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Abstract

This paper will cover three main types of air separation, among these are: Pressure Swing Adsorption, Cryogenic Distillation and Ion Transport Membrane. Emphasis is placed on factors affecting the system, namely pressure, temperature, diffusivity, mass transfer coefficient and tubule and granule diameter.

1. Introduction

1.1 Types of Air Separation

Air separation is the process where air is split up into its constituent species, namely oxygen and nitrogen (as these comprise roughly 21% and 78% of air respectively). This process is industrially carried out in oxygen plants to manufacture a pure oxygen or nitrogen stream for other industrial applications. Air separation may be accomplished through a number of methods, among these are:

- Pressure Swing Adsorption Technology (PSA)
- Cryogenic Distillation Method
- Ion Transport Membrane (ITM)

PSA takes advantage of the species affinity to an adsorbent material. This process involves multiple adsorber vessels each containing beds of adsorbent material such as activated carbon or clay typically in the form of granules. The air is pumped from the bottom and forced through the bed of material. The pressure then causes the molecules to adhere onto the surface of the granules. Depending on the nature of the adsorbent, certain species in the air will have an affinity to the granules and easily (in comparison to the other present species) diffuse through the pores and thus they will be selectively removed from the stream. The air will then exit the system from the top depleted of said species. [1]

Cryogenic distillation is the preferred method for producing streams with high concentrations of oxygen and nitrogen. Depending on the customers the company caters to, the plant may be oxygen or nitrogen-only production plants. However to reduce cost, increase capital and increase energy efficiency these may be produced simultaneously. The generalized stages in cryogenic air separation are [2]:

1) Compressing, cooling and filtering of the air
2) Removal of major impurities such as water vapor and carbon dioxide
3) Removal of heat from air to bring the temperature down to cryogenic temperature of -185°C.
4) Distillation to separate the air into desired products

ITM employs two types of membranes. One type requires porous electrodes on each side of the membrane which apply a voltage difference. At high temperatures the oxygen will then ionize and diffuse through driven by the potential difference. The other type of membrane does not use electrodes but instead employs mixed conductor ceramic membranes to extract oxygen from ionized gas. The oxygen ionizes at the surface of the membrane and diffuses through. This process is effective and economical since high selectivity of ITM's allow for lower production and capital costs [3].

Table 1 gives a brief comparison between these methods.

Table 1: Comparison between Oxygen separation methods, [4], [5]

	PSA	Cryogenic distillation	ITM
Temperature	Ambient	-185°C	700°C
Pressure	Up to 150 kPa	Up to 130 000 kPa	--
Purity (% O_2)	95%	97.5-99.5%	99%

1.2 End use of product streams

Table 1 shows a comparison of the three aforementioned methods. This table, coupled with the brief explanations given, shows that the oxygen concentration of the stream is dependent on the method used. Thus, the type of purification system chosen will depend on the final process it will be used for and the purity of the stream needed. There are many industries and processes that require a high grade stream of oxygen and/or nitrogen. Among these are the mining industry, medicine and food preservation.

The mining industry uses oxygen to improve extraction of low grade ores and sulfide ores. The ore mined may be found in the form of a mineral sulfide. Copper, for example, is mined as chalcopyrite ($CuFeS_2$). In this case before the copper can be extracted the surface must be oxidized to remove the sulfur, this is accomplished through roasting. Roasting will occur in a furnace such as a multiple hearth roaster or fluidized bed reactor. In a fluidized bed the ore is fed into the furnace where a wind box from the bottom will blow air (high grade of oxygen) upwards. The oxygen will then react with the copper sulfide to form copper oxide and sulfur dioxide. The resulting copper oxide can now be introduced into a blast furnace and reduced, with the aid of carbon and carbon monoxide, to metallic copper.

If the sulfur is not removed first then the following process would be rendered useless as carbon cannot reduce sulfides. Thus the goal in roasting is to convert as much of the sulfide as possible. This may be achieved with larger contact times or higher concentrations of oxygen in the air streams. In order to maintain a steady supply of oxygen for these processes some mining companies have introduced on site oxygen plants. Xstrata copper in Mount Isa, Australia built two oxygen plants in 2006 to supply gaseous oxygen to their copper and lead smelting operations. These plants produce roughly 525 tonnes per day per plant of oxygen. [6]

Oxygen may also be used in medicinal purposes such as the treatment of gangrene. This treatment is known as hyperbaric oxygen therapy, it involves increasing the pressure of the oxygen stream into the lungs meaning that the oxygen concentration in the blood will also increase (as the oxygen is also carried by the plasma as opposed to just the haemoglobin). This oxygen rich blood will slow the growth of anaerobic bacteria and aid in the healing of infected wounds [7]. PSA is the preferred method to create on site oxygen in hospitals as it is a safe process with energy and area requirements within reason.

Nitrogen is often used to preserve food. The process is known as modified atmosphere, it involves removing the oxygen from the air leaving only the nitrogen and trace elements already present. The lack of oxygen slows down the growth and propagation of aerobic microorganisms present in the food. This effectively slows down oxidation reactions and slows the decay of the food [9].

The following section will explore the aforementioned oxygen/nitrogen separation processes in more depth, meaning that the transport of oxygen through the process will be explained using a mass transfer analysis. Before this can be done the definition and nature of a "mass transfer analysis" must be explained.

2. Mass transfer equations

Mass transfer refers to the movement, or flux, of mass. The driving force behind the movement of mass is a concentration gradient. This is defined as the difference between concentrations from one point to another. Mass will naturally transfer from areas of high to low concentration. The most general flux term of a species A through B can be shown by [8]:

$$N_A = -C_A D_{AB} \frac{dy_A}{dZ} + y_A N \qquad \text{Equation 2.1}$$

Where:

$$N_A = flux\ of\ A$$
$$C_A = concentration\ of\ A$$
$$D_{AB} = diffusion\ coefficient\ of\ A\ through\ B$$
$$y_A = partial\ pressure\ of\ A$$
$$Z = distance$$
$$N = N_A + N_B$$

The first term refers to the molar diffusion and is represented by Fick's Law. Depending on the nature of the movement of both species (counter current diffusion or diffusion through stagnant film) this equation can be integrated to find the required flux equation. This equation, however, does not account for convective mass transfer.

When convection is involved a new type of analysis called a dimensionless analysis is employed. This relates various dimensionless numbers to each other using specific equations depending on the nature of the flow. Among these dimensionless numbers are Reynolds number (N_{Re}), Schmidt's number (N_{Sc}), Sherwood's number (N_{Sh}) and Stanton's number (N_{St}). These numbers are functions of system constants such as density, viscosity, diffusion coefficient, flow velocity, diameter (of cylinder or sphere) or length and mass transfer coefficient.

