Development of enclosed life support system for underground rescue employing a photocatalytic metal oxide thin film to generate oxygen from water and reduce carbon dioxide

by

Meghna S. Trivedi

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF SCIENCE
AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

JUNE 2006

Signature of Author:______________________________________
Department of Mechanical Engineering
May 12, 2006

Certified by:______________________________________
Richard J. Gilbert MD
Research Scientist, Department of Mechanical Engineering
Thesis Supervisor

Certified by:______________________________________
Professor Roger Kamm
Professor of Mechanical Engineering
Thesis Supervisor

Accepted by:______________________________________
John H. Lienhard V
Professor of Mechanical Engineering
Chairman, Undergraduate Thesis Committee

Development of enclosed life support system for underground rescue employing a photocatalytic metal oxide thin film to generate oxygen from water and reduce carbon dioxide

by

Meghna S. Trivedi

Submitted to the Department of Mechanical Engineering
on May 12, 2006 in Partial Fulfillment of the
Requirements for the Degree of Bachelor of Science in
Mechanical Engineering

Abstract

Despite major improvements in technology and safety regulations, coal mining continues to be a hazardous industry. Catastrophic accidents, related largely to underground explosions and generation of toxic gases, commonly result in the trapping of miners without oxygen for an extended period of time. As an example, in January 2006, an accident at the Sago Mine in West Virginia trapped 12 coal miners underground for 41 hours and resulted in the deaths of all but one. According to the account of the sole survivor, four of the emergency oxygen sources, or "air packs," failed. While devices capable of supplying oxygen to miners trapped underground exist, these systems are limited by the need for an exogenous gas supply, the large size of the devices, and unreliability. We propose here the design of an enclosed life support system functional for up to 12 hours, which employs photocatalytic mechanisms to generate oxygen from water and provides chemical reduction, or "fixation", of carbon dioxide. Oxygen is generated through a photolytic reaction involving the interaction of UV light and a titanium dioxide thin film, resulting in the generation of oxygen gas at a rate of 0.0507 L O_2 / min per m^2 of photolytic surface. Exhaled carbon dioxide is mechanically segregated from the oxygen and then fixed to a 5 carbon sugar molecule, ribulose, through a mechanism that includes the addition of carbon dioxide and water, the cleavage of the C2-C3 bond, and the ultimate generation of glyceric acid and its enolate. We contend that the system proposed here has the ability to significantly exceed the capacity of current emergency life support systems employed underground, and thereby improve the safety of coal miners and the overall productivity of the coal mining industry.

Thesis Supervisor: Richard J. Gilbert, MD
Title: Research Scientist in Mechanical Engineering

1. Introduction

1.1 United States Mining Industry

The United States contains the world's largest coal reserves, about 270 billion short tons. The value of the coal produced in 2005 was $22.7 billion. Coal has many uses but its most prevalent use is to generate electricity. Of the 1.13 billion short tons produced in 2005, 91.6% was consumed for electric utilities.[1] More than half of the electricity in the United States is generated from coal.[2] Of the 1,400 coal mines in the U.S. in 2005, 625 were underground mines.[1] All of the United States coal reserves are found in twenty six states in three coal producing regions: the Appalachian region (PA, OH, WV, VA, AL), the Mid-West region (IL, IN, KY, TX), and the West region (CO, WY, UT, NM, MN, ND, SD).[3] Figure 1 shows a map of coal deposits in the United States. Though many states have coal mines, over 90% of the coal produced comes from 10 states alone. Montana is the leading producer of coal in the United States (Table 1).[4] Overall the coal mining industry employed 112,449 miners in the United States in 2005, with approximately 43,000 miners working in underground mines.[1]

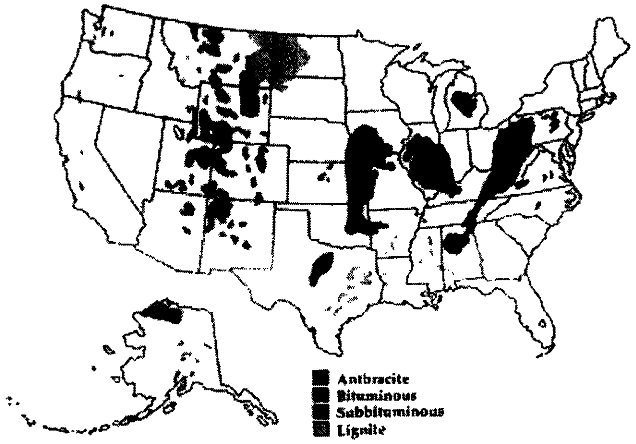


Figure 1: Map of anthracite, bituminous, subbituminous, and lignite coal deposits in the United States[4]

Table 1: Coal output in billions of tons and percent of United States total coal production for top producing states[4]

State	Tons(billions)	Percent of US
Montana	120	25.4
Illinois	78	16.5
Wyoming	68	14.4
West Virginia	37	8.0
Kentucky	30	6.3
Pennsylvania	29	6.1
Ohio	19	4.0
Colorado	17	3.6
Texas	13	2.7
Indiana	10	2.1
Other States	51	10.9
TOTAL	472	100.0

1.2 Conditions and Hazards in Mining

Although many improvements have been made since the inception of the mining industry, coal mines are still very harsh and dangerous. For example, structural inadequacies place miners at risk of slope failure, roof collapse, and explosions. Additional risks include the release of explosive methane gas, spontaneous combustion of coal, inhalation of coal dust resulting in "black lung," rock burst hazard due to mining-induced seismicity, flooding, and extremes of temperature and radiation. [3]

1.3 History of mining legislation

Due to these conditions, the federal and state governments have passed various acts to protect miners over the years. The first national legislation for the protection of coal miners, "An

Act for the protection of the lives of miners in the Territories" was passed in 1891. This act governed safety standards and inspection practices in United States coal mines. The Bureau of Mines was established within the Department of the Interior in 1910 because of the excessive number of coal mine fatalities (over 2,000 deaths annually). The Bureau conducted research and attempted to reduce the number of accidents in the coal mining industry. The next major legislation in coal mining was the Coal Mine Health and Safety Act in 1941, which came in response to the deaths of 257 coal miners in four different methane gas explosions. In this act, the Bureau of Mines was given the authority to send federal inspectors to the mines. The act was revised and strengthened in December 1951 following the deaths of 119 more miners in Illinois.[5]

In 1969, the Federal Coal Mine Health and Safety Act, also known as the Coal Act, was passed after another tragic mining accident. This act was more comprehensive and stringent than any previous federal legislation regarding the mining industry. The act required multiple mine inspections a year, increased the federal enforcement powers, and implemented both monetary and criminal penalties on violations. Safety and health standards for coal miners were also implemented. The Mining Enforcement and Safety Administration (MESA) was created in 1973 to be a separate entity from the Bureau of Mines and enforce the safety and health standards in coal mining.[6]

The Federal Mine Safety and Health Act of 1977, also known as the Mine Act, amended the 1969 act to consolidate all federal health and safety regulations in both coal and non-coal mining under one piece of legislation. With this legislation, the rights of all miners were expanded and they were offered more protection. The Mine Safety and Health Administration (MHSA) was established under the Department of Labor. The Federal Mine Safety and Health Review Commission was also established to provide for independent review of the MSHA's enforcement actions.[6] More recent legislation has been presented in Congress in response to mining accidents that have occurred within the past few years. These regulations lay out the details of an emergency response to disasters and attempt to develop greater safety procedures to protect miners. New legislation could require miners to wear tracking devices and carry communication devices.[7]

1.4 Accidents in Mining

While the rate of accidents in coal mining has significantly diminished in recent years, concern remains high. Mining ranks in the top ten most injury prone industries. Of non-fatal injuries, there were 5,003 incidences in 2005.[1] As of May 1, 2006, 26 coalminers have died from accidents on site.[8] Figure 2 shows the trends in total fatalities and rate of fatalities in coal and non-coal mining from 1911 to 2000.[9] Prior to 1961, the number of fatalities in coal mining was much greater than the number of fatalities in non-coal mining. With the implementation of stricter mining safety and health standards, the rate and number of fatalities has greatly decrease.

