

and were preheated to reactor temperature by the time they emerged. A high excess of preheated steam (about 10 cu. ft. per hour) entered through a distribution ring at the top, flowed downward through straightening vanes, and contacted the narrow stream of carbon particles at the end of the carbon feed-tube. Carbon and steam at the same temperature, in the range of 1,800 to 2,500° F., continued in parallel downflow toward the reactor exit. Partly gasified particles were collected in a glass receiver, while the steam was condensed and some of the particles were recovered from it. This constituted a single "pass" of 40 to 60 minutes duration. The residual carbon was weighed and again passed through the reactor at the same rate. Each run consisted of 4 to 5 passes. The residence time of the particles under gasification conditions was determined for each run.

The initial reaction rates, that is, the rates prevailing during the first infinitesimal increment of time at zero conversion, were determined graphically. This falling-particle technique was found to be a practical method for kinetic rate studies. Its advantages are that (1) particles are uniformly exposed to radiation from the reactor walls, (2) change in the gas composition can be minimized and retarding effects reduced or eliminated, and (3) differential timing technique can be used for rate determination. The accuracy of the method, of course, depends on means for residence-time measurement.

Results of the preliminary runs showed that the initial reaction rate of graphite was much higher than that of petroleum coke, but the rates approached each other as the contact time was increased by repeated recycling of the solid. It was significant that petroleum coke continued to react at a nearly uniform rate with respect to time, but the initially high reaction rate of graphite decreased rapidly.

The data showed further that plots based on the Arrhenius equation gave straight lines for both graphite and petroleum coke, indicating that surface reaction rates controlled throughout the temperature range of 1,800° to 2,500° F.

Effect of Oxygen

Another phase of this research problem, the effect of oxygen on rates of steam-carbon reaction, was investigated. Extrapolation of the carbon conversions to zero oxygen concentration and comparison of the initial rate thus obtained with those determined in the absence of oxygen were used to indicate the inhibiting effect of oxygen.

Before this program, several modifications were made in the original apparatus to improve the accuracy of kinetic data. These included (1) installation of a new alloy-steel conical section with polished interior at the bottom of the reactor, (2) substitution of an improved glass residue receiver, (3) elimination of steam leaks, and (4) insulation of the furnace shell. These changes made the reactor more nearly isothermal and improved both the reproducibility and accuracy of results.

Twenty runs, each consisting of 4 or 5 passes, were made with petroleum coke at temperatures ranging from 1,800 to 2,500° F., each under essentially isothermal conditions and with oxygen concentrations ranging from nil to 1 percent in the gas phase. It is notable that while the curves of cumulative conversion as a function of residence time at 1,800° F. have a slight curvature, the initial rate decreasing toward a constant rate, at 2,400° F. nearly straight lines were obtained. Further experiments now in progress will decide whether this has any significance. Calculations of initial reaction rates showed a rapid acceleration, owing to temperature above 2,200° F. This was true at all oxygen concentrations, although the rate acceleration by the temperature level is particularly rapid at higher oxygen concentrations and, in fact, appears to increase with the oxygen-input ratio.

Evidence on the inhibiting effect of oxygen is not yet conclusive. Further evaluation may also reveal whether the surface reaction rate controls at all temperatures or whether diffusion takes over control at some temperature above 2,200° F. as has been claimed by some investigators for certain fuel bed conditions.

Effects of Particle Size and Adsorption Surface Areas

Investigation of another phase of the same problem, the effects of particle sizes and adsorption surface areas on the rates of steam-carbon reaction, was recently begun with the same apparatus. However, owing to serious defects in its electric heating system, the present equipment may not remain serviceable much longer, so the program may have to be completed in a greatly modified kinetics-research apparatus now under construction. Designed to withstand temperatures to 3,500° F. and pressures of 5 to 45 p.s.i.a., the new reactor will be more isothermal throughout its length. Proposed work in this reactor will include the investigation of coals of various rank and grade, and carbonaceous residues obtained in pilot-plant gasification.

