NASA CONTRACTOR REPORT

NASA CR-496

THE USE OF SILVER OXIDE AS A REGENERATIVE CARBON DIOXIDE SORBER

by John F. Foster

Prepared by
BATTELLE MEMORIAL INSTITUTE
Columbus, Ohio
for Ames Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1966

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THE USE OF SILVER OXIDE AS A REGENERATIVE CARBON DIOXIDE SORBER

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SUMMARY

Silver oxide is a potentially valuable regenerative CO_2 sorbent for space applications because it is a nontoxic solid that reacts with atmospheric CO_2 at room temperature to form nontoxic solid silver carbonate. The temperature at which silver carbonate decomposes is lower and the decomposition energy is also lower than for other reversible oxide-carbonate systems.

Other investigators have found that silver oxide deposited on porous inorganic supports exhibits an initial sorption capability that decreases with successive regenerations. This study was made to develop an improved silver oxide sorbent supported on silver foil, which would retain acceptable sorption capability after repeated regenerations.

Methods have been developed (1) for preforming silver foil into individual sorption modules that permit intimate contact between CO_2-contaminated air and the foil surface, (2) for oxidizing a surface layer of the foil to silver oxide, and (3) for converting the silver oxide layer to an active CO_2 sorbent. Chemical methods were developed for expanding the surface area of the silver foil before oxidation, but silver oxide formed on the expanded surface did not prove superior in sorption characteristics to oxide formed without prior surface expansion.

Sorption and desorption of CO_2 by the activated silver oxide was studied in detail. No gross deterioration in sorption capacity was observed in one module that was carried through six sorption cycles, which included 740 hours at a desorption temperature of 210°C. Other modules were studied for shorter periods. Separate experiments showed that silver oxide on silver removed substantially all the CO_2 from air containing 1 per cent CO_2 until at least 50 per cent of the silver oxide was converted to silver carbonate. Substantially all of the CO_2 could be recovered by prolonged heating at 210°C.

It is concluded that the silver oxide-silver system exhibits no inherent lack of stability on the basis of the results obtained. Further improvements in the mechanical stability and the sorption capacity of the silver oxide layer are possible and necessary for a practical sorption unit. The long-term cycling of a larger prototype unit containing multiple modules is advisable to appraise the performance capability of silver oxide as a practical regenerative CO_2 sorbent.

INTRODUCTION

A program was initiated to investigate the use of silver oxide as a regenerative sorbent for CO_2. As an introduction to the description of the experimental results, the report describes the specific objectives and presents the technical background which indicates that silver oxide should be an effective regenerative sorbent. It was necessary as part of the research to resolve a number of uncertainties as to silver oxide properties that arose because studies reported by other investigators appeared to give contradictory results. The research was planned specifically to appraise these contradictions and to decide whether silver oxide could be developed as a sorbent that approached in actual use its theoretical possibilities.

Objectives

The objective of this study was to develop a reliable, regenerable carbon dioxide sorption system using silver oxide as the active sorption agent. Three intermediate objectives covered all of the work undertaken under the current research contract. They are as follows:

(1) To investigate the formation of silver oxide on a silver metal substrate to form a matrix which has a large surface area of silver oxide

(2) To investigate the ability of the silver oxide-silver matrix to absorb carbon dioxide from a standard air mixture containing 0.5 per cent carbon dioxide.

(3) To investigate the ability of the matrix to be regenerated without reducing its sorptive capacity.

This study was intended to lay the groundwork for a future detailed study of optimizing the assembly and operation of a prototype, regenerative silver oxide sorption system.

Research Plan

In the light of the objectives given above, a research plan was formulated to meet these objectives. It was most important to establish the approximate procedures by which an effective sorbent could be prepared. This over-all preparation required a number of consecutive steps, all of which had to be carried out in sequence before the final product could be tested for sorption and for resorption after a regeneration cycle. Individual procedures for each step were selected somewhat arbitrarily, but selections were guided by preconceptions of sorption mechanisms and of the final form of a practical sorption apparatus. The final criterion for the evaluation of the success of each step was sorption behavior of the prepared material.

The sequence of steps in preparing and testing the silver-silver oxide sorbent was as follows:

(1) Formation of the sorption module blank

(2) Preparation of the silver surface

(3) Formation of a silver oxide sorption layer on the prepared surface

(4) Activation of the silver oxide for CO_2 sorption

(5) Determination of sorption characteristics of the activated oxide

(6) Regeneration of the CO_2-saturated sorbent

(7) Examination of resorption capacity after regeneration.

TECHNICAL BACKGROUND

Characteristics of Silver Oxide

Silver oxide reacts directly with gaseous CO_2 in some manner to form silver carbonate. Three characteristics of this reaction make it favorable for space applications:

(1) Both silver oxide and silver carbonate are solid materials, nontoxic and nonvolatile, with no dangerous properties that would introduce hazards from their use in a closed system.

(2) The energy required to decompose silver carbonate is much less than that necessary to decompose other metal carbonates formed from their corresponding metal oxides.

(3) Silver oxide sorbent does not adsorb moisture to the exclusion of CO_2 when both H_2O and CO_2 are present in air.

Investigations dating back many years of the properties of silver oxide and silver carbonate permit calculations of the equilibrium pressures of CO_2 over silver carbonate and of oxygen over silver oxide. Figure 1, a plot of these equilibrium pressures as functions of temperature, shows that the pressure of oxygen in the silver-silver oxide system is always 5 to 10 times higher than that of CO_2 in the silver oxide-silver carbonate system at corresponding temperatures in the temperature range of interest. It has been inferred from these data that regeneration of silver oxide from the carbonate by raising its temperature to drive off CO_2 might result in simultaneous irreversible decomposition of the oxide to silver metal. If this were true, the capacity of the silver oxide for resorption of CO_2 would be progressively reduced in successive sorption-regeneration cycles. Development studies of silver oxide as a regenerable CO_2 sorbent have been focussed primarily on preparation of an active form of silver oxide which would sorb CO_2 rapidly and would have a high capacity. Studies of stability have been secondary, and the problem of stabilizing the sorbent had not been satisfactorily solved when this research was started.

Chandler and his coworkers at the Isomet Corporation have described work on using silver oxide as a CO_2 sorbent. [1]* Silver oxide was prepared in various forms by precipitation or coprecipitation on expanded silica or

*References are given on page 50.

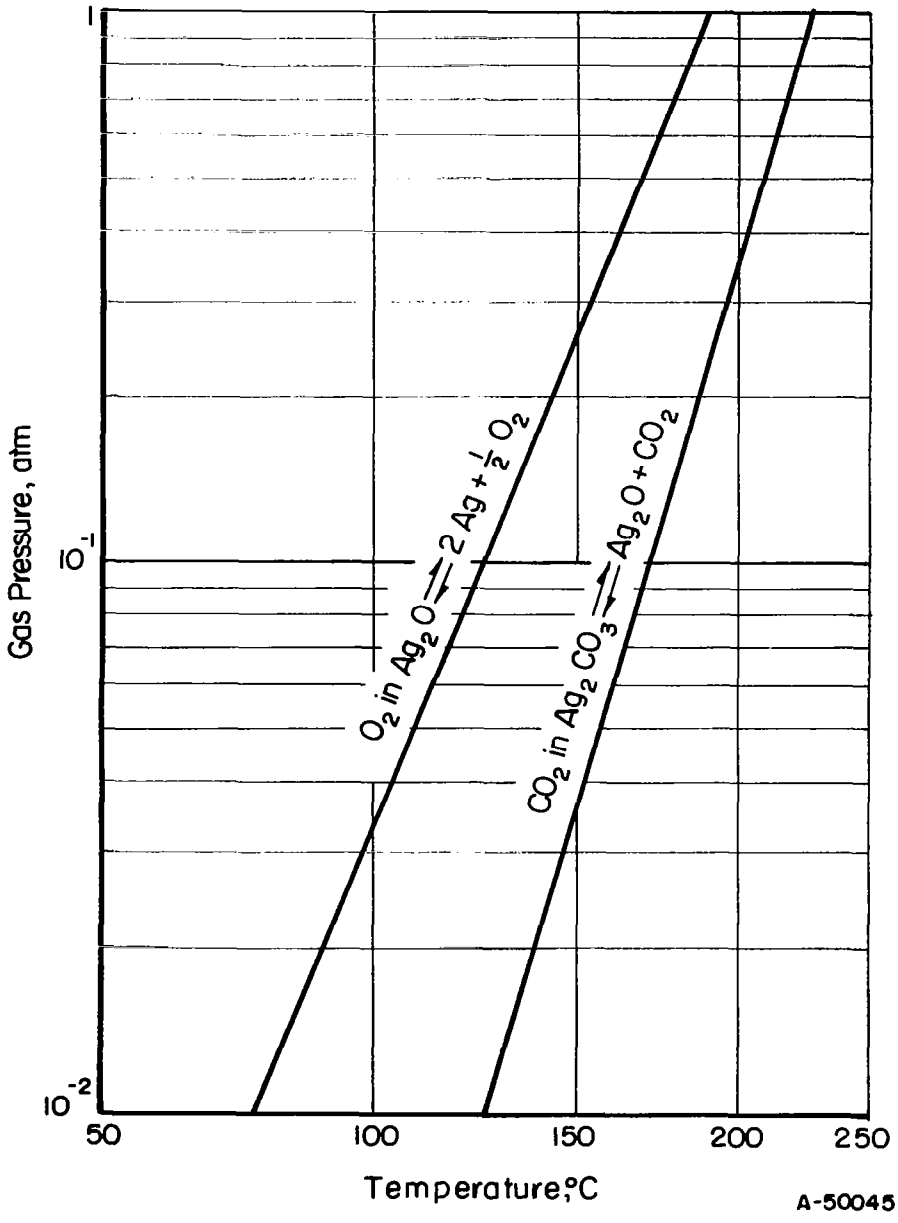


FIGURE 1. EQUILIBRIUM PRESSURES IN SILVER OXIDE SYSTEMS

alumina gels of high surface area, or in one case by precipitation without a substrate. The methods used are described in detail in Reference (1). Of nine different products made, only one removed a 1 per cent concentration of CO_2 effectively from air when used in a sorption column. This material was produced by the coprecipitation of silver carbonate and aluminum oxide and subsequent conversion of the carbonate to silver oxide by heating. The product contained nominally 80 per cent silver oxide, and it remained an active sorbent during exposure to the CO_2-air stream until it was more than 90 per cent saturated with CO_2.

There was evidence that the oxide-carbonate cycle is not as simple as it is usually written:

$$Ag_2O + CO_2 \rightleftharpoons Ag_2CO_3.$$

In some manner water enters into the reversible reaction, and water vapor is necessary for the sorption reaction. There was no opportunity to investigate within the limits of the study, the optimum method for regenerating the effective CO_2-sorbent material described above, which was developed near the end of the contract period. Preliminary experiments indicated a slow decrease in CO_2 absorbing capacity over a period of several cycles, but no data were given.

An oral report was received that experimental work was completed on another study of silver oxide as a sorbent at Denver Research Institute under Air Force Contract No. AF 33(657)-10928. The sorbent was similar to the Isomet material, but it differed in that yttrium was incorporated in the silver oxide lattice. Apparently sorption rate was improved significantly, but stability after cycling was unsatisfactory.

The work of Herley and Prout[2] indicates that the temperature range for the complete regeneration of silver carbonate to silver oxide does not overlap the temperature range in which significant decomposition of silver oxide occurs. In fact, there may be an interval of at least 70°C between complete decomposition of the carbonate to oxide and incipient decomposition of the oxide to silver. Herley and Prout undertook a study of the possible effect of pre-irradiation of specimens of silver oxide by ultraviolet light and cathode rays on the kinetics of thermal decomposition of the silver oxide. In order to make this study it was necessary to establish a reproducible thermal decomposition curve without pre-irradiation. Earlier work which they cite in their publication did not show such reproducibility. They found that the difficulty experienced by other investigators had apparently resided in the use of impure specimens of silver oxide contaminated with Ag_2CO_3 by exposure to atmospheric CO_2. In fact, Herley and Prout themselves

were unable to prepare silver oxide in pure form by chemical means alone. They could prepare reproducible specimens by heating their prepared oxides for 3 hours at 280°C under vacuum. They then showed by a series of independent experiments that this preheat resulted in a pure, stable oxide. During the preheating period, the gases evolved showed the presence of CO_2 and no oxygen, and analysis of the resulting solid residue for silver content gave the purity of the silver oxide as 99.94 per cent. They further showed that the silver oxide decomposition process was definitely not autocatalytic. The decomposition of a sample of preheated silver oxide was unaffected when mixed with the solid (silver metal) residue obtained from a previous decomposition of silver oxide to silver in an atmosphere of nitrogen. Preheating at 280°C for 3 hours in oxygen at one atmosphere did not alter the decomposition at 350°C, as compared to preheating at 280°C under vacuum. Neither was the decomposition at 350°C affected by exposing the decomposing sample to the gaseous decomposition products from a previous decomposition. Anticipating the results reported herein, it was found that substantially all the CO_2 could be removed from a saturated sorption sample by heating at about 210°C; therefore, there is a range of perhaps 70°C, (e.g., 210-280°), in which silver carbonate should be regenerable to silver oxide without substantial loss in activity for resorption.

Preferred Chemical Composition of the Sorbent

Details of the actual sorption-desorption mechanism are obscure, so the philosophy of eliminating possible interfering materials was adopted. The simplest chemical system would contain only silver oxide formed directly on silver, with no additional material present as a porous support. Whatever material might be used as a support, it could conceivably interfere with regeneration by reacting at the mating surfaces between support and silver oxide, since it is well established that the surface atoms of any newly formed solid may be highly active at the instant of formation.

The silver-silver oxide system also minimizes the possibility of temperature extremes at hot spots, which might decompose and deactivate adjacent sites on the silver oxide. The chemical reaction that forms the carbonate releases heat at the sorpiton site that should be dissipated rapidly by the thermally conductive metal, thus minimizing localized temperature rises. Further, in regeneration, heat must be introduced and distributed uniformly throughout the sorption mass without exceeding the temperature at which silver oxide is stable. In this respect the high thermal conductivity of silver in the silver-silver oxide system should be a distinct advantage over the inherently low thermal conductivity of porous inorganic supports.

Preferred Physical Structure of Sorbent

The sorbent must be spread out in a thin layer to allow maximum contact between gaseous CO_2 and the solid surface of the silver oxide. The advantage of the high surface area of a porous supporting material must be approximated in the chemical system containing only silver oxide on silver, if an effective sorbent is to be developed with this system. Therefore, a thin silver foil is used to support the silver oxide.

An additional expansion of the microscopic surface area of the foil can be produced by chemical pretreatments, which cause recrystallization of the silver into fine needles or "hairs" attached at one end to the metal surface. Keil and Meyer[3] showed that needles of silver sulfide form on silver under certain conditions. They established by experiment that needlelike crystals form on freshly cleaned silver exposed at 50 to 80°C in a closed container to sulfur vapor saturated with moisture. Some crystals reached up to 1/10 millimeter in length in 12 hours. In dry gas no needle-like growth occurred. The surface of the sample showed pitted formations near the base of the crystals.