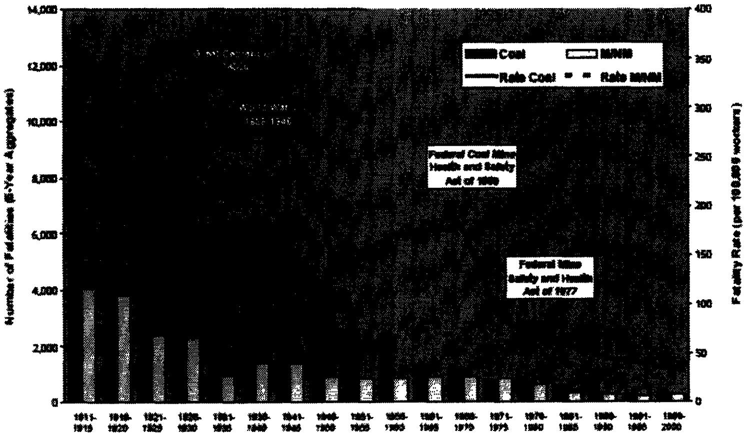


Figure 2: Rate and number of both coal and non-coal mining fatalities from 1911 to 2000 in the United States. Key events in American history and mining legislation are noted on graph.[9]

Figure 3 shows the decrease in total injuries from 1990 to 2004. In addition to the implementation of safety laws, improvements in mining technology and safety gear have helped to decrease the number of injuries.

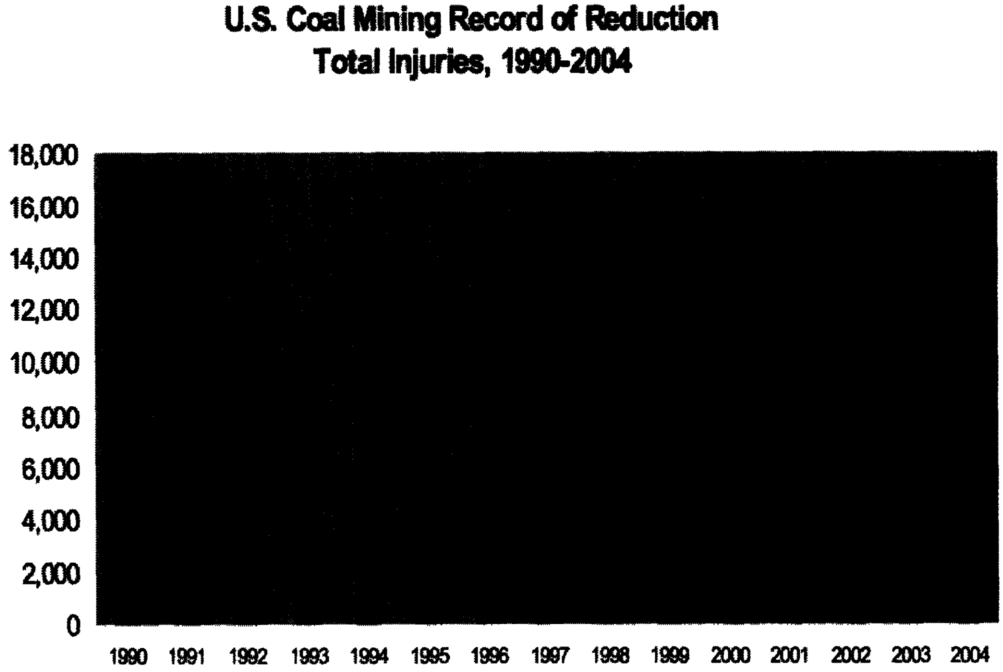


Figure 3: Total injuries in coal mining in the United States from 1990-2004 showing a downward trend with a 68% decrease in total injuries from 15,826 injuries in 1990 to 6,129 injuries in 2004.[10]

Despite the above noted improvements, the occurrence of adverse events has provoked great interest in coal mining safety in the U.S. and abroad. The most recent tragic incident occurred on January 2, 2006 at Sago Mine in West Virginia. An explosion in the mine killed one miner and trapped 12 coal miners 260 feet underground for 2 days. Of the 12 miners trapped underground, 11 slowly asphyxiated from carbon monoxide poisoning and one was found alive but seriously injured. After waking from a coma and spending months recovering in the hospital, the sole survivor, 27 year old Randal McCloy Jr, was able to share his story of the incident. According to

McCloy, four of the air packs, or self-rescuers, were not functioning, leaving the miners to share each others packs. Each pack only had a one hour supply of oxygen.[11] Concern regarding fatalities is particularly high in developing nations. For example, China, the largest producer of coal in the world, had 6,000 deaths in 2004 officially attributed to coal mining accidents, though it is believed that the unofficial number of deaths is much higher. Coal mining fatalities in China account for 80% of the world's total deaths in coal mining.[12] As energy shortages have provoked a return of interest in coal as a source of fuel, there is an ever increasing need to minimize or eliminate the physical risks of mining.

2. Personal Protection Equipment: Respirators

The National Institute for Occupational Safety and Health (NIOSH) and MSHA have developed standard requirements for respirators to be used in coal mines and issued a list of approved devices that coal mine operators can purchase for their employees. There are currently three types of devices that are used by miners in the case of an emergency underground in the coal mines: an air-purifying respirator, an open-circuit self-contained breathing apparatus (SCBA), and a closed-circuit SCBA. The choice of respirator depends on the environment of the mine during the emergency. Figure 4 shows the conditions for the usage of the three types of respirators.

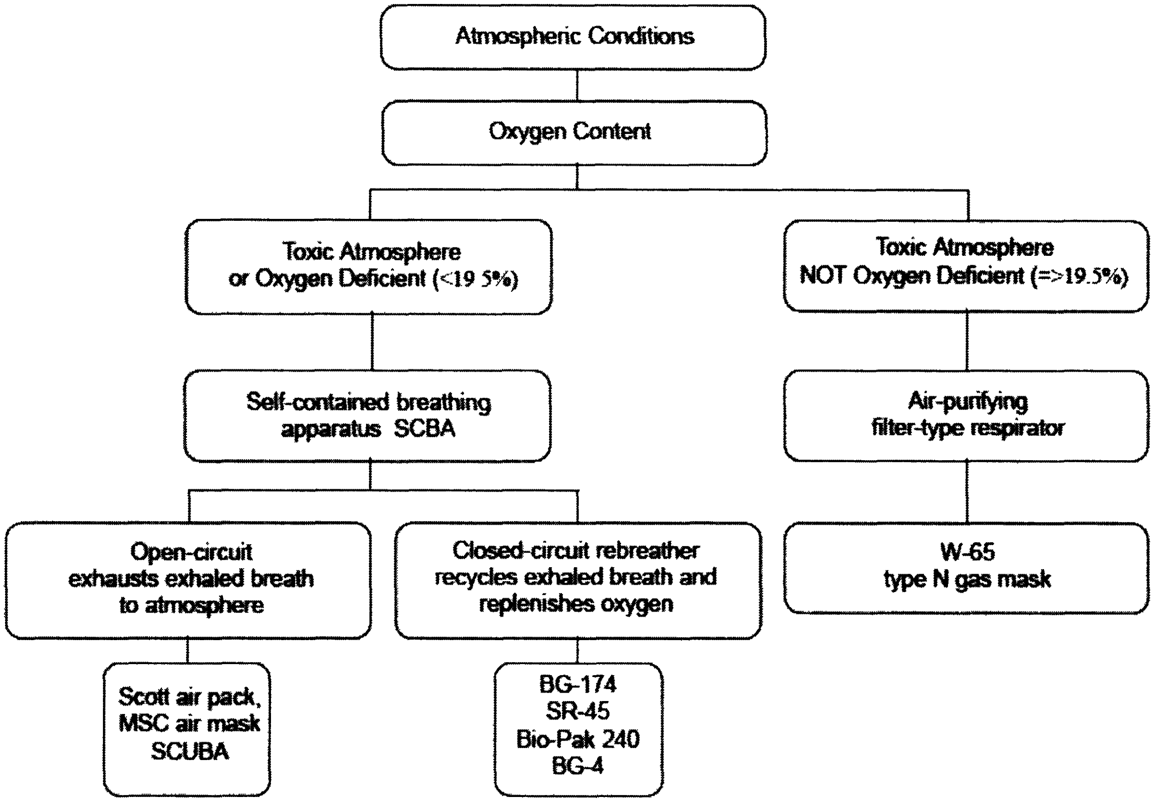


Figure 4: Chart organizing currently available respirators for underground mining applications in different atmospheric conditions. In toxic, oxygen deficient atmospheres (less than 19.5% oxygen), two self-contained breathing apparatus exist: the open circuit device and the closed circuit rebreather. In toxic, not oxygen deficient atmospheres (greater than or equal to 19.5% oxygen), the air-purifying filter-type respirator is used.[13]

2.1 Filter Self-Rescue Device

The first type of respirator is a filter self-rescue device. This device is a small filter-type respirator that is neither self-contained nor oxygen supplying and thus must be used in an oxygen containing environment (=>19.5% oxygen). The filter self-rescue device only protects against carbon monoxide (in concentrations up to 1% by volume) and does not protect against any other noxious fumes. Since the device only works for 20-60 minutes, it may be used during escape only. A commonly used filter self-rescue device is the Mine Safety Appliances Company Model W-65 (Figure 5).[14]

Figure 5: Mine Safety Appliances Company Model W-65 filter self-rescue device shown being worn by a miner. The device clips the nose shut and delivers filtered air to the mouth.[13]

