SME Annual Meeting
Feb. 25 - 28, 2018, Minneapolis, MN

Preprint 18-098

ADVANCING CO_2 SCRUBBER CHEMISTRIES USED IN RESPIRATORY PROTECTIVE DEVICES AND REFUGE ALTERNATIVES

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ABSTRACT

The Mine Improvement and New Emergency Response (MINER) Act included the need for improved chemical technologies to address respiratory protective device inadequacies and refuge alternative development.

The National Institute for Occupational Safety and Health's (NIOSH) National Personal Protective Technology Laboratory (NPPTL) invests in research and development to improve the carbon dioxide (CO_2) scrubbing technologies built into these mine safety systems. Testing at NIOSH NPPTL is performed using a custom-designed test system containing a chemical reactor and sensors in a constant flow of simulated expired breath to evaluate chemical performance for the scrubber materials. Current testing procedures focus on device duration or capacity, but do not report criteria needed to effectively optimize chemical performance. In this presentation, testing results which identify the chemical performance roles for CO_2 scrubber components will be reported, and specific component chemical activities will be linked to both duration and CO_2 absorption capacities. Chemical components being evaluated include hydroxyl, superoxides, metal, and amine active sites, distributed in salts, zeolites, metal-organic frameworks, and microporous materials.

INTRODUCTION

CO_2 absorbents and oxygen sources are at the heart of closed circuit breathing air supply systems used in mining escape and rescue operations. CO_2 absorbent technology was first developed for diving rebreathers and has been in use for over a century. Typically these devices include a soda lime formulation of pellets in the 8-12 mesh range. Larger 4-8 mesh particles are used in medical grade "low-flow" applications, since these particles present a lower flow resistance regime more amenable for use with resting individuals. Potassium superoxide and lithium hydroxide formulations are also used, where in each case the formulations involve bulk solid pellets or materials affixed to surfaces. CO_2 capture technologies are now under intensive study in the energy and automotive industries, where the pursuit of optimal combustion processes has led to the development of new materials to capture, convert and store CO_2, oxygen and carbon monoxide gases. Recent advances in nano-structured and high surface area catalysis have produced novel materials demonstrating chemical performance improvements in these industries, and these improvements may now also be adapted to enhance chemical efficiency and performance in escape and rescue devices. Higher surface area materials offer promise for improving the efficiency, or decreasing the burdens associated with the use of closed circuit respiratory protective devices containing CO_2 absorbents. Novel chemicals that display advantages in chemical performance or decreased burden will be examined for inclusion in developing systems such as the next-generation closed-circuit mining escape respirator or refuge alternatives.

TESTING METHOD

The National Institute for Occupational Safety and Health (NIOSH) is charged with certifying the performance of respiratory protective devices. This testing is performed within its National Personal Protective Technology Laboratory (NPPTL). Whole intact devices are tested under physical and physiological conditions simulating their expected field performance. Closed circuit devices such as Closed Circuit Escape Respirators are approved for duration and capacity testing according to 42 Code of Federal Regulations (CFR) 84.303 (in subpart O) on an automated breathing and metabolic simulator (ABMS) in addition to man tests. Long-term field evaluation testing is also performed on the ABMS to evaluate how well mine-deployed Self-Contained Self-Rescuers, previously approved under 42 CFR 84.97 (in Subpart H) using human subjects, endure the mine environment with regard to both physical damage and the effects of aging. Chemical components in the intact devices are subjected to humidified breathing gas containing 5% CO_2 in pulsed cycles to simulate the breathing process. Breathing and metabolic simulation (BMS) tests are terminated when the breathing gas supply (O_2) is expended (as indicated by a collapsing breathing bag and peak inspired breathing resistance <-300 mm H_2O). Duration or capacity derived from these tests depend on the performance of the oxygen sources, and the tests yield no certain means to calculate CO_2 absorbent performance directly. Capacity in BMS tests refers to the amount of oxygen generated, not CO_2 absorbent capacity.

