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Original Article

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The development and evaluation of a non-pressurised, chemical oxygen reaction generation vessel and breathing system providing emergency oxygen for an extended duration

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Short title:

Extended duration emergency chemical oxygen generator.

Summary

The objective was to develop a sodium percarbonate/water/catalyst chemical oxygen generator not using compressed gas. Existing devices utilising this reaction have a very short duration. Preliminary experiments with a glass reaction vessel, water bath and electronic flowmeter indicated many factors affected oxygen production rate including reagent formulation, temperature, water volume and agitation frequency. Via full scale experiments using a stainless steel vessel, an optimum combination of reagents was found to be 1 l water, 0.75 g manganese dioxide catalyst, 60 g sodium percarbonate granules and 800 g of custom pressed 7.21 (0.28) g sodium percarbonate tablets. This combination of granules and slower dissolution tablets produced a rapid initial oxygen flow to "purge" an attached low flow breathing system allowing immediate use, followed by a constant flow meeting metabolic requirements for a minimum of 1 h duration.
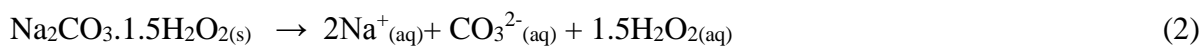
In 2009 the UK Ministry of Defence (MOD) Centre for Defence Enterprise issued an open call for a system to provide emergency medical oxygen to casualties on the battlefield and for subsequent evacuation to a forward medical post [1]. It was specified that no compressed gas must be used, the proposed apparatus should be portable, and the possibility of "regenerating the oxygen supply" should be considered. Comparable requirements also currently exist for the provision of compact emergency oxygen supplies of moderate duration in potentially challenging environments for the initial treatment and evacuation of diving emergencies e.g. decompression sickness, arterial gas embolism.

Possible mechanisms for generation of oxygen *in situ* include battery powered electrochemical devices such as oxygen concentrators and chemical methods [2]. Chemical means of generating oxygen without use of compressed gas cylinders include "oxygen candles", decomposition of hydrogen peroxide [3], and decomposition of sodium percarbonate in water, a reaction evaluated in past anaesthesia literature but which to date has been of too short a duration for widespread use [4-6].

Oxygen candles are used in personal escape rebreathers for smoke filled environments, submarine escape apparatus (e.g. Scott Emergency Escape Breathing Device, Scott Aviation, Lancaster, NY, USA), spacecraft oxygen generators, and emergency oxygen generators for commercial aircraft. The chemical reactions involved are all highly exothermic, the exterior temperature of the canister may exceed 260 °C and this has resulted in a series of catastrophic fires [7-9].

Liquid hydrogen peroxide (H_2O_2) may undergo catalytic decomposition to produce oxygen and water (reaction 1); however it is unstable and the associated apparatus requires an electrical forced-draft cooling system to prevent overheating [3]. Alternatively, H_2O_2 may be generated *in situ* by dissolution and decomposition of sodium percarbonate in water (reaction 2). Sodium percarbonate is a peroxohydrate with H_2O_2 molecules held in a crystal lattice in an analogous way to the water of crystallisation in many salts [10]. Dissolution of the solid liberates H_2O_2 which, in the presence of a catalyst, decomposes to oxygen and water. At 25°C and 1 atmosphere pressure, one mole, 157 g, of pure sodium percarbonate generates 16.8 l of oxygen, with non-toxic by-products of water and sodium carbonate. Provided that it is kept dry, it is stable and may be stored until needed for use.

$$H_2O_{2(l)} \rightarrow H_2O_{(l)} + 0.5O_{2(g)} \tag{1}$$

$$Na_2CO_3.1.5H_2O_{2(s)} \rightarrow 2Na^+_{(aq)} + CO_3^{2-}_{(aq)} + 1.5H_2O_{2(aq)} \qquad (2)$$

A number of materials catalyse chemical reaction 1 and one of the most commonly used is finely divided manganese dioxide, MnO_2 [11].

