

OCDO--95010712

OHIO COAL RESEARCH CONSORTIUM

SUBCONTRACT AGREEMENT NO. OCRC/93-4.8

OCDO Grant No. CDO/R-87-2C/B

EVALUATION OF OHIO FLY ASH/HYDRATED LIME SLURRIES AND
TYPE I CEMENT SORBENT SLURRIES IN THE U.C. PILOT SPRAY
DRYER FACILITY

Final Report for the Period
September 1, 1993 to August 31, 1994

by

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DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

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February 1995

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This project was funded in part by the Ohio Coal Development Office, Department of
Development, State of Ohio.

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EXECUTIVE SUMMARY

Objectives.

The objectives of this year's work included an evaluation of the performance of fly ash/hydrated lime as well as hydrated cement sorbents for spray drying absorption (SDA) of SO₂ from a simulated high-sulfur flue gas. These sorbents were evaluated for several different hydration methods, and under different SDA operating conditions. In addition, the physical properties of surface area and porosity of the sorbents was determined.

Conclusions.

The most reactive fly ash/hydrated lime sorbent studied was prepared at room temperature with milled fly ash. Milling fly ash prior to hydration with lime did have a beneficial effect on calcium utilization. No benefit in utilization was experienced either by hydrating the slurries at a temperature of 90°C as compared to hydration at room temperature, or by increasing hydration time. While the surface areas varied greatly from sorbent to sorbent, the pore size distributions indicated "ink bottle" pores with surface porosity on the order of 0.5 microns. No correlation could be drawn between the surface area of the sorbents and calcium utilization. These results suggest that the composition of the resulting sorbent might be more important than its surface area.

The most effective sorbent studied this year was produced by hydrating cement for 3 days at room temperature. This sorbent provided a removal efficiency and a calcium utilization over 25 percent higher than baseline results at an approach to saturation

temperature of 30°F and a stoichiometric ratio of 0.9. A maximum SO₂ removal efficiency of about 90 percent was experienced with this sorbent at an approach to saturation temperature of 20°F.

The hydrated cement studies indicate a clear benefit in milling the cement slurry during hydration. As in the fly ash/hydrated lime studies, no clear relationship between surface area and reactivity was exhibited. The pore size distribution of the reactive sorbent indicates a bimodal pore size on the order of 1 micron and 0.1-0.2 microns. The larger surface pore size may contribute to the enhanced reactivity.

Future Objectives.

In the following year the performance of hydrated cement in the spray dryer will be more fully investigated. Bench scale experiments at elevated temperatures will be performed. Sorbent reactivity will be related to spray dryer operating parameters, as well as to ball mill hydration conditions. Surface area and porosity will continue to be evaluated. Also, the effect of additives such as fumed silica and diatomaceous earth will be determined.

A wet chemistry procedure for determining the calcium content of cement will be evaluated. The procedure, from ASTM C 114, consists of removing silicon, aluminum, iron, titanium, phosphorus, and manganese from a sample of cement through a series of precipitations and filtrations. Calcium is then precipitated as an oxalate. After filtering, the oxalate is redissolved and titrated with potassium permanganate (KMnO₄).

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INTRODUCTION

Fly ash has shown promise as a calcium-based sorbent additive in several studies on dry sorbent injection into a humidified gas stream^{1,2,3,4,5} and in a few bench scale spray drying simulations^{5,6}, but little work has been done to evaluate this sorbent in a pilot scale SDA. In previous spray dryer studies conducted with the U.C. pilot spray dryer a significant increase in calcium utilization was experienced for specific hydration conditions⁷. A calcium utilization of 95 percent was obtained for a fly ash/hydrated lime sorbent prepared at 4:1 ash to lime weight ratio hydrated for 15 hours at 95°C, treating a simulated flue gas with an SO₂ concentration of 2500 ppm. This result compares quite well with a typical utilization of around 60 percent for slaked lime sorbents under similar conditions. This increase in calcium utilization identified fly ash as a potentially effective calcium-based sorbent additive for SDA. Objectives of this years work include further fly ash/hydrated lime sorbent studies to verify previous results, and to evaluate sorbent performance in terms of several sorbent preparation parameters. These include hydration temperature, hydration time, and fly ash preparation. In addition, sorbent surface area and porosity before and after reaction were evaluated.

The increase in calcium utilization associated with the fly ash/hydrated lime sorbents has been linked to the formation of amorphous calcium silica hydrate (C-S-H), which is a result of the pozzolanic reactions that occur due to the alumino-silica content of fly ash in the presence of calcium.^{2,8,9,10} C-S-H is highly amorphous and precipitates in a sponge-like mesh of foils and fibers on unreacted fly ash during hydration with quicklime. One researcher determined the amount of C-S-H formation for different fly ash/hydrated lime slurry

conditions⁸. Hydration conditions resulting in formation of the most C-S-H material appeared to occur when the fly ash/hydrated lime sorbent was hydrated by stirring a 3:1 Ca(OH)₂:fly ash solution at 90°C for 6 hours. However, his results indicated that the formation of the reactive product is very sensitive to hydration conditions and the type of fly ash used. Variability in product formation was experienced for similar fly ash types under similar hydration conditions, indicating a problem with the fly ash/hydrated lime sorbents associated with the inconsistency in fly ash constituency.

Therefore, it has been proposed¹¹ that to reduce this variability, highly reactive sorbent mixtures containing C-S-H could be made from Type I Portland Cement which has a uniform and fixed composition. One researcher investigated the silicate formation and relative SO₂ reactivity of hydrated cement sorbents.⁸ He found that under favorable conditions the sorbent produced consisted mainly of C-S-H and Ca(OH)₂, and exhibited a relatively high SO₂ reactivity and calcium utilization. The most reactive sorbent in this study was produced by hydrating cement at 10:1 water:cement ratio by weight for three days in a bench scale ball mill at room temperature. A sorbent of similar reactivity was also produced by hydrating at 10:1 water:cement for 9 hours in a bench scale ball mill at 60°C.

Another objective of this year's work was to evaluate the effectiveness of hydrated cement sorbents in the pilot spray dryer. The effect of preparation methods and resulting physical parameters of the sorbents were investigated. Hydration parameters include method of mixing, time, and temperature.

EXPERIMENTAL SETUP

Pilot Spray Dryer Facility

An updated flow diagram of the integrated pilot plant spray drying system is presented in Figure 1. The spray drying chamber was designed in-house and consists of a cylindrical section with a diameter of 0.92 m and a conical constriction at the bottom. The overall height of the unit is 2.13 m and the air flow capacity of the system is 250 m³/hr.

The inlet heater has a 10 kw capacity capable of heating the ambient air drawn through it up to 150°C. A kerosene blower was used to boost the inlet temperatures to around 160°C. Simulated sulfur-laden flue gas was created by injecting SO₂ just upstream of the spray drying chamber. The inlet SO₂ concentration was kept around 2500 ppm to simulate high-sulfur coal combustion conditions.

A two-fluid atomizer with external mixing was used to atomize the feed slurry by shearing the liquid with a cross-current flow of compressed air after the slurry was forced through a central orifice. Slurry feed rates were measured by an electromagnetic flow meter and had typical values ranging from 0.3 to 0.4 lpm.

The particulate control device downstream of the spray drying chamber consists of a single compartment self-cleaning pulse jet fabric filter with 42 individual bags providing a total surface area of 9.1 m². The pressure drop across the fabric filter was measured by a differential pressure gage and was kept between 1.5" and 3" w.g. SO₂ removal efficiency and flue gas temperature is monitored continuously with nondispersive infrared analyzers and

thermocouples, respectively, at the inlet and outlet of the spray dryer and at the outlet of the baghouse.

The slurry preparation system consists of two 0.6 m, 30 gallon capacity HDPE tanks with one used for lime slaking and the other for feed slurry hydration. Liquids in each tank were mixed with a 1/4 hp mixer. Heated slurries were prepared in a stainless steel drum which was outfitted with a steam jacket. The desired temperature of the slurry was maintained by a steam solenoid actuated by a temperature controller. Slurry is agitated in the cooker with a pneumatic mixer. A ball mill was used in this study to grind the fly ash prior to hydration with slaked lime, and to grind the water:cement sorbents during hydration. The ball mill consists of a drum roller and a 55 gallon drum loaded with 130 pounds of 1/4" diameter alumina spheres.

System Modifications.

Several system modifications and/or repairs were incorporated into the spray drying system this year, including:

Ductwork was extended from a 30,000 btu diesel blower to the air.

All of the old piping in the slurry system was replaced and redesigned to incorporate the new equipment.

A ball mill was installed consisting of a U.S. Stoneware drum roller and a 30 gallon drum with a removable lid and bolt ring loaded with 130 pounds of 1/4" alumina spheres.

A Moyno pump and a Fischer & Porter electromagnetic flow meter donated by IT, inc. in Cincinnati were installed. The Moyno pump should provide a steadier flow than the existing membrane pump, which is to be used to move slurries to and from various components of the slurry system.

A 1.4 hp slurry tank mixer was purchased to replace an inoperative mixer.

A second Nalgene HDPE mixing tank, identical to the existing feed tank, was purchased to replace the existing metal slurry tank. The new tank, with a smaller diameter than the metal tank, provides better mixing for slaking quicklime.

A cyclone was installed in the return line to the lime slaking tank to remove lime grit.

A sampling train was installed for SO₂ analysis at the outlet of the fabric filter. However, the third SO₂ analyzer had to be sent to the manufacturer for replacement of the reference cell and recalibration.

A 2" diameter x 10' tall pvc stack was attached to the blower outlet to provide better dispersal of exhaust gases.

A replacement for the heating element of an old Chromolox boiler found on-site was purchased. The intent is to use the boiler as a permanent source of steam for the cooker and the heated ball mill currently being developed.

EXPERIMENTAL RESULTS

Baseline Slaked Lime Studies

An extensive series of baseline slaked lime tests were conducted to classify the performance of the hydrated quicklime used for the fly ash studies in the pilot spray dryer. Calcium hydroxide slurry was prepared by hydrating quicklime at a weight ratio of 4:1 water to CaO in the lime slurry tank. The quicklime (Dravo Lime Company 1/8" x 0 ") has a typical inert content of 15 weight percent with the balance CaO. A typical analysis of the lime provided by Dravo is presented in Table 1. The slurry was continuously recycled during hydration so that most of the grit could be removed in the cyclone. Hydration was continued until all solids were suspended in solution and the slurry had returned to approximately room temperature. The slurry could was then diluted to a desirable solids content for baseline slaked lime tests. The results of the baseline tests have been presented in Figures 2 and 3.

The theoretical removal line is generated assuming that one mole of calcium can react to remove one mole of SO_2 . These results indicate a maximum removal of 69 percent, corresponding to a calcium utilization of 67 percent, at an approach to saturation temperature of 30°F at the exit of the spray drying chamber. The curves, which appear on subsequent graphs representing this data, are polynomial fits. The removals shown here and in subsequent results represent the integrated desulfurization across both the drying chamber and the baghouse.

Ohio Fly Ash/Lime Sorbent Studies

The fly ash used was obtained from the Ohio Power Company Muskingum River Plant Unit 3 precipitator. The results of analyses on the ash are presented in Tables 2 and 3. The mineral content was analyzed by Standard Laboratories, Inc. in Charleston, WV. The combined silicon dioxide and aluminum oxide content, which should correlate to the reactivity of the resulting sorbent, is about 68 percent. The content of these minerals is almost identical to that of one of the ashes used in a previous UC pilot spray dryer study⁷ and should yield comparable results. Since there is no standard procedure for determining the pH of the ash in solution a procedure similar to the EPA SW-846 method for soil in solution was used. The porosity and surface of the fly ash, and subsequent materials, was determined by high pressure mercury intrusion using a Quantachrome Autoscan-60 Porosimeter, and a Quantachrome Monosorb Surface Area Analyzer, respectively.