A simplified test method was developed to directly measure the chemical performance of CO_2 absorbents used in closed circuit devices. This method was adapted from the North Atlantic Treaty Organization (NATO) Standard Agreement (STANAG) 1411 method[1], which uses a constant flow of 5% CO_2 in humidified N_2 through a 105 mL reactor bed. In NIOSH testing, a constant flow of 4% CO_2 in 50% relative humidity room temperature air is delivered by mass flow controllers into a 1 L polymer entry vessel. Sensing and control devices in the entry vessel are used to control CO_2 concentration and relative humidity in the test system entry air. An identical set of sensors is placed in an exhaust vessel to measure and report changes in the air when the flow is switched through a reactor bed containing CO_2 absorbent. Passive CO_2 sensors in these vessels rely on diffusion to fill the nondispersive infrared (NDIR) cell located on the sensor board. The CO2S-PPM-20 CO_2 sensors (SST Sensing) are ultra-low power NDIR sensors mounted on a PC boards providing CO_2 analysis over a 0-20% or 0-5% range in air at 50 ppm accuracy. The LuminOx oxygen sensors (SST Sensing) utilize fluorescence quenching and operate in a range of 0-25%. Humidity is sensed using HTM2500LF (Measurement Specialties) humidity and temperature modules, which operate over 0-100% relative humidity at room temperature. The reactor bed is an inert 225 cm^3 polycarbonate cylinder. Entry air flow into the vertical cylindrical reactor is from top to bottom. A set of solenoid valves directs air flow through a reactor bypass until test conditions are established. Gas concentrations are recorded over time while flow and control conditions are maintained to provide a dynamic flow determination of chemical absorbent performance. The system uses National Instrument data acquisition (NI-DAQ) modules to interface with the sensors and mass flow controllers. A custom-designed LabVIEW program controls test system activities and sends data to a spreadsheet at six second intervals.

This test method is not a certification test, as it uses constant flow rather than breathing and metabolic simulation and incorporates different physical test conditions. Chemical components are tested separately from the devices in reactors, and are subjected to a constant CO_2 concentration and air flow rates. Loadings and flow rates are chosen that mimic absorbent manufacturers' CO_2 weight capacities, typically 110 L/kg for medical grade CO_2 absorbents and 140 L/kg for diving grade CO_2 absorbents. Chemical performance for solid CO_2 absorbent chemicals is typically reported by equipment and chemical manufacturers in terms of capacity, as either mass (in L CO_2/kg) or volume (L CO_2/L absorbent) capacity, or sometimes mass gain. CO_2 absorption processes for higher surface area materials are most often reported as molar capacity, moles of CO_2 absorbed per absorbent mass or volume.

A test begins when flow is diverted into the reactor. Exhaust CO_2 concentration is plotted in real time to monitor absorbent performance. The amount of CO_2 absorbed is the difference between entry and exhaust vessel concentrations times the CO_2 flow rate (112 mL per minute in this case). Capacity is the absorbed CO_2 volume divided by the sample mass (L/kg) and can be determined at every point in the test process. Time and capacity where the CO_2 concentration begins to rise above 0 is described here as "breakthrough" time or capacity. "Effective" times and capacities are defined here as the point where the CO_2 concentration $\geq 0.5\%$. The STANAG 1411 test method terminates the test at 0.5% CO_2, reporting the test time at that point as "activity". This concentration is significant in NIOSH, Occupational Safety and Health Administration (OSHA), and the American Conference of Governmental Industrial Hygienists (ACGIH) occupational exposure standards, which limit exposure to 0.5% CO_2 (5,000 ppm) averaged over a 40 hour week, and short term exposure to 0.3% (30,000 ppm) average for 15 minute exposure. Actual "instantaneous" physiological effects to CO_2 exposure begin to occur between 0.5% and 1% CO_2. Flow continues in this testing scheme until the CO_2 concentration at the exhaust is 4%, with the capacity at that point reported as "end of test" capacity.

MATERIALS

Commercial CO_2 absorbents were obtained from six manufacturers, and represent a variety of ages and two grades, since manufacturers typically offer both medical and diving grades. Products were coded with a three character designation: first by manufacturer (A-F), then by grade (either medical grade M or diving grade D), then a sample number (1-4). Materials with expiration dates before September 2017 were classified as "expired", while the remaining materials were classified as fresh. Most products were soda lime materials, calcium hydroxide with a few percent of sodium and/or potassium hydroxide included as a catalyst. There was typically 12-18% water by weight included in the formulations, though the locations or distribution of water was never described. Most had a small amount of indicator (<1% by weight) to provide visual evidence of exhaustion in clear or opaque canisters. Several did not use sodium or potassium but included lithium or calcium salts to avoid concerns over anesthesia gas decomposition by sodium hydroxide.