In other experiments pellets of silver sulfide were heated for 10 hours in air at 400°C. Fiberlike crystals of metallic silver were thus formed, preferentially on the edges, of the pellets. This growth process could be followed microscopically on silver sulfide in the form of coarse-grained powder at temperatures above 200°C.

Drott[4] also studied the formation of silver sulfide "whiskers" on silver. Samples of cleaned silver foil were suspended at room temperature in air containing 2 per cent hydrogen sulfide and varying amounts of water vapor. The layer of silver sulfide formed on the silver was examined with an electron microscope using replicas of the surface. Various forms of sulfide were found. Whiskers of sulfide predominated only when the surrounding atmosphere was saturated with water vapor. After sulfidation times as long as 100 hours, the surface was completely covered with matted whiskers. Electron micrographs in silhouette showed whiskers as long as 25 microns. These experiments indicated that the optimal condition for the sulfidation of silver by hydrogen sulfide is a condensed aqueous medium with free access to oxygen. The layer of matted whiskers provided crevices suitable for condensation from the saturated atmosphere and was still open enough to allow oxygen free entry.

Interpretation of the Technical Background

The studies of Herley and Prout[1] appear to establish the practical stability of silver oxide at temperatures up to 280°C for periods of many hours. Comparison of the equilibrium pressures of CO_2 over silver carbonate and of oxygen over silver oxide is not valid evidence of oxide instability during regeneration, because decomposition rates may be too low to be of practical significance, and/or because the equilibrium equations do not represent the reactions actually taking place during sorption and regeneration. Observations in other laboratories that silver oxide is not satisfactorily stable and regenerable probably apply specifically to the systems studied, in which the silver oxide was dispersed on a porous support. A system using only silver covered with silver oxide eliminates possible interference by a support and could approximate the large surface area needed for an effective sorbent if the silver surface is suitably expanded. Physical expansion is attained by using silver foil, and expansion by chemical means, if necessary, can be attained by forming whiskers of silver needles on the foil surface.

EXPERIMENTAL METHODS

Methods for Forming the Sorption Module

Construction of the Sorption Module. - Considerations of cost and convenience dictated that small modular units of sorbent be used so that they could be tested individually and could eventually be incorporated into a full-scale sorption bed without major alterations in design.

The prototype sorption apparatus was conceived as a chamber filled with sorbent in a form that would permit free flow and intimate contact of the gas with all material contained in the sorption volume. It seemed desirable to minimize the necessity for diffusion transfer of CO_2 to the sorbent surface and to depend mostly on convection to carry gas close to the silver oxide surfaces. Furthermore, flow distribution should approach complete uniformity without requiring great care in packing the bed. Thus an open structure somewhat different from a conventional catalyst bed was indicated. Therefore, a preformed module was constructed which permitted a maximum of material to be put into the bed, which promoted uniform flow distribution, and which resisted attrition of the silver oxide by mechanical shock or

vibration during assembly and operation. This sorption module was a cylinder about 1 inch in diameter and 3 inches long, formed by wrapping a strip of perforated and embossed silver foil, 3 inches wide and of suitable length, around a removable mandrel.

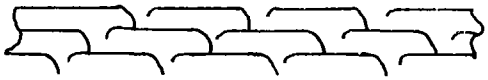
The foil strip was profusely perforated to permit gas flow in all directions through the module by embossing the foil so deeply that each boss burst open at the center and left a burred structure around each opening. The burrs themselves acted both as spacers between turns and as miniature baffles to insure intimate contact between the gas flowing through the module and the solid surface of the sorbent.

Apparatus and Procedure for Forming the Sorption Module. - Embossing and perforating was accomplished by passing the foil strip between a pair of rollers, one of which was covered with laboratory-grade red rubber tubing as the resilient bed for the embossing die. The embossing pattern of four-sided pyramids with protruding tips on 1/8-inch centers was cut into the surface of the mating chrome-plated brass roller. The two rollers were forced together by a spring-loaded clamp with an adjustable load. The resulting embossed pattern produced square holes at each pyramid tip. The total open area was about 20 per cent of the total foil area. A triangular pointed burr protruded from each of the straight sides of the square hole to a height of about 3/64 inch. It was found that an embossed strip of foil about 30 inches long could be wound on a 1/8-inch split mandrel with about 12 complete turns to form a cylinder with an outside diameter of approximately 1 inch.

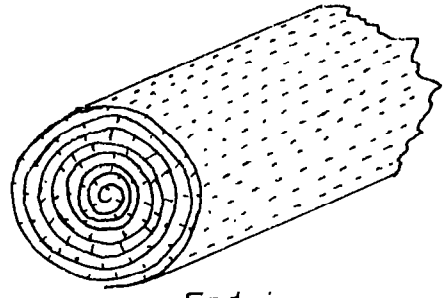
As the study proceeded some of the results were interpreted as indicating that this structure was not sufficiently open to allow the best oxidation and sorption. Therefore, in later experiments coils were made with about the same outside dimensions but with fewer turns and wider spacing between turns. The length of foil used in these modules was about 10 inches, and a separate spacer was interleaved between turns. In one design the spacer was a layer of glass-fiber mat interposed across the whole width of the strip and sufficiently long to extend around the outside of the finished module. Since it was questionable whether a foreign material such as glass fiber could be tolerated, another design was used in which a narrow strip of the same embossed foil was laid separately lengthwise along the primary foil strip midway between its edges. The two were wound together into a cylinder with the desired wider spacing between turns.

Figure 2 shows diagrammatically the structure of the silver foil sorbent module. Figure 2a indicates that the burred hole spacers do not

fall into register with the holes in the next turn as the coil is wound. In fact, a hand-wound module cannot be formed with such close spacing as indicated by the diagram, and usually there is a line of contact in only one or two positions in each revolution of the coil. Figure 2b indicates the appearance of the end of a sorption module after it is wound into roughly cylindrical form without a separate spacer between turns. Air flow is parallel to the axis of the cylinder, but cross flow can occur through the perforations. Optimization of the openwork structure of the module was not attempted because of the priority given to other studies.



a. Burred Hole Spacers



b. Formed-Foil Sorbent Unit A-50046

FIGURE 2. SORBENT MODULE

Methods for Preparation of the Silver Oxide Sorbent

Test Cell for Exposure of the Module to Flowing Gas. – Figure 3 shows a test cell which was used to contain the sample for exposure to a flowing gas stream under controlled conditions. It was used to direct the gas flow through the sample with a minimum of dead space in the system, and it served both for the ozonization experiments and for later experiments in the study of rates of CO_2 sorption. It was constructed of Pyrex glass, so that the appearance of the surface of the outside turn of the coiled sample could be examined for color changes during oxidation. When visual examination was not important, the sample was often wrapped with an extra layer of aluminum foil and glass wool to reduce flow along the cell walls. At times a glass-fiber plug was inserted at each end to help to distribute the gas flow uniformly across the cross section of the cell. For experiments at less than

room temperature, the cell was modified by incorporating a U-turn in the exhaust tube which was lengthened to extend to the inlet end so that the cell could be inserted vertically into a cooling bath.

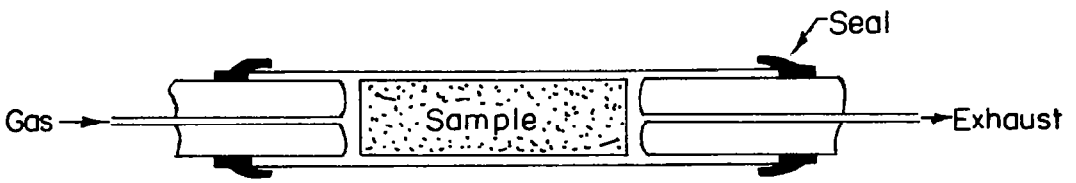


FIGURE 3. TEST CELL FOR FLOWING-GAS STUDIES

For experiments above room temperature, the cell was inserted into a tube furnace, or was wrapped with heating tape backed up by insulation. The temperature at the outer surface of the heated cell was measured and controlled by a thermocouple with its junction at the outer surface. Since the temperature within the cell was lower than that at the surface, the internal temperature was estimated from calibration curves of the temperature differential, as measured by an additional thermocouple inserted at the center of the test sample during preliminary calibration experiments.

The seals at each end of the cell were made with pressure-sensitive vinyl tape, and the whole cell was long enough that the seals were outside the heated zone to prevent deterioration. This arrangement permitted convenient exchange of samples between tests by opening the seal at one end and removing and replacing the sample.

Apparatus for Expanding the Silver Surface by Sulfiding and Reduction. - The apparatus for sulfiding and reduction of the silver module is shown in Figure 4. The coiled module was fitted tightly into a Vycor tube that was long enough to extend through a tube furnace. With the module centrally located in the heated zone the tube was connected to a gas flow system which exposed the heated sample to flowing gas. The flow rate, composition, and temperature of the gaseous atmosphere were separately controlled. Gas was supplied from cylinders of compressed H_2S, hydrogen, and air, each fitted with reducing valves to control individual gas flows and with flowmeters to meter individual flows and total flow of circulating gas. Energy input into the furnace was modulated with a Variac autotransformer, and constant temperature was maintained by a controller with its thermocouple junction inside the furnace at the tube wall. A humidifier was in the flow system upstream from the furnace to permit addition of water vapor to the gas stream.

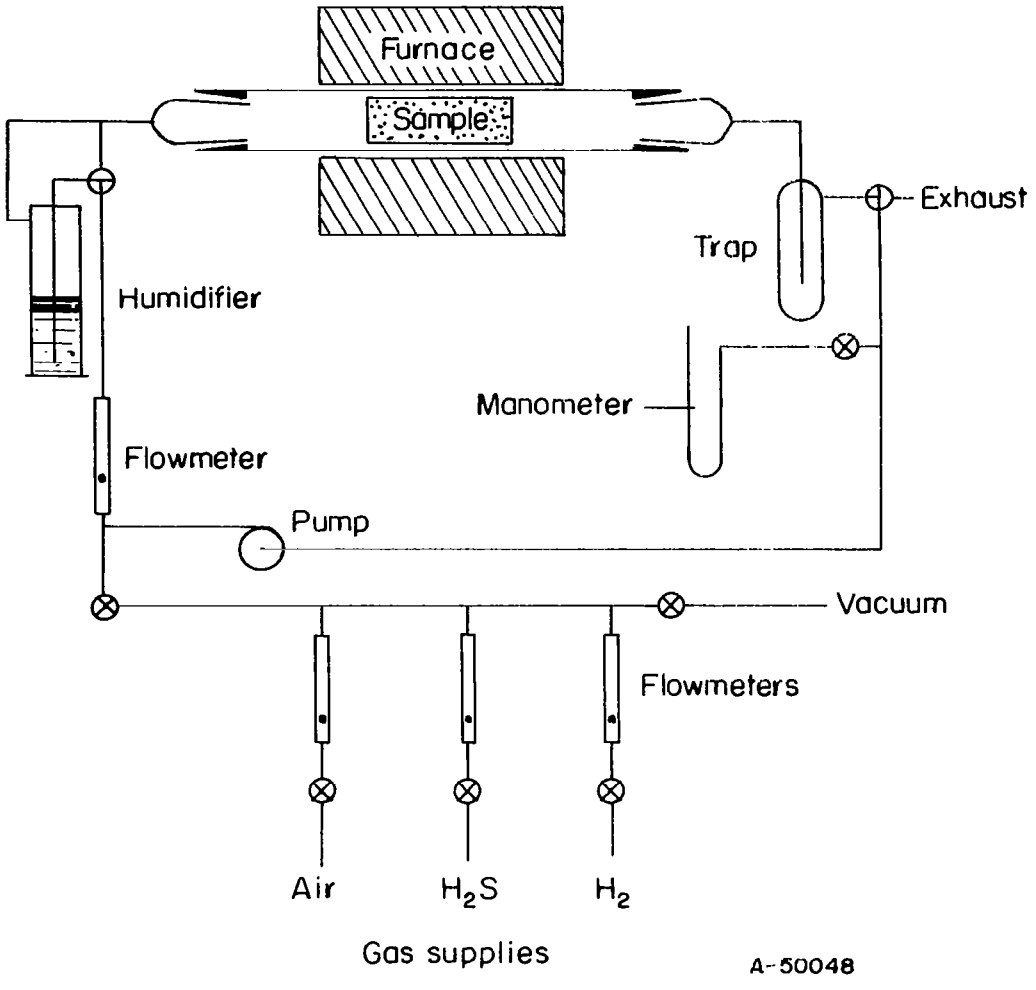


FIGURE 4. APPARATUS FOR SULFIDING AND REDUCTION

Procedure for Sulfiding and Reduction. - Two different procedures were used in the flow system. At first, the flow system was charged with a selected gas composition, which was a mixture of hydrogen sulfide and air for the sulfiding tests, or hydrogen and water vapor for the reduction of the sulfide layer formed previously. After the system was charged to atmospheric pressure, the gas inventory was recirculated through the sample by a diaphragm pump which drew gas from the tube outlet and pumped it back to the tube inlet continuously. A manometer attached to the system indicated the reduction in pressure as gas was consumed by reaction with the silver sample. Periodically the system was returned to atmospheric pressure by adding more gas. The total amount of gas added could be calculated from the known volume of the system and the pressure before and after a gas addition. By this procedure information was collected on the rate of reaction of the silver sample with the gas atmosphere as a function of sample temperature, flow rate, and gas composition. With the information so obtained, it was possible to select conditions for sample treatment that would produce the best rates of sulfiding and reduction.

The second procedure was to admit a gas mixture of constant composition to the sample and exhaust the effluent gas from the system after a single pass. By this procedure the sample was exposed to gas for the much longer periods that were required for substantial surface alteration without determining the rate of reaction of the sample during the experiment. In all experiments the sample was weighed before and after exposure in order to determine the extent of reaction. From these data the amount of silver sulfide and unconverted silver could be calculated without examining the interior structure of the sample and thereby destroying it.

Procedure for Thermal Pretreatment. - The apparatus shown in Figure 4 was used for the thermal pretreatment of some samples that were not pretreated by sulfiding and reduction. The sample was heated at about 500°C for a convenient period of 5 to 15 hours, while air was passed slowly through the system. In some experiments the surface of the foil was roughened by scratching it with a wire brush before the thermal pretreatment.

Apparatus for Gas-Phase Oxidation with Ozonized Oxygen. - Figure 5 shows, in diagrammatic form, the apparatus for gas-phase oxidation with ozone. Oxygen was supplied from a cylinder of high-pressure USP oxygen, and the flow was controlled by a gas pressure regulator. The oxygen stream passed through a Welsbach ozonator, Type T-23, which converted a part of the oxygen to ozone by electrical discharge. The ozone

generator incorporated a calibrated flowmeter and had two exit lines with throttling valves. It was intended that one line would supply ozonated oxygen and the other would feed to a Welsbach photoelectric ozone meter to monitor continuously the ozone content of the oxygen stream. For Battelle's purpose it was convenient to use both streams for the oxidation of two samples simultaneously. Each sample was encased in a test cell, as shown in Figure 3. Since the ozone content of the stream was quite stable, it was sufficient to check the ozone concentration occasionally for a short period by directing the stream temporarily through the ozone meter and then returning it to the sample. Two humidifiers were inserted in the stream of ozonized oxygen ahead of the two samples, after it was found that better results were obtained when the oxidizing gas was saturated with water vapor.