The following are the equations used to find the dimensionless numbers.

$$N_{Re} = \frac{D_p v \rho}{\mu} = \frac{L v \rho}{\mu} \qquad \text{Equation 2.2}$$

$$N_{Sc} = \frac{\mu}{\rho D_{AB}} \qquad \text{Equation 2.3}$$

$$N_{Sh} = \frac{k_c L}{D_{AB}} \qquad \text{Equation 2.4}$$

$$N_{St} = \frac{N_{Sh}}{N_{Re} N_{Sc}} \qquad \text{Equation 2.5}$$

Where:

$$D_p = diameter\ of\ granules$$
$$L = length$$
$$v = velocity\ of\ flow$$
$$\rho = density$$
$$\mu = viscosity$$
$$k_c = mass\ transfer\ coefficient$$

These are related to each other through equations that depend on the flow and system:

$$N_{Sh} = f(N_{Re}, N_{Sc}) \qquad \text{Equation 2.6}$$

There equations are picked based on system variables such as whether it is turbulent or laminar flow. The flow may be labeled turbulent or laminar depending on the Reynolds number. The range of Reynolds that dictates turbulent or laminar flow changes depending on whether the flow is occurring within a cylinder or over a flat plate.

These numbers may also be related to each other through j factors. The j factor refers to the Chilton-Colburn analogy. This is useful when the Schmidt number is not equal to 1. Much like equation 6, the equation relating the j factors to the dimensionless numbers will differ depending on the system. The j factor (for mass transfer) can be related to system constants through:

$$j_D = \frac{k_c}{v}(N_{Sc})^{\frac{2}{3}}$$ Equation 2.7

If the constants are known these equations can be used to find the mass transfer coefficient, use them in a flux equation and determine the flux (or concentrations) needed to complete a process.

3. Pressure Swing Adsorption

In this process, as mentioned in the introduction, the air is pumped through cylinders containing a filtering medium. In air separation a compressor is used to supply the air into the vessel where it will first encounter a silica gel bed used to remove water vapor and impurities (such as carbon dioxide). Depending on the area available and the required daily output, the system may have two to four adsorption columns.

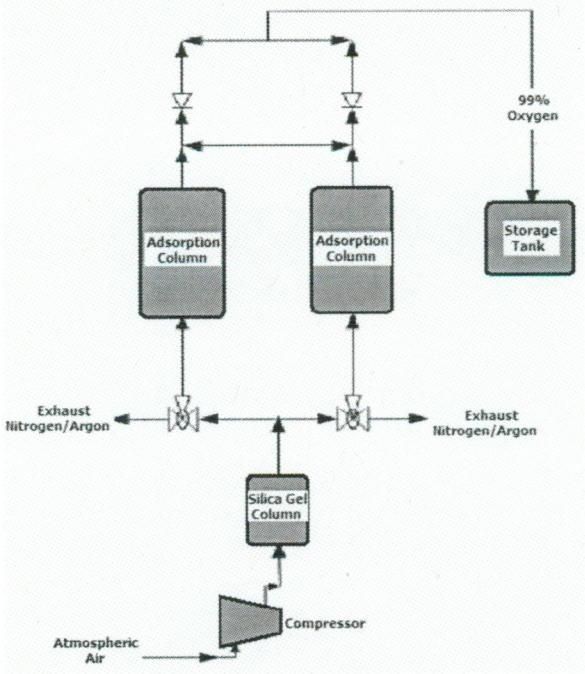

Figure 1: PSA flow diagram [10]

Figure 1 shows a process diagram for a PSA setup with a two cylinder system. Once the air is cleaned of some of the impurities it will be introduced into the first adsorption column. Here nitrogen (and some argon) molecules will be adsorbed onto the bed while Oxygen will be allowed to exit through the top. Once the adsorbent in the first bed is saturated the flow will now be fed into the second vessel. At this point the first bed will be depressurized, this allows for the reversal of the adsorption of the nitrogen and argon. The gas can then be purged from the vessel and the adsorbent material may be reused.

During PSA two important features of this process are:

1) the flow of oxygen through a packed or fluidized bed and
2) the removal of nitrogen from the air stream

The flow of oxygen through a packed bed is a factor of the velocity, density and viscosity of the air stream and the void fraction of the packed bed. The mass transfer of air through a packed bed depleting the air of a species can be calculated using the following equations depending on the range of Reynolds and Schmidt numbers.

For a Reynolds range of 10 – 10,000 [8]:

$$j_D = \left(\frac{0.4548}{\epsilon}\right)(N_{Re})^{-0.4069} \quad \text{Equation 3.1}$$

Where:

$$j_D = \text{j factor for mass transfer}$$
$$\epsilon = \text{void fraction}$$

For a Reynolds range of 0.00165 – 55 and a Schmidt range of 165 – 70,600:

$$j_D = \left(\frac{0.25}{\epsilon}\right)(N_{Re})^{-0.31} \quad \text{Equation 3.2}$$

Assuming all the system constants (density, length, viscosity, and diffusion coefficient) are known, then equation 2.7 and the j_D factor can be used to find the mass transfer coefficient. From this k_C value, the flux can be found using the following equations [8]:

$$N_A A = A k_c C_{A,LM} \quad \text{Equation 3.3}$$
$$N_A A = V(C_{Ai} - C_{A1}) \quad \text{Equation 3.4}$$

Where:

$$C_{A,LM} = \frac{C_{A2} - C_{A1}}{\ln\left(\frac{C_{Ai} - C_{A1}}{C_{Ai} - C_{A2}}\right)}$$
$$C_{A1}, C_{A2} = inlet\ and\ outlet\ concentrations\ respectively$$
$$C_{Ai} = concentration\ at\ solid\ surface$$

3.1 Factors affecting design of PSA

Consider equation 3.1 combined with equation 2.7:

$$\frac{k_c}{v}(N_{Sc})^{\frac{2}{3}} = \left(\frac{0.4548}{\epsilon}\right)(N_{Re})^{-0.4069}$$
$$\frac{k_c}{v}\left(\frac{\mu}{\rho D_{AB}}\right)^{\frac{2}{3}} = \left(\frac{0.4548}{\epsilon}\right)\left(\frac{D_p v \rho}{\mu}\right)^{-0.4069}$$

$$k_c = v^{0.5931}(D_{AB})^{\frac{2}{3}}\left(\frac{0.4548}{\epsilon}\right)D_p^{-0.4069}\rho^{0.2598}\mu^{1.07} \quad \text{Equation 3.5}$$

From equation 3.5 it can be seen that most of the variables are directly proportional to the mass transfer coefficient. This in turn is directly proportional to the flux. If the flux, area and inlet concentration were maintained constant, increasing the mass transfer coefficient would result in a decrease in outlet concentration. In the case of nitrogen being removed by the packed beds this would result in an outlet stream with a higher degree of oxygen purity.