A medical emergency oxygen system based on this reaction exists, using 300 g percarbonate powder, 3 g of manganese dioxide catalyst and 1 l of water in a plastic container (emOx, Exmed UK Ltd, Whitestone, Herefordshire, UK). This and other similar devices are available commercially but the slow onset, variable oxygen production rate and short duration (< 18 min) limits their practical use [6]. The rate of decomposition of hydrogen peroxide is temperature dependent and exothermic ($\Delta H°_{298\ K}$ = 98 kJ.mol^{-1} [12]). Therefore, the rate of both percarbonate dissolution and heat transfer must be controlled to maintain a reasonably constant rate of oxygen generation.

The minimum recommended quantity of compressed oxygen to be carried on dive boats for emergency use is 600 l which, when delivered at $\geq$ 10 l.min^{-1} via a non-rebreathing mask, will provide an endurance of up to 1 hour. This can be extended by attaching it to a very low flow circle portable breathing system (e.g. Wenoll MO2R, DDRC Healthcare, Plymouth UK and DAN MO2R, DAN Europe Foundation, Roseto, Italy) [13,14]. To improve the endurance of a water-percarbonate chemical oxygen generator one approach, therefore, might be (i) to slow down the reaction rate and (ii) combine it with a portable circle breathing system. Our objectives were therefore to:

i) Develop, by iterative laboratory evaluations, a compact percarbonate/water/catalyst chemical oxygen generator with a combination of reagents and formulations producing a rapid-onset initial oxygen flow to "purge" an attached circle breathing system and so allow immediate use, followed by a constant oxygen flow exceeding metabolic requirements for a minimum of 1 h duration.

ii) Control the reaction rate to increase the duration of oxygen production with only modest exothermia.

iii) Optimise efficiency by combining this oxygen generator with a low flow circle breathing system.

iv) Evaluate the potential of the combined apparatus as a means of supplying emergency oxygen.

Methods

Following standard safety procedures, all laboratory investigations were carried out at the College of Engineering, Swansea University. Opinion was sought from our Joint Scientific Review Committee and also the Regional Ethics Committee and formal review was not required for the final evaluation conducted off-site.

In a series of small scale experiments with sodium percarbonate granules we investigated the effect of varying quantities of catalyst and the effect of temperature on oxygen generation rates. Based on this information we then conducted a series of full scale experiments where in particular we investigated the potential use of sodium percarbonate granules to provide an initial rapid oxygen purge for any attached breathing circuit, in combination with sodium percarbonate tablets to provide a subsequent sustained release of oxygen. We also examined the effect of varying catalyst concentration and temperature on the rate of oxygen generation. The materials used were 2mm diameter granules of sodium percarbonate (`sodium percarbonate$_{(granules)}$'), (20-30% available H_2O_2) (Sigma-Aldrich, Gillingham, UK); manganese dioxide (precipitated, GPR grade) (BDH, Poole, UK); distilled water; and artificial seawater, prepared following the formulation of Kester et al [15]. Round tablets ('sodium percarbonate$_{(tablets)}$') were custom made from the sodium percarbonate$_{(granules)}$ by Alchemy Technologies Ltd. Port Talbot, UK using a modified Manesty D3B tablet press operating with an 8 tonne stroke. Tablet parameters [mean (SD)] were: mass: 7.21 (0.28) g; diameter: 24.51 (0.17) mm; thickness 10.44 (0.42) mm.