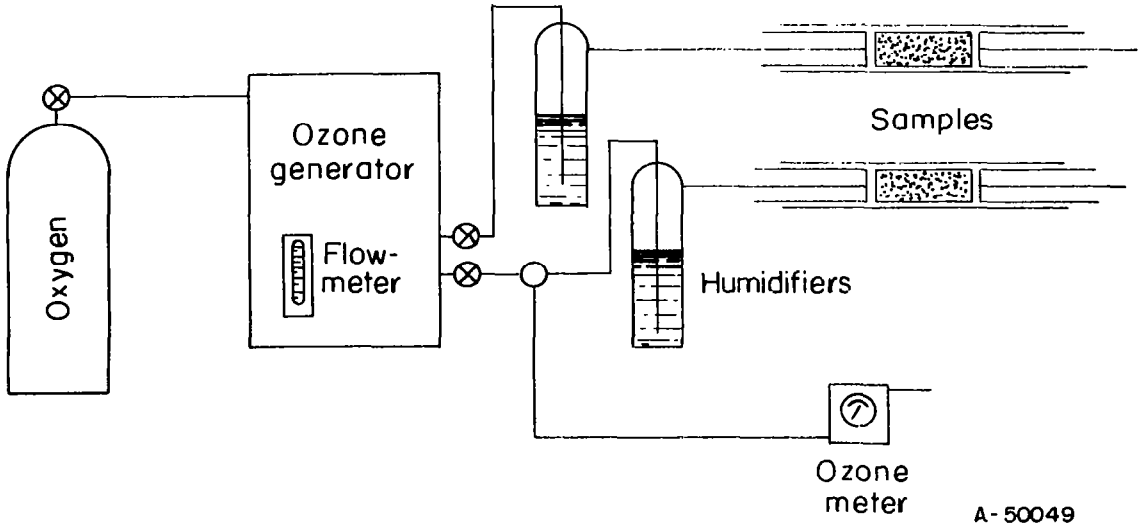


FIGURE 5. APPARATUS FOR GAS-PHASE OXIDATION OF SILVER FOIL WITH OZONE

Procedure for Gas-Phase Oxidation with Ozonized Oxygen. - A flow rate of 400 cc of oxygen per minute (STP) was arbitrarily selected for comparing various oxidation procedures. The ozone concentration was generally set at 0.1 weight per cent ozone as determined by the calibrated ozone meter. A few tests were also run at 1 weight per cent ozone, and on one occasion the ozone concentration was raised inadvertently to a value estimated at greater than 1 per cent because of a reduction in oxygen flow rate by low pressure in the oxygen supply system. The distribution of flow was divided equally between the two samples, at the standard rate to each, by

setting the rate through one sample with the valve to the other sample closed and then opening the closed valve and increasing the total flow to twice the standard rate. This procedure compensated for any differences in flow resistance between the pairs of samples and directed equal flows through each of the pairs.

In experiments on the oxidation of wet silver surfaces the sample surface was wetted by adding about 2 cc of distilled water with a pipette whose tip was placed on the end of the sample before the cell was closed. The sample surface was sufficiently hydrophilic that the distribution of liquid water over the surface was fairly uniform. With a humidified stream of oxygen appreciable evaporation of the liquid film did not appear to occur. For oxidations at temperatures below room temperature the modified cold cell was immersed in a cold-water bath. At the same time the humidifier was surrounded by a second cold-water bath maintained at a temperature about 1° C colder to avoid condensation of water in the sample chamber. For experiments at higher than room temperature the outside surface of the cell was heated by wrapping with heating tape, as described previously.

Progress of the oxidation process was followed by weighing the sample periodically. The sample was removed from the cell, dried to constant weight in a vacuum oven at about 100°F, weighed, and returned to the cell for further oxidation.

Apparatus for Electrolytic Conversion of Silver. – A laboratory-scale setup was used for electrolytic expansion of the surface area of silver foil and for electrolytic oxidation of the silver surface. A 600-ml tall-type Pyrex glass beaker was a convenient container in which the single module could be immersed in electrolyte. The counter electrode was a platinum foil cylinder placed against the inner surface of the container wall so that it surrounded the module suspended at the center of the container. Electrical connection to the silver coil was made by wrapping the cylindrical module with several turns of silver wire and clipping the lead onto one of the wire ends. Auxiliary electrical equipment was provided to pass a controlled direct current in either direction through the cell and to measure and record its magnitude.

Procedure for Electrolytic Expansion of the Silver Surface. – A pretreatment of the silver was necessary to expand the surface so that subsequent oxidation could be accomplished in greater depth. This process is analogous to the surface expansion of silver by sulfide cycling, except that a porous layer is formed instead of whiskers.

A chloridation-reduction cycle was selected, in which the electrolyte consisted of 1 part concentrated hydrochloric acid (37 per cent HCl) diluted with 9 parts of water. With the module as the anode, a constant current of 3.3 ma per sq cm was passed through the cell at room temperature until the voltage rose to the point at which gas was discharged at the electrodes. This limit of AgCl formation in the anodic phase was reached after about 20 minutes. After each anodic phase the current was reversed for about the same length of time, and silver was regenerated by decomposing the silver chloride. In three successive cycles the surface was progressively expanded. A fourth cycle had no further effect. The module was rinsed thoroughly with distilled water in preparation for electrolytic oxidation.

Procedure for Electrolytic Oxidation of Silver. – The module was made the anode in the electrolytic cell containing a 30 per cent aqueous solution of KOH. A constant current of 0.8 ma per sq cm was passed through the cell until oxidation was completed as far as possible. The oxidation period was about 3.5 hours.

Apparatus and Procedure for Oxidation of Silver With High-Pressure Oxygen. – The coiled module was treated with oxygen in a high-pressure bomb with an internal volume of 540 cc. The module was preheated in air at 500°C for a few minutes, cooled, and weighed. It was placed in the bomb, and the cover was sealed with a copper gasket. Oxygen was admitted through a high-pressure valve to a pressure at room temperature of about 165 psi. The pressure was released and the bomb was repressurized one to six times to flush out air and leave an atmosphere of oxygen. In one test, 2 ml of water was added to the bomb before it was closed to give an atmosphere of oxygen and steam during the oxidation test.

The pressure of 165 psi was selected in the first experiment so that the final internal pressure would increase to about 280 psi when the closed bomb was heated to about 250°C in an oven. In two other experiments, the valve was left open to the oxygen supply regulated at about 300 psig until the bomb had reached the oven temperature of 305°C. These pressures and temperatures correspond approximately to the equilibrium between silver oxide and oxygen according to independent determinations by Pollitzer, the Bureau of Mines, and Lewis and Randall, quoted by Chandler in Reference (1).

The bomb was maintained at temperature for about 4 hours. It was then cooled overnight before the residual pressure was released. The

module was removed and weighed to measure the weight change during the exposure to oxygen. In the experiment with water vapor present, the module was vacuum dried at 41°C before the final weight was determined.

Methods for Sorption Studies

Test Atmospheres for Sorption Studies. - Sorption studies were conducted using two different gas mixtures. The test gas used first was a mixture with the nominal composition 5 parts of carbon dioxide and 95 parts of oxygen. This was a convenient composition because it is a stock mixture available locally and because measurement of residual CO_2 in the gas after sorption is easier at higher concentrations. In later experiments a gas mixture containing nominally 1 part CO_2 and 99 parts air was used to correspond more closely to conditions under which the sorbent would be used in actual service.

Apparatus for Sorption of CO_2 From Flowing Gas. - The sorption sample was contained in the test cell shown in Figure 3. Figure 6 shows the sample in the test cell incorporated in a flow system, which was set up to measure flow rate and composition of the effluent gas, as well as to assay the actual composition of the gas supply. The system components were standard Orsat gas analysis pipettes (Fisher Scientific Company valve bubbler pipettes, Catalog No. 10-600-75) for determining oxygen and CO_2, a storage pipette, and a burette for measuring gas volumes with its associated levelling bottle to adjust the measured gas volume to atmospheric pressure. A series of three-way stopcocks in the gas manifold of the Orsat equipment directed the gas samples into and out of the appropriate pipettes for analysis. Gas-pressure regulators on the three independent gas supplies were used to control the flow rate of the gas through the system. Two types of measurements of sorption from flowing gas were made in the same equipment. These were batch-flow and continuous-flow studies.

Procedure for Batch-Flow Studies of CO_2 Sorption. - Batch-flow studies were used to measure the sorption of CO_2 from a single batch of gas during successive exposures to the sorbent sample. It was possible by this procedure to repeat the exposures until the CO_2 was reduced to a minimum and then to repeat the whole experiment with another batch of gas as often as required. A rapid qualitative evaluation of the sorption characteristics of a sorbent sample was thus possible.

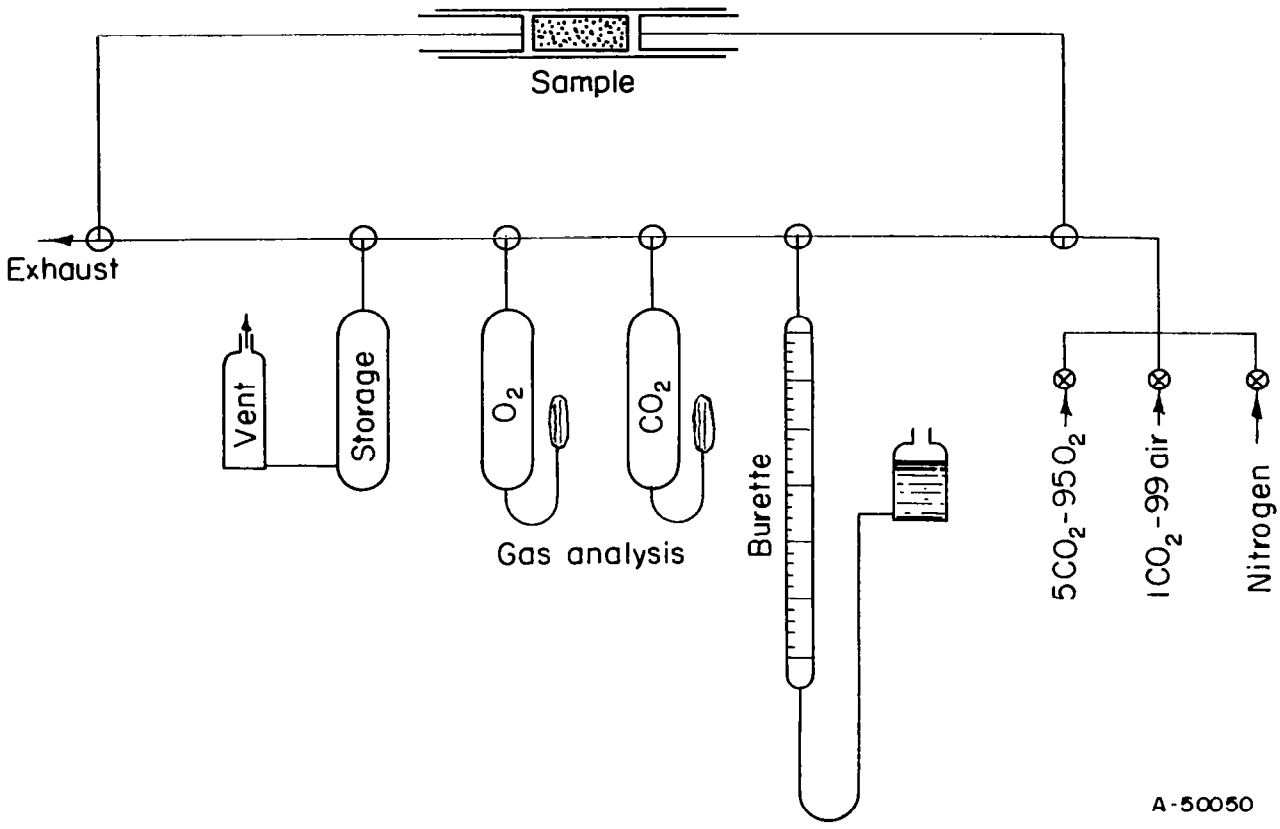


FIGURE 6. APPARATUS FOR SORPTION STUDIES WITH FLOWING GAS

The test cell and its sample was first purged with nitrogen by directing a nitrogen flow from the supply through the cell and to the exhaust. When purging was completed, the test cell was isolated to prepare the system for CO_2 exposure. Gas volume in the isolated system was measured prior to the experiment. In many experiments the nitrogen purge was omitted, and the CO_2-depleted gas remaining in the system from the previous experiment was retained, since the objective of the purge was to limit the CO_2 content of the system to the known amount introduced in a measured gas sample.

After purging the manifold, a measured volume of the 5 per cent CO_2 gas mixture (usually 100 cc) was transferred to the gas burette; and the system was isolated. Sorption characteristics were studied by passing the gas sample from the burette through the test cell into the storage pipette and then returning it in reverse direction to the burette for a volume measurement. This gas flow was accomplished by manual manipulation of the levelling bottle with appropriate settings of the three-way stopcocks. The reduction in volume after each exposure cycle (or group of successive cycles) was a measure of CO_2 adsorbed. To appraise the effect of flow rate on adsorption, flow through the sample could be maintained constant during a pass by the operator, but the rate of flow could be varied three- or fourfold, as desired. After the volume of the gas sample approached a minimum, the composition of the gas residue could be analyzed for oxygen and CO_2 to confirm the sorption results indicated by the volume measurements. The experiments were carried out with suitable precautions against leakage and against temperature changes that might alter the gas volume at atmospheric pressure. These experiments could be repeated as often as necessary to check reproducibility with the sample under essentially constant conditions. If desirable, the experiments could be alternated with continuous-flow studies, as described in the next section, to study sorption by the same sample at various levels of CO_2 saturation.

The results obtained by batch-flow studies served to indicate the minimum CO_2 concentration that could be reached by sorption on a particular sample and gave an indication of the sorption activity of the oxide layer. If the sorption did not reach the ideal objective of total CO_2 removal, the results were then useful as a guide to further development. Such results are not reported in detail in the experimental part of this report.

Procedure for Continuous-Flow Studies of CO_2 Sorption. – In continuous-flow studies the regulated flow from the gas supply was directed continuously through the test sample and out the exhaust. Periodically the exhaust valve was closed to direct the total flow to the burette for a measured time period to determine flow rate. The collected flow-rate sample

was then analyzed to measure effluent-gas composition. Optionally the total flow was switched directly to the burette from the gas supply to measure similarly the flow rate and composition of the input gas. Since the gas analysis at low CO_2 concentrations was not sufficiently precise for an exact determination of the total amount of CO_2 sorbed during long periods of continuous flow, the sorbent sample was removed periodically and weighed to indicate total CO_2 sorption.

