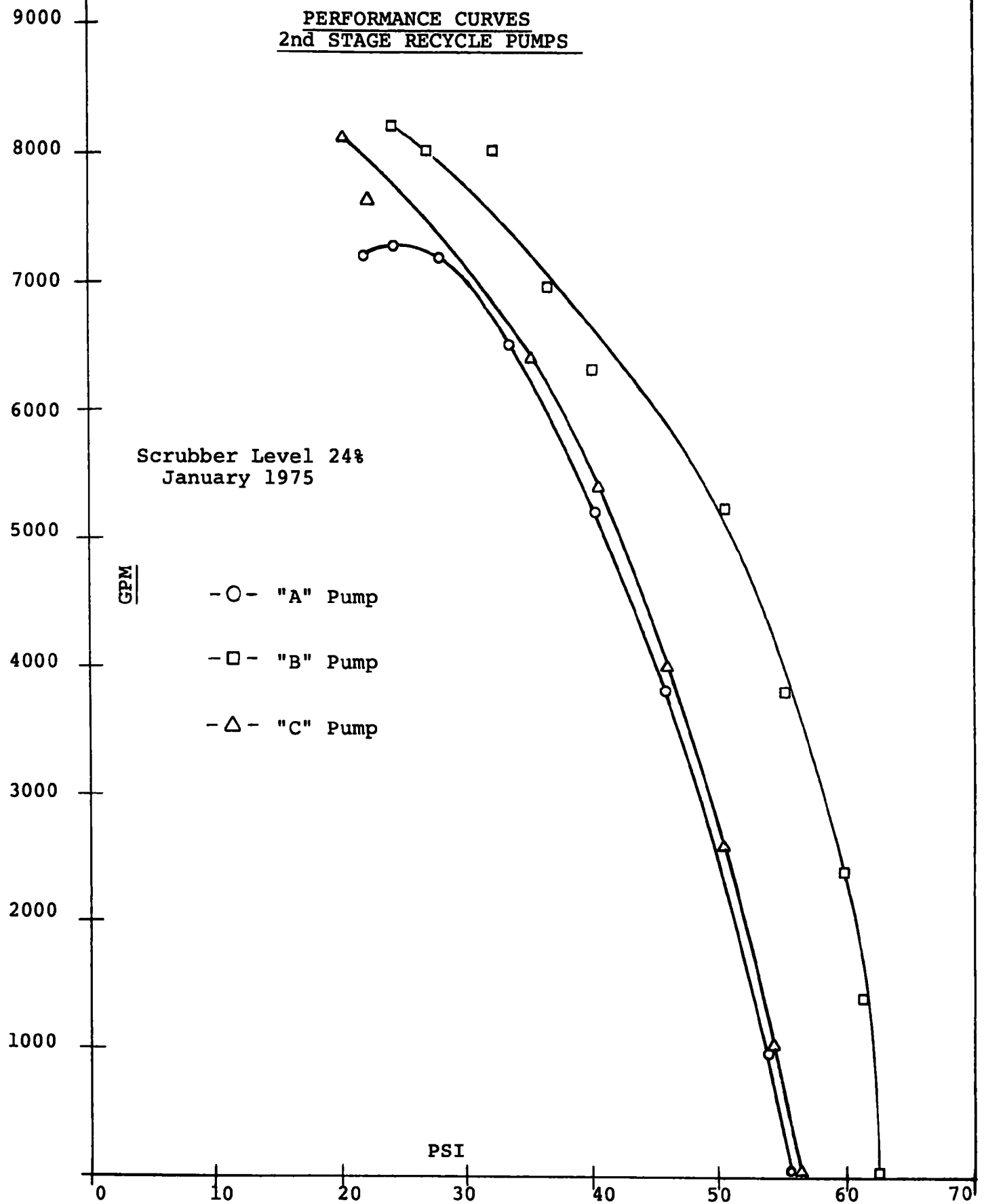
(9) MgO Slurry Tank

Operation has been satisfactory except that the steam
sparger has plugged repeatedly. During the current
boiler outage, the location of the steam inlet line
has been changed. The line now enters through the
top of the tank and is so arranged that the sparger
may be unplugged if plugging should continue. It will
also be possible to change to other sparger designs if
such becomes necessary in order to eliminate plugging.

(10) MgO Slurry Feed Pumps

Operation has been satisfactory since October 1974,
at which time a larger pump was installed as the east
MgO pump. One remaining problem with this system is
that it is necessary to operate both pumps in order to
obtain correct reading of the temperature control ele-
ment. A change in the location of this element is
planned so that the operation may be carried out with
only one pump, reserving the other as a spare.

Solids Systems

(1) MgO Unloading

This system has operated satisfactorily in all respects
except that a leak developed in the elbow at the top of
the loading line, as was to be expected. Repairs were
made by welding which will be adequate for the remain-
ing three months of expected operation of this system.
For a commercial installation materials more resistant
to erosion would be specified for the elbows in unload-
ing lines.

(2) MgO Storage Bin

Operation has been satisfactory.

(3) MgO Weigh Feeder

Operation of this system has been acceptable since

changes were made in the summer of 1974. However, the reliability of this system leaves something to be desired and for future commerical installations, other designs would be investigated. There have been several belt failures during the operation of this system. Near the end of operation in late January, the weigh feeder became most unreliable in its operation and during the outage, moderately extensive repairs and replacements have been carried out.

(4) <u>Centrifuge</u>

Operation of the centrifuge has been generally quite satisfactory and very substantially improved over operation experienced at Boston Edison Company. A major difference between the two installations, of course, is that at Boston Edison the centrifuge feed contained primarily magnesium sulfite trihydrate where-as at PEPCO the feed has been primarily magnesium sulfite hexahydrate. There are four areas that require comment:

(a) There has been no evidence of the type of binding between the conveyor and the bowl (internally) that was so troublesome at Boston Edison. Rotation of the centrifuge was continued most of the time, although there were substantial periods when the machine was shut down and binding might have taken place. The washing procedures developed at Boston Edison were applied at PEPCO from the start of the operations. The extent of internal wear, which is probably directly related to binding, could not be determined. The desirability

of dismantling the centrifuge for inspection
was recognized, but when weighed against the
cost involved, the decision was made to resume
operations without inspection of the internal
portions of the centrifuge.

(b) There was excessive erosion-corrosion of the
case at the liquid end, as shown in photograph
3-2. A patch was applied around the entire 180°
circumference of the casing. Wear continued and
the casing, which was originally 1/4 inch thick,
was worn through completely, exposing the patch
for a longitudinal distance of about 1-1/2 inches.
Although replacement patching internally with
stainless steel would probably have provided a
permanent cure to this erosion problem, the deci-
sion was made, in the interest of economy, to
patch the casing with carbon steel. A coupon of
316 stainless steel has been installed and obser-
vation will be made at the conclusion of the operat-
ing period as to the ability of type 316 to with-
stand this service.

(c) One plow failed and all of the plows were replaced
in September 1974. One plow from the new set
failed in January 1975 and a complete third set of
plows has now been installed. An improved design
of plow may be expected to eliminate this problem
in future installations. The photographs 3-5 (the
failed plow) and 3-11 (normal plows) suggest that
some machines are designed with three bolts per
plow.

(5) Screw Conveyors

These have given generally satisfactory performance.
There is, of course, considerable evidence of wear,
but it is not regarded as excessive. The bearing at
the inboard end of the dryer feed screw was dislodged
due to a spreading of the bearing support as illustra-
ted in photograph 4-3. The screw continued to operate
without any inboard bearing, using the solids in the
trough as support, for several weeks. This bearing has
now been replaced.

(6) Dryer

The dryer has given excellent performance. Buildup
has been limited in amount and it has been possible
to clean the dryer usually by an adjustment in operat-
ing conditions, although occasionally it has been neces-
sary to use a pipe or rod for this purpose. At the con-
clusion of operations in late January, the dryer was
remarkably clean, as illustrated in photograph 4-1.
The refractory of the burner block and the metal casing
around it failed as indicated in photograph 4-6 and
have been replaced.

(7) Dryer Off-Gas Cyclone

The double gate at the base of this cyclone has never
operated properly and a rotary valve has now been in-
stalled to replace it. In the past, failure to remove
solids from the base of the cyclone has led to an ex-
cessive carry-over of fines and recycle to the scrubber.
This situation should be substantially improved as a
result of the installation of the rotary dust valve.

(8) Dryer Off-Gas Fan

Operation has been satisfactory.

(9) <u>Bucket Elevator</u>

It appears that the bucket elevator was sized for a product of higher density and possibly sized in expectation of continuous operation at a uniform rate. In any event, the capacity of the bucket elevator has been inadequate to handle the full load of the scrubber system and has made it necessary to operate at rates approximating 75% of gas flow capacity and somewhat less than 75% of magnesium sulfite capacity. Larger buckets have now been installed on the bucket elevator and it is expected that capacity operation can be achieved at this point in the system as well as elsewhere.

(10) <u>Magnesium Sulfite Storage Silo</u>

Operation has been satisfactory.

(11) <u>Magnesium Sulfite Loading System</u>

Mechanical operation of this system is considered satisfactory. The repeated problems that have been experienced with excessive spillage of magnesium sulfite during loading are considered due to operating problems rather than to defects in the mechanical design or condition of the equipment.

