A Review of Pure Oxygen Generation and Alternative Oxidants for Wet Oxidation of Fecal Sludge for Novel Sanitation Technologies

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

Advanced oxidation technologies have great potential for the effective treatment of fecal wastes, septage, and other sanitation wastes. However, they all rely on the provision of an oxidant, which serves as final electron acceptor for those electrons released from the oxidation of the electron-rich organic molecules that make up the fecal waste. In many cases, this oxidant is oxygen from air. For treatment process that operate under pressure, as is the case in supercritical water oxidation systems and other wet oxidation systems, compressing air which contains roughly 80% (inert) nitrogen can be very energy intensive and expensive.

This literature review summarizes currently available information about oxidant alternatives to compressed air for use in supercritical water and wet oxidation systems for fecal sludge treatment. These alternatives included oxygen enrichment techniques (to avoid compressing inert nitrogen) such as pressure swing adsorption and membrane separation, or using liquid oxygen, reactive oxygen species, electrolysis, and chemical looping combustion. Complexity, energy requirements, cost, and safety were discussed for each technology. Prominent commercial players and research in progress were identified. When possible, costs were estimated.

Of all the alternatives examined, provision of liquid oxygen, vacuum-pressure swing adsorption (VPSA), and vacuum swing adsorption VSA to produce enriched or pure oxygen have the potential to be competitive with air compression. Safety concerns and materials compatibility have to be addressed with all enriched oxygen systems beyond a certain threshold oxygen concentration. Also, energy recovery from the expansion of exhaust gases has the potential to decrease the energy costs associated with air compression.

The following recommendations are made for further investigations:

1. Conduct further evaluation of air separation system utilizing VPSA and VSA. In particular document costs and sweet spots for costs, system reliability, maintenance costs, requirement for consumables and how to best integrate these alternatives with advanced oxidations such as supercritical water oxidation systems and wet oxidation. The recommended study is a paper study that could take about 3-6 months.
2. Develop and demonstrate a high pressure electrolyzer that generate hydrogen peroxide and other reactive species and O_2 directly at elevated pressure, evaluate its efficacy, and how it could be best integrated with advanced oxidations such as supercritical water or wet oxidation systems. This recommended study is a laboratory study that could take about 9-12 months. It could lead to new IP.

The learning from these recommended activities is expected to benefit several projects in the WASH portfolio of the Bill & Melinda Gates Foundation

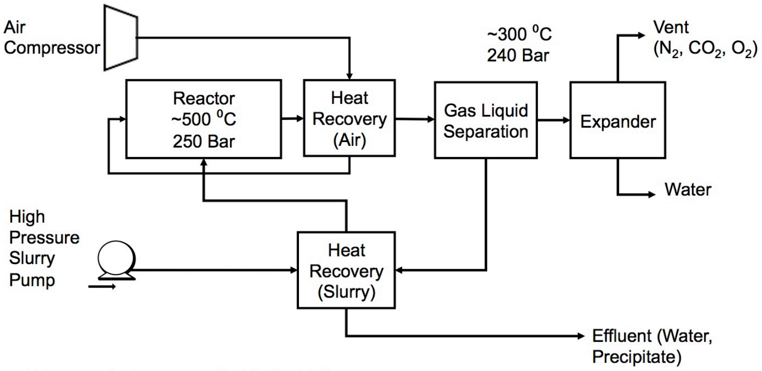
Contents

Abbreviations

ASME	American Society of Mechanical Engineers
ASU	Air separation unit
CLC	Chemical looping combustion
DO	Dissolved oxygen
ITM	Ion transport membrane
Nm^3	Normal meter cubed
OER	Oxygen evolution reaction
PEM	Polymer electrolyte membrane
PSA	Pressure swing adsorption
ROI	Return on investment
ROS	Reactive oxygen species
SCWO	Supercritical water oxidation
SOE	Solid oxide electrolyzer
SPE	Solid polymer electrolyte
SY	Sonochemical yield
TSA	Temperature swing adsorption
VPSA	Vacuum pressure swing adsorption
VSA	Vacuum swing adsorption

1. INTRODUCTION

Supercritical water oxidation (SCWO) shows potential as a method for decentralized neighborhood-scale sludge treatment for both urban and remote areas. SCWO has been used industrially for oxidation of sludges, chemical weapons, hazardous waste and more (Bermejo and Cocero). Water enters the supercritical phase at temperatures above 374^{o} C and pressures above 22.1 MPa. At supercritical conditions, reduction in water polarity and an increase in miscibility with oxygen at supercritical conditions allows fecal sludge to be dissolved and then rapidly oxidized to clean water with production of carbon dioxide and precipitated mineral salts. Because the organic compounds can be completely dissolved in supercritical water, the reaction can occur quickly and uniformly throughout the solution, without mass-transfer related constraints (Bermejo and Cocero). The reaction is exothermic, and the heat of reaction can be recovered in the form of hot water or steam, which part of it is generally used to preheat the incoming sludge, while the excess can be provided to the local community, or directed through a turbine to power a generator. No pre-drying of fecal waste, an energy-intensive and smelly process, is required. An example process flow diagram for a SCWO system is shown in Figure 1. Process input streams include the fecal slurry and air, while the output streams include vent gas and water with suspended salts. Unit operations include an air compressor, a reactor for oxidation of the sludge, a series of heat exchangers, and a pressurized gas-liquid separator.



* Reactor design patent filed in the U.S.

Figure 1. Process flow diagram for Duke's University's supercritical water oxidation system for fecal slurry treatment

In order for SCWO to be a viable technology, energy use must be minimized. One target component of SCWO systems in reducing energy consumption is the air compressor. Many systems use compressed air as an oxidant, but since air comprises of close to 80% of inert nitrogen, a large fraction of the power consumed is directed towards compression of nitrogen, thus affecting the overall energy usage.

To illustrate this, the continuous SCWO system at Duke University can treat the fecal waste of about 1,000 people, or a dry mass of solids of about 110 kg_{dry}, per day. Including a 1.3 stoichiometric excess, approximately 7 kg/h O_2 is needed. The air compressor on the Duke unit pressurizes 36.3 kg air per hour to 27.6 MPa and uses an estimated 9.48 kW. This is a large number in comparison to the calorific loading of the feed to the process, which is about 19 kW. The energy usage of the air compressor translates to a normalized value of 1.35 kWh per kilogram pressurized O_2. Because air is comprised of 79% N_2 and other non-oxygen gases, the maximum energy savings possible is 1.07 kWh/kg. Assuming an electricity cost of 0.12 \$/kWh, this conveys a maximum savings of 0.128 \$/kg, or 0.899 \$/h per 1,000 people serviced. Given the various pressures to minimize the costs of treatment, means to minimize the cost to provide the oxidant to the SCWO process are of paramount interest.

This literature review summarizes currently available information about oxidant alternatives to compressed air for use in supercritical water and wet oxidation systems for sludge treatment. These alternatives include oxygen enrichment techniques such as pressure swing adsorption and membrane separation, using liquid oxygen, reactive oxygen species, electrolysis, and chemical looping combustion. Complexity, energy requirements, cost, and safety are discussed for each technology. Prominent commercial players and research in progress is identified. When possible, costs are estimated. Finally, recommendations for future research or implementation are given.

The objectives were to examine the variety of oxidants available for wet oxidation as a treatment method for fecal sludge. This is of special interest to the Bill & Melinda Gates Foundation, which funds several fecal sludge treatment projects using different wet-oxidation approaches. This review describes the system requirements and advantages and disadvantages of several possible oxidant alternatives. It also makes recommendations to the Bill & Melinda Gates Foundation about promising technologies.

More specifically, the goals of the literature review include:

- Compiling and investigating potential alternative oxidants and generation methods
- Comparing safety considerations of the technologies considered
- Comparing the complexity of technologies considered, and they likelihood they could be implemented in a remote area
- Identifying relevant commercial entities, research in progress, and consultants
- Providing an estimate of the capital and operating cost involved with each method
- Identifying promising technologies and making recommendations to the Bill & Melinda Gates Foundation

Technologies considered in the review include oxygen purification by swing adsorption methods and membrane separation technology, purchase of liquid oxygen, oxygen generation by water electrolysis, and alternative oxidants such as reactive oxygen compounds including peroxides and ozone, oxides, ferrate, and chemical looping combustion.

2. METHODS

2.1 Search Strategy

The following databases were used to search for academic literature relevant to the research questions: NC State University Libraries search engine, Duke University Libraries search engine, SciFinder Scholar, and PubMed. Commercial information and health and safety data was searched for with different techniques. Summaries of market analyses were consulted for each technology. The major players for each technology were noted and the companies websites were located using Google Search. Some commercial information was provided by vendors. For health and safety information, risk assessments relevant to the individual technologies were initially searched for using PubMed. If this resulted no results or irrelevant results, Google Search was used to locate health and safety information from a U.S. or Canadian government agency.