From equation 3.5 it can be seen that the mass transfer coefficient can be increased a number of ways. If we assume that the density of air, viscosity of air and the type of adsorbent are constant (seeing as it is selected to specifically target Nitrogen ions), then the only remaining variables are the air velocity, inlet concentration, granule diameter and void fraction.

The velocity of the air flow is directly proportional to the mass transfer coefficient. From equation 3.5 and 3.3 it can be seen that increasing air flow would cause a decrease in outlet concentration. Similarly, an increase in inlet nitrogen concentration would also result in an increase in the nitrogen concentration of the outlet stream thereby decreasing oxygen purity.

Change in the diameter of the granules inversely affects the mass transfer coefficient. Decreasing the granule diameter would cause a decrease in mass transfer coefficient and a decrease in outlet concentration (purity of oxygen decreases).

The void fraction is another word for porosity, this refers to the amount of empty space in a packed bed and it is the ratio of the void volume to the total bed volume. A large void fraction means that there is a large amount of empty space in the bed. Air flowing through such a bed would have fewer opportunities to come in contact with the adsorbent meaning that it would not properly adsorb the material. From equation 3.5 this shows that a large void fraction would decrease the mass transfer coefficient resulting in an increase of outlet concentration. Jain et al [11] performed a study showing the effects of varying porosity and pressure on the outlet concentration.

Their results showed that an increase in porosity caused the expected decrease in product purity. Figure 2shows a plot of product purity vs. bed porosity for three systems that differed in their inlet concentrations.

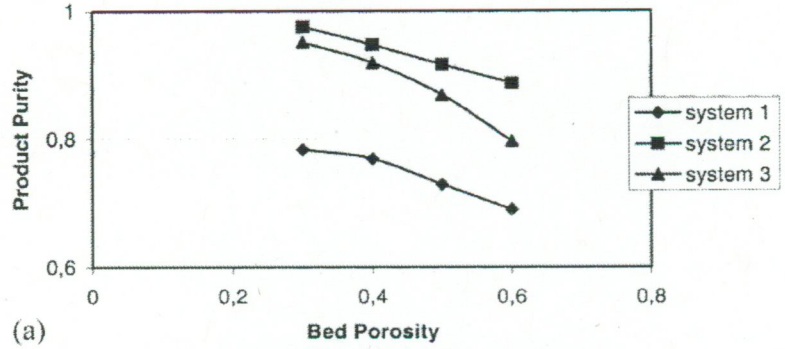

Figure 2: Bed porosity vs product purity [11]

Equation 3.3 can be altered to show the effect of pressure:

$$N_A A = Ak_c C_{A,LM}$$
$$N_A A = Ak_c C y_{A,LM}$$
$$N_A A = Ak_c \left(\frac{P}{RT}\right) y_{A,LM} \qquad \text{Equation 3.6}$$

Where:

$$P = pressure$$
$$R = gas\ constant$$
$$T = temperature$$

From this equation an increase in pressure would also result in a decrease in outlet concentration. Experiments performed by Jain et al [10] study the effects of pressure and prove this hypothesis (Figure 3).

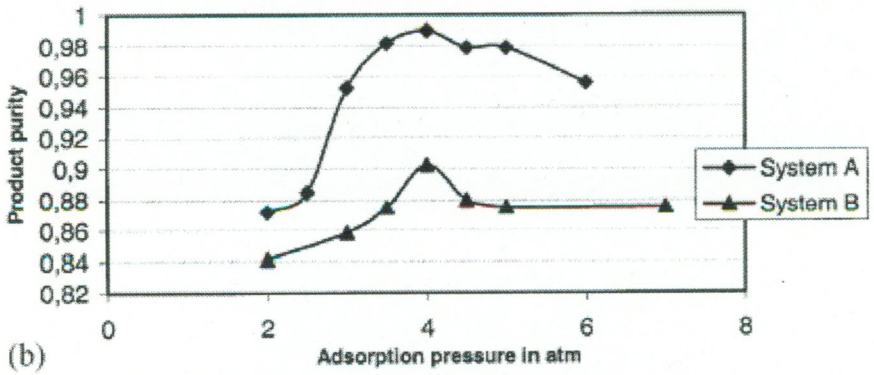

Figure 3: product purity vs pressure [11]

Initially, from this graph one might conclude that the pressure should be as high as economically possible, however at high enough pressures, quality becomes a concern. Jain et al showed that the increase in pressure will eventually lead to a decrease in selectivity. This causes an increase in purity as shown in Figure 3 at around 4 atm.

In equation 3.6, temperature is introduced. This shows that temperature is directly proportional with outlet concentration. There is an entirely different process referred to as temperature swing adsorption (TSA) that uses the influence of temperature instead of pressure. In PSA, temperature is kept constant at all times (the plots in Figures 2 and 3 are isotherms), typically it is held at ambient temperature.

Thus, when performing PSA the key factors that must be controlled are air flow velocity, granule diameter, inlet concentration, bed porosity and pressure.

4. Cryogenic distillation

4.1 Heat Exchanger

In this process, prior to distillation the air is liquefied. This is done by lowering the temperature below the critical point of air. For air the critical point is -140.7°C and 37.2 atm. This means that air can only be liquefied at temperatures below -140.7°C, thus this is the reason the temperature is lowered to -185°C. At this point the air is a boiling liquid.

The air is cooled by means of a heat exchanger. This piece of equipment is capable of transferring heat from one medium to another. There are a number of different heat exchangers used in oxygen plants to subcool the air. Among these is the cascade-vapour compression system [12].

A cascade setup consists of two vapor-compression cycles in series and five different components: refrigerant, condenser, compressor, expansion valve and evaporator. The refrigerant is a compound used to accept the heat being rejected by the refrigerated space. In the case of a two cycle cascade system there are two different refrigerants located in "upper" and "lower" cycle. A typical setup is shown in the left hand side of Figure 4; on the right hand side is a plot of entropy vs. temperature (s vs. T). This plot is helpful in showing the change of entropy and temperature as the refrigerants (labeled A and B in this case) progress through the different components.

