NASA-CR-195262

NATIONAL AERONAUTICAL SPACE ADMINISTRATION (NASA)
Johnson Space Center

IN-25-CR
3942
49 P

FINAL REPORT

ELECTROCHEMICAL INCINERATION OF WASTES

NASA RESEARCH GRANT: NAGW-1779

Prepared and Submitted by:

Dr. J. O'M. Bockris, Principal Investigator

Dr. R. C. Bhardwaj, Senior Research Associate

Dr. C. L. K. Tennakoon, Research Associate

Surface Electrochemistry Laboratory

Texas A&M University

College Station, Texas 77843

January 1993

ELECTROCHEMICAL INCINERATION OF WASTES

C. L. K. Tennakoon, R. C. Bhardwaj and J. O'M. Bockris

Surface Electrochemistry Laboratory

Department of Chemistry, Texas A&M University
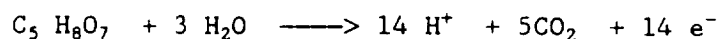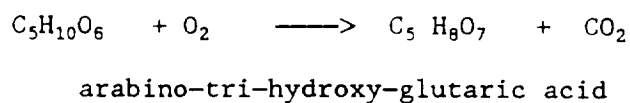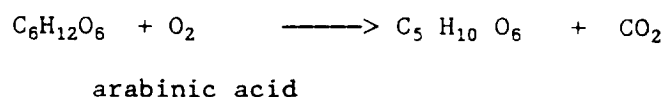
College Station, Texas 77843

INTRODUCTION

There is an increasing concern regarding the disposal of human wastes in space vehicles. It is of utmost importance to convert such wastes into harmless products which can be recycled into an Environmental Life Support System [CELSS] [1], which incorporates the growth of plants (e.g., Wheat) and algae to supplement the diet of the astronauts. Chemical treatments have proven relatively unsatisfactory and tend to be increasingly so with increase of the mission duration. Similarly, the use of heat to destroy wastes and convert them to CO_2 by the use of air or oxygen has the disadvantage and difficulty of dissipating heat in a space environment and to the inevitable presence of oxides of nitrogen and carbon monoxide in the effluent gases [2,3]. In particular, electrochemical techniques offer several advantages including low temperatures which may be used and the absence of any NO and CO in the evolved gases.

Workers in our laboratory at Texas A&M University, College Station, have carried out successful research in the electrochemical oxidation of wastes over the last several years. The commencement of the project was based on the pioneering work of Bockris et al. [4] where it was shown that cellulose could be broken down to CO_2 with a current efficiency of nearly 100% and only 2 Faradays of electricity were involved in the evolution of 1 mol of CO_2, perhaps because of the preliminary hydrolysis of cellulose to glucose.

Thereafter, one possibility would be the electrochemical oxidation of glucose for which the overall reaction is:

$$C_6H_{12}O_6 + 6\ H_2O \longrightarrow 6\ CO_2 + 24\ H^+ + 24\ e^-$$
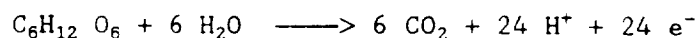
However, this would predict 4 Faradays to produce 1 mol of CO_2. The remaining discrepancy between this expectation and the observations of the original paper was explained by postulating that preliminary chemical oxidation reactions are coupled with the degradation of the glucose unit.

$$C_6H_{12}O_6 + O_2 \longrightarrow C_5H_{10}O_6 + CO_2$$

arabinic acid

$$C_5H_{10}O_6 + O_2 \longrightarrow C_5H_8O_7 + CO_2$$

arabino-tri-hydroxy-glutaric acid

$$C_5H_8O_7 + 3\ H_2O \longrightarrow 14\ H^+ + 5CO_2 + 14\ e^-$$

According to this scheme 2.8 Faradays will be used per mole of CO_2 evolved, a value that is much more in accord with the experimental results.

The other contributions in the electrochemical oxidation of wastes includes the conversion of cattle manure and wood chips into pollution-free effluent containing no CO or oxides of nitrogen by Dhooge [5]. In this study they have extensively used different redox couples for example, iron (II)/iron (III); cobalt (II)/cobalt (III); vanadium (IV)/vanadium (V). The oxidation of urea in urine electrochemically was reported by Tischer et al. [6].

The systematic study of the oxidation of human wastes commenced with a fundamental investigation into their composition and the oxidizability of the components by electrochemical means. In this initial study, Kaba, Hitchens and Bockris [7,8] showed that an artificial waste mixture could be prepared having a similar composition to that of human feces, and that the individual components comprised of cellulose, oleic acid, casein and microbial biomass consisting of

Torpulina, could all be electrochemically oxidized on a platinum electrode. Initial experiments were conducted in 5–12 M sulfuric acid, up to a temperature of 150°C. The total organic carbon decreased by about 95% in 96 hours of electrolysis. The electrodes used were mainly platinum and lead dioxide. The latter electrode was shown to be more effective than the former.

The effect of the addition of Ce^{+3}/Ce^{+4} redox couple was also studied. An oxidation rate increase in the presence of the redox couple about 40% compared to that in its absence was reported [8].

At this stage (1990), it was decided to attempt to exclude the use of H_2SO_4; and to carry out the oxidation of fecal–urine mixture at temperatures less than 100°C. The supporting electrolyte available in human urine is largely NaCl. When this mixture was electrolyzed, at about 90°C, 95% consumption of the fecal–urine content was obtained in about the same time as that used for the consumption of waste mixture in concentrated sulfuric acid at 150°C.

This unexpected increase in rate of oxidation may be due to a partial hydrolysis of the Cl_2 now evolved from the urine.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$HOCl \longrightarrow H^+ + OCl^-$$
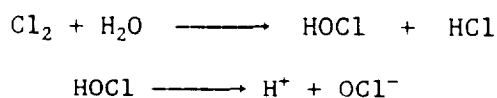
A hypothetical possibility for the partaking of this ion in the oxidation of organic materials is:

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- \ +OCl^- \longrightarrow -\overset{|}{\underset{\diagdown}{C}}-\overset{|}{\underset{O\diagup}{C}}- \ +Cl^-$$
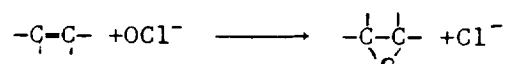
The Cl^- would then migrate to the anode and forms chlorine. A catalytic cycle is thus implied.

Reactions of this type are likely to be the origin of the decoloration and deodorization which is so strikingly observed when urine is involved in the oxidation of the solid wastes (Indeed, HOCl is a well known bleaching agent).

However, it was noted at this early stage that PbO_2 coatings are attacked in the presence of urine presumably forming $PbCl_2$.

The next phase of development was to research a suitable electrode material for the oxidation of the fecal-urine mixture. This work also been performed in our laboratory by Bhardwaj, Sharma and Bockris [9]. In this study seven different electrocatalysts were investigated in the electrochemical oxidation of urine-feces mixtures. The electrodes studied were Pt, PbO_2, gold, graphite, perovskite, tungsten carbide and Ebonex (Ti_4O_7) coated with RuO_2. The current-voltage curves indicated that the waste can be oxidized in the potential range of 1.2-1.6 V vs NHE. Using the amounts of CO_2 generated during long term experiments, measuring TOC values before and after such experiments and by comparing mechanical stabilities, it was found that the perovskite ($La_{0.79}Sr_{0.21}MnO_3$) and RuO_2 coated Ebonex are superior to the other electrodes investigated, in respect to the rate of completion of the oxidation reaction and mechanical stability. These studies were performed in 'U' type cells.

In 1991, mass balance studies were carried out whilst still working with 'U' tube cells, using platinum electrodes. H_2, O_2, CO_2, N_2 and Cl_2 were all collected and analyzed in respect to the dry weight of starting and final material. TOC was also measured before and after electrolysis. (Appendix I). The relative advantages of working at constant potential and constant current were examined. Theoretically, it would be best to work at constant potentials, but it was found that improved results are obtained at constant current density but increasing potential. This is probably due to increased HOCl generation at higher potentials and possibly due to the generation of OH radicals.

At this stage, Tennakoon, Bhardwaj and Bockris [10], commenced work on devices which would increase the rate of consumption per unit cell volume. At
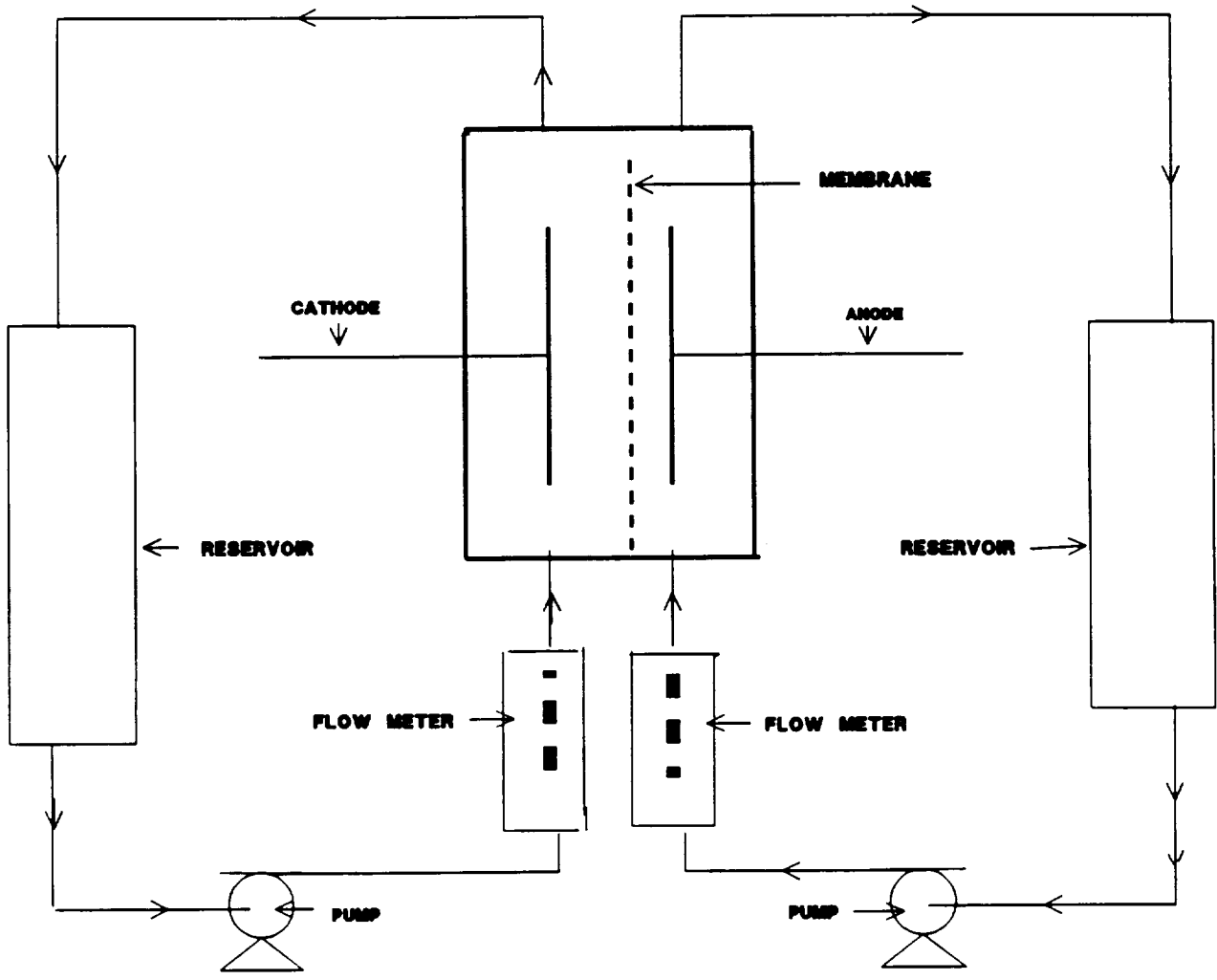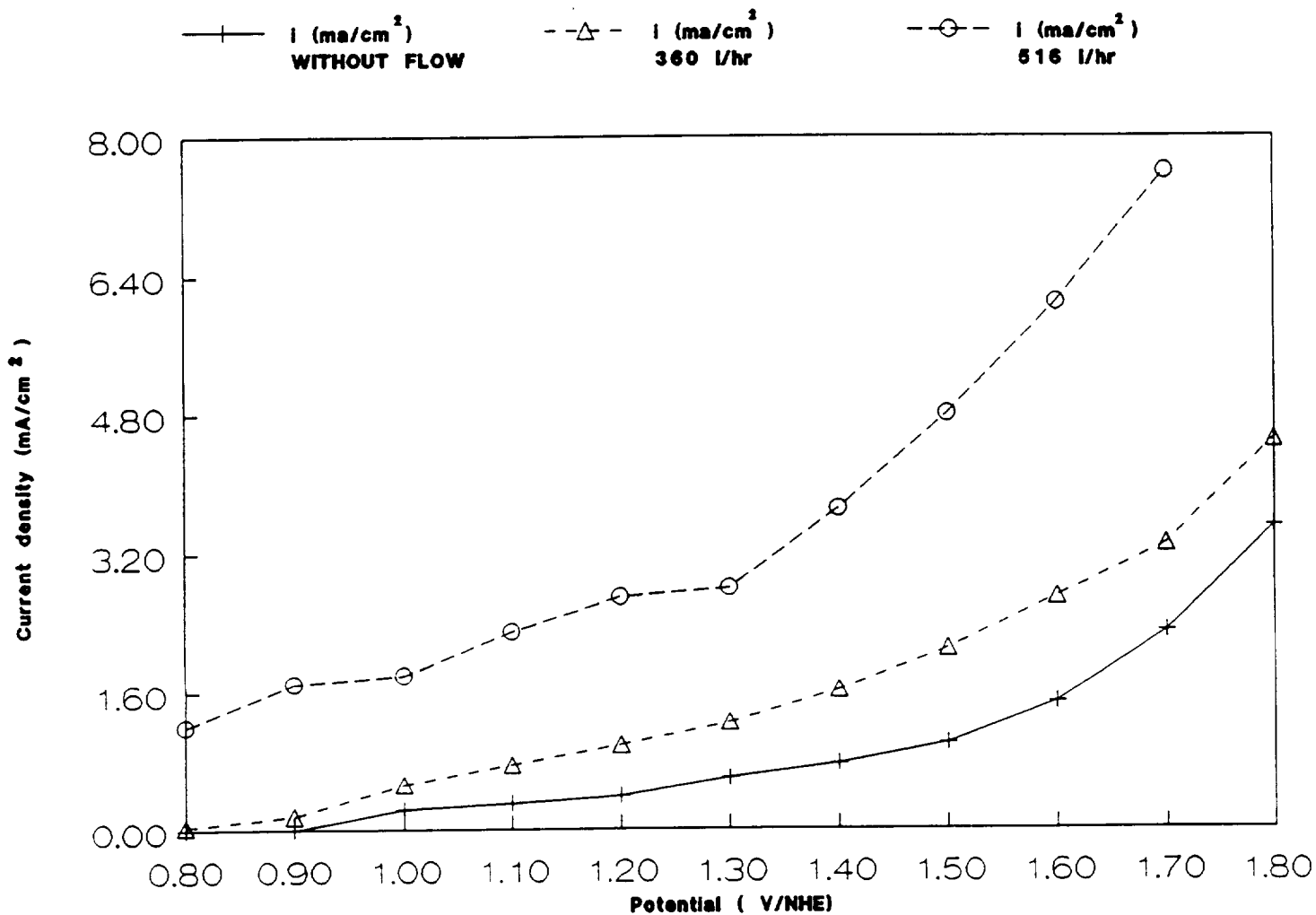
Fig 1. PARALLEL PLATE FLOW THROUGH CELL

Fig 2. HYDRODYNAMIC EFFECT ON CURRENT DENSITY

this point (May 1991), a consultation was held with Dr N. Weinberg, regarded as the leading electrochemical engineer of the time. (Weinberg has extensive experience in the design of electrochemical reactors.) His view was that an optimal design could be achieved by the use of a parallel plate flow-through cell, as shown in Figure 1.

