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CARBON DIOXIDE REDUCTION WITH ALKALI-METAL AMALGAMS

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AUGUST 1968

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Charles F. Kettering Research Laboratory
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FOREWORD

This research was initiated as an unsolicited proposal to the Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio, from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio. The proposal was implemented as a joint research effort under Air Force contract no. F33615-67-C-1333 and in support of project no. 6373, "Equipment for Life Support," and task no. 637306, "Aerospace Sanitation and Personal Hygiene." Alton E. Prince, PhD, was technical contract monitor for the Aerospace Medical Research Laboratories. Richard W. Treharne was principal investigator for the Charles F. Kettering Research Laboratory. The laboratory phase of the research at the Aerospace Medical Research Laboratories was conducted by Charles M. Cox, Chemist, Biotechnology Branch, Life Support Division.

The research performed under this contract was a continuation in part of research conducted at the Charles F. Kettering Research Laboratory by a number of investigators over a period of several years dating back to 1955. The authors wish to acknowledge the contributions of the former Charles F. Kettering Research Laboratory investigators listed here: R.M. Miller, H.V. Knorr, H.J. Eichel, C.M. Meyer, H.C. Eyster and H.A. Tanner. In particular, Mr. C.M. Meyer, currently of the Aerospace Medical Research Laboratories, served as a valuable link in the continuity of research between the Charles F. Kettering Research Laboratory and the Aerospace Medical Research Laboratories.

The authors also acknowledge the expert technical assistance of M. Cappechi, T. Shroyer, R. Davidson and E.R. Thomas of the Charles F. Kettering Research Laboratory.

This technical report has been reviewed and is approved.

WAYNE H. McCANDLESS
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ABSTRACT

The reduction of carbon dioxide (CO_2) by alkali-metal amalgams has been studied as a potential means for reclamation of CO_2 waste gas in space systems. The CO_2 reduction reactions were investigated at moderate temperatures and pressures - typically 25 to 200 C and 1 to 1.1 atmospheres. The investigations demonstrated that CO_2 can be reduced effectively by an appropriate alkali-metal amalgam system. Moreover, the alkali-amalgam expended in the CO_2 reduction process can be reclaimed by electrolysis from an aqueous or nonaqueous salt solution containing the fixed CO_2 products. The CO_2 fixation products can be drained-off or, in some cases, recycled for further reduction. In the CO_2 reduction reactions by alkali-amalgam systems, a wide variety of products ranging from simple organic acids, such as formic and oxalic acid, to totally reduced CO_2 in the form of carbon black have been identified. The types of products formed are dependent upon such factors as the type of alkali-metal amalgam used, temperature, pressure, and electrolytic reducing conditions. In electrolytic recovery of the alkali-metal amalgam from aqueous media, oxygen also is produced as a useful by-product of the CO_2 reduction system.

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SECTION I

INTRODUCTION

BACKGROUND

As early as 1868, according to Henglein (ref 1), E.Drechsel of Germany reported that carbon dioxide (CO_2) reacted with potassium amalgam at the temperature of boiling mercury (356.9 C) to form potassium oxalate. Since that time, many investigators (ref 2, 3, 4) have confirmed the formation of oxalates in comparable experiments using alkali metals or amalgams of alkali metals.

In 1955, several researchers at the Charles F. Kettering Research Laboratory (CFKRL) began to investigate CO_2 reduction by alkali-metal amalgams. The concept that the alkali-amalgam approach to CO_2 reduction appeared to present the possibility of a cyclic system for CO_2 fixation was the impetus for this research. The rationale was that if an efficient system for CO_2 reduction by alkali amalgams could be developed, the alkali amalgam expended in the reaction could be recovered by electrolysis to reduce CO_2 in a continuous cycle. In effect, then, the reduction of CO_2 appeared to be possible under relatively mild temperature and pressure conditions, driven solely by low level electrical energy. Since CFKRL has been actively engaged for several decades in photosynthesis research, the mild processes involved in CO_2 reduction by a cyclic amalgam system were of interest as a crude nonbiological system analogous to the photosynthetic process.

A considerable research effort over a period of several years was devoted by CFKRL to a wide variety of alkali-amalgam CO_2 reduction systems. R. M. Miller, C.M. Meyer, et al (ref 5) of CFKRL made a comprehensive investigation of product formation by alkali-amalgam reactions with CO_2. This work also included a study of alkaline earth-amalgam reactions with CO_2.

These authors (ref 5) reported the formation of three carbon compounds, such as tartronic acid, and higher energy products under properly controlled conditions. In addition, several attempts at the development of a cyclic CO_2 fixation system were made.

