WASTE RECYCLE PRESSURE SWING ADSORPTION

TO ENRICH OXYGEN FROM AIR

by

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A dissertation submitted for the degree of Doctor of Philosophy in the University of Surrey Guildford, Surrey, GU2 5XH

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Summary

Pressure swing adsorption is a method for separating gases by selective adsorption. It is being used increasingly in industry where for some applications, including air separation, the number of plants have increased at a near exponential rate in recent years. However, despite the many hundred different plant configurations and cycles, there is still a lack of understanding of the basic process steps and plenty of scope for achieving even better plant performances. This study examines experimentally and theoretically a two bed process for separating oxygen from air using a zeolite adsorbent.

A plant was designed and built to incorporate the novel feature of recycling waste gas from the purge and depressurization steps back into the feed line and also to investigate conventional purge, backfill and combined cycles. Theoretical modelling had predicted that large amounts of waste gas could be recycled without loss in product oxygen concentration, but causing an improvement in oxygen yield. This was verified experimentally, demonstrating potential energy savings. For each cycle investigated the product oxygen concentration and yield were optimized over a range of product amounts per cycle while continually monitoring the main process variables.

Other experimental work included studies of the bed temperature and pressure profiles, the waste gas oxygen concentrations, unsymmetrical operation and supplying purge from different sources.

The theoretical aims were to further develop the instantaneous local equilibrium (ILE) model used by Kirkby (1984). The model was made more efficient and developed to include novel options for waste recycling and the previously neglected, but common, design feature of supplying purge directly from one bed to another. The model's qualitative agreement with experiments was verified over a wider range of cycles and the quantitative agreement was improved for some cycles.
Preface

The work described in this dissertation was carried out in the Chemical and Process Engineering Department, University of Surrey, from October '85 to October '88. It is the original and independent work of the author, except where otherwise stated in the text. No part of this dissertation has been submitted for a degree at any other university.

I wish to express my gratitude to my supervisor, Dr. N F Kirkby, for his unfailing guidance and enthusiasm. I am especially grateful for his contribution to the modelling sections of this work and for allowing me to extend the model he wrote while at the University of Cambridge.

I am very grateful to BOC Limited, firstly for allowing me as an employee to do this research and also for entirely financing the project. I am especially grateful to my boss, Mike Garrett, for his encouragement and to Andy Bush for his help on numerous occasions.

My time in the Chemical and Process Engineering Department at the University of Surrey was made most enjoyable by its friendly and helpful members. I would like to thank them all, but especially Prof. R Clift, who acted as my second supervisor and Dr. F A Farhadpour for many interesting conversations. The technical support staff in the department also merit recognition and special thanks go to Simon Poole and Ian Wilkinson for their help in building the PSA plant.

Finally, I would like to thank my parents and wife Christine for everything!

Paul Espitalier-Noel
November 1988
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BWR for Backfill Cycle: 4 l/part cycle

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<td>Bed cross sectional area</td>
</tr>
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<td>a</td>
<td>External area for mass transfer per unit volume</td>
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<tr>
<td>b</td>
<td>Langmuir Isotherm constant</td>
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<tr>
<td>C⁺</td>
<td>Gas phase concentration in equilibrium with the adsorbed phase</td>
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<td>C</td>
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<td>C</td>
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<td>D</td>
<td>Diffusivity</td>
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<td>Air feed amount</td>
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<td>F'</td>
<td>Feed to the bed</td>
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<td>f(t)</td>
<td>Arbitrary function of time only</td>
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<td>Y</td>
<td>Augmented mole fraction</td>
</tr>
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<td>y</td>
<td>Mole fraction in the gas phase</td>
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<td>z</td>
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<td>Total voidage in the beds</td>
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Subscripts

A  Least adsorbable component, (oxygen)
B  Most adsorbable component, (nitrogen)
F  Air feed
F'  Feed gas to the bed
G  Overall mass transfer coefficient
g  Single mass transfer coefficient
i  Component in the gas phase
L (v & y)  At z = L, the product end of the bed
o (v & y)  At z = 0, the feed end of the bed
P  Product
R  Recycled waste gas
s  Adsorbent saturated condition
t  Cycle step time
W  Net waste gas

PSA Cycle Abbreviations

DP  Depressurization step  DPT  Depressurization time
PU  Purge step  PUT  Purge time
PS  Purge Snatching step  PST  Purge Snatching time
PR  Pressurization  PRT  Pressurization time
PD  Product Release step  PDT  Product Release time
BF  Backfill step  BFT  Backfill time
WR  Bulk Waste Recycle step  WRT  Bulk Waste Recycle time

Other Abbreviations

UOP  =  Upper Operating Pressure
LOP  =  Lower Operating Pressure
DEPRES  =  Depressurization
PRESS  =  Pressurization
PROD  =  Product, (appendix 4)
Av  =  Average, (appendix 4)
CONCN  =  Concentration
temp  =  Temperature, (appendix 4)
O2  =  Oxygen
N2  =  Nitrogen
WRR  =  Waste Recycle Ratio (defined on page 142)
Ex  =  Experiment, (appendix 4)
l/C  =  Litres per cycle, (appendix 4)
accum  =  accumulation, (appendix 4)
Back'l pres  =  Backfill pressure, (appendix 4)
Y1  =  % oxygen yield calculated from the measured flows
Y2  =  % corrected yield for over predicted waste flows
REC  =  the amount of waste gas recycled per cycle, (appendix 4)
(Re)p  =  Particle Reynolds number, (appendix 4)
CPU  =  Central Programming Unit
ASI  =  Advanced Science Institute, (references)
CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter contains some general information on Pressure Swing Adsorption (PSA). The adsorbents, plant designs, process variables and cycle steps are reviewed. Finally the background and aims of the work reported in this dissertation are presented.

1.2 PSA in General

Pressure Swing Adsorption refers to a group of processes in which gas mixtures are separated due to either selective adsorption or the molecular sieving properties of the adsorbents. Although the potential for PSA was realized as early as 1932, [Finlayson & Sharp], it was not exploited until the 1960's, when synthetic zeolite adsorbents were first manufactured, [Milton, 1959]. It is now widely accepted in industry as a technique for gas separation, where it competes with other techniques such as distillation, liquid absorption and membrane processes for a large number of different separations. The main current applications of PSA are:

i. hydrogen purification,
ii. many separations in the petroleum industry,
iii. the purification of trace components,
iv. gas drying,
v. rare gas separations,
vi. the isolation of radioactive isotopes, and
vii. air separation.
The growth of interest in adsorbents and PSA may be illustrated by the increase in the number of related publications. For example, between 1948 and 1972 over 7000 papers and 2000 US Patents relating to zeolites were accepted. The graph below, [Sircar, (1988)], shows the continued near exponential increase in publications since 1971.

Figure 1.1 The Number of PSA Patents Accepted Annually Worldwide Since 1971

Both the number of PSA plants and their maximum economic sizes are increasing. The largest plants purify hydrogen from varying feed gas compositions. Union Carbide Corporation have built in excess of 200 hydrogen plants worldwide, with their largest plant capable of producing 33 m³ s⁻¹ of 99.9999 % hydrogen from synthesis gas (carbon monoxide and hydrogen). In terms of the greatest number of plants, the enrichment of oxygen from air is the main application for PSA. There are many tens of thousand domiciliary oxygen PSA units in use for medical applications, [Bush, (1988)]. They produce only a few litres per minute (or about, 0.0001 m³ s⁻¹) of enriched oxygen, but the largest oxygen PSA plants supply over 1 m³ s⁻¹ of 93 % oxygen to the Japanese steel industry.
The economics of PSA are complicated and vary for different applications and plant capacities. Generally, the larger plants are more intricate, and have the highest yields. However, the processes have similar basic steps which despite the increasing popularity of PSA are still poorly understood.

In this project the purification of oxygen from air using a 5A zeolite adsorbent was studied. Due to the small separation factors between the components in air the development of PSA processes for air separation was slower than in the hydrogen or hydrocarbon fields. It was only in the early 1970's that the first oxygen and nitrogen plants were commercialized, [Cassidy & Holmes, 1984].

1.3 Adsorption and Adsorbents

The phenomenon of adsorption has been understood by scientists for over 100 years, and it is widely discussed in the literature, [Ruthven, 1984]. Adsorption occurs when molecules in a fluid phase adhere, or "adsorb" on a solid surface. The types of adhesion can be classified into two major categories: chemisorption and physisorption. Chemisorption generally involves the formation of strong chemical bonds, which are not normally broken again by moderate changes in physical conditions. In physisorption, such as in PSA processes, the molecules are loosely bonded by Van der Waal forces and the adsorption is easily reversible, for example water on alumina. In some cases the physisorption bond can be much stronger and of the same order as chemisorption, due to additional electrostatic forces between crystalline adsorbents and polar molecules. For example, water being a small polar molecule forms a very strong bond on zeolites, but no chemical bond is formed.
An adsorbent is a porous solid which allows fluid phase molecules to adhere to its surface. The requirement for adequate adsorptive capacity restricts the choice of adsorbents, for practical gas separation processes, to microporous adsorbents with pore diameters ranging from $10^{-10}$ to $10^{-9}$ m. Two adsorbent types are used in air separation PSA process: zeolites and carbon molecular sieves (CMS). Their properties are discussed in chapter 2.

Adsorption data is normally presented as adsorption isotherms which give the equilibrium loading for a component on the adsorbent versus the partial pressure of that component in the gas phase surrounding the adsorbent, at a constant temperature. The adsorption loading increases with both increasing partial pressure and decreasing temperature. The rate at which equilibrium is obtained is also important because gas separations by PSA can be either kinetically or equilibrium dominated, as illustrated by the following examples.

The enrichment of oxygen from air on 5A zeolites is equilibrium dominated, because the rates of adsorption for both oxygen and nitrogen are both rapid and similar, while at equilibrium significantly more nitrogen is adsorbed than oxygen. Examples of pure gas isotherms for oxygen and nitrogen on the zeolite type used for this work are shown in figure 1.2. In contrast, the enrichment of nitrogen from air using CMS is kinetically dominated. The equilibrium loadings of oxygen and nitrogen on CMS are similar, but oxygen is adsorbed more rapidly than nitrogen. Typical kinetic and equilibrium data for oxygen and nitrogen on CMS are presented in figure 1.3.
Figure 1.2  Pure Gas Isotherms for Oxygen and Nitrogen on Bayer 5A Zeolite

![Pure Gas Isotherms for Oxygen and Nitrogen on Bayer 5A Zeolite](image)

Figure 1.3  Typical Equilibrium and Kinetic Data for Oxygen and Nitrogen on CMS

![Typical Equilibrium and Kinetic Data for Oxygen and Nitrogen on CMS](image)

Equilibrium Data

Kinetic Data

![Equilibrium Data](image)

![Kinetic Data](image)
1.4 PSA Configurations

This section describes the main steps in PSA processes and illustrates the large number of variables that exist in both plant design and operation.

