



Preliminary investigation of the carbonizing properties of Montana coals
by Rudy Herzel

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering

Montana State University

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Abstract:

Presented in this thesis are the results of the first year of work in a program designed to evaluate the carbonizing properties of Montana coal to produce a metallurgical grade coke as an ultimate goal.

Described here is the performance of test equipment constructed for this project. This equipment includes a 21 K. V. A. electrical furnace, tar trap, water cooled condenser, Cottrell precipitator, scrubbing columns, and a gas sampler.

Discussion of the results of two carbonization tests at 840° C and 1000° C, conducted on a Montana coal from the Cokedale field, is included. The two tests indicated that unwashed coal ground to minus 1/4 inch size will not carbonize to coke of metallurgical grade quality.

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by

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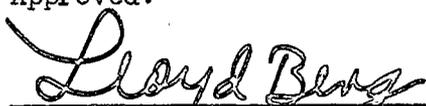
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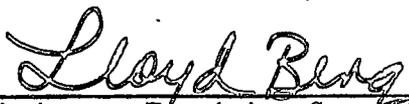
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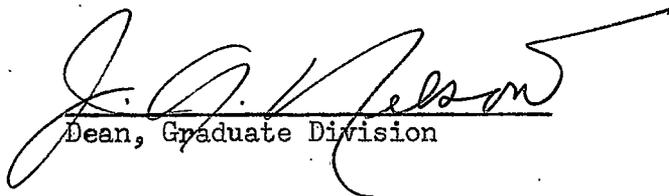
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ABSTRACT

Presented in this thesis are the results of the first year of work in a program designed to evaluate the carbonizing properties of Montana coal to produce a metallurgical grade coke as an ultimate goal.

Described here is the performance of test equipment constructed for this project. This equipment includes a 21 K. V. A. electrical furnace, tar trap, water cooled condenser, Cottrell precipitator, scrubbing columns, and a gas sampler.

Discussion of the results of two carbonization tests at 840° C and 1000° C, conducted on a Montana coal from the Cokedale field, is included.

The two tests indicated that unwashed coal ground to minus 1/4 inch size will not carbonize to coke of metallurgical grade quality.

INTRODUCTION

Montana, with vast and varied coal resources, today finds that its coal industry is being faced with a decreasing market for its products. The coal industry of Montana has problems which reflect the general nationwide trend of economic difficulties within this major industry. Increased railroad dieselization coupled with decreased use of coal for domestic heating are the prominent reasons for decreased coal consumption in Montana.

This problem certainly warrants profound thought and consideration by anyone interested in the economic welfare of Montana. An answer to this enigma would simply be a market utilizing the product of the coal mine. Of course, as stated, the demand for coal itself is diminishing; however, there exists today within the north-west area of the United States a demand for appreciable amounts of coke, metallurgical grade and otherwise. Smelting operations and phosphorous production utilize amounts of coke measured in tens of thousands of tons. This demand for coke, accented by the known value of coal by-products, indicated that studies and investigations of the carbonization properties of Montana coals be initiated.

On October 1, 1952 the Engineering Experiment Station of Montana State College sponsored a research program to investigate the carbonization properties of Montana coals. Although coke is not being produced commercially at the present time in Montana, an investigation of the literature indicated that coals with coking properties exist in quantity within the

state. Tryon and Young (2) reported that during the year 1897, 67,849 tons of bee-hive coke were produced from Montana coals for the smelters at Butte, Anaconda, and East Helena. The four localities that produced coke were Cokedale and Electric in Park County, Storrs in Gallatin County, and Belt in Cascade County. Coking operations ceased during the year 1911 and have never been resumed.

To investigate the carbonization properties of Montana coals, it was decided to utilize a modification of the Bureau of Mines-American Gas Association apparatus as reported by Reynolds and Holmes (1). This type of apparatus was chosen because the coke samples produced are of relatively large size (60-100 pounds) for a test process and yet the equipment is small enough to allow close control of conditions.

After selection of the manner of investigation, all efforts were directed toward design and construction of the necessary apparatus.

EQUIPMENT, MATERIALS, AND PROCEDURE

Figure 1 indicates schematically the components of carbonization study apparatus which were constructed at Montana State College. It was realized at the outset of this project that the apparatus was not the ultimate in equipment but rather a basic design which could be improved upon and modified as the project progressed. At the time of this writing the project is being extended and plans for necessary modifications are underway. It should be noted that most of the equipment was constructed and assembled by chemical engineering graduate students at Montana State College.

A cross sectional view of the electric furnace is shown in Figure 2. The furnace, rated at 21 K. V. A., is operated from a 3-phase 220 volt supply. Three resistor elements, each of 85 foot length, are arranged in a delta connection. These resistors, constructed of 1/2 inch by 26 gauge Nichrome V ribbon, were formed into a wave shaped to fit the nine 2.5 inch shelves formed by the split brick refractory. The resistors were supported in the shelves by the inherent strength of the Nichrome and maintained in position and shape at a temperature of 1000° C. Temperature control was accomplished by controlling the voltage with a three-phase ganged Variac. During the period necessary to heat the furnace to the desired temperature, the Variac was employed until the temperature reached 300° C at which time full load, by-passing the Variac, was impressed upon the resistors. Once the desired temperature was reached, Variac control of the voltage was

again used to hold the temperature within a small range.