3-2

3-5
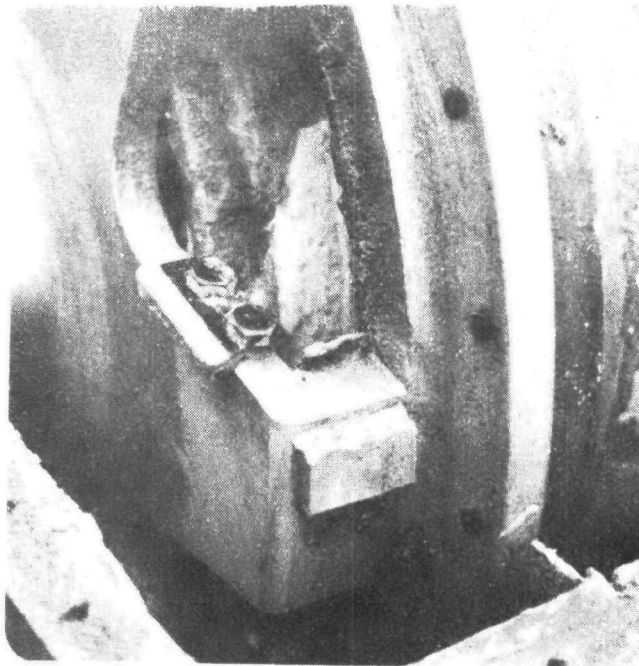
3-11
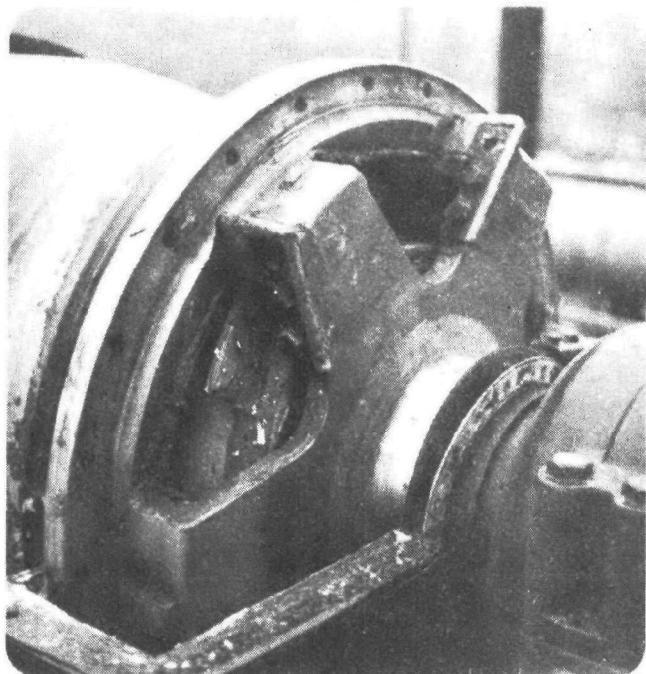
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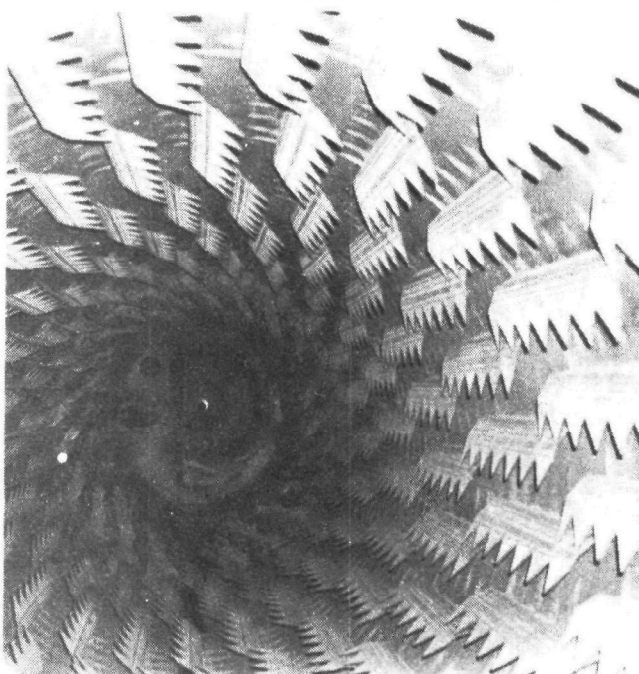
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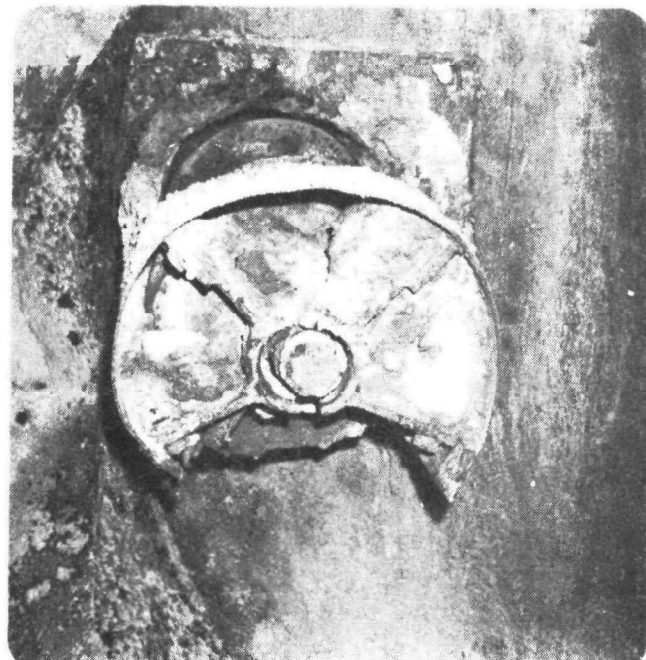
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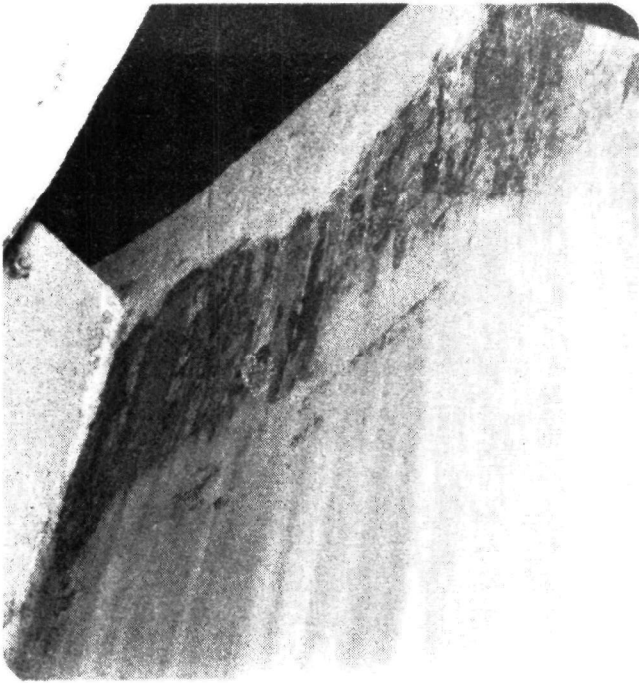
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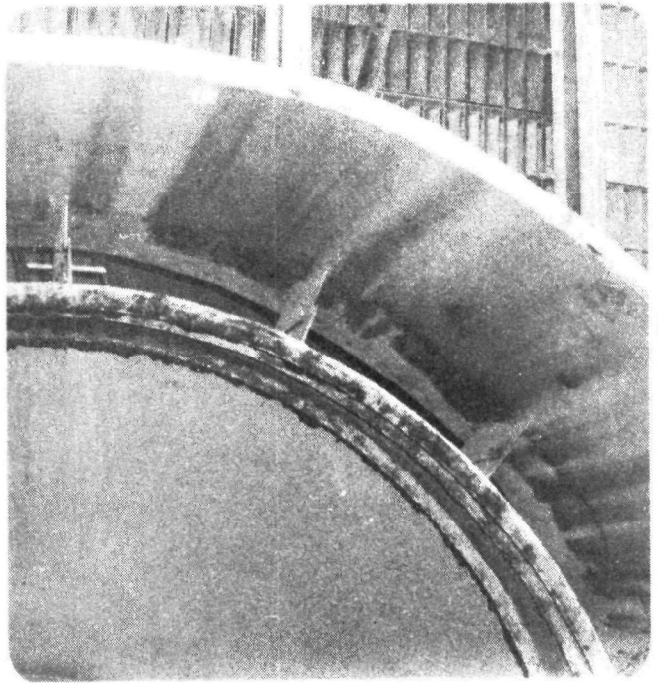
APPENDIX 2

SULFUR OXIDE REMOVAL FROM POWER PLANT STACK GAS

Magnesia Scrubbing-Regeneration: Production of Sulfuric Acid

The Thermal Dehydration of Magnesium Sulfite
Hexahydrate ($MgSO_3 \cdot 6H_2O$) and Magnesium Sulfite
Trihydrate ($MgSO_3 \cdot 3H_2O$);

A mechanistic Study using Thermo-analytical
Techniques and the Development of an Analytical
Method for Quantitating Mixtures of the Hydrates

by

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ABSTRACT

The thermal dehydration of $MgSO_3.3H_2O$ and $MgSO_3.6H_2O$ have been studied by differential thermal analysis, differential scanning calorimetry and thermal gravimetric analysis.

Similar studies by other groups led to contradictory conclusions. In this investigation, these results were reconciled and it was concluded that $MgSO_3.6H_2O$, under equilibrium conditions, dehydrates in two steps through the intermediate formation of $MgSO_3.3H_2O$.

One consequence of this work is the development of a simple analytical procedure, using TGA, for the quantitative determination of both hydrates in mixtures and in the presence of thermally in-active material.

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INTRODUCTION

The thermal dehydration of the two known stable hydrates

of magnesium sulfite, namely, magnesium sulfite hexahydrate

($MgSO_3 \cdot 6H_2O$) and magnesium sulfite trihydrate ($MgSO_3 \cdot 3H_2O$)

have been studied. On the one hand, this work is of practical

importance because in the Magnesia Scrubbing Regeneration

Process (CHEMICO)[9] the thermal dehydration of the magnesium

sulfite hydrates is a significant step. On the other hand,

this study is of scientific interest because the mechanism of

the dehydration has been the subject of controversy.

In the Magnesia Scrubbing Regeneration Process (CHEMICO),

sulfur dioxide in the flue gas is removed by scrubbing with a

magnesia (MgO) base slurry. Hydrates of $MgSO_3$ are formed;

also $MgSO_4$ is formed by oxidation. A portion of the slurry is

withdrawn and centrifuged. The solid is separated from the

liquid, which is recycled. The solids are then dehydrated in

a dryer and, afterwards, calcined at $1400°F$-$1600°F$ with coke

added to the solids. Heating is sufficient to effect the

thermal decomposition of $MgSO_3$; the coke reduces $MgSO_4$ to

$MgSO_3$. The useful products of calcination are MgO, which is

recycled back to the slurry, and SO_2, which is converted to

sulfuric acid.

Turning to the scientific relevance of this study,

thermal dehydration studies have been reported by three groups

and the results were apparently contradictory. Okabe and

Hori[5] used three different techniques to study the dehydration:
Differential Thermal Analysis (DTA), X-ray and Infrared (IR).
From the DTA and X-ray results, they concluded that $MgSO_3.6H_2O$
loses three water molecules between 60°C and 100°C to form
$MgSO_3.3H_2O$. The latter at 200°C completely dehydrates to
yield amorphus anhydrous $MgSO_3$. But in the infrared investi-
gation, they reported that the spectra does not change when
the trihydrate goes to the anhydrous state at 200°C. It does
not seem plausible that the transformation suggested could
h a v e o c c u r red without any change in the infrared spectra.
The band in the 3500 cm^{-1} region is obviously an O-H stretching
band, therefore, if the salt is dehydrated it would be expected
that this band would disappear.

Two other investigations using DTA were carried out by
groups at the Tennessee Valley Authority (TVA). These studies
were not published, but are presented, in part, in an EPA-
sponsored critical analysis of the Magnesia Process prepared
by TVA[6]. In the above cited report, Jordan's work based upon
DTA leads to the conclusion that the thermal dehydration of
$MgSO_3.6H_2O$ takes place in one step starting at 100°C and that
$MgSO_3.3H_2O$ dehydrates in one step, starting at 160°C.

In the other study, Hatfield and co-workers reported that
$MgSO_3.6H_2O$ loses nearly all its water when heated in a stream
of argon or air at 104°C for 16 hrs. This, too, supports the
inference that the thermal dehydration of the hexa-
hydrate occurs in one step. It is also reported that

$MgSO_3 \cdot 3H_2O$ is partially dehydrated when heated in air for 16 hrs. at 160°C.

In the above-cited EPA report, it is suggested that the apparently contradictory results may be due to differences in experimental conditions. It was speculated that the samples were heated in sealed tubes in the work of Okabe and Hori, although such information was not provided in that paper. Without presenting a critical analysis of the effects of having the samples open or closed to the atmosphere, it is concluded in the TVA report that the results of the TVA groups, in which the samples are open to the atmosphere, are valid and that $MgSO_3 \cdot 6H_2O$ dehydrates in one step to $MgSO_3$ at 100°C.

The purpose of this study is to reconcile the contradictory results. Thermoanalytical techniques are used exclusively: Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA). Other groups in this laboratory have studied the thermal dehydration using Mass Spectroscopy and Infrared Spectroscopy. These results will be reported separately.

EXPERIMENTAL

$MgSO_3 \cdot 3H_2O$ (97.9%) and $MgSO_3 \cdot 6H_2O$ (99.0%) used in this study were laboratory prepared samples. Each hydrate was studied individually; also synthetic mixtures of both hydrates were studied.

The DuPont thermal analyzer was employed in this investigation. This included the DuPont 900 differential thermal analyzer (DTA) equipped with both the standard DTA cell and the differential calorimetric cell (DSC). The DuPont 950 TGA unit, which is an attachment to the DuPont 900, was also used.

DTA[9] is a thermal technique in which the heat effects, associated with chemical or physical changes, are recorded as a function of temperature or time as the substance is heated at a uniform rate. Enthalpic changes, either-endothermic or exothermic, are recorded. The sample temperature is continuously compared with a reference material temperature; the difference in temperature is recorded as a function of furnace temperature or time. DTA is reported to have been first used by LeChatelier[4] in 1887 for studying clay. Since that date many developments have been introduced and the literature has grown exponentially. DTA has been used for the study of the thermal dehydration of hydrates. For example, the reader is referred to the work of Wendlant and Hoiberg[10].

In contrast to DTA, in which the temperature difference

between the sample and the reference is measured, in DSC it is the heat necessary to equalize the temperature between the sample and the reference which is measured. This technique thus can be used to measure enthalpic changes quantitatively.

TGA is a technique in which a sample is continuously weighed as it is heated at a linear rate. The resulting thermogram gives information concerning the thermal stability of the substance under investigation. TGA was first described by Honda [2] in 1915. Griffith [1] has applied TGA to the study of mixtures of hydrates and anhydrous salts.

Thermal methods of analysis are uniquely applicable for study of dehydration processes. Dehydration can be observed as endothermic changes in DTA, heats of dehydration in DSC, and as weight losses in TGA.

RESULTS AND DISCUSSION

First, the DTA results will be considered. A typical thermogram for the dehydration of $MgSO_3 \cdot 3H_2O$ is shown in Figure 1. Only one endothermic transition is observed, starting at 190°C. On the other hand, in the thermogram of $MgSO_3 \cdot 6H_2O$ shown in Figure 2, two endothermic transitions are observed. One starts at 90°C and the other coinciding with the endotherm observed for the trihydrate, starts at 190°C. The inference to be drawn from this data is that the hexahydrate does degrade in two steps and that the two steps involve a transition from the hexaform to the triform.

Next, studies were carried out using DSC. In this case, it is the heat input rather than the temperature which is measured. The DSC thermogram of $MgSO_3 \cdot 3H_2O$ is shown in Figure 3. Only one endothermic transition was observed starting at 100°C with a peak maximum at 160°C. Both DTA and DSC analyses indicate that the thermal dehydration of $MgSO_3 \cdot 3H_2O$ is a one step process. From DSC data, it appears that the dehydration of $MgSO_3 \cdot 3H_2O$ starts at a low temperature, 100°C, in contrast to the DTA data from which it is inferred that 190°C is the starting temperature.

The DSC thermogram of $MgSO_3 \cdot 6H_2O$ is shown in Figure 4. It is significant to note that only one endothermic transition was observed starting at 45°C with a peak maximum at 90°C. DSC results suggest that the thermal dehydration of $MgSO_3 \cdot 6H_2O$

takes place in one step starting at 45°C, in contrast to the two step mechanism starting at 90°C to be drawn from the DTA results.

Since the phenomena measured by DTA and DSC is the same, it was expected that the results would be consistent. Surprisingly, this was not the case. From the DSC data, it appears that the dehydration of both hydrates starts at a lower temperature and the hexaform dehydrates in one step and not in two steps as was inferred from the DTA results.

The apparent contradiction between the DTA and the DSC results can be rationalized by considering the relationship between the dehydration reaction and the sample environmental conditions. In any dehydration reaction water is liberated; if the latter is continuously removed from the reaction atmosphere two consequences are observed. First, the dehydration starts at a lower temperature, and, secondly, equilibrium is not attained.

On the one hand in the DSC studies, the sample is placed in an open dish and is heated under a sweeping stream of nitrogen. Under these conditions the liberated water is continuously removed from the reaction environment. On the other hand, in the DTA studies, the sample is heated in a self-generated atmosphere because it is placed in a capillary tube. Under the open conditions encountered in DSC, thermal dehydration starts at a lower temperature, 45°C versus 90°C

and only one endothermic transition is observed for the hexa-form, whereas in the DTA studies two were observed.