It was found during the course of the flow studies that water vapor was necessary in the gas stream for maximum CO_2 sorption, and a humidifier was subsequently placed in the input gas stream. The measured weight increase then would represent both CO_2 and water vapor that was removed from the gas stream by the sorbent.

Test Cell for Static-Gas Sorption Measurements. - The need for a rapid method of evaluating the relative sorption characteristics of individual modules led to a study of a method of measuring sorption from a static gas sample in contact with the sorbent module. Figure 7 shows a test cell constructed from a heavy-gage brass tube about 6-1/4 in. long x 1-1/8 in. ID x 1/8-in. wall thickness, which accommodated two modules end to end. The cell was supplied with a solid brass filler for half the internal volume, so that only one module could be tested if desired. The open ends of the brass tube were closed with threaded brass caps, which were made vacuum tight with O-ring seals on the machined flat ends of the tube. The heavy construction was used to provide high heat capacity, and thus temperature stability, to the cell during the course of an experiment. One of two ports in the cell wall was connected to pressure-measuring equipment and the other to a supply of test gas.

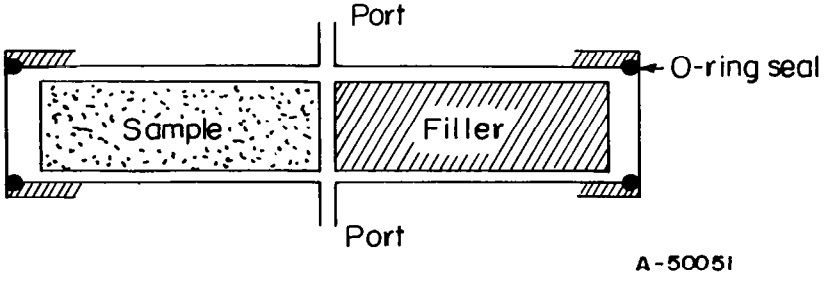


FIGURE 7. TEST CELL FOR STATIC-GAS SORPTION MEASUREMENTS

Apparatus for Measurement of Sorption From Static Gas. - Figure 8 shows a block diagram of the apparatus used for static sorption measurements. One port of the test cell is connected through the gage valve to one side of a differential pressure gage. The other side of the pressure gage is open to atmospheric pressure, which is used as the reference pressure. With the gage valve open, the recorder shows the gas pressure inside the test cell as a function of time. Since the test-cell pressure decreases as gas is adsorbed by the sample, the recorded pressure is a measure of the amount of gas adsorbed.

The master gas valve attached to the other port of the test cell controls the introduction and removal of test gas between experiments. It remains closed to isolate the test cell from the gas supplies during a sorption measurement. This system is so arranged with valves and gas lines that the test cell can be evacuated and then refilled exactly to atmospheric pressure from a gas supply contained in flexible plastic bags. The gas in these bags can be replenished as necessary from gas cylinders. This was always done in anticipation of a series of experiments so that the gas samples were in temperature equilibrium with the surrounding room air. The volume of gas stored in each of the flexible containers is sufficient for many repetitions of the static-gas sorption measurements.

Procedure for Measurement of Sorption From Static Gas. - The apparatus was assembled as indicated in Figure 7 with vacuum-tight connections, as confirmed by leak tests before each series of experiments. For use in later calculations applied to the experimental data, the volumes of various parts of the system were determined by measuring the pressure difference that resulted when a known amount of gas was added to the system. The differential pressure gage was calibrated against an absolute pressure differential measurement made with an inclined U-tube manometer.

After the test cell and its contained sample were in temperature equilibrium with the surrounding room atmosphere, a series of experiments was started. The pressure gage was isolated by closing the gage valve with both gage chambers at atmospheric pressure. All four gas-supply valves on the gas manifold were closed and the vacuum valve was opened together with the master gas valve. The test cell was thus completely evacuated prior to the admission of a gas sample. The master and vacuum valves were then closed. Then in quick succession three valve changes were made: (1) the master valve was opened to fill the test cell with gas sample equilibrated to atmospheric pressure; (2) the gage valve was opened to the test cell; (3) the master valve was closed to isolate the system, and

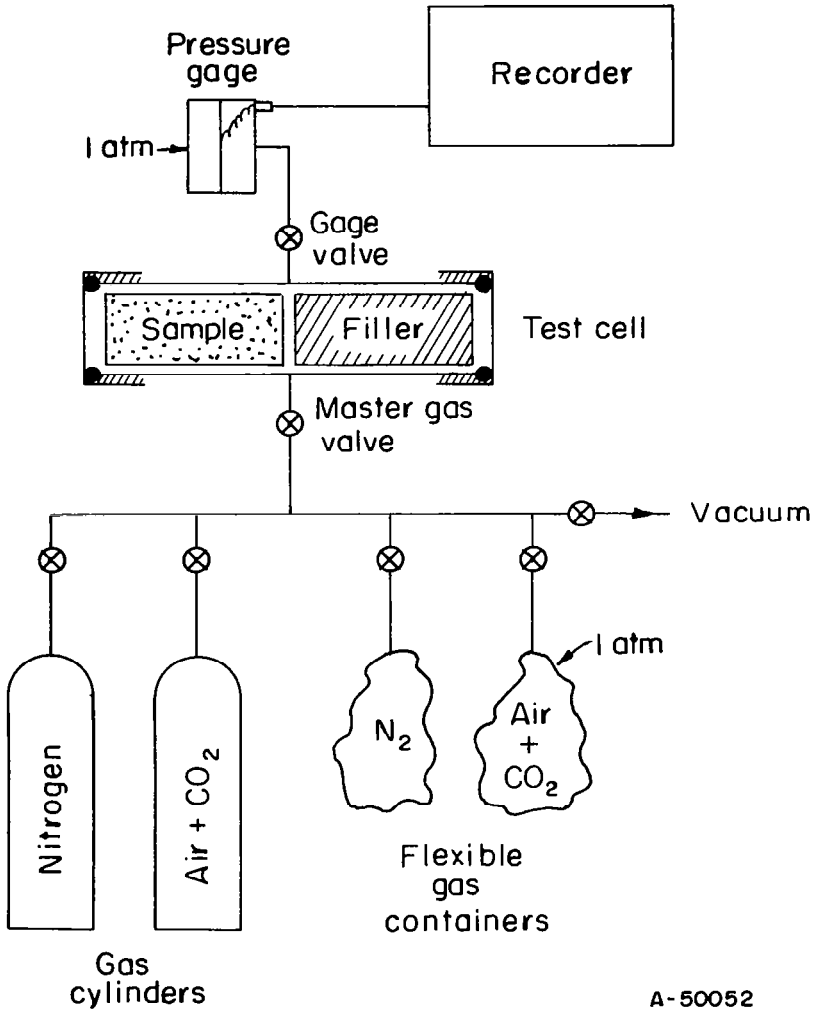


FIGURE 8. APPARATUS FOR STATIC-GAS SORPTION MEASUREMENTS

thus to start the differential pressure measurement as the gas in the cell-gage system decreased in pressure because of CO_2 sorption. It was necessary to use manually operated hemostats applied to the flexible tubing connecting the parts of the system, to cut off or release gas flow, instead of conventional valves. These gave leak-proof cutoff and rapid operation without heat effects. Where vacuum-tight cutoff was not critical, as in the gage valve, a brass stopcock that closed with a quarter turn was used. Manually operated vacuum gate valves were too slow for use in other parts of the system. Solenoid-operated gate valves were fast enough but prevented temperature stabilization by radiating heat from the solenoid coils.

Expansion and compression during admission of a gas sample to the evacuated chamber produced heat and temperature changes in the gas phase. These in turn caused a pressure change unrelated to sorption as the admitted gas sample equilibrated to the temperature of the chamber. It was also found that there was a consistent displacement in the pressure-time curve for both nitrogen and test gas as these were admitted alternately to the chamber. However, reproducible differences were obtained when the test-gas measurement involving both CO_2 sorption and temperature changes was corrected by subtracting the following nitrogen gas measurement, involving similar temperature changes alone.

A second effect on the measurement of total sorption is the time interval between admission of the gas sample into contact with the sorbent and isolation of the system to start the pressure measurement. In the interval during which two valves are being set sorption proceeds without pressure change and thus without being measured. It is conceivable that no pressure change would be detected in this apparatus if sorption were so rapid that CO_2 was exhausted from the admitted sample before the system could be isolated. A correction was introduced for this effect by normalizing the curve so that the portion which showed no adsorption at the end of the experiment corresponded to exhaustion of sorbable CO_2 from the gas sample.

Procedure for Regeneration and Activation of Silver Oxide. – The experimental studies included cycling the modules that showed promising sorption capacity to test their ability to resorb CO_2 after they had been heated to remove sorbed CO_2. The apparatus shown in Figure 6 for sorption of CO_2 from flowing gas was also used for regeneration.

The regeneration temperature was limited to about 210°C corresponding to a measured wall temperature of about 225°C. The amount and composition of gas that was released during the regeneration phase was measured. After the sample was weighed following the sorption phase, it was

replaced in the test cell which was then flushed with nitrogen. Some nitrogen was added to the burette at the same time for subsequent use as a carrier for the gases evolved from the heated sorbent module. The system was closed and the test cell was raised to regeneration temperature. At temperature equilibrium the system thus contained a fixed amount of nitrogen of constant volume, but at temperatures varying between that in the test cell and that in the burette. As gases were released from the heated module, they displaced nitrogen into the measuring burette. The increase in volume with time was a measure of the rate of gas evolution.

Periodically the collected nitrogen was used as a carrier to remove the evolved gases from the test cell for analysis, as follows. The nitrogen in the burette was transferred through the Orsat manifold to the storage pipette, and thence back to the burette through the test cell. Assuming slug flow of the transferred gas through the test cell, all of the gases evolved were thus collected in the burette and analyzed for CO_2 or for CO_2 and oxygen. The CO_2-free gas remaining after analysis was retained in the burette to be used as the carrier in the next transfer. Since only traces of oxygen were present, the oxygen in the system was usually allowed to accumulate over a considerable number of transfer cycles until its concentration reached a measurable level. Even though slug flow might not have been perfectly achieved in each pass, the measurements were cumulative so that the over-all results would not be significantly affected.

Periodically, the system was cooled and the module was removed and weighed so that the total weight loss could be compared with the calculated cumulative weight of the evolved gases determined by analysis. The calculated weights of evolved gases were always less than the weight changes observed in the module. Since some condensate was observed in the gas-transfer line, it is probable that the discrepancy is caused by evolved water vapor.

Exactly the same procedure was used to activate the silver oxide formed by treating the silver with ozonized oxygen. During the experimental program this was found necessary to produce an active CO_2 sorbent. The initial activation differed from regeneration only in the evolution of substantial quantities of oxygen during activation.

RESULTS AND DISCUSSION

Surface Expansion of Silver by Sulfiding and Reduction

A series of ten samples of silver modules was used in exploratory studies of sulfiding and reduction in the apparatus shown in Figure 4. These experiments determined that a mixture of equal parts of air and H_2S flowing through a module at 150 to 200°C reacted with the silver surface to form sulfide without substantial gas phase oxidation of the H_2S by air to release elemental sulfur, which occurred at higher temperatures. It was necessary to use temperatures of 600 to 700°C to achieve reduction of the silver sulfide to silver in an atmosphere of humidified hydrogen.

It was possible to convert the silver completely to sulfide by exposing the module for a sufficiently long time and, similarly, to convert the sulfide completely to silver by reduction. Specifically, Samples 5, 6, and 10 were sulfided for 8.7 hours at 200°C in equal parts of flowing air and H_2S with conversions of 98, 100, and 100 per cent, respectively, based on weight increases. After 13 hours in humidified hydrogen at 700°C, all three samples were reduced to within ±0.2 per cent of their initial weights.

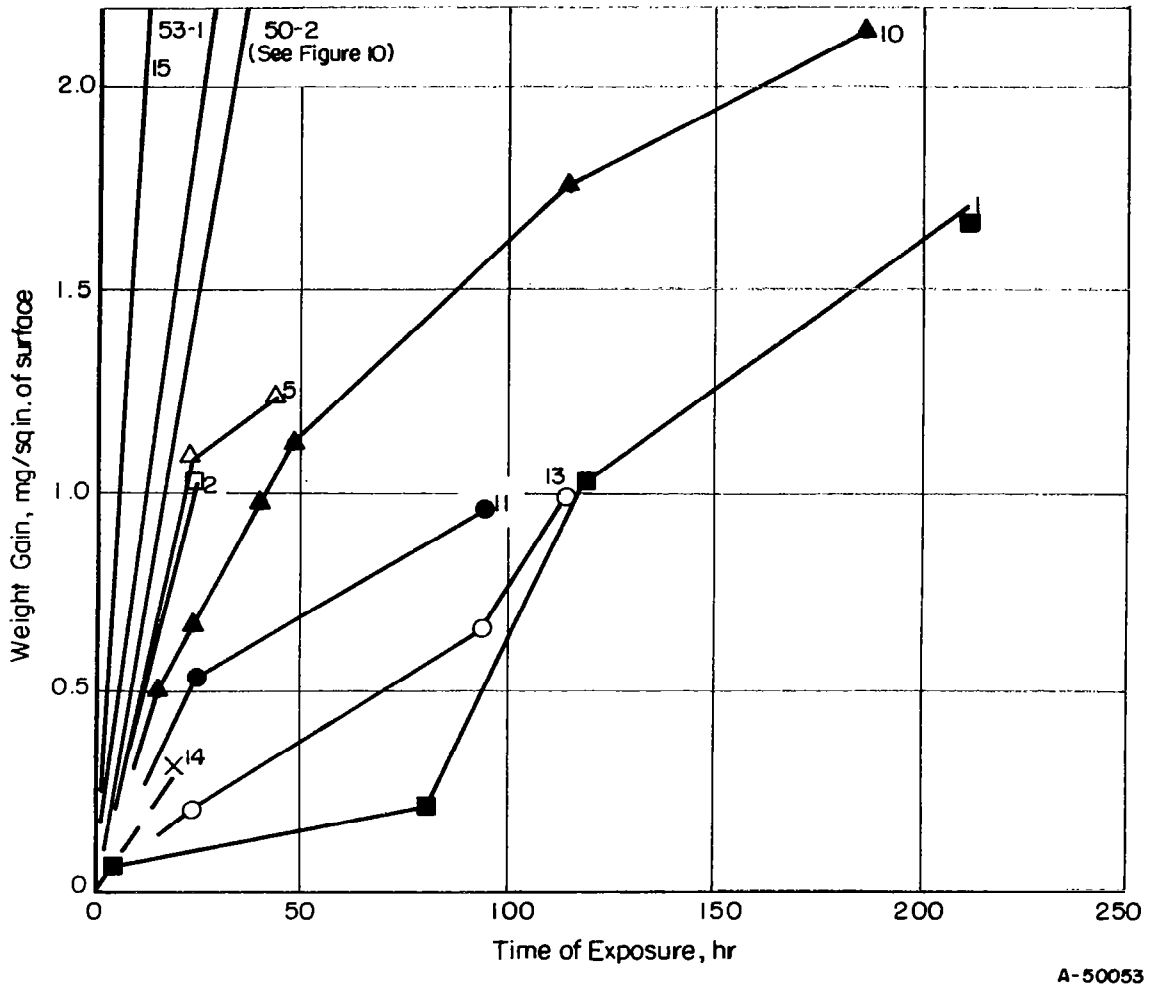
Some needlelike crystals developed on the surfaces of these samples, particularly at the edges, but the inner turns of the modules were not expanded as much as seemed desirable. Samples 11 and 12 were then constructed for tests at slower rates of reaction (lower temperatures) in an attempt to obtain better surface expansion. The two samples were treated together to provide a check on the reproducibility of the results. The temperature was raised to 146°C, and a flow of gas containing equal parts of H_2S and air was passed through the system at a total flow rate of about 1 liter or more per minute. After 16 hours of treatment, the samples were cooled and weighed. Calculations showed that Sample 12 had been sulfided to a level representing 13.0 per cent conversion of the silver to silver sulfide. Sample 11 showed 10.8 per cent conversion. The two samples were returned to the system and exposed under the same conditions for 72 hours. During this period the temperature control failed, so that the samples were not at temperature for the full period although the flow of gas continued. The two samples were again returned to the system for another 72 hours at a temperature of 150°C with the same gas flow and composition. At the end of these three exposures the conversion was 57.0 per cent for Sample 12 and 49.0 per cent for Sample 11.