Refractory fire brick of standard shapes were used as constituents of the retort pedestal and the refractory wall. The retort pedestal has a hollow cross section with an 18 inch square exterior dimension. This pedestal, 17.5 inches in height, is constructed of forty-two 9 inch by 4.5 inch by 2.5 inch standard fire bricks mortared in position. Considering the refractory walls from the base of the furnace, the first five layers of fire brick are of the circle shape, 36 inch inside diameter, 45 inch outside diameter, 2.5 inches thick, with 16 bricks per circle. Resting atop these first five layers is a layer of twenty-one insulating bricks, 9 inches by 4.5 inches by 2.5 inches arranged in a circular shape having an effective internal diameter of 31 inches. This 31 inch diameter layer forms the first resistor shelf. The next 18 layers of refractory brick are alternating layers of circle brick and split brick, 9 inches by 4.5 inches by 1.25 inches. The split bricks and the insulating bricks were arranged in a circle which resulted in an inside diameter of 31 inches. Again 21 bricks per circle were used. The top four layers of the refractory wall were constructed of circle brick. All bricks in the refractory wall were mortared in position. Four 5/8 inch steel bolts serve as electrical leads to the furnace interior.

The refractory walls are encased in a 14 gauge sheet metal cylinder 52 inches in diameter and 60 inches high. The furnace rests in a sheet metal dish with a 2 inch lip; the top of the furnace is covered with a similar dish made of 1/4 inch sheet metal which has a central 2 foot

square opening to allow access to the furnace. A portion of the top metal plate is exposed to the interior furnace temperature. The annular space between the refractory wall and metal wall was filled with vermiculite insulation. The bottom of the furnace interior was filled with vermiculite to a height of 15 inches supplying adequate insulation to the supporting concrete floor. Heat losses from the furnace proved so excessive that an upper temperature of only 850° C could be reached where 1000° C was designed. This problem was remedied by adding 4 inches of vermiculite insulation to the sides and top of the furnace. The added insulation, held in place by 1/4 inch hardware wire backed with heavy aluminum faced paper, reduced heat losses to a practical minimum.

The original furnace door, a sheet metal shell filled with glass wool, did not prove satisfactory and was replaced by a two piece door made of insulating fire brick.

Cylindrical retorts constructed of 14 gauge sheet metal with welded seams were used to contain the coal during the carbonization process. A 2 inch standard black iron pipe serves as an outlet pipe for gases formed within the coal charge. The retorts are equipped with two 1/4 inch pipes with ends placed in the center of the charge and one 1/4 inch pipe welded to the outside of the retort. The outside 1/4 inch pipe and one central pipe serve as thermocouple wells while the remaining 1/4 inch pipe, connected to a mercury filled manometer, forms a system capable of measuring internal pressures within the retort. Two sizes of retorts, one 18 inches in diameter by 26 inches high and 14 inches in diameter by 26 inches high,

were used in the carbonization tests. By placing the vertical outlet pipe two inches off-center and welding a semi-circular strap over the top and center of the retort, the retort will hang plumb when suspended from a chain hoist. It is imperative that the operation of loading the furnace be well planned because the retort is inserted after the furnace reaches the desired carbonization temperature.

The first component of the tar condensing and gas scrubbing train, the tar trap, is simply an air cooled cylindrical expansion chamber made of 6 inch standard pipe 15 inches high. The gas from the retort enters the tar trap through a 2 inch standard pipe and expands into the chamber with resultant tar and water separation. The gas leaves the tar trap through a 1.5 inch standard pipe and enters the water cooled condensing system.

The function of the water cooled condenser, shown in Figure 3 is to lower the temperature of the gas sufficiently to decrease the water content by an appreciable amount. The gas from the tar trap enters a 1.5 inch cross fitting where the stream is split into three portions which are further subdivided until the gas passes through six parallel streams. The inner condensing tubes are made of stainless steel, resistant to the corrosive action of H_2S in the presence of liquid water. Water condensed from the gas stream drains into three 1000 ml. Erlenmeyer flasks. The flasks have to be emptied only once during a carbonization operation.

The Cottrell precipitator, used in removing tar mists from the gas stream, is essentially the same type of apparatus as described by Reynolds

and Holmes (1), differing only in the manner of obtaining a source of direct current. The direct current is obtained by stepping a 110 volt AC source up to a maximum of 15,000 volts by using a neon size transformer. The AC current is then rectified to DC by employing a 5BG3A rectifying tube. The primary voltage is regulated from 0 to 110 volts by Variac control. Normal operation is to utilize a primary voltage of 75-80 volts which is decreased to approximately 40 volts to avoid arcing as the operation proceeds.