To confirm the above rationalization of the differences between the DTA and the DSC studies, the thermal dehydration was studied by another independent technique, TGA, in which it was possible to heat the samples either in an open condition or in a self-generated atmosphere. TGA thermograms, under open conditions, were obtained by the conventional procedure in which the sample is placed in an open platinum dish under a sweeping blanket of nitrogen. TGA, under self-generated atmosphere, was achieved by placing the sample in a capillary tube with a thermocouple inside. Then, the whole tube was placed in the platinum dish.

In Figure 5, the TGA of $MgSO_3.3H_2O$, under open conditions is shown. Thermal dehydration starts at 100°C and takes place in one step. The weight loss of the sample is 34.0%, which corresponds to the loss of 3 moles of water. The effect of operating under open conditions is shown in Figure 6 for $MgSO_3.6H_2O$. Thermal dehydration of the hexaform starts at 70°C and takes place in one step. The weight loss of the sample is 51%, which corresponds to the loss of 6 moles of water.

The thermograms for the trihydrate and the hexahydrate, respectively, under the conditions of a self-generated atmosphere are shown in Figures 7 and 8. $MgSO_3.3H_2O$, as

shown in Figure 7, loses 34.5% of its weight in one step.

This is in a very good agreement with TGA under open conditions, but thermal dehydration starts at 220°C, i.e., at a higher temperature, because of the self-generated atmosphere conditions. The weight loss for the hexahydrate under a self-generated atmosphere, as shown in Figure 8, is 51%, which corresponds to the loss of 6 moles of water. It is significant to note that the thermal dehydration of the hexaform starts at a higher temperature and takes place in two steps, with a weight loss of 25.5% in each step. In other words, $MgSO_3.6H_2O$ loses 3 moles of water in each dehydration step.

Thus, when the TGA study of the hexaform is carried out under a non-equilibrium condition, because of heating the sample under a sweeping blanket of nitrogen, equilibrium is not attained due to the continuous removal of the liberated water. As a result, thermal dehydration starts at a lower temperature and takes place in one step. On the other hand, if equilibrium is attained, because of heating the sample in a self-generated atmosphere, the TGA results showed that thermal dehydration starts at a higher temperature and takes place in two steps. First, dehydration leads to the formation of $MgSO_3.3H_2O$, then, to the anhydrous $MgSO_3$. These TGA observations are consistent with the explanation of the differences observed in the DTA and the DSC studies. The results are summarized in Table 1 for $MgSO_3.3H_2O$ and in

Table 2 for $MgSO_3 \cdot 6H_2O$. The onset of the endotherms as a function of the method are compared.

APPLICATION

The observations made in the TGA studies were used as bases for developing a new analytical method for quantitating mixtures of the tri- and hexahydrates. It had been observed that although the second weight loss for the hexahydrate overlapped that of the trihydrate, nevertheless, from a knowledge of the first weight loss of the hexahydrate, the contribution of the hexahydrate to the second weight loss could be calculated.

The accuracy of the method was investigated by analyzing the thermograms of synthetic mixtures of the hexahydrate and the trihydrate ranging from 10% to 90%. The thermograms are shown in Figures 9-19.

From these thermograms, the water content and the magnesium sulfite content could be calculated. First, the water content calculations will be considered and compared to the theoretical values. The water content of each hydrate in a mixture can be obtained from the TGA thermogram, by taking into account the fact that the weight loss in the first dehydration step at 175°C represents the first three moles of water in $MgSO_3.6H_2O$, i.e., 50% of the water content of the hexaform. Thus the water content can be calculated, from the TGA thermogram, as follows:

$$\% \text{ } H_2O \text{ in } MgSO_3.6H_2O \text{ in a mixture} = (\% \text{ weight loss in the first step at } 175°C) \text{ (2)}$$

% H_2O in $MgSO_3.3H_2O$ in a mixture = (% weight loss in

the second step at 400°C)-(% weight loss in the first step at

<div align="right">175°C)</div>

The theoretical values of the water content are calculated

as follows:

% H_2O in $MgSO_3.6H_2O$ in a mixture = % $MgSO_3.6H_2O$ in the mixture

$$X \frac{6H_2O}{MgSO_3.6H_2O}$$

$$X \ 100$$

$$= \% \ MgSO_3.6H_2O \ \text{in the mixture}$$

$$X \frac{108}{212.3} \ X \ 100$$

$$= \% \ MgSO_3.6H_2O \ \text{in the mixture}$$

$$X \ 50.9$$

% H_2O in $MgSO_3.3H_2O$ in a mixture = % $MgSO_3.3H_2O$ in the mixture

$$X \frac{3 \ H_2O}{MgSO_3.3H_2O} \ X \ 100$$

$$= \% \ MgSO_3.3H_2O \ \text{in the mixture}$$

$$X \frac{54}{158.3} \ X \ 100$$

$$= \% \ MgSO_3.3H_2O \ \text{in the mixture}$$

$$X \ 34.1$$

Both theoretical and observed values of the water content are

shown in Table 3. The percent water (observed values) is

plotted versus magnesium sulfite content in Figure 21 for

$MgSO_3.3H_2O$ and in Figure 22 for $MgSO_3.6H_2O$.

The magnesium sulfite content can be calculated from the TGA thermograms by considering the same aspects mentioned in the water content calculations, and, taking into account that 6 moles of water represent 50.9% by weight of $MgSO_3 \cdot 6H_2O$, and that 3 moles of water represent 34.1% by weight of $MgSO_3 \cdot 3H_2O$. Thus the percent of each hydrate in a mixture is calculated as follows:

$$\% \ MgSO_3 \cdot 6H_2O \ in \ a \ mixture = \% \ weight \ loss \ at \ 175^\circ C \times 2 \times \frac{100}{50.9}$$

$$\% \ MgSO_3 \cdot 3H_2O \ in \ a \ mixture = (\% \ weight \ loss \ between \ 175^\circ \ and \ 400^\circ C \ \_\% \ weight \ loss \ at \ 175^\circ C) \times \frac{100}{34.1}$$

The data obtained is compared versus the theoretical values in Table 4 for the triform and in Table 5 for the hexaform. The accuracy of the method, as shown in Tables 4 and 5, was found to be ± 3% if no calibration curve is used. A value of less than 1% is to be expected if a calibration curve is used.

Furthermore, the TGA method was tested in the presence of TGA inactive material. This was achieved by analyzing a mixture of $MgSO_3 \cdot 3H_2O$, $MgSO_3 \cdot 6H_2O$ and glass beads. The mixture was subjected to the same experimental conditions of a self-generated atmosphere. The TGA thermogram is shown in Figure 20. From the results summarized in Table 6, it is concluded that this method does not suffer any interferences due to the presence of thermally inactive materials.

Relevant to the nature of the materials obtained in the Magnesia Process, the quantitative analysis of mixtures of $MgSO_3 \cdot 3H_2O$ and $MgSO_3 \cdot 6H_2O$ has to be considered in the light of the following contexts: one, only these two hydrates are present; two, in the presence of MgO, three, in the presence of another hydrate, $MgSO_4 \cdot 7H_2O$. The latter is a common product in the Magnesia Process.

When only the two hydrates are present, methods available include total sulfite by iodine titration[3], X-ray analysis[5], and a wet chemical method developed by Dr. Ray which will be referred to as Ray's Method[7].

In the presence of MgO and/or $MgSO_4 \cdot 7H_2O$ the measurement of the sulfite content cannot be used to determine the ratio of the hydrates. From the available literature which is limited to the one paper previously cited[5], it is not clear as to whether or not quantitative analysis is possible using the X-ray method in the presence of MgO and/or $MgSO_4 \cdot 7H_2O$. Ray's method is applicable in the presence of these materials.

The TGA method is simpler than Ray's method but it is not applicable in the presence of $MgSO_4 \cdot 7H_2O$. On the other hand, Dr. Ray[7] has developed a simple procedure for quantitatively stripping $MgSO_4 \cdot 7H_2O$ from mixtures of $MgSO_3 \cdot 3H_2O$, $MgSO_3 \cdot 6H_2O$ and MgO. Therefore it appears that the TGA technique in conjunction with Ray's stripping procedure is the optimum method.

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Table 1

Starting Temperature of Thermal

Dehydration of $MgSO_3 \cdot 3H_2O$

Technique	Experimental Conditions	Onset of the Endotherm
DTA	self-generated	190°C
DSC	open conditions	100°C
TGA	open conditions	100°C
TGA	self-generated	200°C

Table 2

Starting Temperature of

Thermal Dehydration of $MgSO_3.6H_2O$

Technique	Experimental Condition	First Endotherm	Second Endotherm
DTA	self-generated	90°C	190°C
DSC	open conditions	45°C	not observed
TGA	open conditions	70°C	not observed
TGA	self-generated	125°C	220°C

Table 3

Calculated and Observed Values

of Water Content in

Synthetic Mixtures

| Std# | Composition | | Calculated H$_2$O content in | | | Observed H$_2$O content in | | |
	%MgSO$_3$·3H$_2$O	%MgSO$_3$·6H$_2$O	Triform	Hexaform	Total	Triform	Hexaform	Total
1	0.0%	100%	0%	50.9%	50.9%	0%	52%	52%
2	10.29%	84.71%	3.5%	45.56%	49.06%	3.4%	44.4%	47.8%
3	18.96%	81.04%	6.46%	41.19%	47.65%	6.6%	39.4%	46%
4	29.37%	70.63%	10%	35.9%	45.9%	9.0%	35.0%	44%
5	38.24%	61.76%	13.03%	31.39%	44.42%	12%	32%	44%
6	50%	50%	17.04%	25.42%	42.46%	16.4%	26%	42.4%
7	59.84%	40.16%	20.39%	20.41%	40.8%	19.8%	20.4%	40.2%
8	70.19%	29.81%	23.91%	15.15%	39.06%	23%	16%	39%
9	79.34%	20.66%	27.03%	10.5%	37.53%	26.4%	10.6%	37%
10	90.18	9.82%	30.72%	4.99%	35.71%	30.2%	5%	35.2%
11	100%	0%	34.1%	0%	34.1%	34.8%	0%	34.8%

Table 4

$MgSO_3 \cdot 3H_2O$ Content from TGA

Std#	Theoretical Value	Observed Value	Deviation
1	0%	0%	0%
2	10.29%	10.26%	-.03%
3	18.96%	19.35%	+.39%
4	29.37%	26.39%	-2.98%
5	38.24%	35.24%	-3.00%
6	50.0%	48.1%	-1.9%
7	59.84%	58.06%	-1.78%
8	70.19%	67.45%	-2.74%
9	79.34%	77.42%	-1.92%
10	90.18%	88.56%	-1.62%
11	100.00%	102.0%	+2.0%

Table 5

$MgSO_3 \cdot 6H_2O$ Content

From TGA

Std#	Theoretical Value	Observed Value	Deviation
1	100%	102.2%	+2.2%
2	89.71%	.87.3%	-2.41%
3	81.04%	78.45%	-2.54%
4	70.63%	68.8%	-1.83%
5	61.76%	62.9%	+1.14%
6	50%	51.11%	+1.11%
7	40.16%	40.1%	-.06%
8	29.81%	31.45%	+1.64%
9	20.66%	20.84%	+.18%
10	9.82%	9.83%	+.01%
11	0%	0%	0%

Table 6

TGA results of a synthetic

mixture containing thermally

inactive compound

	Theoretical Value	Observed Value
$MgSO_3 \cdot 3H_2O$	44.3%	43.2%
$MgSO_3 \cdot 6H_2O$	30.0%	29.3%
glass beads	25.7%	27.5%*

*This value was obtained by difference

SAMPLE: $MgSO_3 \cdot 3H_2O$

Fig. No. 1

ORIGIN:

SIZE ___6 mg___

REF. ___glass beads___

PROG. MODE ___heat___

RATE __10__ $\frac{°}{min}$,START _30_ °C

ATM. ___self-generated___ MM

	T	$\triangle$ T
SCALE	50 $\frac{°}{in}$	2 $\frac{°}{in}$
SHIFT	0 IN.	0 IN.