The lower cycle with refrigerant A is in contact with the refrigerated space, it is also at a lower temperature meaning that the refrigerated space will reject heat to this cycle in the evaporator. At this point the refrigerant enters the evaporator at a low pressure and low temperature and it is heated in an isobaric (meaning constant pressure) process. The principle behind this step is Charles's law which states that volume is proportional to temperature thus an increase in volume will result in an increase in temperature. This is shown in the s vs. T diagram (Figure 4) from states 4 to 1.

The second law of thermodynamics shows a relationship between change in heat (Q) and change in entropy (S):

$$dQ = TdS \qquad \text{Equation 4.1}$$

Assuming there is no heat exiting the refrigerant and the change in entropy occurs between states 4 to 1 (in this case), then the above equation can be integrated to yield:

$$\int_{Q_{out}}^{Q_{in}} dQ = T\int_{S_4}^{S_1} dS$$

$$Q_{in} = T(S_1 - S_4) \qquad \text{Equation 4.2}$$

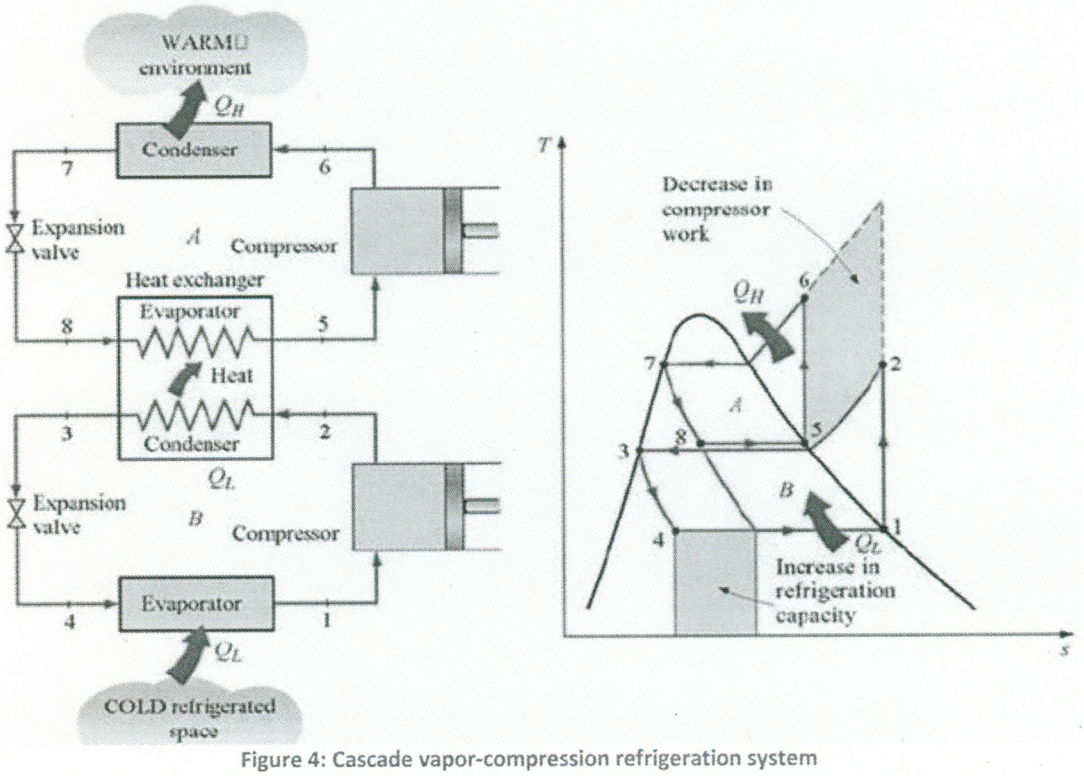

Figure 4: Cascade vapor-compression refrigeration system

The refrigerant vapor will now enter the compressor at a state which is dictated by the pressure and temperature (liquid or saturated vapor). It is then compressed into state 2, this process is said to be isentropic (no change in entropy) and adiabatic since there is no flow of heat energy into or out of the system (Figure 4, state 1):

$$dQ = dS = 0$$

In order to compress the system there must be an input of work. This work (w) is a function of pressure (P) and the change in volume (V). For a reversible process in a closed system, the work equation can be expressed as:

$$dw = PdV \qquad \text{Equation 4.3}$$

If the volume changes between states 1 and 2 and assuming the work is being done on the system then the previous equation can be integrated as follows:

$$\int_{w_{out}}^{w_{in}} dw = P\int_{V_{in}}^{V_2} dV$$
$$w_{in} = P(V_2 - V_1) \qquad \text{Equation 4.4}$$

Using Charles's law, equation 4.4 can then be changed to:

$$w_{in} = Pk(T_2 - T_1) \qquad \text{Equation 4.5}$$
$$T_2 = \frac{w_{in}}{Pk} + T_1$$

Equation 4.5 shows the relationship between work input and temperature, where k is the constant that relates the volume to the temperature in this system. From this equation it can be seen that an input of work will cause an increase in temperature. This change is shown in states 1 to 2 in Figure 4.

The hot compressed refrigerant now enters a condenser where it is cooled in an isobaric (constant pressure) process. The heat expelled by the condenser of B is released into the surrounding fluid stream which in this case is refrigerant A. Thus heat from the lower cycle is used to heat the upper cycle shown by states 8 to 5.

The heat transfer between refrigerants A and B occurs as conduction and convection. Convective heat transfer can be shown through Newton's law of cooling [13]:

$$\frac{dQ}{dt} = hA(T_{A,s} - T_B) \quad \text{Equation 4.6}$$

Where:

$$\frac{dQ}{dt} = change\ in\ heat\ over\ time$$
$$h = heat\ transfer\ coefficient$$
$$A = area$$
$$T_{A,s} = surface\ temperature\ of\ container\ of A$$
$$T_B = temperature\ of\ B$$

Conductive heat transfer is shown through Fourier's law [13]:

$$\frac{dQ}{dt} = -kA\frac{dT}{dz} \quad \text{Equation 4.7}$$

Where:

$$k = thermal\ conductivity$$
$$\frac{dT}{dz} = temperature\ gradient\ across\ z$$

The ratio between the heat transfer coefficient and the thermal conductivity is expressed as the Nusselt number:

$$N_{Nu} = \frac{hl}{k} \quad \text{Equation 4.8}$$

Depending on whether the convection is forced or natural, Nusselts number can be expressed as a function of the Rayleigh number, Prandlt number and/or Reynolds number.

$$N_{Nu} = f(N_{Ra}, N_{Pr}) \rightarrow free\ convection \quad \text{Equation 4.9}$$
$$N_{Nu} = f(N_{Re}, N_{Pr}) \rightarrow forced\ convection$$

Where:

$$N_{Ra} = \frac{\rho g \beta}{\mu \alpha}(T_s - T_\infty)l^3$$
$$N_{Pr} = \frac{C_p \mu}{k}$$
$$\beta = thermal\ expansion\ coefficient$$
$$\alpha = thermal\ diffusivity$$
$$C_p = specific\ heat$$

Similar to what was explained in PSA, if the system constants and the coefficients (and in some cases exponentials) are known that relate nusselts to prandtl and Raleigh or Reynolds, then the ratio between the heat transfer coefficient and thermal conductivity can be found. These values can then be used to calculate the rate of convective and conductive heat transfer.