Generic chemical materials with CO_2 absorption potential were obtained from Sigma-Aldrich. Soda lime chunks consisted of irregular chunks roughly 4 mm in length (similar in size to diving grade CO_2 absorbents). Their water content was only 5.6%. Lithium hydroxide also consisted of irregular 4 mm chunks, but contained <3% water. Potassium dioxide (or superoxide, KO_2) consisted of much larger chunks, irregular and roughly 10 mm in length and were likewise dry.

RESULTS

A study of CO_2 absorbent types was conducted using generic solid particles obtained from commercial chemical suppliers relative to a standard AM2 soda lime pellet. These studies used a constant volume of irregular solid chunks exposed to a constant flow of 4% CO_2 in 50% relative humidity (RH) room temperature air at a rate of 2.8 Liters per minute (Lpm). A 60 g loading of commercial AM2 soda lime pellets served to establish a standard volume of 76 cm^3, about a third of the full reactor volume. Plots are presented in Figure 1, while times and capacities are given in Table 1. CO_2 concentration in the 1 L exhaust vessel dropped to 0 within 2 minutes in each case, then remained at 0 until the solid bed neared exhaustion, where it rose to match entry vessel CO_2 concentration. The end of test capacities were also reported.

Effective time for AM2 was 75 minutes, very similar to times observed for 1 hour escape devices containing CO_2 absorbents that pass ABMS certification testing. Effective capacity was nearly 140 L/kg, much better than the manufacturers' reported value of 110 L/kg for this medical grade material. Capacity at the end of the test, where CO_2 is approaching a minimal absorption near 4%, was about 190 L/kg, or about 69% of the theoretical capacity calculated from the number of base sites available. Figure 2 presents plots of capacity by weight versus time for these same generic solid particle tests. Generic soda lime (blue dotted line) was a poor performer, in spite of the 60 g loading with a higher molar loading of hydroxyls (0.76 moles because of 5.6 % water content). This material consists of irregular 100 mesh chunks, smaller than AM2 pellets. On the surface, poor performance might be attributed simply to low water content, though earlier efforts to add water prior to testing did not improve performance. It could also be that the material was not isolated from atmospheric CO_2 in production, packaging or storage.

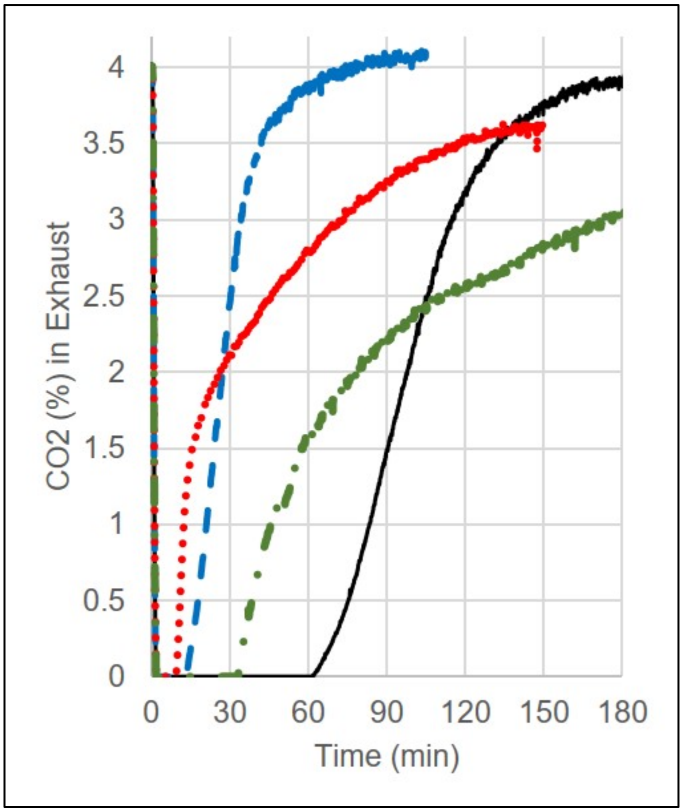

Figure 1. Carbon dioxide absorption versus time for generic solid base chemicals using the constant flow test system: AM2 (black line); lithium hydroxide chunks (green dot dash); soda lime chunks (blue dash); potassium dioxide chunks (red dots).

Table 1. Relative carbon dioxide absorption times and capacities of solid chemical absorbent particles.