The device has a small canister that filters carbon monoxide through a heat generating chemical reaction and delivers the clean air to the user through a mouthpiece. The user's nose is clipped closed and the air must be breathed in through the mouth. The air is then exhaled to the atmosphere. Miners are trained in the use of these devices and are required to carry the devices on them whenever in the mines.[13]

There are several risks associated with the filter self rescue device. The first is that its protective effects are limited to carbon monoxide. There are numerous other toxic gases that are found in coal mines, especially during times of emergency. Such toxic gases include ammonia, chlorine, hydrogen sulfide, and sulfur dioxide. Another deficiency of these devices is that they are only capable of life support for up to one hour, while it can reasonably be estimated that rescues crews may be located up to two hours away.[15] The third danger of the filter self-rescue device is that the unit may overheat and burn the user when the carbon monoxide concentration exceeds 1% by volume. At concentrations lower than 1%, a built in heat exchanger is able to remove most of the heat created by the chemical reaction filtering the carbon monoxide from the air.[13]

2.2 Open Circuit Self Contained Breathing Apparatus

The second type of device is an open circuit self-contained self-rescuer (SCSR). Unlike the filter self-rescue device, the SCSR provides its own supply of oxygen to the user. The exhaled air is released into the atmosphere. There are two different technologies that are used to provide the oxygen. One uses a chemical reaction to generate oxygen and the other uses compressed oxygen. Importantly, SCSRs can only provide up to an hour of oxygen and are to be used only for escape. The first generation SCSR devices were 10.5" by 7.75" by 3.375" and weighed about 8.5 pounds. Second generation SCSRs are smaller at 7.75" by 5.5" by 4.0" and 5.7 pounds.[16] The newer devices are easier to carry and wear. One of the commonly used SCSRs is the Mine Safety Appliances Company Model Auer SSR30/100 (Figure 6). This device is belt mounted and weighs 4.4 pounds. It can provide oxygen for 20 minutes at a consumption rate of 35 liters per minute.[17] The small size allows miners to carry the device into the mines on a regular basis for instant use if necessary. However, like the filter device, these devices have the capacity to sustain life for only one hour, a period of time unlikely to be sufficient to allow a trapped miner to reach safe ground.

Figure 6: Mine Safety Appliances Company Auer SSR30/100 open circuit self contained breathing apparatus being worn by a miner. The 4.4 pound device includes a 20 minute oxygen supply worn around the waist on a belt and a facemask.[17]

2.3 Closed Circuit Self Contained Breathing Apparatus

The third type of device is the closed circuit self-contained breathing apparatus (SCBA), also known as a rebreather. This device provides its own supply of oxygen, usually through a gas cylinder, and recycles the exhaled air through the device. One of the crucial components of this device is the removal of carbon dioxide in the exhaled air. The method of carbon dioxide removal depends on the device. Such a closed circuit SCBA can be used in an oxygen deficient environment and can sustain a user for up to four hours.

One of the commonly used closed-circuit SCBAs is the Biomarine BioPak 240S (Figure 7). The BioPak 240S weighs approximately 35 pounds, is worn on the back, and costs approximately $5,500.[18] The flow diagram of the system is shown in Figure 8. The system has 3 components: a breathing loop, high pressure plumbing, and low pressure plumbing. The high pressure plumbing delivers the oxygen to the system from the oxygen cylinder. The cylinder can provide enough oxygen to sustain a user for four hours regardless of the exertion of the user. The low pressure plumbing allows the flow of the oxygen to the breathing loop and contains an alarm whistle that alerts the user when the oxygen supply is at 25%.[19]

The exhaled air enters the breathing loop through the exhalation breathing hose. The flow then continues to the carbon dioxide scrubber canister where the carbon dioxide is removed so that the air can be recycled. An exothermic chemical reaction occurs to bind the carbon dioxide.

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$

The recycled air then combines with the oxygen from the low pressure plumbing and enters the diaphragm. The diaphragm and diaphragm spring act as a counterlung to maintain the positive pressure within the respirator. The air then passes by a coolant canister to be cooled and dehumidified since the air is heated and has water from the exothermic reaction in the scrubber.

The oxygenated air is delivered to the user through the inhalation breathing hose. Overall, the system provides a steady supply of 1.78 liters of oxygen per minute to the user.[19]

One of the obvious disadvantages of this system is its large size. Because it weighs 35 pounds, miners are not able to carry the system around with them as they work. In case of an emergency, the miners would have to find the rebreather so its use would not be immediately available. In some situations, it may not even be possible to access the respirator storage area because of collapsed walls or explosions. The use of a high pressure cylinder oxygen source is also an area of concern. The cylinder needs frequent attention to ensure that there is no leak, depressurization, or explosion. Finally, though a 4 hour support system is an improvement over a one hour system, it would be ideal in light of recent incidents to have a system that could support its user for an even longer period of time.

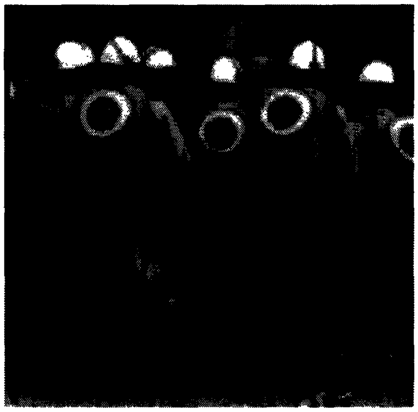


Figure 7: Picture of underground mine rescue team wearing the Biomarine Incorporated BioPak 240S closed circuit self contained breathing apparatus. The 35 pound device is worn on the back with a face mask that delivers oxygen to the user for 4 hours.[18]

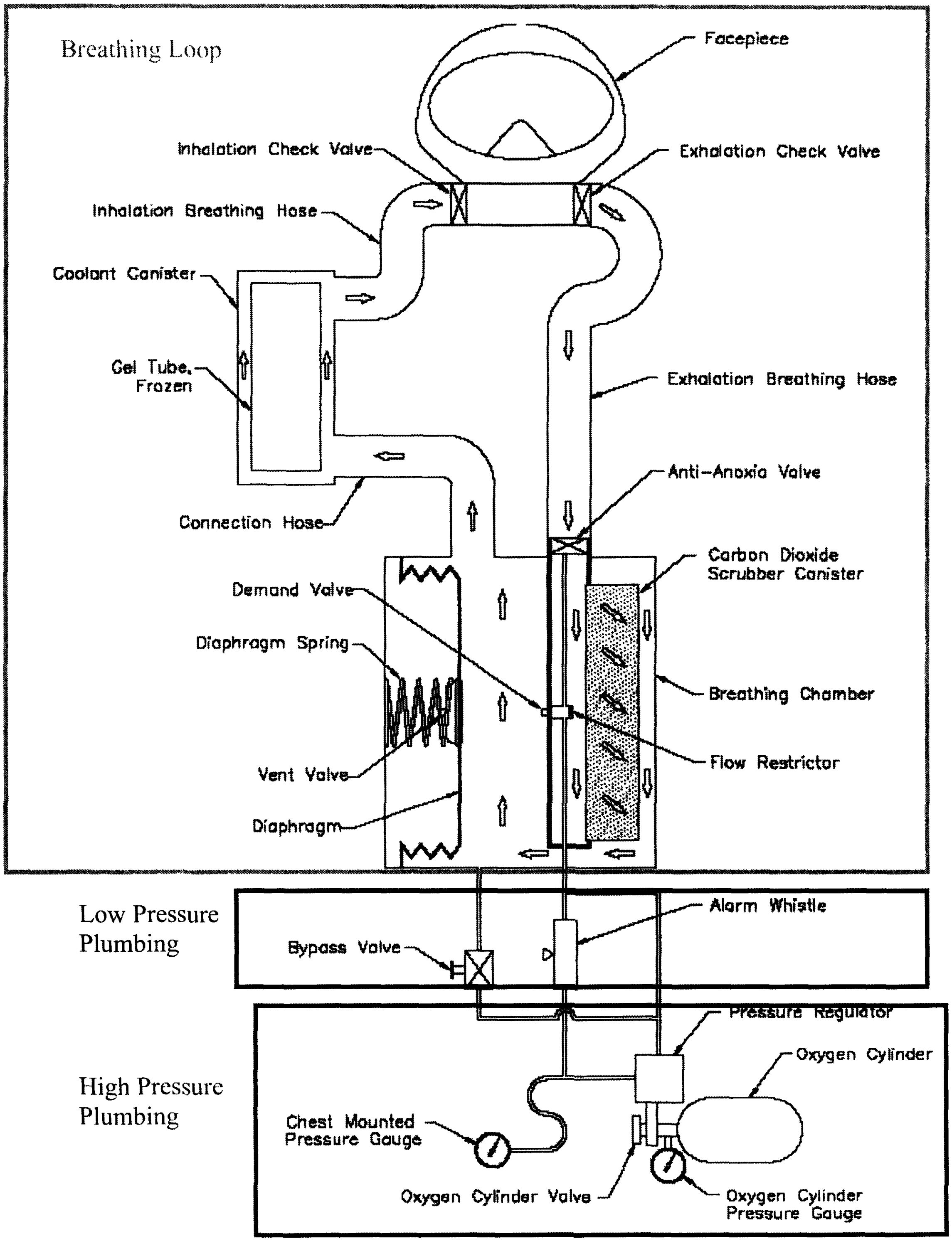


Figure 8: Flow diagram of Biomarine BioPak 240S showing the three components: the breathing loop, the low pressure plumbing, and the high pressure plumbing. Oxygen is delivered to the low pressure plumbing system from the high pressure plumbing system. The low pressure plumbing system allows the oxygen to join the recycled, exhaled air in the breathing loop where it is passed to the user.[19]