RUN NO. ___1___

DATE ___11/8/74___

OPERATOR ___RM___

BASE LINE SLOPE __0__

EXO

$\triangle$ T

ENDO

– 179 –

SAMPLE:

RUN NO.:

190

205°C

T °C (CHROMEL · ALUMEL)

DU PONT INSTRUMENTS
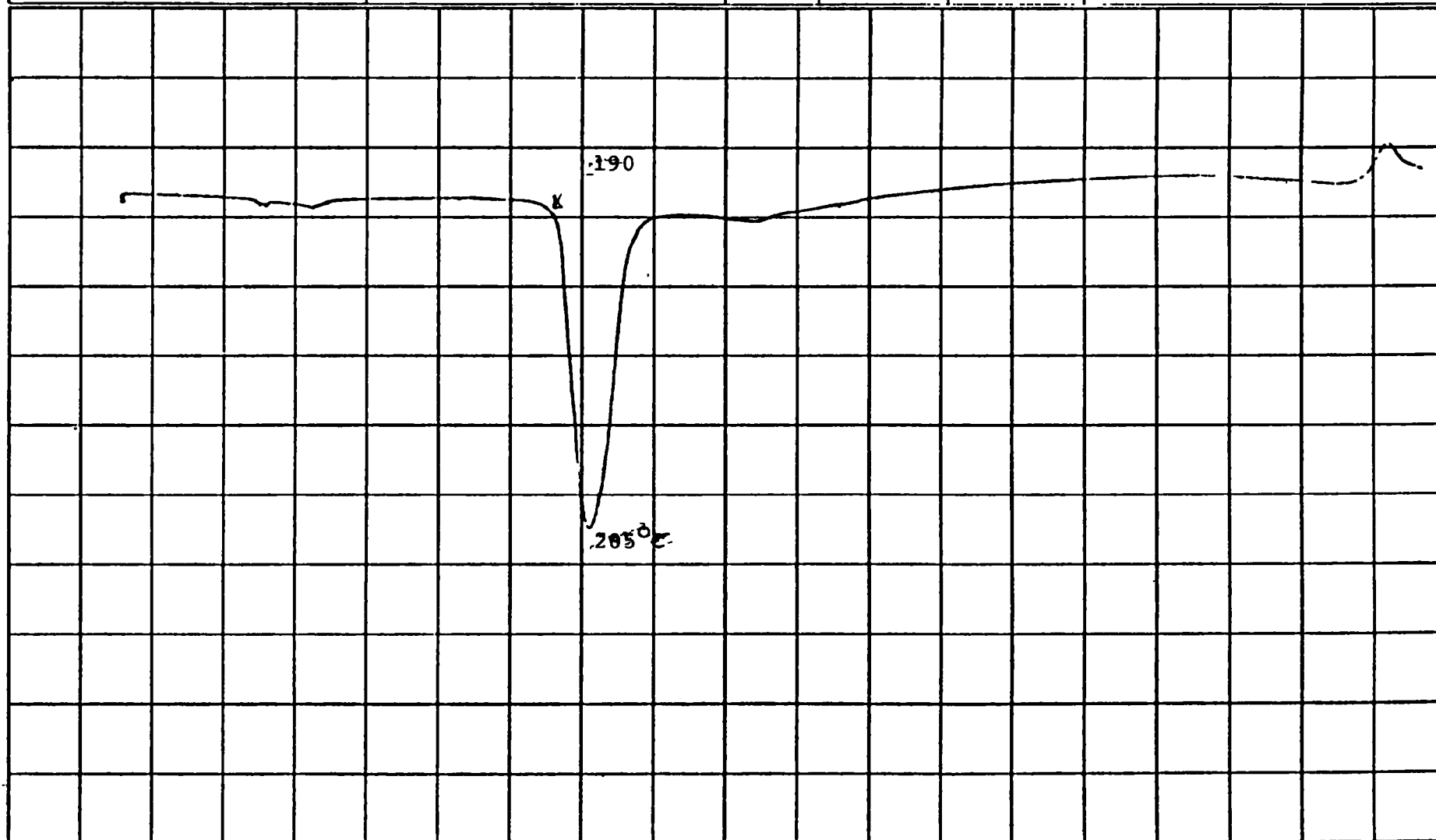
SAMPLE: $MgSO_3 \cdot 6H_2O$ Fig. No. 2 **ORIGIN:**	**SIZE** 8 mg **REF.** glass beads **PROG. MODE** heat **RATE** 10 $\frac{°C}{min}$.**START** 30 °C	**ATM.** self-generated **MM**	**RUN NO.** 1

	T	△ T
SCALE	50 $\frac{°C}{IN}$	2 $\frac{°C}{IN}$
SHIFT	0 IN.	0 IN.

DATE 11/8/74
OPERATOR RM
BASE LINE SLOPE 0

EXO ↑ △ T — (1:82) — ↓ ENDO

Values on graph: 90°C, 190°C, 205°C, 107°C

T, °C (CHROMEL: ALUMEL)

SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

DU PONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 3H_2O$	SIZE 12 mg	ATM. N_2 30 MM	RUN NO. 1
Fig. No. 3	REF. empty pan	T / ΔT	DATE 11/9/71
	PROG. MODE heat	SCALE 50 / 1	OPERATOR RM
ORIGIN:	RATE 10 .START 25 °C	SHIFT 0 IN. / 0 IN.	BASE LINE SLOPE 0
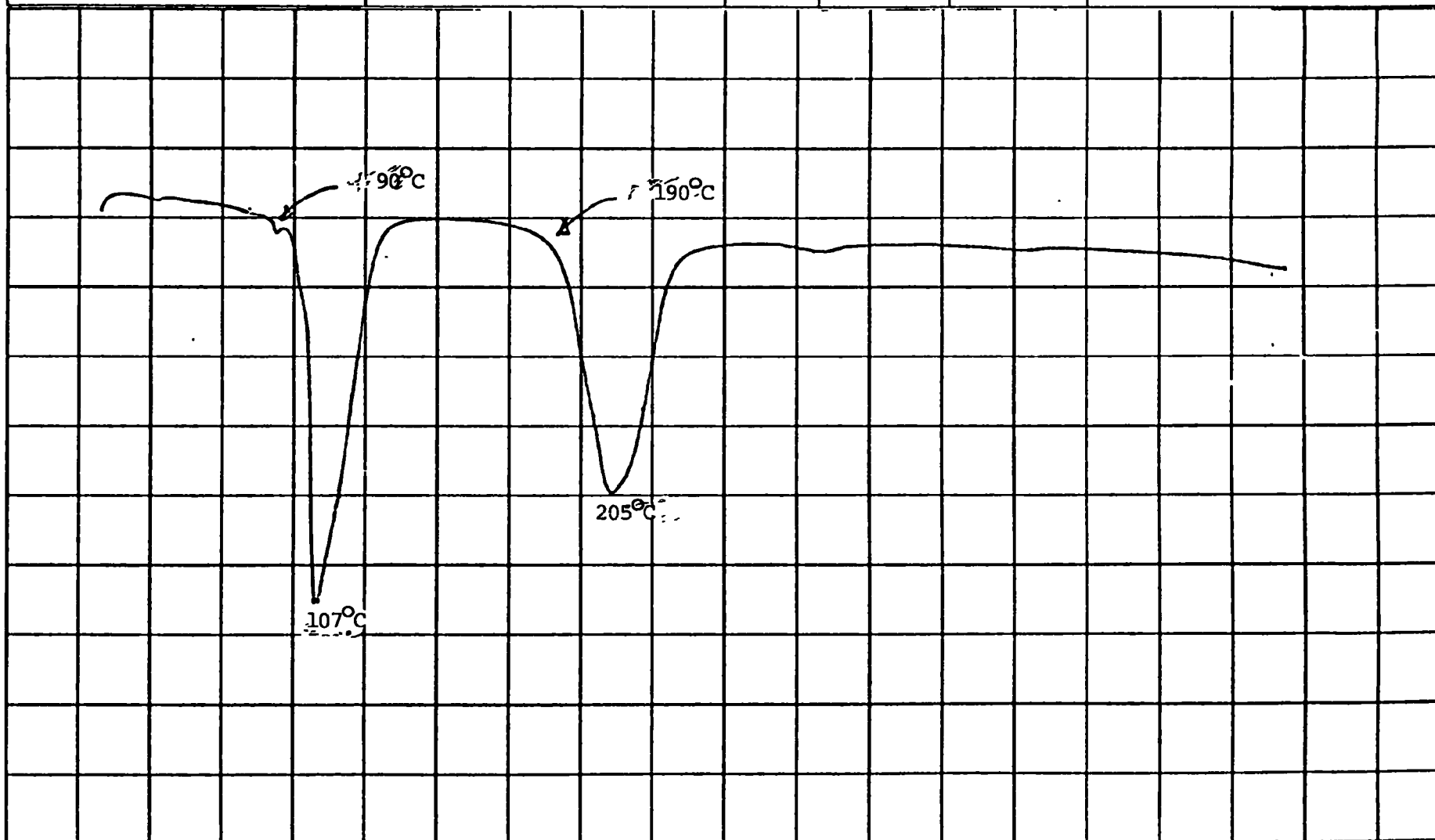
T, °C (CHROMEL: ALUMEL)*

*SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

DU PONT INSTRUMENTS

SAMPLE: MgSO$_3$.6H$_2$O

Fig. No. 4

ORIGIN:

SIZE 5 mg

REF. empty pan

PROG. MODE heat

RATE 10 °C/min .START 30 °C

ATM. N$_2$, 30 MM

	T	△ T
SCALE	50 °C/IN	1 °C/IN
SHIFT	0 IN.	0 IN.

RUN NO. 1

DATE 11/9/74

OPERATOR RM

BASE LINE SLOPE 0

– 182 – OXE 1△ ENDO

SAMPLE: RUN NO.:

45°C

90°C

T. °C (CHROMEL: ALUMEL)*

* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

DU PONT INSTRUMENTS

| SAMPLE: MgSO₃·3H₂O | X-AXIS | Y-AXIS | RUN NO. 1 DATE 11/12/74 |

$MgSO_3 \cdot 3H_2O$

Fig. No. 5

SIZE 20 mg.

X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 4 mg/inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

RUN NO. 1 DATE 11/12/74

OPERATOR RM

HEATING RATE 10 °C/min.

ATM. N₂, 30 ml/min.

TIME CONSTANT 1 sec.

Start of Dehydration

% WEIGHT, mg.

TEMPERATURE°, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
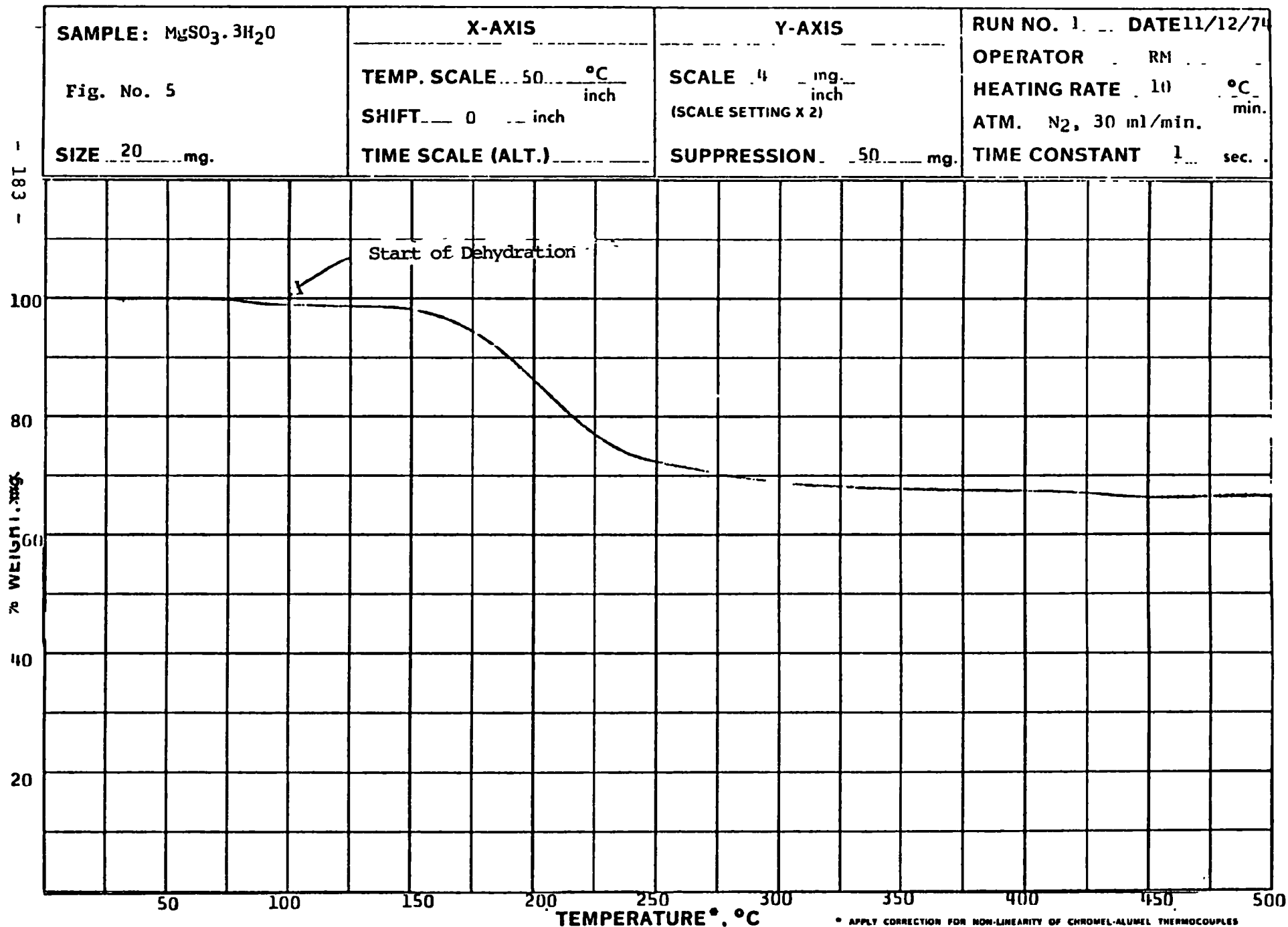
SAMPLE: $MgSO_3.6H_2O$

Fig. No. 6

SIZE 20 mg.

X-AXIS

TEMP. SCALE 50 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 4 $\frac{mg.}{inch}$

(SCALE SETTING X 2)

SUPPRESSION 5 mg.

RUN NO. 1 DATE 11/12/74

OPERATOR RM

HEATING RATE 10 $\frac{°C}{min.}$

ATM. N_2, 30 ml/min.

TIME CONSTANT 1 sec.

184

% WEIGHT. mg.