	AM2	LiOH	Soda Lime	KO_2
Loading (g)	60.04	23.05	60.03	48.05
Time (min)				
Breakthrough	61	33	13	10
Effective	75	39	18	11
Capacity (L/kg)				
Breakthrough	113	156	23	20
Effective	137	181	31	23
Effective (L/L)	106	89	24	15
End of test	190	535	53	110

Potassium dioxide (or superoxide, KO_2) was also a poor performer, but in this case these were 10 mm irregular dry chunks. Water is not needed for the CO_2 absorbent reaction. Again, exposure to CO_2 in preparation, or packaging may have effected performance, but it was more likely a function of chunk size. Lithium hydroxide was tested as 3-4 mm chunks. Though the breakthrough and effective times were significantly less than AM2, breakthrough and effective weight capacities were 156 and 181 L/kg, superior characteristics to all soda limes. Chemical performance testing of the respective powders is needed to sort through the effects of particle size.

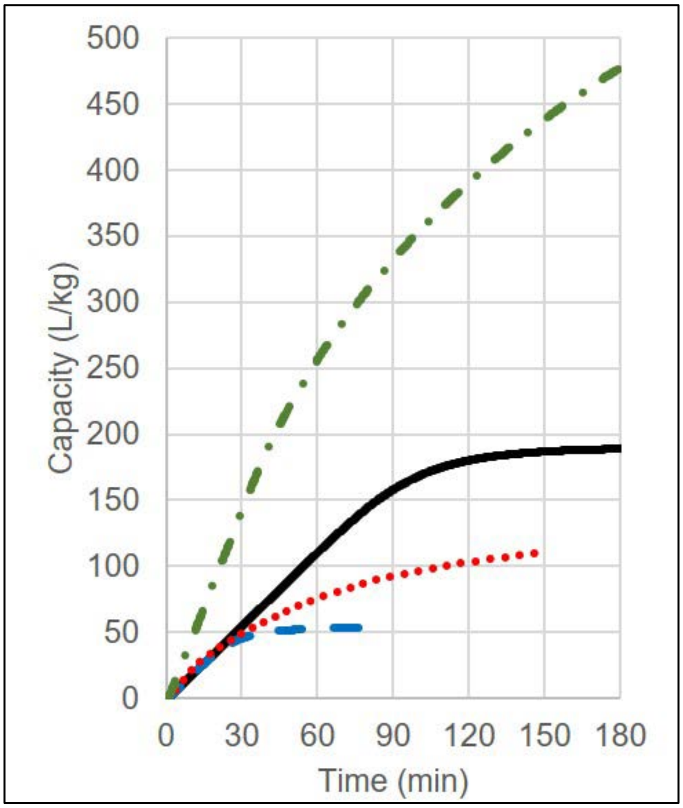

Figure 2. Carbon dioxide capacity versus time for generic solid base chemicals. Curve assignments are: AM2 (black line); (2) lithium hydroxide chunks (green dot dash); (3) soda lime chunks (blue dash); and potassium dioxide chunks (red dots).

A survey of commercial low flow CO_2 absorbents was then conducted using the same 60 g loading and flow conditions. Since a significant number of the stock obtained had reached its expiration date, the data has been divided into two separate figures, where Figure 3 and Table 2 (see APPENDIX) contain data from fresh or unexpired commercial CO_2 absorbents. Effective capacities ranged from 109-138 L/kg for the fresh materials, and all met or exceeded the manufacturers' claims of 100-110 L/kg. AD2 is a diving grade absorbent clearly superior to its co-product AM2, showing the extension in times and capacities attributed to the particle size. The exhaustion portion of the curve was nearly vertical for these fresh materials, occurring usually in 10-20 minutes. The curves were fairly uniform in shape. EM1 and DM1 are two of the better medical grade absorbents, yet are limes formulated without sodium or potassium. Clearly the absence of sodium and potassium is not a detriment, as lithium or calcium salts seem to possess favorable characteristics perhaps in managing water in the predominant reactive lime component.