Figure 4 illustrates the 4 inch diameter acid and caustic columns which remove NH_3 and H_2S respectively from the gas stream. The gas leaving the Cottrell precipitator enters the bottom of the 8 1/2 foot high lead column and passes countercurrent to a recirculating stream of 4N sulfuric acid. The acid column is packed with alternating one foot layers of 1 inch carbon Rashig rings and broken Rashig rings. This procedure of alternating layers of different sized packing was used to minimize channeling of the scrubbing liquid. The caustic column is of similar dimensions as the lead column but is constructed of 4 inch standard black iron pipe. The caustic column was packed with carbon Rashig rings in the same manner as the lead column.

The gas sampler, shown in Figure 5, is operated at regular intervals during an operation to obtain a composite gas sample. Gas is sampled from the stream leaving the caustic scrubber and stored in a 12 gallon glass bottle. The bottle is filled with water before the start of an operation and as sampling proceeds the water is allowed to drain. There are two man-

ometers attached to the inlet gas line. The open end manometer permits measurement of pressure within the bottle and the other manometer is used to indicate gas flow into the system. After collection of a sample the gas is forced through a water cooled condenser and an insulated dry ice cooled condenser. This method of sampling permits the collection of gas samples with low concentrations of water and organic oil. Any portion of the gas sample not saved for analysis is returned to the waste gas line.

The quantity of gas flow is measured by an orifice meter which had been calibrated by using a Thomas flow meter. After the gas passes the orifice meter, it is discharged from the building and flared, ignition of the gas being accomplished by means of an automobile spark plug.

Once the equipment was installed and ready for operation the choice of coals for investigation was made. It was decided to evaluate the carbonization properties of the coals which had been used in commercial coke production.

Near Cokedale, Montana there exists a seam of coal which though not being mined commercially, is easily accessible. This seam lies in the coal field where coal for coking operations was once mined. With the aid of Dr. E. B. McCormick, lessee of the coal seam, several hundred pounds of coal were obtained for testing. Dr. McCormick, in an independent investigation, conducted a carbonization experiment on this coal in July 1953. Employed in this test was a gas heated 6 inch cylindrical retort approximately 12 inches high. The coal was sized by breaking it into random sizes with a hammer, the mean size being approximately 1/2 inch. The retort was heated

to a temperature range of 1600° F to 1900° F for a period of 3 hours. The coke produced in this test was of homogeneous structure, high lustre, and with apparent high inherent strength. The coke was analyzed for ash content, which proved to be 16.8 per cent. It should be stated that for the physical properties of the coke only visual observations are reported here.

Two carbonization operations were performed at Montana State College utilizing the Cokedale coal. The first operation was conducted in the temperature range 740-840° C and the second in a temperature range of 930-1000° C. These two operations served a dual purpose; the study of the coal's carbonization properties at two different temperatures and a test of the equipment.

Preparation of samples for both tests consisted of jaw crushing unwashed, run-of-mine coal to a minus 1/4 inch size. The coal used in the second test was more moist than that used in the first test as it had been more recently mined. In the first test an 18 inch diameter retort was charged by pouring 161.5 pounds of crushed sample through the vertical gas outlet pipe. This method of charging is not recommended as size segregation results within the retort.

When the furnace temperature reached 740° C the retort was inserted. A chain hoist suspended from a track above the furnace was used to load the retorts into the furnace. After the retort is placed on its pedestal the condensing and gas scrubbing train must be quickly connected to the retort by the double union connection shown in Figure 2. Gas evolution from the coal starts practically as soon as the retort is lowered into the furnace.

This situation necessitates that all fittings be aligned and in good working order prior to the start of a run.

After a period of 11 hours the furnace reached a maximum temperature of 844° C. This temperature was maintained for an additional three hours, at which time the electrical supply was shut off and the furnace allowed to cool. The end of the test was determined by noting when gas evolution ceased as indicated by the manometer attached to the orifice meter. All temperatures measured during this first test were taken at the outside wall of the retort.

When the furnace temperature declined to 600° C the door to the furnace was opened and the retort withdrawn. The retort was then removed from the building on an iron cart and air cooled. After cooling, the retort top was removed by using an acetylene cutting torch. Weighing, water quenching and reweighing of the empty retort completed the operation.

The second test was conducted at a higher temperature range ($930-1000^{\circ}$ C), utilizing a 14 inch retort containing 107 pounds of crushed coal. In this test the coal was charged into the retort before the retort top was welded in place. The retort was placed in the furnace when the temperature reached 930° C. The temperature increased to 1000° C at the end of 9.5 hours and was maintained at this level until total test time reached 11.5 hours. Temperatures during the second test were measured at the center of the retort as well as at the retort wall. The end of the operation was indicated when the temperature at the center of the retort reached 960° C. After the electrical power was shut off the procedure followed was the same as that for the first test.

RESULTS

Since the manner in which the test equipment functioned was one of the prime objectives of the first two test runs, consideration will now be given to the problems that incurred during operation.

All iron components of the furnace directly exposed to the interior furnace temperature were noted to deteriorate severely. Refractory and Nichrome components of the furnace showed no evidence of decomposition from the extreme temperature. The vermiculite insulation expanded under high temperature treatment but did not decompose in any manner. The glass wool insulation however, melted to hard nodules with entire loss of insulating value.