TEMPERATURE*. °C

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DuPont INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 3H_2O$	X-AXIS	Y-AXIS	RUN NO. 1 DATE 11/15/7?
Fig. No. 7	TEMP. SCALE 50 °C / inch	SCALE 2 mg. / inch	OPERATOR RM
	SHIFT __.0 __ inch	(SCALE SETTING X 2)	HEATING RATE 10 °C / min.
			ATM. self-generated
SIZE 5 mg.	TIME SCALE (ALT.) __	SUPPRESSION 60 mg.	TIME CONSTANT 1 sec.

Start of Dehydration

34% weight loss

% WEIGHT, mgx

185

100

80

60

40

20

50   100   150   200   250   300   350   400   450   500

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

SAMPLE: $MgSO_3 \cdot 6H_2O$

Fig. No. 8

SIZE 5 mg.

X-AXIS

TEMP. SCALE 50 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 1 $\frac{mg.}{inch}$

(SCALE SETTING X 2)

SUPPRESSION 60 mg.

RUN NO. 1   DATE 11/16/74

OPERATOR RM

HEATING RATE 10 $\frac{°C}{min.}$

ATM. self-generated

TIME CONSTANT sec.

198-1

% WEIGHT, mg.

100
80
60
40
20

51% weight loss

TEMPERATURE, °C

50 100 150 200 250 300 350 400 450 500
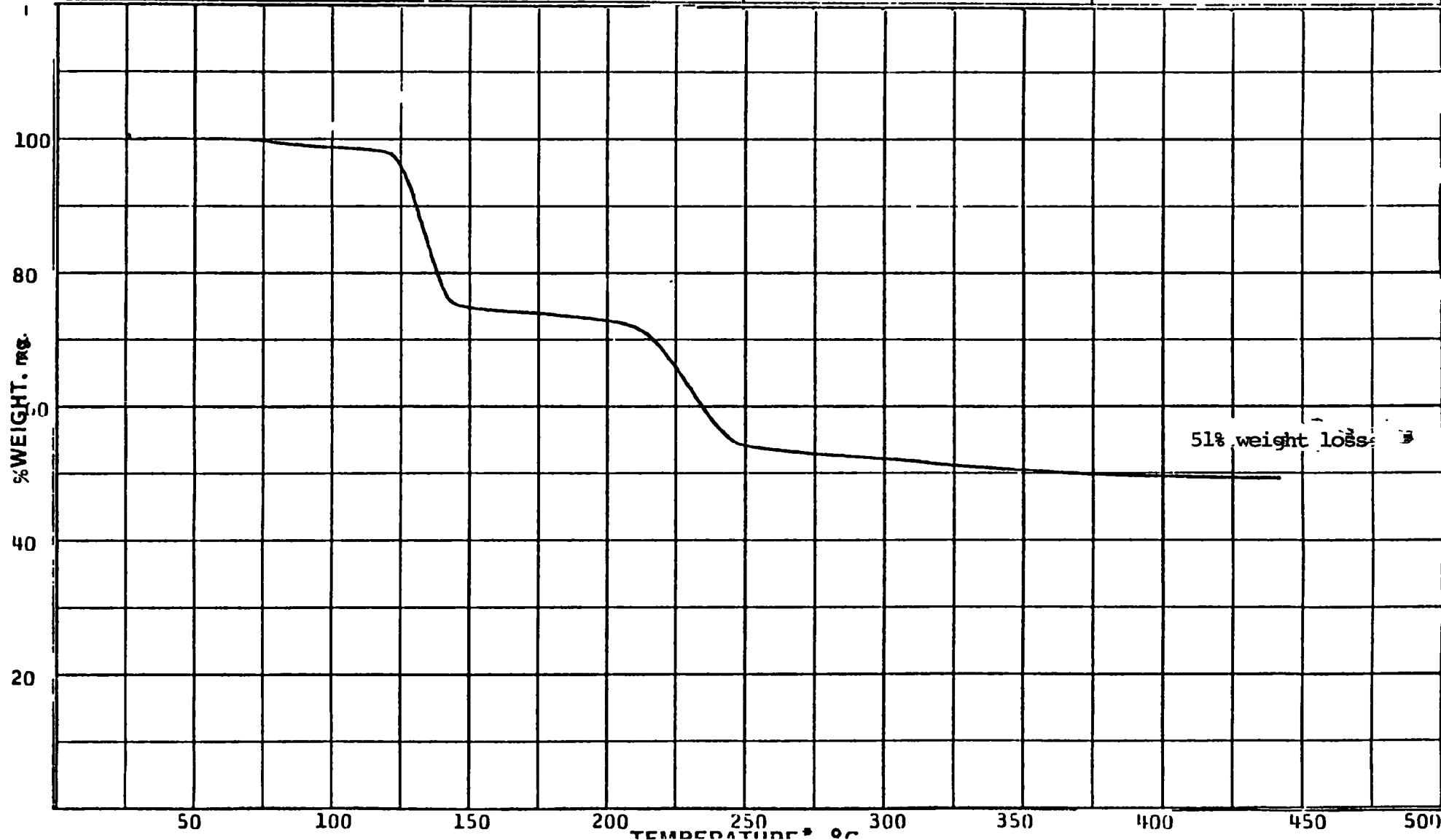
DU PONT INSTRUMENTS

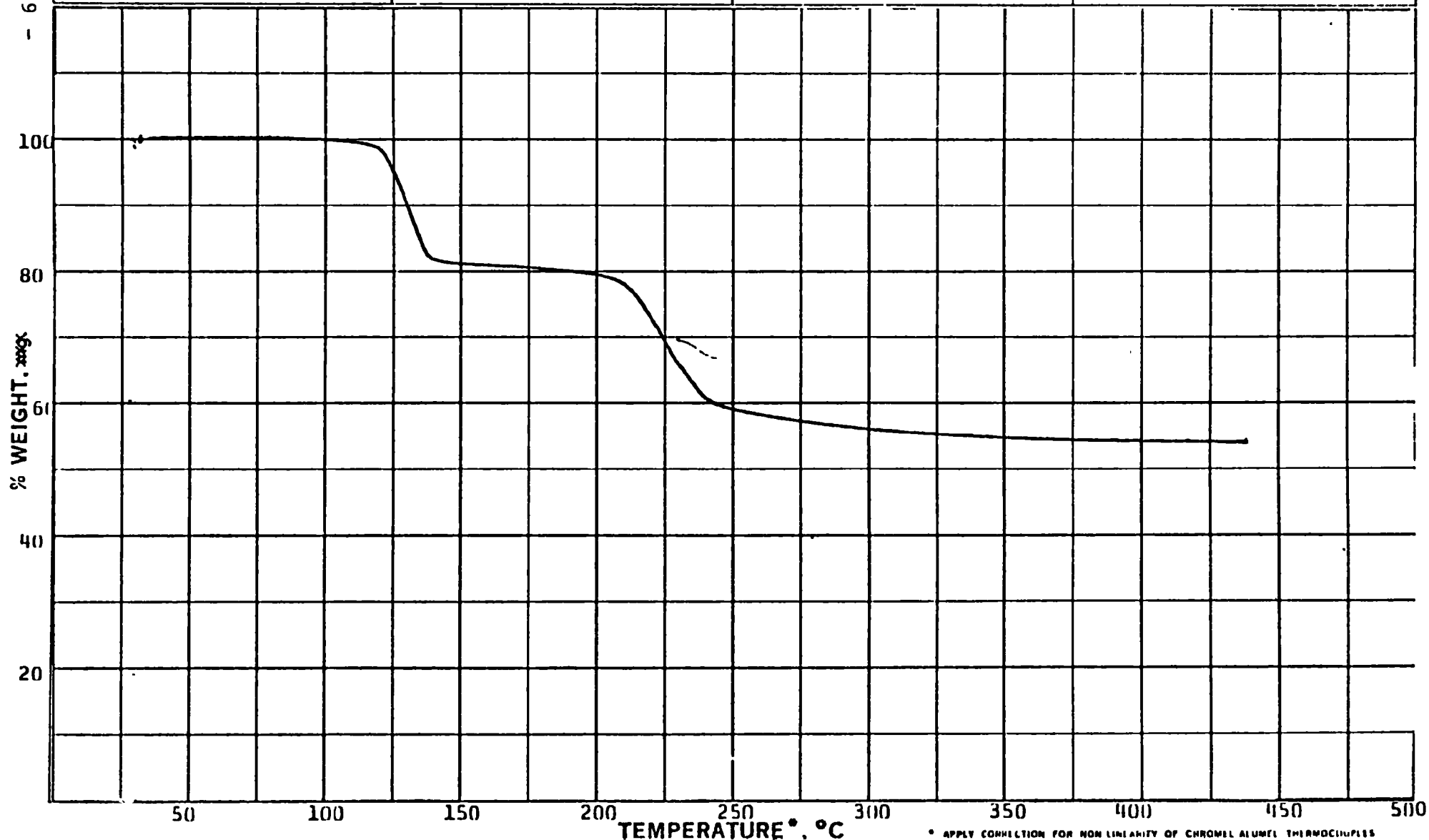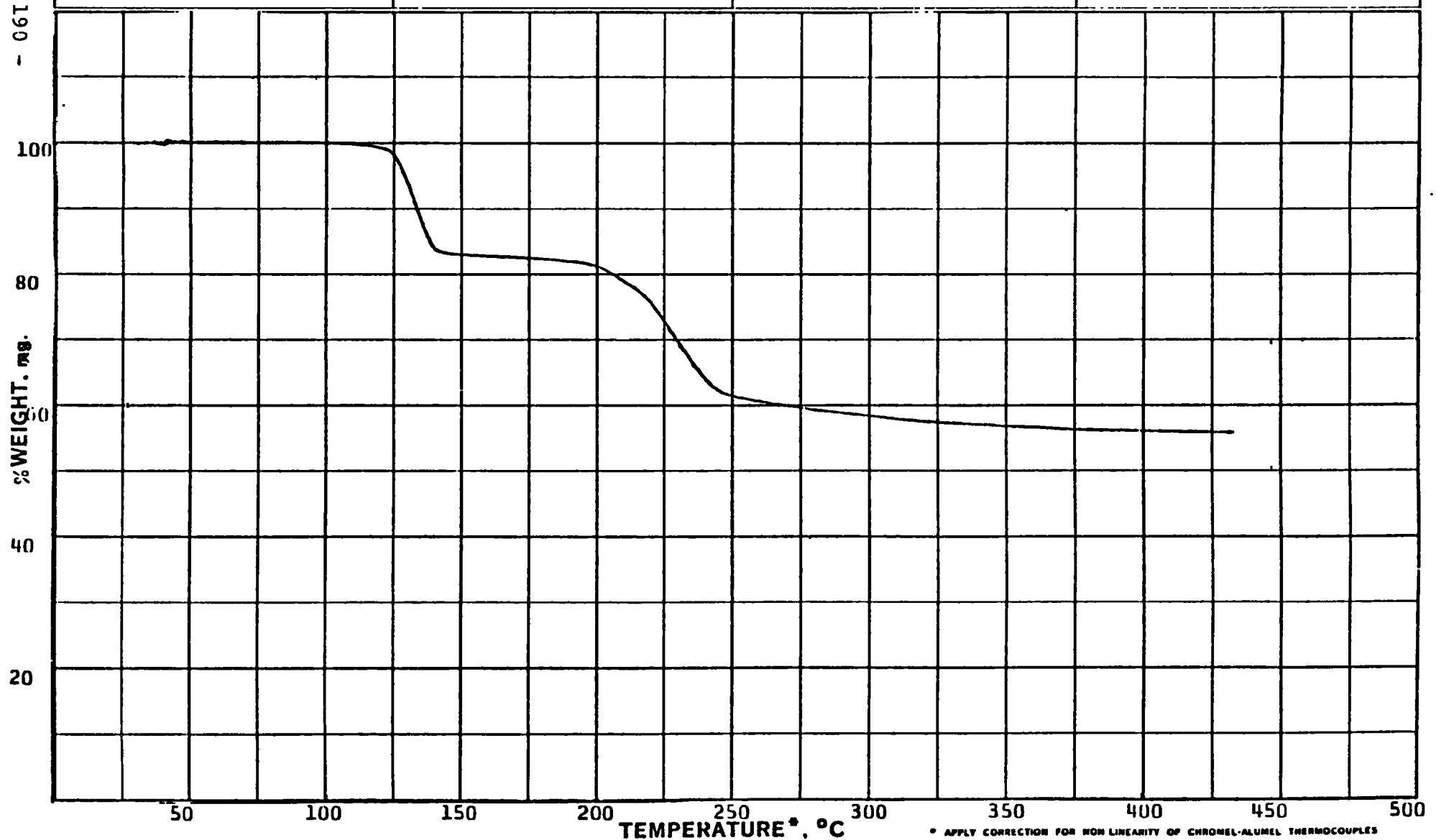| SAMPLE: Std #1
100% MgSO$_3$.6H$_2$O

Fig. No. 9

SIZE ___12__ mg. | X-AXIS

TEMP. SCALE ..50 ___°C__
                                    inch
SHIFT___ . 0 _ inch

TIME SCALE (ALT.) ___ ____ | Y-AXIS

SCALE 2_ ___mg.__
                inch
(SCALE SETTING X 2)

SUPPRESSION . __50____mg. | RUN NO. 1   DATE 11/17/74
OPERATOR   RM
HEATING RATE   10   °C
                                  min.
ATM. self-generated
TIME CONSTANT _1   sec. . |

% WEIGHT. mg.

TEMPERATURE° °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

SAMPLE: Std #2
10.29% MgSO$_3$.3H$_2$0
89.71% MgSO$_3$.6H$_2$0

Fig. No. 10
SIZE 10 mg.