End of test capacities ranged from 55-70% of the theoretical capacity of CO_2 expected from the active hydroxyl concentration in soda lime. This limit is related to physical or chemical conditions common to all lime-based CO_2 absorbents. It suggests that there are structural limitations to how much CO_2 can actually fit in the bulk lime solid, as if the formation of carbonates makes some remaining hydroxyl sites inaccessible. Conversely, some of the expected hydroxyls may be used in the pellet making process, where small amounts silicate or polymeric binders may use up hydroxyls or render them inaccessible. End of test moisture analysis of the products revealed that water remained in every product, and the range observed was 3.45-6.70%. This indicates that the reaction does not cease because of a lack of water in the product. The remaining water may be around cations and these hydrated species may be competing for hydroxyl sites much as they do in zeolites which only seem to hit about 10-20% of their theoretical capacity. This would provide an upper limit to carbonate formation. Or it could be that water is bound up in carbonate structures and unable to catalyze reactions at the hydroxyl sites.

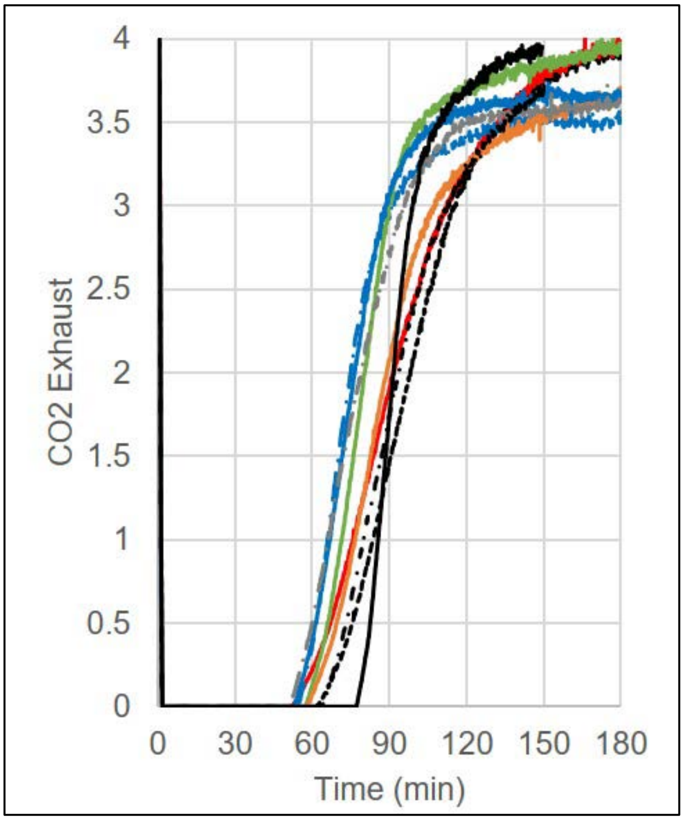

Figure 3. Carbon dioxide absorption versus time for various commercial lime products using the constant flow test system. Curve assignments are AM2 (black dash-dash-dot), BM1 (red), CM2 (blue dash), DM1 (green), EM1 (orange), CD1 (blue solid line), FM2 (gray dash), AD2 (black dash dot) and AD3 (black solid line).

Figure 4 presents the CO_2 absorption curves for various expired commercial products, while times and capacities are given in Table 3 (see APPENDIX). Expired materials generally exhibit premature exhaustion evident in decreased breakthrough and effective times, and elongated exhaustion processes taking >20 minutes. Expired CO_2 absorbents offered a wider variety of breakthrough and effective time and capacity characteristics. Effective time for AM1 was 53 minutes, significantly shorter than that of fresh AM2, and the 96 L/kg capacity measured were also significantly below 110 L/kg. The difference in performance was attributed to sample age: AM1 had an expiration date of July 2016. End of test capacity still averaged 67% of theoretical capacity, suggesting that age does not result in a loss of active hydroxyl sites, just a change in their access.

Breakthrough times and capacities were diminished for AM1 compared to unexpired materials, and this premature rise characteristic was common for the other expired materials. Three products still demonstrated effective capacities near 110-120 L/kg (BM1, BM2 and CM1). Three expired materials, (AM1, FM1 and BD1) were only marginally underperforming, with effective capacities ranging from 90-100 L/kg, through breakthrough time and capacities consistently revealed premature exhaustion. Generally, the older the sample, the flatter the curve, but the BM1 material was a significant outlier, as it expired in April 2010. The FM3 sample expired in July 2016, but clearly showed another dimension of poor absorption performance, perhaps suffering from a long exposure to atmospheric CO_2 or other mishandling. Likewise, the second FM1 test (only in Table 3, see APPENDIX) showed diminished times and capacities due to atmospheric exposure to CO_2 prior to laboratory testing.