In "Principles of Heat and Mass transfer" Incropera et al has a chapter dedicated on the different relationships in the form of equation 4.9 [13]. If we consider the condenser to be a shell and tube heat exchanger submerged inside refrigerant B with refrigerant A flowing inside, then the Zukauskas relation can be used to model it.

$$N_{Nu,D} = CN_{Re}^{m}N_{Pr}^{n}\left(\frac{N_{Pr}}{N_{Pr,s}}\right)^{\frac{1}{4}}$$ Equation 4.10

This equation assumes the surface temperature of the cylinder is constant. If we assume that the flow of A inside the tube is continuous then the surface temperature could also be assumed to remain the same.

Equation 4.10 has the Prandtl number calculated at the temperature of the surrounding B (N_{Pr}) and at the surface of the tube ($N_{Pr,s}$). All the other properties are evaluated at the surface temperature. C, m and n are constants that depend on the Reynolds number. Incropera et al tabulated some of these values as shown in Table 2.

Table 2: constants for equation 4.10, [13]

N_{Re}	C	m
$0.4 - 4$	0.989	0.330
$4 - 40$	0.911	0.385
$40 - 4000$	0.683	0.466
$4000 - 40000$	0.193	0.618

Additionally:

$$if\ N_{Pr} \leq 10, n = 0.37$$
$$if\ N_{Pr} \geq 10, n = 0.36$$

From equation 4.10 it can be seen that Nusselts number is proportional to the Reynolds number. From equation 2.2, Reynolds is shown to be a factor of cylinder diameter, velocity, density and viscosity:

$$N_{Re} = \frac{Dv\rho}{\mu}$$

An increase in cylinder diameter, fluid velocity and density will also yield an increase in Reynolds number. This in turn will yield a larger Nusselts number. A larger Nusselts number shows that the ratio between the convective heat transfer coefficient and the thermal conductivity increases. This means the heat transfer coefficient is larger thereby increasing heat transfer by convection. Conversely if the fluid viscosity increases, Reynolds number will decrease resulting in a corresponding decrease of Nusselts number. This means that the ratio is smaller showing a possible increase in thermal conductivity. This would be expected for a viscous liquid.

Refrigerant A is now heated and will proceed to state 6 through a compressor in the same manner as the lower cycle compressor. It then enters the upper condenser where it releases the heat into a heat sink. Refrigerant B, now cooled, will proceed to the expansion valve and then cycle back to the evaporator.

In an oxygen plant the double cycle allows for the air to be cooled to extreme temperatures. While it inters the cascade VC system as a gas, it will exit as a boiling liquid suitable for distillation.

4.2 Distillation

The compressed cold air is now introduced into a distillation tower where the temperature will rise. Nitrogen has a lower boiling point than oxygen. This means that the nitrogen will boil off leaving behind an oxygen stream and effectively separating the air into its two most significant components. The nitrogen is removed from the top of the column and the oxygen from the bottom. The oxygen-rich stream may be further cooled and used to condense the top nitrogen stream or cool incoming air.

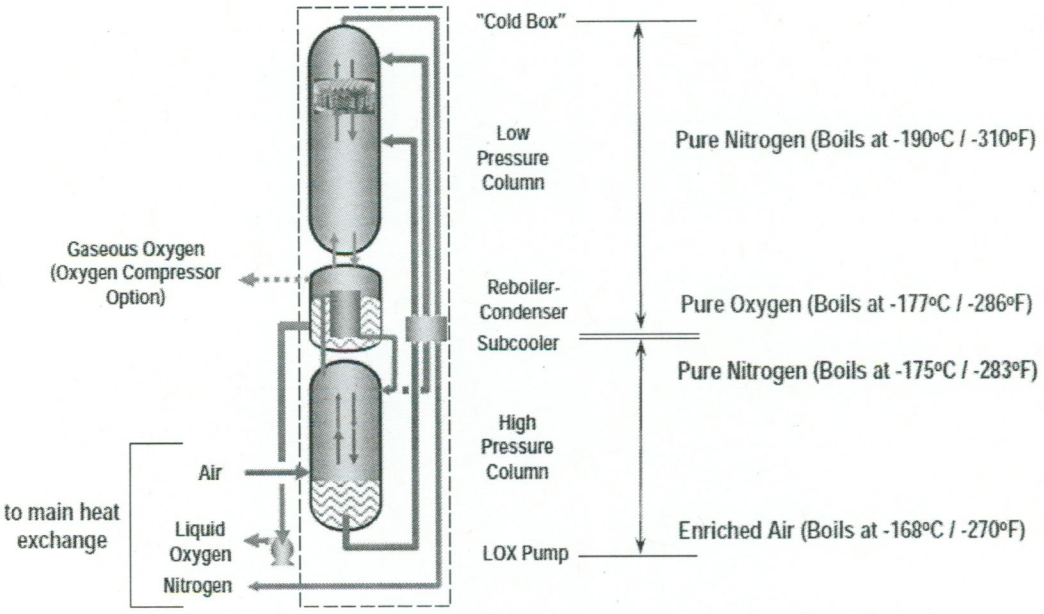

Figure 5: distillation column

A distillation system will typically consist of two columns in series that differ in terms of pressure. Such a setup can be seen in Figure 5. Initially the liquefied air stream will enter the lower column at a high pressure where the boiling point of nitrogen is -175°C. The nitrogen will begin to boil off and diffuse through the column upwards. If we assume the environment inside the distillation column is a stagnant gas then the diffusion flux can be modelled simply by [8]:

$$N = \frac{PD_{AB}}{RTl} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right) \qquad \text{Equation 4.11}$$

Where:

$N = flux$
$P = total\ environmental\ pressure$
$y_{A2}, y_{A1} = partial\ concentration\ of\ the\ gas\ at\ points\ 1\ and\ 2$
$D_{AB} = diffusivity\ of\ A\ in\ B$

The diffusivity coefficient is directly proportional to the flux of the gas. An increase of this value would yield a faster diffusion rate. This can be accomplished by a decrease in temperature:

$$D_{AB} = D_o e^{-\frac{E_A}{RT}} \qquad \text{Equation 4.12}$$

Where:

$D_o = maximum\ diffusion\ coefficient$
$E_A = activation\ energy\ for\ diffusion$

An increase in temperature results in an increase of the diffusivity. While one would assume this causes an increase in flux, there is also a temperature variable in equation 4.11. Overall an increase in temperature results in a decrease in diffusion.