Suspension of Coal in Steam

The objective of this investigation is to develop a method for feeding a coal-water slurry at a constant rate into a heated coil that will vaporize the water and pulverize the coal. Such a device may prove suitable for feeding coal and steam into a large-scale gasifier.

Apparatus now in use is shown in figure 33 and a flowsheet in figure 34. The feeder is batch loaded. Air from the bottom agitates the coal and keeps it in suspension. The coal slurry flows through a preheater coil and enters the flashing coil close to its boiling point. Water in the slurry vaporizes, and the steam formed carries the coal rapidly downward through the coil, with considerable impact between the particles and the tube wall as well as between the particles themselves, causing pulverization. The stream leaves the coil and enters a baffle chamber, where the largest particles are removed. Progressively smaller sizes are removed in the subsequent cyclone and bag filter. A condenser recovers the steam, permitting calculation of material balances.

The conditions that are being varied are (1) pressure and temperature, (2) feed size, (3) slurry concentration, (4) fuel type, and (5) coil design. The most significant result to date pertains to the effect of coil length. The particle break-up in a 60-foot coil is many times that in a 20-foot coil, as seen from figure 35, but there are not yet enough data to correlate quantitatively the size reduction with coil length.

Thus far, the immediate objective has been to develop a bench-scale apparatus for the investigation; it is now nearing completion.

Together with this development, a study has been made of methods for analyzing the product delivered and comparing its size and size-consist with that of the feed coal. Several methods have been tried - the microscope, sedimentation, and permeability. The microscope is slow and tedious, although it is generally accepted as the most accurate. The permeability method is useful for quick determination of the mean particle diameter in a given sample but gives no information on the size consist. Between these two methods lies the usefulness of the sedimentation method. A recent test showed that the results obtained with sedimentation apparatus deviated about 25 percent from that obtained with the microscope. The sedimentation method is rapid enough for ordinary particle sizes but too slow for subsieve sizes and gives a size consist from which an average particle size can be calculated.