CYCLIC CO_2 FIXATION SYSTEM

A flow diagram of the basic concepts involved in the cyclic CO_2 reduction systems investigated is shown in figure 1. The CO_2 reduction reactions were studied mostly under ambient room temperature and pressure conditions - that is near 25 C and 1 atmosphere pressure. The net overall reaction desired for the process outlined in figure 1 may be described by the general equation:

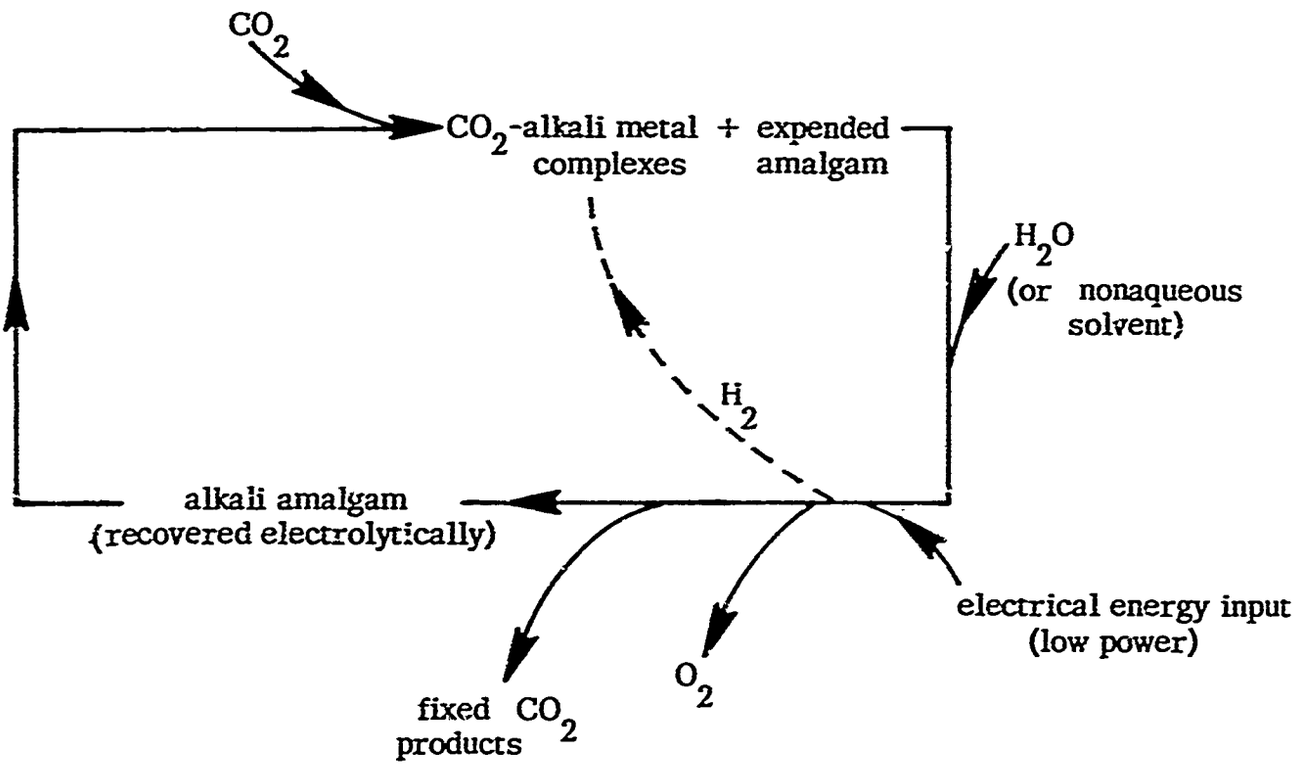

Figure 1. CO_2 Reduction or Fixation Flow Diagram

All reactions can occur under ambient room temperature and pressure conditions - that is near 25 C and 1 atmosphere pressure.

$$CO_2 + H_2O + \text{electric power} \xrightarrow[\text{alkali-amalgam}]{\text{recoverable}} \text{Fixed } CO_2 \text{ products} + O_2\uparrow$$

In this equation, any hydrogen evolved from the decomposition of water is assumed to appear as part of the CO_2 reduction products. For the recovery of the alkali-amalgam by electroysis, a nonaqueous solvent, such as N,N-dimethyl-formamide or ethylenediamine, could be used in place of water.

CO_2 FIXATION MECHANISM

Several mechanisms for CO_2-alkali-metal amalgam reactions have been proposed (ref 5). However, the net overall reaction in a typical CO_2-sodium amalgam reaction is given by:

$$\underset{\text{Carbon Dioxide}}{2C{=}O} + \underset{\text{Sodium (In amalgam form)}}{2Na} \xrightarrow[\text{1 atm pressure}]{\text{25 C}} \underset{\text{(Sodium oxalate)}}{\begin{array}{l} O \\ \| \\ C - O - Na \\ | \\ C - O - Na \\ \| \\ O \end{array}}$$

Sodium oxalate in aqueous solution can be converted to free oxalic acid by electrolysis. This can be accomplished concurrently with the recovery of sodium (in amalgam form) to start the CO_2 fixation cycle again.