A large collection and various combinations of terms relevant to each technology were searched for. An incomplete list of combinations of terms for each technology is listed below:

- **Swing adsorption:** air separation, pressure swing adsorption, temperature swing adsorption, vacuum swing adsorption, hybrid pressure vacuum swing adsorption, PSA, TSA, VSA, VPSA, zeolite molecular sieve for air separation, swing adsorption risk assessment, swing adsorption safety, swing adsorption review
- **Membrane technology:** membrane air separation, membrane air separation review, membrane oxygen generation, membrane oxygen separation operation safety
- **Liquid Oxygen:** liquid oxygen market analysis, oxygen on-site generation, oxygen on-site storage, oxygen cylinder cost, cryogenic oxygen supply, liquid oxygen safety, liquid oxygen storage ASME
- **Reactive Oxygen:** peroxide oxidant supercritical water, peroxide decomposition oxidation, peroxide wastewater treatment, advanced oxidation process, on-site ozone generation, ozone wastewater treatment, ozone advanced oxidation process, methanol oxidant supercritical water, hydrogen peroxide risk assessment, hydrogen peroxide safety, ozone industry risk assessment, ozone exposure safety
- **Metal Oxides and Chemical Looping:** chemical looping combustion, iron oxide market analysis, iron oxide safety
- **Electrolysis:** water electrolysis oxygen production, water electrolysis review, on-site electrolysis unit, spacecraft oxygen generation, electrolysis market analysis
- **Ultrasonic irradiation:** sonolysis water review oxidation, ultrasonic irradiation oxygen production, ultrasonic irradiation industry, sonolysis water hydroxyl radical yield

2.2 Screening Process

Results returned by the above searches were screened for inclusion with the following criteria. Foremost, they must be relevant to the technological specifications of a SCWO unit, as well as relevant to at least one of the following considerations: complexity, power consumption, cost, and safety. For developing technologies and information on the basic science of all technologies, the literature must be peer-reviewed. For pricing information and details about commercially mature technologies, commercial literature that had not been peer-reviewed was included when the required information was not available in the primary literature. There was no publication date before which literature would be excluded, but preference was given to more recent literature when relevant information was available in more than one source with a significant age difference.

3. RESULTS AND DISCUSSION

3.1 Air Separation

The aim of employing air separation methods is to reduce the amount of energy used to compress air by reducing the volume of parasitic nitrogen present in air before compression. However, it is important that the reduction in power required for compression be greater than the power requirements of air separation units. The air separation techniques discussed in this report include various swing adsorption and membrane separation methods.

3.1.1 Swing adsorption methods

Swing adsorption systems can produce large volumes of oxygen at high purities, typically between 93-95 vol% (Smith and Klosek, 2000). For small applications (O_2 production requirements under approximately 300 kg/h), they are more energy efficient than distillation methods (Haruna et al., 2005). There are several variants of swing adsorption technology, the most mature of which is pressure swing adsorption (PSA) (Nelson, 1993). Swing adsorption is comprised of two steps that are generally operated in parallel in order to approach a continuous process. During the adsorption step, a gas mixture, in this case air, is passed at high pressure through one or more columns packed with selectively adsorbent material (Banaszkiewicz and Chorowski, 2015). In the case of oxygen enrichment, this material is a zeolite molecular sieve that selectively adsorbs nitrogen gas. Lithium-containing zeolite is most commonly used due to its high adsorption capacity and affinity, allowing for smaller column size and lower energy consumption (Haruna et al., 2005). In the regeneration step, the pressure is lowered to release the adsorbed nitrogen completing the cycle. A typical PSA process flow diagram is shown in Figure 2

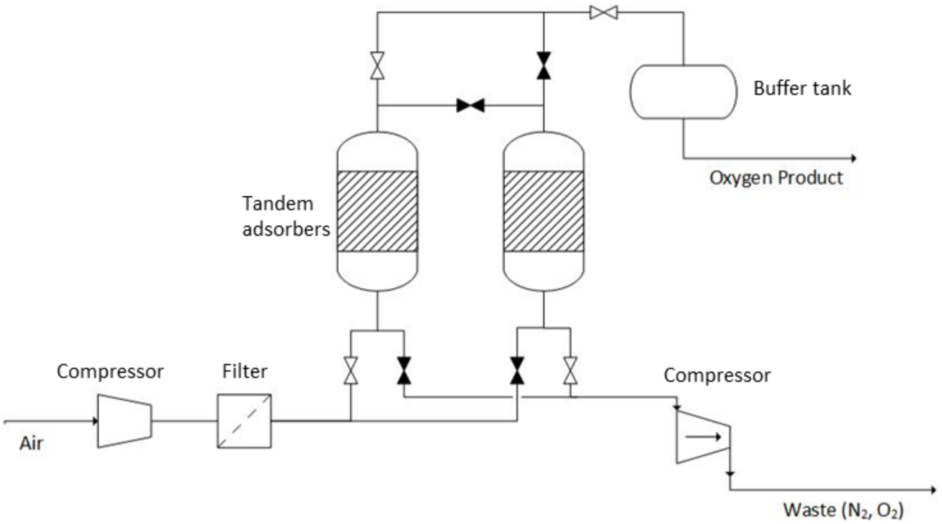


Figure 2. Process flow diagram for a pressure swing adsorption system (PSA).

PSA can produce oxygen with a purity up to 95%, at an outlet pressure of up to 100 kPa (Banaszkiewicz and Chorowski, 2015). Efficiency and capital cost are affected by any pretreatment of air to remove water or carbon dioxide before oxygen enrichment (Smith and Klosek, 2000).

While PSA is commonly used industrially for O_2 separation from air, temperature swing adsorption, or TSA, is a more recently developed technology (Nelson, 1993). TSA process flow is similar to PSA. Rather than the adsorption step occurring at high pressure and the regeneration step at low pressure, the adsorption step occurs at low or ambient temperature and the regeneration step occurs at high temperature (Banaszkiewicz and Chorowski, 2015). However, PSA is usually preferred over TSA for its faster cycle time and simple operation procedures (Smith and Klosek, 2000). A TSA process flow diagram is shown in Figure 3.

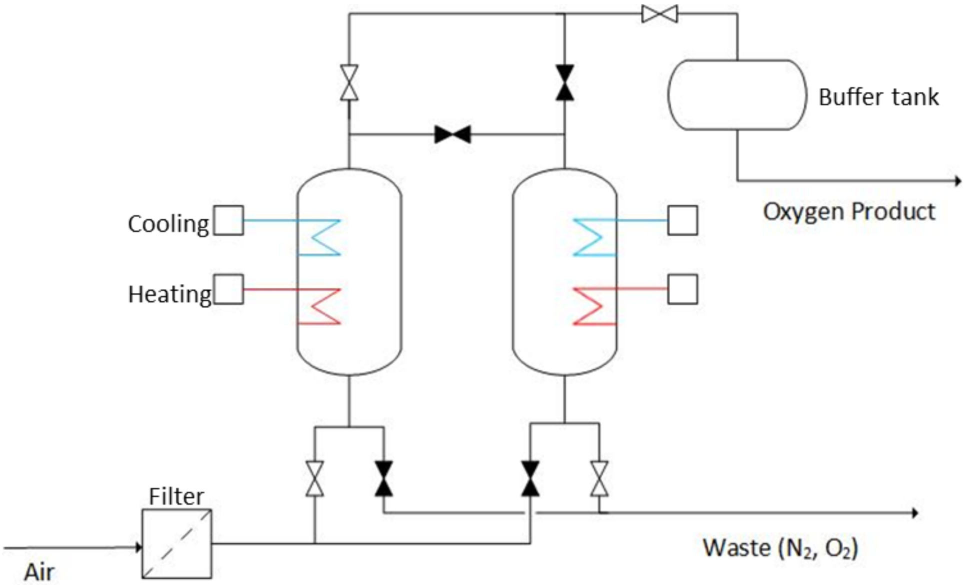


Figure 3. Process flow diagram for a temperature swing adsorption system (TSA).

Some companies, such as PCI Gases and Air Liquide, offer Vacuum Swing Adsorption (VSA) systems. Advantages of VSA over PSA include reduced power consumption and reduced complexity. Additionally, VSA systems are less susceptible to oil contamination of the adsorbent material, and the lower pressure operation results in longer packing material life (Schneider et al., 2011). However, VSA systems have a higher purchase cost than PSA systems. A hybrid process, the Vacuum Pressure Swing Adsorption (VPSA) has been developed to optimize energy efficiency. These systems operate at an elevated pressure in the adsorption phase and at a vacuum in the regeneration phase (see Table 1), but in both cases the differential between these pressures and operating pressure is lower than that for either a PSA or a VSA (Haruna et al., 2005). A VSA process flow diagram is shown in Figure 4, and a VPSA process flow diagram is shown in Figure 5.

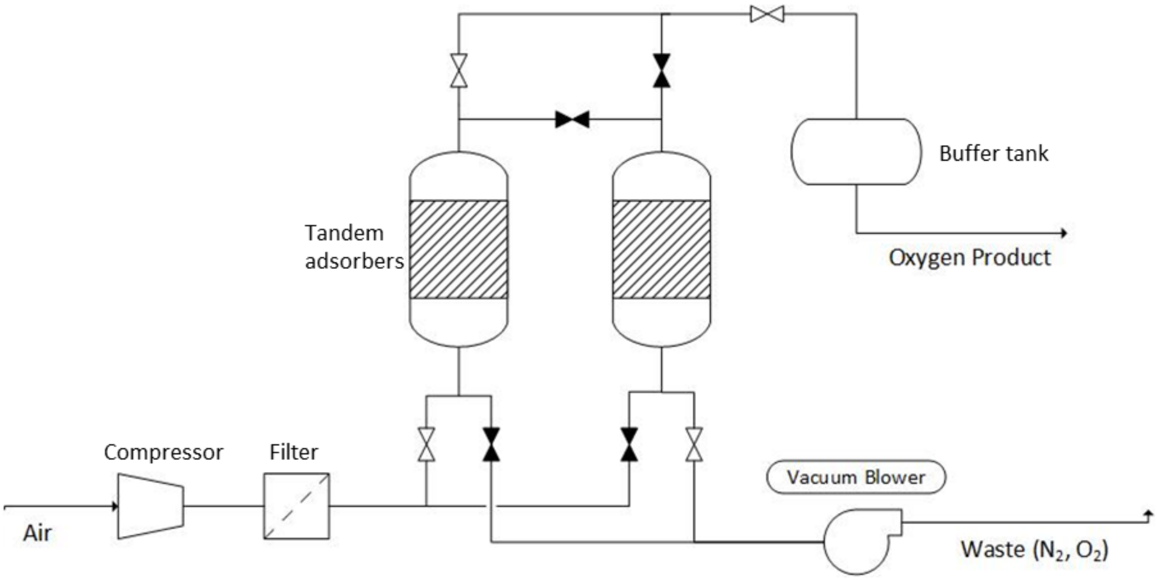


Figure 4. Process flow diagram for a vacuum swing adsorption system (VSA).