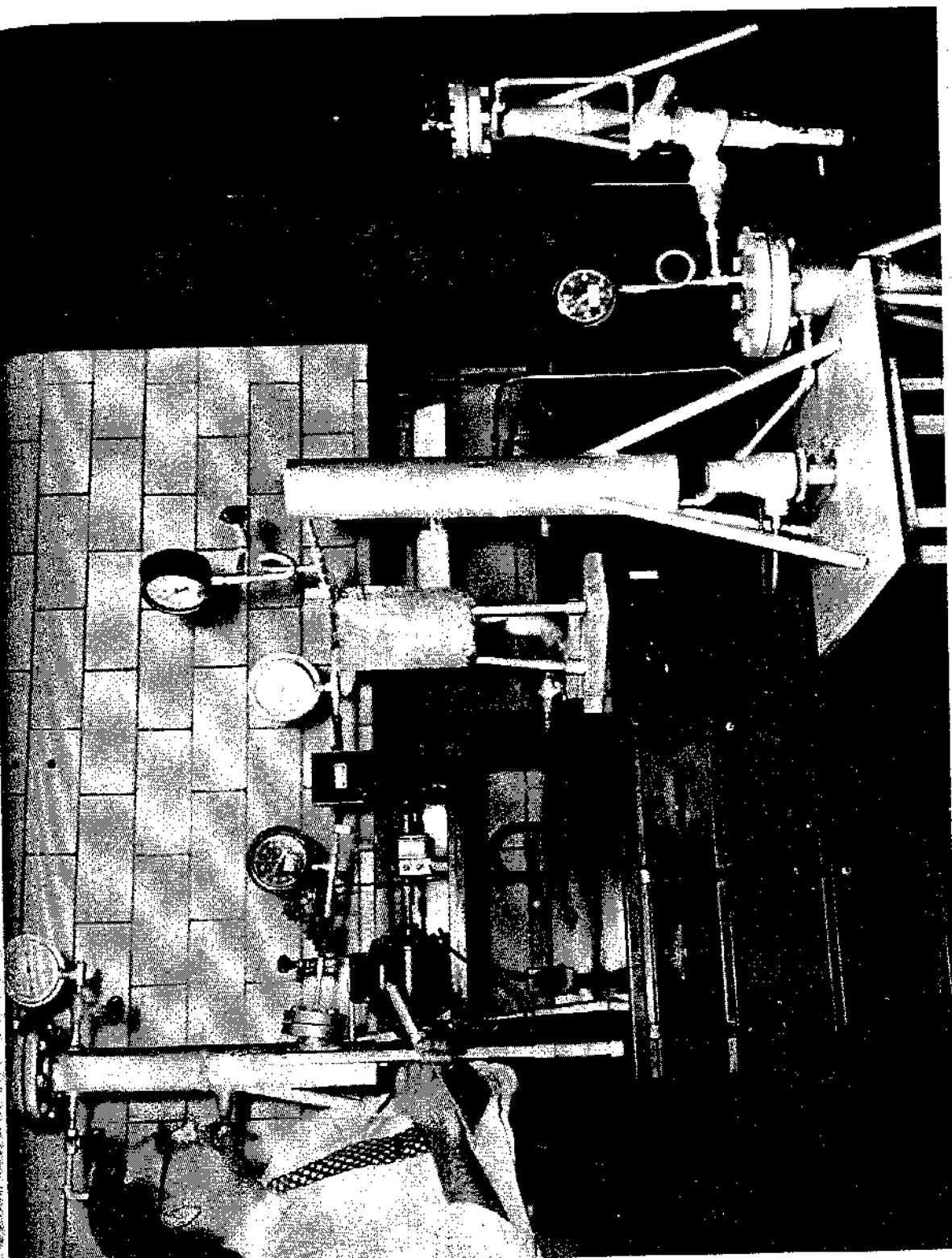


Figure 33. - Apparatus for preparing micronized coal by flashing water-coal slurries in heat coils.

KEY:

- PI - PRESSURE INDICATOR
- TI - TEMPERATURE INDICATOR
(THERMOCOUPLE)
- FI - FLOW INDICATOR
- P_dCV - DIFFERENTIAL PRESSURE
REGULATOR