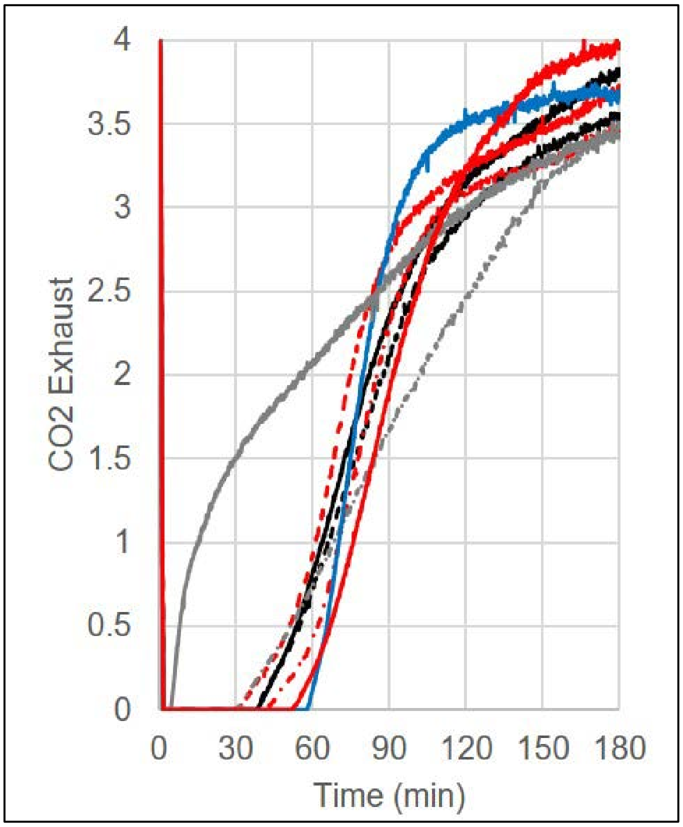

Figure 4. Carbon dioxide absorption versus time for various expired commercial lime products using the constant flow test system. Curve assignments are AM1 (black dash), AM1 (black line), BD1 (red dash), BM2 (red dash dot), FM1 (gray dash dot), CM1 (blue), FM3 (gray line), and BM1 (red solid line).

A series of interrupted experiments with AM2 was performed, in which equivalent 60 g loadings were exposed to CO_2 for increasing reaction times. The product was removed for thermogravimetric analysis to determine moisture and carbonate composition. The range used was 3 hours, with the interval at 15 minutes up to 2 hours, then 30 minutes for the third hour. The CO_2 absorption curves are presented in Figure 5. The data set allows for statistical analysis for breakthrough and effective times and capacities. Breakthrough time averaged 55 minutes with a standard deviation of 9, while the effective time range was tighter, with an average of 70 minutes and a standard deviation of 3. Effective capacity averaged 129 L/kg, with a standard deviation of 6, while breakthrough capacity was 99 L/kg with a standard deviation of 20. So standard deviations were within 5% for effective values, while for breakthrough values they were within 20%. This reinforces the utility of effective time and capacity as desirable chemical performance measurements over breakthrough time and capacity.

The extent of carbon dioxide reaction can be determined in two ways; (1) by mass analysis of carbonate (CO_3^{2-}) formation in the spent solid product, or (2) by determining the volume of CO_2 absorbed from air flow in the exhaust vessel. These capacities were determined by these independent means for 11 time points. Capacities were equivalent, and in each case, 65-70% of the hydroxyl sites had reacted at the end as determined by either carbon dioxide absorption or by solid carbonate formation. An equivalent series with made using AD2, with capacities determined over eight time points, to reveal an endpoint at around 65% of the hydroxyl sites present. This comparison demonstrates that the chemical process occurring in these different grades of soda lime are equivalent and that both are equally reactive towards CO_2 and form the same product. The difference in breakthrough and effective times and capacities are most likely a function of particle size, attributed to differing diffusion processes for CO_2 to reach hydroxyl sites as the material reaches exhaustion. Still in both cases, 30-35% of the hydroxyl sites are inaccessible and were not able to absorb CO_2.