Table 4 summarizes the slurry preparation methods for the fly ash/hydrated lime

slurries. Note that the F7 sorbent was inadvertently hydrated 6 hours at room temperature after an 18 hour hydration at 90°C due to problems with the operation of the pilot plant and data acquisition system. All slurries were prepared at a 1:1 fly ash:hydrated lime weight ratio so that the effect of different preparation methods on spray dryer performance could be determined. Each slurry was agitated by stirring either in the feed tank for room temperature hydration or in the cooker at 90°C for the indicated times of hydration. Hydration was conducted at a total solids content between 10 and 15 percent. The effect of milling the fly ash prior to hydration with calcium hydroxide was investigated using the ball mill. A slurry of water and fly ash was milled for either 24 or 48 hours and then removed from the mill and hydrated with slaked lime.

The overall SO₂ removal efficiencies, including removal across both the spray dryer and baghouse, and calcium utilization of several of the fly ash/hydrated lime sorbents are presented in Figures 4 and 5. These results show that the sorbents provide neither additional removal efficiency nor a benefit in calcium utilization over the slaked lime sorbent. These results compare well with previous pilot plant studies for similar sorbent preparation methods.⁷

Figure 6 shows the effect of milling fly ash 48 hours prior to hydration with slaked lime. While over a 43 percent increase in utilization was experienced for the unheated fly ash sorbents (F1 and F2), the heated fly ash showed no improvement and provided a utilization that was no better than the unheated sorbent prepared with unmilled fly ash. The additional hydration of sorbent F7, however, may have had an adverse effect on the performance of that sorbent. This stresses the notion that the products of hydration are very sensitive to hydration

conditions.

The effects of hydration temperature and time on calcium utilization are presented in Figures 7 and 8. No increase in utilization could be shown by hydrating the fly ash/hydrated lime slurry at an elevated temperature. In fact, the sorbent (F1) hydrated at room temperature may have provided a slightly higher utilization than the heated sorbent. Figure 8 shows the result that the sorbents hydrated for 4 hours (F3 and F5) performed as well if not slightly better than the sorbents hydrated for 18 hours (F4 and F6).

The BET surface area results for the fly ash/hydrated lime sorbents is summarized in Table 5. The results here seem contradictory. While an increase in surface area for the F2 sorbent over the F1 sorbent translated to an increase in calcium utilization, The reactivities of sorbents F5 and F6 were indistinguishable even though F6 had a surface area 3 times that of F5. The effect of milling on the surface area of the fly ash was dramatic in that over a 3-fold increase was seen by milling the ash 24 hours, and over a 9-fold increase was seen by milling for 48 hours. This increase in area did result in a more reactive sorbent.

Figure 9 represents a porogram typical of the fly ash sorbents. In general, the porosity data indicates the majority of pore size on the order of 0.5 microns. However, this pore size indication is probably misleading. The hysteresis curve here is typical of a Type E de Boer's hysteresis, indicating the presence of "ink bottle" pores where the inner pore necks in to form a smaller pore at the surface of the solid¹². This conclusion is supported in that the surface area calculated by assuming cylindrical pores is much higher than the BET surface area.

Type I Portland Cement Studies

The cement was supplied by Quikrete and was produced to adhere to the ASTM C 150 specifications for Type I Portland Cement. Typical composition of Type I Portland Cement is presented in Table 6^{13,14}. Sorbent C1 was stirred at room temperature (about 25°C) for 17 hours in the feed tank, sorbent C2 was milled at room temperature for 18 hours in the ball mill, and sorbent C3 was stirred in the cooker at about 60°C for 24 hours. Before slurry C3 was fed to the spray dryer it was split with half going to the ball mill for an additional 18 hour hydration at room temperature to produce C4. Sorbent C5 was ball milled at room temperature for 3 days. Each cement-based slurry was prepared at 10:1 water to cement weight ratio. The different slurry preparation methods for these sorbents are summarized in Table 7.

One problem associated with the hydrated cement sorbents not experienced with the fly ash/hydrated lime sorbents is in determination of the calcium content of the hydrated sorbent in that the relative decrease in weight concentration of calcium as hydration proceeds must be established. One way to do this is to compare the solids content before and after hydration. This procedure was used to determine the calcium content for the C5 sorbent, but was not used for C1 through C4. For these sorbents the decrease in calcium content with hydration was neglected. Although inaccurate, this approximation is conservative and yields calcium utilization values that are slightly lower than actual.

Figures 10 and 11 summarize the results of spray drying tests performed for the hydrated cement sorbents. These results indicate that sorbents C1 through C4 have both SO₂ removal efficiencies and calcium utilization values lower than the baseline results. Sorbent C5, however, exhibited a reactivity well in excess of the baseline results. This sorbent

provided a removal efficiency and a calcium utilization over 25 percent higher than baseline results at a stoichiometric ratio of 0.9. Another item of note from Figures 10 and 11 is that the sorbents that were milled (C1, C2, and C5) performed better than the sorbents that were only stirred. Figure 12 shows an increase in SO₂ removal efficiency with milling time.

The performance of sorbent C5 at various approach to saturation temperatures at the outlet of the spray dryer is presented in Figures 13 and 14. A maximum SO₂ removal efficiency of about 90 percent was experienced at an approach to saturation temperature of 20°F. Note that the reactivity of the sorbent at a 45°F approach to saturation temperature was even greater than baseline tests where the approach to saturation was 30°F.

BET surface area data is summarized in Table 8. As in the fly ash studies, the correlation between a high surface area and greater reactivity is unclear. The most reactive sorbent (C5) did have the greatest surface area, and the least reactive sorbent (C1) did have the smallest surface area. However, sorbent C2 was more reactive than C3 even though the surface area of the C2 sorbent was about 2/3 that of C3.

A porogram typical of the hydrated cement sorbents is presented in Figure 15. The porograms for these sorbents were generally bimodal with a pore sizes on the order of 1 micron and 0.1-0.2 microns. The hysteresis curves generally look more like that of a Type A, indicating cylindrical pores¹². The surface area calculated from the pore size distribution is also higher than the BET surface areas, indicating that "ink bottle" pores may be present. The larger pore size, which appears to be more prevalent in the C5 sorbent, may contribute to sorbent reactivity.

Bench Scale Tests.

A bench scale ball mill was used to determine the change in physical properties of the hydrated cement sorbent with time. A slurry of 10:1 water:cement was introduced into a glass jar with alumina spheres and milled at room temperature. Aliquots of slurry were drawn from the jar periodically and vacuum dried overnight so that BET surface area and porosity tests could be performed.

Figure 16 shows the development of surface area with hydration time. The surface area of the hydrated cement starts from a value of $24 \text{ m}^2/\text{g}$ and appears to approach a constant value near $70 \text{ m}^2/\text{g}$ within 5 days. Figures 17, 18, and 19 show the appearance of a bimodal pore size distribution as hydration occurs.

Ball Mill Enhancements.

Ball milling operations will be enhanced for future studies. A 30 gallon drum with a flanged lid has been built which should alleviate leakage problems experienced with the drum lids secured with a bolt ring. Also, a steam drum has been designed and is currently under construction. This drum consists of a 30 gallon drum fixed inside a 55 gallon drum. A sketch of the steam drum is presented in Figure 20.

CONCLUSIONS

The most reactive fly ash/hydrated lime sorbent studied was prepared at room temperature with milled fly ash. Milling fly ash prior to hydration with lime did have a beneficial effect on calcium utilization. No benefit in utilization was experienced either by hydrating the slurries at a temperature of 90°C as compared to hydration at room temperature, or by increasing hydration time. While the surface areas varied greatly from sorbent to sorbent, the pore size distributions indicated "ink bottle" pores with surface porosity on the order of 0.5 microns. No correlation could be drawn between the surface area of the sorbents and calcium utilization. These results suggest that the composition of the resulting sorbent might be more important than its surface area.

The most effective sorbent studied this year was produced by hydrating cement for 3 days at room temperature. This sorbent provided a removal efficiency and a calcium utilization over 25 percent higher than baseline results at an approach to saturation temperature of 30°F and a stoichiometric ratio of 0.9. A maximum SO₂ removal efficiency of about 90 percent was experienced with this sorbent at an approach to saturation temperature of 20°F.

The hydrated cement studies indicate a clear benefit in milling the cement slurry during hydration. As in the fly ash/hydrated lime studies, no clear relationship between surface area and reactivity was exhibited. The pore size distribution of the reactive sorbent indicates a bimodal pore size on the order of 1 micron and 0.1-0.2 microns. The larger surface pore size may contribute to the enhanced reactivity.

ACKNOWLEDGEMENTS

This work is funded by the Ohio Coal Development Office in Columbus, Ohio. The researchers would like to thank the Dravo Lime Company for donating quicklime, CG&E for donating fly ash, and IT inc. for donating two moyno pumps and an electromagnetic flow meter. Dr. Malcolm E. Kenney and Ray-Kuang Chiang, from Case Western Reserve University, have provided valuable technical assistance.

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Table 1: Typical Quicklime Analysis

Mineral	% Ignition
Calcium Oxide	90.0
Magnesium Oxide	2.5
Silicon Dioxide	2.8
Ferric Oxide	0.5
Aluminum Oxide	1.0
Sulfur	0.05
Phosphorus	0.004
Carbon Dioxide	2.1
Water	0.4

Table 2: Fly Ash Mineral Analysis

Mineral	% Ignited
Silicon Dioxide	45.94
Aluminum Oxide	22.11
Calcium Oxide	2.59
Sodium Oxide	2.84
Magnesium Oxide	1.31
Sodium Oxide	0.83
Ferric Oxide	21.22
Sulfur Trioxide	0.38
Titanium Dioxide	1.63

Table 3: In-House Analysis of Fly Ash

BET Surface Area	3.2 m ² /g
Mean Pore Population Radius	47 Å
Free Moisture Content	< 1 %
pH in Solution	3.1

Table 4: Fly ash/Hydrated Lime Hydration Conditions

Sorbent	Hydration Temperature	Hydration Time	Fly Ash Preparation
Slaked Lime			
F1	Room Temperature	18 hours	Unmilled
F2	Room Temperature	18 hours	Milled 48 hour
F3	90°C	4 hours	Unmilled
F4	90°C	18 hours	Unmilled
F5	90°C	4 hours	Milled 24 hours
F6	90°C	18 hours	Milled 24 hours
F7	90°C Preceding Room Temperature	18 hours Preceding 6 hours	Milled 48 hours

Table 5: BET Surface Area Results for the Fly Ash/Hydrated Lime Sorbents

Sorbent	Unreacted Sorbent (m ² /g)	Spent Sorbent (m ² /g)
Slaked Lime	31	8
Unmilled Fly Ash	3	
Fly Ash Milled 24 Hours	12	
Fly Ash Milled 48 Hours	28	
F1	16	9
F2	35	11
F3	41	11
F4	23	13
F5	24	13
F6	73	21
F7	30	12

Table 6: Typical Cement Composition

Composition	Percent by Weight
Cao	63
SiO ₂	20
Al ₂ O ₃	6
Fe ₂ O ₃	3
MgO	1.5
SO ₃	2
K ₂ O/Na ₂ O	1
Others	1