The samples were then exposed to a flow of humidified hydrogen gas at about 630°C for 23 hours. After both were cooled and weighed, calculations indicated that Sample 12 had 3.5 per cent of its silver in the form of silver sulfide and that 3.0 per cent silver sulfide remained in Sample 11. Both samples were re-exposed at 695°C to hydrogen for 18 hours, after which time weight differences indicated 0.4 per cent silver sulfide in Sample 12 and 2.4 per cent in Sample 11. The reduction process was terminated.

The appearance of the samples supported the interpretation that Sample 12 was somewhat more completely regenerated to silver than was Sample 11. A few blackened areas remained on the outer turn of Sample 12, and the discoloration on Sample 11 was somewhat greater in area. Examination of the inner structure of the silver between the edges of the turns at the ends of the samples showed that a mass of needle-like projections of metallic apparance extended between turns. No examination was attempted in the interiors because they were to be used in further tests. Conversions of about 50 per cent, as arbitrarily selected for these samples, were believed reasonably certain to leave a coherent supporting structure of unconverted foil. It was observed, however, that the external dimensions of the cylindrical coils were reduced slightly as though there had been some collapse of the individual turns inside. The expanded structure was prone to flake slightly with possible loss of material as small particles. Although the expanded surfaces were not necessarily in optimum condition, it was decided that these samples would permit qualitative evaluation of any advantages obtained by expanding the silver surface. The length of time required in these tests to produce fibrillated silver was regarded as a considerable disadvantage, and it was decided that this treatment would be deleted from the preparation steps if possible.

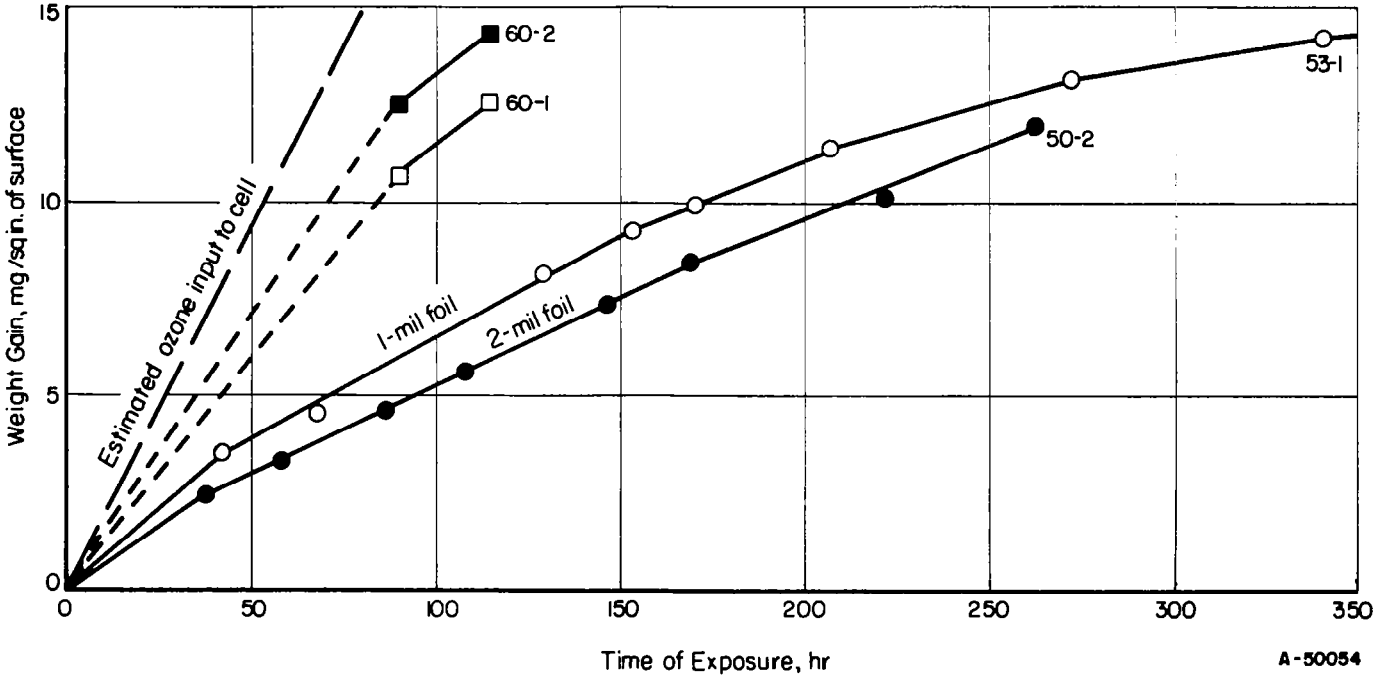
Oxidation of Silver With Ozonized Oxygen. – The progressive gain in weight of modules exposed to ozonized oxygen is summarized graphically in Figures 9 and 10. Figure 9 illustrates a number of exploratory experiments in which modules that had been prepared with various surface treatments were oxidized under different conditions of humidity and temperature. Since there were some differences in the amount of foil contained in the various modules, the weight gains are presented on a common basis of weight per unit area of exposed surface of foil. The curves of Figure 9 show that the rate of weight gain tends to decrease as the total amount of oxide formed increases.

Surface preparation has little effect on the rate of oxidation or the total amount of oxide that can be formed. Temperatures either below or



Sample	Surface Preparation	Oxidation Cond.
1	Expanded, pierced	80°C, dry gas; then at 80 hr humidified gas
2	Ditto	13°C, wetted foil + hydrogen
5	"	26°C, humidified gas
10	Expanded	25°C, humidified gas
11	Expanded, pierced	11°C, wetted foil + hydrogen
13	Scratched, pierced	Ditto
14	Expanded, pierced	10°C, wetted foil + hydrogen
15	Scratched, pierced	26°C, wetted foil + hydrogen
50-2	Heated in air, pierced	Ditto
53-1	Heated in air	"

FIGURE 9. OXIDATION OF FOIL MODULES WITH OZONIZED OXYGEN



Sample	Dimensions, in.	Spacer	O_3 Conc., wt. %	Surface Preparation	Oxidation Cond.
● 50-2	10 x 3 x 0.002	Fiber	0.1	Pierced, heated in air	26°C, wetted foil + hydrogen
○ 53-1	10 x 3 x 0.001	Fiber	0.1	Heated in air	Ditto
□ 60-1	10 x 3 x 0.002	Fiber	Unknown	Pierced, heated in air	"
■ 60-2	10 x 3 x 0.002 +10 x 0.5 x 0.002	Foil	Unknown	Pierced, heated in air	"

FIGURE 10. OXIDATION OF FOIL MODULES WITH OZONIZED OXYGEN

above room temperature do not give higher rates and more oxide than oxidation at room temperature. Room-temperature oxidation is more convenient and was used after it was shown to be effective. Sample 1 shows that humidifying the gas stream increases the oxidation rate above that initially measured with a dry-gas stream. Therefore, in later experiments the gas was humidified and in some instances the sample was wetted before placing it in the test apparatus.

The four modules which exhibited the highest initial rates of oxidation, Numbers 5, 15, 50-2, and 53-1, differed in construction from the tightly wound cylinders 3 inches long that were made up according to the design of Figure 2b. In Number 5 the 3-inch pierced foil strip was folded lengthwise and then rolled into a cylinder 1.5 inches long. Number 15 was rolled from a 2-inch foil strip into a cylinder 2 inches long. Numbers 50-2 and 53-1 were cylinders rolled from 3-inch foil with a glass-fiber spacer between turns.

The highest oxidation rate shown by Number 15 did not give an adherent oxide. The upstream edges of the foil tended to disintegrate during oxidation, and the oxide layer was mechanically weak and flaky. From these experiments it was concluded that a relatively open structure of the module was required for effective oxidation, but the initial oxidation rate must be limited to give a satisfactory sorbent.

Figure 10 shows again the data for Samples 50-2 and 53-1 plotted on a different scale to show the total weight increase. These modules differed only in the thickness of the foil used and showed no significant difference in oxidation rate. Both used a glass-fiber mat to maintain the spacing between turns, and there was a question of whether the glass-fiber mat structure or the increasing spacing it produced was important for relatively rapid and complete oxidation.

Accordingly, a second pair of specimens was prepared which differed only in the use of a narrow foil spacer in Number 60-2 as compared with a glass-fiber spacer in Number 60-1. Figure 10 shows the weight increases during the oxidation. For the first 90 hours of exposure to the ozone stream the experiment was left unattended over a weekend, and the ozone concentration varied in an unknown way. This occurred because the oxygen supply approached exhaustion, and the rate of flow decreased. Since the ozonizer continued to operate, the concentration of ozone in the flowing stream undoubtedly increased to higher levels as the flow velocity dropped. Nevertheless, the two samples appeared to have no significant difference in oxidation results because of the difference in spacers. Also, both samples appeared to exhibit a higher rate of oxidation than any previous sample after the ozone

concentration was returned to normal during the final 22 hours of exposure shown as the solid portions of the two curves.

The data have been examined for consistency by estimating the weight increase that would be observed if all the ozone reached the silver surface and reacted. The ozone decomposes during reaction to release an active oxygen atom and simultaneously forms an oxygen molecule:

$$O_3 \rightarrow O^{\cdot} + O_2.$$

The active atom combines directly with the silver and increases the weight of the module.

The oxidizing gas was ozonated to contain 0.1 weight per cent O_3 and then was introduced into the oxidation cell at a rate of 400 cc per minute. This is equivalent to introducing ozone of a rate of 34.2 mg per hour, or 11.4 mg of active oxygen atoms per hour. Sample 50-2 with 60 sq in. of surface area could gain weight at a rate of no more than 0.19 mg per sq in. of surface per hour if all the active oxygen reacted. This maximum weight gain is plotted as the estimated ozone input at the left of Figure 10. Comparison of the slopes of the experimental and the calculated maximum curves indicates that about one-fourth of the ozone generated reacted with Sample 50-2 at the silver surface under experimental conditions.

Sample 50-2 was examined after oxidation to determine how much of the metallic silver remained unreacted. The coil was opened, and practically all of the friable oxide layer was removed from the metallic silver base by rubbing and gentle scraping. Initial weight of the silver foil was 9.43 g, and 4.64 g of foil remained unoxidized. By difference, 4.79 g was oxidized. Experimentally, the sample gained 0.724 g during oxidation. Conversion of the oxidized silver to AgO would produce a calculated weight gain of 4.79 x 16/108 = 0.71 g, where the ratio 16/108 is the ratio of molecular weights of O and Ag. The close agreement between calculated and observed gains supports the assumption that AgO is the product of the reaction between ozone and silver.

Similar calculations of the extent of conversion of Sample 53-1, based on the measured weight increase, indicated that over 90 per cent of the silver was oxidized to AgO. The weight increase was greater than would have been possible if the silver was oxidized only to Ag_2O.

The rate of oxidation, Figure 10, decreases with time, presumably because the ozone oxidant reaches the surface more slowly through the layer of oxide previously formed. The rate was almost zero after 350 hours

(not shown) because the silver still available for oxidation is approaching zero. This sample was not examined but was reserved for later studies of CO_2 sorption.

Electrolytic Expansion and Oxidation of Silver. – In a pilot experiment a strip of perforated silver foil 19 x 1 x .002 inches was coiled into a cylinder about 0.75 inch in diameter and 1 inch long and bound with several turns of silver wire to make contact for surface expansion by electrolytic treatment. Table 1 shows the conditions of treatment.

TABLE 1. ELECTROLYTIC SURFACE EXPANSION OF COILED SILVER FOIL

Conditions: Electrolyte, 1 part 37% HCl + 9 parts H_2O
Room temperature
Constant current, 0.024 amp/sq in.

	Time, min		Cutoff Potential, volts	
Cycle	Anodic	Cathodic	Anodic	Cathodic
1	15	13	+0.67	-0.52
2	14	17	+0.68	-0.53
3	14	22	+0.76	-0.54

The coil was removed from the electrolyte, rinsed in running water, and dried at 110°C before weighing. It was noted that the rinse water was clouded by particles loosened from the surface of the foil.

The coil was oxidized by anodizing the surface in a 30 per cent solution of KOH at room temperature. A constant current of 0.230 amp was maintained for 150 min, when the potential had increased to +0.44 v. Current was then reduced to 0.115 amp at +0.40 v and maintained for an additional 36 min, when the potential had risen to +0.52 v.

The coil was rinsed in water, dried, heated, and weighed after each treatment. Table 2 shows the treatments and corresponding weights. The coil was not processed further.

TABLE 2. DRYING AND HEAT TREATMENT OF PILOT COIL

Treatment	Coil Weight, g	Weight Change, g
Initial	6.420	--
Surface expanded, rinsed, and dried 1.5 hr at 110°C	6.392	-0.028
Oxidized, stored in desiccator 90 hr	6.541	+0.149
Heated 2.5 hr in air at 110°C	6.531	-0.010
Stored in closed container 14 days	6.542	+0.011
Heated in dry flowing air 9 hr at 200°C (apparatus Figs. 3 & 4)	6.482	-0.060
Net weight change		+0.062

Sample 62-1 was assembled from two strips of perforated foil 10 x 3 x 0.002 and 10.5 x 0.5 x 0.002 inches. The narrow strip was laid coaxially on the wide strip, and the two were rolled together into a cylinder 3 inches long and about 0.8 inch OD, with 7 turns spaced 0.05 inch apart. Table 3 shows the conditions for surface expansion of the sample.