Though the iron retorts scaled severely, they did not fail structurally, however, the use of any one retort for more than three tests is not anticipated. It was noted that pin-hole sized leaks in the welded seams of the retort presented no problem, as they were sealed shut in a matter of minutes after the retort was charged into the furnace. During the carbonization process internal retort pressures were noted to rise from an average of 1 inch of Hg to 8 inches of Hg when coke and carbonization products forming in the vertical outlet pipe restricted gas flow. Pounding on the outlet pipe with a hammer freed the gas passage allowing unrestricted gas flow. Though subjected to high temperatures, the two unions in the gas line above the retort were easily removed at the end of a test because they had been well lubricated with graphite grease.

The tar trap functioned well with no undue attention during either test. For the test conducted at 740-840° C, water as well as tar condensed in the tar trap. For the test conducted at a higher temperature little water condensed in this trap.

Both water and tar condensed from the gas stream in the water cooled condenser, however the amounts of tar precipitated from the gas stream were small as compared to the amount of water formed. Although gas volume was greatest through the two central tubes of the water cooled condenser, the temperature of the exit gas was practically the same as the temperature of the cooling water.

The degree of performance of the Cottrell precipitator was difficult to evaluate as the secondary voltage was not measured. After completion of each test the electrical precipitator was dismantled and inspected. Though the walls of the precipitator were coated with tar after each test, its performance was questionable as large amounts of tar and sludge-like material formed to such an extent in the two scrubbing columns so as to prevent recirculation of the caustic and acid solutions. The caustic and acid columns were by-passed in the second test. Since large amounts of tar were present in the two solutions from the first run they were not analyzed for NH_3 or H_2S .

The remaining components of the apparatus, the gas sampler, the orifice meter, and waste gas flare, operated to satisfaction.

After two coking operations residual tar was evident throughout the apparatus and connecting pipes. An attempt to remove this tar with a high-

ly chlorinated hydrocarbon solvent, Tromex, proved only partially successful. The application of live steam might be the preferred tar removal method.

Iron-constantan thermocouples, employed in the first test, proved unsatisfactory as they broke at the hot junction after several hours exposure to the furnace temperature. Chromel-alumel thermocouples were used during the second test and no failure occurred.

The coke produced during the first two tests differed little in physical characteristics, indicating that coking at a temperature higher than 850° C has little effect on the quality of the coke. As compared to the coke prepared from the same coal by Dr. McCormick, the coke from the first two tests was of significantly poorer quality. The product was softer with more fractures and the grain was coarser with larger cells.

Considering the product obtained, with respect to the retort walls, a lack of homogeneity was apparent. The external edges were hard and the product was progressively softer as the center of the retort was approached. In both tests the coke charge contained a 5 inch core of a soft uncoked product. The product of the second test also had variation with respect to vertical position within the retort. An outside layer approximately 4 inches thick yielded a superior grade coke. This layer contained coke of significant lustre, fingery structure, fine grain, small cells, and thin celled walls. This better product did not appear to be of quite as high quality as that produced in the independent test previously mentioned. It was evident that the ultimate product had not yet been obtained.

Analysis of by-products was not determined at this time since the quality of coke produced was the primary factor and improvements on the gas scrubbing analysis should be made to insure significant and accurate results.

SUMMARY AND RECOMMENDATIONS

Unwashed coal from the Cokedale area when ground to a minus 1/4 inch size, will not form metallurgical grade coke when carbonized at 840° C or 1000° C. This is no positive indication that coke of metallurgical quality cannot be produced, for there are several variables to be applied to this operation. Wilson and Wells (3) report factors that can influence coking properties as follows: fineness of the charged coal, charge density, oven size and dimensions, coking temperature and rate of heating. It should also be noted that addition of a non-coking coal to a blend has often yielded an improved coke.

A sample of Cokedale coal for testing underwent washing with only sizes above 3/4 inch chunks being saved for a third test conducted at Montana State College. The temperature of this third run was approximately 1000° C and the resulting coke had the most desirable physical properties of any yet produced. The report of this investigation, conducted by Gordon Smith who is presently continuing the coal carbonization studies, though beyond the scope of this thesis, is presented as an illustration of the effect of variables on a coal's coking properties. Further investigation of the indicated coking variables, coal blending, and testing of coal from many of Montana's varied sources, are steps recommended by this writer.

There are improvements that should be made on the condensing and scrubbing equipment. All metal components of the furnace directly exposed to interior furnace temperature should be replaced with refractory material. The

The output voltage of the electric precipitator should be a measurable quantity allowing proper evaluation of its efficiency. Tar condensing in the scrubbers should be prevented. Scrubbing the gas with an organic solvent prior to its entrance into the lead column has been suggested. A final recommendation is to have steam available for cleaning the interior of the apparatus of tar after each test operation. At the time of this writing some of the recommendations stated above were being incorporated into the test apparatus.

It is felt by the author that the first year's work on this project served as merely the inauguration of a study which if expanded in scope and duration, will prove of great benefit to the state of Montana.