A schematic of the apparatus and photograph of reagents is shown in Figure 1. For preliminary small scale experiments, a glass reaction vessel of 200 ml volume was used with a ground taper-fit stopper incorporating the exit tube for the generated gas. For subsequent full scale experiments a general purpose reaction vessel was made from stainless steel (AIR Engineering, Swansea, UK) with a wide necked airtight screw-on lid sealed by an "O" ring. This had a gas tight hose connection in the centre of the lid from which the generated gases could exit and was partially submerged in a water bath. The generated gases were bubbled through water and then passed through a drying chamber containing silica-gel which absorbed water vapour from the gas. The dry gas then passed via a mass flowmeter (Model 4140, TSI Instruments Limited, High Wycombe, UK) and oxygen analyser (Model GKM-03, INSOVT, St. Petersburg, Russia) to the environment. Each experiment was started by adding

water to the solid reactants in the reaction vessel and replacing the stopper or screwing on the lid for the small and full scale experiments, respectively. In the full scale laboratory studies the experiments were terminated when the generated oxygen flow fell below 250 ml.min^{-1}, as this would not meet metabolic demands. Flowmeter and oxygen analyser data were sampled at 0.1Hz via serial port connections and captured to a spreadsheet (Excel, Microsoft Corp, WA) for subsequent analysis using bespoke software written in the open source scientific programming language *Python* (www.python.org). Temperatures of the room and water bath were measured with mercury thermometers, and the reaction vessel temperature was measured using a pyroelectric thermometer (Model OSXL450, Omega Engineering Ltd., Manchester, UK) every 5 min.

The laboratory investigations included the use of simulated seawater [15], to see whether this would have any effect on reaction kinetics, as in some potential applications seawater might be readily available.

A very low flow circle breathing system was made by modifying a Russian IDA 71 military diving apparatus (Figure 2). The standard IDA 71 oxygen cylinder was replaced by the stainless steel chemical oxygen generator reaction vessel. Each of the two standard soda lime canisters contained 1.7 kg of soda-lime and one of these was removed to make available two connection ports to the gas circuit. An oxygen feed line from the chemical reaction vessel and the oxygen sensor cell of an oxygen analyser were connected to these two ports via custom made screw-on adapters. The combined apparatus (oxygen generator and breathing system) had dimensions of 58 x 40 x 16 cm and weighed 12 kg (total weight of approximately 13.9 kg when chemical reagents and water were added to the reaction vessel). Two evaluations were performed with this apparatus by one of the authors. No additional apparatus or circuit priming manoeuvres were used to provide pre-oxygenation and denitrogenation, as in a practical situation this would not be possible. In both evaluations the reagent combination used was 800 g percarbonate pellets, 60 g percarbonate granules, 0.75 g catalyst and 1 l of water.

Results

The preliminary small scale experiments provided an insight into the effects of reducing the quantity of catalyst to slow the rate of oxygen generation but increase the duration of oxygen production. It was also noted that too little catalyst would lead to an extremely prolonged reaction however and we also found that increasing the temperature of the reactants would increase the reaction rate, as expected. These are summarised in Table 1.

When sodium percarbonate$_{(granules)}$ only were used in these small scale experiments, the oxygen flow curve was characterised by oxygen generation of rapid-onset, the rate of which increased but also decayed quickly (Figure 3). The rapid-onset reaction obtained from use of granules was therefore considered suitable as an initial means of supplying oxygen to purge the breathing system of air, but too short in duration for prolonged use. Although on a smaller scale, these results were similar in profile to those described with the emOx system [6]. When the compressed percarbonate$_{(tablets)}$ alone were used in full scale experiments, the rate of dissolution and reaction was reduced presumably because of the lower surface area/volume ratio (Figure 3). This suggested that a combination of granules and tablets could be found which gave both an initial rapid onset of oxygen generation followed by a slower but sustained rate of production thereafter.