X-AXIS

TEMP. SCALE 100 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.) _____

Y-AXIS

SCALE 2 $\frac{mg.}{inch}$
(SCALE SETTING X 2)

SUPPRESSION 50 mg.

RUN NO. 1 **DATE** 11/20/7�
OPERATOR RM
HEATING RATE 10 $\frac{°C}{min.}$
ATM. self-generated
TIME CONSTANT 1 sec.

– 188 –

%WEIGHT, mg.

| | | | | | | | | | | |
100
80
60
40
20

TEMPERATURE*, °C

100 200 300 400 500 600 700 800 900 1000

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DU PONT INSTRUMENTS

SAMPLE: Std #3	X-AXIS	Y-AXIS	RUN NO. 1 DATE 11/21/71
18.96% MgSO$_3$.3H$_2$0			OPERATOR RM
81.04% MgSO$_3$.6H$_2$0	TEMP. SCALE 50 °C/inch	SCALE 2 mg./inch	HEATING RATE 10 °C/min.
Fig. No. 11	SHIFT 0 inch	(SCALE SETTING X 2)	ATM. self-generated
SIZE 15 mg.	TIME SCALE (ALT.)	SUPPRESSION 50 mg.	TIME CONSTANT 1 sec.

T189 —

% WEIGHT, mg%

TEMPERATURE°, °C

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DU PONT INSTRUMENTS

SAMPLE: Std #4
29.37% $MgSO_3 \cdot 3H_2O$
70.63% $MgSO_3 \cdot 6H_2O$

Fig. No. 12

SIZE 10 mg.

X-AXIS

TEMP. SCALE 50 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 $\frac{mg.}{inch}$
(SCALE SETTING X 2)

SUPPRESSION 50 mg.

RUN NO. 1   DATE 11/22/7

OPERATOR RM

HEATING RATE 10 $\frac{°C}{min.}$

ATM. self-generated

TIME CONSTANT 1 sec.

Y-axis: %WEIGHT, mg. (190, 100, 80, 60, 40, 20)

X-axis: TEMPERATURE*, °C (50, 100, 150, 200, 250, 300, 350, 400, 450, 500)

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

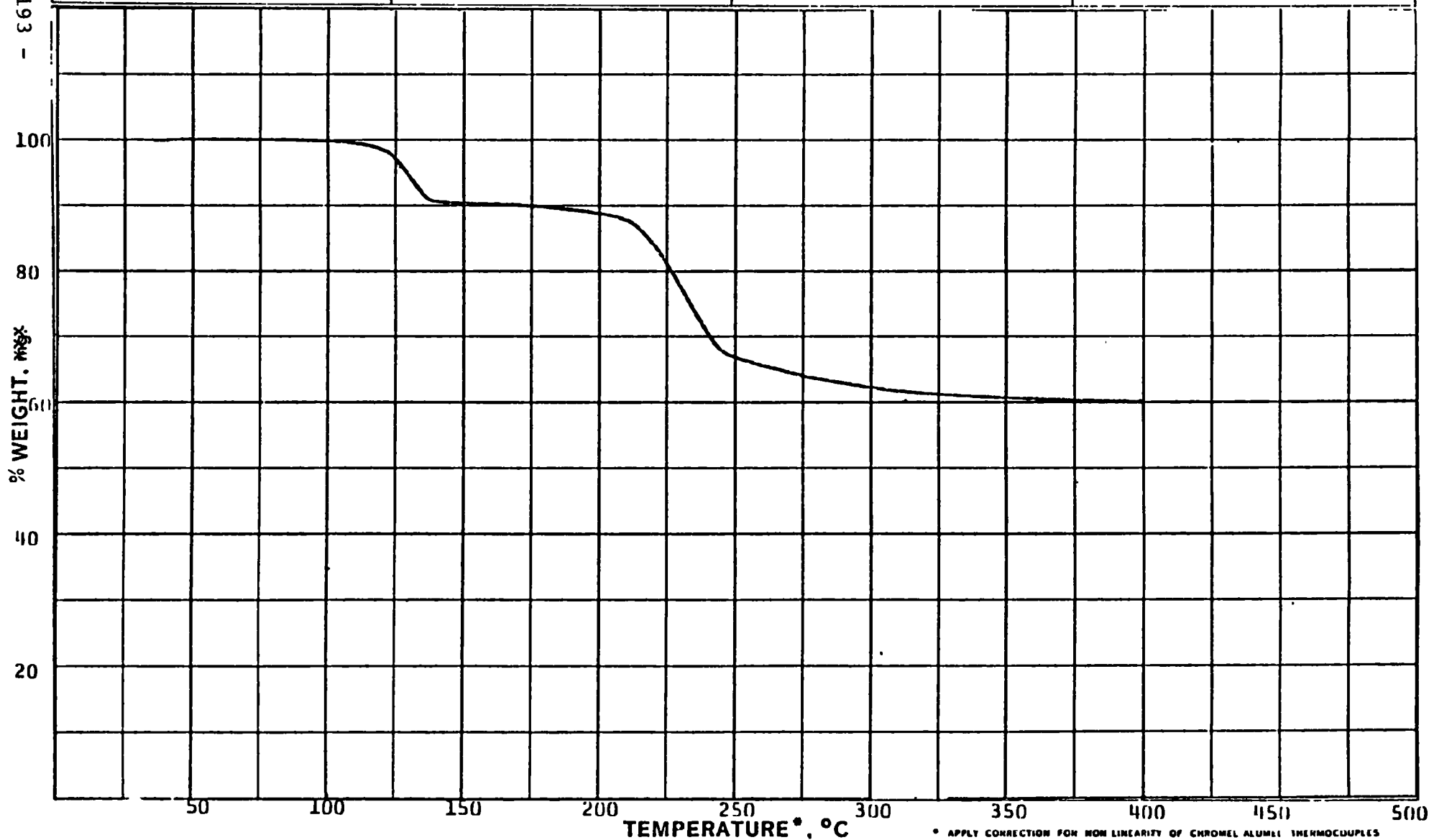| SAMPLE. Stil #5
38.24% MgSO₃·3H₂O
61.76% MgSO₃·6H₂O

Fig. No. 13

SIZE 12 mg. | X-AXIS

TEMP. SCALE 50 °C/inch

SHIFT 0 inch

TIME SCALE (ALT.) | Y-AXIS

SCALE 2 mg./inch
(SCALE SETTING X 2)

SUPPRESSION 50 mg. | RUN NO. 1 DATE 11/25/74
OPERATOR RM
HEATING RATE 10 °C/min.
ATM. self-generated
TIME CONSTANT 1 sec. |

$SAMPLE$: Stil #5, $38.24\% \ MgSO_3 \cdot 3H_2O$, $61.76\% \ MgSO_3 \cdot 6H_2O$

− 191 −

% WEIGHT, mg.

TEMPERATURE, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

SAMPLE: Std #6
50% MgSO$_3$·3H$_2$O
50% MgSO$_3$·6H$_2$O

Fig. No. 14

SIZE 10 mg.

X-AXIS

TEMP. SCALE 50 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 $\frac{mg.}{inch}$

(SCALE SETTING X 2)

SUPPRESSION _____ mg.

RUN NO. 1 DATE 11/25/74

OPERATOR RM

HEATING RATE 10 $\frac{°C}{min.}$

ATM. self-generated

TIME CONSTANT 1 sec.

% WEIGHT, mg.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

DUPONT INSTRUMENTS

SAMPLE: Std #7	X-AXIS	Y-AXIS	RUN NO. 1 DATE 11/27/74

SAMPLE: Std #7
  59.84% $MgSO_3 \cdot 3H_2O$
  40.16% $MgSO_3 \cdot 6H_2O$
Fig. No. 15
SIZE _12_ mg.

X-AXIS
TEMP. SCALE 50 $\frac{°C}{inch}$
SHIFT __ _0_ __ inch
TIME SCALE (ALT.) __ __

Y-AXIS
SCALE 2 $\frac{mg.}{inch}$
(SCALE SETTING X 2)
SUPPRESSION _50_ mg.

RUN NO. 1   DATE 11/27/74
OPERATOR RM
HEATING RATE 10 $\frac{°C}{min.}$
ATM. self-generated
TIME CONSTANT 1 sec.

— 193 —

% WEIGHT, mg %

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

DU PONT INSTRUMENTS

SAMPLE: Std #8	X-AXIS	Y-AXIS	RUN NO. 1 DATE 11/25/7?
70.19% $MgSO_3.3H_2O$			OPERATOR RM
29.81% $MgSO_3.6H_2O$	TEMP. SCALE 50 $\frac{°C}{inch}$	SCALE 2 $\frac{mg.}{inch}$	HEATING RATE 10 $\frac{°C}{min.}$
Fig. No. 16	SHIFT 0 inch	(SCALE SETTING X 2)	ATM. self-generated
SIZE 12 mg.	TIME SCALE (ALT.)	SUPPRESSION 50 mg.	TIME CONSTANT 1 sec.

TEMPERATURE°. °C

% WEIGHT. mg.

194

* APPLY CORRECTION FOR NON LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

| SAMPLE: Std #11 | X-AXIS | Y-AXIS | RUN NO. 1 DATE 12/1/74 |
| 100% MgSO₃·3H₂O | | | OPERATOR RM |

SAMPLE: Std #11
100% $MgSO_3 \cdot 3H_2O$

Fig. No. 19

SIZE 14 mg.

X-AXIS

TEMP. SCALE 50 °C / inch

SHIFT 0 inch

TIME SCALE (ALT.)

Y-AXIS

SCALE 2 mg. / inch

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

RUN NO. 1 DATE 12/1/74

OPERATOR RM

HEATING RATE 10 °C / min.

ATM. self-generated

TIME CONSTANT 1 sec.

197

% WEIGHT. mg.

TEMPERATURE*, °C

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

SAMPLE: A mixture of:
44.3% MgSO$_3$.6H$_2$O
30.0% MgSO$_3$.3H$_2$O
25.7% glass beads
Fig. No. 20
SIZE 15 mg.

X-AXIS

TEMP. SCALE 50 $\frac{°C}{inch}$

SHIFT 0 inch

TIME SCALE (ALT.) _ _ _

Y-AXIS

SCALE 2 $\frac{mg.}{inch}$

(SCALE SETTING X 2)

SUPPRESSION 50 mg.

RUN NO. 1   DATE 12/1/74
OPERATOR RM
HEATING RATE 10 $\frac{°C}{min.}$
ATM. self-generated
TIME CONSTANT 1 sec.

198

% WEIGHT, mg.

• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL ALUMEL THERMOCOUPLES

TEMPERATURE*, °C
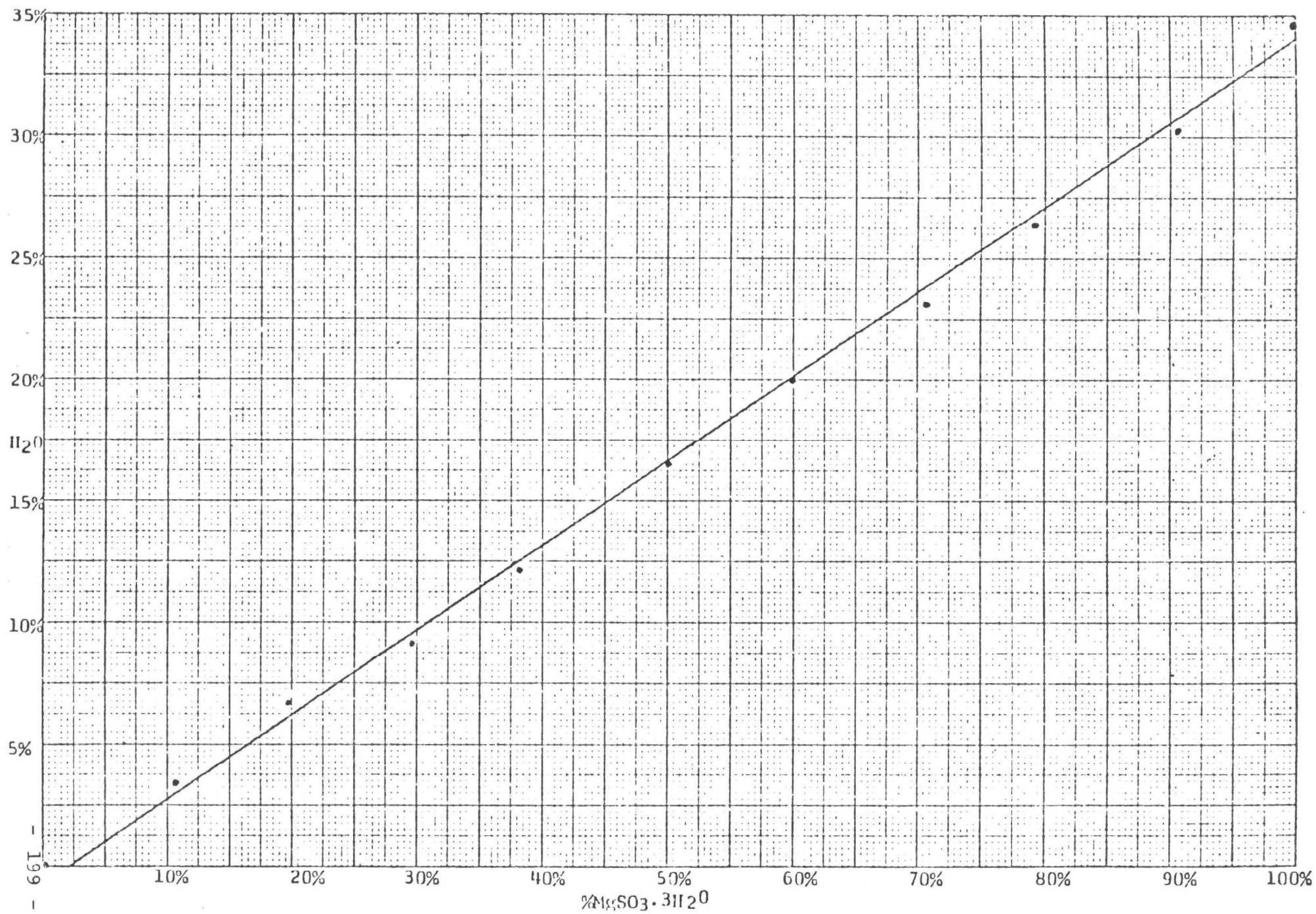
Fig. No. 21
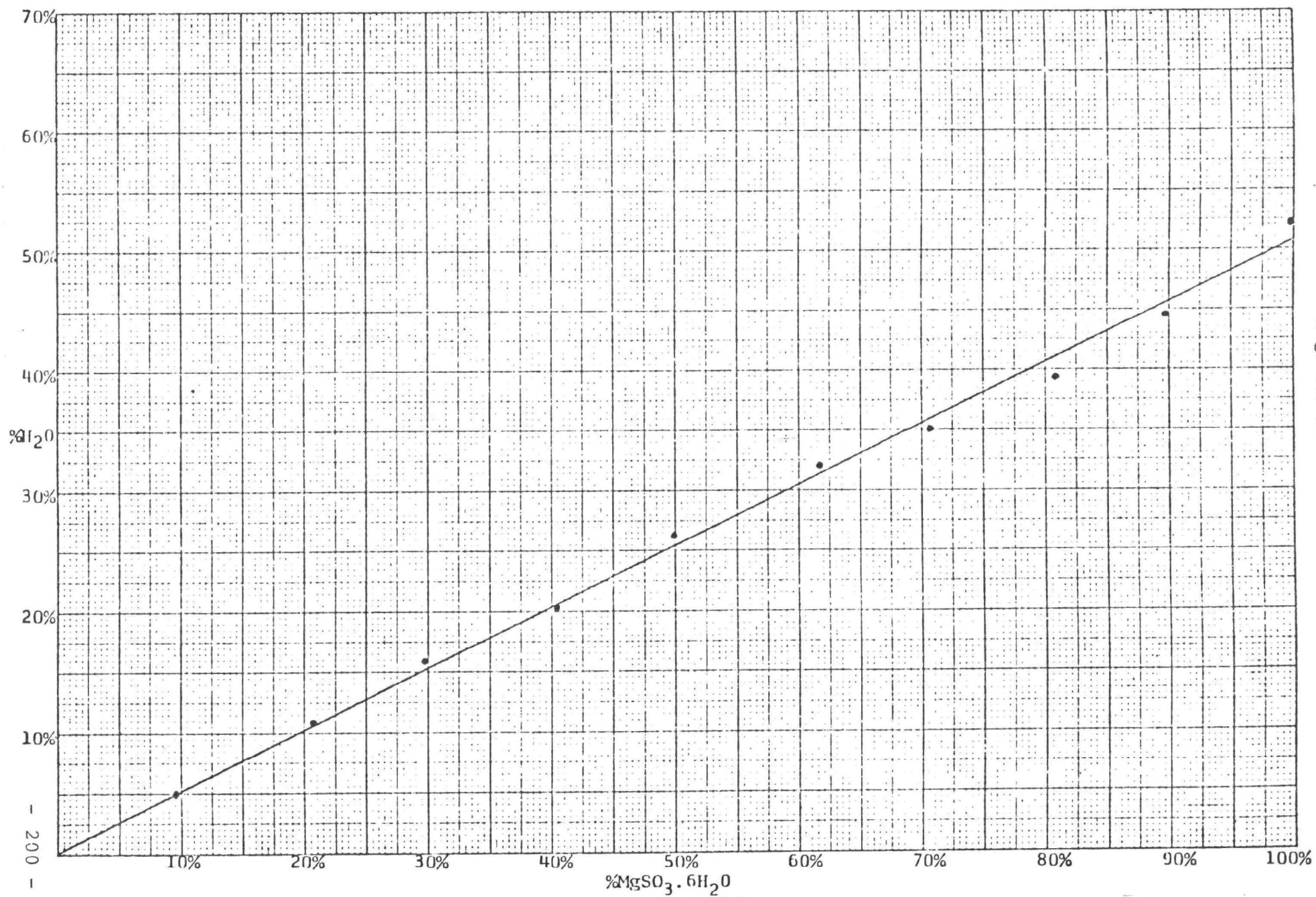
%MgSO3·3H2O

- 199 -

Fig. No. 22

%H₂O

%MgSO₃.6H₂0

APPENDIX 3

SULFUR OXIDE REMOVAL FROM POWER PLANT STACK GAS

Magnesia Scrubbing-Regeneration: Production of Sulfuric Acid

A Mass Spectrometric Study of the Thermal Degradation
of $MgSO_3 \cdot 3H_2O$ and $MgSO_3 \cdot 6H_2O$

by

Prof. Leonard Dauerman
Department of Chemical Engineering and Chemistry
New Jersey Institute of Technology
Newark, New Jersey

INTRODUCTION

In the Magnesia process for the removal of SO_2 from the flue gas and power plants, two hydrates of magnesium sulfite - the trihydrate and the hexahydrate - are formed. At a later stage these hydrates are calcined; MgO is formed which is recycled and, also, SO_2, which is converted into sulfuric acid.

It was the aim of this study to answer several questions pertaining to the calcining process: How do the hydrates decompose under vacuum conditions? Are trace amounts of H_2S formed in the thermal decomposition? How valid is the thermodynamic calculations on the partial pressure of SO_2 as a function and temperature. [1](K. Schwitzgebel and P. S. Lowell, "Thermodynamic basis for existing experimental data in $Mg-SO_2-O_2$ and $Ca-SO_2-O_2$ systems," Env. Sci. & Tech.,7, No. 13, 1147 (Dec. 1973).

The technique used in this study was mass spectrometry.

EXPERIMENTAL:

Samples of the hydrates were heated in the ionization source of the Finnigan Quadrupole 1015 mass spectrometer by utilizing the solid inlet probe. The temperature of the solid could be heated up to $400^{\circ}C$ and the ambient pressure was approximately 10^{-6} mm. Samples were heated to a given temperature and spectra were taken after the spectral pattern had stabilized.

RESULTS AND DISCUSSION

Two series of runs are presented as representative of the data obtained. In Run #370, the spectra presented are those for the decomposition of $MgSO_3 \cdot 3H_2O$. Spectra are recorded from 35° to $400^{\circ}C$. The three parallel recordings on each spectrum represent data recorded at three different sensitivities

1:3:9. A similar set of records for $MgSO_3 \cdot 6H_2O$ are presented in Run #371 series of spectra. As a reference record, the spectrum of SO_2, H_2O is shown in Figure 1.

To determine whether or not there is a difference in the thermal decomposition between the two hydrates, the ratios of the peak heights of $\frac{SO2}{H_2O}$ as a function of temperature were calculated.

In making these calculations data from an additional run for the trihydrate, and two additional runs for the hexahydrate were used. In Tables 1-5, the relevant data taken from the spectra are tabulated, and the value of the $\frac{SO2}{H_2O}$ ratio is calculated. In Table 6, the ratios for the three runs for $MgSO_3$ $\cdot 6H_2O$ are averaged at each temperature, and the logs are calculated. In Table 7, similar operations are carried out on the two $MgSO_3 \cdot 3H_2O$ runs.

The log $(\frac{SO2}{H_2O})$ as a function of temperature for the hydrates is plotted in Figure 1. The trend is similar. And in the light of the precision of the data, it can not be concluded that there is a difference in the way that the hydrates decompose.

Another question raised is whether H_2S, even in trace amounts, is observed. The peak characteristic of H_2S is observed at an m/e equal to 34. This m/e is observed in some spectra, for example, Run #370 at $400^{\circ}C$. The ratio of $\frac{m}{e}32/\frac{m}{e}64$ is 0.00547. In spectra Figure #1, for SO_2, where the intensity of m/e 64 is of a similar value the ratio is 0.00550. The fact that the difference in the ratio is the within the error in measuring the intensities means that the 34 is not an independent peak due to a separate species. It is, therefore, concluded that H_2S does not form even in trace amounts when the hydrates thermally decompose.

Note that SO_2 is observed at very low temperatures. In Run #370, it is observed at $35^{\circ}C$. But the pressure is ~ 10^{-6} mm. From Figure 2 in the previously

cited paper by Schwitzgebel and Lowell, in which the equilibrium constant is plotted against temperature for the system $MgSO_3 \rightleftharpoons SO_2 + MgO$, it is seen that at $35^\circ C$, the predicted value of the SO_2 pressure is 1.2×10^{-6} mm. This prediction is consistent with the observation made in this study, therefore, it is concluded that the equilibrium calculations are verified for the low temperature region.

CONCLUSIONS

1. Under vacuum conditions, $MgSO_3 \cdot 3H_2O$ and $MgSO_3 \cdot 6H_2O$ degrade similarly.

2. H_2S is not a thermal degradation product of the magnesium sulfite hydrates.

3. The thermodynamic calculations for the equilibrium $MgSO_3 \rightleftharpoons MgO + SO_2$ were confirmed in the lower temperature region, $50-100^\circ C$.

The numerous mass spectra taken at the temperature
intervals given in the table are not presented here
since the pertinent data have been reduced in the
subsequent tables and graphs.

Tables 1-5. CALCULATION OF $\frac{SO_2}{H_2O}$ INTENSITY RATIOS AS A

FUNCTION OF TEMPERATURES FOR RUNS OF VARYING

DETECTION SENSITIVITY FOR $MgSO_3 \cdot 3H_2O$ and

$MgSO_3 \cdot 6H_2O$.

Table 1. $MgSO_3 \cdot 3H_2O$; Run #370; Detection Sensitivity, 1000 microamps.

Temp	m/e[1] 64	m/e 18	m/e 17	$\dfrac{SO_2}{H_2O} = \dfrac{64}{18}$
35°C	17	1500	480	0.01133
50	8	40	11	0.20
100	11	47	13	0.234
150	13	33	9	0.394
200	13	26	7	0.50
250	28	34	9	0.823
300	42	17	5	2.47
350	110	25	7	4.40
400	350	47	13	7.445

[1] m = atomic weight
   e = charge

Table 2. $MgSO_3 \cdot 6H_2O$; Run #371; Detection Sensitivity, 1000 Microamps

Temp	m/e 64 [1]	m/e 18	m/e 17	m/e 16	$\dfrac{SO_2}{H_2O} = \dfrac{64}{18}$
40^oC	36	4610	1540	90	0.007810
50	250	15600	4900	320	0.01603
100	250	1830	580	40	0.1366
150	46	150	38		0.307
200	86	180	45		0.478
250	200	260	52		0.769
300	440	260	50		1.692
350	940	200	42		4.70
400	3250	350	68		9.286

[1] m = atomic weight
    e = charge

Table 3. $MgSO_3 \cdot 6H_2O$; Run #372; Detection Sensitivity, 500 Microamps.

Temp	m/e[1] 64	m/e 18	m/e 17	$\frac{SO_2}{H_2O} = \frac{64}{18}$
35°C	5	450	150	0.0111
70	24	1674	558	0.01434
150	50	315	100	0.1587
200	33	80	22	0.4125
250	50	61	18	0.8197
300	98	63	18	1.556
350	207	35	10	5.914
400	423	72	18	5.875

---

[1] m = atomic weight
e = charge

Table 4. $MgSO_3 \cdot 3H_2O$; Run #373; Detection Sensitivity, 600 Microamps.

Temp	m/e [1] 64	m/e 18	m/e 17	$\frac{SO_2}{H_2O} = \frac{64}{18}$
35°C	- -	16	5	- -
50	13	500	130	0.026
100	10	350	80	0.0286
150	2	33	9	0.0606
200	2	32	8	0.0625
250	12	150	30	0.080
300	20	140	28	0.143
350	36	26	7	1.385
400	113	42	11	2.69

[1] m = atomic weight
e = charge

Table 5. $MgSO_3 \cdot 6H_2O$; Run #374; Detection Sensitivity, 750 Microamps.