The oxalic acid in turn can be reduced further to glycolic acid at the mercury cathode during electrolysis in a reaction of the form shown below:

$$\underset{\text{(Oxalic acid)}}{H{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H} \xrightarrow[\text{(from electrolysis)}]{+4H} \underset{\text{(Glycolic Acid)}}{\begin{array}{l} H \\ O\ O \\ |\ \| \\ H{-}C{-}C{-}OH \\ | \\ H \end{array}} + H_2O$$

The electrolytic reduction of other organic compounds at a mercury cathode also has been studied. In fact, we have demonstrated the electrolytic reduction of numerous compounds of the form $R{-}\underset{\underset{O}{\|}}{C}{-}R$ or R=R. With the notable exception of oxalic acid, we found that organic acids of the form R-COOH exhibit virtually no reduction by electrolysis in aqueous medium. In the photosynthetic process, nature apparently circumvents the energy barrier imposed by the reduction of an organic acid by inserting a phosphorylation step in the reduction process. For example,

one of the first reduction steps in the photosynthetic process is the reduction of 1-3 phosphoglyceric acid (ref 6) and not the reduction of glyceric acid itself.

If the organic acid reduction barrier can be overcome by electrochemical means, the reduction of CO_2 to almost any desired organic compound appears feasible. We have been able to demonstrate, for example, that several steps in the metabolic Krebs cycle can be driven by electrolysis to higher energy organic intermediate compounds. Thus, we envision the distinct possibility of a nonbiological CO_2 fixation system that could be analogous in some aspects to a photosynthetic process. The late C.F. Kettering, in fact, dramatized this possibility even more strongly with his prediction that, within a few decades, it should be possible to produce hardware that could sustain life in a completely sealed room for any desired length of time if a source of electrical power was available to the room.

SECTION II

EXPERIMENTAL METHODS

The research at Aerospace Medical Research Laboratories was initiated by duplicating some of the early research efforts of CFKRL on CO_2 fixation by alkali-metal amalgams. The equipment as outlined in figure 2 was assembled. Basically, the system consisted of a gas manometer to measure CO_2 uptake, coupled with a reaction vessel in which CO_2 was exposed to any of several types of alkali-metal amalgams. At first, the reactions were run in a 500 ml, three-necked flask fitted with a mechanical stirrer. The procedure was to flush the system with CO_2, introduce the amalgam into the reaction flask, and observe CO_2 uptake while maintaining a slight differential pressure head manometrically. The differential pressure head maintained usually was 5 inches of water equivalent. To relieve the tedium of constant operator surveillance in maintaining the slight pressure head, a servomotor control system operating through electrical contacts on a differential pressure gage was constructed.

Initially, an active alkali-amalgam will wet the surface of a glass reaction flask with a mirror-like appearance. As the CO_2 reduction reaction proceeds, the amalgam becomes pasty in appearance and finally separates into a black powder and liquid mercury. At this point water can be added to start the product separation and initiate the alkali-amalgam recovery by electrolysis. At first, this was done as a two step operation in which the water-treated CO_2 fixation products and expended amalgam were transferred to a separate electrolysis cell for the amalgam recovery. Later we developed the modified reaction vessel shown in figure 3, which permitted reclamation of the alkali-amalgam within a closed system. This modification removed the need for physical handling of the expended amalgam during the alkali-amalgam recovery cycle. Although we experienced mechanical difficulties, such as clogged porous frits, in our first design of this particular type of cell, we feel that a cell design similar in principle to that shown in figure 3 could serve as the prototype of a cyclic CO_2 fixation apparatus.

AMALGAM PREPARATION

All the alkali-amalgams, with the exception of magnesium, were prepared, initially, by the electrolysis of a concentrated solution or suspension of the corresponding reagent grade hydroxide or carbonate. For the batch type (noncyclic) experiments, the electrolytic reduction apparatus used was the "Dyna-Cath" manufactured by Eberbach Co., Ann Arbor, Michigan. In this