The parallel plate cell used was purchased from Electrocell AB of Sweden. This cell constructed in a similar manner to a plate and frame filter press, consisted of a cathode, an anode, a separator and plastic frames into which the electrolyte is introduced. The cell had an active area of 100 cm^2, an inter-electrode gap of 0.5 cm. A maximum electrolyte flow rate of about 500 liters per hour could be established through the inter-electrode gap. The two electrodes were separated by a "celgard" membrane. Turbulence promoting nets provided by the manufacturers were used in both anodic and cathodic compartments. Anodes used were graphite, lead dioxide and ruthenium dioxide coated titanium. The cathode was a stainless steel plate.

Figure 2 shows the current-voltage curves obtained with this flow cell for various flow rates. A number of attempts were made to increase the flow rate of the solution through the inter-electrode gap. A large centrifugal pump from the Chemical Engineering Department of the University was obtained to give a flow rate of 512 liters per hour. Even under these conditions, it was only possible to obtain a three fold increase in current density. As such, the research work using this parallel plate cell was discontinued at this stage.

As the use of the parallel plate flow through cell was not successful, it was necessary to investigate the use of other electrodes systems available for electrochemical processes. The use of three dimensional electrodes was considered as the next alternative. In recent years considerable attention has
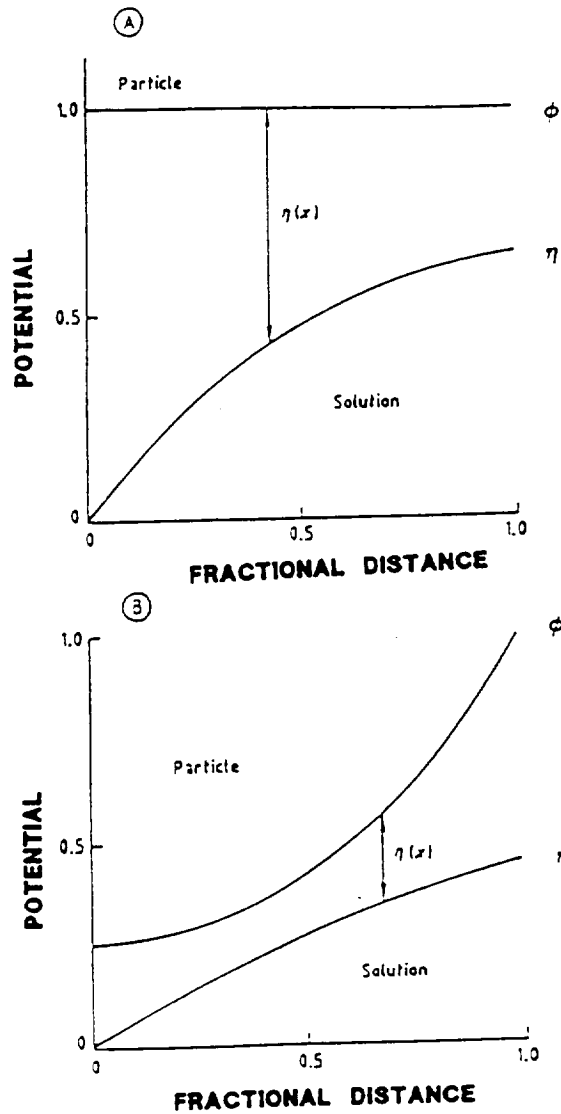
Fig 3. SCHEMATIC POTENTIAL DISTRIBUTIONS.

(a) PACKED BED ELECTRODE

(b) FLUIDIZED BED ELECTRODE

ϕ represents the potential of the metal phase with respect to an electrode outside the bed; and η is the potential in the solution. In the fluidized bed, particles are only sporadically in contact. Such systems are used in electro-winning from dilute solutions.

been given to cell designs employing electrodes in the form of small particles rather than planar or cylindrical sheets. The primary advantage of these designs is to provide a high ratio of electrode surface area to cell volume. The two main types are the packed bed and the fluidized bed electrodes. These two electrodes were simultaneously developed at the universities of Southampton and Newcastle Upon-Tyne in the United Kingdom, by Fleischmann [11-16] and Goodridge [17-21], respectively.

Out of the two possible electrode systems, the packed bed was chosen for our study by considering the potential distributions of the two electrode systems. Figure 3 shows the schematic potential distributions of packed and fluidized bed electrodes [22]. It is seen that the potential of the metal phase remains constant in a packed bed, whereas in a fluidized bed the potential change along the metal phase is significant. This is due to the fact that the particles in a fluidized bed are having only an intermittent contact with each other.

The first electrode material tested on a packed bed consisted of graphite particles of diameter about 0.5-1.0 mm supplied by the Electrosynthesis Company and it was observed that the electrochemical stability of the particles was poor as the particles slowly disintegrated with oxygen evolution on the surface. The next electrode material tested was approximately 1 mm in diameter, Ebonex particles, coated with RuO_2. 0.1M solution of $RuCl_3$ in 50% aqueous solution of ethanol was used for coating the particles. The particles were prepared by crushing a plate of Ebonex and by subsequent separation using standard sieves. The particles were then washed in distilled water, etched in 10 % solution of HF and dried at 120°C. The coating solution was then applied on to the particles taken in a beaker using a brush. Care was taken to see that all the particles were wet with the coating solution. The solvent was allowed to evaporate at
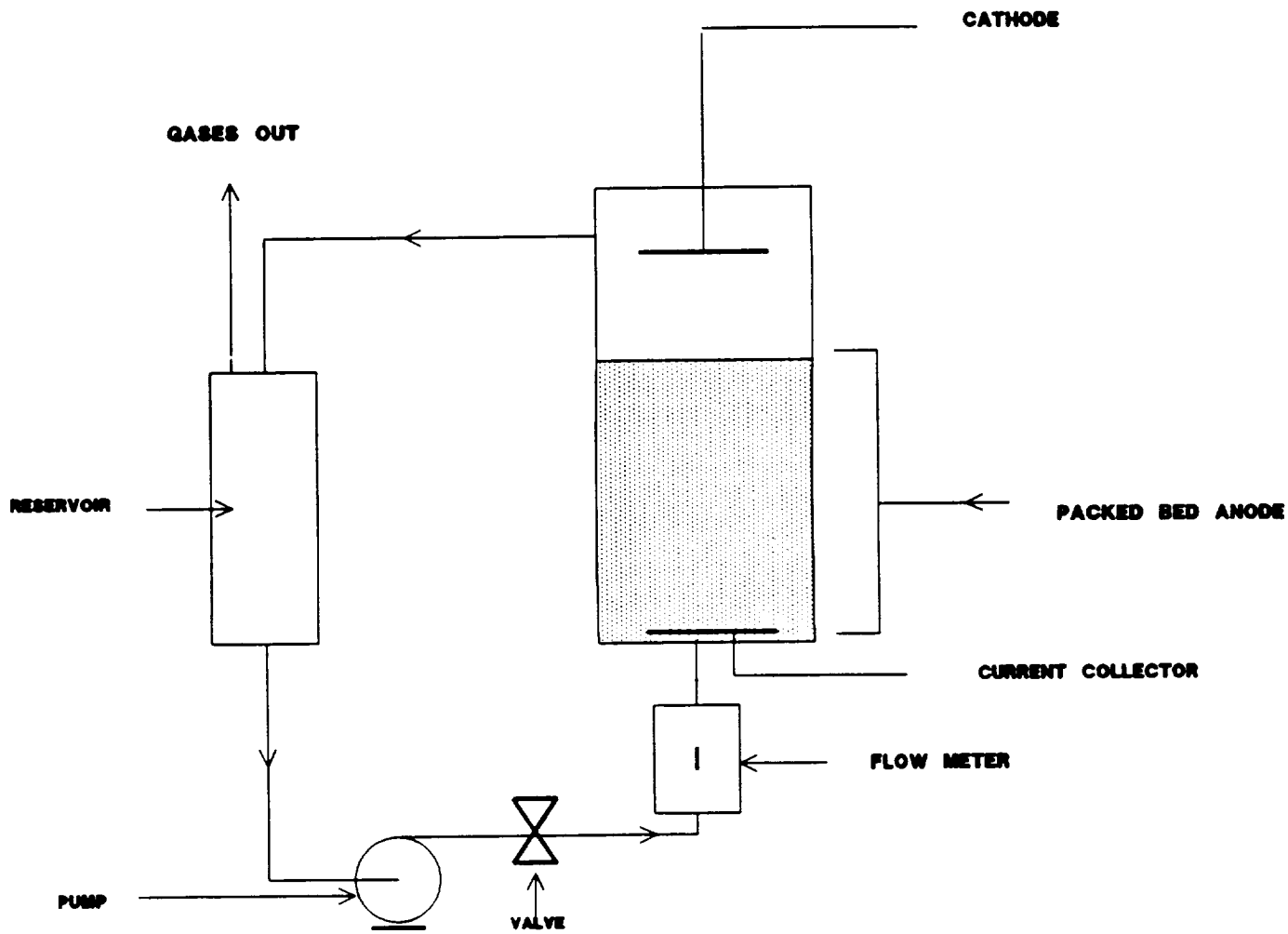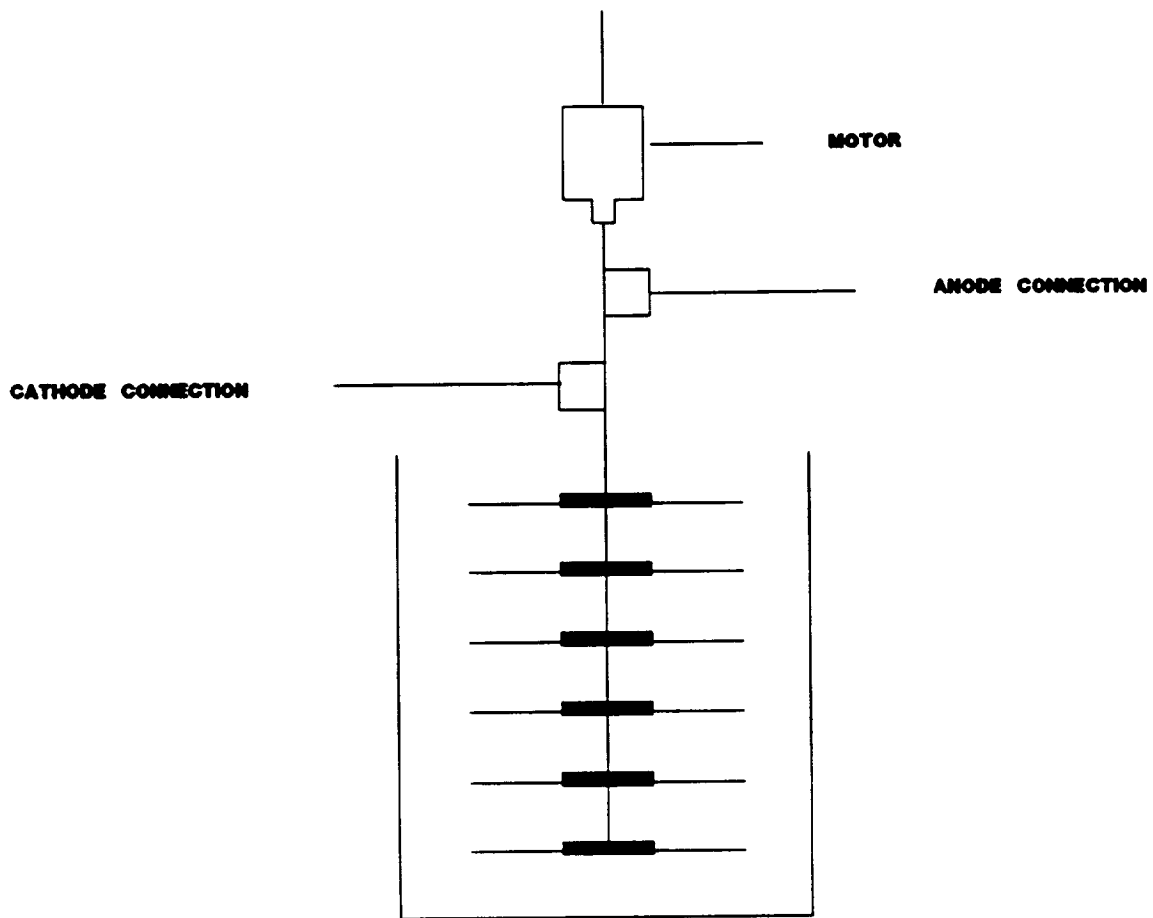
Fig 4. PACKED BED FLOW CELL

110°C and then the particles were placed in an oven at 400°C for 5 minutes. The procedure was repeated four times and the final annealing was done at 400°C for one hour. Thereafter, the particles were cooled in air, washed in distilled water and stored for use in the experiments.