Equation 4.11 shows that an increase in pressure results in an equal increase in flux. Thus it can be seen that since the liquefied air first enters a high pressure column, then diffusion will initially occur very fast. This may decrease selectivity meaning that the nitrogen stream will not be as pure as required. The exiting nitrogen stream of this first column is condensed again and then introduced into a second low pressure column. This decreases the boiling point of the nitrogen to -190°C meaning it will boil sooner.

A more complicated model would consider the diffusion nitrogen through the liquid and the separation. The flux between the liquid and gas interphase to the gas phase can then be described by [8]:

$$N_A = k_G(P_{A,i} - P_{A,G}) \qquad \text{Equation 4.13}$$

Where:

$$k_G = convective\ mass\ transfer\ coefficient\ in\ the\ gas\ phase$$
$$P_{A,i} = interphase\ pressure$$
$$P_{A,G} = bulk\ \ pressure$$

The pressure difference between the interface and the bulk is the driving force for diffusion. A similar equation to 4.13 can be shown for the liquid phase where the concentration gradient becomes the driving force. However, seeing as nitrogen represents 79% of the bulk concentration then this concentration gradient is not very large. In this case the majority of the nitrogen is already at the interface since it is boiling off (lower density than the other constituents). The liquid phase concentration gradient becomes more relevant when the majority of nitrogen is boiled off. Then the nitrogen becomes a minor component in the now oxygen stream. At this point the diffusion nitrogen through the oxygen liquid becomes important.

The mass transfer of nitrogen from the liquid to the liquid/gas interface can be shown by [8]:

$$N_A = k_L(C_{A,L} - C_{A,i}) \qquad \text{Equation 4.14}$$

Where:

$$k_L = convective\ mass\ transfer\ coefficient\ in\ the\ liquid\ phase$$
$$C_{A,i} = interphase\ concentration$$
$$C_{A,L} = bulk\ concentration$$

At this point the interfacial pressure can be related to the interfacial concentration through Henry's law:

$$P_{A,i} = mC_{A,i} \qquad \text{Equation 4.15}$$

As mentioned previously the driving force for the flux of nitrogen is the pressure gradient. As the nitrogen boils off, the concentration in the liquid and the partial pressure will eventually reach equilibrium. This will prevent and/or slow down further nitrogen from boiling off. This shows the importance of removing the nitrogen through diffusion shown in equations 4.14 and 4.11.

5. Ion transport membrane

At room temperature ion transport membranes are impervious to all gases but become permeable to oxygen at high temperatures. Typically they are tubular, thin walled (less than half a millimetre thick), a few millimetres in diameters and can be up to 2 cm long. A general ceramic ion transport membrane is shown in Figure 6.

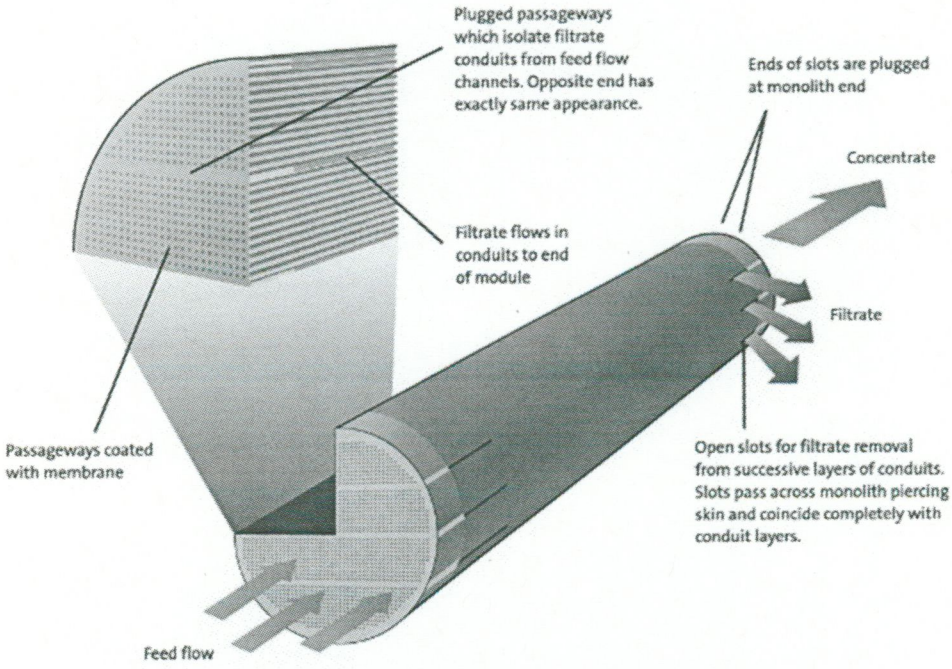

Figure 6: Ceramic Ion Transport Membrane [14]

In Figure 6 it is seen that the air flow is fed through the length of the cylinder. This cylinder is comprised of smaller parallel tubes used to maximize the surface contact area of ceramic to air. While the bulk air diffuses through the length of the tube, the oxygen will diffuse out of the sides [14].

As mentioned in the introduction, two types of membranes are used: one that requires electrodes and one that uses mixed conductor membranes. The term mixed conductor refers to materials that are effective at ionic and electronic conduction. These membranes are crystalline in structure, have an affinity only to oxygen and have vacancies through which oxygen ions may diffuse. In this process the membrane is heated to a temperature of around 700°C. Once the oxygen reaches the ceramic membrane it will ionize and diffuse through. On the other side the oxygen will bond together to reform a stable molecule and create a pure stream of oxygen.