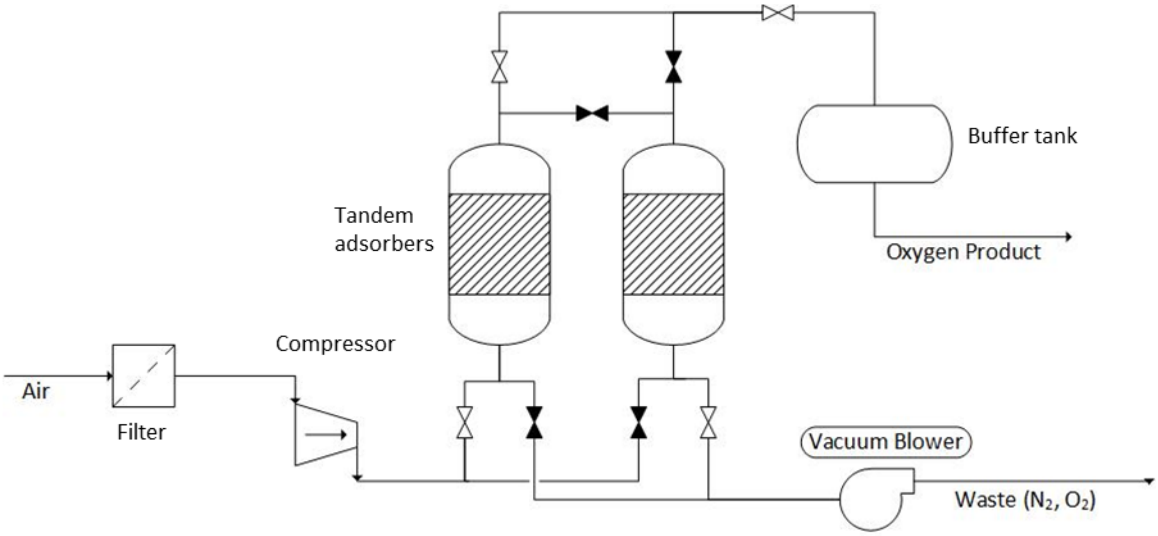


Figure 5. Process flow diagram for a vacuum pressure swing adsorption system (VPSA).

Minimum complexity is desired in order to minimize maintenance costs and to ease the deployment of wet oxidation systems. Most VSA systems have four major unit operations and three process valves, as opposed to the six major unit operations and ten process valves for a PSA or TSA unit (Schneider et al., 2011). VPSA systems are the most complex of all systems.

A chart giving typical operating pressures for PSA, VSA, and VPSA systems are given in Table 1 (Haruna et al., 2005, Shen et al., 2012, Maruti Corporation).

Table 1. Operating pressures for PSA, VSA, and VPSA units

Unit Type	Adsorption Pressure (kPa)	Regeneration Pressure (kPa)
PSA	200-400	atmospheric
VSA	atmospheric	3-50 (gauge)
VPSA	10-50	3-50 (gauge)

3.1.2 Membrane separation

Membrane separation of oxygen from air can be accomplished with polymeric materials. With an upper limit of 25-50% vol. O_2 purity depending on the membrane material and operating conditions, this method produces the least concentrated oxygen (Smith and Klosek, 2000). However, this method is the least energy and capital intensive, has low complexity, and is operated at near ambient conditions. This tradeoff may be considered acceptable for wet oxidation processes, especially when the safety modifications required for operating in a high-oxygen environment are considered (Smith and Klosek, 2000). A typical separation process employing polymeric membranes is shown in Figure 6. Air is compressed, typically to pressures between 1,000 and 3,000 kPa and passed over hollow fiber membrane modules (Brunetti et al., 2011). An enriched oxygen gas stream is recovered as the permeate while the reject gas stream is wasted.

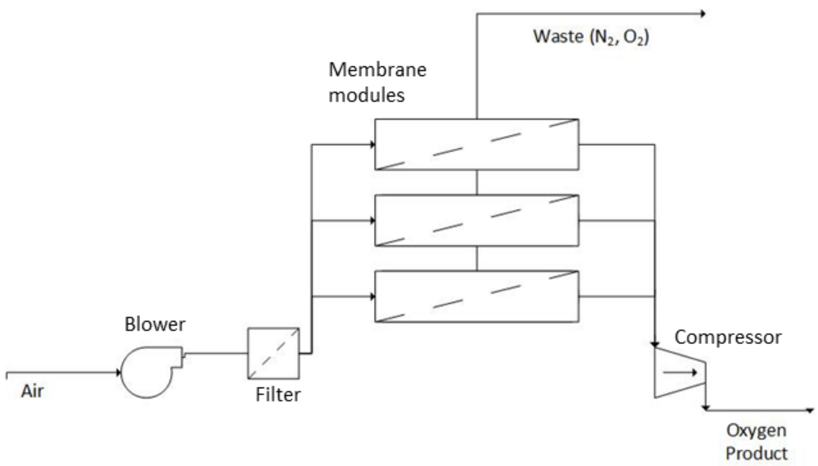


Figure 6. Process flow diagram for a polymeric membrane system.

When choosing a material for a polymeric membrane for oxygen enrichment, it is important to consider the flux and the specificity. The flux, expressed in units of $kg_{O2}\ m^{-2}_{membr}.\ h^{-1}$, is the flowrate over area and found as a function of pressure drop divided by membrane thickness and multiplied by a permeability factor, can be used to determine the necessary membrane surface area. It can be calculated by the difference in pressure on the two sides of the membrane divided by the membrane thickness and multiplied by a permeability factor. The selectivity is the ratio of the permeability of the membrane to the gases to be separated (Smith and Klosek, 2000). Typical selectivities and permeabilities for oxygen separation membranes vary depending on the type of polymer used. There is a tradeoff between high selectivity and high permealility. Common polymeric materials used for air separation are polyimide, polysulfone, and poly(2,6-dimethyl-1,4-phenylene oxide). A high-performing membrane may have a permeability and selectivity of 60 GPU and 4.6, respectively (Chong et al., 2016).

Ion transport membrane (ITM) technology can be used to produce an O_2 stream of greater than 99 vol.%. However, this process is more capital-intensive and operates at temperatures over 600°C and thus requires significant energy input. Furthermore, ITM is a developing technology that is not yet fully mature. ITM membranes are made of inorganic oxide materials that allow oxygen ions, but not nitrogen, to pass through the membrane's crystal structure. The ions reassemble into oxygen gas on the other side of the membrane. A voltage differential may be applied across the membrane to increase flux. A sweep gas can be applied in order to increase yield, at the cost of decreased product purity (Smith and Klosek, 2000).

3.1.3 Power consumption for air separation

Banaszkiewicz and Chorowski (Banaszkiewicz and Chorowski, 2015) stated that a minimum energy consumption for production of oxygen using swing adsorption technology was approximately 1.57 kWh/kg. They concluded that oxygen production with swing adsorption is efficient for large applications, but that smaller applications such as pilot plants and laboratories, should consider using membrane technology instead. However, the minimum energy requirement they found is much lower than that reported by many vendors. The reasons for the discrepancy could not be determined. Within the literature, Nelson (1993) reported over 20 years ago, that PSA units have been proven in small operations in remote areas, as with the medical oxygen plants in a small number of hospitals in South Africa.

Estimates for power requirements of various air separation techniques were collected from several industrial vendors. In order to determine whether each air separation technique would be competitive with air compression in a 6,000 person per day SCWO unit, total power requirements and power required per mass of oxygen gas generated were estimated. The following assumptions were made:

- The target capacity is 42 kg/h oxygen gas.
- Enriched oxygen exits the air separation unit at the unit's working pressure. It is then compressed to 25 MPa by a gas compressor.
- The air compressor currently on the Duke University SCWO system requires 9.48 kW to produce 7 kg/h O_2, or 1.35 kWh/kg O_2 produced. In order to be competitive, the air separation method and the compression of the enriched oxygen gas to 25 MPa must have a power requirement of less than 1.35 kWh/kg O_2.
- The power requirements of any air inlet compressors, filters, or other pieces of accessory equipment were included in the vendor's power estimate for each air separation unit, with the exception of the membrane module.
- There is a logarithmic relationship between the change in pressure imparted by the air compressor and the power it requires. See Appendix A for the derivation of the relationship. When an air separation technology is available at multiple working pressures, the highest working pressure is chosen.
- For the EcoGen™ Oxygen VPSA Onsite Generator, an extrapolation from the power use at the two pressures available suggested the power requirement increased by 1 kW with each 69 kPa increase in working pressure.
- For the PCI VSA, operating cost was known, but power consumption was not. An estimate of the power consumption was back-calculated from the operating cost by assuming all operating costs are the result of electricity usage and that the cost of electricity is 0.12 $/kWh.

The calculated values are given in Tables 2-4. See Appendix A for calculations and vendor provided information.

Table 2. Estimated power requirements for enrichment and compression of 42 kg/h O_2 using VPSA systems. Note that the 42 kg/h corresponds to a unit that can treat the waste of 6000 people, i.e., the size of the next prototype considered by Dr. Deshusses team.