Figure 4 shows a schematic diagram of the solution flow circuit used with packed bed electrodes. The rate of carbon dioxide evolution from the oxidation of urine-fecal waste in a packed bed of height 4 cm and cross sectional area of $7cm^2$ was measured using the usual procedure of collecting and analyzing the gases by gas chromatography. The rate of CO_2 evolution was found to be 12.9 mmols per hour. Comparing with a 'U' tube cell of volume 100 cm^3 producing 1.5 mmols of CO_2 per hour, the rate of CO_2 generation in a packed bed cell per cm^3 per hour was 30 times more than that obtained in a 'U' tube cell.
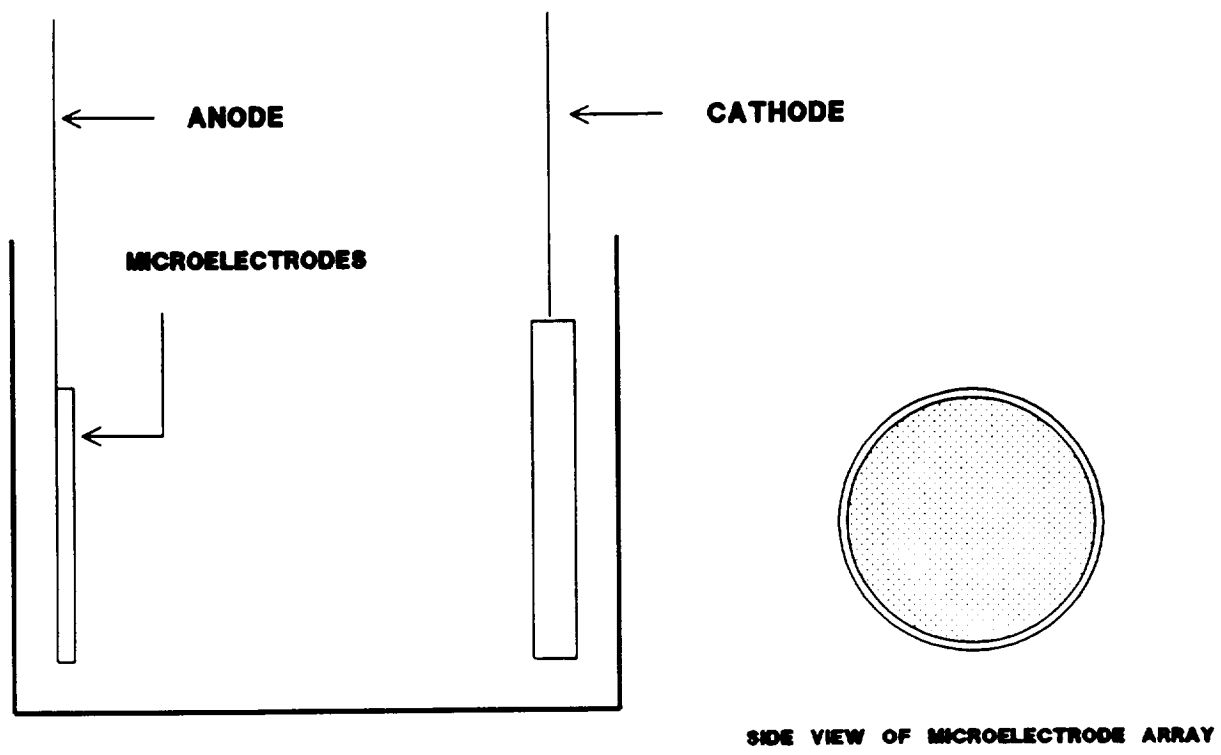
WORK DONE IN 1992

One of the important tasks in the design of an electrochemical process is to determine the mass balance for the system. The mass balance work done in 1991 was reviewed again, and the amounts of gases that would dissolve in the water used in the collection of gases by the downward displacement of water was calculated. The final mass balance was improved accordingly and the calculations are presented in Appendix 1.

The major task for 1992 was to conduct parametric studies in preparation for the building of a breadboard system, i.e., an actual practical device to consume the daily waste output of one astronaut in 24 hours. electrochemical incineration of human wastes in space vehicles.

Fig 5. STACK OF ROTATING DISCS

MOTOR

ANODE CONNECTION

CATHODE CONNECTION

ANODE

CATHODE

MICROELECTRODES

SIDE VIEW OF MICROELECTRODE ARRAY

Fig 6. MICROELECTRODE ASSEMBLY

FIXED CATHODE

VIBRATING ANODE

VIBRATING TABLE
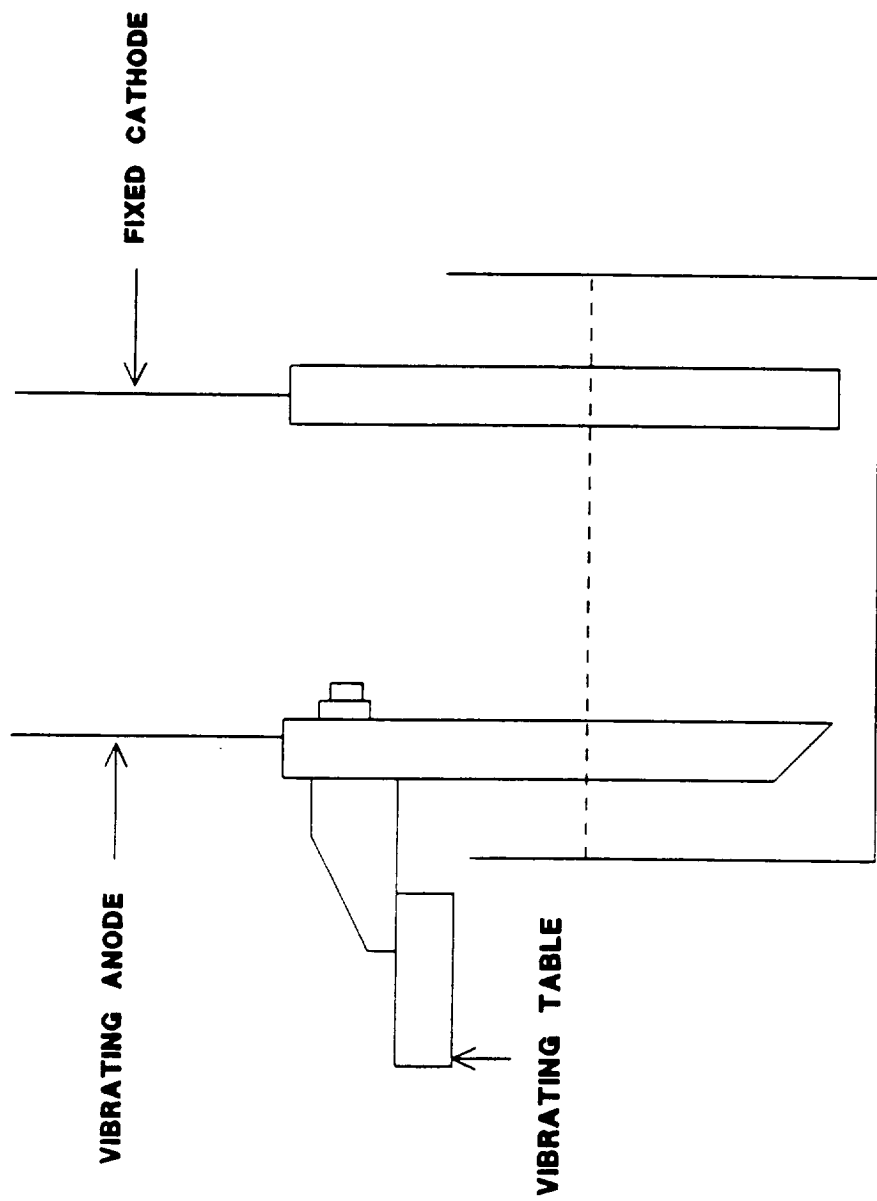
Fig 7. VIBRATING ELECTRODE CELL

REFERANCE
ELECTRODE   ANODE

NOZZLE
COUNTER
ELECTRODE

LEAD TO COUNTER ELECTRODE

FLOW OUT   FLOW IN
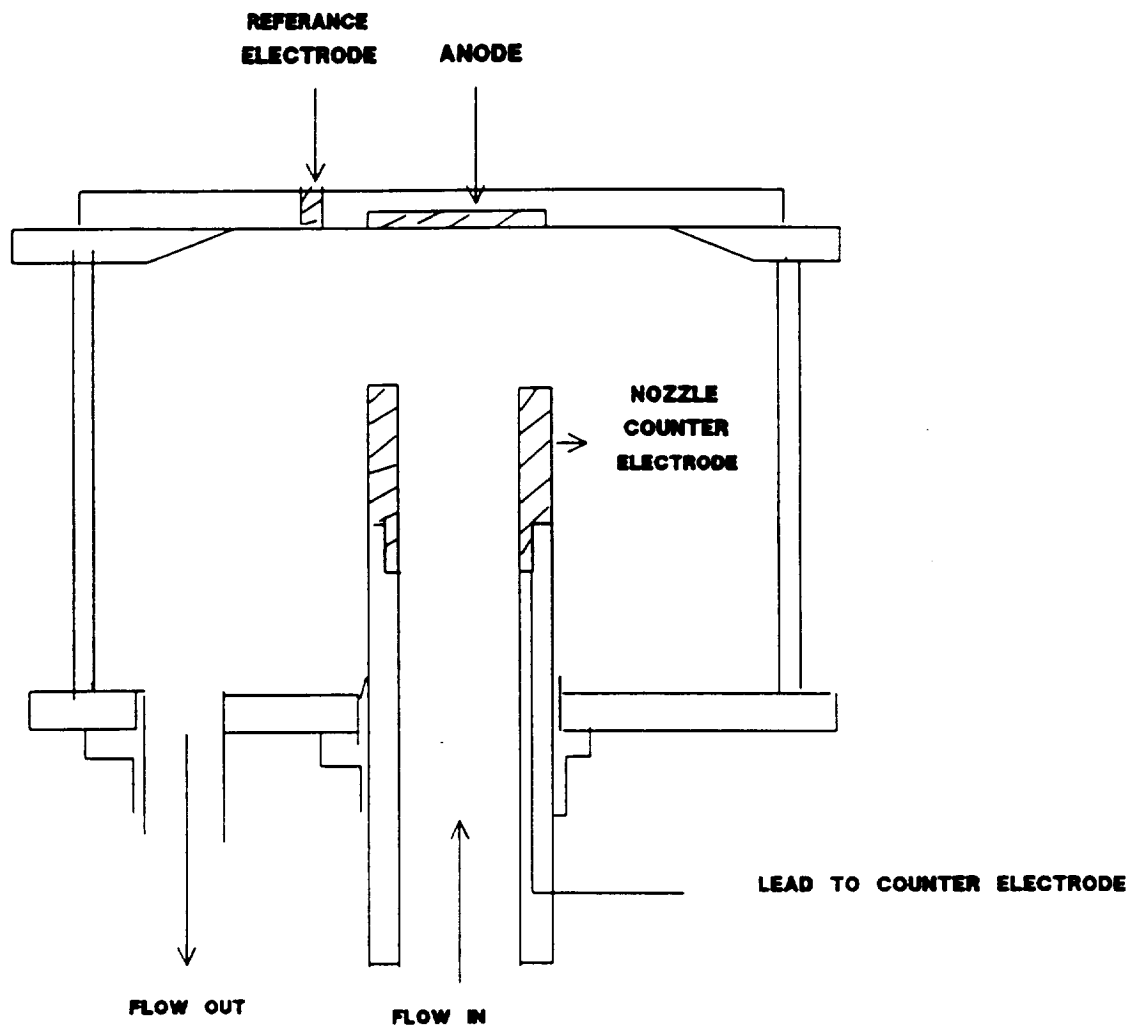
Fig 8. JET ELECTRODE CELL

Thus, one of the main objectives was to decide on the type of three dimensional or other electrode system that would suit this purpose. The various types of electrode systems which were considered for this purpose included:

(1)   Rotating disc electrode   (2)   Micro-electrode – an array

(3)   Vibrating electrode   (4)   Jet electrode

(5)   Packed bed electrode

1. Rotating Disc Electrode

The electrode assembly considered consists of a set of metal discs positioned close to each other assembled on a single shaft.   Discs are electrically insulated from the central shaft, so that the shaft is made the cathode and the discs the anode of the electrolyzer.   Rotation of the disc assembly produce enhanced mass transfer onto the electrode surfaces. A schematic diagram of this assembly is shown in Figure 5.

2. Micro-electrode System

The micro-electrode assembly considered consists of a large number of micro-electrodes assembled together.   That is 10^5 micro-electrodes each of 5 μm radius embedded in a slab of epoxy of surface area of one cm^2 [23].   A schematic diagram is shown in Figure 6.

3. Vibrating Electrode

The vibrator electrode considered consisting of a variable speed motor, a variable eccentric, and an oscillating shaft connected to a vibrating table is shown in Figure 7 and reference 24.

4. Jet Electrode

A schematic diagram of an electrolyte cell for a circular jet impinging on a flat electrode surface is shown in Figure 8.   The nozzle acts as the counter-electrode.   The reference electrode is positioned close to the working electrode

and both these electrodes are mounted on a Plexiglas sheet and machined in such a way so that the electrode surfaces are flush with the surfaces of Plexiglas [25].

5. Packed Bed Electrode

The packed bed electrode [12] consists of a bed of conducting particles through which the waste solution is pumped. The packed bed is made the anode. The electrical contact to the bed is provided by using a current collector which is usually a metal mesh. The counter electrode is kept separated from the working electrode by using either a suitable ion exchange membrane or by physically separating it from the anode bed.

In order to assess the performance of the various electrode systems, the quantitative criterion used is the space time yield (STY), which is defined as

$$STY = \frac{\text{Amount of carbon dioxide Obtained}}{\text{Time x Cell Volume}}$$

To use this criterion, it is necessary to determine the amount of carbon dioxide formed as a function of time, by experiment.

Alternatively, Beck et al. [27] suggest that for theoretical comparisons, the parameter I/V can be used to compare the performance of different electrode systems, where I is the current and V the cell volume. This parameter, also called the current concentration is equal to the space time yield when the current efficiency is 100%.