The module was rinsed well with running water after surface expansion. The water appeared more heavily clouded with loosened silver particles than the rinse water from the pilot sample. The coil was not dried and weighed as before but was transferred to the oxidizing bath after rinsing. The module was anodized in 30 per cent KOH at a constant current of 0.380 amp for 3.5 hr, when the potential was +0.38 v. The module was rinsed, dried, and heated in preparation for sorption tests. Table 4 shows the drying and heat treatments and the weights after each treatment.

TABLE 3. ELECTROLYTIC SURFACE EXPANSION OF SAMPLE 62-1

Conditions: Electrolyte, 1 part 37% HCl + 9 parts H_2O
Room temperature
Constant current, 0.021 amp/sq in.

Cycle	Time, min		Cutoff Potential, volts	
	Anodic	Cathodic	Anodic	Cathodic
1	20	23	+0.66	-0.50
2	19	26	+0.72	-0.52
3	19	32	+0.74	-0.53

TABLE 4. DRYING AND HEAT TREATMENT OF SAMPLE 62-1

Treatment	Coil Weight, g	Weight Change, g
Initial	11.043	--
Expanded, oxidized, stored in desiccator 66 hr	11.251	+0.208
Stored in closed container 9 days	11.247	-0.004
Heated in dry flowing air 9 hr at 200°C	11.095	-0.152
Net Weight change		+0.052

Sample 62-1 was used in tests of CO_2 sorption and regeneration, as described later. It now appears that it would have been useful to have weighed the sample following surface expansion to determine the amount of silver that was lost during rinsing. This was not done because it was believed, at the time, that the weight loss of 0.028 g in the pilot experiment was not significant. Furthermore, the decrease in weight of the pilot sample during heat treatment at 200°C (-0.060 g) and in similar treatment of Sample 62-1 (-0.152 g) is not satisfactorily explained by assuming a

conversion of AgO to Ag_2O, with loss of a part of the fixed oxygen. The net weight increase of Sample 62-1 during preparation (+0.052 g) is insufficient to account for the capacity for CO_2 sorption measured in later experiments. A direct determination of fixed oxygen by decomposing the oxide would have destroyed Sample 62-1. Clearly, additional experiments will be required to clarify the oxidation and activation reactions occurring during the preparation of electrolytically oxidized sorption modules.

Oxidation of Silver With High-Pressure Oxygen. – A strip of silver foil 3 x 12.8 x .002 inches was embossed and perforated, and wound into a cylindrical module. It weighed 12.065 g after it had been heated for 5 minutes at 500°C in air to remove any volatile surface contaminants.

Table 5 shows the conditions used and the results obtained in three successive measurements of oxidation on the same module. In Experiment 1 at 237°C the weight of the module increased only 0.001 g after 3.8 hr exposure. Experiment 2 produced an added weight gain of 0.011 g in 3.5 hr at 305°C. In the third experiment the module was wetted with 2 ml of distilled water before the bomb was closed, and the weight decreased 0.007 g after 4.1 hr. Presumably the presence of water vapor in the oxygen atmosphere induced decomposition of some of the oxide formed in the preceding experiments.

TABLE 5. EXPOSURE OF SILVER FOIL TO HIGH-PRESSURE OXYGEN

Experiment	Test Conditions				Weight Change, g
	Time, hr	Pressure Range, psi	Temperature, °C	Water Vapor	
1	3.8	280-249	237	No	+0.001
2	3.5	286-255	305	No	+0.011
3	4.1	325-301	304	Yes	-0.007

The specific weight increase during Experiment 2 was 11/77 = 0.14 mg per sq in. or 0.04 mg per sq in.-hr. Specific weight increase during ozonized oxygen treatment of Sample 53-1 was 3.6 mg per sq in. in 42 hr, or 0.09 mg per sq in.-hr, as shown on Figure 10. Specific weight increase during electrolytic oxidation of Sample 62-1 was 208/70.5 = 2.95 mg per sq in. in 4.5 hr, or 0.65 mg per sq in.-hr.

The pressure in the heated bomb decreased during the course of the experiments by an amount which was equivalent to the reaction of about 760 mg of oxygen to form a nonvolatile oxide. At most, 11 mg reacted to form silver oxide; the remainder of the oxygen consumed probably reacted with the bomb wall to form iron oxide.

The objective of these exploratory experiments was to find a rapid method for oxidation of silver. Since the oxidation rate was substantially less than that of the other two methods, the study was discontinued.

Sorption of CO_2 and Regeneration of Silver Oxide

Long-Term Cyclic Sorption-Desorption With Flowing Gas. - Sample 12 was tested to determine whether a gross deterioration in sorption capability would occur because of sorption-desorption cycling. Preliminary measurements by batch-flow sorption indicated that a gas mixture of 5 per cent CO_2 in oxygen could be reduced to a negligible concentration of CO_2 after a number of passes over Sample 12. Accordingly, the sample was carried through a series of six consecutive continuous-flow sorption and desorption cycles.

Table 6 gives the weight changes observed at the end of each phase of the six cycles. The times of the sorption and desorption phases are listed in Columns (2) and (5), with the corresponding weights gained and lost in adjacent Columns (3) and (6). In all instances the phase was continued for a longer time period than would be needed in bringing about a substantial reduction in CO_2 concentration. This was to allow the sorbent time to reach equilibrium with the test gas before terminating the sorption phase. Similarly, it was brought to equilibrium with nitrogen before terminating each desorption phase.

Column (4) gives two results of the calculated cumulative difference in CO_2 content between gas feed and effluent. This is not a very precise measurement in the sorption phase, involving the determination of small differences in concentration by the Orsat method. Therefore this measurement was not always made. However, in the two phases reported, the CO_2 sorbed appears substantially less than the total weight gained by the sorbent. The difference may arise from the simultaneous sorption of water vapor from the gas stream.

TABLE 6. CYCLIC SORPTION-DESORPTION[a] STUDIES WITH SAMPLE 12

	Sorption			Desorption			
Cycle (1)	Time, hr (2)	Weight Gain, mg (3)	CO_2, mg (4)	Time, hr (5)	Weight Loss, mg (6)	CO_2, mg (7)	O_2, mg (8)
1	160	129	--	165[b]	137	51	51
2	18	80	--	28	78	71	5
3	168	144	--	74	156	118	9
4	91	147	94	70	149	108	7
5	20	105	76	26	96	74	9
6	164	118	--	23	124	106	4

(a) Conditions for sorption: room temperature, 5% CO_2, 95% O_2 water vapor at 20 cc per min to CO_2 saturation.
Conditions for desorption: 210°C, intermittent nitrogen flush to negligible CO_2 content.
(b) First thermal treatment; high oxygen desorption shows that this is an activation phase.

Columns (7) and (8) give the measured amounts of CO_2 and oxygen desorbed in each cycle. The measured weights of these gases are always less than the total weight loss of the module, presumably because of desorption of water vapor. This module had not been activated by preheating before the sorption phase of the first cycle, because the necessity for activation was not recognized. The comparatively large amount of oxygen released during the first desorption phase may have come from the decomposition of AgO by the reaction $2AgO \rightarrow Ag_2O + 1/2\,O_2$. The fact that some desorbed CO_2 was also recovered presumably means that some Ag_2O was formed spontaneously during or after the primary oxidation to AgO, perhaps by the secondary reaction $AgO + Ag \rightarrow Ag_2O$.

The traces of oxygen found in the desorbed gases in Cycles 2 through 6 may be derived from decomposition of Ag_2O under heating, but this interpretation is not necessarily correct. The oxygen might have entered the system by air leaks in the gas transfer system, because a negative pressure was used to pull the carrier gas from storage through the test cell into the burette.

Three other modules in addition to Sample 12 were examined for weight gains and losses in a manner similar to the study of the cycling of Sample 12. The data are limited, as shown in Table 7, but they indicate by the larger weight changes that higher capacities can be achieved in modules of about the same external dimensions.

TABLE 7. ANALYSIS OF CYCLING CHANGES IN SORPTION MODULES

			Sorption			Desorption			
Sample	Cycle	Test Gas	Time, hr	Weight Gain, mg	CO_2, mg	Time, hr	Weight Loss, mg	CO_2, mg	O_2, mg
53-1	A	5.5% CO_2	70	40	None	5	372	--	(a)
	1	5.5% CO_2	10	815	720	15	531	465	8
60-2	1	1% CO_2	165	1001	--	Experiment terminated			
62-1	1	1% CO_2	99	517	(175)	22	542	494	6
62-1	2	1% CO_2	53	468	390	Experiment terminated			

(a) This was an activation treatment in which oxygen was evolved so rapidly that it could not be measured quantitatively in the apparatus.

When the test on Sample 53-1 was started, the meaning of the results from the first cycle of Sample 12 was not yet clear. Sample 53-1 was not activated by preheating before sorption was attempted in Cycle A. No sorption of CO_2 could be detected by analysis of the effluent gas, and the total weight gain was only 40 mg after 70 hr. This sample had been practically completely converted to AgO, by oxidation, according to results reported in Figure 10, and presumably no Ag_2O was present to adsorb CO_2. When the module was carried on to the first desorption phase, oxygen was evolved so rapidly that it could not be analyzed quantitatively. Thus, this phase was effectively an activation treatment to convert AgO to Ag_2O, and subsequent modules were activated similarly before sorption of CO_2 was attempted.

The low value indicated for CO_2 sorption by Sample 62-1 in Cycle 1 was caused by difficulties in the Orsat gas-analysis apparatus, rather than by poor sorption characteristics. Sorption was normally high during Cycle 2.

The amounts of oxygen found in the gas desorbed from Samples 53-1 and 62-1 were similar to the amounts found during desorption phases of Sample 12. Similar amounts of oxygen would not be expected if the oxygen was formed by decomposition of different quantities of silver oxide, decomposing at a constant rate controlled by the temperature of desorption.

Table 8 gives a summary of the construction and composition of these three modules, with estimated amounts of fixed oxygen present as Ag_2O. Fixed oxygen is present in the three modules in the ratios of about 1:2:4. The large differences in oxide present is the main basis for the interpretation that the similar amounts of oxygen found may be from air leakage into the system during the analyses.

Table 8 includes data for two additional modules for later reference.

TABLE 8. CONSTRUCTION AND COMPOSITION OF SORPTION MODULES

Sample:	12	53-1	60-1	60-2	62-1
Construction					
Spacer	None[a]	Glass fiber, 4 g	Glass fiber, 2.1 g	Silver strip	Silver strip
Dimensions					
length, in.	31.5	10	10	10;10.5	10;10.5
width, in.	3	3	3	3;0.5	3;0.5
gage, in.	0.001	0.001	0.002	0.002	0.002
area, sq in.	189	60	60	70.5	70.5
Sorption Capacity					
Silver, g	16.2	6.3	9.1	11.0	10.9
Pretreatment	Sulfide	Thermal	Thermal	Thermal	Electrolytic
Oxidation	$O_2 + O_3$	$O_2 + O_3$	$O_2 + O_3$	$O_2 + O_3$	Electrolytic
Fixed oxygen, g[b]	0.09_3	0.4_3	0.4_8	0.5_1	0.2_1
Conversion, percent	8	92	71	63	25
CO_2 capacity, g	0.26	1.2	1.3	1.4	0.58

(a) Silver foil in all samples except 53-1 was embossed and pierced with holes on 1/8-inch centers, leaving burrs about 0.045 inch high surrounding each hole. About 20 per cent of foil area is convered to burrs that serve as spacing elements.

(b) There is uncertainty as to what part of the weight gain observed during oxidation should be considered as "fixed oxygen" in Ag_2O and thus available for CO_2 sorption. These are minimum amounts estimated by consistent calculation procedures.

Short-Term Sorption by Three Modules. - The short-term behavior of a freshly prepared or a freshly regenerated sorption module is of practical interest because in actual use the sorbent will be cycled before it is completely saturated with CO_2. It is desirable that the sorbent completely remove CO_2 from the flowing gas and continue to do so until a maximum part of its sorption capacity is utilized. Therefore, the sorption characteristics during the first few hours of exposure were studied.

Figure 11 shows the sorption characteristics at room temperature of Sample 12 over the first 2 hours of exposure during the sorption phases of sorption-regeneration Cycles 2 and 5. With 5.6 per cent CO_2 in the test gas, this module in Cycle 2 passed 3.6 per cent CO_2 in the effluent after 29 minutes of flow and after it had reached a saturation of less than 10 per cent of the calculated CO_2 capacity. The rate of sorption decreased with time, and the amount sorbed approached a maximum of 15 per cent of theoretical saturation after about 2 hours. The data obtained in Cycle 5 demonstrated an improvement in sorption characteristics. The earlier sorption limit of 15 per cent saturation was passed in 1.3 hours, and sorption reached 25 per cent saturation in less than 3 hours.

Figure 12 shows the short-term sorption performance of Sample 53-1, plotted on a scale reduced tenfold compared to Figure 11. The effluent CO_2 concentration rose slowly and reached 1.5 per cent after the module was more than 40 per cent saturated with CO_2.

The next module studied was Sample 62-1, which had been oxidized electrolytically. Figure 13 shows that sorption from a stream of dry gas containing about 1 per cent CO_2 was not very effective. The module ceased to pick up CO_2 after it was only about 5 per cent saturated, and so it was returned to the apparatus for sorption in a humidified stream of the same test gas. With water vapor present, Sample 62-1 was an effective sorbent, and no CO_2 could be detected in the effluent when the short-term test was terminated after almost 6 hours of exposure. At this point the sample was about 25 per cent saturated - 5 per cent from the dry-gas stream and 20 per cent from the humidified stream. The percentage saturation was calculated from the theoretical CO_2 capacity of the oxide present, based on net weight gain of the module following oxidation and activation, and from the amount of CO_2 actually adsorbed, based on the cumulative difference between influent and effluent CO_2 determined by gas analysis. The sorption exposure was continued until complete saturation was attained, as indicated by equal influent and effluent concentrations of CO_2. Then the module was thermally regenerated. After regeneration, it was returned to the sorption apparatus and was checked again at the same flow rate in Cycle 2 to show that it retained a CO_2 sorption capability after regeneration.