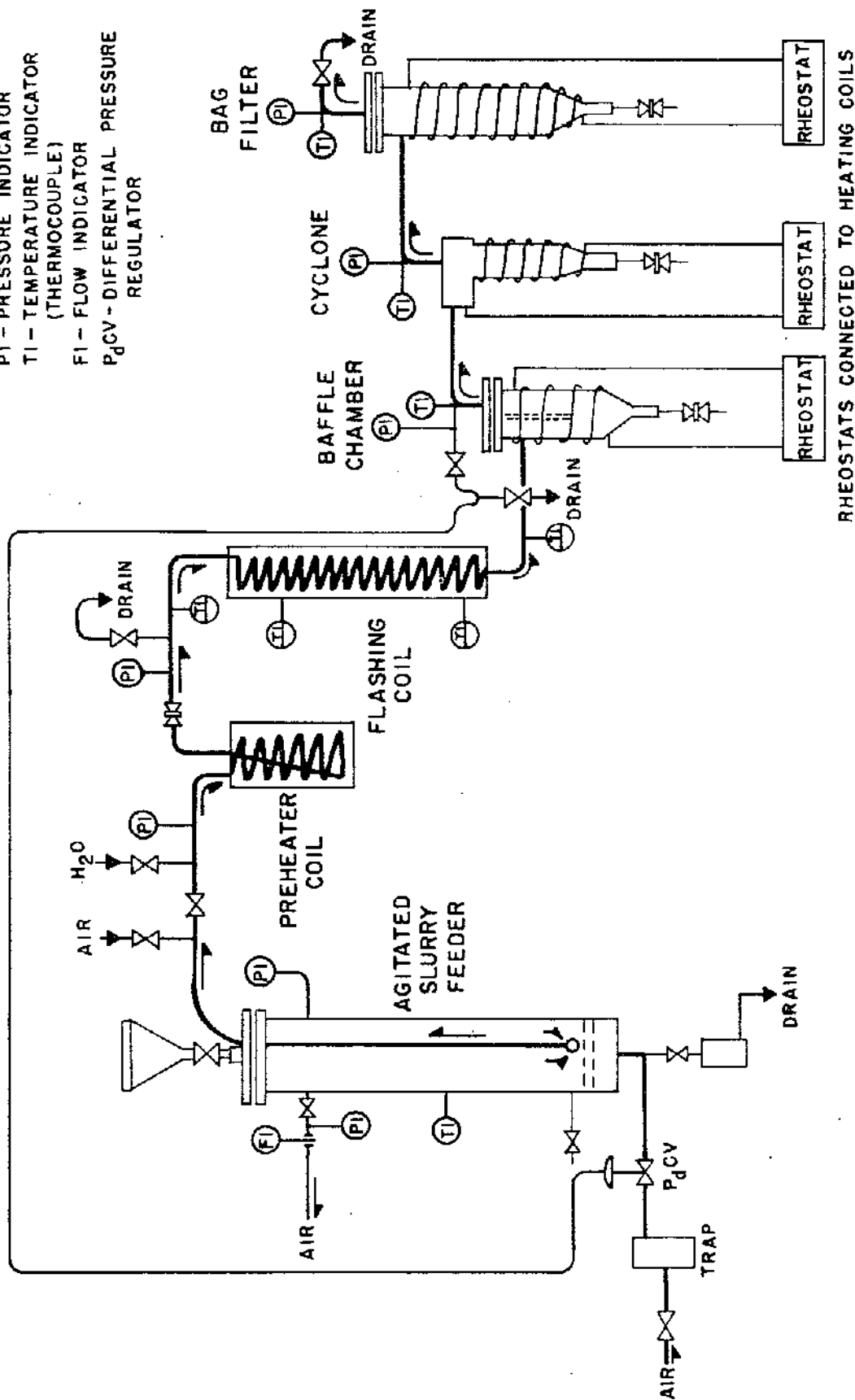


Figure 34. - Improved bench-scale metallic apparatus for flashing coal-water slurries.