Module name	Purity (vol%)	Total power required to produce gas containing 7 kg/h O_2 (kW)	Power required per kg O_2 produced (kWh/kg)	Lower power requirement than air compression? (Y/N)	Source
N/A – General market knowledge	90	25.3-32.7	0.601-0.779	Y	(Honeycutt, 2018)
N/A – General market knowledge	90	25.5	0.607	Y	(Haruna et al., 2005)
EcoGen™ Oxygen VPSA Onsite Generator	90	35.1	0.836	Y	(EcoGen™)
AirSep VPSA Oxygen Systems	93	26.3	0.627	Y	(AirSep Corporation, 2011)
Average	90.8	29.0	0.690	Y	N/A

Table 3. Estimated power requirements for enrichment and compression of 42 kg/h O_2 using a VSA system

Module Name	Pressure at purification outlet (kPa)	Estimated purification power (kW)	Max. total power requirement for VSA to be competitive (kW)	Max. power requirement per kg O_2 produced for VSA required to be competitive (kWh/kg)	Lower power requirement than air compression? (Y/N)	Source
PCI Gases – DOCS 500	379.2	2.49-3.57	N/A	N/A	N/A	(PCI Gases. DOCS 500)
PCI Gases – DOCS 500	689.5	N/A	7.26	1.04	Y (predicted)	(PCI Gases. DOCS 500)

Table 4. Estimated power requirements for enrichment and compression of 42 kg/h O_2 using Generon® membrane systems

Pressure (kPa)	Purity (vol%)	Max. purification power requirement for membrane unit to be competitive (kW)	Max. power requirement per kg O_2 produced for membrane unit required to be competitive (kWh/kg)	Lower power requirement than air compression? (Y/N)	Source
1,400	38.5	4.34	0.621	N (predicted)	Generon, Inc.

The energy requirements of PSA systems were difficult to obtain. The company PCI reports that their VSA has approximately half the energy requirement of a PSA. A 93% purity oxygen stream could be produced by PSA at 1.22 kWh/kg (Schneider et al., 2011). This would suggest PSA is probably a competitive alternative to air compression, but not to other swing adsorption methods. However, it is important to note that PCI is a vendor of VSA systems, so it is desirable to obtain more specific information about the energy requirements of PSA systems before determining definitively that VSA systems are more energy efficient.

For comparison with membrane technologies, it should be noted that the power requirements given for membrane technologies are generally for the membrane module only. They do not include power requirements of the filtering or dewatering units required for membrane separation (Generon, Inc.). These extras, added to already higher power requirements further the argument that air separation by membrane technologies is not competitive for oxygen supply for wet oxidation.

This analysis shows that, of the air separation methods considered, VPSA and VSA appear to be competitive with the currently used air compressor in terms of power requirement. VPSA in particular is promising.

3.1.4 Costs

For swing adsorption methods, the electricity will be a major driver of cost. Therefore, an air separation that is energy efficient should be chosen. A VPSA unit continuously producing 42 kg/h at 90% O_2 purity would have an approximate annual operating cost $38,000, or $900 per kg, adjusted from 2005 prices (Haruna et al., 2005). Bed size plays a very significant role in determining capital cost for swing adsorption units and should be carefully considered (Smith and Klosek, 2000). The frequency of replacement should also be considered. AirSep reports VPSA equipment life of greater than 15 years (AirSep Corporation, 2011). The capital cost of membrane components is nearly linearly related to the O_2 production rate desired. ITMs are still in development, and their prices remain to be determined. ITM is said to be most economically viable when integrated into a power generation scheme (Smith and Klosek, 2000). Capital costs and maintenance costs of each method of air separation should be balanced with any cost savings that may be incurred through the reduction of power from air compression.

3.1.5 Safety considerations

Enriching oxygen poses some safety risks including fires and violent reactions with certain materials. Therefore specialized equipment (e.g., compressors, gaskets, etc.) are needed when using enriched oxygen or pure oxygen. In addition, there are specific hazards associated with swing adsorption. Nitrogen acts as a simple asphyxiant and can displace oxygen. Concentrations of oxygen near the nitrogen exhaust stream from the regeneration step of swing adsorption less than 19.5% present a hazard. Oxygen concentrations below 14% can cause fatigue, loss of coordination, confusion, euphoria, and an inability to diagnose the situation as dangerous in exposed individuals. Exposure to oxygen levels less than 10% can lead to death (European Industrial Gases Association, 2017).

Compressors and blowers for PSA, and especially VSA, units can produce high noise levels that can be nuisance or even hazardous. Methods for noise abatement and personal ear protection should be used (European Industrial Gases Association, 2017).

Deterioration of the molecular sieve packings used in adsorption towers can cause dust that can present a variety of hazards. The dust can plug piping, valves, and sample lines, causing unsafe pressure conditions or inaccurate sampling. It can contaminate condensate, which should be disposed of accordingly (European Industrial Gases Association, 2017). Operator exposure to the dust should also be avoided. Depending on the hazards associated with the particular packing material, exposure could cause respiratory irritation or more serious health effects. Dust masks and eye protection should be used in order to avoid exposure to such dusts (Nelson, 1993).

3.2 Liquid Oxygen

3.2.1 Oxygen supply and storage

A potential alternative to separating oxygen from air on-site is purchasing liquid oxygen. Key players in the gas industry include but are not limited to Air Liquide, Air Products and Chemical Inc., Praxair Technology, Inc., The Linde Group, Air Water Inc., Airgas, Inc., Taiyo Nippon Sanso, Yingde Gases, Baosteel Metal Co., Ltd., Guangdong Haute Gas Co, Ltd., and others (Industrial Gas Market, 2017, Oxygen Market, 2018).

Though oxygen is generally used as a gas, it is commonly liquefied for efficient transport and storage (Air Products Safetygram 6). Oxygen has a boiling point of -183°C and a latent heat of vaporization of 213 kJ/kg (NIST). Oxygen has a volume expansion ratio of 1:861 at atmospheric pressure and 20°C (Air Products Safetygram 6).

Containers commonly used for liquid oxygen storage include dewars, cylinders, and cryogenic storage tanks. Dewars are used to store relatively small volumes of oxygen. The most common dewar volume sold by Air Products is 1 L, but a range of volumes up to approximately 200 L is available (Air Products Safetygram 6). The largest dewar offered by Airgas is 180 L (Ezell, 2018). Dewars are not pressurized. A typical pressure and range of volumes for cylinders is 2.4 MPa and 80 - 450 L. A typical volume for a cryogenic storage tank is between approximately 2 and 1,500 m^3. These can either be stationary or mounted on a railcar or truck chassis for transportation (Air Products Safetygram 6). Tanks are usually made of either carbon steel, stainless steel, or aluminum with 9% nickel content. For thermal insulation, these tanks have an inner and outer shell (Praxair). Between the shells is an insular material under an induced vacuum of 0.16 – 0.3 kPa (Gardner, 2014). Utilization of cryogenic storage tanks requires a pressure control manifold and a vaporizer (Air Products Safetygram 6). Atmospheric vaporizers exchange heat with ambient air, and don’t require external power. Steam or electricity may be required to vaporize oxygen for high-flow systems. It is preferable for the storage tank to be kept at a distance from the operation and oxygen to be transported by a pipe in order to reduce operator exposure to the low temperatures associated with the vaporizer (Praxair). An example of a cryogenic storage tank system is shown in Figure 7.

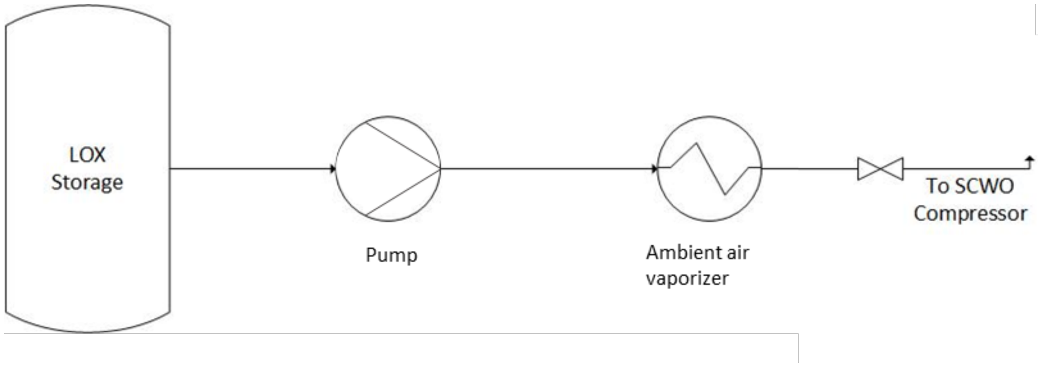


Figure 7. Example of cryogenic storage tank system for feeding a SCWO system. Note that unlike most applications using liquid oxygen, pumping of liquid oxygen to the required pressure occurs prior to vaporization, which greatly reduces power consumption as it eliminates the requirements for gaseous oxygen compression.

It is important to note that some oxygen losses will occur dependent on storage type and ambient temperature. For cylinders approximately 0.4-3.0% volume losses is common (Air Products Safetygram 27). Therefore, O_2 requirements should consider losses. For any oxidation system, a cryogenic oxygen tank system is the recommended storage method. The frequency of refilling will depending on the size of the tank and the system consumption.