3. Human Physiological Needs

At sea level, Earth's pure, dry air in the atmosphere consists of 78.09% nitrogen, 20.94% oxygen, 0.95% argon, 0.03% carbon dioxide, and trace amounts of other gases.[13] Humans require an environment like this to live optimally and oxygen content below 19.5% is considered to be oxygen deficient.[20] Table 2 shows the effects of oxygen deficiency in air.

Table 2: Effect of oxygen deficiency on the health and physiological response of humans for various atmospheric oxygen contents[13]

Percent Oxygen	Health effects and physiological responses
17%	Breathing is faster and deeper; impaired judgment may result
16%	First signs of anoxia appear
15%	Dizziness, buzzing noise, headache and blurred vision may result
12-16%	Breathing and pulse rate increases; muscular coordination is slightly impaired
10-12%	Emotional upset and abnormal fatigue on exertion are evident; a person may remain conscious
6-10%	Nausea and vomiting may occur; victims are unable to move freely and may lose consciousness
<6%	Convulsive movements and gasping occurs; respiration stops and soon after the heart also stops

In a closed circuit self contained breathing apparatus, like the BioPak 240S, pure oxygen is supplied to the user. There are no ill effects from breathing pure oxygen as long as the user is not exposed to pressures greater than atmospheric pressure and the pure oxygen exposure is less than 24 hours.[13] The requirements for oxygen depend on the activity of a human. When a person is at rest, the oxygen requirement is much less than the requirement when a person is performing heavy work. The metabolic oxygen requirements for humans are shown in Table 3.

Table 3: Human metabolic oxygen requirements in liters per minute for various workloads[13]

Work Load	Oxygen required in liters per minute
Rest	0.2-0.5 lpm
Light work	0.75-1.0 lpm
Moderate work	1.0-1.5 lpm
Heavy work	1.5-2.0 lpm
Extremely heavy work	2.0-3.0 lpm

In addition to providing oxygen to the user, it will also be necessary to remove the CO_2 exhaled by the user during respiration. CO_2 is expelled from the body at a rate of between 8 and 50 mg/sec. The average rate of CO_2 production from respiration is 25 mg/sec.[21] There is a great danger if the carbon dioxide accumulates in the breathing environment. At 5% CO2 in the air, respiration is stimulated and at 7-10%, unconsciousness results after a few minutes.[13]

4. Proposed System

Before designing the enclosed life support system for underground rescue, it is important to define the system requirements. The most important system requirement is to meet the physiological needs specified in the previous section. There should be a continuous supply of oxygen for breathing and a continuous removal of exhaled carbon dioxide. The removed CO_2 should be disposed of or recycled and should not be affected by any CO_2 in the mine tunnel atmosphere. The device should be operable for at least 12 hours without significant user interface or maintenance. For the ease and convenience of the miner, it is necessary for the device to be lightweight and portable. To ensure the mobility of the miner, the device should be wearable and comfortable while posing no risk to the wearer. One of the limiting requirements of the system will be the power source. There should be minimal power consumption (less than

50 watts) in order to keep the source of power as small as possible. Since the entire system must be carried by the miner as he works in the mine tunnel, the power source should be lightweight and portable as well. Finally, the entire system should be compatible with the underground mine environment. The enclosed life support system should be immune to the levels of methane and carbon monoxide in the tunnel air and the underground temperature. It is also important to ensure that there are no combustible components.

With these system requirements in mind, we propose a novel enclosed life support system for underground rescue. There are 2 major components in the system: photolytic oxygen generation and carbon dioxide removal, connected by a circulation system. The oxygen is generated by shining UV light on a TiO_2 surface, thus creating electron holes that interact with water to produce hydrogen peroxide that decomposes into O_2. The carbon dioxide is removed by a carbon dioxide fixation in a process that is similar in concept to a process that occurs in the Calvin-Benson cycle in photosynthesis.

4.1 Photocatalytic Oxygen Generation

The mechanisms for generating oxygen from water using a photocatalytic interaction of UV light with a titanium dioxide thin film have been previously described.[21,22,23] This reaction fundamentally emulates the capacity of photosynthesis to use light energy to drive the exchange of carbon dioxide for oxygen derived from water. Photosynthetic organisms use an interaction of metal chelate chromophores (chlorphyll) with the transition metal oxides of Mn for the light dependent charge separation.[22] The anatase form of TiO_2, which is known for its ability to serve as a chromophore yielding a charge separation, has been used to generate oxygen through photolysis.[23] The anatase TiO_2 is deposited can be deposited in two ways: sputter coating or sol-gel processing (both described in 22 and 23). When UV light is absorbed into the layer, electrical charge separation occurs and electron "holes" are created. The electron holes promote the oxidation of water molecules to form an active form of oxygen (AO) in the nanopores of the metal oxide film, which then spontaneously decomposes to dissolved oxygen. For photoactivation, the TiO_2 layer absorbs ultraviolet light at a wavelength between 350-389 nm. This reaction creates hydrogen peroxide, which is an active form of oxygen.

$$2H_2O + hv \xrightarrow{TiO_2(anatase)} H_2O_2 + 2H^+ + 2e^-$$

Almost immediately following its formation, the hydrogen peroxide spontaneously disproportionates to dissolved oxygen and water.[21,22,23]

$$H_2O_2 \xrightarrow{MnO_2} \text{Dissolved Oxygen} + H_2O$$

Figure 9 shows the generation of dissolved oxygen over time as the UV light source is turned on and off. In the presence of the UV light, the amount of dissolved oxygen increases and as soon as the light source is turned off, the amount of dissolved oxygen levels off.

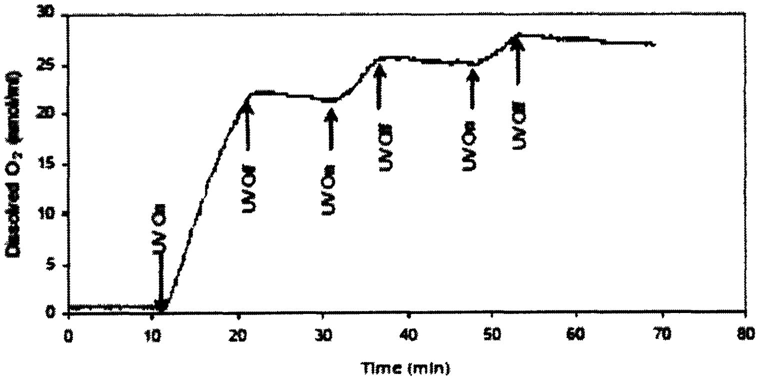


Figure 9: Demonstration of dissolved oxygen generation in a glass substrate containing 1230 Angstrom Ti and TiO_2 in 2.35 mL of Locke's Solution at 36°C as UV light source is turned on and off.[21]

4.1.1 Photoreactive layers

The photoreactive surface is composed of three layers on a transparent glass or quartz substrate (Figure 10). The first layer is a conducting film, the second layer is the anatase form of TiO_2, and the third layer is a MnO_2 film.

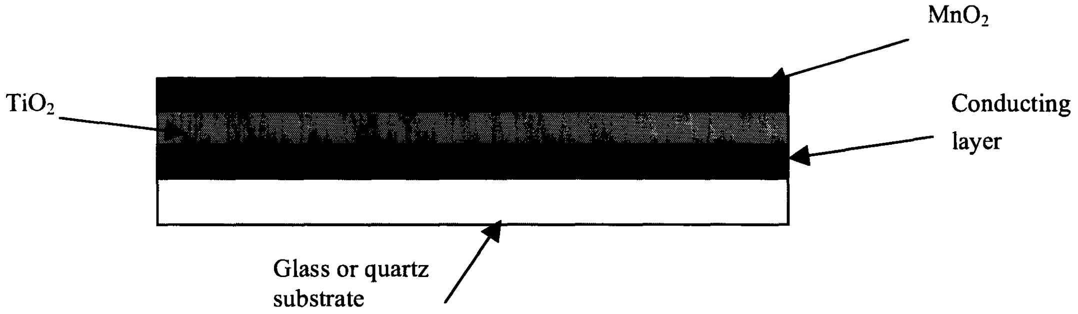


Figure 10: Schematic of photoreactive layers of the photolytic device. The three layers are put onto a glass or quartz substrate. The layer directly on the substrate is the conducting layer (Ti), which conducts away the electrons from the photolytic reaction in the second layer of TiO_2. The top MnO_2 layer promotes the conversion of active oxygen to dissolved oxygen.

