Computer Modeling of the Kinetics of CO_2 Absorption in Rebreather Scrubber Canisters

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Abstract- Despite the ubiquitous use of carbon dioxide (CO_2) scrubbers in life-support equipment, the kinetics of absorption in scrubbers is poorly understood. Furthermore, there are no dependable sensors to indicate when scrubber life has been expended in underwater breathing apparatus. It was thus our aim to model scrubber kinetics, and from that modeling determine whether thermal sensors could reliably indicate remaining scrubber life. To that end, we have exploited a stochastic method for the discrete simulation of CO_2 absorption reactions in scrubber canisters found in closed-circuit underwater breathing apparatus (rebreathers). The model, applicable to both sodalime and lithium hydroxide absorbents, allows us to test the effects of temperature, flow rates, CO_2 production, canister geometry, and granule size on absorption kinetics. The model exhibits some similarities to the finite-element method: the simulated bed contains a minimum of 200,000 volume elements or cells, within which are found the cell temperature and amount of CO_2 stored for each increment of time. However, unlike the usual application of partial differential equations in finite modeling, mass and heat transfer are determined stochastically. Although constrained by the overall physics, chemical absorption within each cell, with its resulting thermogenesis, and CO_2 flow path among cells are probabilistic. The result is a simulation rich in CO_2 absorption and thermal fluctuations. Diffusion of CO_2 within absorbent granules is impeded by diffusion resistance generated by the accumulation of reaction products within the granules. Thermal conductivity of the absorbent granules, granule size and volume, convective flow rate, and heat transfer between air and granules all influence the reaction kinetics. Gas flow can be directed evenly across the canister or toward a point source. We currently use the model to predict and explain the time- and space-varying thermal profiles occurring as CO_2 reaction fronts move through various canister shapes. We are exploring how knowledge of transport coefficients computed from fluctuation analysis would improve estimates of canister survival time. We also use the simulation to visualize the patterns of CO_2 absorption within a scrubber canister. Since the absorption process is inefficient, the model may ultimately aid optimum use of carbon dioxide absorbents and canister geometry.

I. INTRODUCTION

The Navy Experimental Diving Unit (NEDU) develops test procedures and standards for underwater life-support equipment, including rebreathers [1, 2]. NEDU test procedures and standards for rebreather components such as CO_2 scrubber canisters (Fig. 1) have been adopted by both the U.S. Navy and the U.S. Occupational Safety and Health Administration (OSHA) [3].

Recently, after we observed scrubber canister behavior that was not explained by the conventional wisdom, it became apparent that we lacked an investigational tool to explore the complexities of CO_2 absorption kinetics in sodalime-based absorbent beds. To that end, a discrete computer model of absorption kinetics was developed, based on stochastic principles. Since the model was to be used for didactic purposes only, a qualitative model was acceptable. This paper explains the methods and application of the resulting stochastic model.

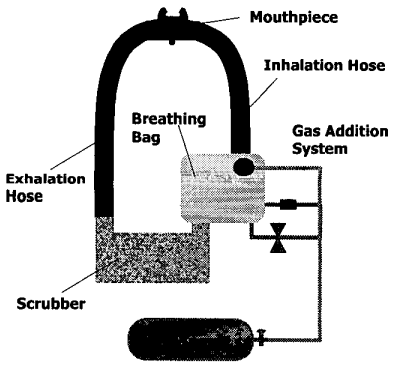

Fig. 1. Simplified rebreather schematic.

II. METHODS

The model was written in Visual Basic 6.0 and run on a PC with 1 GB of RAM to handle large array sizes. It was based on the repetitive application of small forces acting on up to 250,000 discrete volume elements (cells) within a simulated CO_2 absorbent bed in a rebreather scrubber canister (Fig. 1). The resulting heat and mass transfer influenced chemical reactivity in each cell. Dynamics were determined by forces established at discrete time intervals, applied within discrete cells. CO_2 and heat moved according to gradients established during the preceding time interval.

A. Simulation Setup

We assume spherical granules made of concentric shells, with each shell being 0.5 mm thick. Therefore, a 4-mm diameter granule has four shells, and a 2-mm granule has two shells.

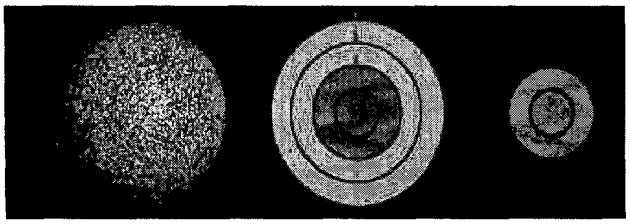

Fig. 2. Granule geometry

The number of absorption sites per granule directly depended on the surface area of each granule shell (Table 1). The total number of sites available in each granule were the sums for all shells. Consequently, 4-mm granules (large

TABLE I
ABSORPTION SITES PER SHELL

	Shell diameter (mm)			
	4	**3**	**2**	**1**
sites	32	18	8	2

granules) contained a total of 60 CO_2 absorption sites, and 2-mm granules (small granules) had 10 sites.