Table 7: Hydrated Cement Hydration Conditions

Sorbent	Hydration Temperature	Hydration Time	Hydration Conditions
C1	Room Temperature	17 hours	Stirred
C2	Room Temperature	18 hours	Milled
C3	60°C	24 hours	Stirred
C4	60°C Preceding Room Temperature	24 hours Preceding 18 hours	Stirred Preceding Milled
C5	Room Temperature	3 days	Milled

Table 8: BET Surface Area Results for the Hydrated Cement Sorbents

Sorbent	Unreacted Sorbent (m ² /g)	Spent Sorbent (m ² /g)
Unhydrated Cement	1.4	
C1	22	Not Meas.
C2	38	Not Meas.
C3	59	14
C4	52	18
C5	71	23

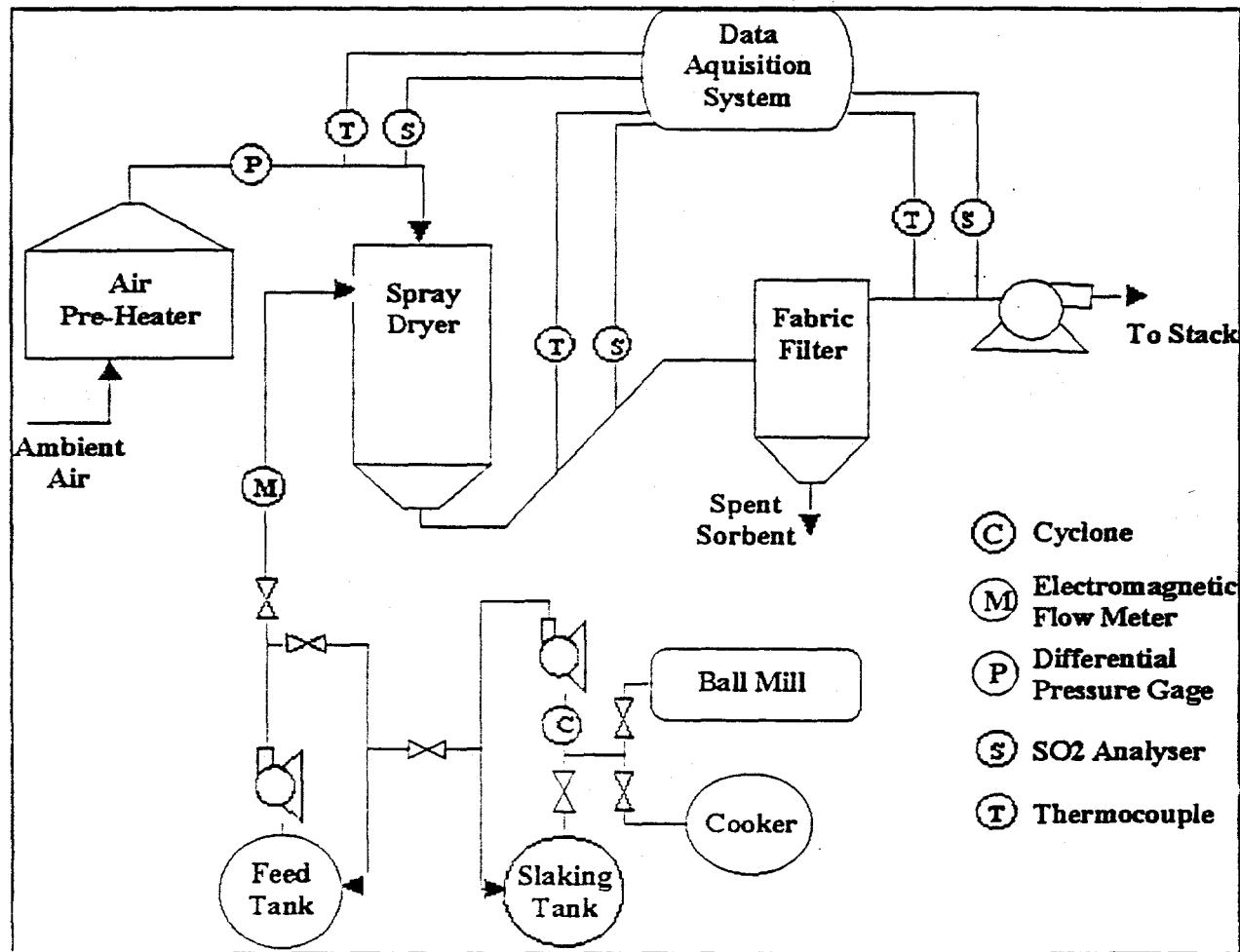


Figure 1: Spray Drying System

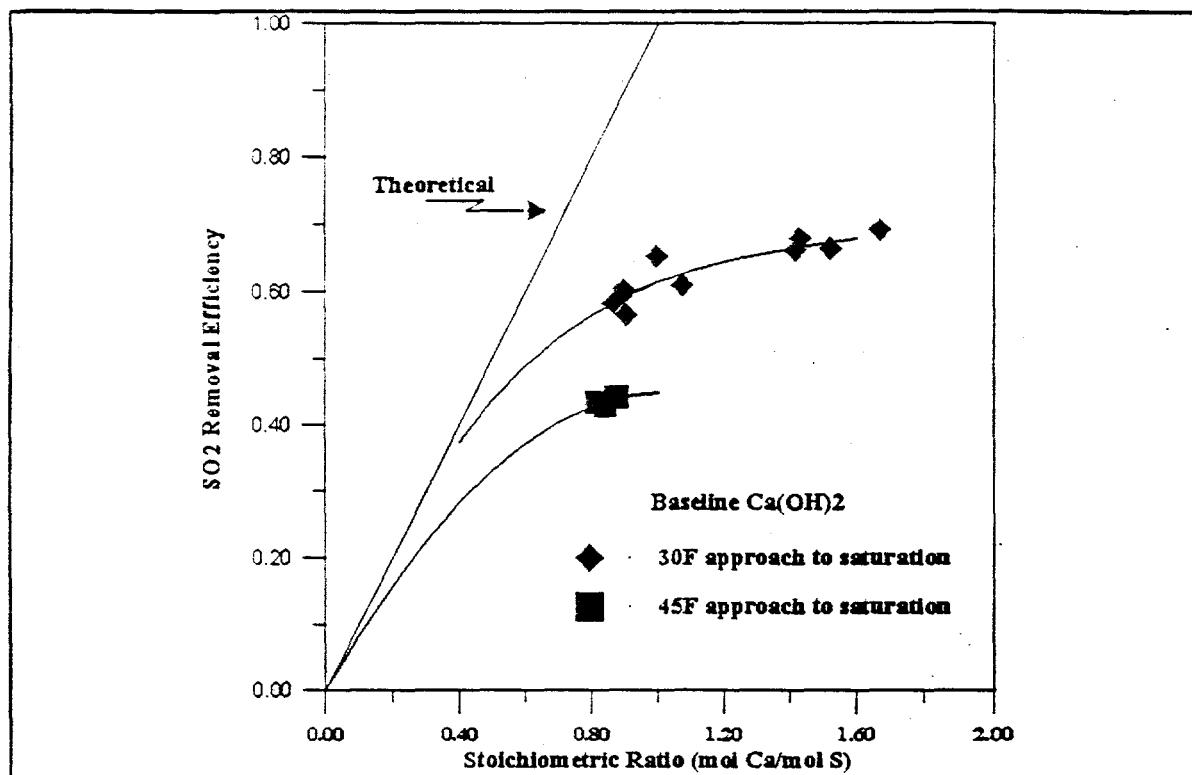


Figure 2: Baseline Ca(OH)_2 , SO_2 Removal Efficiency

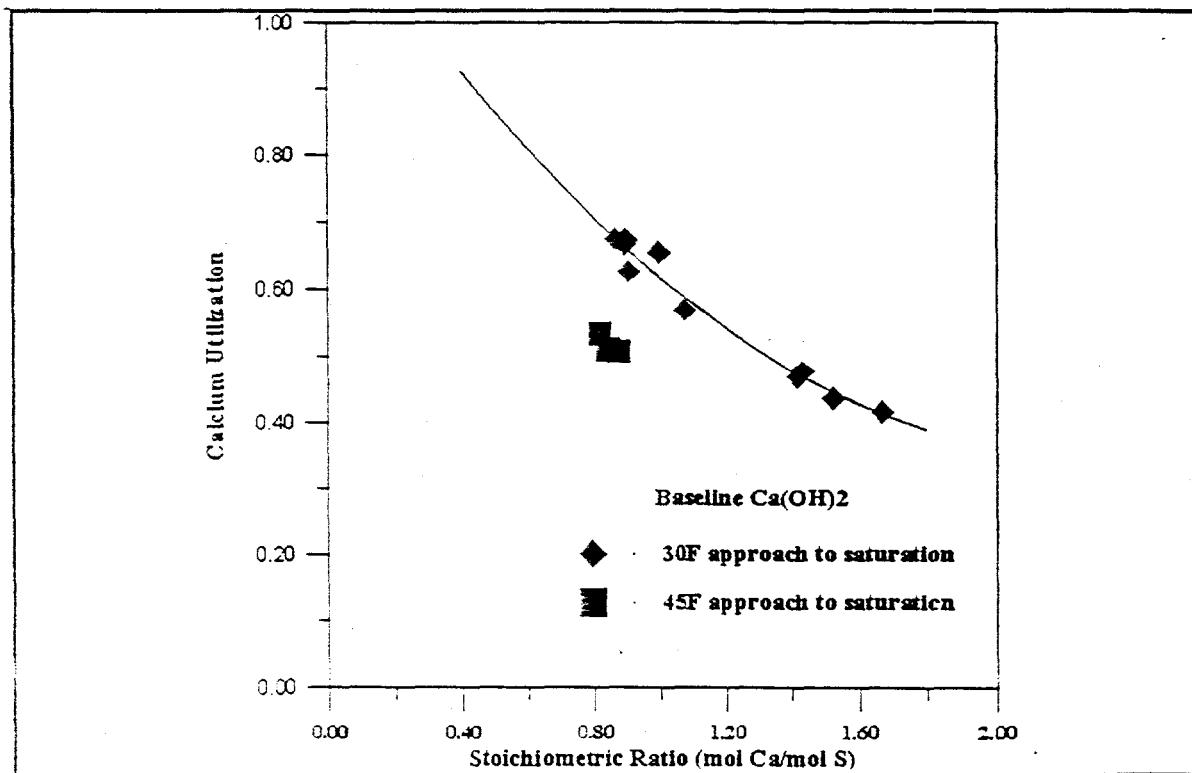


Figure 3: Baseline Ca(OH)_2 , Calcium Utilization