1.4.1 The Basic PSA Steps

PSA processes have three steps in common, namely pressurization, product release and depressurization, (figure 1.4). During pressurization feed gas is compressed into the bed until the upper operating pressure is attained. As feed enters the bed the more adsorbable components are preferentially removed from the gas phase, creating a zone of gas at the closed end of the bed which is enriched in the least adsorbable component. The product release step removes some of the gas enriched in the least adsorbable component as product, while normally maintaining the upper operating pressure by continually adding feed gas to the opposite end of the bed. The depressurization step reduces the bed pressure to its lower operating pressure by exhausting gas counter currently to the feed direction. The exhaust gas is known as waste gas and for air separation it is normally vented to atmosphere. If the lower operating pressure is below atmospheric pressure a vacuum pump is required on the waste line. Lowering the bed pressures gives the driving force for desorption which regenerates the beds.

A cycle consisting only of these three steps is known as a simple cycle. Generally the product concentrations and yields (defined on page 7) obtained from simple cycles are poor, so additional process steps are required to further regenerate the beds, and to enhance the product release. The relative importance of these steps on different gas separations was discussed by Kirkby and Kenney, [1986]. The chromatographic effect of the product release step dominates the recovery of a dilute adsorbable component from a non-adsorbable carrier
gas, (for example hydrogen recovery from a steam reformer). However, for bulk gas separations, such as oxygen enrichment from air, the pressure changing steps have a greater influence on the separation.

Product Yield is defined as the amount of desired gas that leaves the plant in the product stream divided by the amount of desired gas that enters the plant in the feed stream.

Figure 1.4 Simple Cycle PSA Steps

![Diagram of PSA Steps]

1.4.1.1 Further Regeneration (FR) steps

The most common steps in this category are called purge and backfill steps, (figure 1.5). In a purge step, pressurized gas enriched in the desired product is reintroduced into the product end of the bed to be regenerated whilst at its lower operating pressure. The feed end of the regenerating bed is left open, to maintain the lower operating pressure during purge. As purge gas enters the regenerating bed, it lowers the local partial pressure of the more adsorbable component, which desorbes and is carried down the bed where some of it leaves in the waste gas stream.

The backfill step is similar to the purge step except that no waste gas is produced and instead, the pressure in the regenerating bed is allowed to increase while the more adsorbable components are displaced to the bottom of the bed.

Most PSA processes give only one product. They reintroduce their product enriched purge and backfill gas (regeneration gas), counter
currently to product release, to the product end of the bed. However, amongst the 1000's of PSA patents several variations on the backfill theme can be found. For example, gas from different sources may be fed simultaneously to the bottom and top of the bed.

The gas supply for the purge and backfill steps can come from different sources:

1. from a product buffer, [Armond & Webber, (1975)],
2. gas specially stored as regeneration gas, [Marsh et al, (1964)],
and
3. directly from another bed, [Skarstrom, (1960)].

The direct transfer method differs from the former two as the regeneration gas source is not of constant composition. Method 2 is now rare and has been superseded by better use of the just off-specification product, as discussed in the following section. Methods 1 and 3 are both in common use, but to date no systematic experimental or theoretical work has been published to distinguish between the various forms of purge and backfill.

Figure 1.5 Further Regeneration Steps

- purge gas
- backfill gas
- low pressure
- waste
- pressure increasing

PURGE  BACKFILL
1.4.1.2 Enhanced Product Release (EPR) steps

After the product release step there remains at the top of the bed a zone of gas which, although not of product quality, is enriched in the least adsorbable component. The steps described by figure 1.6, under the headings second cut and cocurrent partial depressurization are designed to recover as much of this gas as possible and in so doing they improve the product yield.

The second cut step extends the duration of product release, but as the product concentration start to fall below the desired value the product stream is diverted into the feed of another bed. This step could continue until the concentration of the feed to both beds was equal. The process of second cut has most potential for the separation of dilute components from non-adsorbable carriers, but it has been used by BOC Limited for oxygen production from air, [Armond, (1980)].

During cocurrent partial depressurization the bed pressure is lowered by expelling gas enriched in the least adsorbable component from the product end of the bed. This gas may then be used to feed another bed. The step also improves the product yield by reducing the amount of waste gas produced in subsequent depressurization steps. There are several PSA processes where the bed pressure is allowed to fall during the product release step, see, for example, the early Union Carbide Corporation process for oxygen production from air, [Davis, (1972)].

Figure 1.6 Enhanced Product Release Steps
1.4.1.3 Combined Process Steps

In some processes the product release valve is opened before the end of the pressurization step. In other cycles the depressurization and purge steps may be combined. The advantages of these variations are that the valve switching may be simplified and they allow proportionally more time for bed regeneration in any given cycle.

Some cycle steps combine regeneration and enhanced product release, the most common of these being bed pressure equalization (BPE), which may be considered as a cocurrent partial depressurization followed by a backfill step. BPE occurs when two beds at different pressures are connected so that gas and pressure energy are transferred from one bed to another. In some cases this step continues until the pressures in both beds become equal. Relatively few published PSA studies include BPE even though it is normally used in all but the very small PSA units. In very large PSA units its primary aim is to recover pressure energy. There are many forms of BPE and for multibed processes they can be cascaded, [Berlin, (1966); Wagner, (1969)]. Some of the more usual configurations for two bed processes are shown below.

Figure 1.7 Types of Bed Pressure Equalization

(Pressure decreasing in A and increasing in B)
1.4.2 PSA Design

The obvious aim in PSA plant design is to minimize the capital and operating costs, while giving high purity product at high yields. However, while greater capital costs should reduce a plant's specific energy costs, in some cases the special advantages of PSA such as its simplicity of operation or small plant size may be more important than minimizing the energy costs. Generally, reducing the energy costs is more important in larger plants where the scope for savings is much greater. These points are considered in detail in chapter 2. This section summarizes the stages of PSA design and discusses some of the special problems for the processes.

Stage 1 Defining the Problem

At an early stage the required product flow rate, purity and any design constraints such as the feed gas composition need to be defined. Other considerations at this stage might be the type of separation required, bulk gas separation, or the purification of a dilute mixture and also the treatment and disposal of the waste gas.

Stage 2 Selecting the Adsorbent

In selecting the adsorbent and its particle size the relative properties on the components in the mixture, such as molecular size and polarity must be considered. Small particles improve mass transfer, but increase pressure drops in the bed. For an equilibrium dominated separation the upper and lower operating pressures and isotherm data are used to fix the amount of adsorbent required and the pressure drop is used to assess practical cycle times.
Stage 3  Choice of Operating Process

Decisions must be made on the number of beds, which cycle steps to use and what plant arrangement will best accommodate these steps, while maintaining the required plant flexibility. For air separation on zeolites it is necessary to consider a means of drying the feed air.

Stage 4  Detailed Plant Design

This involves the sizing and selection of each item of equipment, choosing the materials of construction, considering the plant layout, size, weight and deciding on the degree of instrumentation and automation necessary. These decisions influence the plant performance by, for example, determining the shape of the bed pressure and temperature profiles.

Other considerations in the design include the need to:

(a) ensure that the plant construction and operation will be as symmetrical as possible, [Kirkby, (1984)],

(b) to securely fix the adsorbent particles in the beds as they may be subjected to violent pressure changes. If not securely fixed attrition between the particles causes dust formation and a subsequent loss in plant performance, and

(c) to minimize voidage at the ends of the beds, as excess voidage adds to unnecessary compression costs. This point is particularly important for large plants (typically for bed diameters $> 1 \text{ m}$), where the ends of the beds are domed shaped. The design of large plants is further complicated by the need to distribute the feed and regeneration gas evenly over the cross sectional area of the beds.
1.5 This Project

1.5.1 Background

Research into the enrichment of oxygen from air using 5A zeolites has continued, under Kenney, at the University of Cambridge since 1976, [Flores-Fernandez, (1978); Kirkby, (1984); Liow, (1986)]. This project is largely a continuation of the work of Kirkby. The instantaneous local equilibrium (ILE) model first developed by Flores-Fernandez and later refined by Kirkby was extended to include a waste recycle option. The waste recycle simulations predicted that large volumes of waste gas could be recycled to the feed line without any detrimental effect on the product concentration, while at the same time greatly improving the product yield.

The work has also been influenced by BOC Limited, who provided all the financial support for the project.

1.5.2 Experimental Aims

Most effort was placed on the experimental part of this project. A main objective was to try and verify the theoretical waste recycle prediction that, for some cycles, waste recycling could simultaneously improve the oxygen concentration and yield while reducing the oxygen content in the waste gas. It was also an aim to investigate conventional simple, purge, backfill and combined cycles while simultaneously monitoring the main temperatures, pressure, flow rates and compositions. The approach taken was to try and optimize the oxygen concentration and yield for a range of product amounts per part cycle. The novel cycles investigated were to include different modes for selectively recycling waste gas produced during the purge and depressurization steps.

If successful selective waste recycling could improve yields and concentrations beyond the capabilities of conventional cycles. It could show that currently the waste gas streams are not used to their best
potential. Also, by reducing the amount of the oxygen in the net waste, the waste stream may become a useful product. The work on the conventional cycles should improve understanding of cycle steps within PSA processes and the data collected from both the conventional and novel cycles could be used for comparison with theory.

The first stage of the project required the design and construction of the PSA plant described in chapter 4. The design incorporated two beds and required a sufficient degree of instrumentation and automation to allow more detailed studies of the process variables than previously reported for this separation. In addition, the plant had to have sufficient flexibility so that having completed the initial experiments many options existed for some detailed studies of certain cycles. Those options that were taken are described in chapter 5, and include studies of the bed temperature and pressure profiles. A comparison was made between supplying purge gas directly from another bed, or from the product reservoir, and some effects of unsymmetrical operation were investigated.

1.5.3 Theoretical Aims

The development of a new PSA model to improve on those already in the literature is a major task, and given the emphasis on experimental work, it was not an aim of this project. Instead the aim was to further develop the ILE model, which because of its greatly simplifying assumptions is relatively easy to expand for different cycle configurations. The model has some proven qualitative agreement with experimental results, but the large amount of experimental data planned to be obtained from this project should give a better indication as to its predictive qualities.
The model assumed that constant composition regeneration gas was supplied from a perfectly mixed product. It was hoped to expand the model to allow the purge to be supplied perfectly mixed, as before, or of variable composition by transferring purge directly from one bed to another. The transfer of concentration profiles between beds is more difficult to simulate and is generally avoided in other models despite its occurrence in most PSA processes having more than one bed. The model was also to be extended to include different waste recycle modes.