The conducting film is a thin (<100 nm) layer of a metal or semiconductor used to conduct away the electrons that are created from the photolytic reaction. The layer is laid down using conventional vacuum sputter coating procedures. Previous work by Gilbert *et al* determined the effect of the material choice for the conducting layer and layer thickness on the dissolved oxygen generation (Table 4). Various material samples were prepared as described in 22 and 23 with TiO_2 as the photoactive layer and tested in 2.35 mL Locke's Ringer solution at 36°C with a 365 nm light source and +1 voltage bias to determine the dissolved oxygen production. The effect of the thickness of the conducting material was the most significant in the generation of dissolved oxygen.[21] For the Ti conducting layer, a film thickness of 1200 Angstroms showed a significant reduction in resistance and an increase in dissolved oxygen production rate. Of the other materials, ITO was found to have the best DO production rate at 1300 Angstroms. ITO is a good material for the conductive layer because it is transparent, which will allow the direct interaction of the photoreactive layer with the UV radiation.[23]

Table 4: Effect of conducting layer material and thickness on the production of dissolved oxygen. Ti, Ni, Cr, and ITO at various thicknesses, acid treatments, and heat treatments were tested to find most efficient conducting layer with respect to DO production.[23]

Sample Number	**Material**	**Thickness(A)**	**Acid Treatment(s)**	**Heat Treatment (°C)**	**Resistance (Ω)**	**DO Prod Rate (nmol/ml/hr)**
90-32-1	Ti	100	15	250	50000	0.000
90-26-1	Ti	325	0	250	40000	11.77
75-83-2	Ti	1200	120	350	110	186.5
75-55-1	Ti	1230	60	350	110	113.9
75-64-1	Ti	1230	60	350	110	123.3
90-14-1	Ni	450	0	350	---	0.000
90-23-2	Ni	450	0	250	105	0.000
90-16-3	Cr	100	0	350	870	0.000
90-23-4	Cr	100	0	209	690	2.131
75-94-3	Cr	400	30	350	230	57.63
75-100-1	Cr	400	60	350	200	4.115
90-03-1	Cr	1000	0	350	---	0.000
75-94-4	ITO	1300	30	350	55	54.74
90-03-4	ITO	1300	60	350	50	143.3
90-03-4	ITO	1300	60	350	50	34.38
90-52-1	ITO	1300	0	209	47	78.48

The MnO_2 film is the top layer of the photoreactive surface. It promotes the conversion of active oxygen into aqueous phase dissolved oxygen and water during disproportionation. Though it is not necessary for the conversion, it helps improve the rates of oxygen generation.[22]

Under the optimal fabrication of the photoreactive surface using Ti at a thickness of 1230 Angstroms as the conductive layer, Gilbert *et al* were able to reach oxygen generation rates of 3.5×10^{-5} M/(sec m^2). At room temperature the density of oxygen is 1.325 kg/m^3,[24] thus the rate of oxygen generation in liters per minute per surface area of photoreactive surface is 0.0507 LO_2/(min m^2).

$$3.5\times10^{-5}\frac{moles\ \mathrm{O_2}}{\sec\bullet m^2}\times\frac{32\ \mathrm{g\ O_2}}{1\ \mathrm{mole\ O_2}}\times\frac{1000L}{1325g}\times\frac{60\sec}{1\min}=0.0507\frac{L\ \mathrm{O_2}}{\min\bullet\mathrm{m}^2}\ .$$

The BioPak 240S delivers 1.78 L of O_2 per minute, which is 4-9 times more than the required amount at rest.[19] If this much oxygen is to be provided to the user using the photolytic technology, 35.108 m^2 of photoreactive surface is required.

$$\frac{1.78\frac{L\ \mathrm{O_2}}{\min}}{0.0507\frac{L\ \mathrm{O_2}}{\min\bullet\mathrm{m}^2}}=35.108m^2$$

As this is a novel approach to generating oxygen, it is believed that the rates of oxygen can be significantly increased through some modifications. These changes include the modification of the nanocrystal surface and uniformity of deposition, improved photoconductivity, and enhanced photoelectron removal.[23] A ten fold increase in the generation of oxygenation would drastically reduce the surface area of photoreactive surface needed from 35.108 m^2 to 3.511 m^2. It is feasible that enough oxygen to sustain a human working at a heavy workload can be created.

4.1.2 Ultra Violet Light Source

The light source used in the experiments by Gilbert *et al* was the EFOS Lite unit which was directed through a liquid light pipe. It produced UVA light at a wavelength of 365 nm and intensity of 88.1 mW/cm^2.[23] For use in the enclosed life support system for underground rescue, a UV laser by CrystaLaser that contains a wavelength filter and operates at 10 watts from a 9-18 VDC power supply can be used as the light source.[25]

4.1.3 Water Supply

In order to produce enough oxygen for a life support system that will last for 12 hours, it is necessary to have an adequate water supply for the photolytic chemistry. Using the photolytic chemical equation and stoichiometry, the number of moles of water needed for the life support system to operate for 12 hours is

$$3.5\times10^{-5}\frac{moles\ \mathrm{O}_2}{\sec\bullet m^2}\times 35.108m^2\times 12hours\times\frac{3600\sec}{1hour}\times\frac{2\ \text{moles}\ \mathrm{H}_2O}{1\ \text{mole}\ \mathrm{O}_2}=106.167moles\ \mathrm{H}_2O$$

Converting the molar amount of H_2O into a volume of H_2O, it is found that 1.911 L of H_2O is necessary for the life support system to operate for 12 hours.

$$106.167\ \text{moles}\ \mathrm{H}_2O\times\frac{18g\ \mathrm{H}_2O}{1\ \text{mole}\ \mathrm{H}_2O}\times\frac{1\ \mathrm{L}\ \mathrm{H}_2O}{1000\text{g}\ \mathrm{H}_2O}=1.911\ \mathrm{L}\ \mathrm{H}_2O$$

4.2 Carbon Dioxide Removal

The composition of air exhaled by humans is 18% oxygen, 78% nitrogen and 4% carbon dioxide.[26] In our system, the exhaled air will be passed through a filter so that the exhaled oxygen can be recycled into the breathing loop. The carbon dioxide is exhaled by humans at a rate of approximately 25 mg/sec.[22] In order to utilize fixation chemistry, it is necessary to bubble the carbon dioxide into an aqueous medium. In this case, the water in the system can be carbonated using a nozzle that pressurizes the exhaled carbon dioxide gas. The solubility of carbon dioxide in water is 1.45 g carbon dioxide per liter of water[24]; thus, 0.0172 liters of water are needed per second in order to dissolve the exhaled carbon dioxide. This is feasible because at least 1.911 liters of water will already be present for the generation of oxygen.

Various reactions involving carbon dioxide were considered for eliminating the exhaled carbon dioxide[27,28]; however, the reaction chosen was one similar to the reaction that occurs in photosynthesis. In plants, photosynthesis is a process that has two pathways: the light reactions and the Calvin-Benson cycle, that uses water, light, and carbon dioxide to produce carbohydrates and oxygen. Through the Calvin-Benson cycle, high energy compounds from the light reactions of photosynthesis are used to reduce carbon dioxide to a carbohydrate. The first step in the Calvin-Benson cycle fixes a carbon dioxide to a five carbon compound, ribulose 1,5-bisphosphate (RuBP), using the enzyme Rubisco. The six carbon intermediate splits into two molecules of 3-phosphoglycerate (Figure 11).[29]

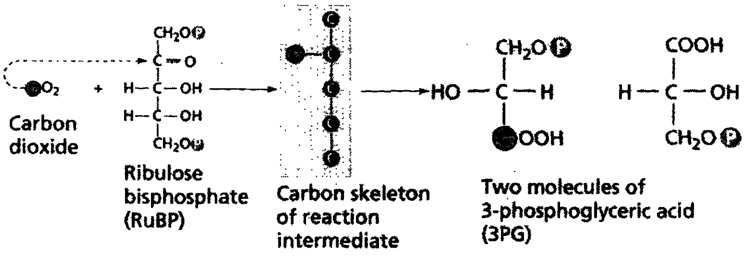


Figure 11: Carbon dioxide is added to ribulose bisphosphate at the carbonyl group in order to make a six carbon intermediate. There is a cleavage at the C2-C3 bond and two molecules of 3-phosphoglyceric, 3PG, result. This entire reaction occurs with the enzyme Rubisco.[30]

A reaction similar to the carboxylation of RuBP could be used to fix the carbon dioxide that is exhaled into the closed loop life support system by the user; however, it is not possible to have the enzyme in the system because of the uncertainty of its degradation over time. Zhan *et al* attempt to characterize the mechanism of the Rubisco reaction in order to determine the energetics of a nonenzymatic pathway for the carboxylation of RuBP.[31] The carboxylation of RuBP involves 3 steps: the addition of carbon dioxide, the addition of water, and the cleavage of the C2-C3 bond (Figure 12). The final product is a ene-2,3-diol(ate).