Calculation of I/V for a Packed Bed

Consider a packed bed of cross sectional area of a cm² packed to a height of L cm. In this calculation the theory developed by Chu, Fleischmann and Hills

[26] for a packed bed working under diffusion controlled conditions is used. The design equations applicable are,

$$I = nFuc_0 [1-exp-(L/\lambda)]$$

$$and \ \lambda = \delta u/DA\epsilon$$

where I = the current in amperes, n = Faradays per mole, u = flow velocity in cm/sec., L = bed height in cm., λ = characteristic length in cm., δ =diffusion layer thickness in cm., D = diffusion coefficient in $cm^2/sec.$, A = surface area of particles in cm^2/cm^3, c_0= concentration of an electro-organic substance subjected to oxidation, λ = characteristic length in cm., and ϵ = the voidage of the bed.

Using typical values, for example: A = 30 cm^{-1}, δ = 0.001 cm., u = 5 cm/sec, D = 10^{-5} $cm^2/sec.$, and ϵ = 0.5,

we get λ = 33.2 cm and then for a bed height of 3 cm.,

$$I = nFa5C_0 [1- exp - 3/33.2)]$$

$$V = 3a$$

Then, I/V = 0.14 n Fc_0

Calculation of I/V for the Micro-electrode System

Consider 10^5 micro-electrodes each of radius 5 μm positioned in an area of 1 cm^2.

$$Active \ area \ (a) \ = 10^5 \ x \ \pi \ [5 \ x \ 10^{-4}]^2 \ cm^2$$

$$= 0.078 \ cm^2$$

If the counter electrode is placed 0.5cm away from the array of micro-electrodes, then

$$V = 0.5cm^3$$

For spherical diffusion the total current for all the 10^5 electrodes is given by

$$I = nFD\ c_0\ a/r$$

Taking $r = 5 \times 10^{-4}$cm, and $D = 10^{-5}$cm^{2}sec^{-1}

$$I/V = 0.003\ nFc_0$$

It is seen that the expressions for I/V contain a common factor (nFc_0)

Similar expressions were derived for other electrode systems considered above and normalizing to make I/V equal to 1 for a packed bed, the I/V values for the different electrodes are summarized in Table 1.

TABLE 1. NORMALIZED I/V VALUES FOR DIFFERENT ELECTRODES

	Packed Bed	Rotating Disc	Micro-Electrode Array	Vibrating	Jet
(I/V)	1.0	0.01	0.02	0.05	0.15

Thus, the packed bed electrode is the most promising configuration for further work on the project.

On February 15, 1992, Mr. C. Verostko of NASA Johnson Space Center and Dr. Nigel Packham of the Lockheed Engineering and Sciences Company visited our laboratory and at the discussion which ensued, the following parametric studies were planned.

(1)   The best method of coating the Ebonex particles with SnO_2 doped with Sb_2O_3.

(2)   Dependence of the rate of reaction upon particle size.

(3)   Dependence of the rate of reaction upon the flow rate of fecal/urine mixture.

(4)   Dependence of the rate of reaction upon the bed height.

(5)   Dependence of the rate of reaction upon current density.

(6)   The effect of the use of stanchions positioned in the bed as cathodes.

(7)   The effect of intermittent addition of fecal matter during the progress of the electrochemical oxidation.

(8)   Use of a colloid mill to reduce the particle size, and study the effect on the rate of electrochemical oxidation of waste.

Coating Optimization

In 1990, Bhardwaj, Sharma and Bockris demonstrated that RuO_2 coated on Ebonex (Ti_4O_7) electrode provides good catalytic activity for the electrochemical oxidation of wastes. Thus, this material was more stable during long term experiments than are graphite, gold and perovskite electrodes. Comparing the Pt and RuO_2 the difference of the anode potential at which the current reaches 1 ma cm^{-2} is 0.2V. In approximate terms, the anode potential will be ~ 1 volt and hence the improvement in energy saving is about 20% for RuO_2 compared to Pt.

Recently, Kotz et al. [14] and Stucki et al. [15] studied the performance of SnO_2 as an anode material for the electro-oxidation of bio-refractory organics in waste waters. The influence of the doping agents (Sb, F, Cl) and doping level on the oxygen overpotential was also studied. The oxidation of phenol was investigated as a test reaction for the oxidizing power of the new anode material when compared to Pt or PbO_2. It was reported that the rate of oxidation of phenol was much greater for SnO_2 than for PbO_2 or Pt. Moreover, the oxygen overpotential on SnO_2 was reported to be 650 mV higher than that on a platinum anode at a current density of 10 mA/cm^2 which is a reasonable current density for technical applications. The higher overpotential would be advantageous because it would diminish O_2 evolution.

The following properties of SnO_2 makes it an attractive electrode material for anodic oxidation of organics in aqueous solution.

(1)   High chemical and electrochemical stability as a consequence of rather large band gap (3.5 eV).

(2)   Low electrical resistivity of the Sb_2O_3 doped SnO_2 ($\sim 1 \times 10^{-2}$ Ω cm).

(3)   High oxygen overpotential.

Kotz et al. have used the spray pyrolysis technique for coating titanium substrates with SnO_2. The composition of the solution used by these workers was,

$$10 \text{ g } SnCl_4 \ . \ 5 \ H_2O$$

$$0.1 \text{ g } SbCl_3$$

$$100 \text{ ml of ethanol.}$$

This solution was sprayed onto the substrate heated to a temperature of 500°C using a spray gun activated with nitrogen gas.

Subsequently, Comniellis and Vercesi [16] have critically discussed the various methods of coating titanium substrate with SnO_2 films. In their studies they have found that the thermal decomposition technique seems to be very sensitive to the geometry of the sample, solvent used and the concentration and nature of the metal salts. One important point brought forward by these workers, was that the boiling point of $SnCl_4$ is 114°C, whereas the melting and boiling points of $SnCl_2$ are 246°C and 652°C, respectively. Thus, at temperatures of 400°–500°C used in the initial spraying, a major part of $SnCl_4$ used in the spraying boils away leaving only a very small fraction on the substrate for conversion to SnO_2. They confirmed this by measuring the deposition yield which was only about 15% when $SnCl_4$ was used in the preparation. On the other hand in their experiments using $SnCl_2$ instead of $SnCl_4$, the deposition yields were about 66%.

Thus, the solution used for coating Ebonex (Ti_4O_7) particles was

6.4 g $SnCl_2$. $2H_2O$

0.1 g $SbCl_3$

100 ml ethanol or propanol.

Two methods of application of the solution onto the Ebonex particles were used.

(1)   Spraying

(2)   Brush painting

The Ebonex particles were initially degreased by using 10% NaOH solution; then, after washing off the alkali, the particles were etched in 10% hydrofluoric acid. Subsequently, the particles were washed in distilled water and dried at 400°C before the application of the coating solution.

Spray Pyrolysis Method

The particles taken in a beaker was sprayed with the coating solution using a spray gun operated with nitrogen gas. The particles were agitated from time to time to inspect whether all particles were wet with the spraying solution. After heating the particles in air up to about 100°C to vaporize the solvent, the particles were dried at 400°C for 5 minutes. The procedure of spraying was repeated three times including the heat treatments after which the final annealing was performed at 400°C for 1 hour.
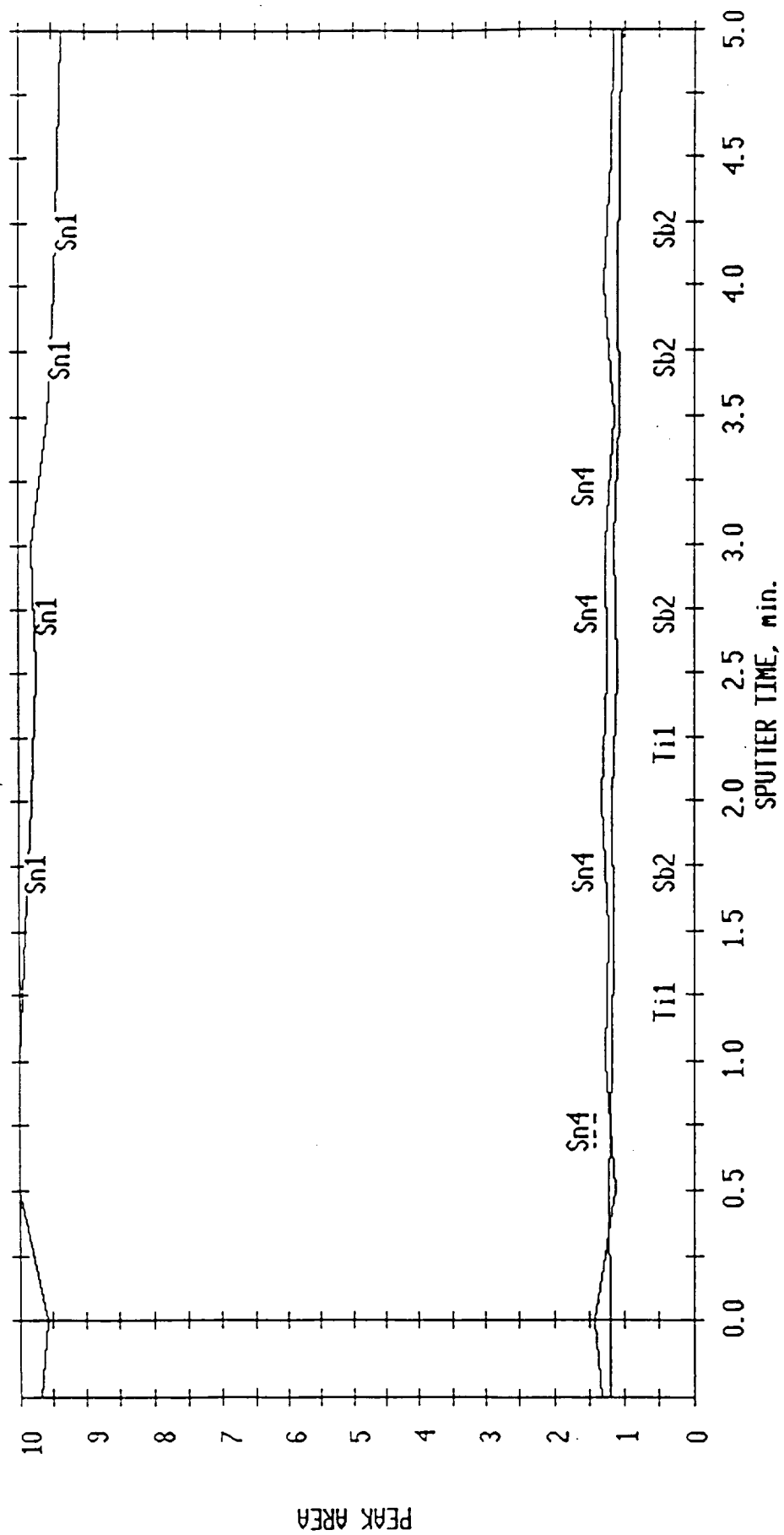
Slurry Painting Method

In using this method propanol was used instead of ethanol to prepare the slurry. The preparation of a viscous slurry was facilitated by the use of propanol. The slurry was brushed onto the particles taken in a beaker. During the brushing operation, the particles were agitated from time to time to see
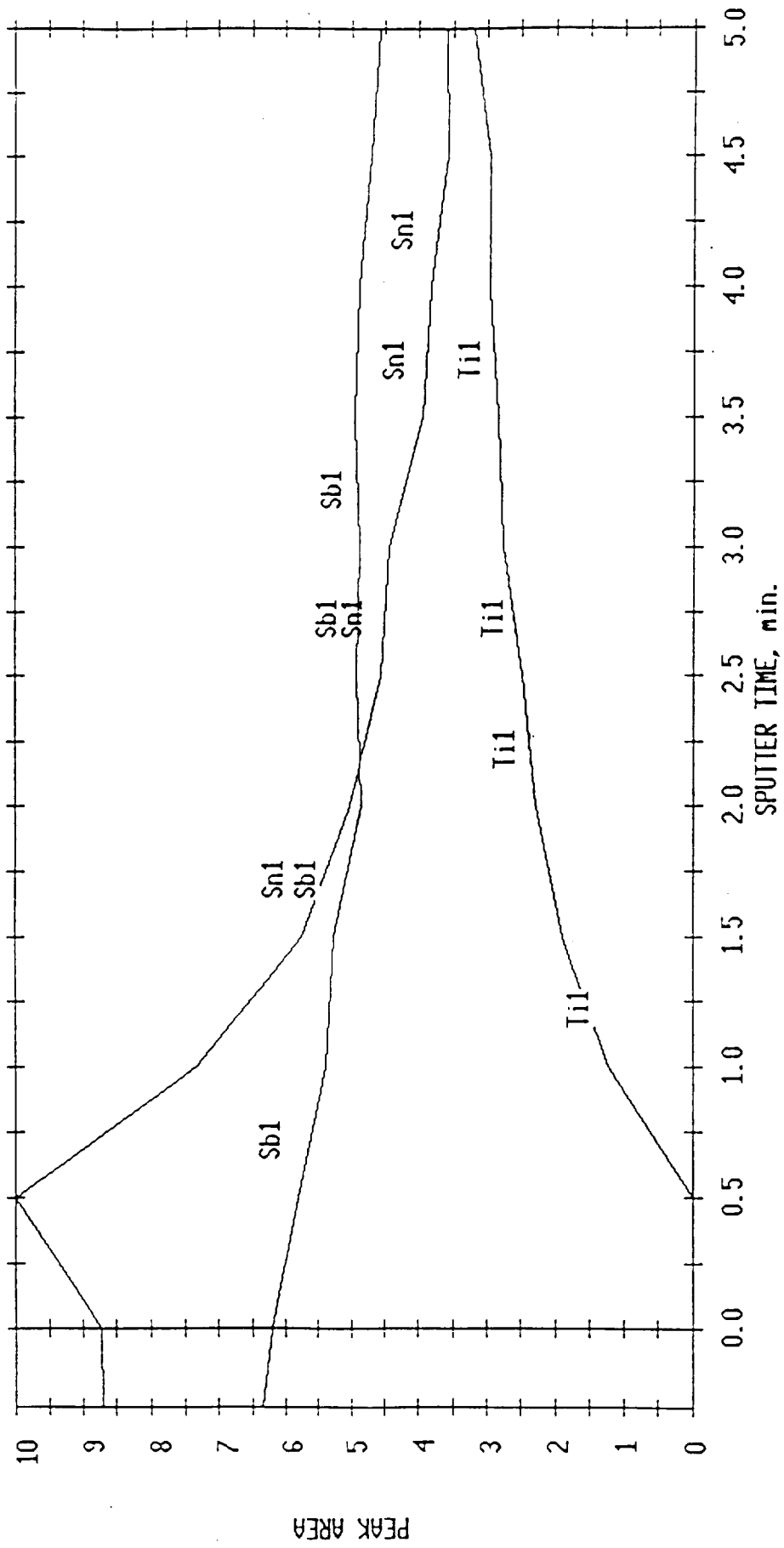
Fig 9. ARGON ION BOMBARDMENT STUDY OF COATING BY SPRAY PYROLYSIS

Fig 10. ARGON ION BOMBARDMENT STUDY OF TIN OXIDE COATNG BY SLUURY PAINTING

whether all the particles were wet with the slurry. The same heat treatment procedure described in the spray pyrolysis method was repeated.