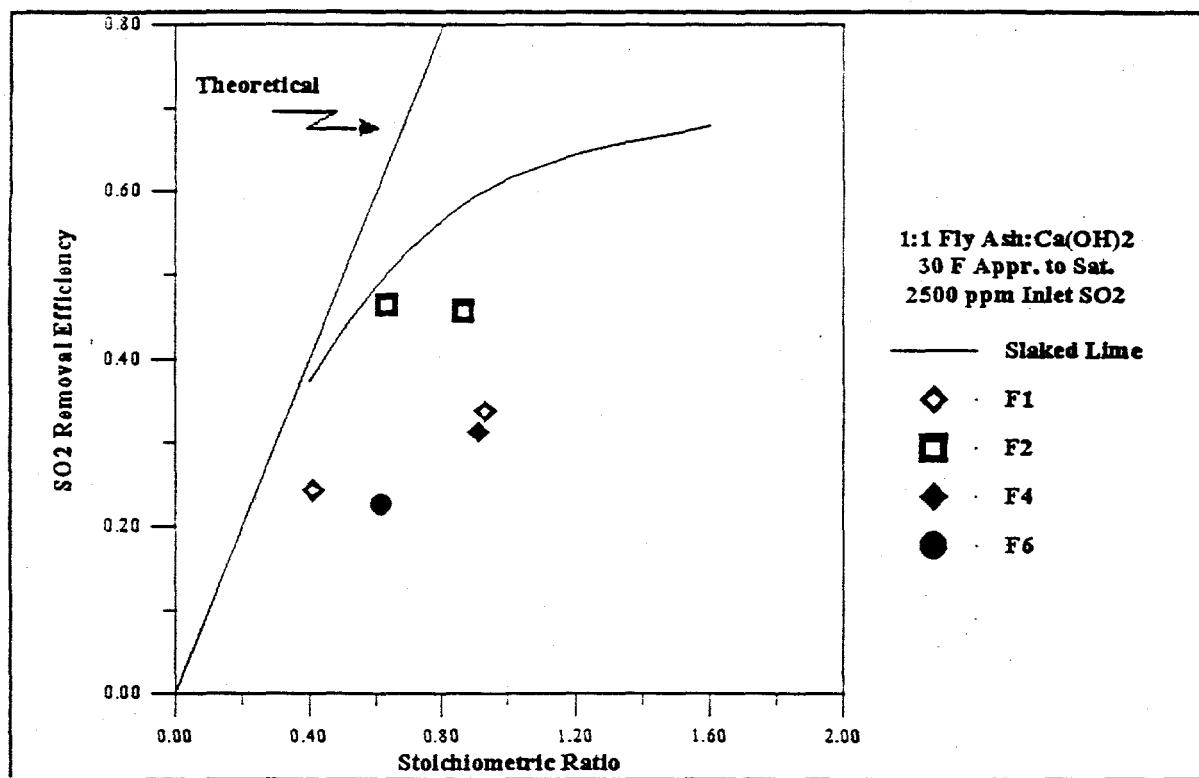


Figure 4: Fly Ash/Hydrated Lime SO₂ Removal Efficiency

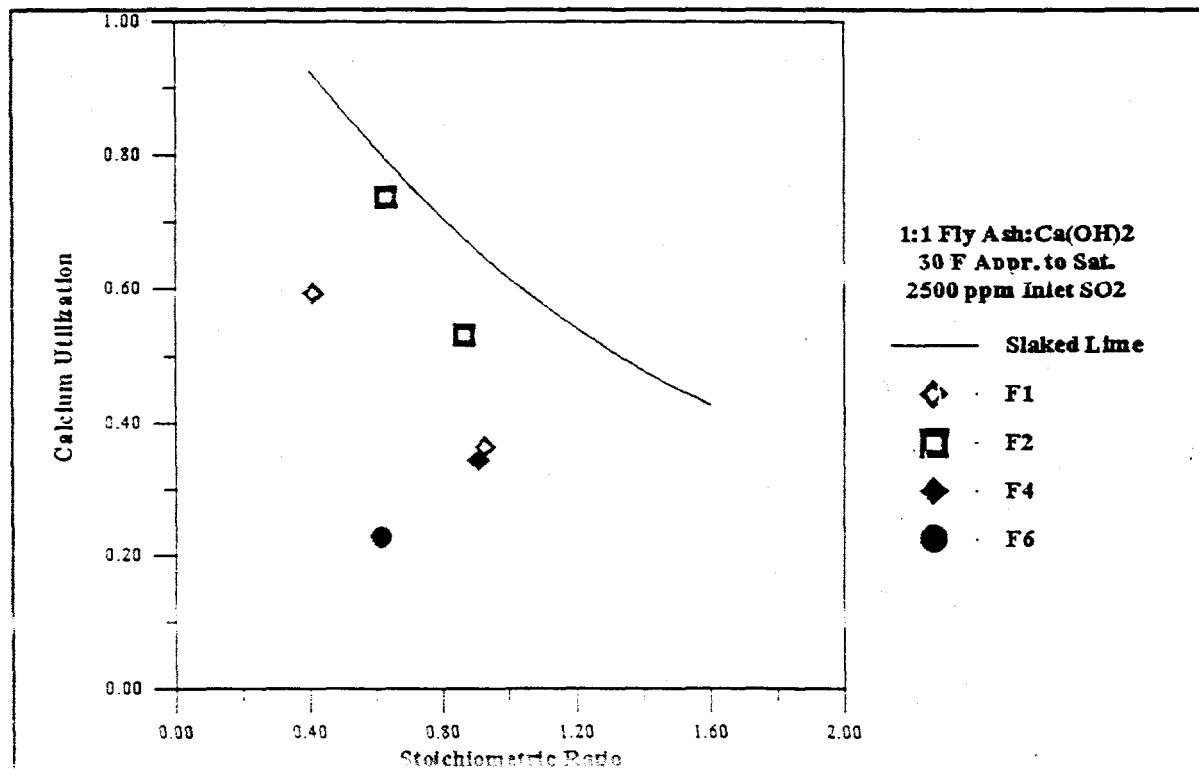


Figure 5: Fly Ash/Hydrated Lime Calcium Utilization

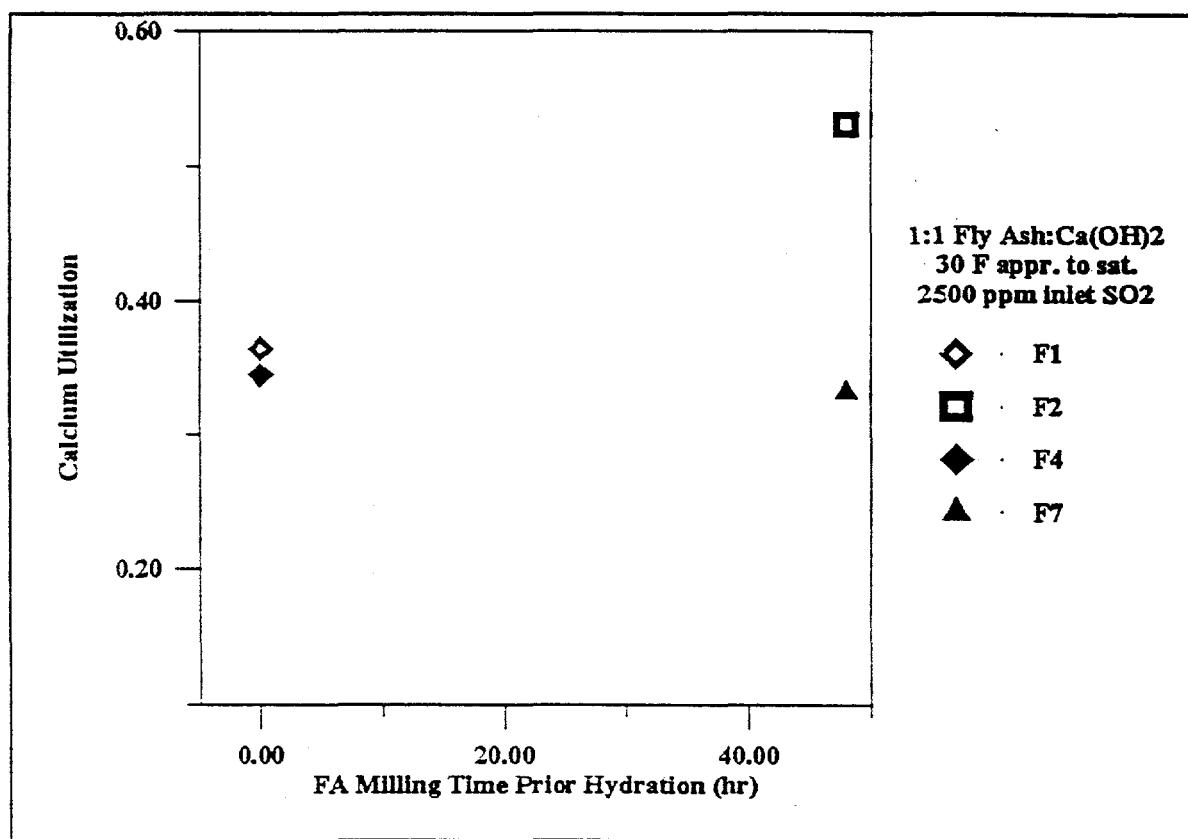


Figure 6: Effect of Milling Fly Ash Prior to Hydration

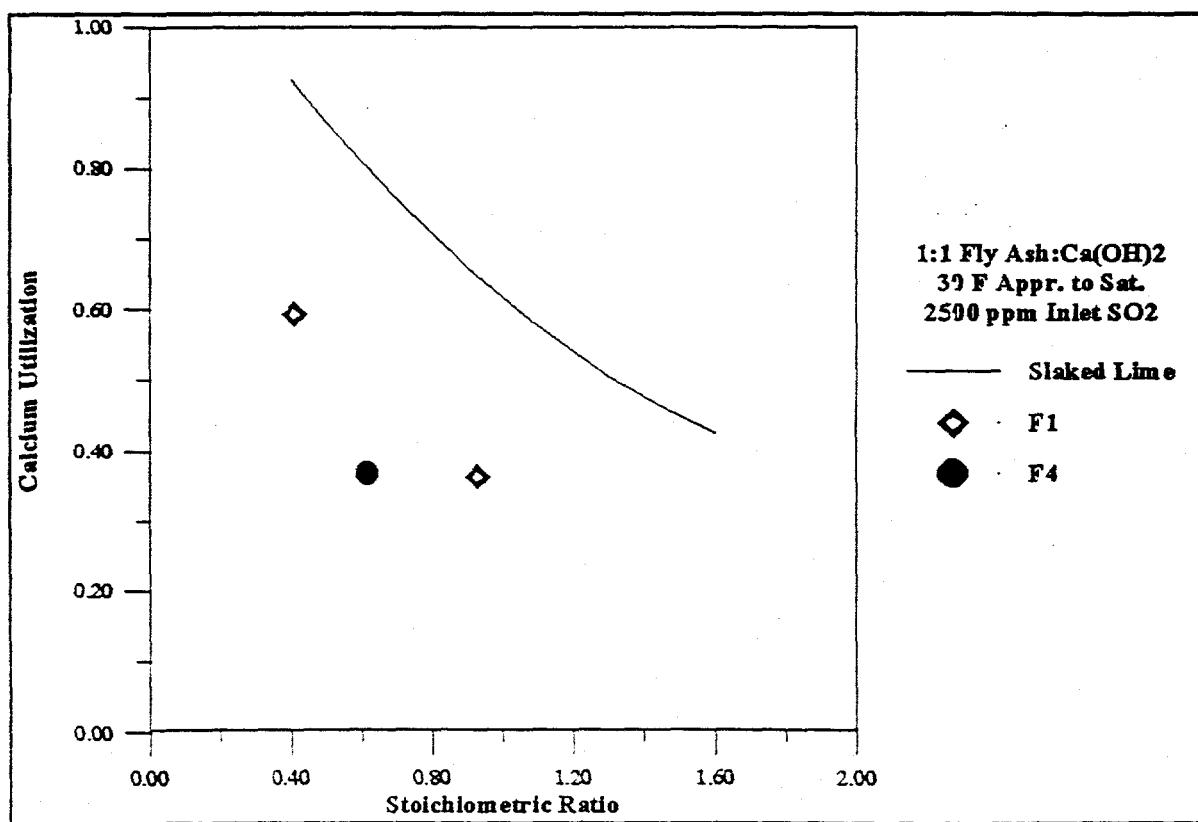


Figure 7: Effect of Hydration Time on Calcium Utilization