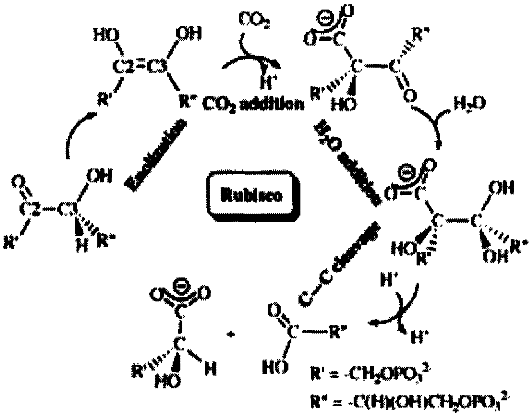


Figure 12: Mechanism of the rubisco catalyzed addition of carbon dioxide to ribulose bisphosphate (RuBP). RuBP enolizes and then carbon dioxide adds to C2. Water is then added to C3 and the C2-C3 bond is cleaved.[31]

Previous studies have shown that the energy barriers for the nonenzymatic carboxylation of RuBP are very high; however, in the study by Zhan *et al*, a more detailed examination of the possible transition state structures and intermediates of differently substituted model systems was undertaken using first-principle calculations. The various potential stabilizing factors in lowering the activation energy of the carbon dioxide addition and carbon-carbon bond cleavage were determined by the calculated structural, energetic, substituent, and solvent effects.[31]

The proposed reaction pathways for the addition of carbon dioxide, the addition of the water, and the cleavage of the C2-C3 bond of a RuBP-like molecule are shown in Figure 13.

In order to simplify the analysis, two models were run, one where R'=R"=H and another where R'=R"=CH_3. The second order Moller-Plesset energy calculations were used to determine the energy barriers. Table 5 shows the energy barriers for the model at each transition step when R'=R"=H and R'=R"=CH_3. The solvent effects are also shown with the shift from gas solvent to aqueous solvent.[31]

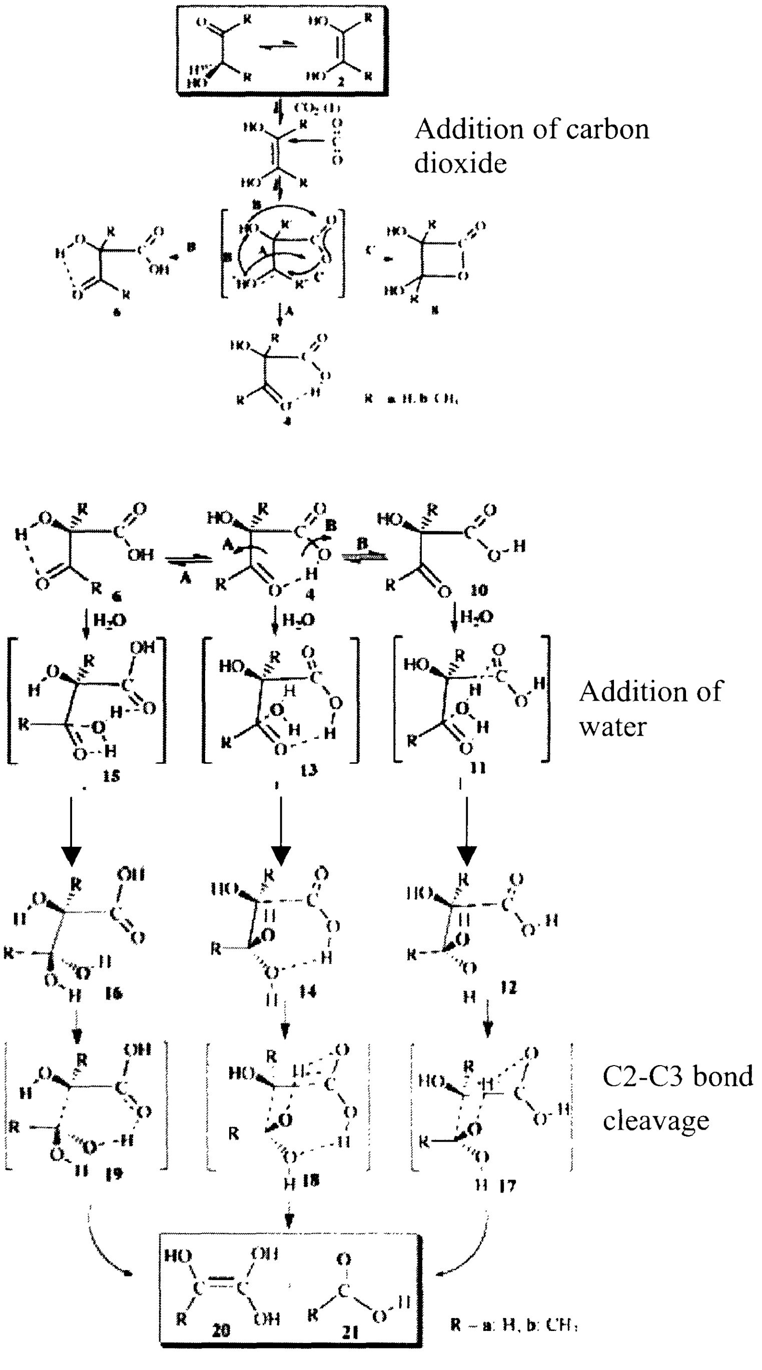


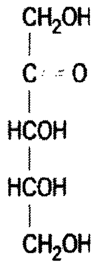
Figure 13: The reaction pathway of the nonenzymatic carboxylation of a molecule similar to ribulose bisphosphate (RuBP). In the first step, the starting molecule enolizes to (2) and carbon dioxide is added to create 3 intermediate molecules: (4), (6), and (8). Intermediate (8) is unstable, so only intermediates (4) and (6) continue to the next step where water is added. (11), (13), and (15) show the transition states of the addition of water to (4), (6), and (10) and (16), (14), and (17) show the product of the water addition. The C2-C3 bond is cleaved, causing transition states (17), (18), and (19). The final products of the pathway are (20) and (21).[31]

Table 5: The calculated relative energies in kcal/mol for R'=R"=H and R'=R"=CH_3 using second order Moller-Plesset calculations. The numbers in the Structure column represent the numbered structures in Figure 13 and $TS_{a\rightarrow b}$ stands for the transition state between structure a and structure b. ΔE_{gas} is the energy in gas phase and $\Delta E_{solution}$ is the energy in aqueous solution.[31]

Mechanism	**Structure**	**R'=R"=H**		**R'=R"=CH_3**	
		ΔE_{gas}	**$\Delta E_{solution}$**	**ΔE_{gas}**	**$\Delta E_{solution}$**
Addition of CO_2	1+2+H_2O	0.0	0.0	0.0	0.0
	$TS_{2\rightarrow4}$+ H_2O	37.0	30.5	29.2	23.1
	4+ H_2O	1.0	2.2	-4.5	-2.3
	$TS_{2\rightarrow6}$+ H_2O	31.8	25.1	19.9	15.2
	6+ H_2O	-0.2	-0.4	-6.0	-4.8
	$TS_{2\rightarrow8}$+ H_2O	37.4	25.4	28.8	19.1
	8+ H_2O	13.8	12.3	9.0	8.4
Addition of H_2O	$TS_{4\rightarrow10}$+ H_2O	9.7	10.1	N/A	N/A
	10+ H_2O	1.2	0.2	-3.3	-7.2
	11+ H_2O	35.1	41.0	30.4	37.5
	12	-4.7	0.9	-6.3	-0.2
	13	32.5	38.4	26.7	35.5
	14	-7.4	0.1	-10.7	-2.6
	15	32.7	41.6	27.0	37.0
	16	-5.4	1.2	-8.2	-1.0
C2-C3 bond cleavage	17	31.8	38.9	28.0	35.7
	18	31.4	39.5	26.4	34.6
	19	30.8	39.5	27.6	36.6
	20+21	24.2	24.2	19.3	21.5

The results by Zhan *et al* indicate that the energy barriers for the CH_3 substituent are lower than the energy barriers for the H substituent. The substituent effect was largest on the addition of carbon dioxide. When the solvent effects are included, the energy barriers for the carbon dioxide addition becomes significantly lower (7-12 kcal/mol lower), the energy barrier for the water addition becomes significantly higher (4-11 kcal/mol higher) and the energy barrier for the carbon-carbon bond cleavage becomes slightly higher (1-2 kcal/mol higher). One of the key findings by Zhan *et al* was that hydrogen bonding plays a key role in transition state stabilization. From the results, the lowest energy barrier in a given reaction stage was associated with the transition state structure with the highest hydrogen bonding.[31]

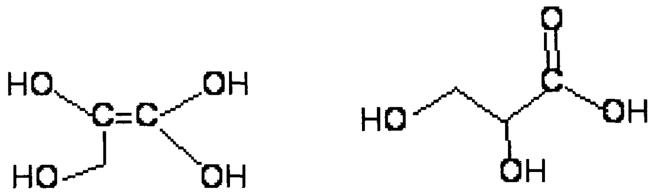
Based on the work done by Zhan *et al*, it is proposed that ribulose be used as an agent to fix the carbon dioxide. Ribulose is a pentose sugar with the chemical formula $C_5H_{10}O_5$ (Figure 14).