Two types of diffusion occur in this system:

- Diffusion of bulk air through the smaller tubes
- Diffusion of oxygen through the ceramic walls

5.1 Bulk air diffusion

Assuming the conditions inside the ceramic tubes are constant then the rate of diffusion can be described by equation 4.11:

$$N = \frac{PD_{AB}}{RTl} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right)$$

Similarly what was explained in the distillation membrane, the rate of flux of air can be controlled by controlling the pressure, temperature and length of the tube. A more complicated model would consider the interaction between the diffusing particles and the walls of the tubules. These tubules can range in diameter from a few millimeters to less than one millimeter. Figure 7 shows the varying sizes and even geometries of the membrane cross sections.

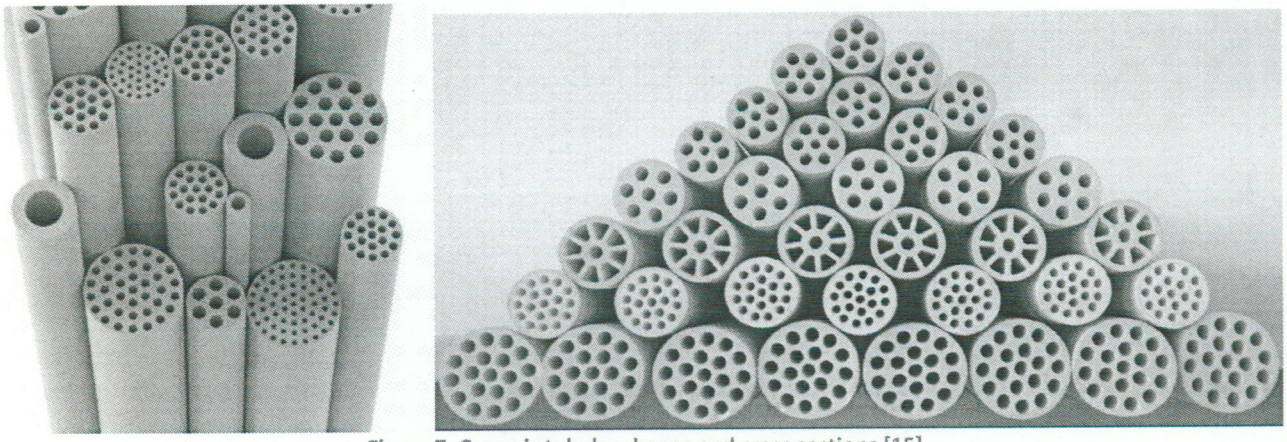

Figure 7: Ceramic tubular shapes and cross sections [15]

Seeing as the membranes are heated to cause ionization, it could be assumed that the kinetic energy supplied to the air is enough to agitate them to the point where their flow is erratic. This means there will be an increase in intermolecular interactions and interactions between particles and membrane walls. At this point both fickian-type (referring to equation 4.11) diffusion and Knudsen diffusion must be considered.

The nature of the intermolecular interactions can be quantified by the mean free path, λ. This value is defined as the average distance a gas molecule travels before colliding against another. The equation used to find it is a function of fluid viscosity, molecular weight, pressure and temperature [8]:

$$\lambda = \frac{3.2\mu}{P}\left(\frac{RT}{\sqrt{2\pi M}}\right) \qquad \text{Equation 5.1}$$

As can be seen at high pressure the mean free path decreases. If the mean free path is small then diffusion will follow fickian diffusion. If it is large then interactions between wall and molecule are considered more dominant and Knudsen diffusion takes over.

From the mean free path the Knudsen number, N_{Kn}, can be found using [8]:

$$N_{Kn} = \frac{\lambda}{2r_{av}} \qquad \text{Equation 5.2}$$

If $N_{Kn} \geq 10$, then then Knudsen diffusion is dominant and the flux can be predicted (to within $\pm 10\%$ error boundary) using the following Knudsen equations.

The Knudsen diffusivity can be calculated using the following equation [8]:

$$D_{KA} = 0.667 r_{av} V_{av} \qquad \text{Equation 5.2}$$

Where:

$$D_{KA} = knudsen\ diffusivity$$
$$r_{av} = average\ pore\ radius$$
$$V_{av} = average\ molecular\ velocity$$

Another equation used is [8]:

$$D_{KA} = 97 r_{av} \sqrt{\frac{T}{M_A}} \qquad \text{Equation 5.3}$$

Where:

$$M_A = molecular\ weight$$

Both of these equations show the direct effect the tubule radius has on Knudsen diffusivity. The molecular mass is inversely proportional meaning a large molecular mass will cause a decrease in the diffusivity. This means that the diffusivity is larger for molecules with small molecular mass and for pores of large radii. The radii of the tubules can be varied depending on system parameters to adjust for faster flux rates.

Once the Knudsen diffusivity is determined, the air flux can be found using the following equation [8]:

$$N_A = -\frac{D_{KA}}{RTl}(P_{A1} - P_{A2}) \qquad \text{Equation 5.4}$$
$$N_A = -\frac{PD_{KA}}{RTl}(x_{A1} - x_{A2})$$

Where:

$$x_A = \frac{P_A}{P}$$

5.2 Oxygen Diffusion

Foy et al do a study investigating the use of different methods to separate oxygen. One of their focuses is ceramic ion transport membranes and the varying factors that affect surface exchange of oxygen. They explained that different materials had varying results. Despite membrane thickness certain membrane material showed larger flux rates than others, their results can be seen in Figure 8 [3].

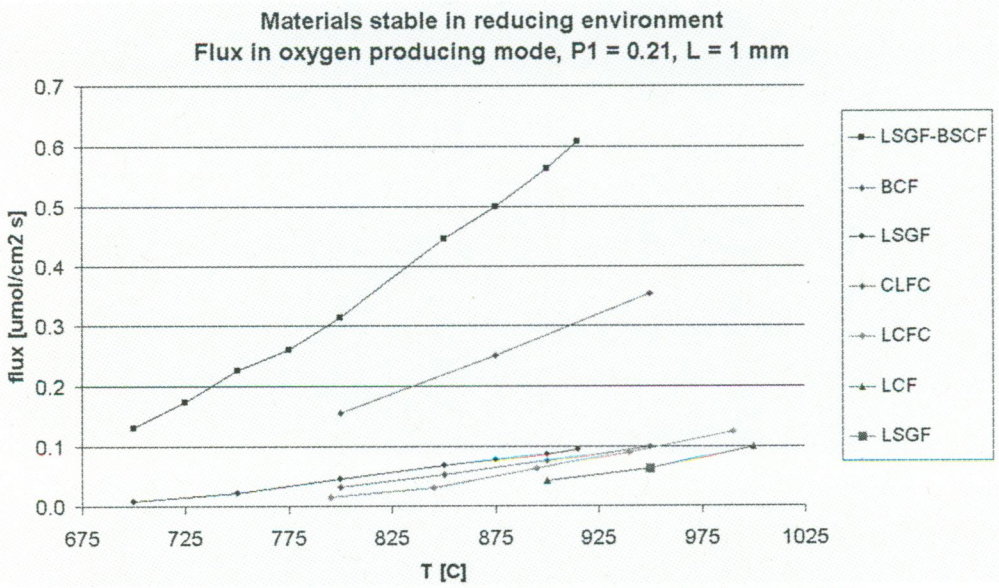

Figure 8: Flux of oxygen with varying temperature and ITM material [8]