<u>3.2.2 Power consumption</u>

Cryogenic storage of liquid oxygen does not require electricity but vaporization will occur at a rate depending on the setup (Air Products Safetygram 6). Ambient vaporizers do not require additional electricity. They are made of conductive material that use ambient heat from the surroundings to convert liquid oxygen to gaseous oxygen. They are available with a variety of working pressures, most around 2.5 MPa, but some over 40 MPa (FIBA Technologies, Inc.). A high-pressure vaporizer is preferable for SCWO application, which eliminated compression associated expenses and limits power requirements to pumping liquid oxygen to the required pressure. Because the expansion ratio for liquid to gaseous oxygen is 1:860, liquid oxygen stored at atmospheric pressure can be pressurized via gasification in a constant volume to over 25 MPa, assuming ideality and a leak-free vessel.

The power required to pump 42 kg O_2 per hour as required for a 6,000 person SCWO unit is reported in Table 5.

Table 5. Power requirements for compression of vaporized liquid oxygen at common purities and pressures

Purity (%vol)	Pressure (MPa)	Normalized Power (kWh/kg O_2)	Total Power (kW per 42 kg O_2 h^{-1})
99.5	2.4	0.030	1.26
90	2.4	0.033	1.39

3.2.3 Cost

Most vendors supply liquid oxygen at high purities of 90% oxygen or above. However, many vendors do offer nitrogen and oxygen gas mixtures at lower costs. The cost incurred by purchasing a higher purity oxygen should be evaluated as the increased in power consumption for pumping lower purity oxygen is marginal.

Though the cost of liquid oxygen will vary with the location of the unit and between vendors. One source lists a typical cost of liquid oxygen as $0.109/kg, as well as a tank rental fee of approximately $500/month (Honeycutt, 2018). Including the rental, this sums up to approximately $1,050 in liquid oxygen per month, for a 1,000 person unit or $0.208/kg. Yet another source gives the purchase cost of liquid oxygen as $0.08/kg close to the $0.109/kg mentioned above (Morgan, 2018).

In Table 6, the cost per kilogram oxygen and monthly cost of oxygen assuming a flow rate of 42 kg/h O_2 are estimated. These numbers consider both the raw cost of the liquid oxygen and the cost of electricity assuming an average cost of $0.12/kWh. The cost of oxygen tank rental fee was not included. Examination of Table 6 shows that the power costs are very low compared to the cost of procuring liquid oxygen.

Table 6. Approximate purchase and compression cost of liquid oxygen products. Note that Honeycutt costs include tank rental is the cost of oxygen (see text for details).

Purity (%vol)	Pressure (MPa)	Liq. O_2 Cost ($/kg)	Power Cost ($/kg)	Total Monthly Cost ($/mo for 42 kg O_2/h)	Source
90	25	0.208	0.0040	6,500	Honeycutt, 2018
90	25	0.08	0.0040	2,570	Morgan, 2018

Pressure at which the vaporized liquid oxygen is provided to the reactor plays an important role in determining the cost operating with liquid oxygen. If oxygen was first vaporized at atmospheric pressure and a compressor was then used to provide the 42 kg/h O_2 for a month, this would require approximately 41,000 kWh electricity. This corresponds to a monthly operating cost of \$4,900 assuming a cost of electricity of \$0.12/kWh.

Overall, the lowest cost figures in Table 6 indicate liquid oxygen could be a viable replacement for air compression.

3.2.4 Safety

Safety considerations specific to liquid oxygen include human exposure to cold temperatures, spills, embrittlement of materials due to cold temperatures, and overpressurization of inadequately insulated vessels. Exposure of skin to the low temperatures of liquid oxygen can cause severe burns. Additionally, liquid oxygen spills on clothes present a combustion risk and should be immediately removed and aired out. Cold temperatures can cause materials to become brittle and shatter, so a regular maintenance schedule should be followed. Inadequate insulation of a pressurized oxygen container can cause gasification and expansion, which presents an explosion risk. Pressure relief valves should be installed appropriately (Air Products Safetygram 6). Furthermore, in the United States, liquid oxygen storage vessels must be built in accordance with American Society of Mechanical Engineers (ASME) regulations (Air Products Safetygram 6). Other safety considerations include those discussed in Section 3.1.5.

3.3 Reactive Oxygen

Oxidation of organic chemical species can be accomplished through a variety of methods that rely on reactive oxygen species (ROS). Many of these methods were developed for the treatment at ambient conditions, but some of them have also been tested with supercritical water systems. For the purposes of this literature review, ROS oxidation methods that involve the addition of a catalyst will not be considered as they are probably not practical for fecal sludges at supercritical conditions. Methods that are considered are oxidation with hydrogen peroxide, ozonation, ultrasonic irradiation, and other reactive oxygen species.

3.3.1 Hydrogen Peroxide

Hydrogen peroxide is first decomposed to water and oxygen gas in a separate reactor before being used to oxidize organic material. Together, these processes can be described by the equation for hydrogen peroxide decomposition combined with the equations for partial oxidation of hydrocarbons. Alshammari and Hellgardt give the equations for reaction of n-hexadecane, as an example organic compound, with oxygen from the decomposition of hydrogen peroxide, as shown in Equations 1-4:

$$H_2O_2 \rightarrow O_2 + H_2O \quad (1)$$
$$C_{16}H_{34} + 8O_2 \rightarrow 16CO + 17H_2 \quad (2)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$
$$C_{16}H_{34} + 24.5O_2 \rightarrow 16CO_2 + 17H_2O \quad (4)$$

Equation 4 is included for stoichiometric purposes; full oxidation will not always be accomplished. Alshammari and Hellgardt report full oxidation occurring at $T > 400^oC$ and residence time > 39 s at a pressure of 27 MPa. Under partial oxidation conditions, vent gas will consist of H_2, CO, CO_2, CH_4, and unreacted hydrocarbon. Increasing the proportion of H_2O_2 to organic substrate results in increased H_2 production (Alahammari et al, 2015).

Small-scale reactor systems using hydrogen peroxide are described in the literature, and foretell challenges for large-scale SCWO. The surface of a stainless steel reactor has a catalytic effect on the oxidation reaction. This can cause uneven mixing at the reactor inlet, where surface area suddenly increases. To prevent this, a high concentration of H_2O_2 can be pumped into the oxidation reactor before use in order to “wall age” the reactor. Partial oxidation of the carbon feedstock leads to coke formation. Accumulated coke will need to be purged from the reactor occasionally (Alahammari et al, 2015). Finally, when the reactor is operating at supercritical conditions, H_2O_2 decomposes to a significant extent in the lines before reaching the reactor, due to heating of the lines (Croiset et al, 1997). This is a very important safety consideration for large reactors, as lines operating at higher than expected pressure can pose an explosion risk. Additional considerations may need to be taken into account for an industrial scale system.

Commercially, hydrogen peroxide is produced on a large-scale using a catalytic method. It is typically delivered in drums. On-site generation of H_2O_2 involves emerging technologies, as H_2O_2 has begun to be commonly used as a disinfectant in place of chlorine. Some of these technologies involve a polymer electrolyte membrane subjected to a voltage gradient. A clean water stream, air stream, and electricity is required (Eltron).

Cost

Major suppliers of H_2O_2 include National Peroxide Limited, Solvay S.A., AkxoNobel N.V, Arkema S.A, Chang Chun Petrochemical Co., Ltd., Mitsubishi Gas Chemical Company, Evonik Industries AG, Guangdong Zhongcheng Chemicals Inc., Ltd., and more (Global Analysts, Inc, Transparency Market Research). Because delivery to remote sites may be difficult, it may be preferable to generate H_2O_2 on-site. However, emerging small-scale H_2O_2 generation techniques often do not use a catalyst as do large-scale operations, which may result in larger electricity costs in producing H_2O_2 on site (Eltron). In 1992, Chemical Marketing Report recorded the cost per kg, adjusted to 2018 values, of a 35% H_2O_2 solution to be 0.97 $/kg. For the oxidation of acetic acid in supercritical water, Chang et al. found this to translate to 34 $/kg of equivalent oxygen (Chang et al., 1993). This would suggest a cost of approximately 240 $/h for H_2O_2 for a 1,000 person SCWO unit. This is clearly cost prohibitive.

Safety

Hydrogen peroxide should be kept away from combustibles, reducing agents, and hot surfaces while in storage. Hydrogen peroxide should be stored in vented containers in a cool, dark area. Care should be taken not to generate a mist, hydrogen peroxide is corrosive and inhalation can cause symptoms such as nausea and vomiting (NIOSH). Decomposition in the lines leading to the reactor poses an explosion risk (Croiset et al, 1997).

3.3.2 Ozonation

Ozone (O_3) decomposes in water to form hydrogen peroxy (HO_2) and hydroxyl (OH) radicals. An added benefit of ozonation is odor reduction (US Environmental Protection Agency). Ozone can be used alone or in combination with other classes of chemical species to result in the formation of hydroxyl radicals for oxidation (Bokare et al 2014).

Ozone must be generated on-site, as it is unstable. For this, a high voltage electrode with voltage between 6 and 20 kV is commonly used (Bokare et al 2014). The feed air must be dry, with a dew point of less than -60 °C. An ozone stream generated from air, without enrichment by oxygen, will be comprised of 0.5 – 3.0 wt% ozone. To enhance the reaction of ozone with the aqueous contaminant, an efficient contactor is required to maximize the interphase mass transfer of ozone. This could take the form of a diffused bubble contactor, a pressure differential driven injector, a packed flow, or mechanical agitation (US Environmental Protection Agency).

Cost

Ozonation is most likely the least economically viable of the reactive oxygen methods for oxidation. Because of ozone's short half-life, continuous supply of ozone is required. Efficiency of ozonation is dependent on mass transfer, but the low solubility of ozone in aqueous solution makes high mass transfer difficult to achieve. Generation of ozone has a high operating cost (Hermosilla et al 2015). Ozone is corrosive and thus can reduce the lifetime of process equipment. This is in addition to the capital cost of the ozone-generating equipment, as well as the cost of any co-reagent used. The following capital cost estimates were provided to the United States Environmental Protection Agency by Champion Technology in 1998 (US Environmental Protection Agency). Dollar values have been adjusted to 2018 values. A caveat is that this installation is for disinfection and not for treatment of organics. The following values are given for disinfection of 3790 m^3/day wastewater (1 MGD).