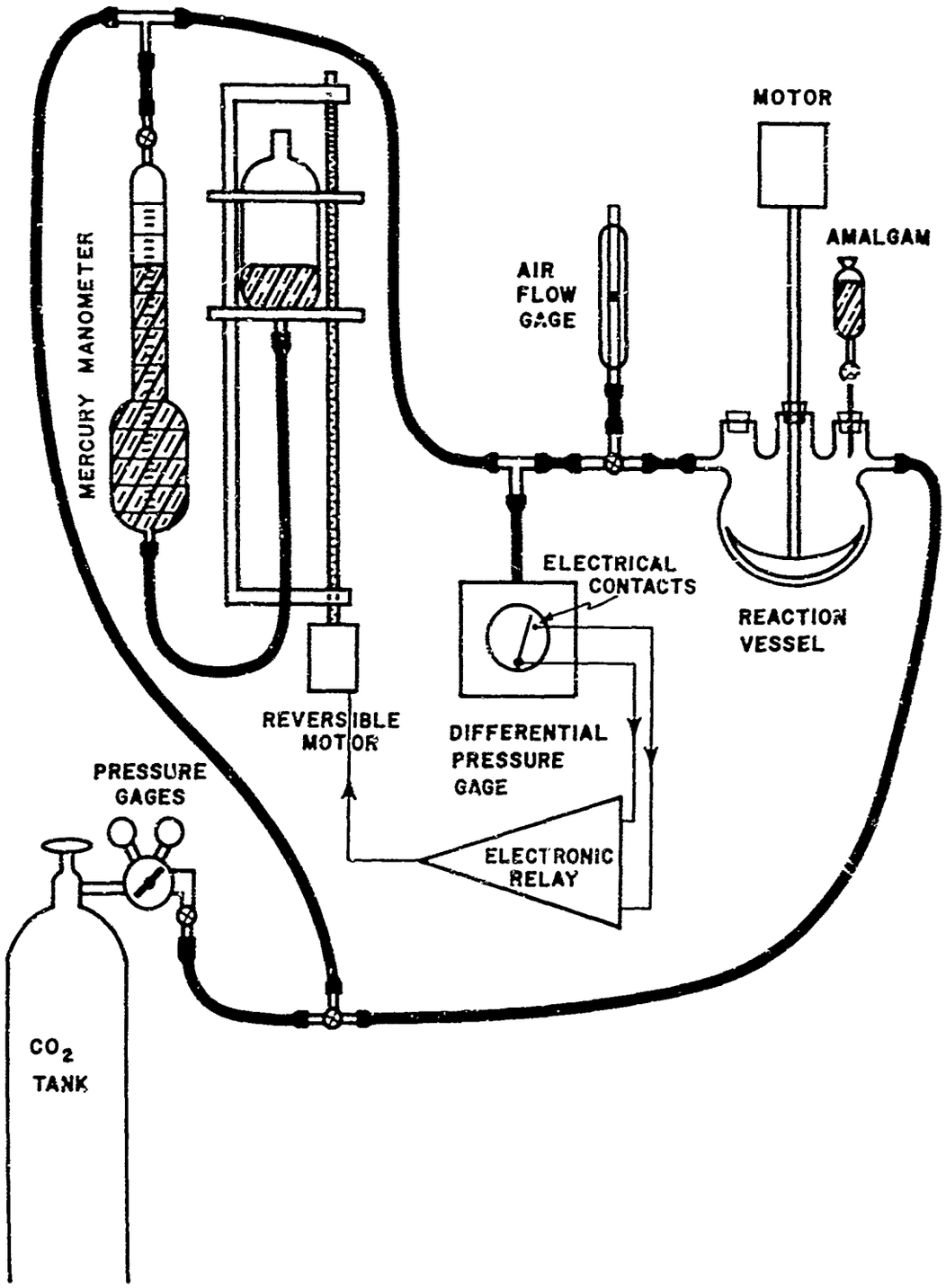

Figure 2. Experimental Apparatus for CO_2 Reduction Studies.