Through subsequent iterative development, an optimum combination was found to be: 60 g sodium percarbonate$_{(granules)}$, 800 g sodium percarbonate$_{(tablets)}$, 0.75 g manganese catalyst, and 1 l water. We found that 60 g sodium percarbonate$_{(granules)}$ produced a rapid onset of oxygen production at an initial flow rate of >1 l.min^{-1} to purge an attached circle breathing system. It was found that 600g of percarbonate$_{(tablets)}$ produced an inadequate subsequent generation rate of oxygen over an extended time period of approximately 1 h and 800g was selected as a more appropriate mass to use. By reducing the mass of catalyst from 1 g to 0.75 g we then found that the early peak in the overall oxygen flow rate could be reduced slightly but extended over a clinically more useful duration. Substitution of simulated sea water for distilled water also had no effect on oxygen yield or flow rate. These are illustrated in Figure 4.

In both of the final full scale evaluations with an attached circle breathing system, using the above optimum combination of reagents, a supply of oxygen sufficient to meet metabolic requirements was maintained for over 90 minutes (Figure 5). In all experiments the measured oxygen fraction was $\geq 99\%$.

Discussion

We have demonstrated that it is technically feasible to extend this method of chemical oxygen generation over a more clinically useful period of time. Further development could potentially optimise such a design for practical use with respect to oxygen yield, temperature regulation and further reductions in the weight of apparatus and reagents. The weight and size of the carbon dioxide absorber could be reduced by using lithium hydroxide as the absorbent, rather than soda lime: lithium hydroxide absorbs more than three times more CO_2 per unit mass which is why it is used in spaceflight, however it is also more expensive compared to soda lime. Weight could also be reduced by using a plastic circle breathing system, possibly as a single use device, in the manner of currently available portable diving-emergency oxygen cylinder / low flow circle combination breathing systems [13, 14].

The relatively large particle size of the catalyst we used caused it to settle out, resulting in peaks and troughs of oxygen production, unless the solution was agitated manually at frequent intervals. This could be addressed by reformulating the catalyst as a rapidly dissolving transitional metal ion salt, bonding it to a surface, or by using catalyst in the form of a colloidal suspension.

If such a device was employed in a diving rescue setting, the surrounding environment (e.g. sea or lake) could be used effectively as a heat sink to control the rate of reaction; as well as providing a convenient source of water to be added to the dry reagents to initiate the reaction. We have shown that the use of seawater made no difference to the reaction characteristics. One could even conceive of a system that might self-fill and so activate on immersion in water. On dry land, especially in high environmental temperatures, a method of thermal management to limit the maximum temperature of the reaction vessel may be required. One lightweight means of achieving this, used with success on Apollo space missions to maintain lunar rover batteries within a stable working temperature range, would be to encase the reaction vessel in a solid wax heat sink of suitable mass and latent heat of crystallisation, such that the heat energy generated by the reaction would make the wax undergo isothermic change of state from solid to liquid [16].

Currently the oxygen generator, as with others using this basic reaction, has to be kept in an upright position. To increase practicality it would be desirable to incorporate a means of preventing spillage such as internal valves or baffles in the reaction vessel and hydrophobic filters to prevent accidental inhalation of dust or liquid.

We envisage several possible applications of this apparatus with suitable development, in addition to supplying emergency oxygen for medical use or diving emergencies. One example would be a single use water-activated diving or submarine underwater escape system. There may also be a role in military conflicts where oxygen supplies can be limited, as was the case in the South Atlantic conflict of 1982 [17], or in military situations where compressed gas supplies are considered undesirable, as in the original MOD open request which inspired this work.

A development of the oxygen generator unit alone could be used as an oxygen source to enrich air in draw-over anaesthesia systems for austere environments or veterinary settings.

In conclusion, we have demonstrated that, by combining a water-activated chemical oxygen generator and a very low flow closed circuit breathing system, with careful choice and formulation of reagents, it is feasible to build a device which can generate oxygen *in-situ* with sufficient control of the reaction rate to sustain life for over 1 h.

Competing Interests

JD, DW, PD, MD, JOD – no competing interests declared.

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Table 1. Early small scale laboratory experiments.