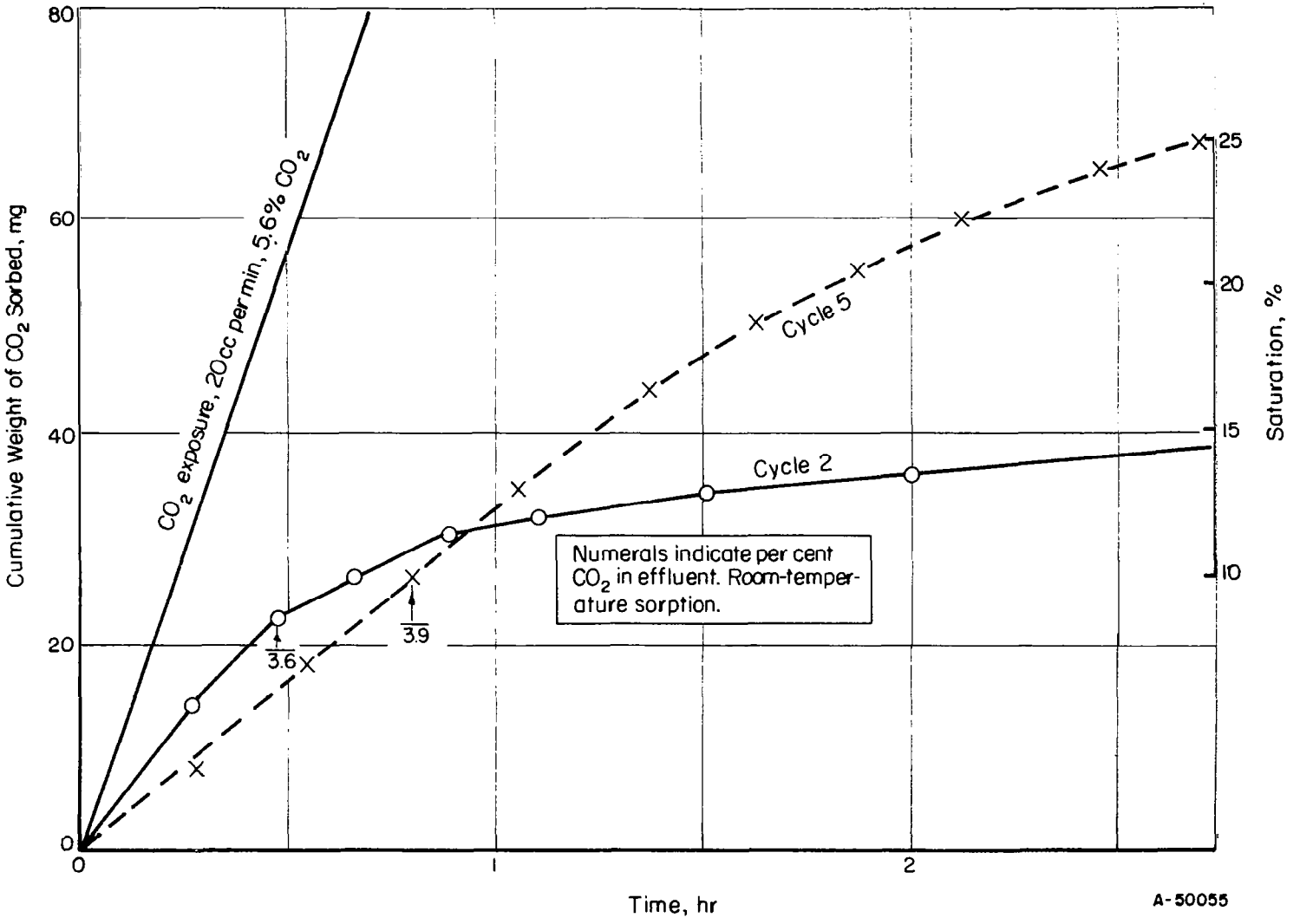


FIGURE 11. CO_2 SORPTION BY SAMPLE 12

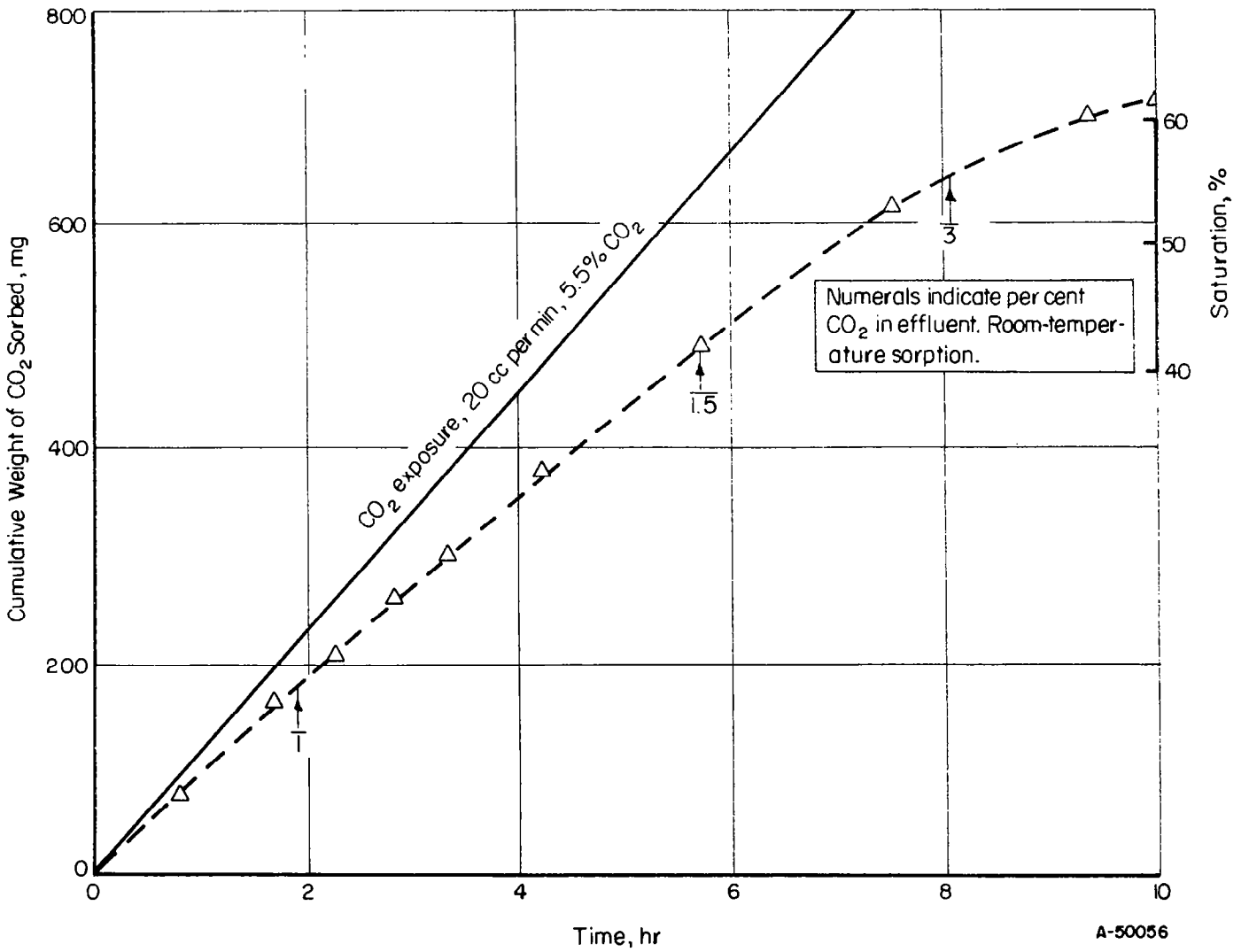


FIGURE 12. CO_2 SORPTION BY SAMPLE 53-1

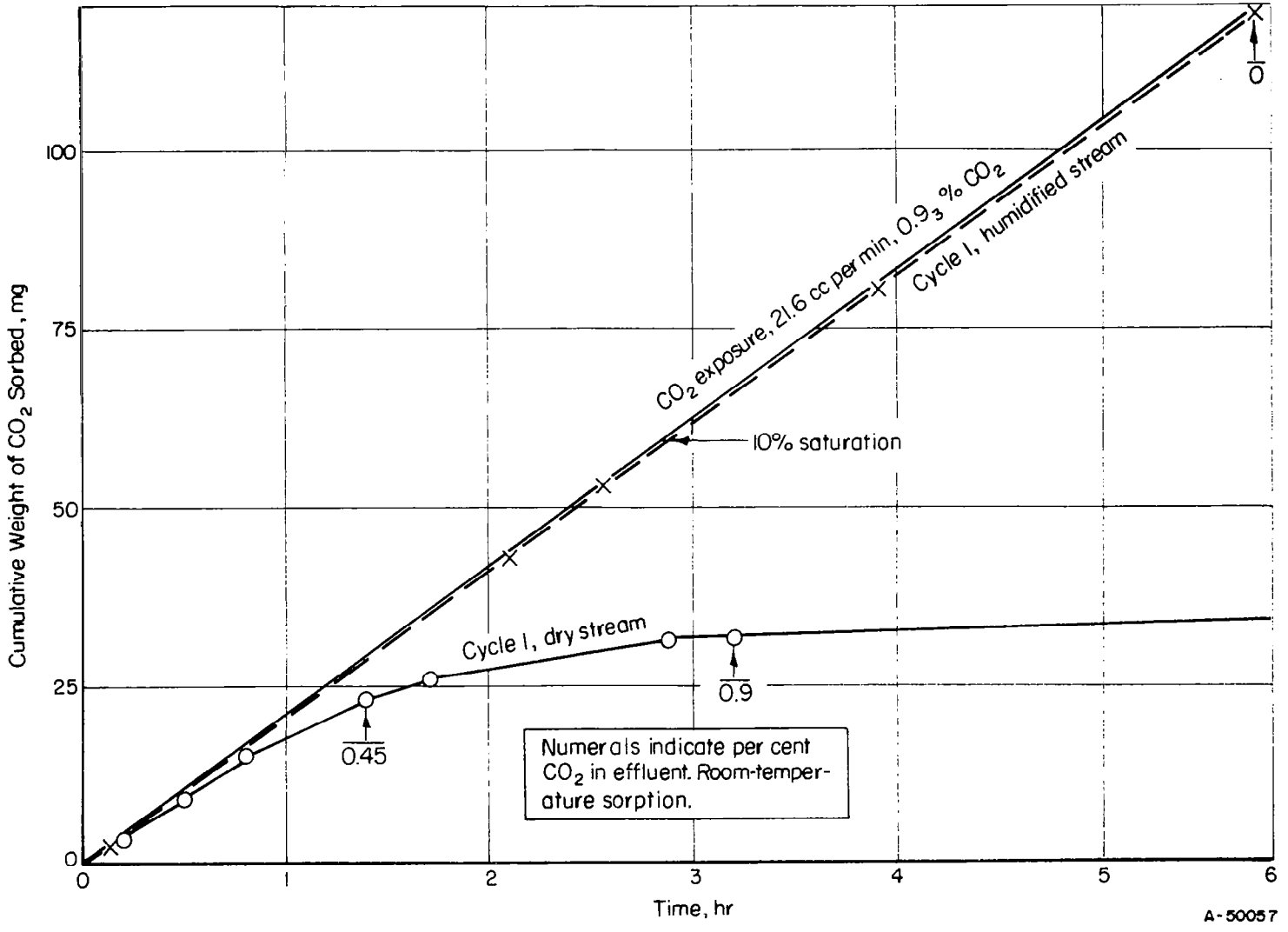


FIGURE 13. CO_2 SORPTION BY SAMPLE 62-1 IN CYCLE 1

Figure 14 shows the results of additional short-term tests at higher flow rates in Cycle 2. Following the initial check at 21 cc per minute, the flow rate was increased by increments to 48, 100, and 175 cc per minute, as shown on the CO_2 exposure curve of Figure 14. It appears that the module was an effective sorbent at 48 cc per minute, removing a substantial part of the CO_2 input, and leaving only 0.15 per cent CO_2 in the effluent. Further increases in flow rate did not increase the rate of CO_2 sorption appreciably, because the concentration of CO_2 in the effluent rose correspondingly, as shown on the sorption curve. Following the test at the highest flow rate, the gas flow was reduced again to approximately its initial value and sorption was continued for 5-1/4 hours. The module reached over 50 per cent CO_2 saturation with 0.05 per cent CO_2 in the effluent gas. At this point the experiment was terminated, and the module was submitted to the Sponsor for his examination and test.

Short-Term Desorption of CO_2 During Regeneration. - The gases released during regeneration of Sample 62-1 were examined by measuring the increments of CO_2 picked up in the carrier gas at 20-minute intervals. Figure 15 shows the data obtained. These are the data that have already been summarized in Table 7, which showed that 494 mg of CO_2 was recovered in the first desorption phase of 22 hr. Table 8 showed a calculated CO_2 sorption capacity of 580 mg for this module.

The most widely scattered data points for increment size are those that were measured following periods in which the apparatus was brought up to temperature at the beginning of the experiment and after two overnight interruptions at 3.3 and 13.0 hr. In each case there was a small increment, followed by a large increment. The other data points show less scatter, and a definite pattern is evident in the incremental evolution of CO_2. The size of the increments decreases quite regularly until the cumulative amount of CO_2 evolved approaches 50 per cent of capacity. Then there is a flattened portion of the incremental curve, which persists until the cumulative amount reaches slightly over 60 per cent. After this, the increments decrease regularly again until they approach zero. This pattern of a three-segment curve is not quantitatively significant, since it probably reflects the arbitrary choice of a 20-minute interval between analyses. During each successive incremental evolution of CO_2 into the carrier gas, the CO_2 concentration approaches equilibrium more quickly, and the amount collected is reduced. The cumulative curve shown on Figure 15 is of more practical significance, because it shows that a substantial proportion of the sorbed CO_2 is released at reasonably rapid rates until the total amount evolved approaches 70 to 80 per cent of the sorption capacity.