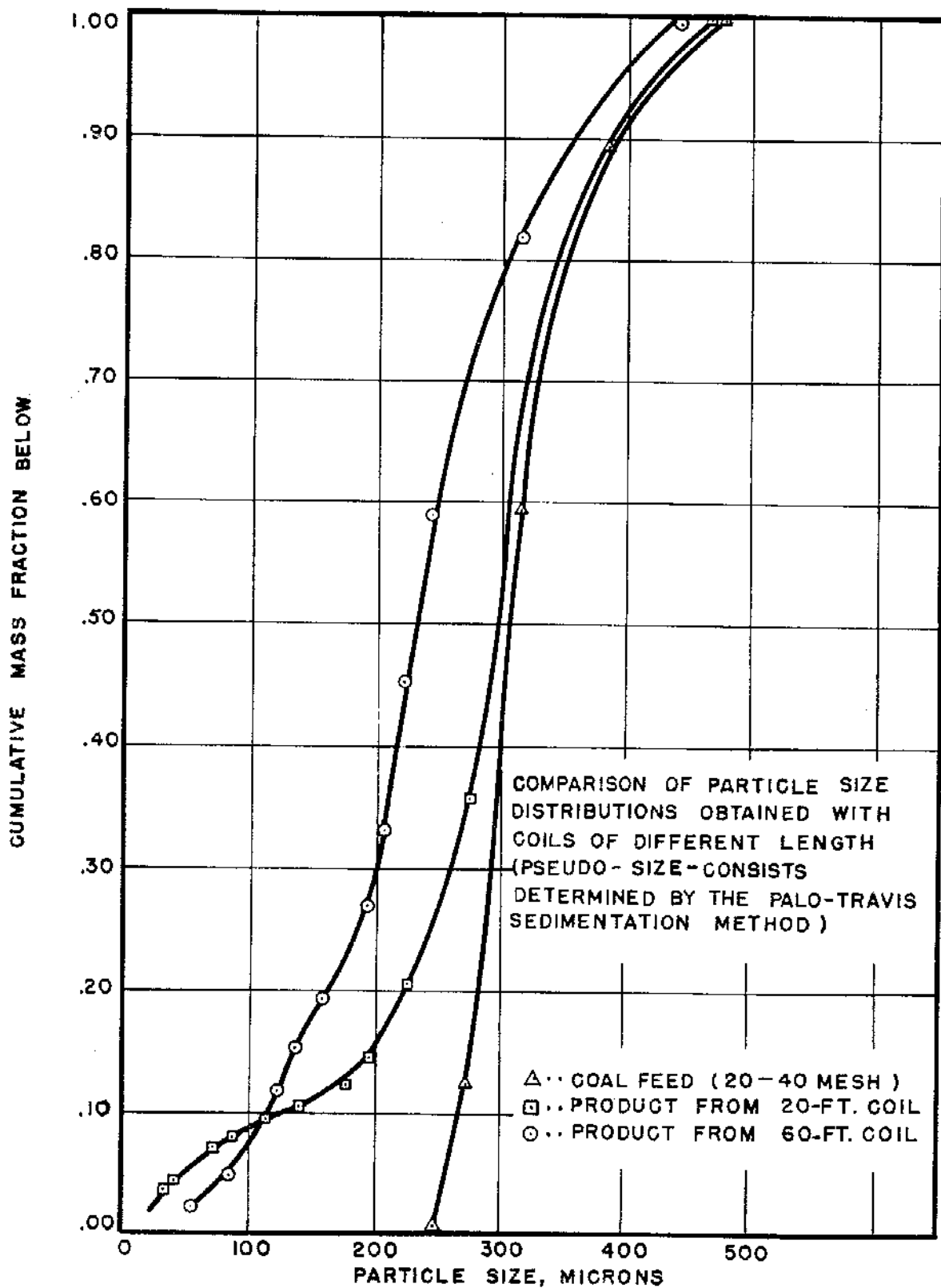


Figure 35. - Comparison of particle-size distribution obtained with coils of different length.

Sorption and Recovery of Oxygen From Air

The objective of this investigation is to develop a process for producing tonnage oxygen at a lower cost than the conventional rectification of liquefied air.

Most of the methods proposed in the past involve physical or chemical sorption of oxygen. Desorption may be done by increasing the temperature with simultaneous reduction of pressure, stripping by steam, or combinations of these. None of these methods has reached the stage of commercial operation and few have ever been examined in the light of recent developments in the field of sorption.

A literature survey on oxygen-carrying compounds now in progress includes: (1) "Salcomine" and derivatives, (2) "versene" and derivatives, (3) indigo chelates, (4) histidine chelates, (5) acetylacetone chelates, (6) "porphine"-type natural oxygen carriers, and (7) inorganic oxygen carriers. The most promising among these appear to be, at this time, the salcomine and versene type of metal chelates.

One variety of cobalt salcomine, a coordinate covalent compound of a cobalt atom with ethylenediamine and salicylaldehyde, was tested for oxygen production by the United States Navy during the last world war but was abandoned because of the wartime shortage of cobalt and limited life of the absorbent. It appears that poor heat-transfer conditions to and from the granular absorbent, packed tightly into horizontal holders, were responsible for the short life of the compound. In an effort to modify the properties of salcomine, certain alkoxy and fluorine derivatives were prepared by Calvin, Geissman and coworkers, who found that these had a greatly increased life and higher speed at lower pressures than the original salcomine tested by the Navy.