In order to determine which method of application gives the best results in coating Ebonex particles, X ray Photo-electron Spectroscopy (XPS) was used to estimate the thickness of the coating as a function of time. Experiments were carried out using small Ebonex plates, typically 0.5 cm x 0.5 cm x 0.1 cm in size. This size was chosen because this is the best size of the sample for fixing on to the XPS sample holder. The coating of the plate was done by both of the methods mentioned above. The Ebonex plate was heated to about 100°C in air after each application of the coating solution. The plates were dried at 400°C for 5 minutes to evaporate the solvent. This procedure was repeated three times after which the final annealing was performed at 400°C for 1 hour.

The coated samples were subjected to Argon ion bombardment at 4 keV using a Perkin Elmer (PHI 5500) X ray Photoelectron Spectrometer in the Chemistry Department of Texas A&M University. Figures 9 and 10 represent the XPS output when the samples were subjected to argon ion bombardment for 5 minutes.

In Figure 9, it is clearly seen that Ti atoms are exposed after 0.5 minutes of ion bombardment. This is for the sample prepared by spray pyrolysis.

In Figure 10, for the sample prepared by the slurry painting method, the Ti surface is not exposed after 5 minutes of sputtering. Painting is therefore the better method.

Waste Mixture

A synthetic mixture of material which represented the main constituents of feces was made up for the experiments. Though the nature of sewage and fecal mixture [31] can vary considerably, generally, one-third of its contents is made up of micro-organisms from the intestinal flora and approximately one-third is

CONTROL UNIT

CIRCULATING LOOP
(ONE OF FOUR)

HORN
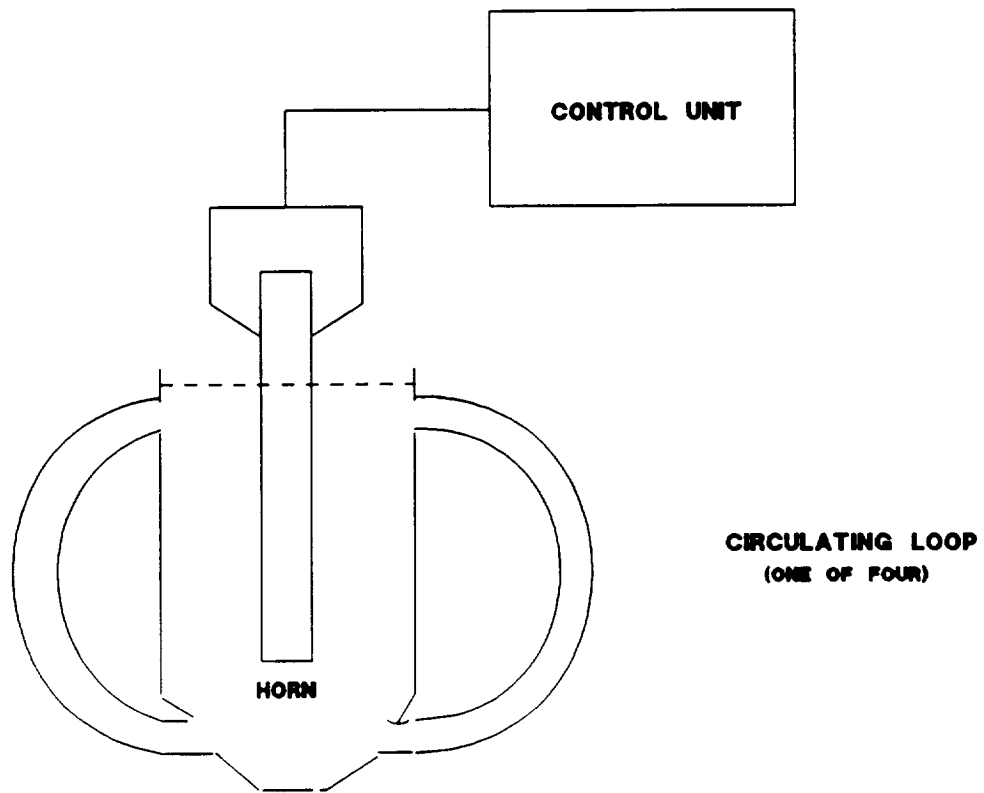
Fig 11. SONICATION VESSEL FOR WASTE MIXTURE

TABLE 2. COMPOSITION OF THE ARTIFICIAL FECAL MIXTURE

COMPONENT	% Total Dry Weight
Cellulose	33
Torpulina	25
E. coli	07
Casein	10
Oleic Acid	20
KCl	2
NaCl	2
$CaCl_2$	1

made up of undigested fiber. The remainder is made up of lipids and inorganic material. The waste mixture shown in Table 2 reflects these proportions. The micro-organisms Torpulina and E.coli were obtained in powdered form from Sigma Chemical Company, and the remaining contents were obtained from standard chemical supplies. All amounts of waste are given in terms of dry weight. A fresh batch of the waste mixture was prepared every month and the mixture was kept frozen between experiments.

Waste solutions were made up in urine without the addition of any expendable chemicals. The solid material used for experiments consisted of 14 g waste (dry feces) in a liter of urine. The material was weighed and treated in a pestle and mortar to which a small amount of urine was added. The mixture was then further homogenized in a 600-watt sonicator (Fisher) for 4 hours, working in a pulse mode with a duty cycle of 60%. The sonication was carried out in a special glass vessel shown in Figure 11. The essential feature of this vessel is that the lower part is conical in shape and the particles at the bottom are subjected to severe bombardment by the sonicator horn. The use of the four circulating loops (see Fig. 11) is to allow the bombarded particles to move from the bottom to the top of vessel. Larger particles settle to the bottom and size reduction takes place as the process is repeated. During sonication the conical vessel was immersed in water at room temperature to prevent the waste solution from getting unduly heated.

Samples of slurry subjected to sonication were placed on microscope slides and examined on a Nikon OPTIHOT microscope using objective micrometers. This microscopic examination revealed that the particle size was reduced to about 25 μm in diameter.

CURRENT COLLECTOR

CATHODE

FLOW OUT

PACKED BED ANODE

BED SUPPORT

FLOW IN
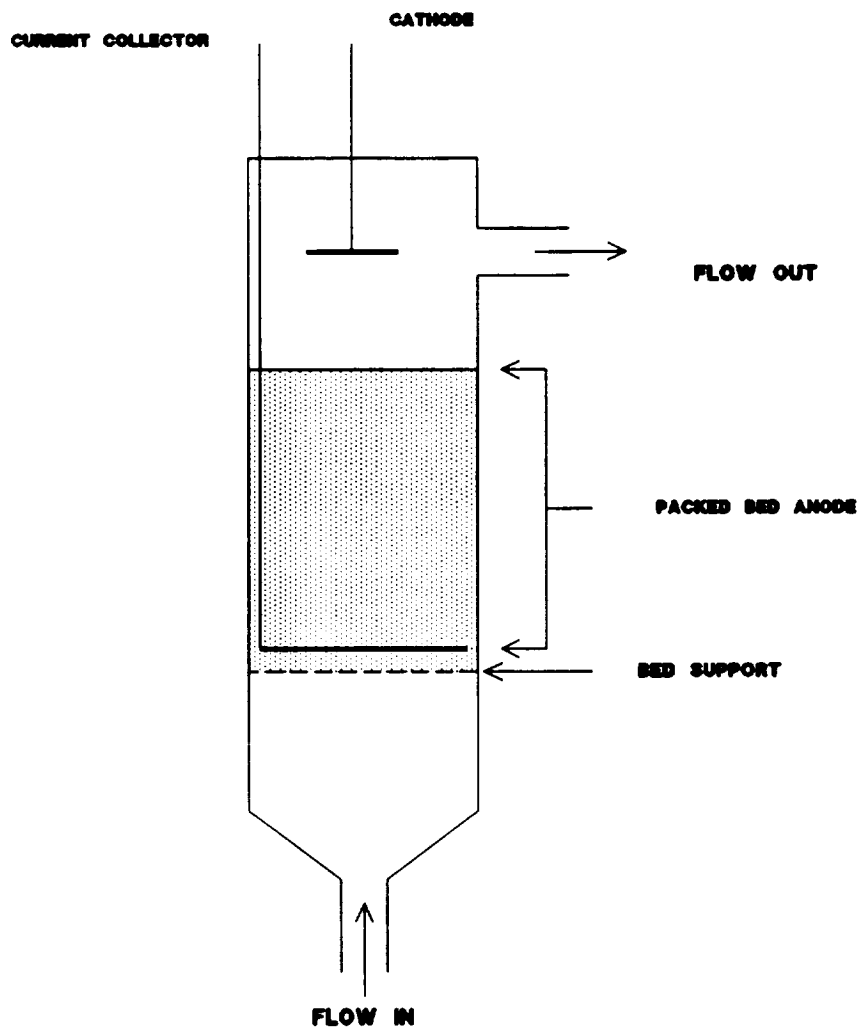
Fig 12. PACKED BED CELL WITH SOLUTION FLOW PARALLEL TO CURRENT FLOW

CURRENT COLLECTOR
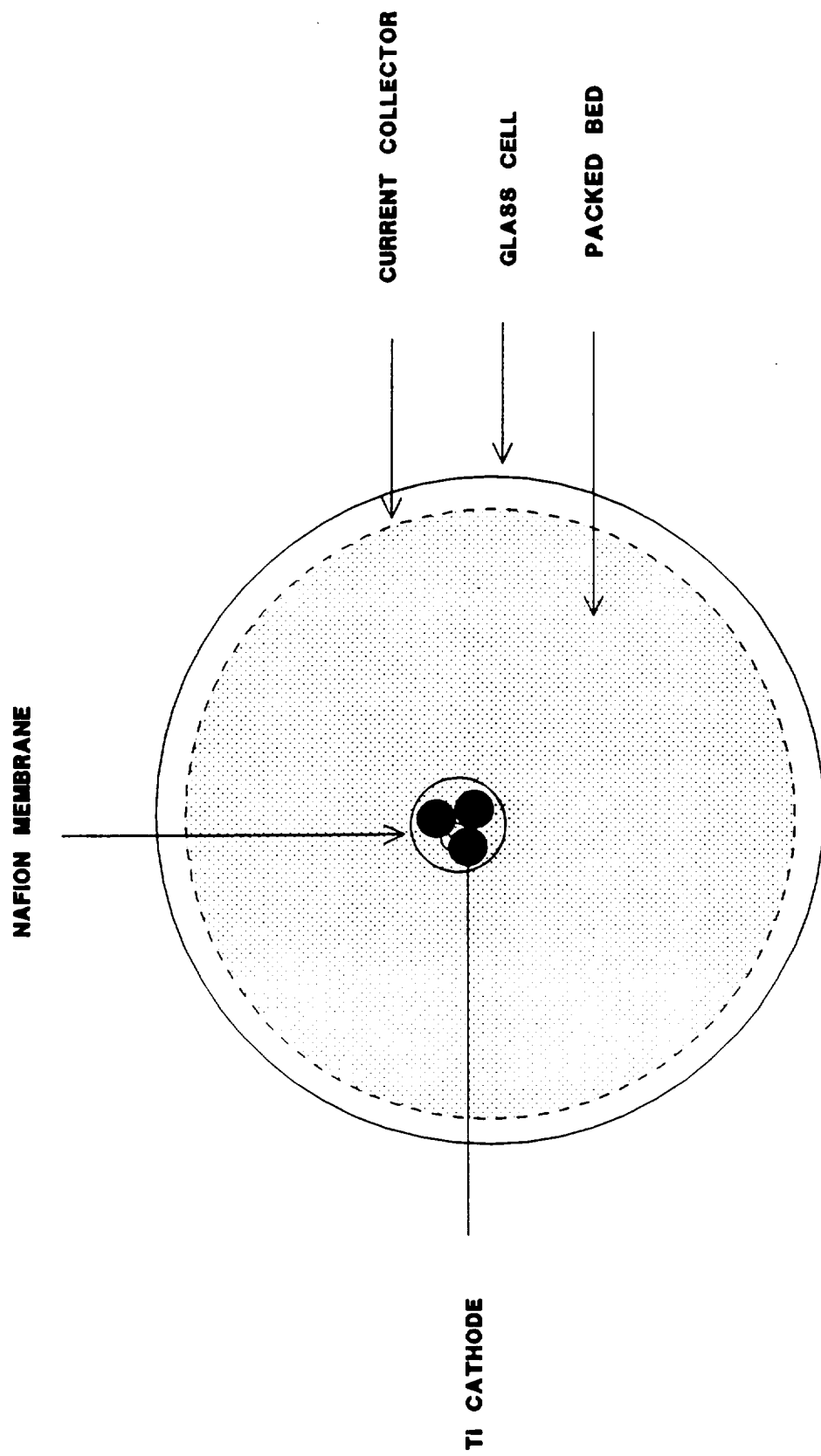
GLASS CELL

PACKED BED

NAFION MEMBRANE

TI CATHODE

Fig 13. CROSS SECTION OF CELL WITH CENTRAL CATHODES AND MEMBRANE

BED DIAMETER = 2 cm

Packed Bed Cell

Figure 12 shows a schematic diagram of a packed bed cell. A glass tube of 3 cm internal diameter fitted with a glass frit served as the support for the particles forming the bed. The height from the bottom of the bed to the flow-exit was 13.5 cm. Particles of several different sizes were used in experiments detailed in the succeeding sections. Similarly, different configurations of the packed bed were used in the experiments.

(a)   Current flow in the direction of the waste solution flow.

In this configuration the feeder (current collector) electrode was placed at the bottom of the bed, which was a platinum mesh of area 7 cm^2. The electrical connection was made to this feeder electrode through a lead sealed inside a glass tube, positioned vertically down from the top of the cell.

The counter electrode was a stainless steel sheet of area 7 cm^2 positioned above the bed of particles. A membrane separating the anode and cathode was not used when using this configuration shown in Fig. 12.

(b)   Current flow in the direction perpendicular to the solution flow.