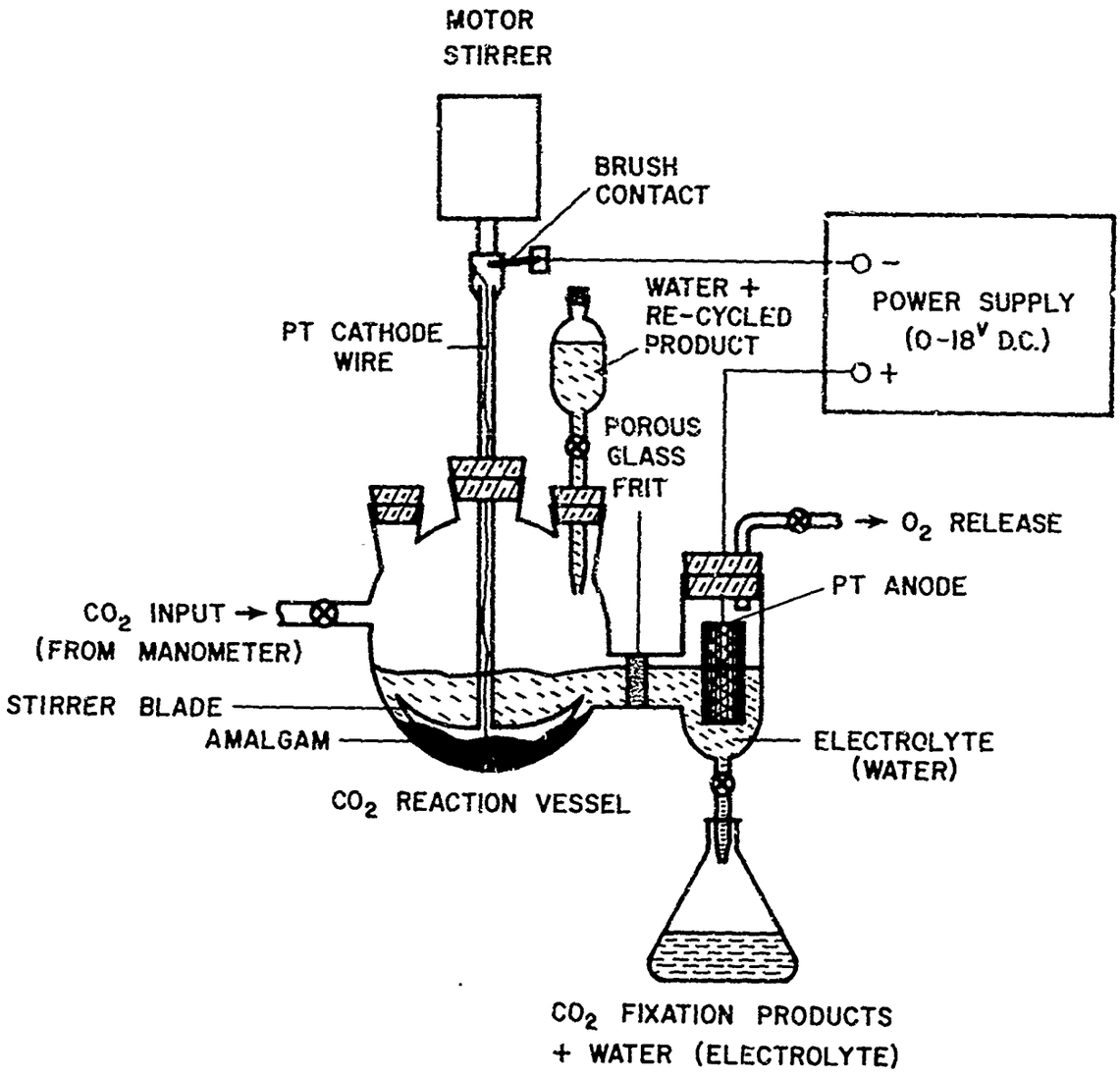

Figure 3. Experimental Apparatus for Cyclic CO_2 Reduction Studies.

apparatus, a platinum ring assembly is used as the anode. We used approximately 100 milliliters of mercury as the cathode. Depending on the conductivity of the electrolyte, the current range varied from a fraction of 1 ampere to 10 amperes and the voltage range from 2 to 20 volts. Cooling of the electrolyte, if necessary, was accomplished by circulating water through cooling coils immersed in the electrolyte. When the desired amalgam concentration was obtained, the amalgam was drained from the electrolysis cell and sealed in a flask to exclude air. The amalgam concentrations were determined by the loss of weight method in which the amalgam was decomposed by acid treatment and the mercury reweighed after thorough washing and drying.

As will be observed later in this report, completely saturated alkali-amalgam solutions apparently cannot be produced by electrolysis of aqueous solutions. One factor that limits the concentration of amalgam is the back reaction rate of the amalgam surface exposed to the electrolyte (water) interface. This can be minimized to a certain extent by rapid stirring of the mercury to expose as much fresh mercury as possible at the interface. A dropping mercury cathode also accomplished the same purpose.

Magnesium amalgam could not be prepared by electrolysis from aqueous magnesium salt solution; therefore, this amalgam was prepared by dissolving magnesium metal turnings in mercury by mechanical mixing.

ANALYTICAL PROCEDURES

The basic analytical procedure used in product determination was gas chromatography using ethyl esters of the CO_2 reduction products formed. An excellent description of the gas chromatography procedures used can be found in the R. M. Miller et al paper (ref 5). For the record we quote, in part, from this paper:

"An exploratory examination, using the silica gel column procedure of Bulen, Varner, and Burrell, (ref 14) showed that the hydrolysates consisted of mixtures of carboxylic acids. The analytical procedure adopted was gas chromatography of the ethyl esters. Dry samples were prepared from the basic reduction product solution by freeze drying, which left the product in the form of a powder. The dried alkaline sample was moistened with 30% sulfuric acid and 25 ml of dry ether was added to elute the organic acids from the column. The ether solution was then evaporated in a stream of nitrogen to a final volume of about 0.4 ml in a 6.5-ml serum tube. The serum tube was closed with a rubber serum cap and a Drierite-filled vent tube was attached to a syringe needle through the cap.

"Some preliminary trials were made on the preparation and esterification reactions of diazomethane,-ethane,-propane,-butane, and -pentane. Diazoethane gave the best over-all results. This material was prepared by the method of McKay (ref 15) from N-ethyl-N-nitroso-N'-nitroguanidine and potassium hydroxide in 2-(ethoxyethoxy) ethanol. A suspension of 2 gm of ethylnitrosonitroguanidine in carbitol was added slowly to alkaline carbitol and the product diazoethane was distilled into a serum tube containing the sample. The sample was cooled to about -70 C in a dry ice-acetone bath during the ethylation. The conclusion of the reaction was determined by the accumulation of yellow color due to excess diazoethane. The ether solution of esters was warmed to 0 C and within 30 min injected into the gas chromatography system.