Table 7. Estimated costs for ozonation for disinfection of 3790 m^3/day (US Environmental Protection Agency)

Item	Cost (USD)
Oxygen feed gas and compressor	378,900
O&M supplies (yearly)	10,000

The power required for the example of Table 7 was 90 kW. It is difficult to extrapolate from this example to the costs of ozonation for sludge treatment in a SCWO system. However, an ozone generator by Lenntech was capable of producing up to 9 kg/h ozone at less than 7 kW/kg from a feed gas of air (Lenntech). This allows an estimated power requirement for a SCWO unit that serves 1,000 people to about 49 kW, assuming that the same mass of ozone and oxygen would be required. This number is significantly higher than that of the currently employed air compressor. Additionally, the ozone would be produced diluted in air, and would need enrichment and compression. This seems impractical and is probably cost prohibitive.

Safety

Exposure to ozone can cause headache, lung damage, and eye and respiratory irritation. Ozone can increase sensitivity to allergens. Exposure should be limited (OSHA). Gaseous ozone is explosive in concentrations above 0.240 kg/m^3. However, occurrence of this high of a concentration is unlikely if the system is purged properly (US Environmental Protection Agency).

3.3.3 Ultrasonic Irradiation

Ultrasonic irradiation causes the formation of hydroxyl radicals, which can oxidize many organic compounds (Hoffmann et al., 1996). Hydrogen peroxide is also formed through combination of hydroxyl radicals (Hua et al., 1997). Typically, water is exposed to frequencies between 20 and 500 kHz. This causes “electrohydraulic cavitation,” in which the radii of existing gas bubbles oscillate in correspondence with oscillations in pressure. These unstable oscillations result in the eventual collapse of the gas bubbles, leading to localized high temperatures and pressures of approximately 4000 ^{o}C and 97.5 MPa respectively. Under these conditions, H_2O dissociates into hydrogen and hydroxyl ions (Hoffmann et al., 1996).

Ultrasonic irradiation has applications in industrial chemistry and food processing. As of 2008, commercial scale applications existed for extraction, emulsification, crystallization, filtration, separation, viscosity alteration, defoaming, and extrusion (Patist et al., 2008). Potential vendors include Branson Ultrasonics Corporation and Lewis Corporation, though this list is quite incomplete (Berlan et al., 1992).

An ultrasonic reactor consists of a transducer, a sonotrode, and a reservoir for the medium. The sonotrode of the reactor receives power through a piezoelectric transducer. A typical energy transmission efficiency between the transducer and the medium is 85% (Patist et al., 2008). The temperature should be high enough to reduce viscosity to the point that it does not suppress cavitation, but low enough to avoid dampening by high vapor pressure (Patist et al., 2008). This may require refrigeration of the sludge. Knowing the sonochemical yield (SY) is necessary in order to determine the power input needed to generate sufficient hydroxyl radical (Berlan et al., 1992). Hua and Hoffmann’s 1997 work contains some differences from the conditions within a SCWO unit, but can be used to give a rough estimate of SY for •OH. The production rate of •OH in O_2 saturated, ultrapure water at 25-30^{o}C treated at 513 kHz was 2.68 μM min^{-1} (Hua et al., 1997). Extrapolation of this number to oxidant production relevant to the management of fecal sludge of thousands of people is greatly impractical. This is probably what motivated Patist and Bates to state that “high power ultrasonics is not an off-the-shelf technology and therefore needs to be developed and scaled up for each application” (Patist et al., 2008). However, ultrasonic irradiation could potentially be combined with reactive oxygen species such as ozone or hydrogen peroxide in order to increase overall hydroxyl radical generation rate.

Cost and Power

Though ultrasonic irradiation is used frequently in the food industry for defoaming and other purposes, it is very difficult to estimate capital and operating costs for an industrial scale unit meant specifically for ROS production. Power usage of a typical laboratory ultrasonic irradiation unit falls between 20 W and 200 W (Faïd et al 1998) which would prorate to well in excess of

4,000 kW for a 1000 person unit. This would result in a very unfeasible cost for the application. If ultrasonic irradiation were to be considered as a method of generating reactive hydroxyl radical, it must be considered in combination with other advanced oxidation processes, such as ozonation.

Safety

Being in the vicinity of ultrasonic irradiation for long periods of time can cause nausea, headache, tinnitus, pain, dizziness, and fatigue. Exposure should be limited and hearing protection should be worn (Health Canada, 2008). Sound-proof cabinets are available for purchase to reduce exposure (Patist et al., 2008).

3.3.4 Other Reactive Oxygen-Containing Species

Some other reactive species that generate oxygen include but are not limited to potassium permanganate, sodium hypochlorite, and potassium superoxide (University of California, Berkeley).

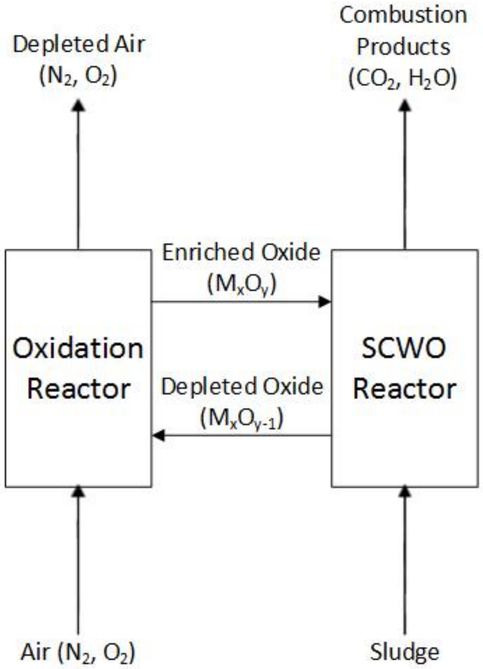
Chang et al. found potassium permanganate ($KMnO_4$) to be more efficient in oxidizing acetic acid in supercritical and sub-supercritical water than H_2O_2 or oxygen gas. In 1992, the Chemical Marketing Report cost per kg of $KMnO_4$, adjusted to 2018 values, to be 4.77 $/kg. The oxidation efficiency of acetic acid in supercritical water Chang et al. found for $KMnO_4$ predicted 106 $/kg of equivalent oxygen (Chang et al., 1993). This would suggest a cost of approximately 740 $/h for $KMnO_4$ for a 1,000 person SCWO unit.

Potassium superoxide is used to generate oxygen for self-sustaining breathing apparatus (Jackson et al., 1957). However, research applicable to its use in SCWO is limited.

3.4 Chemical Looping

A chemical looping combustion (CLC) reactor is a system of two reactors: the air reactor in which the oxygen carrier is regenerated, and the fuel reactor in which combustion occurs. The air reactor receives streams of reduced oxygen carrier from the fuel reactor and air. The air reactor operates at elevated temperature around 800-1000 ^{o}C. Output streams include O_2-depleted air and oxygen carrier oxidized back to its initial state. The fuel reactor receives a stream of oxidized oxygen carrier from the air reactor and a fuel stream. Output streams include reduced oxygen carrier and flue gas (DOE/NETL). This process is shown in Figure 8. No one has yet operated a CLC at supercritical water conditions, however the idea of chemical looping, since it involves a solid oxygen carrier, was retained for further consideration for possible merging with the SCWO technology.

Figure 8. Chemical Looping Combustion Reactor Block Flow Diagram (DOE/NETL, 2013)



Adapted from DOE/NETL,
2013

The overall chemical reactions that occur in the air and fuel reactors are given in Equations 5-7 (DOE/NETL).

Oxidizer: MxOy-1 + ½ O2 → MxOy (5)
Reducer: CnH2m + (2n+m) MxOy → n CO2 +m H2O + (2n+m) MxOy-1 (6)
Net reaction: CnHm + ½ (2n+m) O_2 → n CO_2 +m H_2O + heat (7)

where M represents a metal ion and n and m are variables dependent on the metal ion oxidation number.

CLC reactors are still in the research and development stage, but show promise. Because it is difficult to estimate power and capital cost requirements, this literature review will focus on a variety of pilot plant experiments that were successful in carrying out combustion without an air separation unit (ASU) and which may prove useful in a SCWO unit. Current research challenges include “scale-up issues; solids handling and transport; O_2 carrier capacity, reactivity, and attrition; slow reaction rates between the O_2 carrier and coal char; [and] ash management” (DOE/NETL). Key players in this field include The Ohio State University, Alstom Power Inc., and Babcock & Wilcox Power (DOE/NETL).