Another promising type of oxygen carrier is the versene family of metal chelates. Being combinations of ethylenediamine tetra-acetic acid with iron, cobalt, manganese, etc., these chelates are widely used in agriculture, as ion-exchange mediums, and detergents. Although cobaltous and ferrous chelates of versene are known to be powerful absorbents of oxygen, none of them has ever been investigated for its oxygen-sorption capacity. The literature survey revealed further that an iron chelate of indigo exhibited strong activity for oxygen absorption, and so did a cobalt chelate of histidine. Also worthy of consideration are inorganic chemicals, such as barium oxide, a mixture of alkaline lead and manganese oxides called "Plumboxan", etc. A thermodynamic evaluation of several of these reactions will be made.

A number of samples were procured from manufacturers and other sources. For their screening, that is, elimination of compounds of low activity for either sorption or desorption, a bench-scale glass apparatus was constructed that permits testing a few grams of sample. Results of these tests are correlated with polarographic tests of the same samples, which similarly require only a few grams of material. Shifts in the half-wave potential in the polarogram indicate affinity for oxygen. Results of this work, now in progress, should be available soon.

A metallic bench-scale apparatus design for pressures up to 100 p.s.i.g. was constructed for a more exhaustive investigation of compounds indicated in these preliminary tests as promising oxygen carriers. In this apparatus (see figs. 36 and 37) all sorbents are tested under cycling conditions. The apparatus also can be used to determine weight-percent saturation and equilibrium oxygen partial pressures at various temperatures and to estimate the energy requirements for air compression. Thus, it may be decided whether the cost of compression would make use