ACKNOWLEDGMENTS

The author thanks the Engineering Experiment Station of Montana State College for sponsoring this project. The author acknowledges aid and suggestions supplied by the entire staff of the Chemical Engineering Department of Montana State College. Special thanks are extended to Gordon Smith whose efforts and aid in construction and operation of equipment, promoted completion of the initial phase of this work.

LITERATURE CITED

- (1) Reynolds, D. A. and C. R. Holmes, Bureau of Mines Technical Paper 685, Procedure and Apparatus for Determining Carbonizing Properties of American Coals by the Bureau of Mines - American Gas Association Method, United States Government Printing Office, Washington, 1946.
- (2) Tryon, F. G. and W. H. Young, Bureau of Mines Technical Paper 529, Analysis of Montana Coals, United States Government Printing Office, Washington, 1932.
- (3) Wilson, P. J. and J. H. Wells, Coal, Coke and Coal Chemicals, McGraw-Hill, New York, 1950.

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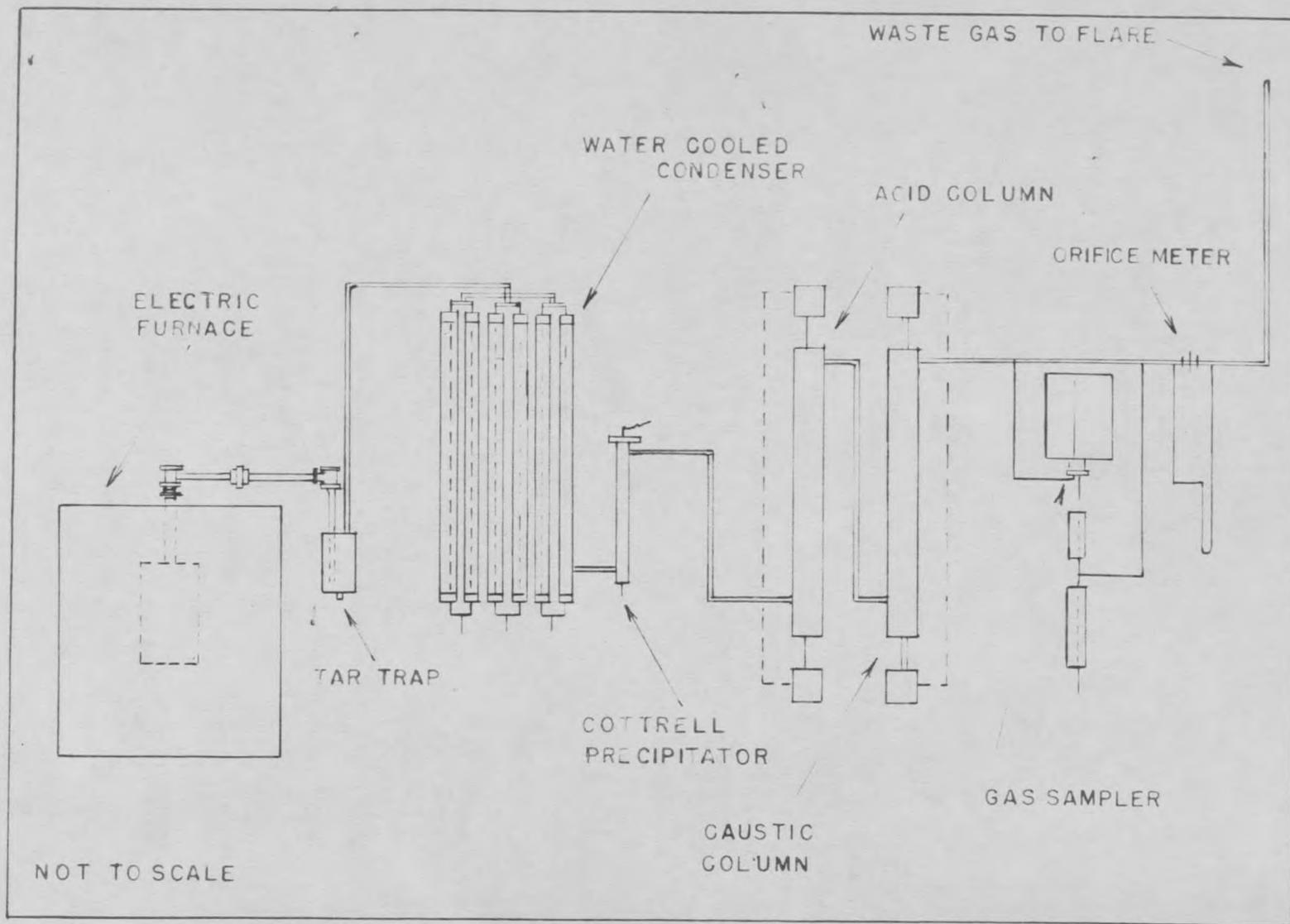