Several alternative configurations were used in the experiments and the first one used is shown in Fig. 13. In this configuration the feeder (current collector) was a platinum mesh formed into a cylinder of internal diameter of 2 cm. The cathode consisted of three titanium rods each 3.175 mm in diameter, electrically connected together, placed centrally in the bed. The three cathode rods were insulated from the anode bed particles by using a proton exchange Nafion membrane. The cell was filled with Ebonex particles coated with SnO_2 doped with Sb_2O_3 to the required height. The particles resting within the current collector and the central cathode are effective in participating in the reaction. The advantage of this configuration is the reduced IR drop between

NAFION MEMBRANE

CURRENT COLLECTOR

GLASS CELL

PACKED BED
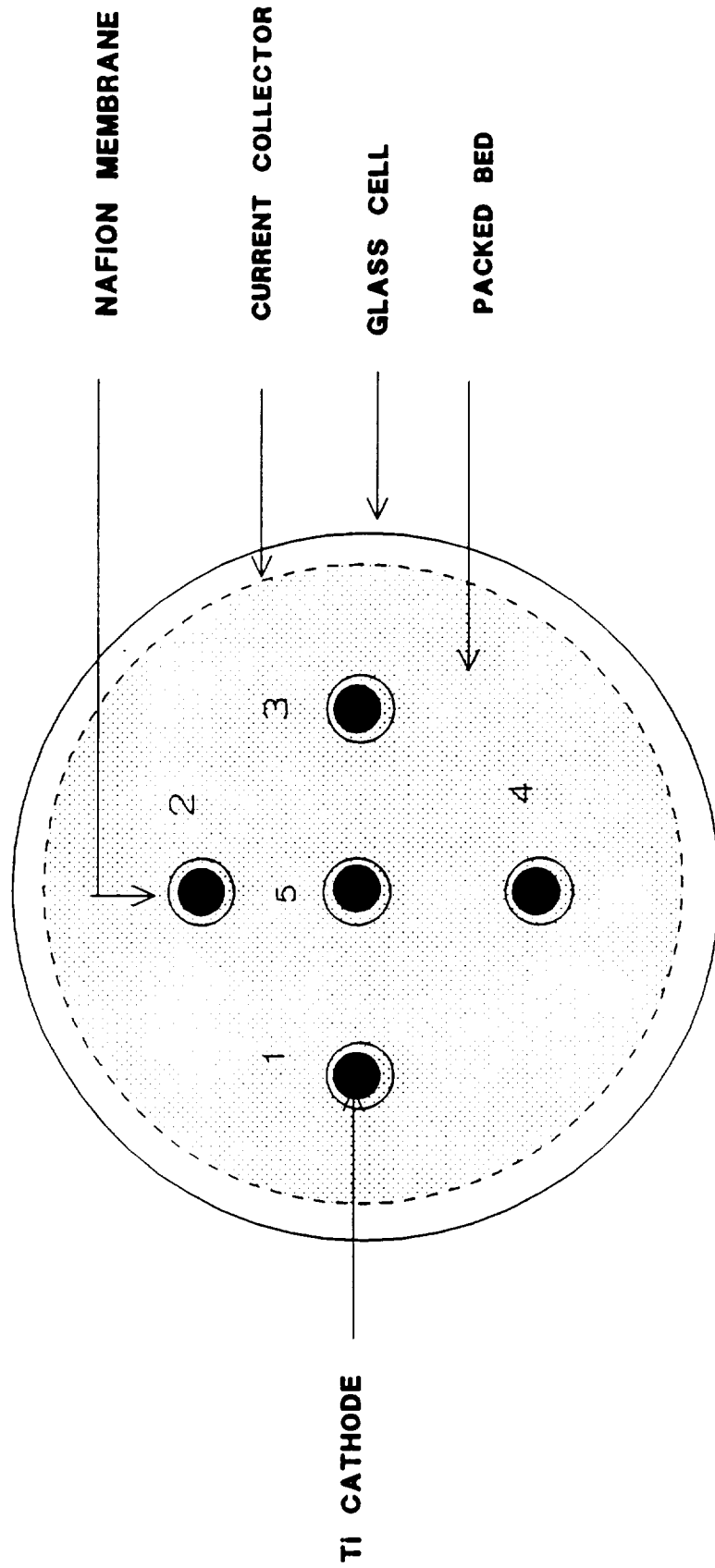
Ti CATHODE

Fig 14. CROSS SECTION OF PACKED BED WITH FIVE CATHODES

BED DIAMETER = 2.6 cm

NAFION MEMBRANE

CURRENT COLLECTOR

GLASS CELL

PACKED BED

TI CATHODE

ANODE

1

2

3

4

5
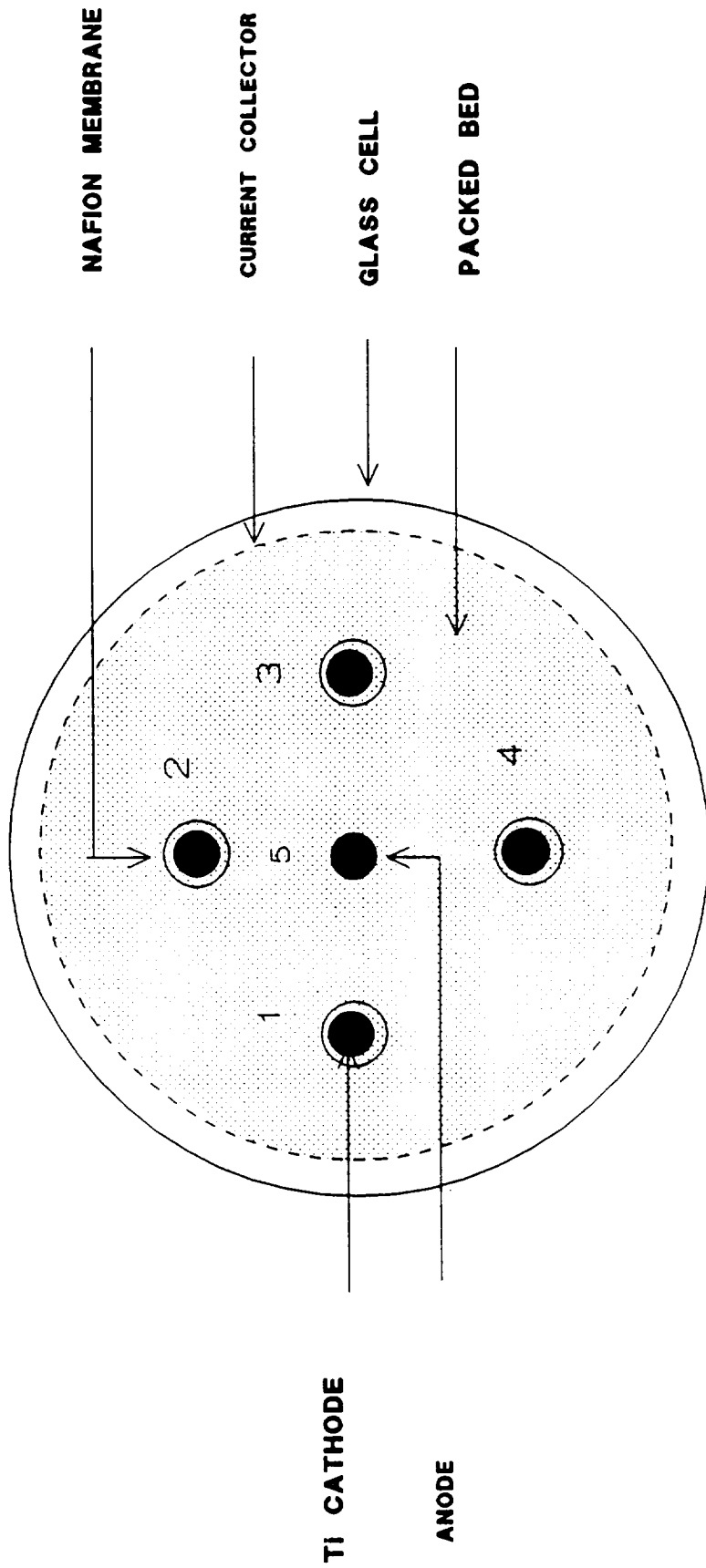
Fig 15. CROSS SECTION OF CELL WITH FOUR CATHODES AND CENTRAL ANODE
BED DIAMETER = 2.6 cm

anode and cathode, as the distance between the cathode and the current collector remains constant irrespective of the bed height. In contrast to the arrangement used in Figure 12, as the bed height is increased the distance between the current collector and cathode is increased, causing the IR drop to increase.

(c) Current flow in the direction perpendicular to the solution flow, with five cathode stanchions.

This configuration is shown in Figure 14. Here the number of stanchions are increased to five. This arrangement brings the cathodes closer to the current collector, reducing the overall IR drop. All 5 cathode stanchions are insulated from the anodic bed particles by using proton exchange membranes surrounding each stanchion.

(d) Current flow in the direction perpendicular to the solution flow.

Here four stanchions (Ti rods (2, 3, 4 and 1) serve as cathodes. These four cathodes are insulated from the anode bed by using Nafion membranes. Stanchion 5 is an additional current contact to the bed, so that the four cathodes now lie symmetrically between the current collectors, stanchion 1 and the mesh. Figure 15 (contrasts Figure 14) shows a cross section of the arrangement.

The flow of electrolyte in such cells is shown in Figure 4. During parametric studies, bed height was varied up to 10 cm and flow rates was varied up to 1250 ml/min., thus the capacity of the pump required varied widely. One of the three pumps given below, depending on the situation was used in the experiments.

1.   Diaphragm Pump — Asti (French) distributed by Cole-Palmer.

2.   Centrifugal Pump — March MFG Inc — Model BC2CPMD.

3.   Centrifugal Pump — March TE MDX MT-3.
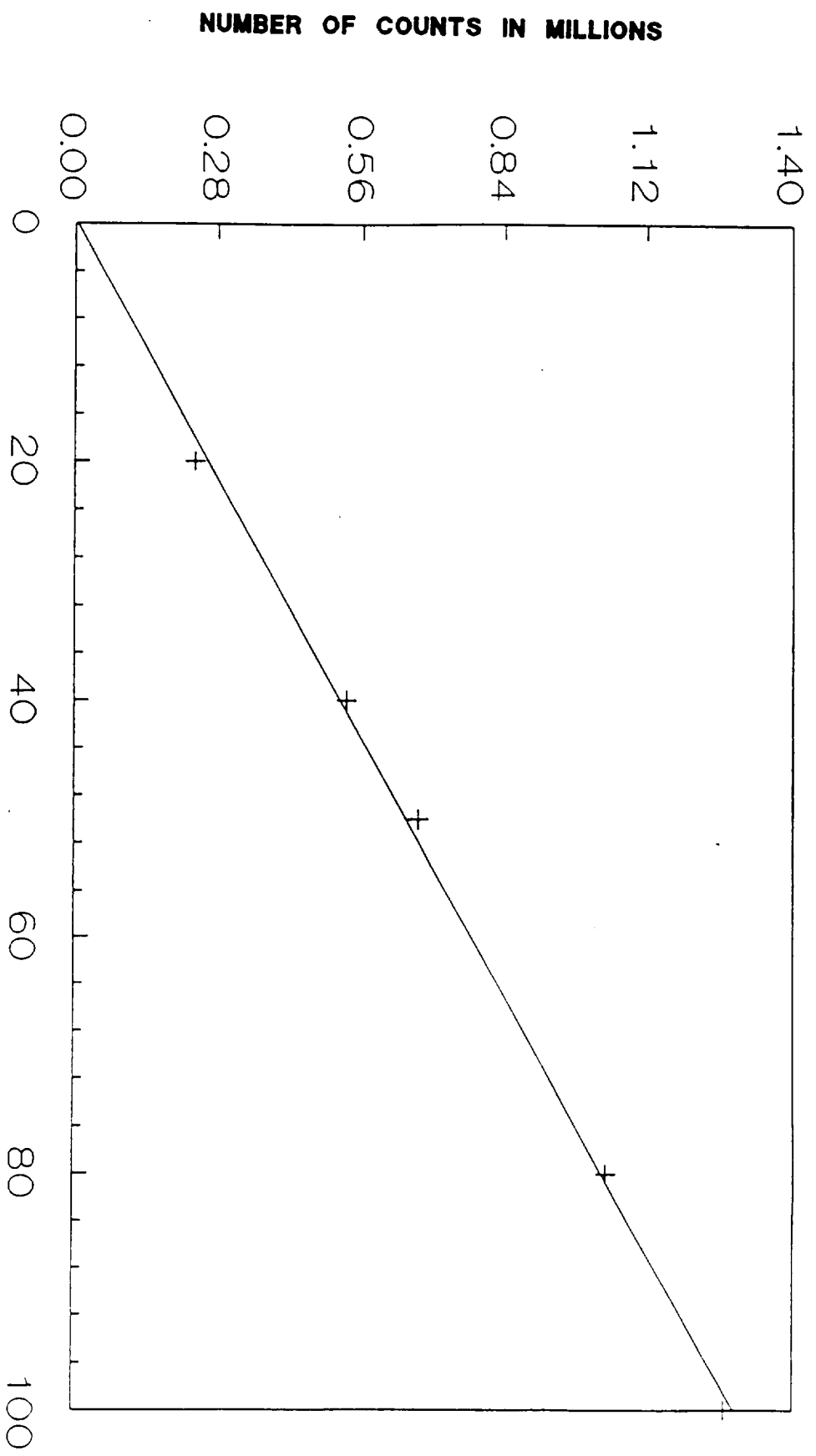
Fig 16. CALIBRATION GRAPH OF CARBON DIOXIDE

The Diaphragm Pump was of the least capacity (50- 400 ml/min.), while the March Pump MDX MT-3 had the highest capacity up to 1750 ml/min.

The method employed in the experiments was to collect all gases generated at the anode and cathode by the downward displacement of water over 4 liter containers. The gas container had to be replaced several times during the experiment, each container being able to hold only 4 liters of gas. The gases collected were analyzed using a Varian Model 3400 gas chromatograph, a carbosieve II column and a thermal conductivity detector. Argon was used as the carrier gas at a flow rate of 28 ml/min. Chromatograms were recorded using an HP 3390A integrator which provided digital readouts of the retention times and integrated areas of the different peaks. Calibration curves for CO_2, O_2, N_2 and H_2 were performed on a regular basis and typical curve for carbon dioxide is shown in Figure 16.