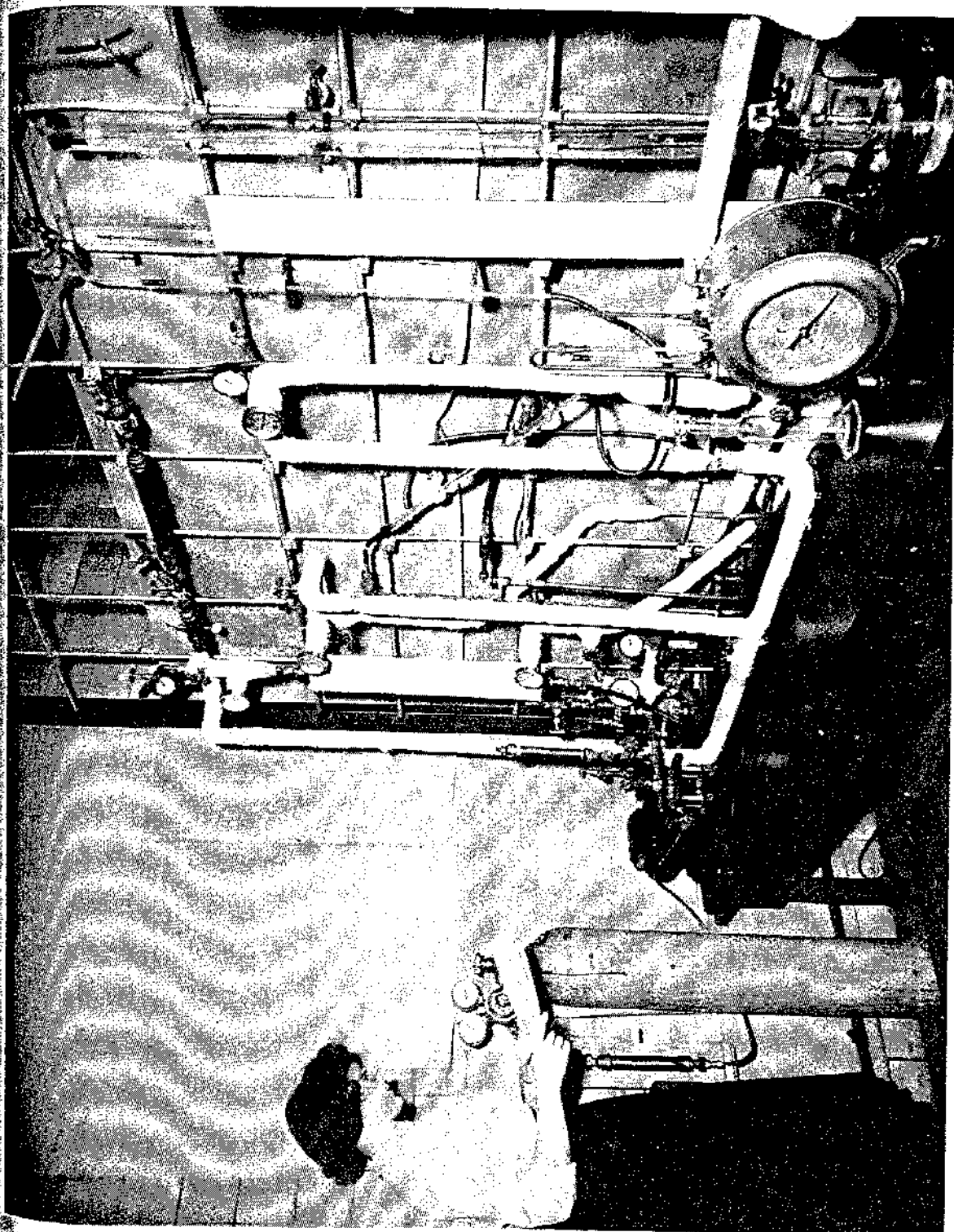


Figure 36. - Apparatus for oxygen absorption and desorption studies in fundamental investigation of metal chelates as oxygen carriers.