Figure 1. Schematic Diagram of Equipment

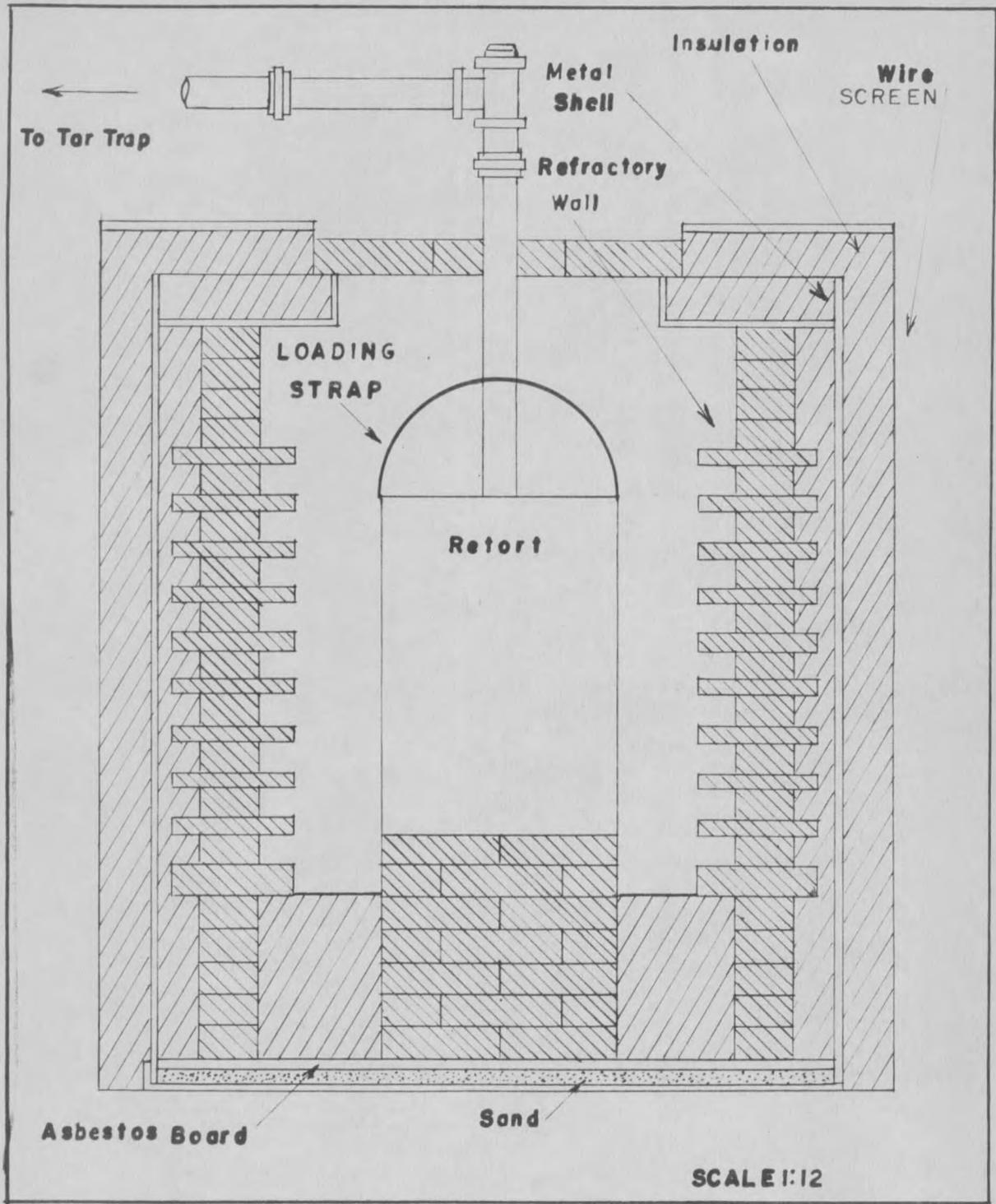


Figure 2. Electric Furnace and Coal Retort