The Dependence of Particle Size on the Electro-oxidation of Human Waste in Urine

Experiments concerning this variable was done in the packed bed configuration shown in Figure 12. The parameters kept constant in this are the bed height (3 cm), the current density (7 mA/cm^2) based on the area of particles in the bed, and the flow rate (550 ml/min). The variable was the particle size.

The reaction of waste destruction was followed by collecting the generated gases and analyzing the gases for H_2, O_2, N_2 and CO_2. The Ebonex particles were prepared by crushing a tube of Ebonex and separating the particles to various sizes using standard sieves. The particles were washed in distilled water to remove the fine powdered Ebonex and were coated with SnO_2/Sb_2O_3 by slurry painting method. Four particle sizes were used in this study. The average diameters were 0.35, 0.60, 1.0, 1.85 and 4.0 mm, respectively.
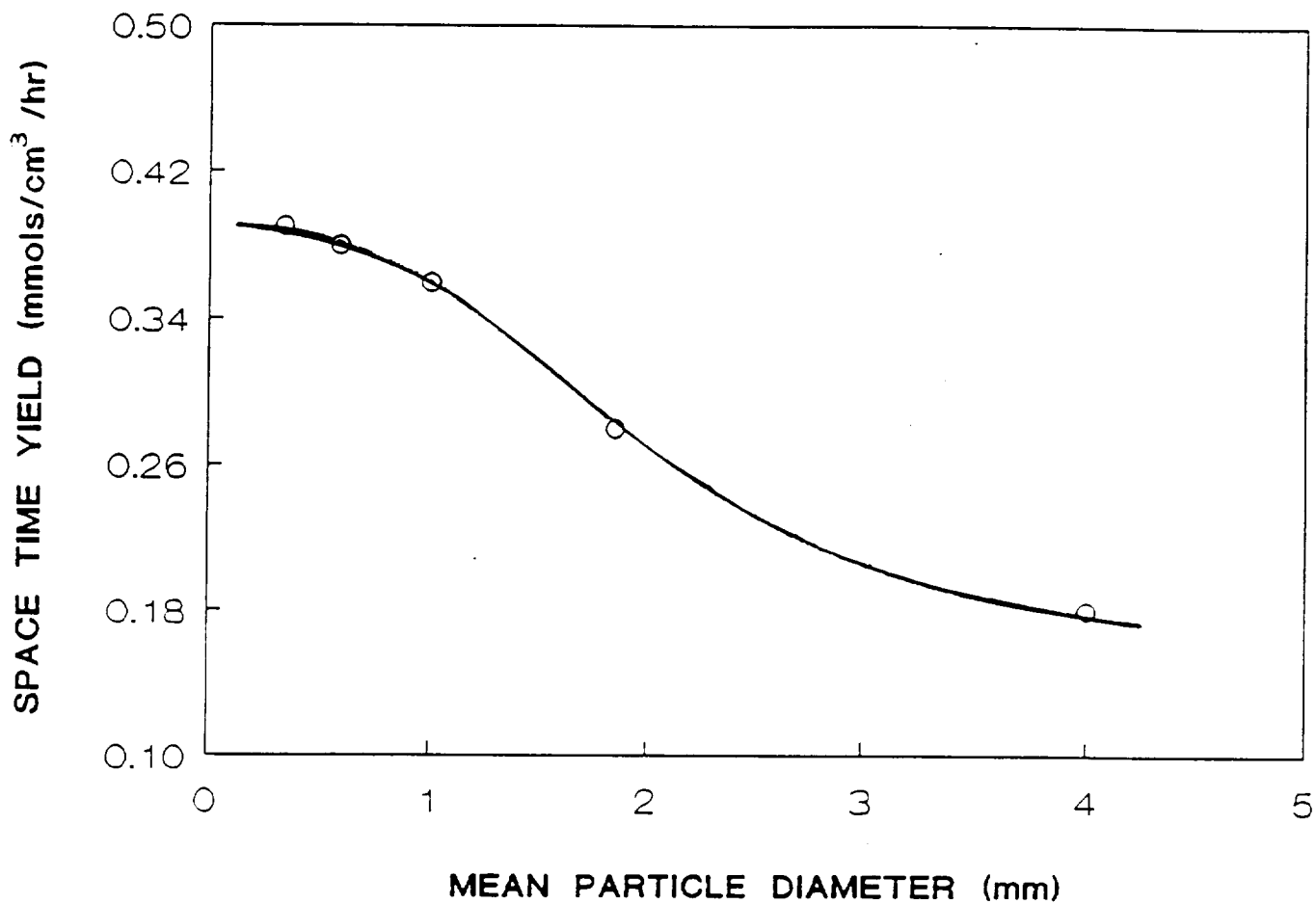
Fig 17. VARIATION OF STY WITH PARTICLE SIZE

The results are shown in Table 3 below.

TABLE 3.   THE DEPENDENCE OF SPACE TIME YIELD WITH PARTICLE DIAMETER

Average Particle Size Diameter (mm)	STY mmoles of CO_2/hr/cm^3	CO_2 in mg/hr/cm^3
0.35	0.39	16.7
0.60	0.38	16.28
1.0	0.36	15.4
1.85	0.28	11.9
4.0	0.18	7.92

The variation of space time yield (STY) is a function of particle size and is shown in Figure 17.

Calculation of Surface Area per Unit Volume for Spherical Particles,

Consider a vessel holding V cm^3 of particles of radius r cm.   If the voidage is ϵ, then the volume occupied by the particles is V (1-ϵ).

The number of spherical particles = V (1-ϵ)/(4πr^3/3)

Thus the total area A of particles per unit volume is

$$\frac{4\pi r^2 V(1-\epsilon)}{V\frac{4\pi}{3}r^3} = \frac{3(1-\epsilon)}{r}$$

When the particle size decreases, the available area per volume increases according to the above equation, where A is the area per unit volume of the bed, ϵ is the bed voidage and r is the mean radius of the particles comprising the bed.

Thus, the rate of generation of CO_2 increases as expected when the particle size decreases.   However, when the particle size is below 1.0 mm in diameter, variation of the rate of generation reaches a plateau region.
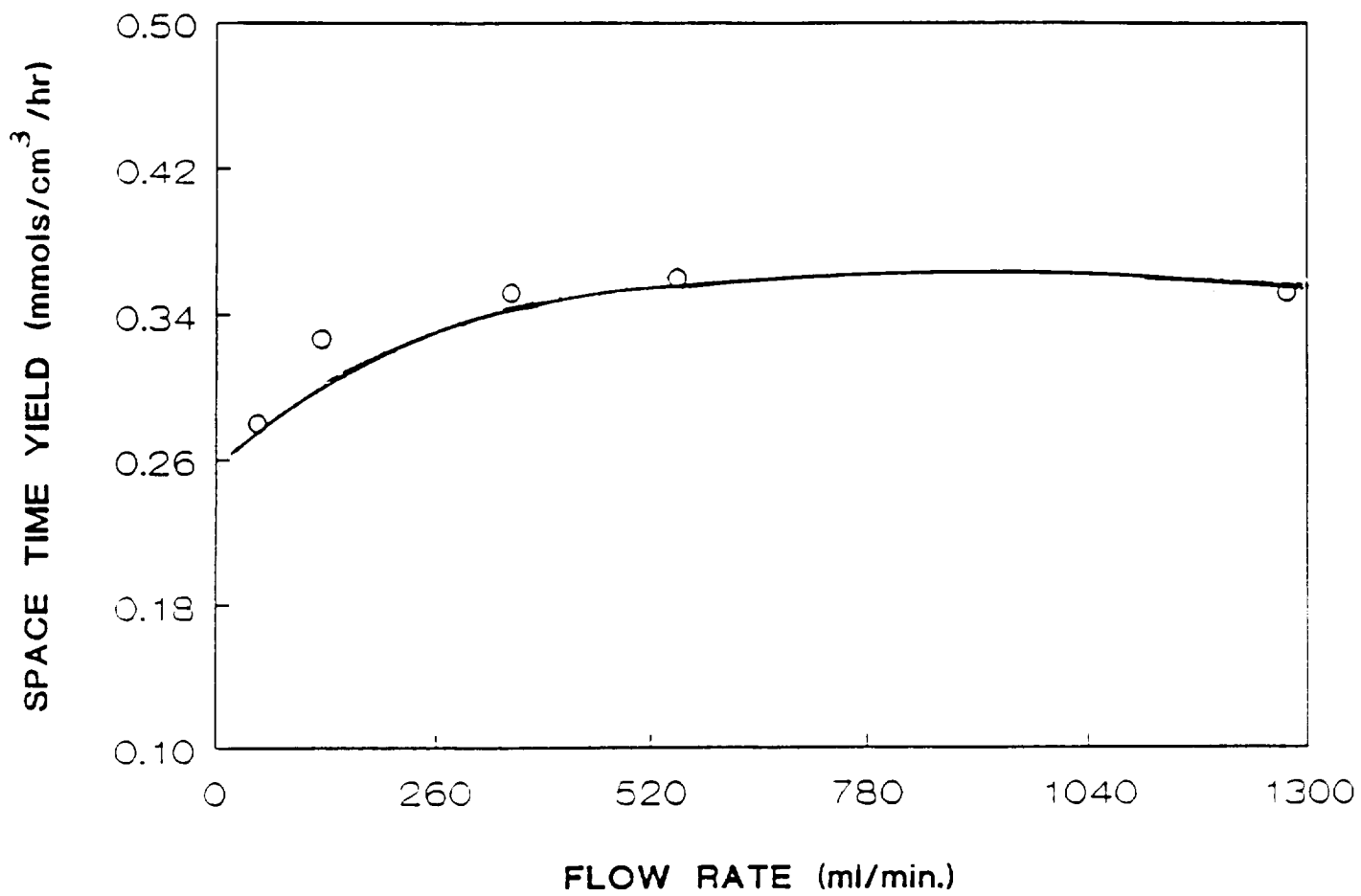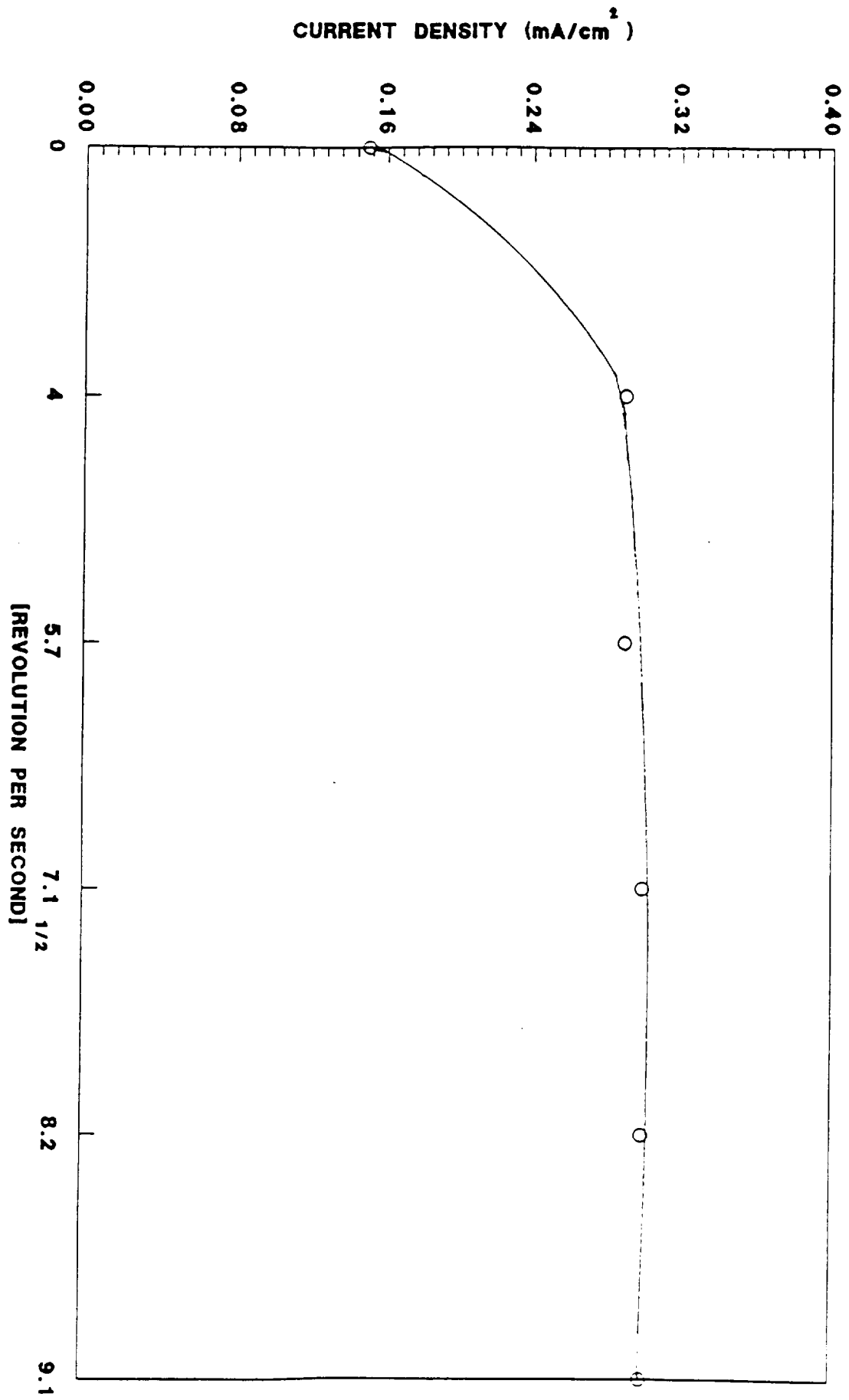
Fig 18. VARIATION OF STY WITH FLOW RATE

CURRENT DENSITY (mA/cm²)

[REVOLUTION PER SECOND]

Fig 19. VARIATION OF CURRENT DENSITY WITH (rps)$^{1/2}$

One reason for this effect may be that as the particles become smaller, the particulate matter remains adherent to the particles. This would increase the contact resistance between particles, making the bed less conducting and less effective. Thus the optimum particle diameter is in the range of 0.5 to 1 mm.

Dependence of the Rate of Generation of CO_2 in the Electrochemical Oxidation of Urine-Fecal Mixture on the Flow Rate

The experiments for this parametric study were carried out using the packed bed configuration shown in Figure 12. The parameters, namely particle size (1 mm), current density (4.2 mA/cm^2), bed height (5 cm) and temperature (90°C) were kept constant and the flow rate was varied from one experiment to the other. Gases generated at the anode and cathode were analyzed by GC, to determine the variation of CO_2 produced as a function of time. The results are summarized in the Table 3 below.