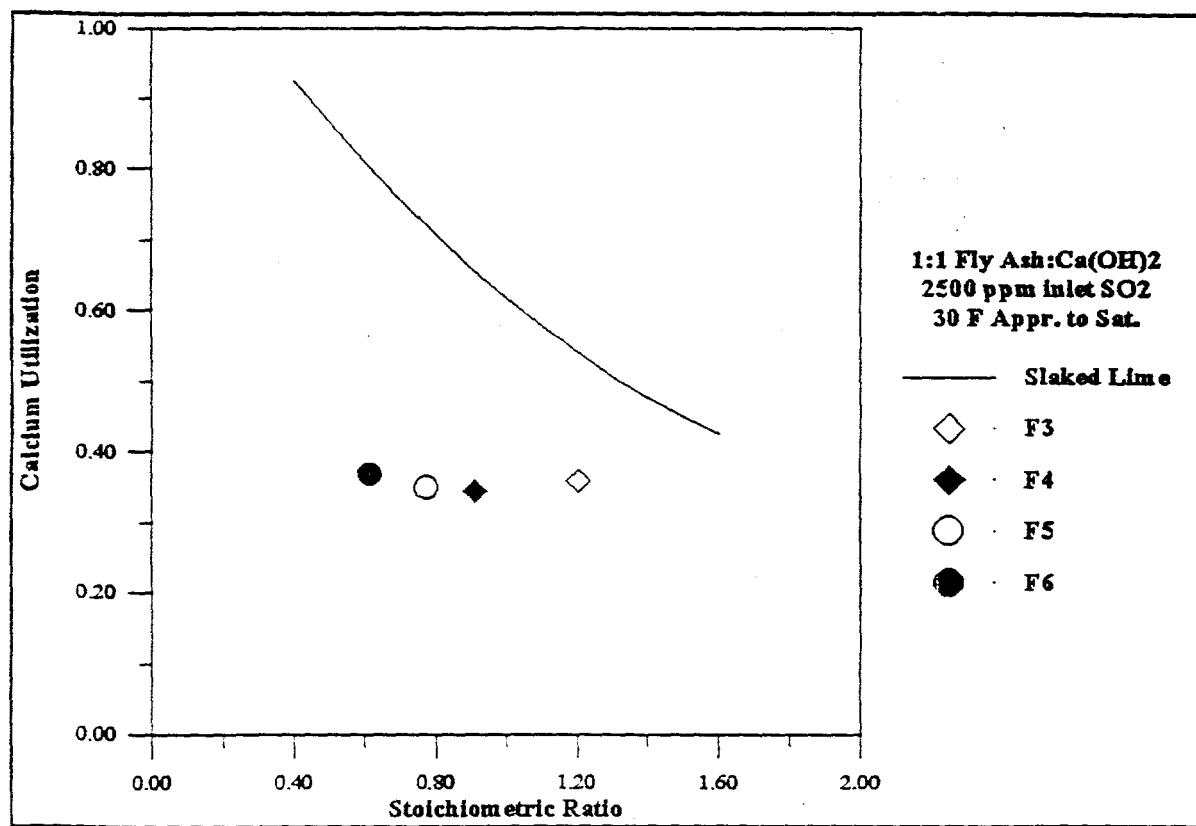


Figure 8: Effect of Hydration Temperature on Calcium Utilization

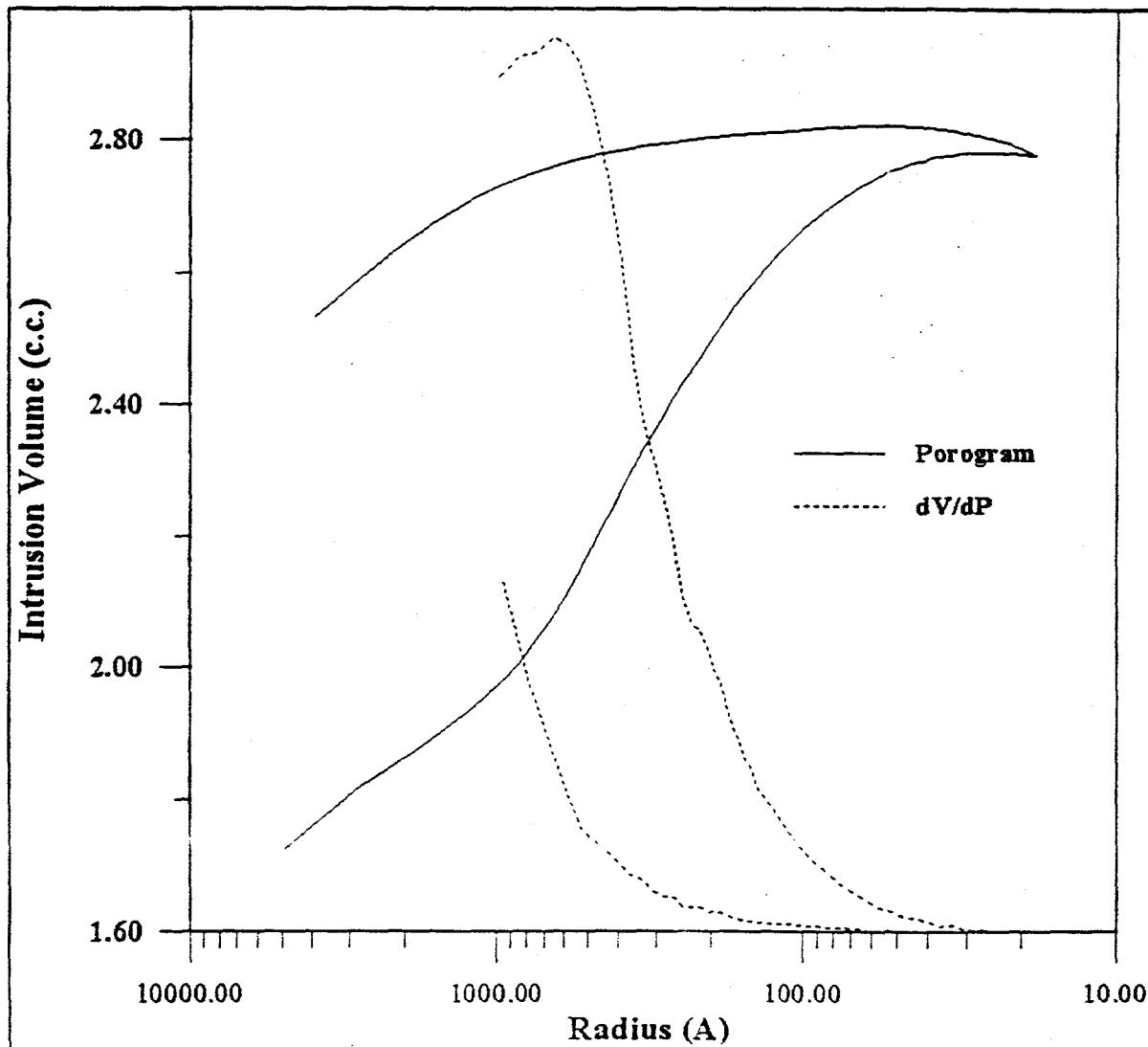


Figure 9: Porogram for Sorbent F6

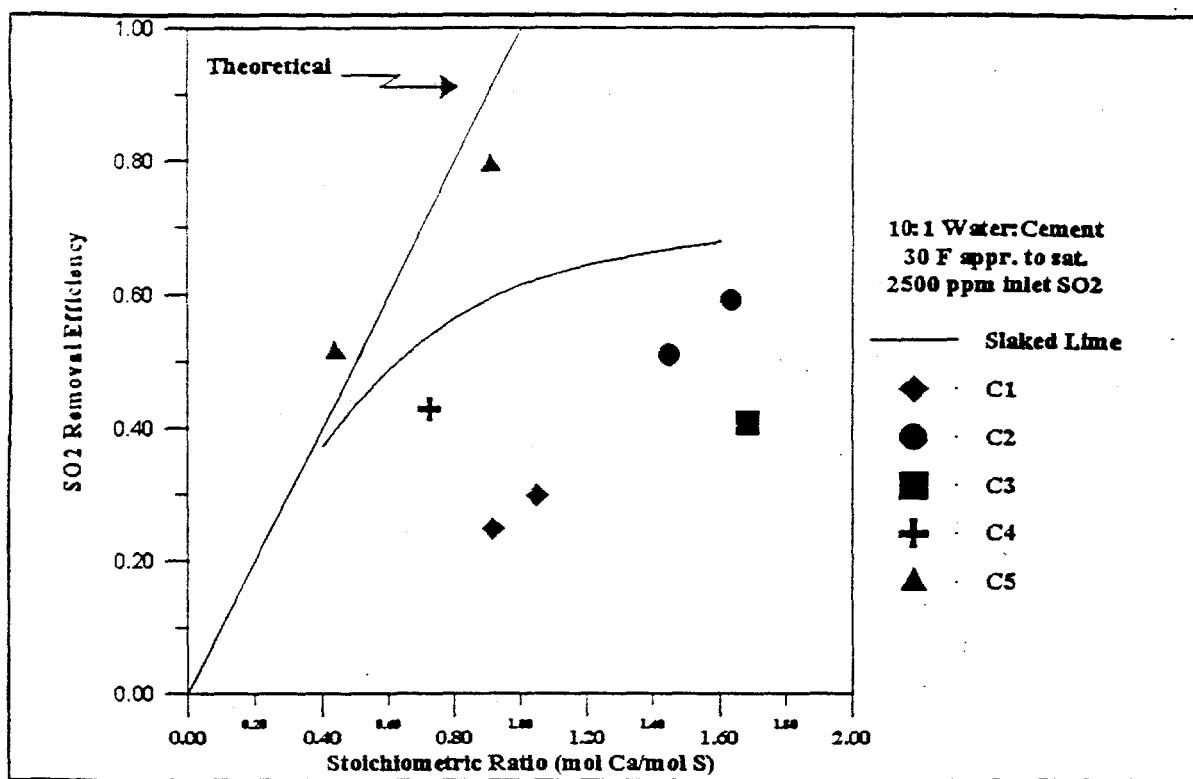


Figure 10: Hydrated Cement SO_2 Removal Efficiency

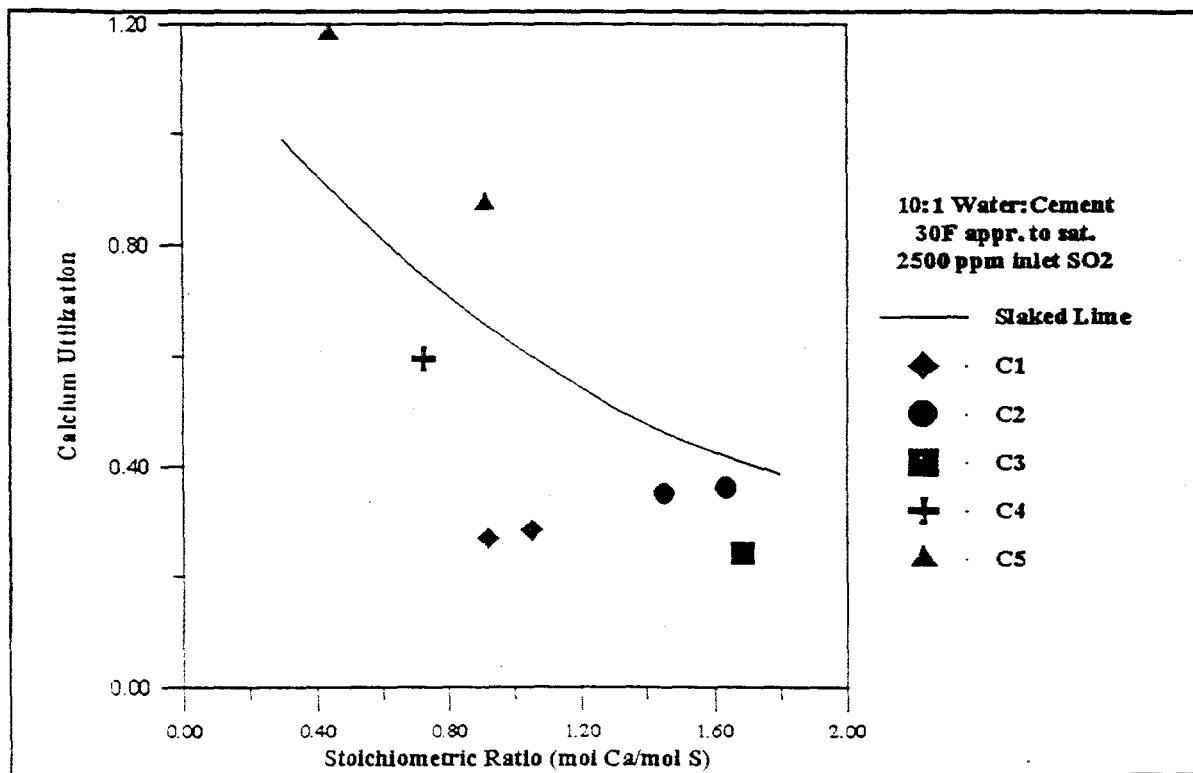


Figure 11: Hydrated Cement Calcium Utilization

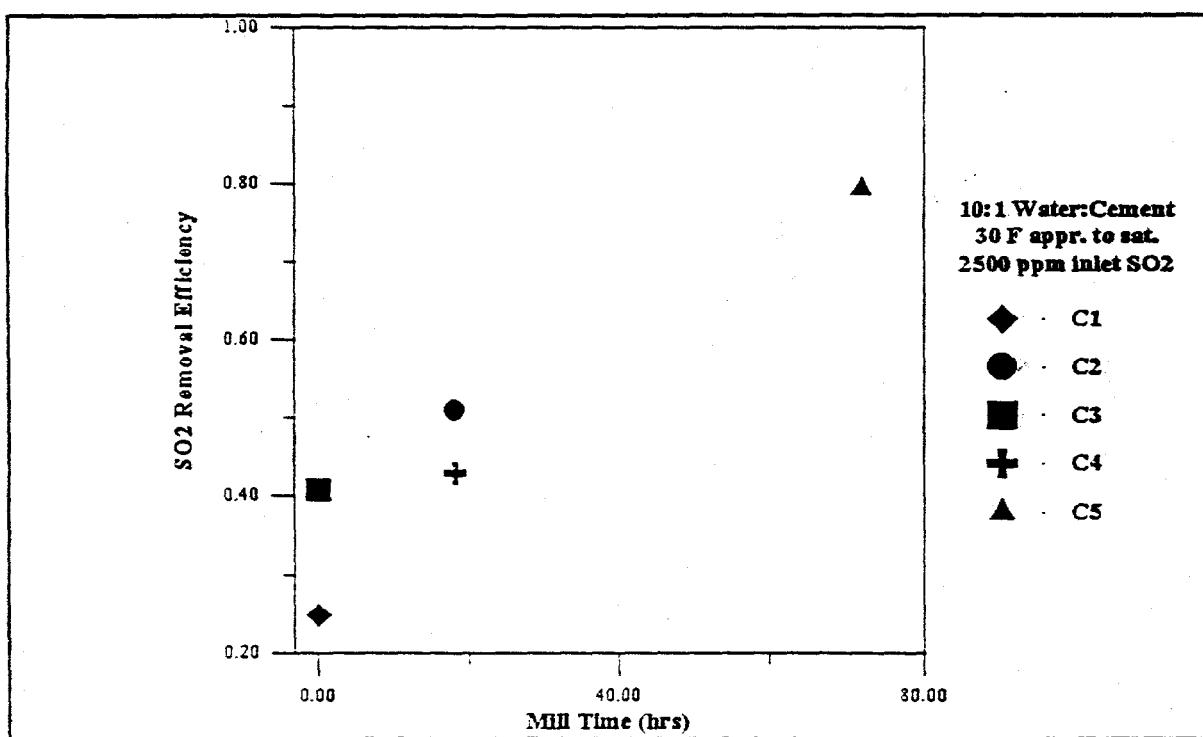