Temp	$m/e^{(1)}$ 64	m/e 18	m/e 17	m/e 16	$\dfrac{SO_2}{H_2O} = \dfrac{64}{18}$
50	13	135	45		0.0963
100	74	4200	1400	91	0.1771
150	160	960	320		0.1667
200	55	160	36		0.3438
250	88	115	30		0.7652
300	200	98	22		2.564
350	520	65	17		8.00
400	850	100	27		8.50

(1) m = atomic weight
e = charge

Table 6. Ave. Ratio of $\frac{SO_2}{H_2O}$ as a function of T ($MgSO_3 \cdot 6H_2O$)

Temp (°C)	Run #371	Run #372	Run #374	Ave	Log Ave
35	--	0.0111	--	0.0111	-1.95
40	0.007810	--	--	0.007810	-2.107
50	0.01603	--	0.0963	0.0562	-1.250
70	--	0.01434	--	0.01434	-1.843
100	0.1366	--	0.1771	0.1569	-0.804
150	0.307	0.1587	0.1667	0.2108	-0.676
200	0.478	0.4125	0.3438	0.4114	-0.386
250	0.769	0.8197	0.7652	0.7846	-0.105
300	1.692	1.556	2.564	1.9373	0.287
350	4.700	5.914	8.00	6.205	0.793
400	9.286	5.875	8.50	7.887	0.897

Table 7. Ave. Ration of $\dfrac{SO_3}{H_2O}$ as a function of T ($MgSO_3 \cdot 3H_2O$)

Temp($^{\circ}$C)	Run #370	Run #373	Ave	Log Ave
35	0.01133	--	0.01133	-1.946
50	0.200	0.026	0.113	-0.947
100	0.234	0.0286	0.1313	-0.8817
150	0.394	0.0606	0.2273	-0.6434
200	0.500	0.0625	0.2813	-0.5509
250	0.823	0.080	0.4515	-0.3453
300	2.47	0.143	1.3065	1.161
350	4.40	1.385	2.893	0.4612
400	7.445	2.69	5.068	0.7048

Figure 2.   Log $(\frac{SO_2}{H_2O})_{ave.}$ as a function of Temperature

for $MgSO_3 \cdot 3H_2O$ and $MgSO_3 \cdot 6H_2O$

LOG $\left(\frac{SO_2}{H_2O}\right)$ V. T(°C)

EQUAL CONCENTRATIONS OF
H₂O AND SO₂

1 $MgSO_3 \cdot 6H_2O$

2 $MgSO_3 \cdot 3H_2O$

T (°C)
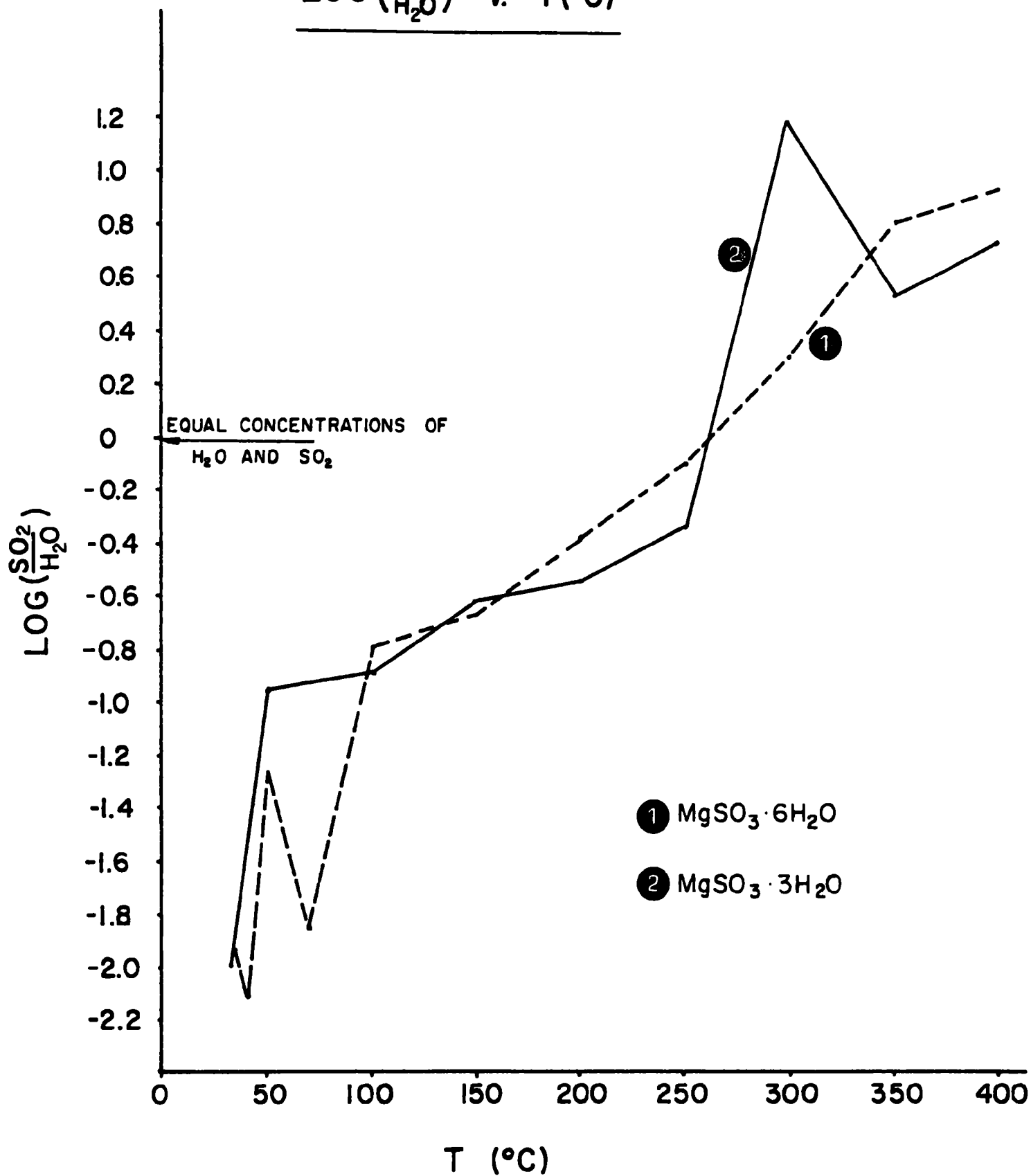
APPENDIX A. Simulation of Calciner in the Laboratory; The Testing

of the Hypothesis that H_2S is Formed When the Burner

Gas is Operated in the Fuel-Rich Region.

INTRODUCTION:

Since the previous study showed that H_2S is not a product of the thermal decomposition of the magnesium sulfite hydrates, and since H_2S had been reported as a product during calcination, it was conjectured that H_2S forms as a result of reactions between SO_2 and hydrocarbons present when the flame used to effect thermal degradation is operated in the fuel-rich region.

A laboratory set-up was designed which simulates many features of a calciner and, also, permits the immediate continuous analysis of volatilized products.

EXPERIMENTAL:

An inverted premix burner and a movable platform on which the sample is situated are housed within a pyrex glass pipe. See Figure A. In the center of the platform just above the sample is a quartz probe which leads to the Finnigan 1015 Quadrupole mass spectrometer. Thus, volatiles are continuously and rapidly characterized. In addition, the temperature in the region is sensed by a thermocouple. Also, the pressure in the "cross" can be varied and controlled. In practice, the pressure was maintained at 100 mm and the burner was operated in the fuel-rich region.

RESULTS:

This study was not carried out in a comprehensive manner. In the survey-type studies carried out, H_2S was not observed.

LAB-SCALE CALCINER SIMULATOR

APPENDIX A
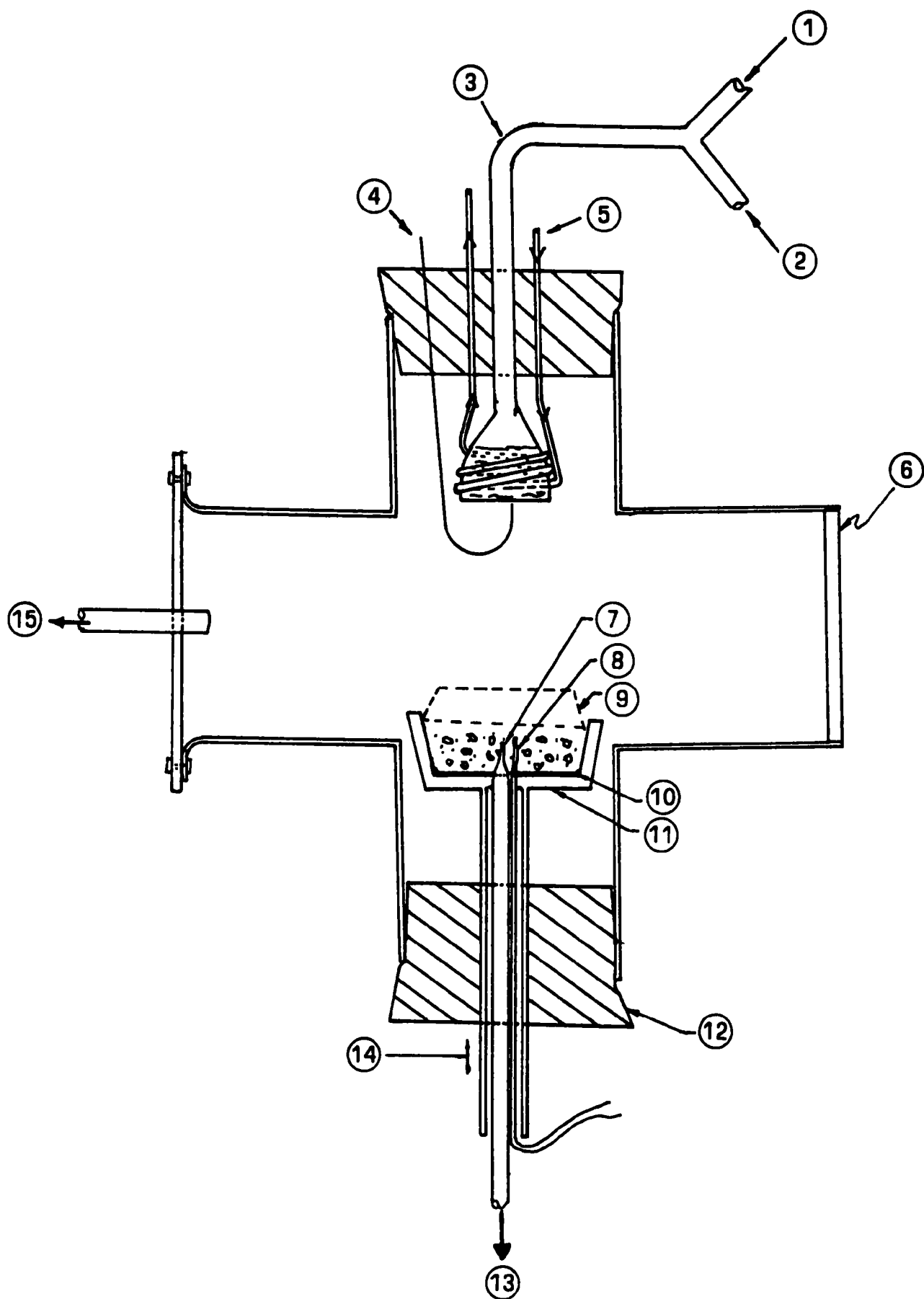
LAB-SCALE CALCINER SIMULATOR

EXPLANATION OF NUMERALS

1. O_2 feed

2. Fuel feed

3. Premix burner

4. Lead for Tesla Coil ignition

5. Cooling water

6. NaCl window

7. Quartz probe

8. Thermocouple

9. Perforated stainless steel cover

10. Asbestos sheet

11. Stainless steel sample holder

12. Rubber stopper

13. To mass spectrometer

14. Position of thermal decomposition stage is adjustable

15. To vacuum

APPENDIX B.   Effect of Wettness of Hydrates on Aggregate Formation

During Calcining

INTRODUCTION:

The prevalent feeling had been that less aggregation, finer particles,
resulted from the calcining of "dry" hydrates. On the other hand, it was thought
in this laboratory that the volatilization of water during calcination should
break up the particles.

EXPERIMENTAL:

Samples of $MgSO_3 \cdot 3H_2O$ were heated in air and vacuum to $500^{\circ}C$. Also,
an extra-moist sample was heated in vacuum.

RESULTS:

Samples heated in air showed less aggregation than samples heated in
vacuum. Extra-moistened samples heated in vacuum show less aggregation than the
drier samples.

CONCLUSION:

Water decreases aggregation by explosive volatization, thus rapid re-
moval by applying vacuum increases aggregation. Ideally, a wet sample should be
rapidly heated to as high a temperature as possible.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-77-018	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Magnesia Scrubbing Applied to a Coal-Fired Power Plant		**5. REPORT DATE** March 1977
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) George Koehler		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemico Air Pollution Control Company One Penn Plaza New York, NY 10001		**10. PROGRAM ELEMENT NO.** EHB528
		11. CONTRACT/GRANT NO. 68-02-1870
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15. SUPPLEMENTARY NOTES IERL-RTP project officer for this report is C.J. Chatlynne, Mail Drop 61, 919/549-8411 Ext 2915.

16. ABSTRACT The report gives results of a full-size demonstration of the magnesia wet-scrubbing system for flue gas desulfurization (FGD) on a coal-fired utility boiler. The system was designed to desulfurize half the flue gas from a 190-MW rated capacity generating unit firing 3.5% sulfur coal. The FGD installation was equipped with a first-stage wet scrubber for particle emissions control, followed by the magnesia unit. The FGD system was able to remove 90% of the inlet SO2 over 2800 hours of operation logged at the generating station. Its particle control capability was also demonstrated by reducing particle emissions to less than 0.01 gr/scf with the unit operated in series with an electrostatic precipitator. A test program, using only the wet-scrubbing unit for particle emissions control, achieved a collection efficiency of 99.6%. Magnesia was regenerated and recycled successfully. The SO2 produced during regeneration was used to manufacture commercial grade sulfuric acid which was marketed. Correlations were developed to determine SO2 removal for varying boiler loads and fuel sulfur content, and to control regeneration of acceptable alkali. Several other studies of the process technology and process chemistry were undertaken as part of the work.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Flue Gases Scrubbers Magnesium Oxides Desulfurization Sulfur Dioxide	Electric Power Plants Coal Combustion Particles Sulfuric Acid	Air Pollution Control Stationary Sources Magnesia Scrubbing Particulates	13B 21B 10B 07A 21D 07B 07D

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