The number of granules per canister was a function of granule size and absorbent bed porosity. For a bed porosity of 0.32 [4], a 4.5-liter canister contained 91,320 four-mm granules and 730,500 two-mm granules.

The number of reaction sites per canister equaled the product of the number of granules and the number of sites per granule. For a bed of large 4-mm granules, there were 5,479,200 absorption sites, and for a bed of 2-mm granules, there were 7,305,000 absorption sites.

B. Model Rules

1) As a CO_2 molecule carried by convection (respiratory flow) approaches a granule, it encounters a potential absorption site at random. If that site is empty, then the probability that CO_2 will react linearly depends upon temperature. As more absorption sites are filled, the fewer the number of available sites. A CO_2 molecule can loiter in a cell and randomly encounter absorption sites until its "residence time" for that cell has expired.

2) If no free site has been found within the allotted cell residence time, the CO_2 molecule moves to the next cell downstream.

3) Cell residence time is an inverse function of mass flow rate.

4) Probabilistic rules determine the diffusion of CO_2 into the lower shells of a granule. The probabilities depend on temperature, availability of an empty site, and diffusion barriers caused by accumulating reactants (Fig. 3). On the left side of Fig. 3 we see CO_2 molecules (red dots) that absorb to the outside of the granule, and then diffuse inward to available sites (lower left). On the right is a similar depiction of diffusion in small granules.

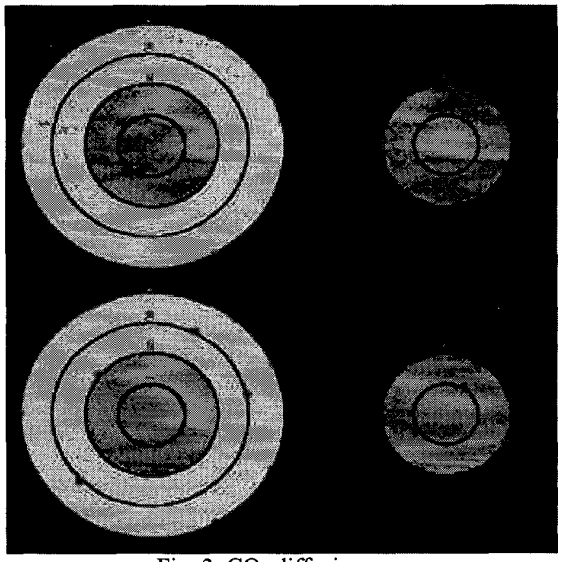

Fig. 3. CO_2 diffusion

5) When a temperature gradient exists between cells within the bed and the surrounding water, heat flows towards the heat sink (the lower temperature) by conduction.

6) Heat generated by the exothermic reaction of CO_2 with sodalime granules is carried downstream by convective transport (gas flow). The heated gas can preheat downstream granules.

C. Additional Porosities

Imperfect canister filling causes porosities not accounted for by the packing of perfect spheres. These porosities are distributed randomly throughout the absorbent bed.

The imperfect packing of granules around container walls results in edge effect porosities and "channeling." These sources of additional porosity are shown in Fig. 4. A slice has been cut out of a rectangular canister to show internal structure. Cells that contain absorbent are white; those lacking absorbent are shaded. Due to the edge effect, porosities are more numerous at the edges of the canister than in the middle.

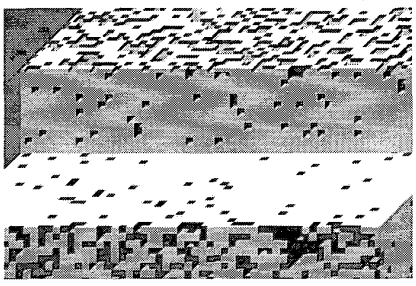

Fig. 4. Edge effect and random porosities.

D. Parameters

The following parameters can be manipulated by the model: size of the absorbent bed, ratio of canister length to width, axial or radial flow, canister insulation, size of granules (2 to 4 mm diameter), water temperature, initial absorbent bed temperature, temperature dependence of reaction, magnitude and temperature dependence of granule internal diffusion coefficient, diffusion resistance of accumulating reaction products, CO_2 residence time, heat of reaction, and heat transfer factor between granules and air.