Once the oxygen has been adsorbed into the membrane surface it is then transported through the ceramic by oxygen ion vacancies. The flux of oxygen across the membrane can be described by the Nernst-Einstein equation:

$$N_{O_2} = \frac{\sigma RT}{4ln^2F^2} ln\left(\frac{P_{1,O_2}}{P_{2,O_2}}\right) \quad \text{Equation 5.5}$$

Where:

$$\sigma = membrance\ ionic\ conductivity$$
$$l = membrane\ thickness$$
$$F = Faraday's\ constant$$
$$n = charge$$
$$P_{O_2} = partial\ pressures$$

The diffusion of oxygen can be seen in figure 9 [17].

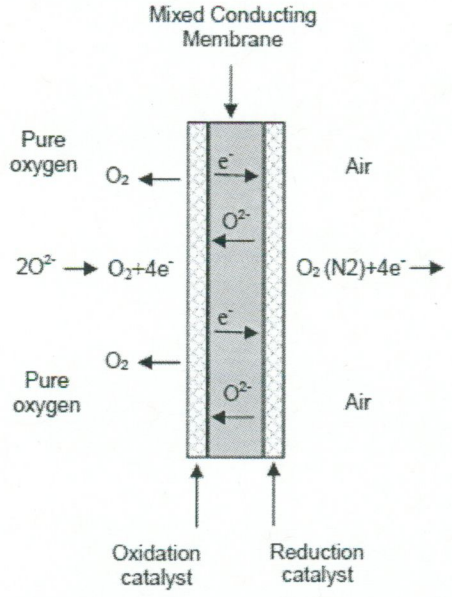

Figure 9: Oxygen diffusion through membrane [4]

Conclusion

The three types of air separation systems explained here are pressure swing adsorption, cryogenic distillation and ion transport membrane. Pressure swing adsorption uses columns filled with adsorbent material that filter out the nitrogen and allow only oxygen through. Cryogenic distillation uses a cascade vapor compression system to cool air until it's a boiling liquid. After it is cooled it is transferred to a high pressure distillation tower where the nitrogen will boil off first (due to its lower boiling point). It is then condensed again and introduced into a low pressure distillation column where it will increase the purity of the nitrogen stream. Ion transport membrane uses a ceramic mixed conductive membrane that is selective towards oxygen. As the air flows through the membrane cylinder the oxygen will diffuse out of the sides.

Picking between these techniques depends on the required purity of the exiting stream (which ultimately depends on the end use) as well as economical demands.

Reference

[1] How do Pressure Swing Adsorption Nitrogen Generators Work?. (2010). *Peak Scientific*. Retrieved April 3, 2013, from www.peakscientific.com/news/148-how-do-pressure-swing-adsorption-nitrogen-generators-work/

[2] Overview of Cryogenic Air Separation and Liquefier Systems. (2003). *Universal Industrial Gas Inc.* Retrieved April 3, 2013, from www.uigi.com/cryodist.html

[3] Foy, K., & McGovern, J. (2005). *Comparison of Ion Transport Membranes*. Retrieved April 3, 2013, from http://www.netl.doe.gov/publications/proceedings/05/carbon-seq/Tech%20Session%20Paper%20111.pdf

[4] Tech Brief. (2009). Oxygen Separation membranes. *Eltron Research and Development*. Retrieved April 3, 2013, from http://www.eltronresearch.com/docs/Oxygen_Separation_Membranes.pdf

[5] Scott, P. (n.d.). Oxygen - Pressure Swing Adsorption. *IChem Ltd.*, *1*, 1.
[6] Xstrata Copper. (2006). Oxygen Plant Control System Upgrade. *Xstrata* , *1*, 1.

[7] Latham, E. (2013). Hyperbaric Oxygen Therapy. *Mescape Reference*, *1*. Retrieved April 3, 2013, from http://emedicine.medscape.com/article/1464149-overview

[8] Subramanian, R. (Professor) (2013). ENGR 3416: Mass Transfer. *Lecture*. Lecture conducted from Laurentian University, Sudbury.

[9] Modified Atmospheric Packaging (MAP). (n.d.). *Food Science Network*. Retrieved April 3, 2013, from www.uoguelph.ca/foodsafetynetwork/modified-atmospheric-packaging-map

[10] Bagajewicz, M. (2007). zeolites and pressure swing adsorption. *n/a*, *1*. Retrieved April 10, 2013, from http://www.ou.edu/class/che-design/a-design/projects-2007/Oxygen%20Generator.pdf

[11] S. Jain, A.S. Moharir, P. Li, G. Wozny (N.A.). *Heuristic design of pressure swing adsorption: a preliminary study*. Retrieved April 5th, 2013.

[12] Oxygen Plants| Oxygen Gas Plants| Oxygen Plants Manufacturers. (2013). *Oxygen Gas Plants| Nitrogen Plants India| Acetylene Plants Setup*. Retrieved April 10, 2013, from http://www.oxyplants.com/oxygen-plants.html

[13] Incropera, F. P. (20132012). Chapter 7 external Flow. *Principles of heat and mass transfer* (7th ed., p. 458). Singapore: John Wiley & Sons Singapore Pte. Ltd..

[14] Extracting oxygen using ceramics | CSIRO. (2008, January 9). *Commonwealth Scientific and Industrial Research Organisation (CSIRO) | CSIRO*. Retrieved April 14, 2013, from http://www.csiro.au/en/Outcomes/Climate/Reducing-GHG/Extracting-Oxygen-Using-Ceramics.aspx

[15] Ceramic membranes. (n.d.). *Likuid Nanotek*. Retrieved April 14, 2013, from www.likuidnanotek.com/en/membranes-cartridges/membranes/ceramic_membranes/