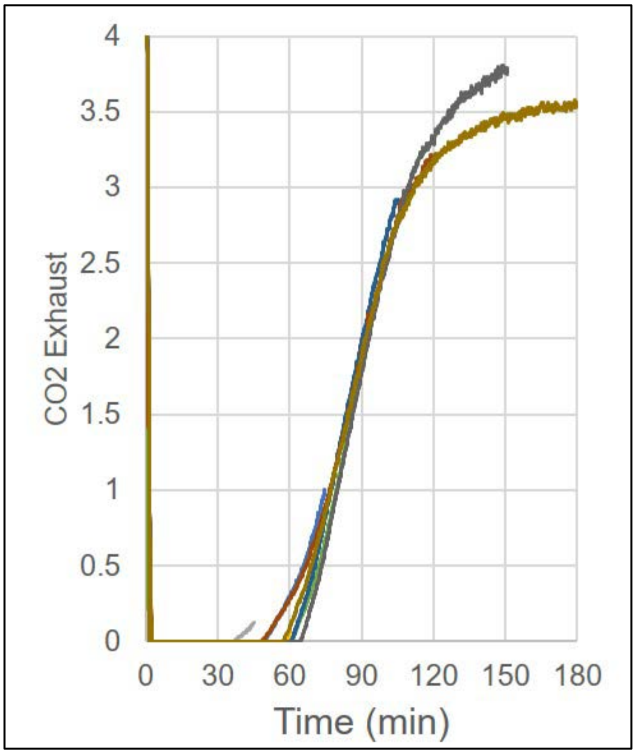

Figure 5. Carbon dioxide absorption versus time for equivalent loadings of AM2 interrupted for moisture and carbonate analysis. Interrupted times (in min) are 0, 15, and 30 (olive), 45 (light gray), 60 (yellow), 75 (violet), 90 green), 105 (navy), 120 (red), 150 (dark gray), and 180 minutes (gold).

CONCLUSIONS

The CO_2 capacities of generic solid bases and commercial lime CO_2 absorbents were studied using a custom built constant air flow test system. Lithium hydroxide demonstrated somewhat superior weight capacity over soda lime and potassium superoxide, though particle size had a significant effect on breakthrough and effective times and capacities. Test results for commercial lime products correlated well with manufacturers' reported capacity claims, with the smaller diving grade materials displaying longer times and capacities relative to corresponding medical grade products. However, only 55-70% of the base sites were active at the "end of test" times, and the percentage is even lower (40-55%) at breakthrough and effective times. Test results for a set of expired materials displayed premature breakthrough and effective times and capacities for materials more than five years after manufacture. Elongated exhaustion slopes suggest the base sites are present but not accessible to CO_2 molecules.

REFERENCE

(1) North Atlantic Treaty Organization (NATO) Standardization Agreement (STANAG) 1411 (Edition 2) "Standard to Quantify the Characteristics of Carbon Dioxide (CO2) Absorbent Material for Diving, Submarine and Marine Applications." 5 July 2006.

DISCLAIMER

The findings and conclusions in this report are those of the author and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention." Mention of product name or depiction of product does not constitute endorsement by NIOSH.

APPENDIX

Table 2. Relative carbon dioxide absorption times and capacities of commercial lime products.

Product Label-→	**AD3**	**AD2**	**AM2**	**EM1**	**BM1**	**DM1**	**CM2**	**CD1**	**FM2**	**Soda Lime**
Time (min)										
Breakthrough	77	64	62	58	43	57	54	53	51	13
Effective	82	73	76	70	67	66	62	62	60	18
Capacity (L/kg)										
Breakthrough	142	117	113	106	78	105	99	97	94	23
Effective	151	133	138	127	122	121	112	112	109	31
Effective (L/L)	118	102	106	80	100	75	77	77	73	24
End of test	176	183	190	191	179	159	171	162	171	53

Table 3. Relative carbon dioxide absorption times and capacities of expired commercial lime products.

Product Label-→	**BM1**	**CM1**	**BM2**	**AM1**	**AM1**	**BD1**	**FM1**	**FM1**	**FM3**
Time (min)									
Breakthrough	43	53	42	38	38	31	31	9	5
Effective	67	62	62	55	54	51	51	16	8
Capacity (L/kg)									
Breakthrough	78	97	76	68	70	55	55	14	7
Effective	122	113	112	99	97	91	92	27	13
Effective (L/L)	100	81	92	76	75	74	64	21	10
End of test	179	170	190	187	172	163	203	142	141