"A Podbielniak chromatograph (4975-3) was modified so that the detector (Gow-Max No. 9285) was maintained at 158 C separately from the column compartment. Helium carrier gas flow was adjusted to 75 ml per minute using a soap film meter. In general, two 40-µl samples were used, one with a 20% Octoil S on C-22 firebrick column, 12-ft long programmed from 30 C to 70 C, and the other with a 25% silicone rubber on Washed Chromosorb column, 6 ft long, programmed from 30 to 158 C. The silicone rubber packing used was supplied by F and M Scientific Corp, New Castle, Delaware. For calibration, 2,2,4-Trimethylpentane was used as an internal standard. Peak areas were measured by planimeter and were related to volume of component by individual calibration curves. All data were converted to mM carbon dioxide equivalents for comparison. The peaks were identified by infrared analysis and confirmed by cochromatography with knowns.

"The following compounds are adequately resolved by each of these columns:

Octoil-S 30 to 70 C	Silicone Rubber 30 to 158 C
1. Diethyl ether	1. Diethyl ether
2. Ethyl formate	2. Ethyl acetate
3. Acetone	3. 2,2,4-Trimethylpentane
4. Ethanol	4. Ethyl glycolate
5. Ethyl acetate	5. Ethyl ethoxyacetate
6 2,2,4-Trimethylpentane	6. Ethyl oxalate
	7. Ethyl malonate
	8. Ethyl tartronate
	9. Ethyl ethoxymalonate"

For the references cited in the above verbatim quotation from R. M. Miller et al, the original paper should be consulted.

SECTION III

RESULTS

EXPERIMENTALLY OBSERVED RATES OF CO_2 FIXATION

In table 1, an attempt has been made to summarize, in as concise form as possible, all available data from CFKRL and AMRL that pertain to rates of CO_2 uptake using alkali amalgam systems under ambient room temperature and pressure conditions.

The rates of CO_2 uptake shown in table 1 are based on the average of a number of experiments employing different types and preparations of alkali-metal amalgams. Because of the difficulties cited above in preparing concentrated alkali amalgams from aqueous alkali-salt solutions, all of the experiments employed relatively dilute amalgams. For any given amalgam, however, we did observe a direct, quantitative relationship between the concentration of alkali in the amalgam and the rate of CO_2 uptake. Thus, we believe the rates of CO_2 uptake shown in table I are extremely conservative rates that can be obtained even in relatively crude cyclic systems.

In general, our experimental data exhibit a close, but not exact, correlation between rate of CO_2 uptake and the corresponding published reduction potentials for each alkali metal. This correlation trend can be observed by comparing the experimentally observed CO_2 reaction rates shown in table I with the alkali-metal reduction potentials shown in table II.

CALCULATED MAXIMUM RATES OF CO_2 FIXATION

In table II, we have extrapolated our experimental results to set upper limits on the maximum rates of CO_2 fixation one could reasonably expect if a practical system for employing saturated amalgams can be developed.

For example, by comparing tables I and II, note that the average concentration of potassium amalgam we were able to prepare by electrolysis of an aqueous potassium salt was only 0.12% by weight. This concentration of potassium amalgam represents less than one sixth of the concentration of potassium in a saturated amalgam solution (ref 7). As reported above, we have observed a direct correlation between concentration of the alkali in amalgam form and rate of CO_2 uptake. Preparation of saturated amalgams by electrolysis may not be possible. However, rates of CO_2 fixation somewhere between the rates shown in table I and table II may be obtainable in a practical cyclic system.

CO_2 FIXATION PRODUCT DISTRIBUTION

The distribtuion of products that have been identified

Table I

Experimentally Observed Rates of CO_2 Fixation

by Alkali-Amalgam Systems *

Type of Amalgam	No. of Experiments	% Alkali in Amalgam by weight †	CO_2 Fixation Rate (Averaged) (cc CO_2/hr/cc amalgam)
Li	6	0.033	8.9
K	8	0.12	7.1
Rb	3	0.19	6.0
Sr	3	0.13	5.5
Cs	3	0.23	4.8
Ca	4	0.025	3.9
Ba	3	0.18	3.4
Na	12	0.036	3.1
Mg	5	0.037	1.0

* All experiments conducted at room temperature (25 C approx) and corrected to 1 atmosphere (760 mm) pressure.

† Amalgams prepared by electrolysis from aqueous alkali hydroxide solution with exception of Mg amalgam which was prepared by mechanically dissolving Mg metal turnings in Hg.

Table II

Calculated Maximum Rates of CO_2 Fixation Possible

Assuming Use of Saturated Alkali-Amalgams

Type of Alkali Metal	Reduction Potential *	Max. Solubility in Mercury % by Weight **	Max. Rate CO_2 Fixation † (cc CO_2/hr/cc amalgam)
Li	-3.045	0.09	24.1
Rb	-2.925	1.54	48.7
K	-2.924	0.80	47.5
Cs	-2.923	4.34	90.0
Ba	-2.9	0.33	6.2
Sr	-2.89	-	-
Ca	-2.76	0.30	47.0
Na	-2.71	0.68	58.8
Mg	-2.375	0.24	6.5

* From CRC, Handbook of Chem. & Physics - 47th Edition
** From Inorganic Syntheses (Tammann & Hinnüber) - Vol I - H. S. Booth, Editor (Ref 7)
† Extrapolated from observed rates shown in Table I to saturated alkali-amalgam conditions.