1.6 Further Comment

Although this project investigated oxygen separation from air, many of the principles researched apply equally well to other PSA uses.

There have been many advances in PSA technology in recent years which have made it more competitive with other separation processes and increased its use in industry. PSA processes can only become more efficient. This will be attained partially by better designs and by improving the understanding of the basic cycle steps, which will help to optimize the processes.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The literature contains numerous references to different gas separations by adsorption using a variety of techniques and adsorbents, [Ray, (1983)]. Since Union Carbide Corporation began developing synthetic adsorbents [Milton, (1959)], zeolite science and PSA have both been the subject of several thousand publications. There have been many general reviews on PSA, and these are summarized in table 2.1.

The aim of this chapter is to summarize the main work in PSA, to emphasize in particular the studies on oxygen separation from air and to identify other work directly relevant to this project. General aspects of PSA, such as its development, the adsorbent properties and plant configurations are discussed. A review of the recent theoretical and experimental developments is then presented, and finally PSA as a means of air separation is compared to other air separation techniques.

2.2 The Development of PSA

2.2.1 Background

Most of the advances in adsorption and PSA have occurred this century, [Cassidy & Holmes, (1984)], and they are summarized in chronological order in table 2.2.

The first PSA process was probably invented by Finlayson and Sharp (1932), while working for British Celanese Limited, (now part of Courtaulds Ltd). Their patent describes a single bed process involving a pressurization step and a sequence of depressurizations, each of which produced gas enriched in a different component. Although no record
exists within British Celanese of the commercial use of their process, they foresaw all the major applications to which PSA is applied today.

Kahle (1942), working for Linde A.G., developed a two bed adsorption system for air drying and carbon dioxide removal in the early 1940's. This system was integrated with a cryogenic air separation unit, so that a nitrogen stream from it could be used to regenerate the adsorbers by purging at constant pressure. Later versions of Kahle's system included regeneration by changing the absolute pressure of the adsorber beds during the cycle, leading to the Sorbogen I process, [Reyhing, (1975)].

By 1964 Union Carbide Corporation started to take advantage of their synthetic zeolites. At the same time L'Air Liquide were using adsorption, with a heat or vacuum regeneration step, to produce an oxygen rich product. Two years later Skarstrom, who is widely acclaimed as the inventor of PSA, patented a number of two bed PSA processes, while working for Exxon Research and Engineering. These patents included processes for oxygen enrichment from air, but more significantly they initiated a boom in PSA related patents. At first the processes were simple and used only one or two adsorption beds, but they were followed by some far more complicated configurations.

2.2.2 Influences on PSA Development

The development of PSA was complicated by the largely independent work of a number of companies that simultaneously developed PSA and similar processes for different uses. The directions followed by the main companies are reflected in appendix 1, where a selection of their PSA patents are presented, [Tondeur & Wankat, (1985); Liow, (1986a)].
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Year</th>
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<tr>
<td>Domine &amp; Hay</td>
<td>1968</td>
<td>PSA</td>
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<td>PSA, (air separation)</td>
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<td>1973</td>
<td>Zeolite separation of gases.</td>
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<td>Smith &amp; Armond, (1)</td>
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<td>Cyclic separation processes</td>
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<td>Suzuki</td>
<td>1979*</td>
<td>PSA</td>
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<td>Czaplinski &amp; Mrozek</td>
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<td>PSA</td>
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* Those publications not in English
Zeolite crystals were discovered and named, [Cronstedt, (1756)].
Rutherford first discovered nitrogen by burning air.
Hales prepared oxygen by heating saltpetre in 1731 and Scheele prepared oxygen from various methods in 1771, but Priestley was finally credited with its discovery in 1774.
Damour, (1840), observed that crystals of zeolite could be reversibly dehydrated without any apparent change in their transparency or morphology.
Linde developed fractionating columns to separate oxygen from nitrogen by the distillation of liquid air.
Activated powdered carbon was first offered for sale. It was initially used for sugar decolourisation. In following years adsorption techniques were used for many batch operations. For example, activated carbon was used to remove gasoline from natural gas and adsorption was used at low temperatures to separate the rare gases.
Langmuir (1916), derived a theory of adsorption phenomena assuming only a monolayer forms, adsorption is localized and the heat evolved is independent of the coverage.
McBain introduced the term "molecular sieve" to describe porous solid materials. Further work was necessary to classify the new zeolites continually being identified.
Finlayson and Sharp (1932), developed the first PSA single bed process.
Barrer (1938), published data showing selective properties of chabazite for air and correctly explained that this was due to the quadropole differences of the molecules.
Kahle (1942), released a German Patent describing a two bed PSA process. Later, in 1954, Kahle employed a pressure swing into his more famous "Sorbogen Process".
A major advance came with the invention by Union Carbide Corporation scientists of synthetic zeolites, [Hilton, (1959)].
Skarstrom (1960), developed several PSA cycles. Most early applications for PSA were for gas drying.
L'Air Liquide started filing patents on adsorption processes in 1957. Their first plant was built in 1964 and produced 0.02 m³ s⁻¹ of 99.95 % hydrogen from cracked ammonia, [Guerin de Montareuil & Domine, (1964)].
Union Carbide Corporation, who had several plants working by now, began selling PSA hydrogen plants, [Cassidy & Holmes, (1984)]
Parametric Pumping was invented in the 1960's, [Sweed, (1984)].
Juntgen & Knoblauch, (1971), of Bergbau-Forschung GmBH (BF) developed carbon molecular sieves that were remarkably oxygen specific.
Small oxygen PSA units producing 2-4 litres per minute of 85-95 % oxygen became widely used in hospitals for treating patients with respiratory illnesses.
PSA plants for separating nitrogen from air became readily available. The market was dominated by plants using the BF CMS.
Large scale PSA hydrogen systems were exploited, [Carr et al, (1979)].
Rapid PSA was developed, [Jones, Keller & Wells, (1980)].
Nitrogen production using zeolites adsorbents was commercialized.
2.3 Adsorbent Properties

Some general adsorption information was given in chapter 1, and the characterization of adsorbents was reviewed recently by Sing, (1988). In this section the properties of existing adsorbents and the development of new ones for air separation are discussed. The ideal adsorbent for PSA would be one which had a large selective adsorption capacity and a diffusional resistance favouring a single component, but despite considerable research efforts, such an adsorbent is still unavailable for air separation.

Established adsorbents such as silica gel and alumina are not widely used for PSA other than for drying applications, and instead those used for air separation are generally zeolites, or carbon molecular sieves, (CMS).

2.3.1 Zeolites

The structure, chemistry, manufacturing processes and uses of zeolites have been studied by numerous people including Barrer (1938) and Breck (1974). Unlike traditional adsorbents, zeolites are crystalline, and consequently have virtually no pore size distribution. They are porous hydrated alumino silicates, of general stoichiometry $M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$, where $M$ is normally a group I or II metal of valency $n$ and $x,y$ and $z$ are integers. Within the structure the ratio of silicon to aluminium atoms, which is normally in the range 1 to 5, influences the hygroscopic properties of the adsorbent. Each $AlO_2$ group donates one negative charge which has to be balanced by a metal cation.

There are 34 naturally occurring zeolites and about 100 synthetically manufactured ones. Those of practical significance conserve their alumino silicate skeleton when dehydrated, leaving a structure with a typical intraparticle voidage of between 0.2 and 0.5, and ideally suited for gas separations by adsorption. Their structure is
bidispersed, consisting of roughly spherical cavities (or cages), interconnected with passages (or windows). The windows consist of 4, 5, 6, 8, 10 or 12 oxygen atoms, which join together groups of AlO₂ and SiO₂ tetrahedra. The aperture of these windows depends on the number of oxygen atoms present, but generally falls in the range of 3 to 10 Ångstrom. The cations have several preferred locations in the structure and their size, location and number also influence the diameter of the windows. Careful ion exchange of cations during manufacture of synthetic zeolites enables adsorbents to be produced with favourable micropore sizes for many different gas separations. Several companies have manufactured their own zeolites, (appendix 1).

2.3.1.1 Air Separation Using Zeolites

The ionic structure of the zeolites means that often strong electrostatic forces are formed between them and adsorbate molecules. This is illustrated for oxygen enrichment from air on 5A zeolites (as used in this project), where, despite being the larger molecule, nitrogen is preferentially adsorbed to oxygen due to it possessing a higher quadropole moment. The rates of adsorption for both nitrogen and oxygen are extremely fast, so the separation is equilibrium dominated. Ruthven, (1984), suggested that diffusivities on 5A zeolites were generally less than $10^{-12}$ m² s⁻¹, except for very small molecules, and activation energies were typically above 10 kJ mole⁻¹.

The cages, for 5A zeolites, have internal diameters of about 11 Ångstrom and the windows, which comprise of 8 oxygen atoms, have diameters of about 4.5 Ångstrom. Liow (1986), compared two 5A zeolite types for his oxygen enrichment PSA work, (see section 2.5.1.1).

Shin and Knaebel, (1988), used a 4A zeolite to purify nitrogen from air using a kinetically dominated PSA system. In this case the smaller window size resulted in the rate of adsorption for oxygen being...
significantly greater than that for nitrogen.

2.3.2 Carbon Molecular Sieves (CMS)

A large number of starting materials have been used to prepare CMS, [Nandi & Walker, (1976)], but most are prepared from anthracite and hard coal by controlled oxidation and subsequent thermal treatment. The early work on CMS is reviewed by Walker, Austin and Nandi, (1966). Using special activation procedures adsorbents can be produced with micropore size distributions much narrower than activated carbons, and therefore can be used as molecular sieves. The pore sizes range from 4 to 9 Angstrom and can be altered by changing the manufacturing process, but it is difficult to reproduce exact properties in successive batches. However, as with synthetic zeolites, specific carbon sieves can be produced for different separations.

The pore size distributions in CMS are not as narrow as for zeolites, but CMS have the advantage that their non polar structure tends to make them hydrophobic, and organophilic. Hence, for air separation on CMS there is no need to pre-dry the air feed.

2.3.2.1 Air Separations Using CMS

Although there are several current and proposed uses for CMS, [Schroter & Juntgen, (1988)], the main large scale application is in nitrogen purification from air. Early work in this area was dominated by processes using the CMS produced by Bergbau-Forschung GmbH (BF) of West Germany. Within BF, Juntgen, (1977), developed activated carbons that were remarkable oxygen specific, having diffusion ratios for oxygen to nitrogen of over 100. Subsequently Knoblauch et al, (1975, 1978), described processes using the BF material. Many other companies tried to manufacture sieves with comparable properties, but at first they were largely unsuccessful. However, Calcon Carbon Corporation claim to be able to produce a CMS for air separation with an oxygen to nitrogen
selectivity of 6.5 to 8.5 and a diffusional rate ratio between 9 and 400, [Sutt, (1984)]. Other companies that have also produced their own CMS include Takeda Chemical Company in Japan and Union Carbide Corporation. Kitagawa and Yuki, (1980), were particularly active in their search for new carbons for air separation.