Figure 12: Effect of Milling Time on Removal Efficiency

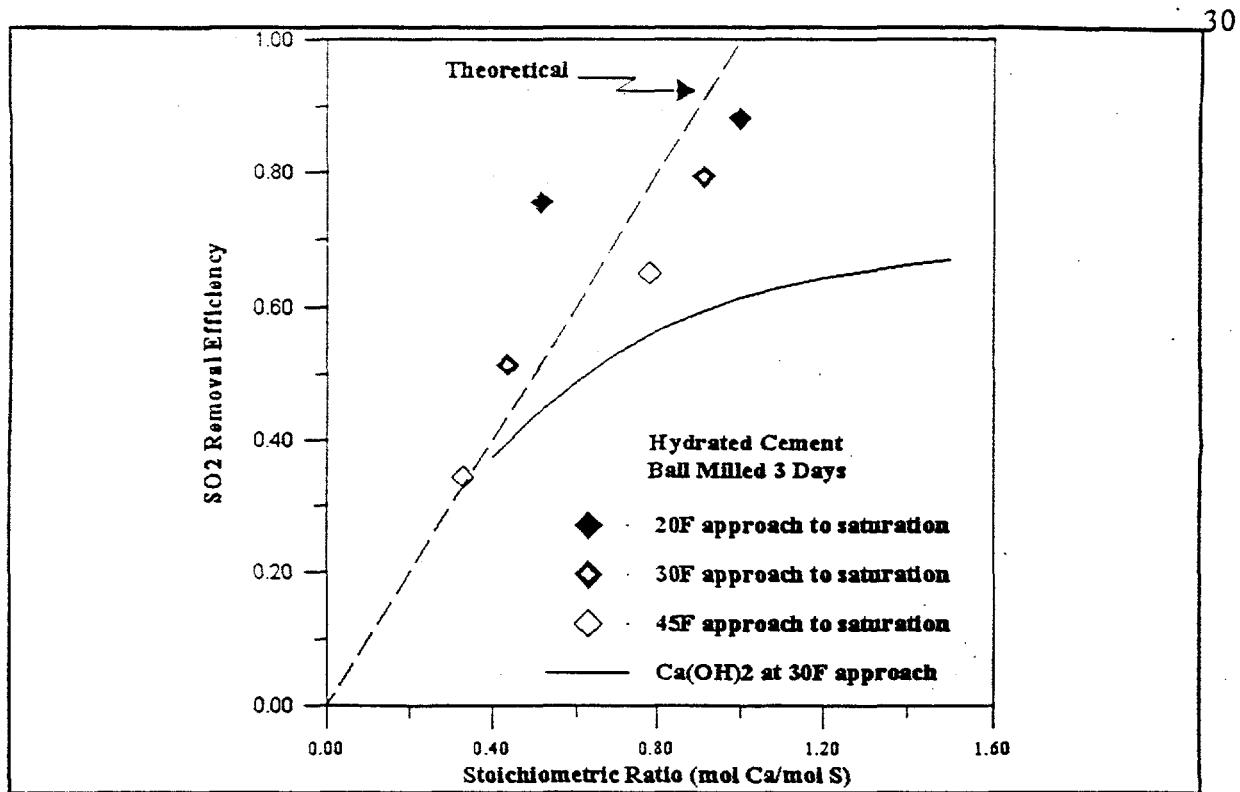


Figure 13: SO_2 Removal Efficiency of Sorbent C5

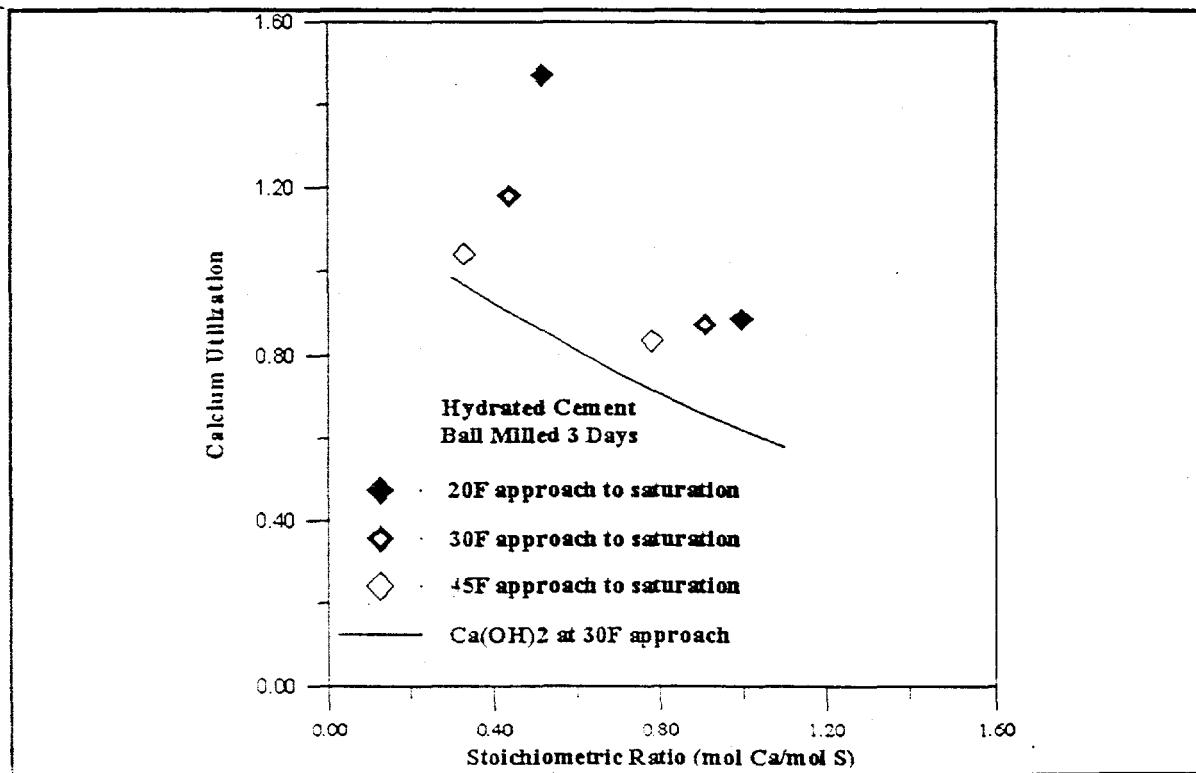


Figure 14: Calcium Utilization of Sorbent C5

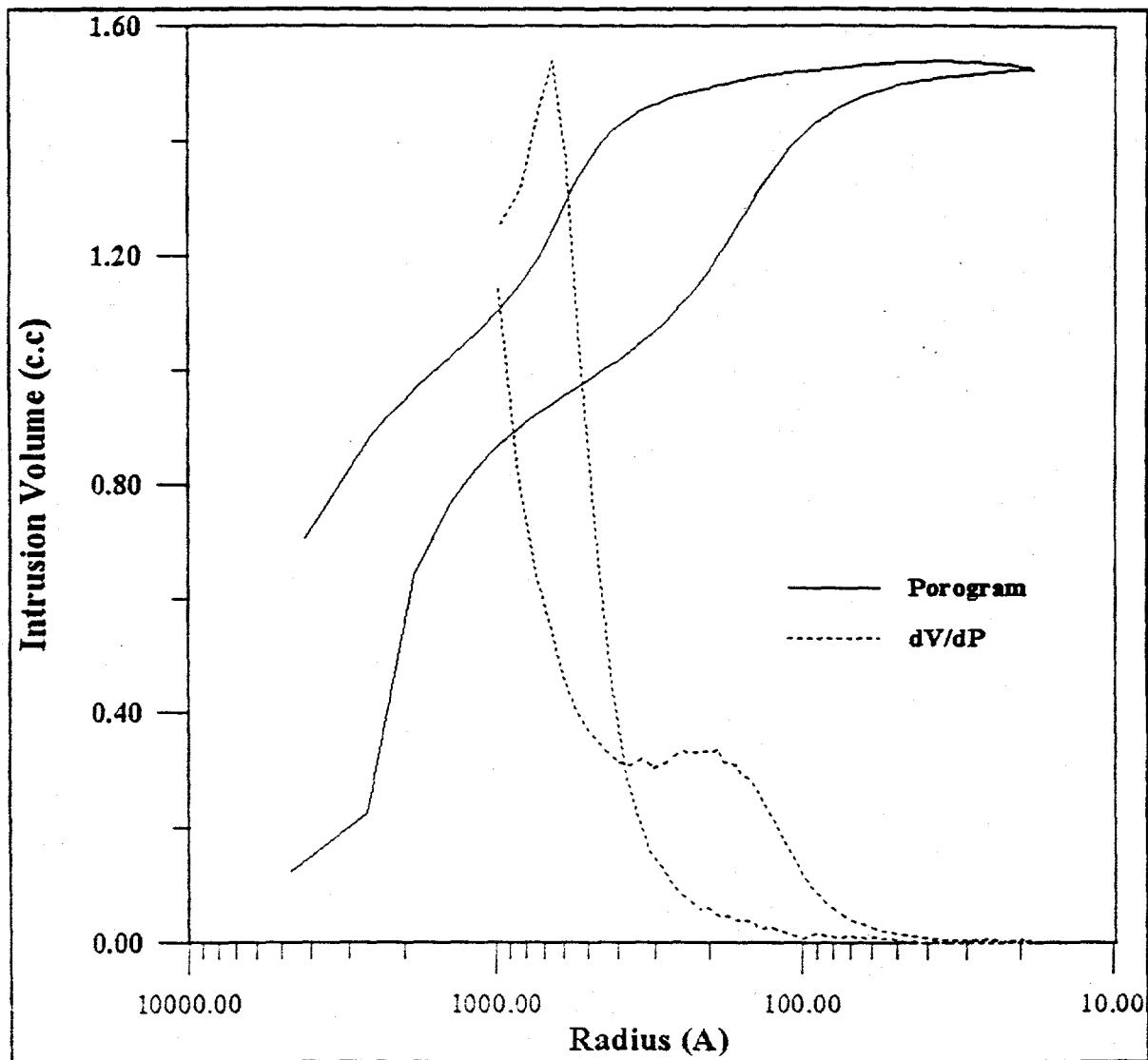


Figure 15: Porogram for Sorbent C5

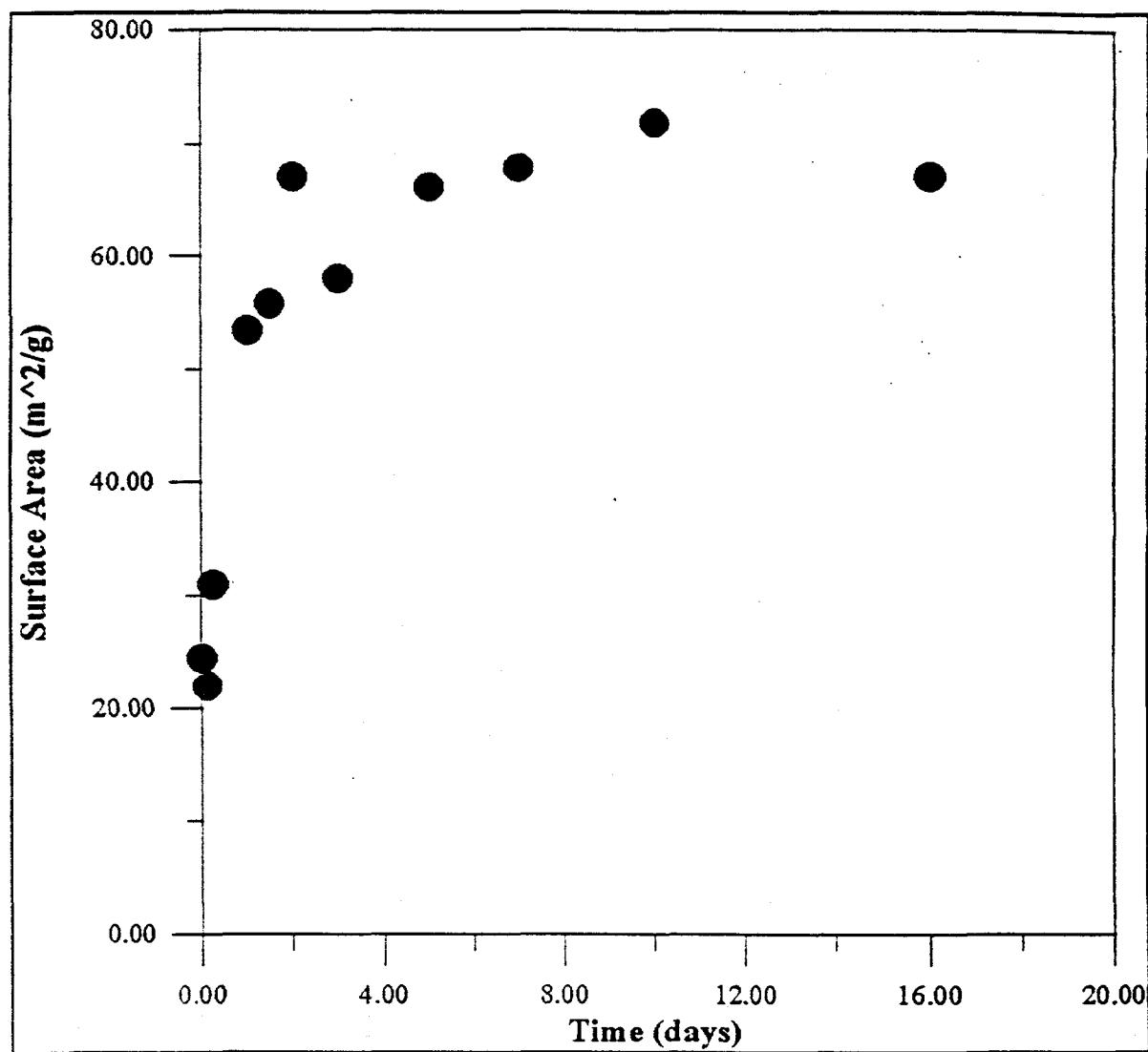