in the reduction of CO_2 by different alkali amalgams is summarized in the chart shown in figure 4. These data, based mostly on earlier CFKRL experiments of R. M. Miller et al(ref 5), were obtained under three separate sets of experimental conditions. All reactions were run at normal atmospheric pressure, but at two different temperatures 25 and 200 C. In addition, one set of data was obtained in which the amalgam was not completely expended (i.e. excess amalgam remained). The effect of the excess amalgam is to produce hydrogen upon addition of water in the product separation stage. The hydrogen serves to further reduce the products formed by the alkali amalgam alone. For example, note that sodium amalgam at 25 C produces mainly oxalic acid (83%) from CO_2. However, with excess alkali amalgam, this particular product is reduced further to glycolic acid This reduction is discussed under the CO_2 Fixation Mechanisms section above. Although all the CO_2 reduction mechanisms are not clearly understood at present, multiple step reduction processes, such as outlined for the CO_2 to glycolic acid conversion described above, may account for the wide variety of CO_2 reduction products reported in figure 4.

The more salient features of figure 4 are the large percentage (83%) of oxalic acid produced by sodium amalgam under ambient conditions; the significant production (43%) of 3 carbon compounds, tartronic acid, produced by lithium amalgam; and the traces of hydrocarbons produced by magnesium amalgam. The high percentages of carbonate produced by amalgams, such as rubidium and cesium, appear of less interest because the formation of carbonate does not represent a reduction of CO_2.

However, the product distribution shown in figure 4 was not obtained using a cyclic CO_2 fixation system. We have demonstrated that recycling of products results in the formation of compounds of a more reduced form. In fact, we have observed the reduction of CO_2 to traces of carbon black in at least one type of cyclic system. In this cyclic system we employed sodium amalgam and recycled the CO_2 reduction products concurrently with the sodium amalgam recovery. Thus, we demonstrated that CO_2 could be reduced to carbon under ambient temperature and pressure conditions. The product distribution (fig 4), therefore, should serve only as an indication, not a complete picture, of the CO_2 reduction products available from a cyclic system.