E. Model Outputs

While the simulation is running, the following data can be obtained: temperature within each cell at any moment during the simulation, and the amount of CO_2 stored in each cell. *Slicer/Dicer* 3-D visualization software (Visualogic, Inc., Bellevue, WA) aided depiction of both temperature and CO_2 content data. The model also outputs the average temperature of the absorbent bed, average temperature of the canister effluent, CO_2 released into the effluent per calculation cycle, cumulative CO_2 in the canister effluent, cells with free CO_2, and cells with active absorption reactions.

III. RESULTS

The higher the flow rate through the canister, the less time CO_2 resides within a canister cell, and therefore within the canister. Fig. 5 shows the direct effect of residence time on "canister breakthrough", the point where absorption is no longer complete and CO_2 begins to rise in the canister effluent. "Cycles" in Fig. 5 refers to computation cycles and directly relates to simulated time. Residence time varies left to right from 2 to 4 in arbitrary units. The longer the residence time, the longer the canister duration.

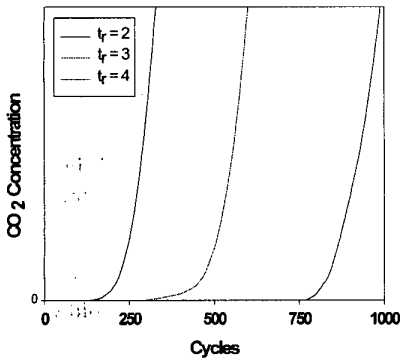

Fig. 5. Effect of CO_2 residence time (t_r) on canister breakthrough.

Edge effects, in which packing against the canister walls is imperfect, dramatically reduce breakthrough time. From right to left in Fig. 6, the probability of having a cell close to the canister wall filled with absorbent ranges from 100% to 80%.

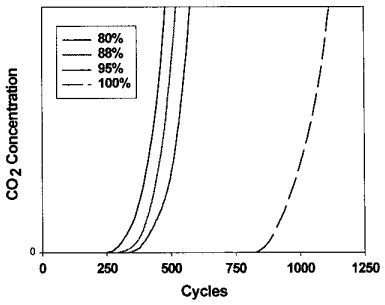

Fig. 6. Effect of filling probability and edge channeling on breakthrough.

A. Temperature Profiles

The absorption of CO_2 by sodalime is exothermic, meaning that heat is produced. The following sequence progressing left to right and down the page shows the heat from a CO_2 absorption reaction front progressing from left to right through a rectangular canister. As in Fig. 4, a rectangular portion of the canister has been removed to reveal internal temperature profiles. Black is the coldest temperature, in this case 50° F, and yellow is the warmest temperature (~105° F). Time progresses from left to right and down the page. Heat is carried downstream by both convection and conduction.

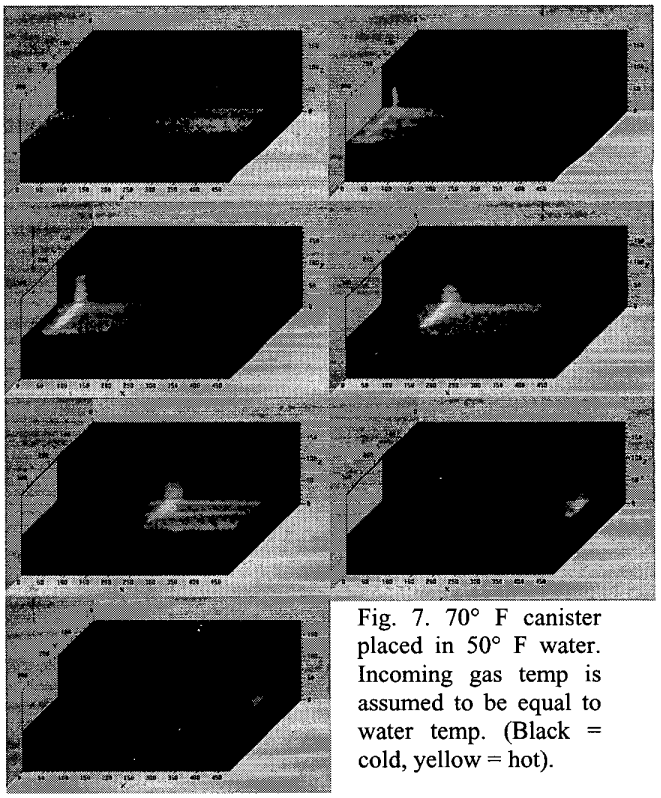

Fig. 7. 70° F canister placed in 50° F water. Incoming gas temp is assumed to be equal to water temp. (Black = cold, yellow = hot).