2.3.3 New Adsorbents

Most developments in the adsorbent field have been concerned with the improvement, or development, of synthetic zeolites and CMS. Other materials have been investigated, but as yet their properties have not proven more advantageous to the existing adsorbents. Union Carbide Corporation, for example, describe a series of new compounds that can adsorb oxygen preferentially from nitrogen. One compound Ce[Fe(CN)6] had a separation factor for oxygen from nitrogen of 10 to 48 in 10 minutes, in which time about 70% of the equilibrium oxygen loading was achieved, [Mulhaupt & Berwaldt, (1984)].

2.4 PSA Processes

This section expands on the information presented in section 1.4, where the main design and operational parameters in PSA processes were discussed. It was also illustrated that the processes can vary greatly, making general theoretical, experimental and economical studies difficult. The aim here is to provide an overview of PSA processes. In this section typical plant configurations and possibilities for classifying them are discussed. A general review on optimizing the processes and additional information on the operating parameters are also included.

2.4.1 Cyclic Adsorption Processes

Since Skarstrom patented two bed processes in the mid 1960's, over 1000 patents describing other PSA systems have been granted. Even
though many of these patents were sought by companies wishing to ensure a share of potential PSA markets, and do not describe fundamental changes in the process, the plant configurations differ greatly.

PSA is the most popular method for separating gases by adsorption. There are however other cyclic adsorption techniques, which may be grouped together under headings like Parametric Pumping (PP), and Thermal Swing Adsorption (TSA). These are reviewed in many of the references given in table 2.1 and are also discussed in detail by Sweed (1984), and LeVan (1988). Some workers separate PSA and Vacuum Swing Adsorption (VSA), [Sircar, (1988)], although the only difference is a change in operating pressures, and it is normal to regard vacuum regeneration as an extension to the depressurization step.

Keller and Jones, (1980) and Jones et al, (1980), describe rapid PSA (RPSA), which is the use of very fast cycles for single bed units using small particles. The process basically incorporates low pressure PSA using only one bed and a cycle time of less than 10 seconds, but it can result in a 6 fold improvement in adsorbent productivity for a minimal energy penalty. Thus, RPSA is ideally suited to small scale applications, such as supplying oxygen in aircrafts, where minimizing the plant size and weight are important advantages.

Distinguishing between these techniques is not always easy, especially as in some cases they can be combined into single plants.

A variety of up to date plant configurations have been reviewed by Keller (1983), Ray (1983), Tondeur and Wankat (1985) and Yang (1987). In addition, a selection of the major patents are described in appendix 1, and some of the more unusual designs are presented in table 2.3. The discussion in this chapter is confined to conventional PSA processes, except where air separation applications have been considered.
Table 2.3 Some Unusual PSA Design Features

1. Crowley et al, (1968), used concentric beds for an air drier, where 2 beds were placed one inside the other and separated by a highly conductive wall.
2. Graham (1979), proposed a fluidized bed PSA unit for nitrogen enrichment from air.
3. Several designs combine TSA and PSA. For example, Amitani et al, (1979), coupled a PSA oxygen generator to a furnace to help regenerate their beds.
4. Hitachi Limited, (1981), developed an air separation unit, using both a 5A and a 4A zeolite in their beds. They claim improved plant performances.
5. Wilson (1982), proposed inverted PSA to recover the more adsorbable component in the gas mixture.
6. Microwave regeneration has been suggested in many patents. For example, Mezey and Dinovo, (1982), used microwaves on 4A zeolite to remove carbon dioxide and hydrogen sulphide from natural gas.
7. Japan Oxygen Company (1983), coupled a PSA unit with a membrane unit to purify further their oxygen product. The purer oxygen was then used to regenerate the beds, resulting in a shorter regeneration time.
8. Mattia (1984), used a design where the beds rotated, and as they did so they came in contact with various chambers which were maintained at different pressures.

2.4.2 PSA Classification

Even having limited the discussion to conventional PSA plants using the cycle steps described in chapter 1, there are still many different plant configurations. The processes can vary greatly for different applications, [Sircar, (1988)]. This is illustrated by considering three simple separation types;

Case 1) the recovery of a dilute adsorbable component from a non adsorbable carrier over a selective adsorbent,

Case 2) the separation of a binary adsorbable mixture over a selective adsorbent, and

Case 3) the separation of a binary mixture over a molecular sieve.

In case 1, the purification of dilute mixtures, the chromatographic effect during the product release and purge steps dominate the separation, while for cases 2 and 3 the pressure changing
steps are of major importance to the separation. Case 2 is equilibrium dominated, but case 3 is kinetically dominated. Most applications of PSA can be satisfactorily approximated by one of these groups, which is especially useful when considering PSA mathematical modelling, because the normal simplifying assumptions for each case vary, (section 2.7).

Since modern PSA processes sometimes involve many columns with complex cycles a common framework for their description is helpful. Such a framework was suggested by Tondeur and Wankat, (1985). They proposed the following useful criteria to distinguish between designs:

1) the number of columns and buffer vessels,
2) the number of distinct steps to each column,
3) the phase shift between columns for each step,
4) the coupling between the columns,
5) the relative flow directions, and,
6) the coupling to other processes or energy recovery systems.

When considering the economics of PSA, which is quite different for each application, it is often convenient to subdivide the processes into ranges of plant capacity. This will be illustrated when the economics of air separation are discussed in section 2.8.3.

2.4.3 PSA Operating Variables and Plant Optimization

Having selected the plant configuration and process cycle to be used there remain many operating variables such as temperatures, pressures, flow rates, step times and compositions that can significantly alter plant performances. There is a lack of understanding as to how the process variable affect each other and the overall plant performance. There is also considerable potential for optimizing the process variables especial as the number of cycle steps increases. This is illustrated in table 2.4, which shows the increase in degrees of
freedom for a two bed process as additional process steps are added to the cycle.

Table 2.4 Degrees of Freedom for a Two Bed PSA Process

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1.</td>
<td>Feed temperature</td>
</tr>
<tr>
<td>2.</td>
<td>Particle size</td>
</tr>
<tr>
<td>3.</td>
<td>Adsorbent type</td>
</tr>
<tr>
<td>4.</td>
<td>Bed length</td>
</tr>
<tr>
<td>5.</td>
<td>Bed area</td>
</tr>
<tr>
<td>6.</td>
<td>Upper operating pressure</td>
</tr>
<tr>
<td>7.</td>
<td>Lower operating pressure</td>
</tr>
<tr>
<td>8.</td>
<td>Pressurization time</td>
</tr>
<tr>
<td>9.</td>
<td>Product flow rate</td>
</tr>
<tr>
<td>10.</td>
<td>Product release time</td>
</tr>
<tr>
<td>11.</td>
<td>Depressurization time</td>
</tr>
<tr>
<td>12.</td>
<td>Purge flow rate</td>
</tr>
<tr>
<td>13.</td>
<td>Purge time</td>
</tr>
<tr>
<td>14.</td>
<td>Purge source and composition</td>
</tr>
<tr>
<td>15.</td>
<td>Backfill pressure</td>
</tr>
<tr>
<td>16.</td>
<td>Backfill time</td>
</tr>
<tr>
<td>17.</td>
<td>Backfill source and composition</td>
</tr>
</tbody>
</table>

PSA mathematical models are being continually improved to account for more variables and process cycles, but there is also a need for detailed experimental work where the main operating variables may be simultaneously monitored. Such experimental work is both time consuming and expensive and there have been relatively few published works of this type.

Most experimental work aimed at optimizing the product concentration or minimizing energy costs has been for the Skarstrom cycle, (1960), which has two beds and operates a four step purge cycle, [Espitalier-Noel & Kirkby, (1988); Shin & Knaebel, (1987)]. Conclusions from the optimization work on air separation are discussed in section 2.5.1.1.
There have been some general observations of improved plant performances by manipulating certain operating variables and these are discussed in section 2.4.3.2.

2.4.3.1 Computer Control

One advantage PSA processes have in common is their simplicity of operation, and it is unusual for the plants to be computer controlled. However, there are some examples of control systems in the patent literature where variables such as bed temperatures, pressures, or waste gas concentrations have been used to optimize performances, [White & Christel, (1983)]. Computers have also been used to correct unsymmetrical plant operation. Kirkby (1984), showed that unsymmetrical operation was detrimental to the performance of an oxygen PSA plant.

2.4.3.2 Operating Variables

This section includes some of the general comments on PSA operating variables, [see also Yang, (1987)].

As gas flows through the beds, zones of changing concentration (concentration fronts) are formed, [Tondeur et al, (1988)]. The concentration fronts are self sharpening provided gas enriched in the least adsorbable component is followed by gas enriched in the more adsorbable component. If the reverse is true then the zone of changing composition expands. These effects occur because gas enriched in the more adsorbable component is able to move through the bed at a faster rate to gas enriched in the least adsorbable component.

In practice the sharpness of the concentration fronts is limited by finite mass transfer rates and dispersion. However, Kirkby's ILE model, described in chapter 3, neglects these effects and so predicts discontinuities in concentration or shock waves.
It is widely accepted that producing sharp concentration fronts is advantageous to plant performance. The separation of oxygen on 5A zeolites is equilibrium dominated, but the kinetic driving force favours the separation of nitrogen. Therefore, care must be taken to ensure that the gas superficial velocities in the beds are not so fast that equilibrium is not approached. A technique to increase their sharpness was suggested by McCombs, (1973). He described a cycle which starts with a partially pressurized bed. The feed is introduced to the beds at rates such that the bed pressure keeps rising. This is done by restricting the discharge flow rates. Improved air separation has been claimed by using this technique.

It is also widely agreed that the local temperature rise during adsorption and local temperature drop during desorption are both detrimental to the separation process. That being the case short cycles and low throughput per cycle should be maintained in order to conserve heats of adsorption. This idea was derived from the observation that long cycles and high throughputs would result in hot beds during adsorption, and cold beds during regeneration. However, short cycles are not always feasible for multibed processes, and where truly adiabatic operation is approached in large beds the greatest temperature variations are observed. It was shown experimentally, [Collins, (1977)], that the use of heaters inside the adsorber beds, or even the addition of highly conductive inert particles to the beds, greatly improved the performance for large oxygen PSA plants by reducing the temperature fluctuations in the beds.