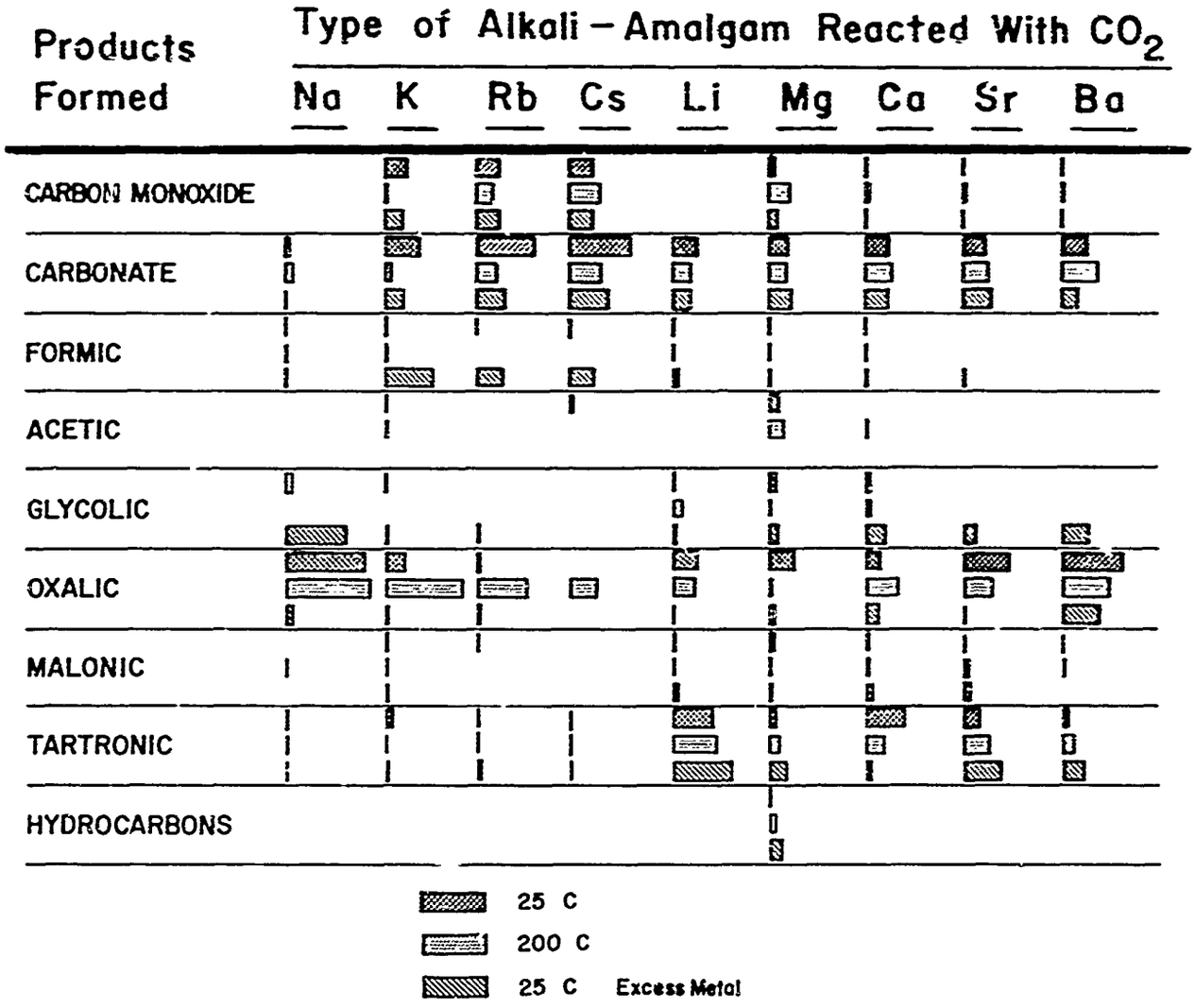

Figure 4. CO_2 Reduction Product Distribution

Bar graphs indicate relative amounts of each product formed by reaction of CO_2 with the type of alkali-amalgam indicated. See text for details.

SECTION IV

DISCUSSION

POTENTIAL APPLICABILITY TO SPACE MISSIONS

The main objective of this research was to conduct a feasibility study of the use of alkali amalgams for CO_2 fixation in space systems.

In a closed space system, the CO_2 removal requirements are 2.32 lb of CO_2 per man per day (ref 8). This corresponds roughly to 44 gm of CO_2 per hour per man or approximately 22.4 liters of CO_2 per hour per man under ambient temperature and pressure conditions.

Based on the actual observed rates of CO_2 fixation shown in table I, at least 2.5 liters, or 75 pounds approximately of alkali-amalgam would be required to handle the CO_2 recovery requirements of one man. However, depending upon how closely one could approach the maximum CO_2 rates obtainable with saturated amalgams, as shown in table II, the alkali-amalgam requirement could be decreased by a factor of 5 or more. It seems reasonable to expect, for example, that a system for CO_2 fixation can be devised that would require only a few hundred milliliters of alkali-amalgam and probably could weigh less than 15 pounds per man.

From the wide variety of CO_2 reduction products shown in figure 4, the possibility exists that, on extended space missions, some of these products could serve as precursors for crude forms of fuel (or, conceivably, even food) for reuse on the space mission. This, of course, is only a remote, but distinct possibility that must be considered as space missions become of increasingly longer duration.

The overall efficiency of an alkali-amalgam - CO_2 reduction system appears particularly attractive. The temperature and pressure requirements are minimal and the electrolytic recovery of the alkali amalgam is inherently efficient. The voltage and current requirements are low enough that adequate power could be drawn from a source, such as a photovoltaic cell panel exposed to solar energy. Thus, a CO_2 reduction system employing alkali-amalgams may be feasible for space systems.

SECTION V

CONCLUSION

We have demonstrated that:

CO_2 can be reduced by alkali-metal amalgams under mild temperature and pressure conditions.

The alkali-amalgam expended in the CO_2 reduction process can be reclaimed by low power, low cost electrolytic procedures to provide a cyclic system for CO_2 fixation.

A wide variety of CO_2 reduction products can be produced by alkali-amalgam systems. The product distribution is determined by such factors as the type of alkali-amalgam used, temperature, pressure, and electrolytic procedure for recovery of amalgam.

A practical, cyclic system for CO_2 reclamation in space systems based on the above principles appears feasible.

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Aerospace Medical Research Laboratories Aerospace Medical Div., Air Force Systems Command, Wright-Patterson AFB, OH 45433

13. ABSTRACT

The reduction of carbon dioxide by alkali-metal amalgams has been studied as a potential means for reclamation of carbon dioxide waste gas in space systems. The carbon dioxide reduction reactions were investigated at moderate temperatures and pressures - typically 25 to 200 C and 1 to 1.1 atmospheres. The investigations demonstrated that carbon dioxide can be reduced effectively by an appropriate alkali-metal amalgam system. Moreover, the alkali-amalgam expended in the carbon dioxide reduction process can be reclaimed by electrolysis from an aqueous or nonaqueous salt solution containing the fixed carbon dioxide products. The carbon dioxide fixation products can be drained-off or, in some cases, recycled for further reduction. In the carbon dioxide reduction reactions by alkali-amalgam systems, a wide variety of products ranging from simple organic acids, such as formic and oxalic acid, to totally reduced carbon dioxide in the form of carbon black have been identified. The types of products formed are dependent upon such factors as the type of alkali-metal amalgam used, temperature, pressure, and electrolytic reducing conditions. In electrolytic recovery of the alkali-metal amalgam from aqueous media, oxygen also is produced as a useful by-product of the carbon dioxide reduction system.

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Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Alkali-metal						
Amalgam						
Carbon dioxide						
Electrolysis						
Fixation						
Gas						
Organic acids						
Reclamation						
Reduction						
Waste gas						

Security Classification