$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{C{=}O} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

Figure 14; Structure of the 5-carbon sugar, ribulose, which will be used to fix carbon dioxide.[32]

Using the previous notation, $R' = CH_2OH$ and $R''=(CH)(OH)CH_2OH$. The ribulose is the un-phosphorylated molecule of RuBP, the molecule upon which this reaction enzymatically occurs. The presence of multiple –OH groups would encourage hydrogen bonding during the transition states which would lower the energy barriers for the nonenzymatic carboxylation of ribulose. For this reason, it is predicted that the energy barrier for the carboxylation of ribulose will be less than the energy barrier for the model when $R'=R''=CH_3$. The energy barrier for the addition of carbon dioxide in solution for the $R'=R''=CH_3$ case was 23.1 kcal/mol. After the carboxylation is complete, the predicted product is glyceric acid, a sugar acid, and its enolate (Figure 15).



(a) (b)

Figure 15: Products of the carbon dioxide fixation to ribulose: (a) enolate of glyceric acid and (b) glyceric acid

In order to fix the carbon dioxide that is produced over the period of 12 hours that the system is being used, it is necessary to make sure there are enough reactants to be consumed. The average carbon dioxide production rate from exhalation is 25 mg/sec and for every mole of carbon dioxide there must be one mole of ribulose for fixation; thus, the total amount of ribulose needed is 3.681 kg.

$$25 \times 10^{-3} \frac{g\ \mathrm{CO_2}}{\mathrm{s}} \times \frac{1\ \mathrm{mol\ CO_2}}{44\ \mathrm{g\ CO_2}} \times \frac{1\ \mathrm{mol\ ribulose}}{1\ \mathrm{mol\ CO_2}} \times \frac{150\ \mathrm{g\ ribulose}}{1\ \mathrm{mol\ ribulose}} \times \frac{3600\mathrm{sec}}{1hr} \times 12hrs = 3.681\ \mathrm{kg\ ribulose}$$

In addition to ribulose, water is also consumed. For every one mole of carbon dioxide, one mole of water is consumed. The volume of water needed for carbon dioxide fixation is 0.344 L.

$$25 \times 10^{-3} \frac{g\ \mathrm{CO_2}}{\mathrm{s}} \times \frac{1\ \mathrm{mol\ CO_2}}{44\ \mathrm{g\ CO_2}} \times \frac{1\ \mathrm{mol\ H_2}O}{1\ \mathrm{mol\ CO_2}} \times \frac{14\ \mathrm{g\ H_2}O}{1\ \mathrm{mol\ H_2}O} \times \frac{1L\ \mathrm{H_2}O}{1000\ \mathrm{g\ H_2}O} \times \frac{3600\mathrm{sec}}{1hr} \times 12hrs = 0.344\mathrm{L\ H_2}O$$

5. Proposed System Design

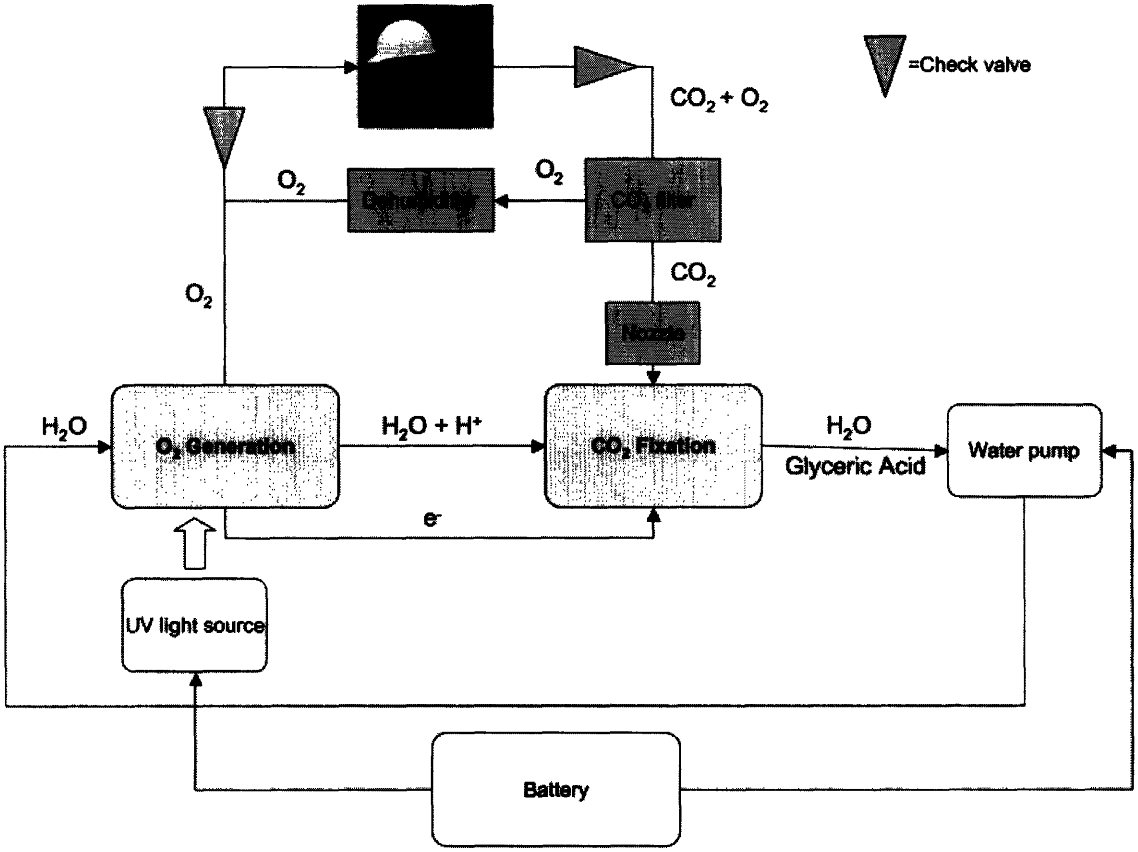


Figure 16: Flow diagram of proposed enclosed life support system for underground rescue. The striped boxes represent the two main components: oxygen generation and carbon dioxide fixation. The white boxes represent the battery and elements that require power (the water pump and light source). The dark gray figures represent mechanical elements in the system, including the check valves, carbon dioxide filter, dehumidifier, and nozzle.

Figure 16 shows the block diagram of the proposed enclosed life support system. The system consists of two functional loops: a gaseous breathing loop and an aqueous loop. Both the oxygen generation component and carbon dioxide fixation component occur in the aqueous phase. A DC powered water pump that can run off of a low voltage (<30V) battery will pump water through the aqueous loop. The water will both constitute the substrate for generating oxygen and contain the ribulose used in the carbon fixation. The products of fixation will be dissolved in the water (ribulose is not found in crystalline form) and are not expected to affect the oxygen generation. The use of a single pump for both reactions will conserve power and reduce system weight.

The water will enter the oxygen generation component where it will interact with the photoreactive surface. In order to maximize the diffusivity of the oxygen generated and to minimize the size of the component, it is proposed that microfluidic chips be used as the reaction environment. The flow rate through the each channel in each chip will be approximately 1 mL/min in order to obtain the oxygen generation rates presented previously. The 365 nm wavelength ultra-violet light source will be powered by the same battery that powers the water pump. As the reaction occurs, the electrons will be conducted to the carbon dioxide fixation component and the unreacted water and H^+ ions will be passed to the carbon dioxide fixation component.