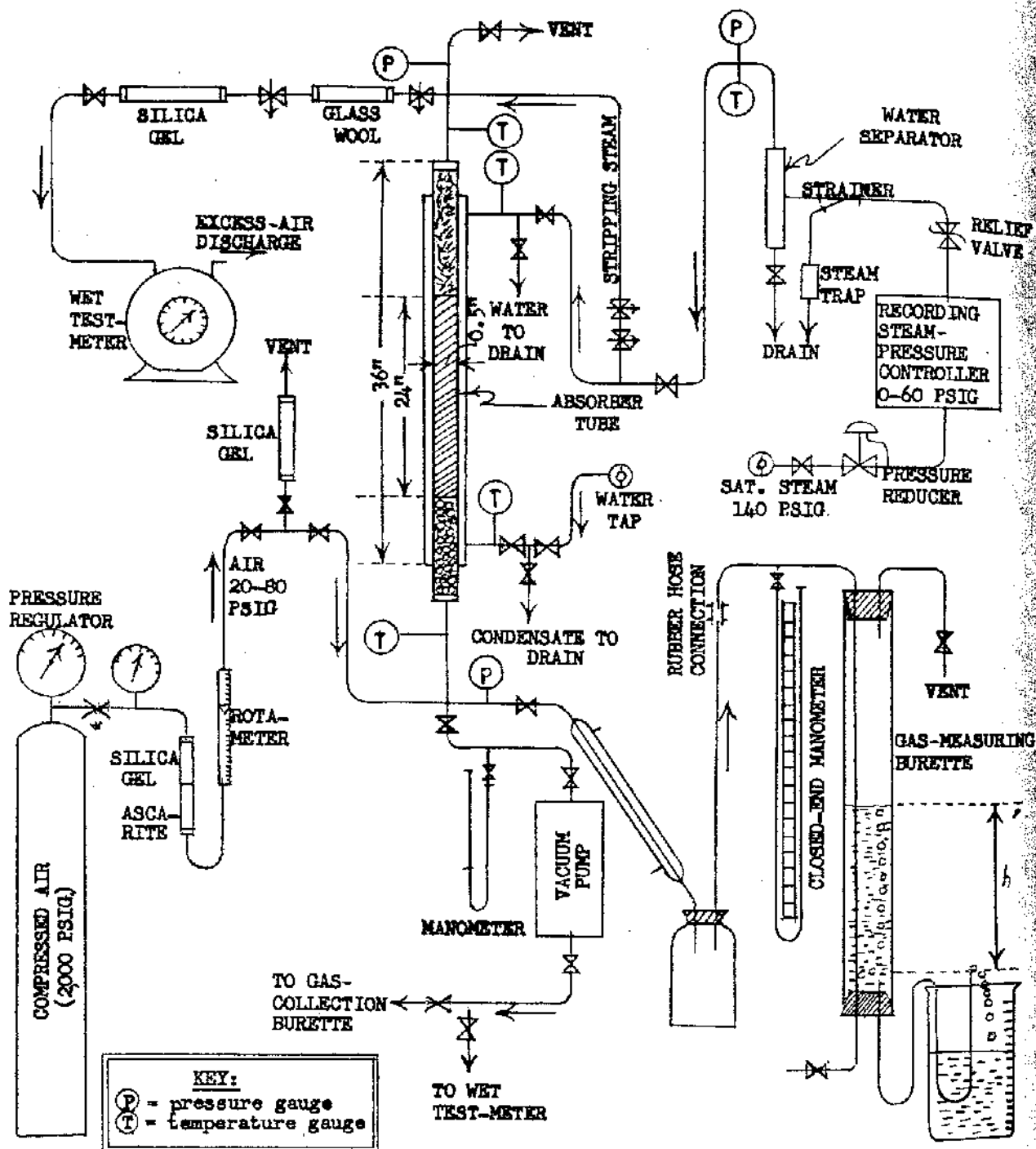


Figure 37. • Flowsheet of apparatus for oxygen absorption and desorption studies.

of the absorbent economical in comparison with the production of oxygen by rectification of liquefied air.

The test apparatus resembles that used by Geissman at the University of California in that cooling water is put through the jacket of a 0.5-inch-diameter packed reactor tube during absorption and heating steam during desorption. Also, air at pressures up to 80 p.s.i.g. is passed through the absorber column during the absorption. However, the desorption period of the cycle is substantially modified in that it may be carried out by (a) merely raising the temperature of the sorbent bed, (b) application of suction up to 20 inches Hg (c) use of stripping steam at desired temperatures of 300° F. or higher, or (d) application of stripping steam as well as suction. Suction and stripping steam may be applied in addition to heating the absorber to various temperatures. The granular sorbent is placed above small glass beads in the vertical reactor and is covered by glass wool. If removal of heat during absorption is found to be inadequate, the reactor will be replaced by other types of absorbers provided with more efficient cooling and heating systems and better temperature control.

Engineering Studies

High-Ratio Centrifugal Compressor

The design, fabrication and testing of the high-ratio, low-flow centrifugal compressor described in the 1953 annual report has continued during the past year. In preliminary tests, the aerodynamic characteristics of the impellers have proved satisfactory. Owing to the high speed (50,000 r.p.m.), bearing and gear design presented many problems; however, it appears that satisfactory solutions have been found and the final assembly and testing are now under way.

The large cost of this development has been underwritten by a private corporation at no expense to the Government.

Nuclear Energy for Production of Synthesis Gas

In the overall search for more economical processes for generating synthesis and high-B.t.u. gas from coal, the use of nuclear energy has been studied. This scheme, if feasible, has several advantages:

1. It eliminates the oxygen plant and oxygen compression, which account for 70 percent of the power used in a gas-synthesis plant.
2. It offers hope of a synthesis plant in which the B.t.u. in the product approaches that in the coal, instead of a mere 45-percent efficiency now obtained.

Electric power companies and electric power equipment manufacturers have been actively engaged since 1946 in an attempt to use nuclear heat for power generation. A plant is now being built in which a nuclear reactor replaces the conventional boiler using coal, oil, or gas. At the present stage of the technology, this has meant a retrogression of a number of years in steam pressure and temperature.

Use of heat from nuclear sources for generating synthesis gas may be nearer economic feasibility than is power generation, in spite of the fact that a 60,000 kw. nuclear power plant is under construction.