In general, processes that are equilibrium dominated get better as they get colder provided they don’t get so cold that mass transfer rates start to restrict the attainment of equilibrium. Similarly, the performances of processes that are restricted by mass transfer improve as they get hotter, but if they become too hot the reduction in
adsorptive capacity becomes significant. Yang (1987), summarized some qualitative results from a mathematical model concerning the importance of the ambient and feed temperatures on PSA separations. He concluded that for separations involving strongly adsorbed gases, such as air separation on zeolites, desorption was the controlling factor. Hence, he inferred that increases in temperature would improve the operation. This is not consistent with other developments, for example, Mitibushi have developed a low temperature oxygen PSA process (247-278 K) for which substantial improvements in plant performance are claimed, [Suzuki, (1988)].

Plant performances can be improved by manipulating the bed pressure profiles. Hitachi Limited (1982) claim for oxygen separation from air, that the use of a pressure control valve on the exhaust line improved their oxygen yield. Also, the pressure variations imposed by Keller and Kuo (1982), on a single bed process improved the oxygen productivity.

The conclusions from optimization work are still vague. There are guidelines for optimizing purge cycles. Yang (1987) suggests that the volume of feed and purge at their respective pressures should be at least equal. Alternatively, an approximation generally accepted in industry, is that the optimum purge amount is obtained when the feed composition is just observed in the waste gas at the end of the purge step, [Kirkby, (1984)]. The understanding of the processes is improving through the advances in mathematical modelling, but again the need for detailed experimental work is emphasized.
2.5 Experimental Work

Many groups of workers combine theoretical studies with specific experimental work for a variety of separations and cycles. In addition, Ray (1983), produced a bibliography of experimental PSA work and Myers (1988a), is producing a data book for adsorption.

The experimental work has been done with numerous plant configurations and operating cycles, for different gas separations, but despite some good research by many groups of workers the overall experimental picture is one of discontinuity, as direct comparisons of experimental results are extremely difficult. Despite extensive corporate research, relatively few results from comprehensive PSA experimental studies have been published. For some newer applications of PSA, such as the separation of hydrogen and carbon monoxide, there is an almost complete lack of published experimental data.

2.5.1 Air Separation by PSA

2.5.1.1 Oxygen Separation on 5A Zeolites

The choice of adsorbent for oxygen separation from air is justified by the work of Kotsis and Argyehan, (1981 & 1982), who investigated 5 different adsorbents.

Work on oxygen PSA using zeolites has continued under Kenney at Cambridge since 1974, [Flores-Fernandez, (1978); Kirkby, (1984)]. Most recently, Liow (1986), reported experimental and theoretical studies of the importance of mass transfer in oxygen production on 5A zeolites. Liow developed a model which included a mass transfer term and was fairly successful in predicting plant performances. Initially his experimental work involved collecting kinetic data by studying breakthrough curves of oxygen and nitrogen on 5A zeolite under different conditions. Interestingly two zeolite types were studied, one from Bayer UK Limited (as used in this project), and one from Laporte Industries.
Limited. Electron microscope studies showed several differences between the zeolite types. The Bayer zeolite consisted of 3-10 micron irregularly shaped crystals which were fused together in a fairly open structure. rods of calcium aluminosilicate, 30-300 microns long, were observed and were probable present to add physical strength. In contrast, a binder was used with the Laporte zeolite, which had more regularly shaped crystals of 2-5 microns in size. Due to the effort placed elsewhere, and the eventual failure of ancillary equipment, relatively few PSA cycles were operated. Liow did observe that there was an optimum purge amount for purge cycles, but did not suggest how this optimum might vary with changing operating conditions. He also states that decreasing the rates of pressurization, depressurization, product release and backfill all improved the product oxygen concentration for backfill cycles. Espitalier-Noel and Kirkby, (1988) have since shown that the relationship between the optimum purge amount and the product amount per part cycle is complex, and that the purge superficial velocity can be critical to the plant performance, (see chapter 5).

Knaebel and co-workers did some similar work to Kenney et al, as both groups developed and tested equilibrium models against the results from two bed PSA units, [Kayser & Knaebel, (1986)].

Two groups of workers chose to study specific respiratory applications of small oxygen PSA units. Pritchard and Simpson (1986), investigated experimentally the best design for single bed RPSA oxygen medical units. Beaman et al, (1983 & 1985), studied the operation of a twin bed OBOGS, (on-board oxygen generating system), for jet pilots.

The use of rapid cycles in PSA was first commercialized for oxygen production by Keller and Jones, (1980). They used a short feed and long exhaust, plus a delay time with both feed and exhaust ends shut to overcome the low product recoveries that were initially obtained with RPSA. In considering the best design for these units, Prichard and
Simpson produced plant performance data, (product concentrations and compression penalties), for two bed lengths and different particle sizes. They found the plant performance was not particularly sensitive to the cycle times for their longer bed (0.61 m). Their shorter bed (0.23 m) was used to produce about 30% oxygen and for this case the cycle times were more critical. Also using course particles in the smaller bed produced a low pressure drop across the bed, which resulted in high flow rates through the bed, a fall in the product concentration and a drop in compression efficiency. At optimum conditions, the bed pressure profiles showed a sharp fall in pressure at the end of the feed step, indicating that the beds had not been fully saturated with feed gas.

Beaman's studies on the OBOGS system were for a two bed process operating a four step purge cycle. He altered the volume fraction of activated zeolite in the beds and showed that the product oxygen concentration and amount were unaffected between volume fractions of 1.0 and 0.75. However, below 0.75 both the oxygen concentration and amount decreased rapidly. Beaman produced a mathematical model for his system, which is discussed in section 2.7.5.

2.5.1.2 Nitrogen Separation from Air

Until very recently nitrogen PSA was dominated by processes using the BF CMS, [Reyhing, (1975)]. Ruthven, Knaebel and their co-workers have presented papers that have investigated kinetically controlled PSA separations.

Hassan, Ruthven and Raghavan, (1986 & 1987) have presented results for a two bed process using the BF CMS. The first paper gives results obtained from operating a purge cycle, while for the second paper there was no purge step, but instead a bed pressure equalization was included.
Shin and Knaebel, (1988) investigated the production of nitrogen from air with bench scale equipment, but using a 4A zeolite (type RS-10, supplied by Union Carbide Corporation) in a four step purge cycle. They studied the duration of the steps in the cycle, flow rates, pressure rates, subatmospheric blowdown and purge amount as well as the column geometry. They produced some thorough experimental results, illustrating the complex relationships between these parameters.

Both these groups claim good agreement between their experimental results and theoretical models.

2.6 Other Processes of Special Relevance to this Project

2.6.1 Waste Recycle PSA

A major aim of this experimental project was to observe the effects of selectively recycling gas from the waste stream back into the feed to the beds, (see chapter 5). Recycling waste gas reduces the amount of product lost in the net waste, improves the product yield and affects the product concentration. These proposed modifications to conventional cycles have not previously been studied in the way described in chapter 5. The ideas behind waste recycling are, however, similar to those used for inverted PSA and some other processes where more than one product is obtained from a single PSA plant.

Most current PSA plants yield a single product, which is generally the least adsorbable gas in the feed mixture. It is possible to purify the most adsorbable component using inverted PSA. Knoblauch et al, (1975), describe a process for producing 60 - 80% oxygen using CMS. They used a two bed PSA unit operating a pressure to vacuum cycle, which could produce either 99.0% nitrogen or 80% oxygen. The nitrogen is the least adsorbable component and the more usual product. However, by increasing the air loading so that more oxygen is adsorbed the "waste" stream can be sufficiently enriched in oxygen as to become a useful
product. The oxygen fraction then recovered from depressurization contained 50-60% oxygen. By dividing the desorption into three phases and recovering only the middle phase 80% oxygen could be recovered. The first and last phases of the depressurization gas are recycled to the feed. This is an example of selective waste recycling, but using CMS rather than a zeolite adsorbent.

Miwa and Inoue, (1980), describe a plant for producing nitrogen using a zeolite adsorbent, where the nitrogen is the least adsorbable component. Their process is complex and includes six beds, two compressors, a vacuum pump and numerous recycles.

2.6.2 Multiple Product PSA

Sircar and Zondlo, (1977), patented a process for the simultaneous production of nitrogen and oxygen enriched gases. The process could, for example, produce 1.92 litres per kg of adsorbent per cycle of 90% oxygen and 6.88 litres per kg of adsorbent of 99.9% nitrogen. The plant consisted of two parallel trains of adsorbers, each with a pretreatment bed for removal of water and carbon dioxide from air and a main air separation bed containing a zeolite. During their cycle nitrogen enriched gas was fed back into the feed end of the beds and oxygen rich gas into the opposite end. The process also included a subatmospheric desorption step.

Szanya, Szabo and Szolosany, (1981), also reported experimental and theoretical work on a process for the simultaneous production of oxygen and nitrogen from air using two beds filled with a 5A zeolite, operating at ambient temperature and at pressures of 3-300 kPa. Their cycle had 10 steps and included both internal and external recycling. The former was realized by the pressure equalization of the adsorbers, the latter by the recycle of the produced oxygen and nitrogen gases. Their experimental unit produced 1.35 litres of 85% oxygen and 5.35
litres of 99.2% nitrogen simultaneously from 15.9 litres of air per part cycle.

Other workers have considered multicomponent PSA, but for separations other than air separation. Sircar (1979) separated hydrogen and carbon dioxide from the off-gas of a hydrogen reformer. Like many of the multicomponent processes, that plant utilized two adsorbent types, [Knaebel, (1984)]. Nataraj and Wankat, (1982), claim to have first proposed multicomponent PSA using a single adsorbent, and more recently Suh and Wankat, (1988), claim to have invented a chromatographic multicomponent PSA process with improved performances.

The common theme in these multiple product PSA processes is that they return some of the waste gas, enriched in the more adsorbable component, to the adsorber beds. Hence, the amount of the least adsorbable component in net waste gas from the plant is reduced and it becomes a useful product. This effect is shown in the waste recycle experimental and theoretical results of chapters 5 and 6 respectively.

2.7 Theory

The literature contains several reviews on theoretical developments in PSA modelling, [Liow, (1986); Yang, (1987); Rousar & Ditl, (1988)]. In this section the problems of PSA modelling, the assumptions made and the methods of solution are discussed. Liow (1986) produced a table summarizing models proposed up to 1985. Table 2.5 lists models published since then.

This section is limited to those models that have been developed specifically for PSA. There are many other groups of workers researching into adsorption on a more fundamental level, or modelling other aspects of gas separation by adsorption. Two recent examples include, Suh and Meunier (1987), who proposed a detailed model for non-isothermal sorption in porous adsorbents by considering a single microporous

36
particle. They accounted for simultaneous heat and mass transfer, and determined the concentration and thermal profiles in the particle as well as obtaining kinetic data. In addition, Kluge et al., (1987), proposed a model for the non-isothermal multicomponent adsorption in adiabatic fixed beds. Their results are relevant to the recent improved PSA models, where bulk gas separations are considered, and heat and mass transfer are more commonly accounted for in the model assumptions.