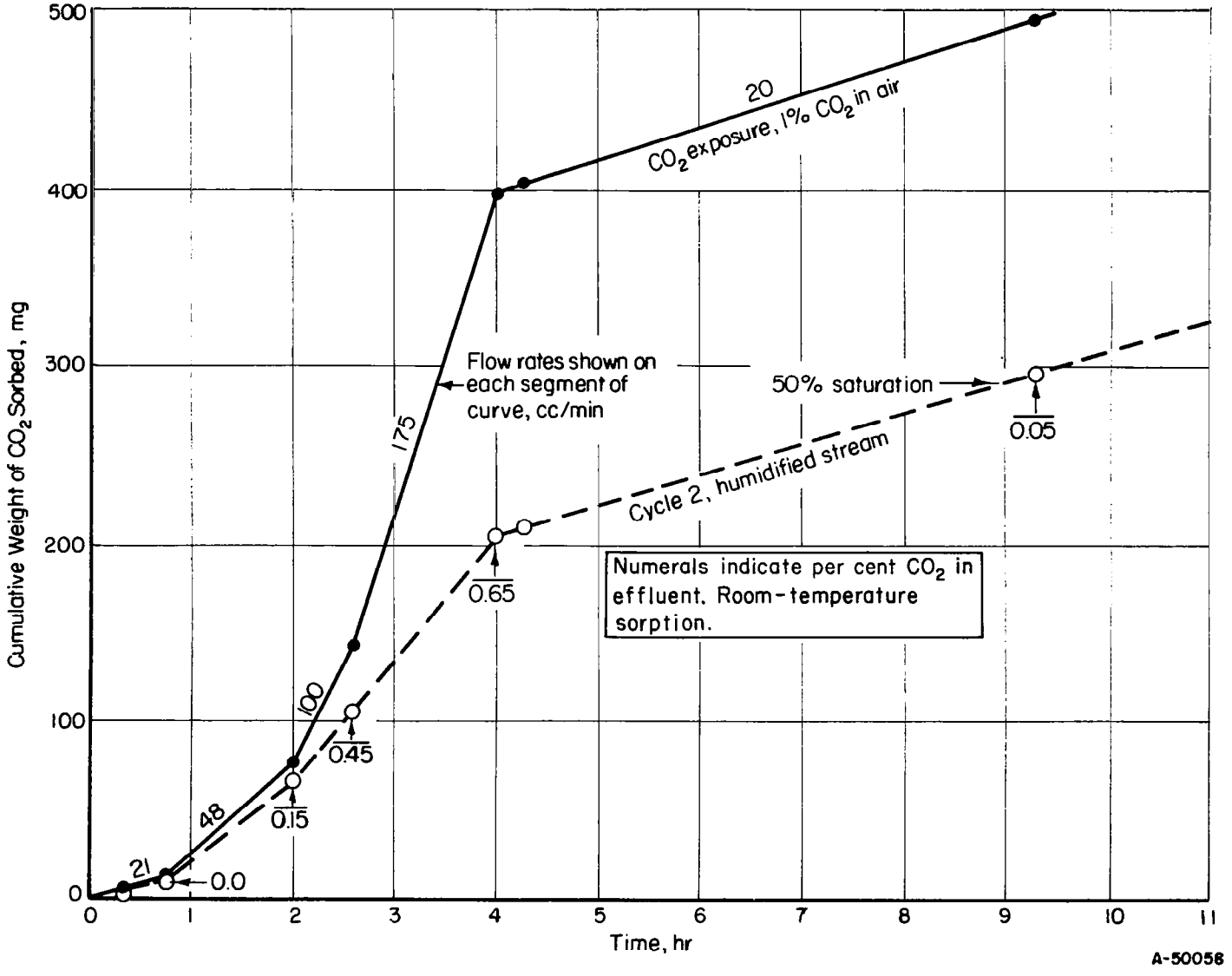


FIGURE 14. CO_2 SORPTION BY SAMPLE 62-1 AT HIGH FLOW RATES, CYCLE 2

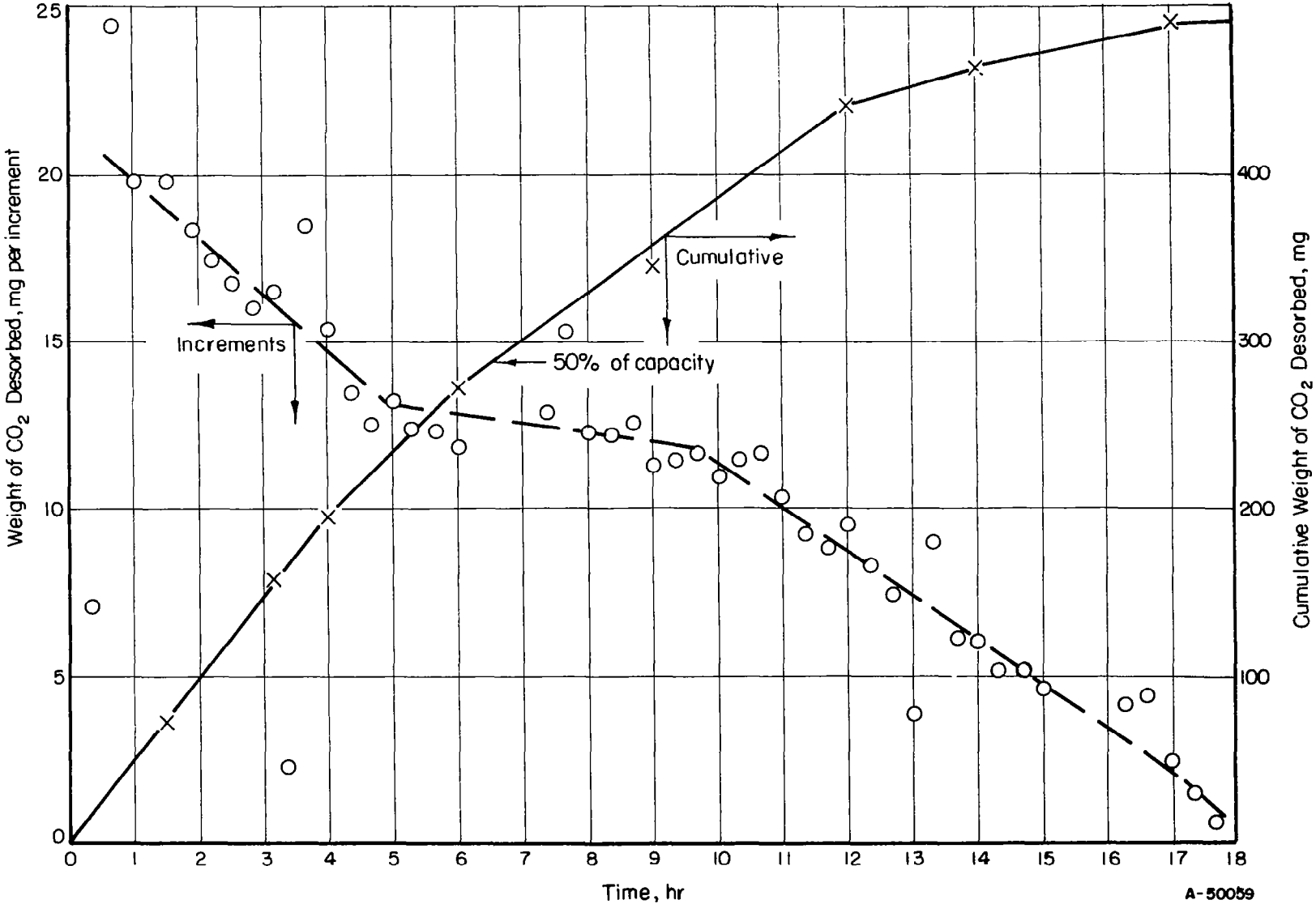


FIGURE 15. DESORPTION OF CO_2 FROM SAMPLE 62-1 DURING THERMAL REGENERATION

Sorption From Static Gas. – The rapid procedure for evaluating sorption characteristics by the change in pressure of a closed system containing a static gas sample was used to compare two modules whose sorption characteristics were already known from previous studies using Orsat analyses. These modules were Numbers 53-1 and 60-2. Sorption characteristics of Number 53-1 were shown in Figure 12. Sample 60-2 had sorption characteristics, as determined by Orsat analyses, similar to those of Sample 62-1, as shown in Figure 13. The capacity of Number 60-2 for sorbing CO_2 from a dry stream of test gas was exhausted at a low level of saturation, but sorption was complete from a humidified stream with no detectable CO_2 in the effluent. (Detailed curves for Number 60-2 have not been presented because of analytical difficulties during the test.)

Figure 16 shows comparable sorption curves from static-gas samples for the two modules. These curves are the average of three or four successive tests that showed reproducible differences in the pressure change observed when the test gas and the nitrogen were admitted alternately to the test cell after prior evacuation. The static sorption curves show the same characteristic differences between the two modules as were present in sorption from flowing gas. Module 60-2 sorbs so rapidly that a substantial amount of CO_2 is removed from the gas phase before the pressure measurement is started. The CO_2 is completely exhausted after about 7 minutes, since the curve shows almost a zero sorption rate at that time. It is known from a calculation of the free volume within the module envelope that about 0.47 cc of CO_2 is available for rapid sorption. After this amount is sorbed, the curve should flatten out, as it does. Therefore, the curve for Number 60-2 was normalized as shown by the dashed line for this sample. This brings the flat portion of the curve to the level calculated for complete exhaustion of the CO_2 content of the test gas within the module, as indicated in the auxiliary scale showing CO_2 residual concentration at the left of Figure 16.

This appears to be a convenient and reproducible method for rapid appraisal of sorption characteristics of individual modules.

CONCLUSIONS

There is no gross deterioration in the CO_2 sorption capability of silver oxide after six cycles of sorption and regeneration of a single sorption module, which was heated at 210°C for a total of 740 hr during the six desorption phases. (Table 6 and Figure 11.)

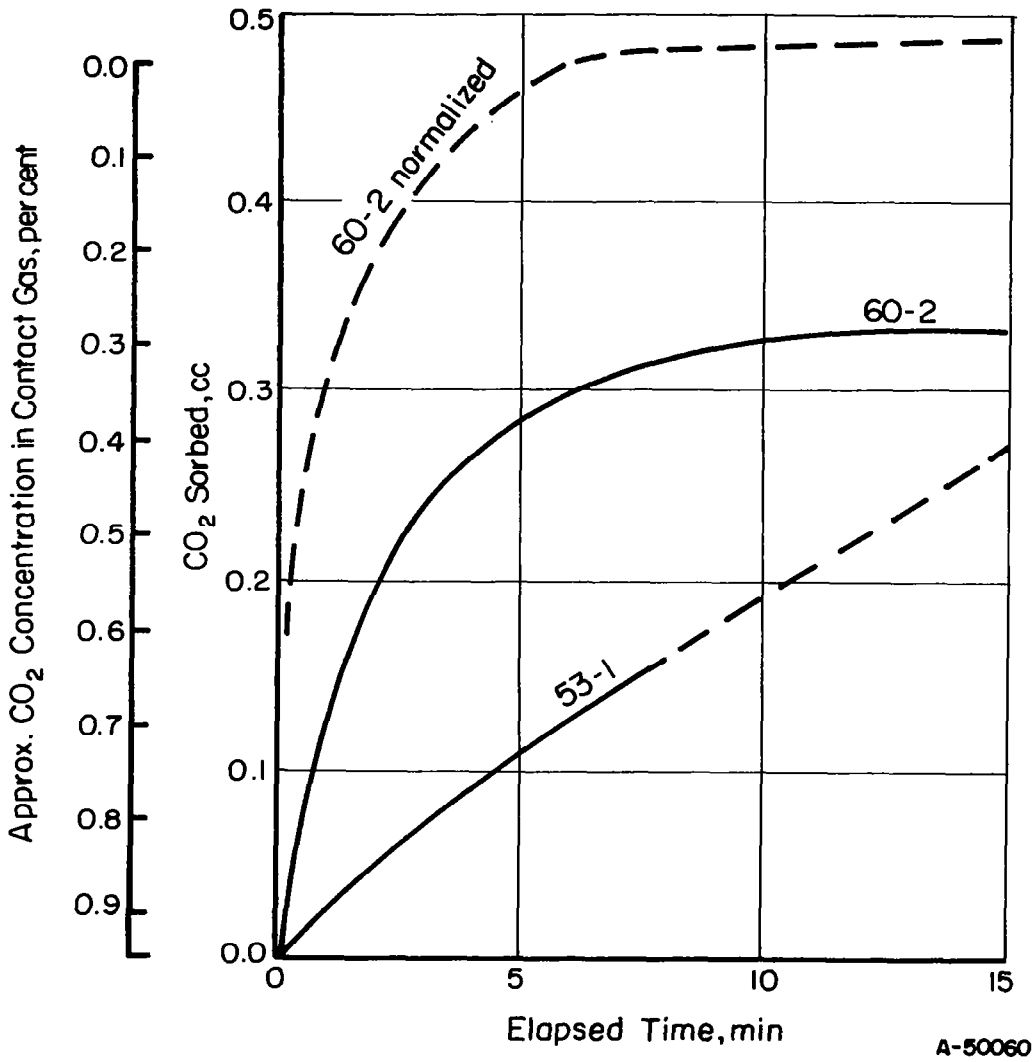


FIGURE 16. SORPTION RATE FOR CO_2 FROM A STATIC-GAS SAMPLE

Silver oxide removes substantially all the CO_2 from a humidified air stream containing 1 per cent CO_2 until at least 50 per cent of the silver oxide has been converted to silver carbonate. (Figure 14.)

Substantially all of the CO_2 sorbed can be recovered by prolonged heating. (Figure 15.)

Further improvements in mechanical stability and specific sorption capacity of the silver oxide-silver system are possible and necessary to develop a practical sorption unit.

The over-all results of this study are sufficiently promising to justify further development studies on a larger scale.

RECOMMENDATIONS

Further work is recommended in two parallel investigations. In one study a prototype unit would be assembled, using two sorption chambers, each containing multiple sorption modules, with a target capacity to remove 1 per cent CO_2 from air at a rate equivalent to the metabolic output of one man. The unit would be operated continuously, with one chamber sorbing and one chamber regenerating alternately. Instrumentation and controls would be provided for measurement of CO_2 in the effluent, for maintaining a preset flow rate of influent air containing 1 per cent CO_2, and for automatic switching and regeneration based on either a preset time period or a preset concentration of CO_2 in the effluent. Various flow rates, sorbent configurations, regeneration temperatures, and switching schedules would be studied to arrive at an optimum and compatible procedure for continuous operation over long periods at the highest efficiencies attainable with the silver oxide sorbent system. Continuous operation for up to a thousand cycles should reveal any slow changes in capacity, rate, and efficiency of CO_2 sorption and would provide engineering data for comparison with competitive sorption systems.

In order to begin the long-term tests, sorption modules would be constructed, oxidized, and activated by the best methods available, on the basis of the study of single modules described in this report. It is estimated that about 300 modules would be required. Sorption efficiency and uniformity of individual modules would be monitored by testing in the static test apparatus developed in this study (Figures 8 and 16) before assembling the modules into the prototype apparatus. It is probable that electrolytic

surface expansion and electrolytic oxidation would be used, because of the shorter time required for sorbent preparation by this method.

In the parallel study, improvements in oxidation, sorption, and regeneration procedures would be investigated, using single modules as in this study. It is probable that more rapid desorption could be accomplished at higher temperatures without reducing the capability for resorption of the regenerated modules. It is possible that resorption capability can be increased by desorption in superheated steam at one atmosphere instead of in nitrogen.

It is possible that oxidation of silver can best be accomplished by a combination of the electrolytic and ozonization procedures. An initial layer of electrolytic oxide laid down after surface expansion may permit additional oxidation in shorter times of exposure to concentrations of ozone of 1 per cent or more. A concentration of 0.1 per cent ozone was the apparent limit for direct oxidation of silver, as reported in these studies, because uneven oxidation and disintegration of the silver substrate could occur at higher concentrations or greater flow rates.

Major improvements in preparation techniques or sorption capabilities found in studies with single modules would be further tested in the prototype sorber, using multiple modules prepared by the improved methods to determine their stability over many cycles.

It is recommended that supporting studies of the role of H_2O in the sorption process and of reaction mechanisms and kinetics should be undertaken when they would be necessary or useful in determining the theoretical limits of efficiency or capacity of the practical sorption system.

REFERENCES

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(4) Drott, J., "Reaction Rate and Growth Forms in the Reaction Between Silver and Hydrogen Sulfide. I. The Influence of Water Vapor Pressure", Arkiv Kemi, 15 (14), 181-194 (1960); in English.