According to the National Energy Technology Laboratory, “CLC technology starts with the selection of the oxygen carrier material. The requirements for a good oxygen carrier are high oxygen transport capacity, high reactivity, high mechanical strength, environmentally friendly, physical/chemical stability, and low production costs” (DOE/NETL, 2013). For most reactor designs, it is also important to consider the tolerance of the oxygen carrier to carbon deposition within the reactor. Oxygen carriers may consist of both a reactive portion that is typically a metal oxide and a high surface-area support such as alumina or silica. The most common types of metal oxide are iron and copper. These are the most successful at temperature ranges of 700-900 ^{o}C. Copper based oxygen carriers are more reactive than iron based ones, and therefore produce more oxygen, but they soften at the upper end of this temperature range. Nonetheless, the Pan group at Western Kentucky University has found them to be an effective, low-cost choice. Fe_2O_3 is the most promising carrier. Fe_2O_3 ore should be doped for increased reactivity. 700-900 ^{o}C is a typical temperature range for traditional CLC reactions using coal (DOE/NETL). However, this range may be different for a SCWO system, which warrants consideration of oxygen carriers outside of the traditionally used iron and copper oxides. The Ohio State University offers a license for a proprietary iron oxide oxygen carrier that is reported to be ten times more reactive than pure Fe_2O_3 and recyclable for more than 100 reduction cycles without loss of activity. Though iron, copper, and nickel are the most commonly used metals in oxygen carriers, there are several other experimental oxygen carriers. For example, Alstom Power, Inc. has used a $CaSO_4$ carrier. Alumina and silica are the most common supports, though experimental support materials are also in testing (DOE/NETL).

Pilot plants have been built using several different reactor designs. The reducing reactor should be designed with the following considerations: sufficient oxygen carrier/fuel contact time, sufficient oxygen carrier/reduced gas contact time, scalability, and ability to sufficiently mix solids with minimum pressure drop (UND Institute for Energy Studies). The Fan group at The University of Ohio employs an entrained flow system to pneumatically transport the oxygen carrier from the air reactor to the fuel reactor (DOE/NETL). Another group at The University of Ohio uses non-mechanical L-valves between the air and fuel reactors (Bayham, 2015). Both the air and fuel reactors in the Fan group were moving bed reactors. The second used a gas-solid countercurrent moving bed (Bayham). Several other groups use fluidized bed reactors. Ash management can pose a significant problem in CLC reactors. They should always be designed with outlets for ash cleaning. A baghouse vented with a fan such as an ID fan, and possibly containing water, should be installed to collect fines. Additionally, the endothermic nature of the reaction of the carrier should be taken into account (DOE/NETL).

A typical oxygen carrier to fuel ratio is 50:1, with the oxygen carrier being 50% iron oxide or other active material. The University of Ohio pilot plant used 2766 kg/s oxygen carrier and an air input rate of 416 kg/s, about 1.5 million kg/h. This resulted in an oxygen production rate of 101 g/s, which is equivalent to 363 kg/h (Bayham). This is certainly larger than the 7 kg/h oxygen gas required for the SCWO unit, meaning CLC technology is available at the scale required for our application. However, the efficiency of oxygen production is low. A low recovery rate of 0.0242% relates air input to oxygen transfer to the fuel reactor. An air intake rate of approximately 30,000 kg/h would be required to produce the 7 kg/h oxygen needed for a 1,000 person SCWO unit. While the 30,000 kg/h air may seem large, a simple 3-5 HP blower can achieve this.

Western Kentucky University's CLC reactor was able to run 24 hours total: eight hours per day for three days (DOE/NETL). In a project meant partly to evaluate the potential of developing a commercial-scale CLC reactor, The University of Ohio built a demonstration unit capable of operating continuously for seventy hours (Bayham). Chemical looping technology is still unable to run continuously for more than a few days, as may be required by later SCWO unit prototypes.

Power

Electricity would be required for the blower to intake the large amount of air required for reaction in the air reactor. However, this can be provided by a simple blower (~4 kW). Pumping or conveying the oxygen carrier would also be required. Details of the power requirements are not yet available. More substantial are the power requirements for heating the oxygen carrier to the supercritical conditions of the reactor and cooling to the conditions of the oxidation reactor. Obviously, effective heat recovery is a prime requirement for such system, to avoid heat and energy wastages. Much development is needed before this can be conceived.

Safety

Because iron oxide is the most promising oxygen carrier, this section will focus on safety issues specific to iron oxide. Iron oxide can cause eye, skin, and respiratory irritation, but overall has fairly mild health effects. It does pose a significant fire and explosion risk. Iron oxide is spontaneously combustible, which may pose particular risk due to the high temperatures of the SCWO unit that will be in the vicinity of a CLC reactor. An iron oxide fire will produce gases that are toxic and corrosive, and that may cause serious injury or even death. Runoff containing iron oxide is also a fire and explosion hazard, and should be contained. Iron oxide is incompatible with carbon monoxide and hydrogen peroxide (OSHA).

3.5 Electrolysis

3.5.1 Introduction

Electrolysis can be used to produce high purity oxygen and hydrogen gas from water through the application of a direct current between two electrodes. Reduction of species occurs at the cathode, while oxidation occurs at the anode. This overall reaction for water electrolysis is $H_2O \rightarrow H_2 + \frac{1}{2} O_2$. Oxygen gas evolution occurs at the anode, while hydrogen gas evolution occurs at the cathode (Sapounti et al., 2017). Though water electrolysis is most commonly used for hydrogen gas production, it is also used for oxygen gas production for some applications such as life-support systems in submarines and spacecraft (Lu et al., 1979).

Packed bed electrolysis is carried out with porous electrodes comprised of electrically-conducting particles (Volkman et al., 1977). Packed bed electrolysis has advantages of high electroactive area per unit reactor volume, and improved energy efficiency of gas production (Khattab et al., 2013). The high electrode surface volume makes them particularly useful for slow reactions. They can also lead to reduced maintenance costs in applications in which peeling of electrodes is an issue (Menon et al., 2015). Disadvantages of packed bed electrolysis include potential drop in the electrolyte, corresponding to increased power requirement (Volkman et al., 1977), and low current efficiency due to non-uniform potential distribution through the electrode matrix (Khattab et al., 2013).

Supporting electrolyte is added to water in order to increase its conductivity. Supporting electrolyte could be a base, dilute acid, or conducting salt. The most commonly used base is KOH. Commercially, 20-30% (w/v) KOH is used, though certain groups, such as Shau et al., have been experimenting with dilute alkaline solutions. HCl is a commonly used acid. However, acids, even dilute acids, are not favored as they are highly corrosive and tend to form mineral deposits that reduce current efficiency (Shau et al., 2015). Typical salts include NaCl, Na_2SO_4 (Khattab et al., 2013), $NaClO_3$ (Menon et al., 2013), and KH_2PO_4 (Thostenson et al., 2018). A commonly used rule of thumb is that a 0.2 M increase in acid or base corresponds to a doubling of conductivity. Salts typically require a greater increase in concentration. The large potential drop in the electrolytic solution of pack bed electrolyzers can be minimized by increasing the concentration of supporting electrolyte. Selection of the species of supporting electrolyte for current efficiency is also important. For example, NaCl has been related to higher current efficiency than Na_2SO_4 (Khattab et al., 2013) although with NaCl, chlorine generation will compete with oxygen generation, which is not the case in Na_2SO_4.

3.5.2 Electrolysis in the Context of SCWO: Ideas and Potential

For the purposes of supercritical wastewater oxidation, it would be desirable to conduct electrolysis at high pressure. This would avoid the energy required to compress oxygen gas after it has been liberated through the electrolysis reaction. Certain companies and U.S. Department of Energy projects have explored high-pressure electrolysis for production of hydrogen gas as a renewable fuel. However, high-pressure electrolysis is an area in which further research and development is still needed. Challenges include masking of electrode surfaces by generated gases, increased side reactions, and excessive leaking (Avalence). It is also desirable for the purposes of SCWO to reduce electricity use by avoiding unnecessary products such as hydrogen gas. Alternatives to traditional splitting of water into oxygen and hydrogen gas were also explored. Reactive oxygen species (ROS), as well as O_2, can be used for oxidation in the SCWO reactor. Using a carbon-based cathode, such as diamond, H_2O_2, a powerful ROS, can be generated at the cathode from the reduction of dissolved oxygen (Thostenson et al., 2018). Ebonex® powder, a Magnéli phase titanium sub-oxide, is a potentially more cost-effective electrode material, that could be used as both anode and cathode with voltage cycling.

We believe that development of a high-pressure water electrolyzer with packed-bed electrodes could beneficial for SCWO and other oxidation technologies. Because the products of both the cathode and the anode could be used for oxidation of sludge, no membrane would be necessary. This would allow for a reactor design in which spiked water can travel directly through the anode and then the cathode of a packed bed reactor. This solution could then be fed to the SCWO reactor. The lack of membrane would also increase energy efficiency of the electrolysis reaction. Na_2SO_4 could be explored as a potential supporting electrolyte. A clean water stream would need to be provided but could be an internal recycle loop. The filtered effluent from the SCWO reactor could be suitable depending on the level and nature of the dissolved salts. Direct electrolysis of sludge would probably lead to fouling of electrodes. Cycling of electrodes in order to avoid fouling could be explored (Thostenson et al., 2018). A high-pressure packed bed reactor for use with SCWO would most likely operate at approximately 2-3 V. Methods of incorporating heat from the SCWO reactor into the electrolysis reaction in order to increase reaction rate could also be explored. A process flow diagram of the proposed system is given in Figure 9. Details about similar projects are describe below.