2.7.1 PSA Modelling

Early work on PSA modelling was for processes separating dilute adsorbable components from inert carrier gases. In such cases analytical solutions are possible by assuming idealized conditions such as isothermal operation, instantaneous equilibrium and by ignoring the pressure changing steps. The cumulative errors from these assumptions are large and when modelling the behaviour of bulk gas separations, such as air separation, they are of limited success. The advantage of these greatly simplified models is their ability to be easily expanded for many cycle steps. Kayser and Knaebel (1986), tested their equilibrium model, which assumed a binary feed gas and linear isotherms, against an experimental oxygen PSA plant. They concluded that the average absolute error in predicting product concentration was 7.1% for a purge cycle at pressure ratios from 6.5 to 840. Their model is very similar to the one which has been further developed in this project, (chapter 3), [Flores-Fernandez and Kenney, (1983); Kirkby, (1984)].

2.7.1.1 Modelling Problems

Two main problems exist in modelling PSA systems. The first is a lack of reliable data for heat and mass transfer parameters, heats of adsorption, equilibrium isotherms and their relationships to changing process conditions. The second arises from the discontinuous nature of PSA, as while in practice this should not alter the fundamental
equations, it does mean separate solutions are required for each new cycle step where boundary conditions vary. Given that sometimes as many as 100 cycles may be required for a plant to stabilize, this second problem results in many models requiring large CPU times, thus reducing their practical usefulness.

2.7.1.2 The Basic Equations

In general PSA is governed by a set of mass balance, heat balance, heat and mass transfer rate and equilibrium isotherm equations. These form a set of coupled partial differential equations (PDE) and algebraic equations for which the PDE are either hyperbolic, parabolic or mixed hyperbolic and parabolic depending on the assumptions made. The type of equations formed will influence the method of solution chosen.

2.7.2 Methods of Solution

Solution methods generally fall into one of the following categories:

1. analytical,
2. finite difference, (implicit and explicit),
3. the method of characteristics,
4. finite elements or cell models, and
5. collocation methods.

Mathematical explanations for these techniques are given by Lapidus and Pinder (1982) and their applications to PSA models, and relative merits are discussed by Liow, (1986) and Kirkby, (1984). The method of characteristics will be discussed in more detail in chapter 3, as it is the solution method used for the model in this project.
2.7.3 Assumptions made for PSA Mathematical Modelling.

The types of assumptions made are discussed below with reference to models in the literature. Examples of the mathematical expressions resulting from these assumptions are presented in chapter 3.

a) Ideal gas behaviour is always assumed.

b) Plug flow is generally assumed.

c) Some recent models account for axial dispersion, [Raghaven et al, (1985)], all models to date ignore radial dispersion.

d) Most workers assume there to be no axial pressure gradients, but an exception to this is the model developed by Sebastian, (1975). In rapid cycling, for which the pressure gradients do not have time to decay, it becomes more important to include pressure drops in the models, [Sundaram and Wankat, (1988)].

e) Most models describing the purification of dilute mixtures ignore the pressure changing steps, while other models make arbitrary assumptions concerning the temporal rates of pressure change. The pressure changes are often assumed to be linear.

f) Most models assume isothermal operation, but since Chihara and Suzuki, (1983), presented their non-isothermal model, several other workers have attempted to account for the thermal effects of PSA processes, [Ishida & Takeuchi, (1987); Doong & Yang, (1987)]. They successfully simulate the non-isothermal behaviour of laboratory scale PSA processes, but the temperature variations observed in large industrial plants have not been reproduced. The process dependence on temperature is complicated and the assumptions made with regard to temperature are still gross simplifications. The models generally assume values for heats of adsorption and their relationships to the changing physical conditions. They also allow for heat transfer through the walls of the beds, but no model as yet includes terms
for the thermal effects of compression and expansion, [Psaras, Leech and LaCava, (1988)].

g) Most models account for velocity changes in the bed, for example [LaCava, Dominguez and Cardenas, (1988)], but no model exists which includes a full transient momentum balance.

h) The majority of workers assume linear independent isotherms, with the remainder adopting either Langmuir, [Nagaev et al., (1974); Flores-Fernandez, (1978)], or Freundlich type isotherms, [Turnock & Kadlec, (1971); Kowler & Kadlec, (1972)].

Some workers have considered multicomponent adsorption equilibria. Knaebel (1984), considered the accuracy of the thermodynamic model, [Ruthven et al., (1973)], and the ideal adsorption solution theory (IAST), [Myers & Prausnitz, (1965)] to the equilibria of oxygen, nitrogen, argon and air on 5A zeolite. These theories have been included in some PSA models, for example Liow (1986) uses the IAST in his model for oxygen purification from air.

i) Models either include a mass transfer or pore diffusion term, or alternatively the assumption of instantaneous equilibrium is made. The continually changing process flow rates, temperatures, pressures and compositions and the non uniform nature of some of the adsorbents make the mass transfer resistance very difficult to model. A further complication results from the differences between the internal structures of each zeolite and CMS, which may produce different mechanisms for the mass transfer, (see section 2.7.4).

2.7.4 Mass Transfer Resistances in PSA

The general subject of adsorption kinetics was reviewed recently by Ruthven, (1988). In keeping with the emphasis on air separation, this section is mainly concerned with microporous adsorbents.
The first PSA model to include a finite mass transfer term was developed by Mitchell and Shendalman, (1973). Similar models were developed by Carter and Wyszynski, (1983), and by Chihara and Suzuki, (1983). (The latter model also included an energy balance). Since then several groups of workers have proposed models which include mass transfer resistances, some of these are discussed in section 2.7.5, (see also table 2.5).

The first workers to model bulk gas separations looked at equilibrium dominated systems. Although equilibrium dominated, mass transfer resistances do play a significant role in these separations, (see chapter 5). Liow (1986) investigated the importance of mass transfer for the equilibrium dominated system of oxygen enrichment from air with a 5A zeolite.

Much of the recent activity in PSA modelling has been for kinetically dominated systems, for which the accuracy of the mass transfer assumptions are more important. The main commercial separation of this type is the purification of nitrogen from air. This has been modelled for systems using 4A zeolites, and more commonly for those using CMS. Recently, Koss and co-workers, (1986), noticed that some CMS deviated considerably from the diffusion controlled mechanism of adsorption. They produced a rate behaviour that could be modelled quite accurately using Langmuir kinetics, which is widely used in catalytic reaction modelling.

2.7.5 Recent Advances in PSA Modelling

There have been many publications in the last three years concerning the mathematical modelling of PSA processes. Many of these models account for thermal effects and mass transfer resistances. They are claimed to have an improved agreement with experimental results,
when compared to some earlier models. Some of the relevant publications are listed in table 2.5.

2.7.5.1 Oxygen Enrichment from Air on 5A Zeolites

For this separation the rates of adsorption are extremely fast, so models have tended to assume instantaneous equilibrium. The mass transfer effects are secondary, but nevertheless important to the separation. Recently, Beaman (1985) and Liow (1986), have both proposed models for oxygen separation from air on 5A zeolites, which included mass transfer resistances, and account for co-adsorption effects. They claim their models have good agreement with experimental results. Beaman's model incorporated overall mass transfer coefficients, valve characteristics and the IAST to predict co-adsorption of oxygen and nitrogen. Liow's model also incorporated the IAST, and is especially unusual because it could handle systems with up to four different adsorber beds.

2.7.5.2 Other Recent Modelling Work

Many recent models have simulated kinetically dominated PSA processes. Included in these, is the study by Shin and Knaebel, (1987), who presented a model for nitrogen purification from air on 4A zeolite. They assumed linear isotherms and isothermal operation, but covered all four steps of a purge cycle and accounted for both film and intraparticle diffusion resistances. They were able to predict concentration profiles within the particles and axially along the beds.

Doong and Yang (1986 & 1987), have produced several models incorporating local equilibrium, pore diffusion, surface diffusion and energy balances. They assumed parabolic concentration profiles in the particles, which may not always be reasonable, [Shin & Knaebel, (1987)].

There have been numerous recent publications from Ruthven and co-workers. Raghaven et al, (1985), presented a model that included both
pressure-dependent mass transfer coefficients and axial dispersion. This was later extended for non-linear trace components, but in both cases they neglected sorption during the pressure changing steps, which, for bulk gas separations, is unrealistic. Raghavan and Ruthven, (1985), then presented a model for kinetically controlled bulk gas separation using CMS supplied by BF and a four step purge cycle, while assuming linear isotherms. Hassan et al, (1986), then extended this to allow for non-linear isotherms.

Hassan et al, (1987), then report the theoretical and experimental study of a modified cycle including BPE, but with no purge. The equalization was top to top and bottom to bottom, (figure 1.4). This model continues to assume that there is no sorption during the pressure changing steps. Instead they assume that the adsorbed phase is frozen during the pressurization and depressurization steps and the mole fraction of the gas phase remains constant. This means that during pressurization the residual gas phase profile is compressed to the closed end of the bed, while the remainder of the bed is filled with feed air. A similar assumption is used for the BPE step, so that at the beginning of pressurization the beds are of two uniform concentrations with a step change in the middle. Good agreement between theory and experiment for a small scale laboratory unit was claimed.

2.7.5.3 Discussion

All these models represent the mass transfer rate by a diffusion controlled mechanism for adsorption. The mass transfer may be modelled with rigorous solutions to the diffusion equations, which computationally is not very practical, or more commonly a linear driving force, (LDF), is assumed.

The use of the LDF approach for PSA models was assessed by Nakao and Suzuki, (1983), and they concluded that mass transfer depends not
only on the pressure, but also on the rate of pressure change. This finding was later verified by Raghaven, Hassan and Ruthven, (1986).

LaCava et al, (1988), reported that the LDF assumption was inaccurate in predicting the rate of adsorption of mixed gases in microbalance experiments on some experimental CMS. They proposed a mass-action rate mechanism, modelled using a Langmuir kinetic expression. They produced a 6 step PSA model including purge and BPE for nitrogen separation from air on these CMS. The BPE assumptions where similar to those of Hassan et al, (1987), but a rigorous solution to all other pressure changing steps was produced. The Langmuir kinetic model was shown to be more accurate than the LDF approach. They also state that the cyclic corrections of Nakao and Suzuki (1983) were inappropriate for their system, but do not disclose the range of pressure changes for which this was shown.

Another interesting development in PSA modelling was observed by Farooq, Hassan and Ruthven, (1988). They presented a model for an adiabatic system involving adsorption of a single trace component. They assumed non-linear isotherms, finite mass transfer resistance and included axial dispersion of mass and axial conduction of heat. The simulation results from this model indicated that more than one cyclic steady state can exist, and that the steady state achieved is dependent on the starting conditions in the beds. Specifically they found that the desirable steady state was achieved when the beds were initially clean. If their process was started with the beds saturated the cyclic steady state obtained had significantly different bed temperature and concentration profiles, and a lower product purity was obtained. The same workers demonstrated experimentally, for an ethylene-helium 5A sieve system, that two different cyclic steady states existed corresponding to clean and saturated initial bed conditions. This is the
only reported instance of multiple steady states experimentally or theoretically.