The oxygen generated will be delivered to the user though a check valve in a hose to a face mask. The entire system will have a positive pressure in order to keep the atmosphere out of the closed system. As the user exhales, another check valve allows the exhaled air to exit to another hose. As the air exits, it is passed through a filter to separate the oxygen from the carbon dioxide. The exhaled oxygen is passed through a dehumidifier to remove the moisture (i.e. saliva) and then recycled back to the user through the delivery hose. The carbon dioxide rich air passes though a nozzle that pressurizes it and carbonates the water in the carbon dioxide fixation component. The dissolved carbon dioxide is fixed to the ribulose using energy from the electrons conducted from the oxygen generation component.

Based on this proposal, the predicted specifications of the enclosed life support system for underground rescue are shown in Table 6.

Table 6: Summary of the specifications of the proposed enclosed life support system for underground rescue

Duration	12 hours
Volume of water	2.255 L
Amount of ribulose	3.7 kg
Water pump	12V DC powered at 35 W
UV light source	365 nm wavelength 9-18 V DC powered at 15W
Battery	30 V
Estimated power consumption	50 W
Estimated mass	7 kg

6. Conclusion

There are many advantages of the proposed system over the existing methods. The most important advantage is the length of time it can support a user. A 12 hour life support system operates three times longer than best life support device currently on the market. By lengthening the duration that the life support system works, the chances of rescue of survivors from underground accidents is greatly increased. The lack of an oxygen cylinder in the proposed system is another advantage. The presence of a cylinder in existing systems poses two problems: the need for constant maintenance and the risk of explosion. An air cylinder must be monitored daily to make sure that the tank is still pressurized and filled. With such a high pressurized gas, there is always a risk of explosion, especially in an environment that is filled with flammable gases. While the proposed system will require some maintenance to ensure functionality, it will not be as demanding as existing devices. Another important benefit of the proposed system is that it is lightweight. Existing self contained breathing apparatuses, i.e. BioPak 240S, are bulky and heavy. The enclosed life support system weighs approximately half of the weight of the

BioPak 240S. This will allow miners to wear the life support at all times so that in case of emergency, the device will be immediately available. Currently, the closed circuit self contained breathing apparatuses are located at safety stations underground and in the case of an emergency, they must be obtained from the safety station. If an accident were to block access to the safety station, the miners would be left without oxygen.

The application of the enclosed life support system is not limited to underground mining, as there are many other important applications. For one, firemen who enter burning buildings that are filled with smoke, carbon dioxide, and carbon monoxide can use the device. Having a source of oxygen will allow firemen to enter oxygen deficient areas to rescue people. Applications in outer space are also useful. Astronauts also need a closed loop system for generating oxygen and eliminating metabolic wastes like carbon dioxide.

The implications of creating a better life support system for miners are tremendous. With the recent tragedies, miners and their families and friends are even more fearful of the risks associated with coal mining. Even coal mine operators and the government have become more cautious and wary. Creating a life support system that could potentially be used by every miner would increase the peace of mind of all people involved in the mining industry and thus help the mining industry to grow even more. With the rising prices of oil, the use of coal as a source of energy has become a preferable option. By creating a life support system that will allow miners and mining officials to feel safer when underground, America's energy problem can also be helped.

Acknowledgments

I would like to thank my thesis advisor Dr. Richard Gilbert for his guidance, encouragement, and assistance throughout the entire process of researching and writing my thesis. I would also like to thank Professor Roger Kamm for his co-sponsorship of my thesis.

References

[1] National Mining Association. Most Requested Statistics-U.S. Coal Industry. Washington, DC: 2006.

[2] Coal Energy. August 2005. Energy Information Administration. 30 April 2006 <http://www.eia.doe.gov/kids/energyfacts/sources/non-renewable/coal.html#uses>.

[3] Golosinski, Tad S., ed. Mining in the New Millennium Challenges and Opportunities. Brookfield: A.A. Balkema, 2000.

[4] 27 Coal-Mining States. 15 Dec 2005. Kentucky Educational Television. 27 April 2006 <http://www.ket.org/Trips/Coal/AGSMM/agsmmwhere.html>.

[5] Legislative History-Federal Mine Safety and Health Act of 1977-House Report No. 95-312. 1997. Mine Safety and Health Administration. 27 April 2006 <http://www.msha.gov/SOLICITOR/COALACT/leghist1.htm>.

[6] History of Mine Safety and Health Legislation. 1996. Mine Safety and Health Association. 27 April 2006 <http://www.msha.gov/MSHAINFO/MSHAINF2.HTM>.

[7] Department of Labor Mine Safety and Health Administration. "Emergency Mine Evacuation; Final Rule." Federal Register 71.46 (2006):12252-12271.

[8] Mine Safety and Health Administration (MSHA)-U.S. Department of Labor. 21 April 2006. Mine Safety and Health Administration. 27 April 2006 <http://www.msha.gov>.

[9] U.S. Department of Health and Human Services. Getting To Zero: The Human Side of Mining. Washington, DC: GPO, 2006.

[10] National Mining Association. Coal Mining Safety Trends. Washington, DC: 2006.

[11] "Sago mine survivor: Our air packs failed." CNN. 28 April 2006. Time Warner. 26 April 2006 <http://www.cnn.com>.

[12] "Small mines pose dangers for China miners." MSNBC. 3 January 2006. MSNBC.com. 9 May 2006 <http://www.msnbc.msn.com/id/10627199/from/RL.5/>.

[13] Occupational Health and Safety. Saskatchewan Mine Emergency Response Program. Saskatchewan, Canada: Saskatchewan Labour, 2001.

[14] MSHA's Occupational Illness and Injury Prevention Program Health Topic- "Filter Self-Rescue Devices". 1996. Mine Safety and Health Administration. 1 March 2006 <http://www.msha.gov/illness_prevention/healthtopics/HHICM03.HTM>.

[15] MSHA and Sago Mine Facts based on questions asked of Mine Safety and Health News editor Ellen Smith. 2006. Legal Publication Services. 1 March 2006 <http://www.minesafety.com/pages/sagominefacts.html>.

[16] Self-Rescue Devices; Use and Location Requirements. 1997. Department of Labor. 1 March 2006 <http://www.msha.gov/REGS/FEDREG/PPOLICY/1997PP/97-25633.HTM>.

[17] Ampac Asia-ISH (Respirators/Apparutus. 2003. Ampac Asia. 27 April 2006 <http://www.ampacasiapacific.com/respiratory.html>.

[18] Biomarine Incorporated. BIOPAK 240. Exton, PA: 1997.

[19] Biomarine Incorporated. Biopak 240S Benchman Instruction Manual. Exton, PA: 2003.

[20] Golosinski, Tad S. and Xie, Heping, eds. Mining Science and Technology '99. Brookfield: A.A. Balkema, 1999.

[21] Gilbert, Richard J. NIH2006-PAL115 Proposal. 2006.

---

[22] Dasse, Kurt A., Monzyk, Brude F., Burckle, Eric C., Busch, James R., Gilbert, Richard J. "Development of a Photolytic Artificial Lung: Preliminary Concept Validation." ASAIO Journal 49 (2003): 556-563.

[23] Monzyk, Bruce F., Burckle, Eric C., Carleton, Linda M., Busch, James, Dasse, Kurt A., Martin, Peter M., and Gilbert, Richard J. "Photolytically driven generation of dissolved oxygen and increased oxyhemoglobin in whole blood." 2005

[24] Air Liquide Group. 2006. 1 May 2006 <http://www.airliquide.com>.

[25] Compact CW UV laser and DPSS Q-switched UV Laser. 2006. CrystaLaser. 10 May 2006 <http://www.crystalaser.com/new/uv-laser.html>.

[26] Respiration. 2002. 25 April 2006 <http://users.rowan.edu/~farrell/hohb/Respiration.htm>.

[27] Inoue, S. and Yamazaki, N. Organic and Bio-organic Chemistry of Carbon Dioxide. Tokyo: Kodansha Ltd., 1982.

[28] Xiaoding, Xu and Moulijn, J.A. "Mitigation of CO_2 by Chemical Conversion: Plausible Chemical Reactions and Promising Products." Energy and Fuels 10 (1996): 305-325.

[29] Purves, William K., Sadava, David, Orians, Gordon H., Heller, H. Craig. Life The Science of Biology Sixth Edition. Gordonsville: Sinauer Associates, Inc., 2001.

[30] Light Independent Reactions. 2002. 1 May 2006 <http://www.geocities.com/barefeetchild/darkreaction.html>.

[31] Zhan, Chang-Guo, Niu, Shuqiang, Ornstein, Rick L. "Theoretical studies of nonenzymatic reaction pathways for the three reaction stages of the carboxylation of ribulose-1,5-bisphosphate." Journal of the Chemical Society-Perkin Transactions 2 (2001): 23-29.

[32] Ribulose. 2000. 1 May 2006 <http://www.accessscience.com>.