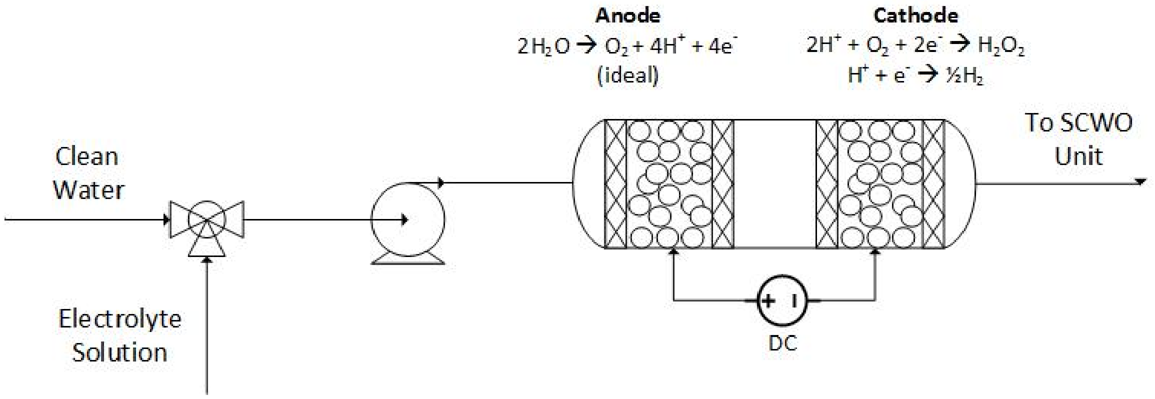
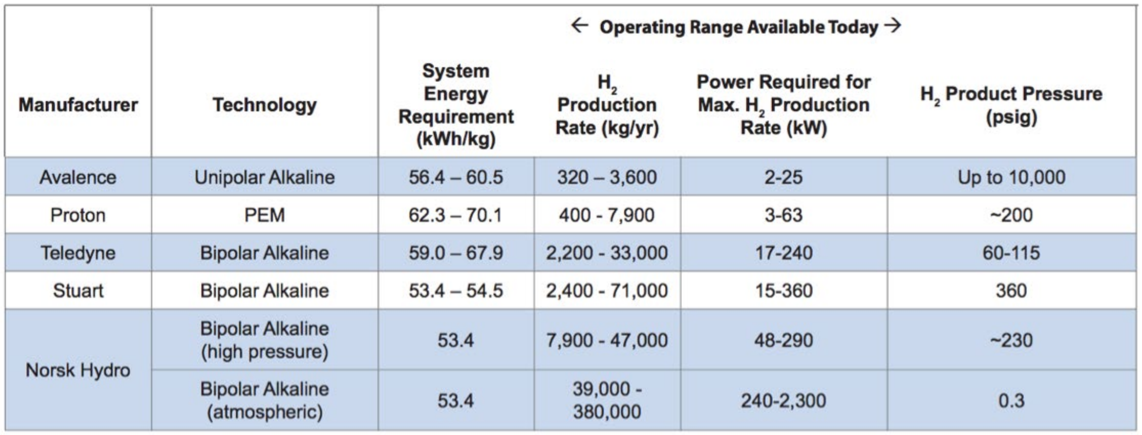


Figure 9. Process flow diagram of the proposed high-pressure packed bed electrolyzer and SCWO reactor.

3.5.3 Related Projects

Commercial projects investigating high-pressure electrolysis for the splitting of water include those by Avalence LLC, Angstrom Advanced, Inc., Giner Inc., Teledyne Energy Systems, Inc., and Norsk Hydro ASA. Information on the operating pressures, volume of H_2 produced, and energy required by the technologies produced by many of these projects are given in Table 8 (NREL).

Table 8. NREL summary of DOE-funded commercial projects involving high-pressure electrolysis for the splitting of water in 2011 (NREL)



		← Operating Range Available Today →			
Manufacturer	**Technology**	**System Energy Requirement (kWh/kg)**	**H_2 Production Rate (kg/yr)**	**Power Required for Max. H_2 Production Rate (kW)**	**H_2 Product Pressure (psig)**
Avalence	Unipolar Alkaline	56.4 – 60.5	320 – 3,600	2-25	Up to 10,000
Proton	PEM	62.3 – 70.1	400 - 7,900	3-63	~200
Teledyne	Bipolar Alkaline	59.0 – 67.9	2,200 - 33,000	17-240	60-115
Stuart	Bipolar Alkaline	53.4 – 54.5	2,400 - 71,000	15-360	360
Norsk Hydro	Bipolar Alkaline (high pressure)	53.4	7,900 - 47,000	48-290	~230
	Bipolar Alkaline (atmospheric)	53.4	39,000 - 380,000	240-2,300	0.3

However, these technologies are optimized for H_2 production, and do not incorporate the generation of ROS or other features desired for use with the SCWO reactor. In first approximation, for each kg of H_2 produced, 8 kg of O_2 is produced. Thus number of Table 8 can be adapted accordingly as first estimates for evaluation. Information on several experimental electrolyzers in scientific literature is given in Table 9 (next page).

Cost

As of 1979, electricity accounted for approximately 80% of all costs associated with electrolysis of water, including capital cost (Lu et al., 1979). Though this may be outdated information, it conveys the importance of considering power consumption when considering cost of electrolysis. Packed bed electrolysis in particular is considered to have low capital cost and high operating cost (Volkman et al., 1977). The latter is due to electricity usage and maintenance, including frequent replacement or cycling, of electrodes.

Table 9. Summary of experimental electrolyzer specifications

Experiment Summary	Supporting electrolyte	Supporting electrolyte concentration (M)	Voltage (V)	Current or Current Density	Current Efficiency (%)	Energy Efficiency (%)	Source
Packed bed electrolyzer for hydrogen reduction and copper deposition	NaCl	0.5		500 A/m^2			(Khattab et al., 2013)
Packed bed electrolyzer for production of sodium perchlorate	$NaClO_3$	6.3	60	200 A			(Menon et al., 2015)
Packed bed electrolyzer for splitting of water	KOH	0.09	3		83.8-96.4	47.7-49.2	(Shau et al., 2015)
Electrolysis of DO for generation of ROS	KH_2PO_4	0.2	2	150 µA			(Thostenson et al., 2018)

Safety

The highly concentrated unused hydrogen gas produced by electrolysis poses several safety risks. These include the fact that hydrogen “burns with an invisible flame,” as well as ignition and asphyxiation risks (Symes et al., 2012). Hydrogen gas can also cause embrittlement of many materials. Additionally, all gaskets should be verified to be compatible with the temperatures and pressures at which the electrolyzer operates. In the United States, hydrogen gas must be stored at least 50 feet from the inlets of air compressors. Hydrogen storage containers should be built to meet the requirements of “ASME Boiler and Pressure Vessel Code, Section VIII - Unfired Pressure Vessels (1968) or applicable provisions of API Standard 620, Recommended Rules for Design and Construction of Large, Welded, Low-Pressure Storage Tanks, Second Edition (June 1963) and appendix R (April 1965), which is incorporated by reference as specified in Sec. 1910.6.” (OSHA).

4. CONCLUSIONS AND RECOMMENDATIONS

Comparison of the power requirements of the methods for which they are known is given in Table 10. A similar comparison concerning price is given in Table 11. For the liquid oxygen costs in Table 11, the lowest cost of Table 6 was reported and a high pressure vaporizer providing the product at 25 MPa was assumed.

Table 10. Comparison of estimated power requirements of alternative oxidation methods for a 6,000 person SCWO unit

Method	Total power requirement (kW)
VPSA	29.0
VSA	14.9-21.4 at 380 kPa
Ozonation	<294

Table 11. Comparison of estimated operating costs of alternative oxidation methods for a 6,000 person SCWO unit

Method	Cost per month ($/month)
Air compression (reference)	4,900
VPSA	2,500
PSA	4,400
VSA	2,200
Liquid oxygen	2,570
Hydrogen peroxide	1.0×10^6
Potassium permanganate	3.2×10^6

From this, the following conclusions were made about whether each method is competitive in terms of power or cost to air compression. VPSA, VSA, and liquid oxygen have the potential to be competitive to air compression. We note here that the cost figures of VPSA and VSA are from a single vendor and need to be confirmed. Membrane purification, ozonation, hydrogen peroxide, ultrasonic irradiation, and potassium permanganate most likely are not cost competitive. Air compression shows here also does not consider any energy recovery from gas expansion.

VPSA and VSA air separation is the most promising method of supplying oxygen with lower electrical requirements than air compression. However, unless high purity (much >40%) oxygen is used, air compression is more energy efficient. High purity oxygen does pose safety and maintenance concerns. Electrical equipment in high-oxygen environments must be designed to prevent sparks. Non-flammable cleaning products must be used. Personnel must not enter areas with unsafe concentrations of oxygen. Depending on the cost of supply, electricity and the capital and maintenance costs of equipment for air separation, liquid oxygen may be a competitive alternative. Liquid oxygen would come with the safety risks of high purity oxygen, as well as concerns with supply chain and availability in remote areas. Oxidation with hydrogen peroxide or potassium permanganate is not practical or economical at industrial scale. Current membrane technologies seem to focus on purification of nitrogen. Only membranes that produce oxygen at a higher purity than those considered in this report (38.5% O_2) could be economically viable. Chemical looping seems to be a promising technology, but it still needs a significant development before it is viable and considerable challenges exist for chemical looping in supercritical water oxidation. Electrolysis is optimized for hydrogen, not oxygen, production. Further development of high-pressure oxygen-producing electrolysis technology is needed. This could include generation of reactive oxygen species which could be used for fecal sludge oxidation.

Based on the findings of this study, the following recommendations are made for further investigations:

1. Conduct further evaluation of air separation system utilizing VPSA and VSA. In particular document costs and sweet spots for costs, system reliability, maintenance costs, requirement for consumables and how to best integrate these alternatives with advanced oxidations such as supercritical water oxidation systems and wet oxidation. The recommended study is a paper study that could take about 3-6 months.
2. Develop and demonstrate a high pressure electrolyzer that generate hydrogen peroxide and other reactive species and O_2 directly at elevated pressure, evaluate its efficacy, and how it could be best integrated with advanced oxidations such as supercritical water or wet oxidation systems. This recommended study is a laboratory study that could take about 9-12 months. It could lead to new IP.

The learning from these recommended activities is expected to benefit several in the WASH portfolio of the Bill & Melinda Gates Foundation

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