<table>
<thead>
<tr>
<th>Author</th>
<th>System/Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hirose &amp; Minoda, (1986)</td>
<td>Periodic steady state solution to PSA with short cycle times.</td>
</tr>
<tr>
<td>Hassan, Ruthven &amp; Raghavan, (1986)</td>
<td>Kinetic separation of nitrogen from air using BF CMS. Assumes linear mass transfer, binary langmuir equilibrium and a frozen solid phase for the pressure changing steps</td>
</tr>
<tr>
<td>Shin &amp; Knaebel, (1987)</td>
<td>Kinetic separation of nitrogen from air using a 4A zeolite. Adsorption and desorption were accounted for in the pressure changing steps</td>
</tr>
<tr>
<td>Ishida &amp; Takeuchi, (1987)</td>
<td>Development of a compiler-type simulator for oxygen enrichment from air</td>
</tr>
<tr>
<td>Farooq, Hassan &amp; Ruthven, (1988)</td>
<td>Numerical simulation for an adiabatic system with dilute adsorbable component in an inert carrier. Showed that depending on the initial conditions different steady states were obtained.</td>
</tr>
<tr>
<td>LaCava et al, (1988)</td>
<td>Nitrogen separation from air using CMS. Compared the linear driving force with a Langmuir kinetic expression to describe the mass transfer for certain types of CMS. Modelled a six step PSA cycle including purge and BPE steps, accounting for changes in the gas velocity.</td>
</tr>
</tbody>
</table>

45
2.8 Air Separation by PSA

Since the beginning of the century when the Linde process replaced the Brin barium oxide route, cryogenic distillation has held a virtual monopoly over other separation techniques as the preferred route for air separation. This situation has now changed, with the development in the last 10 years of competitive adsorbent (PSA), and membrane processes. Currently, the membrane processes are at an early stage of development and are only really competitive at low purities up to say 40% oxygen, or 99.5% nitrogen. They can however produce 96% oxygen if required, [Null, (1979)]. In contrast, PSA processes for both nitrogen and oxygen production have established themselves, and are now rapidly expanding into the market.

2.8.1 PSA Applications

Uses for oxygen and nitrogen PSA plants are given in table 2.6. Standard PSA plants can produce up to 99.9% nitrogen or 96% oxygen, (the remaining 4% of the oxygen product is mainly argon). At these purities nitrogen is easier to produce than oxygen, so nitrogen PSA was first to become attractive to small and medium scale gas users. For example, nitrogen PSA plant have been used on oil rigs where their convenience and ability to be skid mounted has been especially advantageous.

PSA is a particularly flexible process in terms of plant capacities and required product purities, which is useful as the demands in the market vary greatly. This is illustrated by the medical industry which requires 30% oxygen for incubators, and greater than 85% oxygen for the treatment of some respiratory conditions. Other low purity oxygen applications include aviation breathing apparatus and certain chemical and biochemical reactors. The economics of PSA over cryogenic distillation for these purities are very favourable.
Table 2.6 Specific Air Separation Applications for PSA

Oxygen PSA plants

These have found uses in all the following fields, [Lee & Stahl, (1973)];

1. biological treatment of waste water
2. feed to ozone generators
3. oxygenation of rivers and reservoirs
4. black liquor treatment in the paper industry
5. medical use
6. chemical oxidation processes
7. enhanced combustion atmospheres
8. fish farming
9. respiratory equipment, (such as for jet pilots)
10. steel industry

Nitrogen PSA plants

Schroter and Juntgen, (1988), of Bergbau-Forschung GmbH produced these recent figures on the applications of their nitrogen PSA plants.

<table>
<thead>
<tr>
<th>Application</th>
<th>% share of PSA market (number of plants)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert blanketing</td>
<td>46.1</td>
</tr>
<tr>
<td>Laboratories</td>
<td>27.2</td>
</tr>
<tr>
<td>Metal treatment</td>
<td>18.4</td>
</tr>
<tr>
<td>Off shore</td>
<td>3.2</td>
</tr>
<tr>
<td>Refineries</td>
<td>3.1</td>
</tr>
<tr>
<td>Chemicals</td>
<td>2.0</td>
</tr>
</tbody>
</table>

2.8.1.1 The Number of Plants

Exact figures for the number of plants in commercial use is difficult to gather as companies often regard this information as confidential. Yang, (1987), suggests that in 1983 there were about 200 oxygen PSA plants with capacities between 1 and 36 tonnes per day and around 40,000 smaller oxygen plants with capacities of about $5 \times 10^{-8}$ m³ STP s⁻¹. (1 tonne per day is $9 \times 10^{-3}$ m³ STP s⁻¹). Studies of recent company literature suggests that the number of oxygen and nitrogen plants is increasing almost exponentially, and disregarding the
domiciliary oxygen units there are probably around 3000 oxygen and nitrogen PSA units in operation worldwide, [Bush, (1988)].

2.8.2 Comparison of Air Separation Methods

The relative merits of air separation by PSA, cryogenic distillation and membranes are summarized in table 2.7. Distillation although widely used is not an energy efficient process, and as the relative volatilities for gases decrease adsorption processes become more favourable, [Ruthven, (1984)]. This is especially true when the distillation is required to take place at extreme temperatures or pressures, such as for air separation.

The option of choosing a PSA plant involves many considerations other than cost. Springmann, (1977), compared PSA to cryogenic distillation assessing variables like the capital cost, flexibility, state of products, operating cost, constraints on feed or product pressures, maintenance, convenience, size, safety, and reliability. Since 1977 PSA technology has improved considerably.

Advantages of PSA and membrane processes over cryogenic distillation are very similar. The main difference currently is that PSA is more economical at higher product concentrations, than the membrane systems.

2.8.3 The Economics of Air Separation by PSA

Since they were first commercialized in the 1970's the performances, designs and reliabilities of oxygen and nitrogen PSA plants have improved considerably. PSA was initially a more energy intensive option to the cryogenic route, and was only attractive to those small gas users, where the special advantages of PSA were important. Lee and Stahl, (1973), compared commercial oxygen PSA processes, but only for maximum plant capacities of up to 5 tonnes per day. By 1983, Keller was predicting that air separation by PSA would
prove economical for plants capacities up to 20 tonnes per day. Other economic reviews of air separation by PSA include the works of Springmann (1977), and Knoblauch, (1978).

Currently, single PSA units are in use supplying over 40 tonnes per day of oxygen or nitrogen product gas. By combining units, PSA plants have been built in Japan to supply over 100 tonnes per day of 93 % oxygen to their steel industry. At these sizes PSA is competing directly with small cryogenic plants. However, air separation by distillation generally produces at least three products, (oxygen, nitrogen and argon), at greater purities than can be produced by PSA process and plants can process as much as 10,000 tonnes per day of air, [Smith and Armond, (1980)].

For plant capacities of 100 tonnes per day of oxygen, cryogenic distillation would have a power penalty of about 0.5-0.6 kWh m⁻³ for 99.9 % oxygen product at 20.4 kPa and at recoveries greater than 90 %. The best oxygen PSA plants would produce the same amount of product, but at the lower purity of 93 % oxygen, at around 0.5 kWh m⁻³ and 30-60 % recoveries. However, the recoveries obtained from cryogenic processes are already high and power consumption depends on compressor technology which is mature. Also, the need in the Linde double column to condense nitrogen with liquid oxygen fixes the pressure ratio between the upper and lower column for cryogenic distillation. In contrast, there is scope for improving recoveries from PSA processes which will directly reduce energy consumption and there are no fixed pressure ratios in PSA. Claims are already being made by Mitibushi that they have developed a low temperature oxygen PSA process with a power penalty of only 0.2 kWh m⁻³ for 93 % oxygen, [Suzuki, (1988)].

Cryogenic distillation should continue as the main route for air separation, but PSA is still likely to capture a sizeable volume of the market.
Generally nitrogen is easier and cheaper to produce by PSA than oxygen. Bergbau-Forchung GmBH published some recent figures for the power consumption of their nitrogen plants, [Schroter & Juntgen, (1988)].

Power Consumption for BF Nitrogen PSA Plants

<table>
<thead>
<tr>
<th>% oxygen content in product</th>
<th>power consumption kWh m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.74</td>
</tr>
<tr>
<td>0.5</td>
<td>0.47</td>
</tr>
<tr>
<td>1.0</td>
<td>0.37</td>
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<tr>
<td>2.0</td>
<td>0.29</td>
</tr>
<tr>
<td>3.0</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 2.7 Comparison of Air Separation Methods

PSA/Membrane

- Economics favour low purity products.
- Plants are often of simple robust design, and easily operated. Although, membranes are not easy to manufacture or fabricate.
- Generally, low capital and high power.
- Argon is not separated, but remains with the oxygen enriched gas.
- Plants are smaller and may be skid mounted.
- All products are gaseous and from the simpler plants only one product is obtained.
- Plants scale down well, but scale up less well.
- Start-up and shut-down are simple and rapid.
- Plants are lighter.

Cryogenic

- High purity products are readily produced.
- Designs are sophisticated and plant operations are more complex.
- Generally, high capital and low power.
- Argon is obtained as a main product from cryogenic distillation.
- Plants are larger.
- Gaseous and liquid products for all components are readily obtained.
- Plants scale up well, but scale down less well.
- It takes much longer to start-up cryogenic plants.
- Plants are heavier.

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2.9 Conclusions

In the last few years PSA plant sales and the amount of research relating to PSA have both increased sharply. However, there is still a lack of published experimental results for most PSA applications and many of the theoretical and experimental studies consider only the simplest of cycles. Further work is required not only to improve the understanding of the basic cycle steps, but also to increasing the range of cycles investigates which should improve the overall understanding of the cycle steps, allow models to be assessed over a wider range of conditions and hopefully enable higher product concentrations and yields to be obtained.

Many recent theoretical models account for a greater number of process variables and they have produced improved agreements with experimental results, but at the cost of additional computer time which reduces their usefulness.

Recent improvements in plant designs, optimization and adsorbents have made PSA processes more competitive. There is still scope for improving plant recoveries, but possible ways of doing this have been neglected in the open literature. If recoveries may be improved they should reduce energy consumption, hence extending the range of capacities over which PSA is economically preferable to cryogenic distillation.