TABLE 4. THE VARIATION OF SPACE TIME YIELD WITH FLOW RATE

Flow Rate (ml/min)	Space Time Yield (STY) in mmoles $CO_2/cm^3/hr$
50	0.28
125	0.327
350	0.352
550	0.360
1275	0.352

The variation of STY with the flow rate is shown in Figure 18. It is seen that the rate of generation of CO_2 is independent of the flow rate above 350 ml/min. This is in conformity with the data obtained for the oxidation of the waste mixture in urine on a rotating disc electrode (Fig. 19). This shows that the
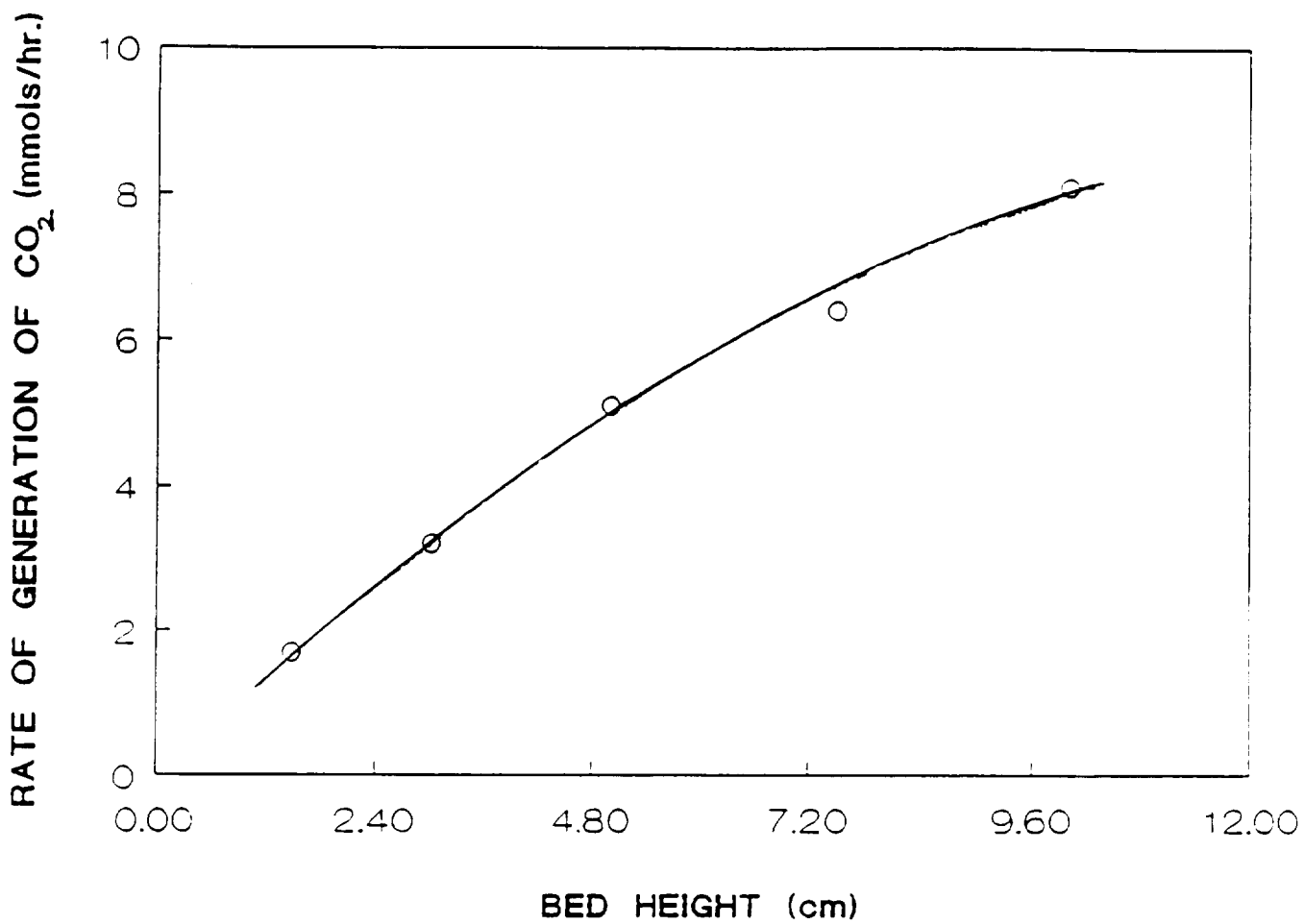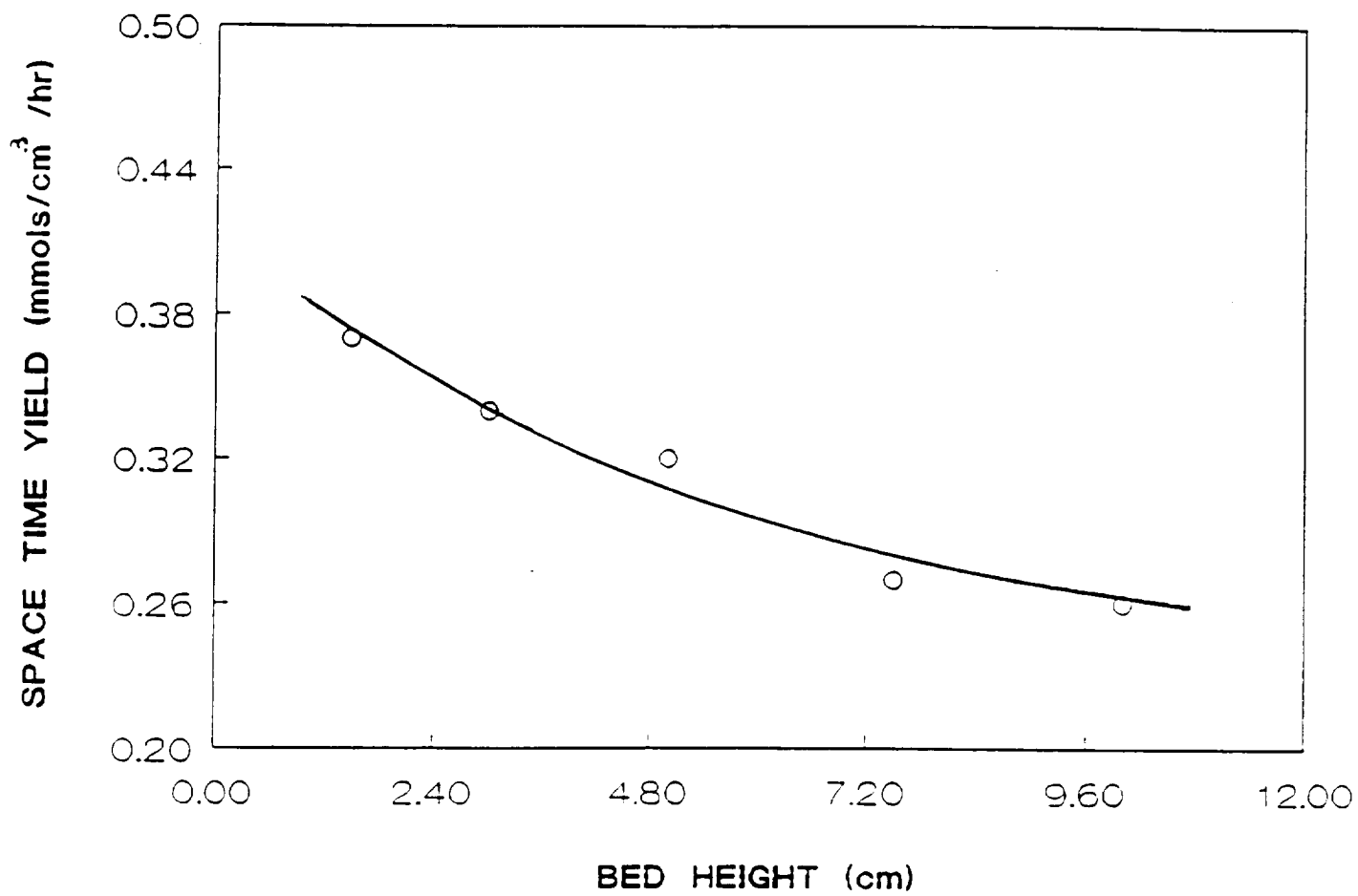
Fig 20. RATE OF GENERATION OF CO_2 WITH BED HEIGHT

Fig 21. VARIATION OF STY WITH BED HEIGHT

electrochemical oxidation becomes no longer mass transfer controlled, i.e. becomes controlled by chemical kinetics.

This study also shows that the flow rate control between 400-600 ml per minute for a bed of cross sectional area of 7 cm^2 is sufficient to enable the electrochemical reaction to take place in the plateau region, shown in **Figure 18**. This corresponds to a linear flow velocity between 0.9 and 1.4 cm/sec.

Dependence of the Rate of Generation of Carbon Dioxide by the Electrochemical Oxidation of Urine-Fecal Mixture on the Bed Height

In this study the configuration of the packed bed used for experiments is shown in Figure 15. The bed height was increased up to 10 cm and at each bed height the generation of carbon dioxide as a function of time was monitored by collecting the gases evolved and analyzing the gas mixture by means of gas chromatography. All other parameters, namely, particle size (1 mm), flow rate (550 ml/min), current density (4.3 mA/cm^2), and temperature (90°C) were kept constant.

The rate of generation of CO_2 in terms of the space time yield in mmoles CO_2 per cm^3 per hour as a function of bed height is shown in Figure 21. The variation of rate of generation of CO_2 in mmoles per hour with bed height is shown in Figure 20. This figure shows that the rate of generation of CO_2 increases with bed height, but Figure 21 shows that the STY decreases with increase in bed height. This shows that when the bed height is increased, the top part of the bed is not as efficient as the lower part of the bed.

This situation can be explained by the following consideration. The waste mixture enters the bed from the bottom, and when it flows up through the particles, the solution gets mixed with progressively increasing amounts of gases, namely, CO_2, N_2 and O_2 evolved due to the electrochemical reaction. Thus,

the percentage of gas bubbles mixed with the waste mixture increases from the bottom to the top of the bed. Thus, the effective conductivity of the bed gradually changes from a higher value at the bottom of the bed to a lower value towards the top of the bed. Then the upper part of the bed is less effective than the lower part of the bed.

One important consequence of this study is that in scaling up of the packed bed reactor, it is necessary to limit scaling up in the direction of solution flow, because when the bed height increases, the upper part of the bed has to accommodate more gas bubbles generated in the bed due to the anodic reactions. However, there are no limitations in scaling up in the direction perpendicular to the solution flow.

MAIN CONCLUSIONS

Thus, the main conclusions of the experiments on the parametric studies on the method of depositing SnO_2 on Ebonex, particle size, flow rate, bed height and current density are as follows.

(1) The Ebonex particles can be coated with Sb_2O_3 doped SnO_2 by the brush painting technique, followed by pyrolysis. The coating obtained is stable and superior to the coating obtained with the spray pyrolysis technique. This was confirmed by depth profile studies using XPS.

(2) Particles of diameter 0.5 mm to 1 mm are the best size for packing the bed.

(3) The best flow rate for a bed of 7 cm^2 cross section area is 60–100 ml/sec, which corresponds to a linear flow velocity of 0.9 to 1.4 cm/s. Higher flow rates above 1.4 cm/s do not produce higher oxidation rates, as the reaction is kinetically controlled.

(4)   The increase of bed height increases the conversion of waste to carbon dioxide, but the upper portion of the bed is not as effective as the bottom part of the bed, due to the accumulation of gas bubbles in between the particles.

(5)   The increase in current density based on the surface area of particles increases the rate of decomposition of waste. This is possibly due to the generation of very active OH radicals and more hypochlorous acid. It is necessary to fix the upper limit of the current density to avoid excessive evolution of oxygen.

In summary, particles of Ebonex (0.5 mm to 1 mm) in diameter coated with SnO_2/Sb_2O_3, a solution flow rate of 0.9 to 1.4 cm/second through the bed based on the cross sectional area of the empty tube holding the particles, bed height of 5 to 8 cm and a current density based on the particle surface area of 5 mA/cm^2 comprise a suitable set of parameters for the scaling up of the process and the construction of the final machine.

SUMMARY OF ACCOMPLISHMENTS IN 1992

(a) In 1991 it was shown that a packed bed electrode can be used for the electrochemical oxidation of human wastes. The better results obtained in a packed bed cell encouraged us to investigate the possibility of using other systems available, namely a stack of rotating disc electrodes, an assembly of micro-electrodes, jet electrode and vibrating electrode. Theoretical values of Space Time Yield (STY)(the number of moles of CO_2 formed per unit volume per unit time) were calculated for each electrode system. The value of STY was found to be the highest for the packed bed configuration. Thus this cell configuration was used for further studies.

(b) Mass balance calculations which are essential for scale up designs were reviewed at this stage. The amounts of gases dissolved in water used in the gas receiving vessels were calculated and used in the mass balance study. The agreement between theoretical amounts of CO_2, N_2, H_2 and O_2 and the experimental values were found to be within $\mp$ 8%.

(c) Parametric Studies in a Packed bed Cell.

1. Selection of electrocatalyst. Ebonex coated with tin oxide doped with antimony oxide was found to be 40 % more efficient than a coating of ruthenium dioxide on Ebonex.

2. Coatings obtained by brush painting and subsequent pyrolysis was found to be more stable than that produced by spray pyrolysis.

3. Experiments on the dependance of STY with particle size, flow rate, bed height and current density based on the area of particles were carried out. When the

dependence on one parameter was studied, values of all other parameters were kept constant.

4. In summary, particles of Ebonex (0.5- 1.0 mm) in diameter coated with SnO_2/Sb_2O_3, a solution flow rate of 0.9 to 1.4 cm/s, based on the cross sectional area of the empty tube, a bed height of 8 cm and a current density based on the total area of particles in the bed of 5 mA/cm^2 comprise a suitable set of parameters for scaling up the process.

5. A preliminary design of the packed bed cell to oxidize the daily output waste of one crew member in 24 hours yielded the following.

Bed height= 8 cm; Bed diameter = 6.4 cm; Number of cathode stanchions (3 mm diameter Ti rod) symmetrically placed in the bed= 5; Number of anode stanchions (3 mm diameter Ti rod) symmetrically placed around each cathodes = 4. Cathodes stanchions insulated from the anodic bed particles by using Nafion membranes.