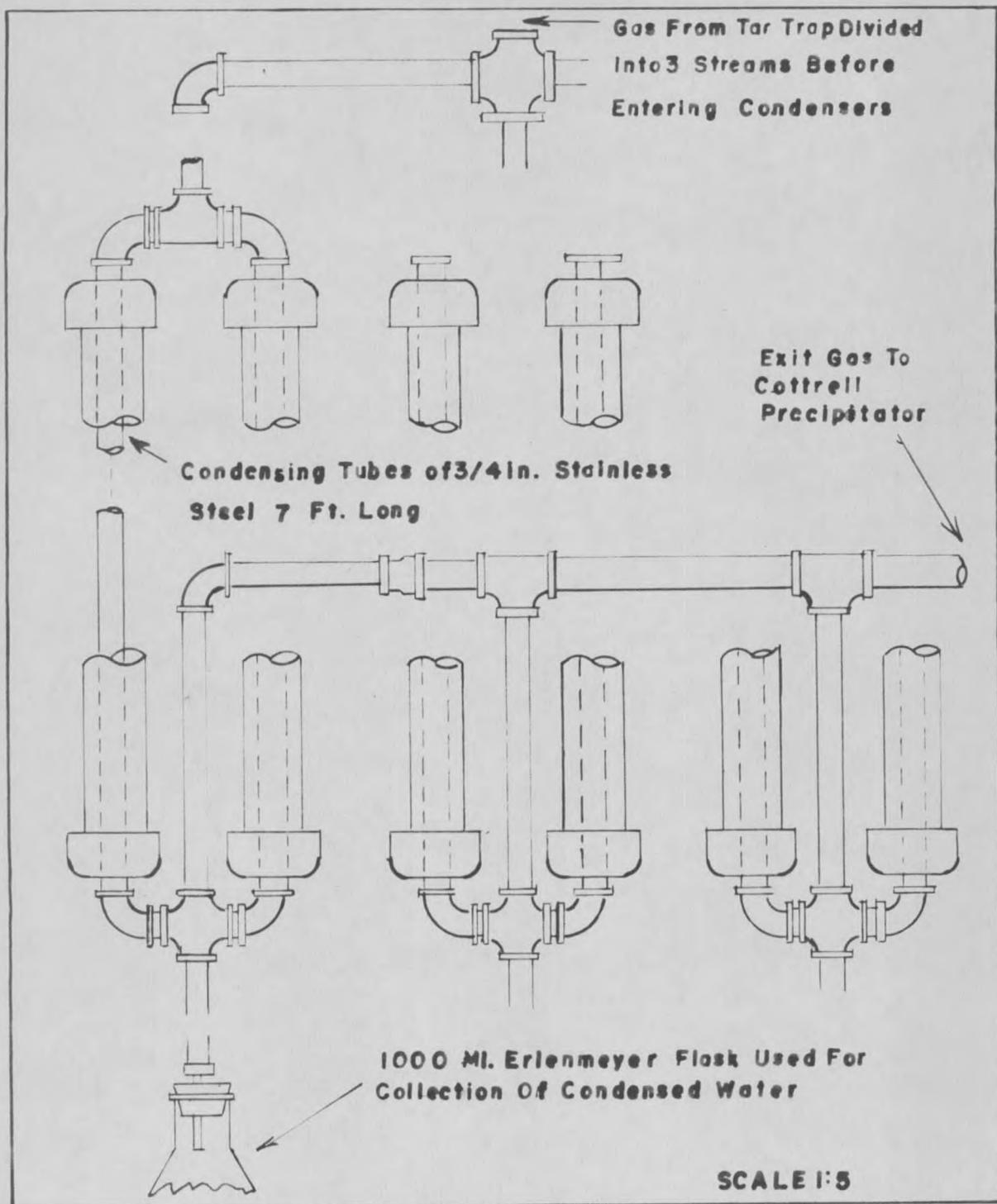


Figure 3. Water Cooled Condenser

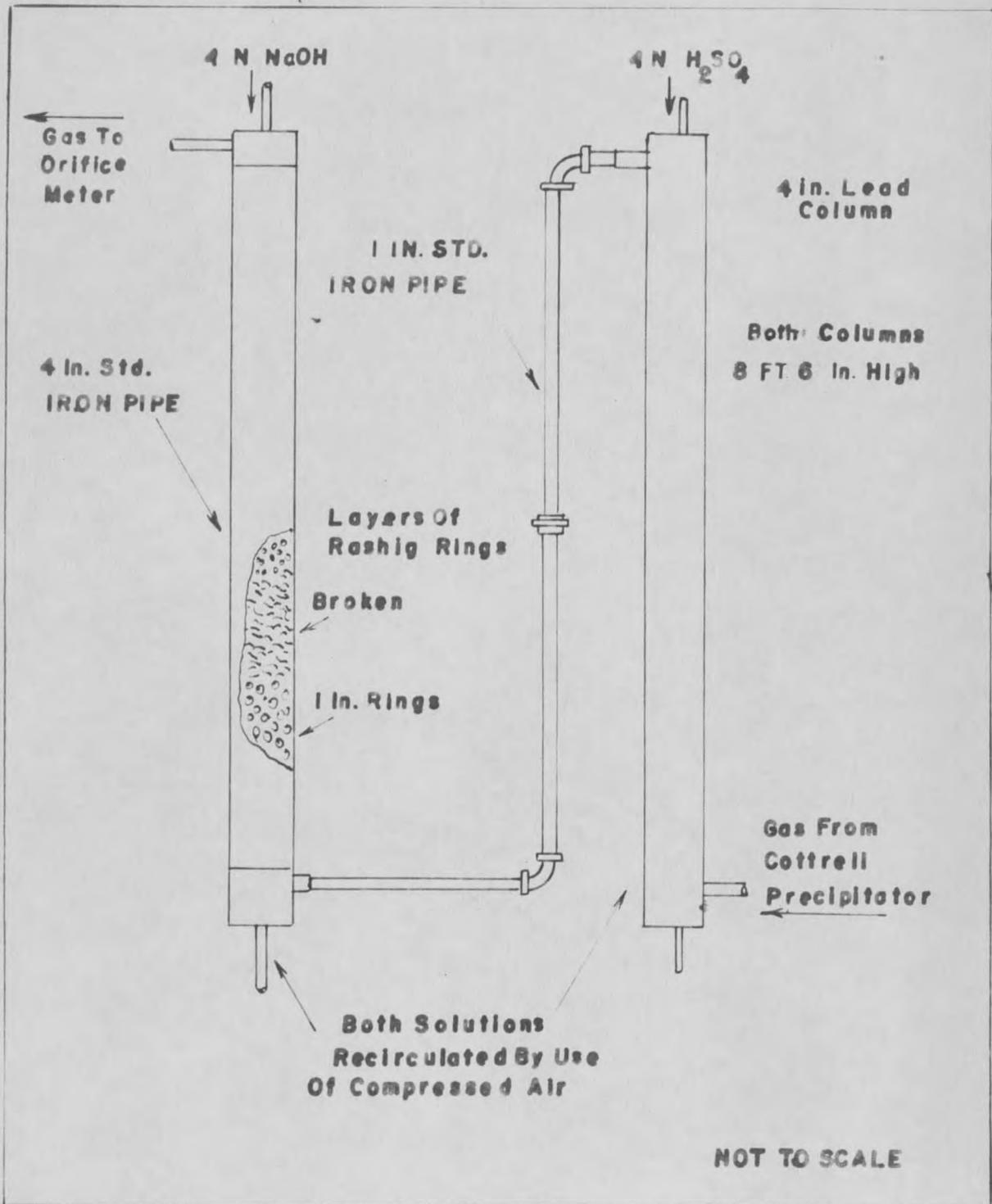


Figure 4. Scrubbing Columns