Figure 16: Surface Area Development for Bench Scale Tests at Room Temperature

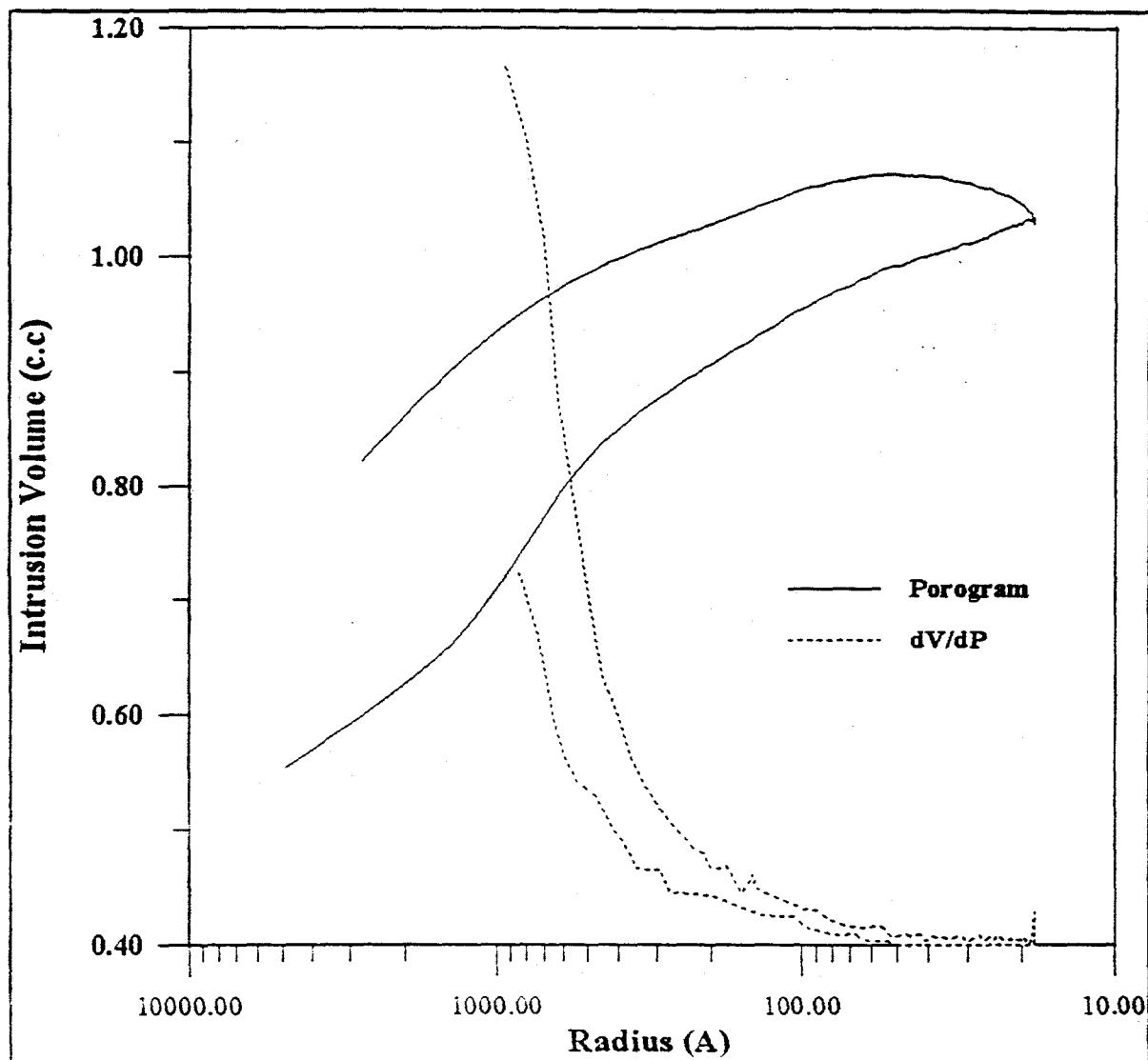


Figure 17: Porogram for Bench Scale Sample at Zero Days

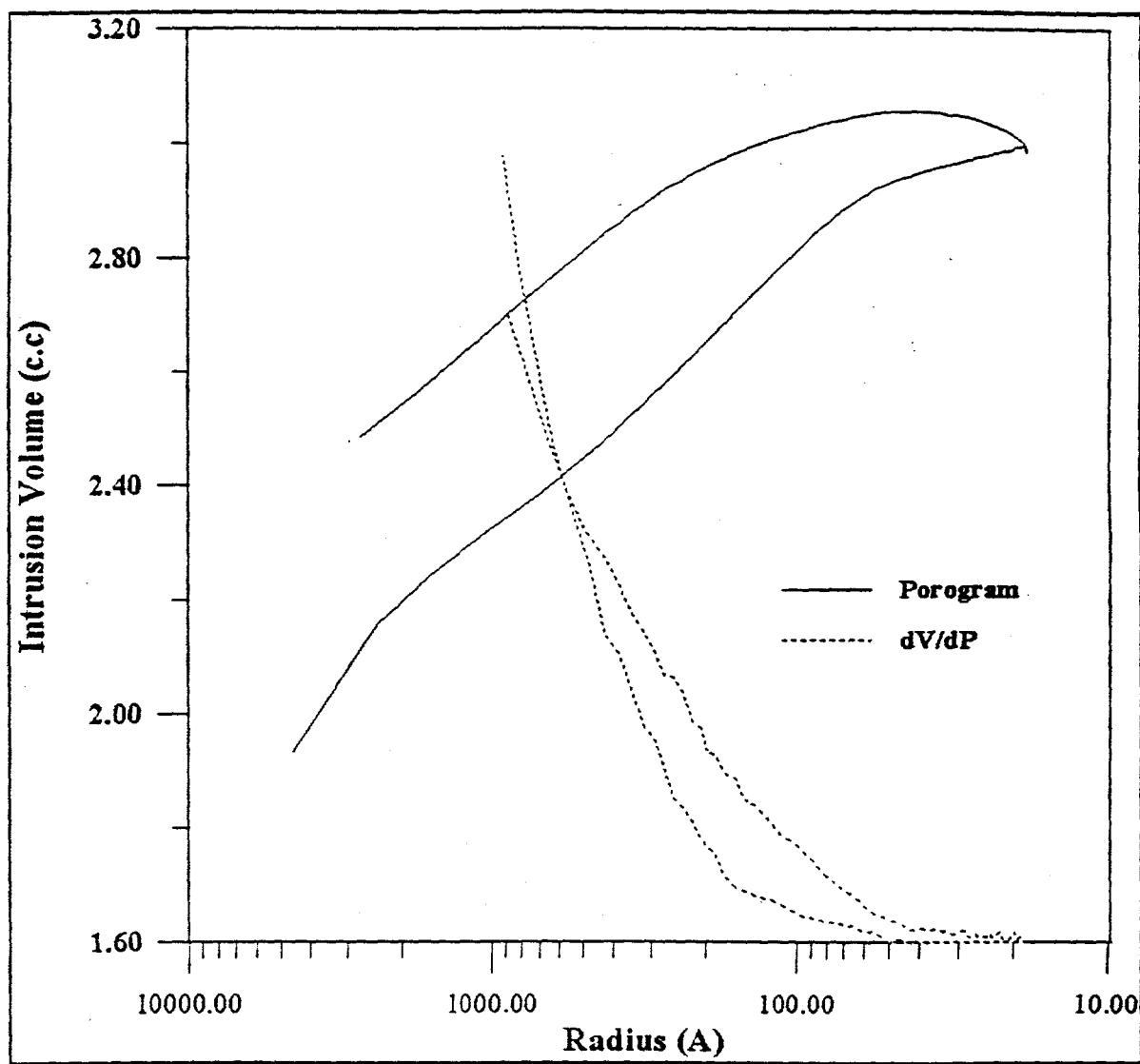


Figure 18: Porogram for Bench Scale Sample at 1.5 days

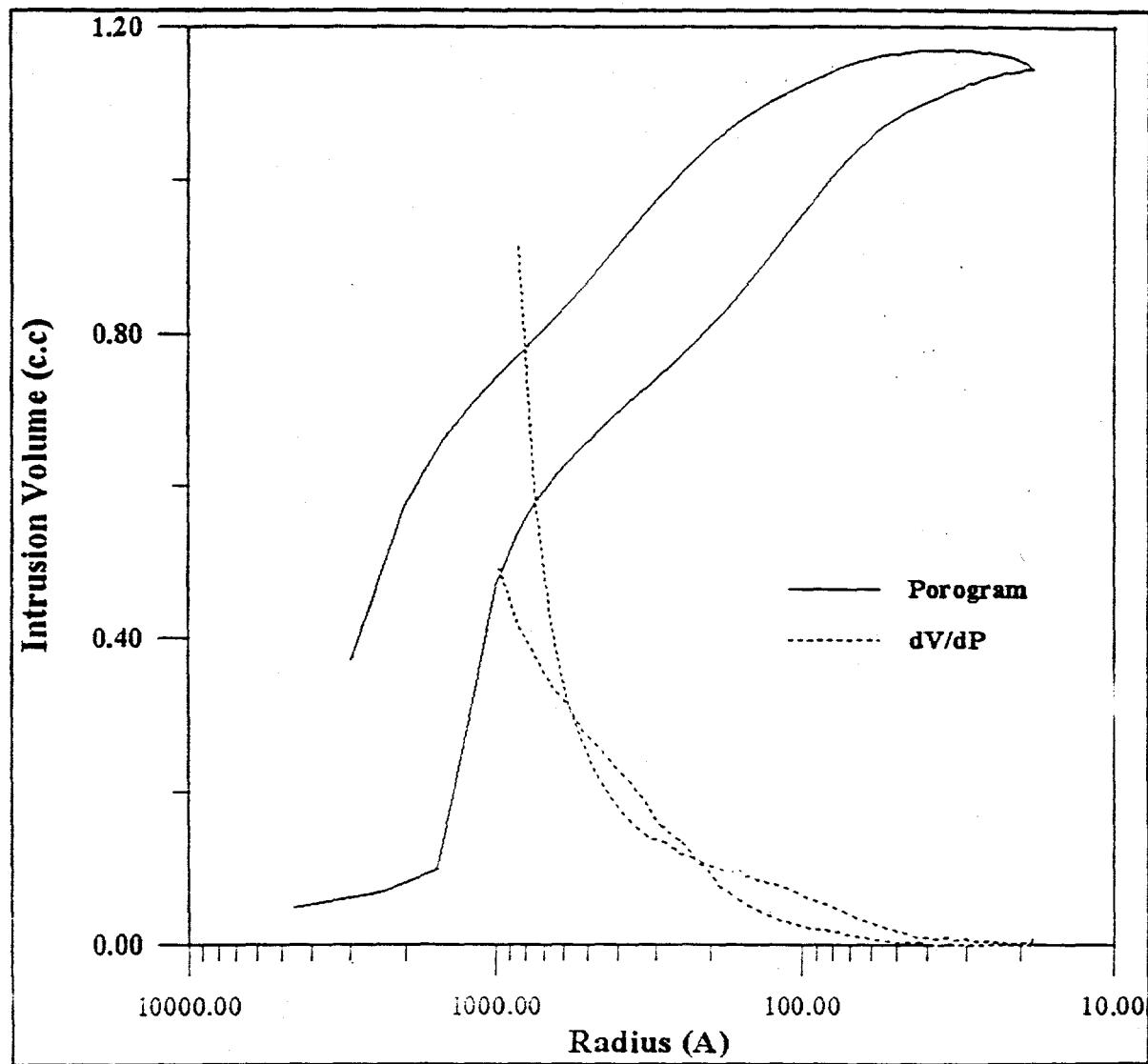


Figure 19: Porogram of Bench Scale Sample at 10 days

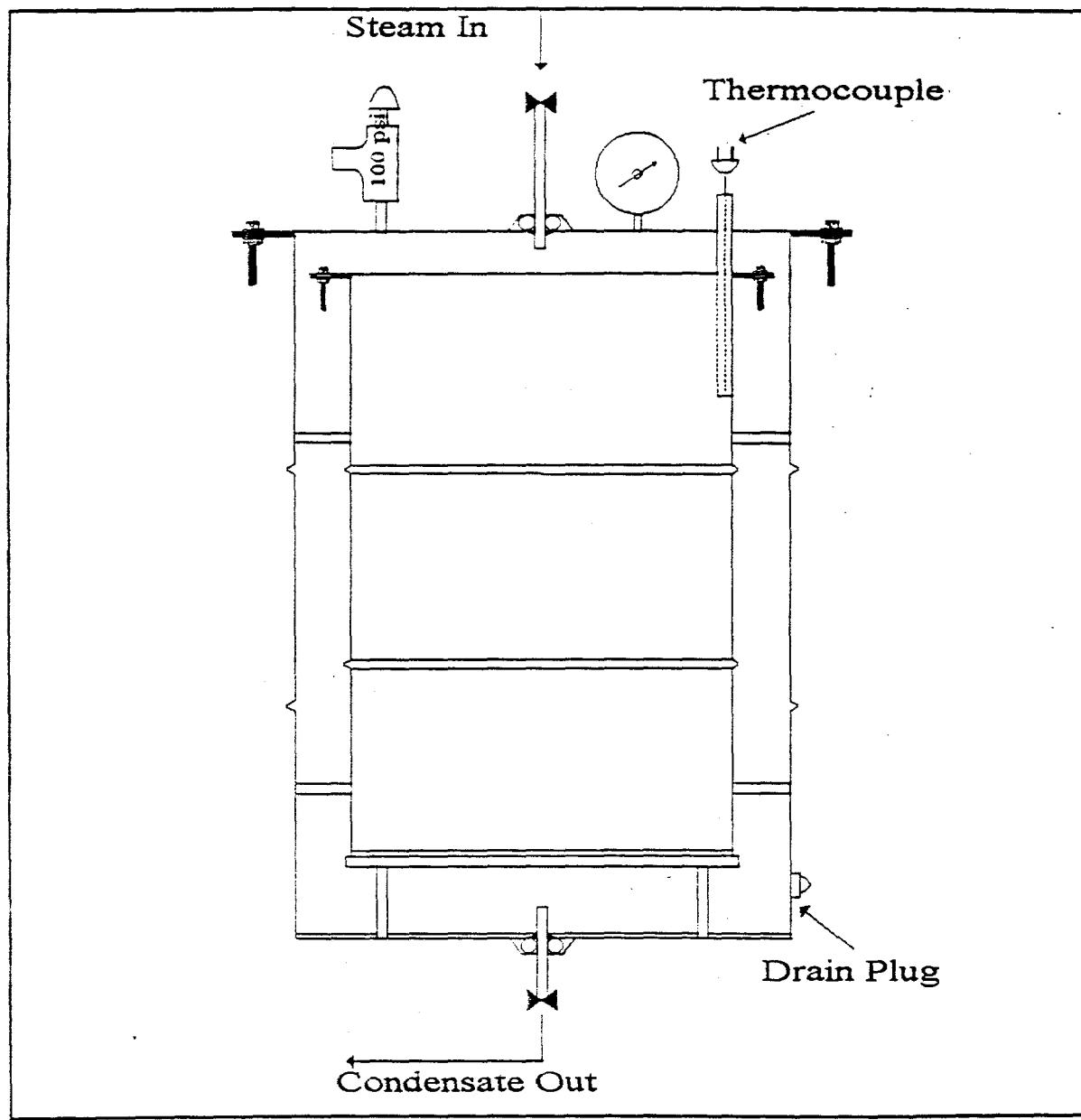


Figure 20: Steam Drum