Plan	Percarbonate granules (g)	Catalyst (g)	Water (ml)	Water bath temp (°C)	Findings
1) Best estimate Start.	20	0.1	50	25	Linear rise to high peak flow by 8 min then rapid exponential decay to minimal flow by 13 min. *Comment:* Duration too short.
2) Effect of increasing catalyst relative to percarbonate	10	0.1	50	24	Almost constant flow until 9 min then gradual more linear reduction to 24 min. *Comment:* Improved duration profile.
3) Effect of reducing catalyst	10	0.05	50	24	Near-constant flow to 12 min at rates approximately half those of experiment (2). Linear reduction in flow to 45 minutes. *Comment:* Improved duration profile.
4) Effect of further reducing catalyst	10	0.025	50	24	Flow rates approximately half those of experiment (3) over longer duration to 18 min. Steady slow flow thereafter. Reaction not complete by 63 min. *Comment:* Reaction slowed too much. Insufficient catalyst.
5) Effect of increasing reactant temperature	10	0.025	50	33.7	Flow rates to 15 min almost double those of experiment (4) then gradual decay. *Comment:* Reaction speeds up with increased temperature as expected.

Figure 1 Diagram of laboratory apparatus and view of reagents used showing (clockwise) percarbonate tablets, manganese catalyst and percarbonate granules.

Figure 2 Apparatus used for in-vivo evaluation. Oxygen from the chemical generator is first dried by passage through a silica-gel dessicant column, its flow is measured using a mass flow sensor and it then enters the breathing system which includes a flexible bag. As the user breathes, this oxygen then circulates around the circuit as illustrated, via the action of unidirectional check valves in the inspiratory and expiratory hoses, passing through the soda-lime carbon dioxide absorbent as it does so. Some oxygen is consumed metabolically and any excess gas exits through a spill valve if the flexible bag is full. An oxygen analyser sensor (S) is mounted in the base of the flexible reservoir bag.

Figure 3 Laboratory investigations: typical results.

Grey line: Small scale laboratory study using percarbonate granules only with catalyst and distilled water with no agitation that shows oxygen output rapidly starting, reaching a maximum then decaying rapidly within 5 min. i.e. a high initial flow but short duration.

Black line: Full scale laboratory run using 800 g tablets only, 1.25 g of catalyst, distilled water and agitation every 5 min demonstrating a prolonged duration but absence of the rapid onset of flow required to initially purge an attached breathing system of air.

It was therefore considered that an optimal mix of reagents might be obtained by using granules to produce a high initial oxygen flow with minimal delay, combined with 800 g of tablets to sustain this flow for a longer duration.

Figure 4 Summary of full scale laboratory experiments.

Experiment (a) agitated every 5min, the remainder every 1min. Starting temperatures given.

a) 800 g tablets, 60 g granules, 1 g catalyst. Reactor 20.75 °C, Water bath 19.5 °C. 1 l distilled water.

b) 800 g tablets, 60 g granules, 0.75 g catalyst. Reactor 17.2 °C, Water bath 18.7 °C. 1 l distilled water.

c) 800 g tablets, 60 g granules, 1.25 g catalyst. Reactor 17.65 °C, Water bath 18.7 °C. 1 l distilled water.

d) 800 g tablets, 60 g granules, 0.75 g catalyst. Reactor 25.0 °C, Water bath 25.0 °C. 1 l distilled water.

e) 800 g tablets, 60 g granules, 0.75 g catalyst. Reactor 19.7 °C, Water bath 20.0 °C. 1 l distilled water.

f) 798 g tablets, 60 g granules, 0.75 g catalyst. Reactor 25.2 °C, Water bath 25.0 °C. 1 l simulated seawater.

Figure 5 Data from the two *in-vivo* evaluations using 60 g percarbonate granules, 800 g percarbonate tablets, 0.75 g catalyst and 1 l water with agitation every 5 min, demonstrating adequate initial purge from the rapid reaction of the percarbonate powder and sufficient duration provided by the slower-reacting tablets to supply oxygen for 90 min to the breathing system.