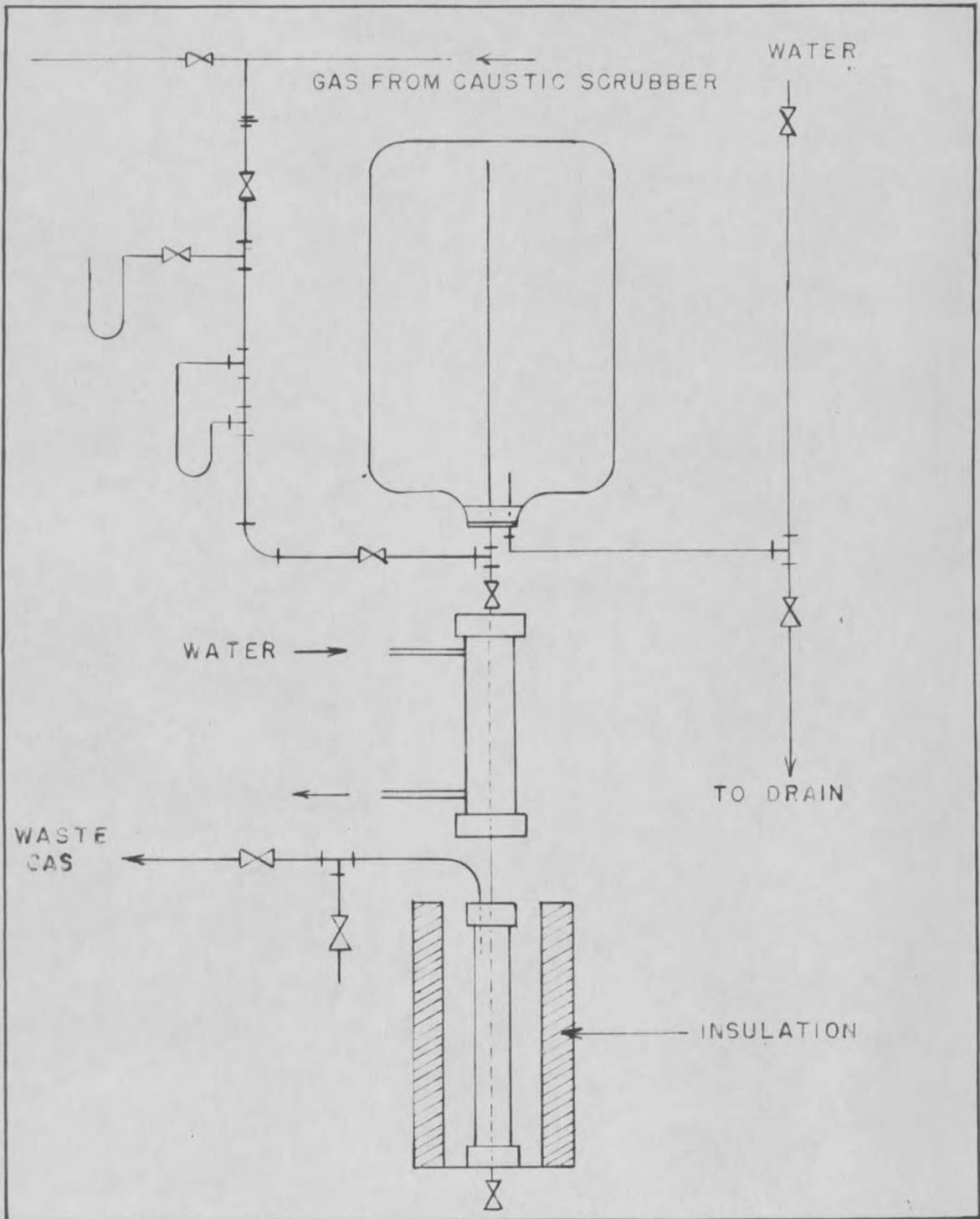


Figure 5. Gas Sampler

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