In this dissertation the product oxygen concentration and yield (recovery) are studied for both conventional cycles and novel cycles. The novel cycles include the selective recycling of waste gas back into the feed line. The model described in the next chapter had shown that large amounts of waste gas could be recycled without loss in product oxygen concentration, but while improving the oxygen yield.
CHAPTER 3

THEORY

3.1 Introduction

This chapter includes a summary of the instantaneous local equilibrium (ILE) model, which has been used and further developed in this project. The model originates from the work of Flores-Fernandez, (1978), and was refined by Kirkby, (1984). In this project several modifications have been made, which include the addition of waste recycle modes, but the fundamental theoretical basis for the model has not been changed. For this reason only a summary of the fundamental equations and assumptions are given, but the modifications and new cycle configurations are discussed in detail, (section 3.5).

The ILE model has proven qualitative agreement for the application used in this project, but it is a greatly simplified model. Other more complicated models have been proposed, but generally at the cost of additional computer time, which hinders their development. Section 3.6 summarizes some more advanced theories and relates them to the modelling assumptions of PSA processes.

3.2 Summary of the ILE Model

The key assumptions and equations describing the equilibrium model are summarized below:

1. The feed consists of two adsorbable components with no inerts present.
   
   (Argon is assumed to behave as oxygen, and the feed is treated as a binary mixture of oxygen and nitrogen).
Linear, independent isotherms are assumed.

\[ C_A = C_{A0} + K_A p_A = C_{A0} + K_A P_Y A \]  \hspace{1cm} (3.1)

\[ C_B = C_{B0} + K_B p_B = C_{B0} + K_B P_Y B \]  \hspace{1cm} (3.2)

2. Ideal gas behaviour.
3. Instantaneous local equilibrium,
4. Isothermal operation,
5. Plug flow with no axial dispersion,
6. Radial diffusion and wall effects are ignored.
7. The pressure drop over the bed is neglected.
8. The bed pressures are considered to be a function of time only and the rates of change of pressure are assumed linear.
9. Perfect product mixing is assumed. As the model simulates the supply of regeneration gas from the product reservoir this assumption means that constant composition regeneration gas is used for each purge and backfill step.
10. The beds and cycles are assumed to be symmetrical.
11. The beds are assumed to be completely and uniformly filled with identical adsorbent particles.

Equations
A mass balance for component A over an element in the bed, allowing for linear isotherms and ILE, gives

\[ \frac{-\delta (v_Y A)}{\delta z} = \frac{1}{P} \frac{\delta (P_Y A)}{\delta t} \]  \hspace{1cm} (3.3)

where \( \varepsilon \) = the total voidage in the beds,
and \( w \) = the bulk density of the adsorbent.
If \( k_A = \epsilon + \text{wRTK}_A \) equation 3.3 simplifies to

\[
-\frac{\delta (vY_A)}{\delta z} = \frac{k_A}{P} \frac{\delta (PY_A)}{\delta t}
\]  
(3.4)

This is a quasi-linear partial differential equation which expresses the velocity and composition of the gas phase as a function of time and distance along the bed.

Similarly,

\[
-\frac{\delta (vY_B)}{\delta z} = \frac{k_B}{P} \frac{\delta (PY_B)}{\delta t}
\]  
(3.5)

Equations 3.4 and 3.5 may be rearranged allowing for \( y_A = 1 - y_B \) to eliminate the temporal derivative in \( PY_A \). Hence,

\[
\frac{(k_B - k_A)}{\delta z} = \frac{k_A k_B}{P} \frac{\delta P}{\delta t} + \frac{\delta v}{\delta z} k_A
\]  
(3.6)

Two further definitions are made to simplify the algebra

\[
p' = \frac{1}{P} \frac{\delta P}{\delta t} \quad \text{and} \quad Y = (k_B - k_A)y_A + k_A
\]

where \( Y \) is the augmented mole fraction.

Substituting the above definitions into equation 3.6 gives,

\[
\frac{\delta (vY)}{\delta z} = -k_A k_B p'
\]  
(3.7)
Equation 3.7 can be integrated with respect to distance since \( p' \) is a function of time only, so

\[
\nu Y = -k_A k_B p' z + f(t) \tag{3.8}
\]

\( f(t) \) is an arbitrary function of time only and may be determined from the boundary conditions which may be known at either:

a) \( z=0 \),

\[
\nu Y = \nu_0 Y_0 - k_A k_B p' z \tag{3.9}
\]

or

b) \( z=L \),

\[
\nu Y = \nu_L Y_L + k_A k_B p' (L - z) \tag{3.10}
\]

**Application of the Method of Characteristics**

The objective is to identify trajectories in the distance time plane for which the partial differential equations 3.4 and 3.5 may be reduced to ordinary differential equations. Such trajectories are called characteristic ground curves.

By manipulating 3.4 * \( Y_b \) - 3.5 * \( Y_A \) and substituting for \( \delta y_A = -\delta y_b \) to eliminate the derivative for velocity with respect to time equation 3.11 may be produced.

\[
\frac{\delta Y}{\delta t} + \frac{\nu}{\delta z} \frac{\delta Y}{\delta z} = \frac{P}{(Y - k_A)(Y - k_B)} \tag{3.11}
\]

Equation 3.11 can be compared to the equation for the total derivative, equation 3.12.

\[
\frac{\delta Y}{\delta t} + \frac{\nu}{\delta z} \frac{\delta Y}{\delta z} = \frac{DY}{Dt} \tag{3.12}
\]
Hence, the characteristic ground curve velocity is defined as,

\[ v = \frac{dz}{Y \, dt} \]  \hspace{1cm} (3.13)

and the change in augmented mole fraction along the trajectories is given by,

\[ \frac{DY}{Dt} = -(Y - k_A)(Y - k_b) \frac{p'}{Y} \]  \hspace{1cm} (3.14)

Substituting boundary conditions from equations 3.9 and 3.10 into equation 3.13 gives,

\[ \frac{dz}{dt} = \frac{(v_o Y_o - k_A k_b p' z)}{Y^2} \]  \hspace{1cm} (3.15)

or

\[ \frac{dz}{dt} = \frac{(v_L Y_L - k_A k_b p' (L - z))}{Y^2} \]  \hspace{1cm} (3.16)

Equations 3.15 and 3.16 describe how the position of the characteristics vary with time. They are coupled to equation 3.14, which expresses the change in composition along these trajectories as a function of time only.

The boundary conditions for the steps modelled by Kirkby are summarized on page 65, (see table 3.1).

3.3 Interpretation of Characteristics

The method of characteristics was discussed by Kirkby, (1984). This section defines some terms which are used in chapter 6, where typical characteristic plots are presented.
In general, characteristics are neither straight, nor of constant composition, nor do they change position with the same velocity as the gas phase. There are some simplifying cases, such as product release steps, where constant pressure and feed composition are assumed, so \( p' = 0 \) and \( v_0 Y_0 \) is constant. For these circumstances straight characteristics of constant composition are produced.

Characteristics may converge or diverge. Where they diverge "simple waves" form and where they converge and ultimately intersect "shock waves" are formed. For the model described above, the shock wave velocity is the geometric mean of the velocities of the characteristics converging at that point. Physically shock waves form when zones of the less adsorbable gas (oxygen), are displaced by the more adsorbable component, (nitrogen). The region between the zones contracts as it moves because the volume of the oxygen desorbing is less than that of the nitrogen replacing it. By a similar logic, simple waves are formed when oxygen rich gas is chasing nitrogen rich gas.

3.4 Structure of the ILE model

Kirkby, (1984), fully described the structure of the model. He included block diagrams to summarize the operation of the programs and the arrangement of the program subroutines. Similar diagrams to these are included in this report, (figures 3.1 and 3.2), but they include the modifications from this work, (see section 3.5 and appendix 2). Appendix 2 contains a summary of the functions of each subprogram and block diagrams explaining their arrangement in the model. Diagrams describing the operation of the two main subprograms which produce the characteristic maps for each step, (CHARCL and FILLUP) are included. This appendix also describes the modifications made to existing subprograms and the functions of the new subprograms added as part of this project.
Collect 1) cycle data,
2) initial values
3) simulation options, etc.

Select the next cycle step

Set the characteristic and boundary value arrays

Remove any redundant characteristics produced in the previous step

Calculate the characteristics for this step

Fill any gaps in the characteristic profiles

Check that data has been loaded into the characteristic arrays in the correct order

Calculate the step mass balance

YES NEXT STEP?

NO

Summarize the cycle mass balance

control action on product release velocities

YES NEXT CYCLE?

NO

Output summary
Store graphics
Store bed profiles

STOP
Figure 3.2 Simulation Options

**CYCLE OPTIONS**

A maximum of 10 steps in any order may be chosen from the following:

1. PRESSURIZATION
2. PRODUCT RELEASE
3a. DEPRESSURIZATION
3b. DEPRESSURIZATION with waste recycling
4a. PURGE (mixed purge source)
4b. PURGE (mixed purge source) with waste recycling
4c. PURGE (direct purge source)
5. BACKFILL

**CONTROLLER OPTIONS**

Controller modes are available for:

1. product amount,
2. product purity, and
3. feed amount control.

PI control is used in each case.

**INPUT**

- Equilibria data
- System dimensions
- Cycle configuration
- Control requirements
- Printing options
- Graphics options
- Tolerance levels
- Starting step
- Waste recycle requirements
- Initial conditions

**PRINTING OPTIONS**

1. Mass balance summary
2. Numerous messages to aid fault finding, or for more detailed studies.
3. Working arrays

**GRAPHICS OPTIONS**

1. Mass balance summary
2. Characteristic profiles
3. Bed profiles
4. Product concentration profiles

The above printing and graphic options are available for all cycles, or just the last cycle.
3.5 Additional Operating Modes for the Model

This section describes the new operating modes for the ILE model that were added in this work. They include two ways of selectively recycling waste gas back into the feed line. In addition, the model was altered so as to simulate purge supply directly from another bed as well as from a product reservoir as before. For any given purge step, the latter case produces constant composition purge gas, while the former case produces variable composition purge gas. No other workers have published models incorporating these options. This is not surprising for the waste recycle modes, which are novel, but direct purge is commonly used in PSA processes.

Although these new modes do not alter the fundamental equations, they do change some boundary conditions, (table 3.1).

3.5.1 Bulk Waste Recycling (BWR)

This involved recycling a fixed amount of the waste gas produced during the depressurization and purge steps back into the feed line. By recycling gas into the feed stream the amount of air feed required was reduced and could only be calculated by iterative methods.

In this mode all the waste gas was mixed together before recycling, so that the net waste and recycled waste were the same composition. The model assumes perfect mixing, so $Y_w = Y_r$.

Figure 3.3 BWR Process Simulations

- air feed $F \frac{Y_F}{Y_F}$
- collector and mixer
- product $P \frac{Y_p}{Y_p}$
- bed
- $F' \frac{Y_F}{Y_F}'$
- net waste $W \frac{Y_w}{Y_w}$
The overall and component mass balances over the beds with or without recycling produce

\[ F = P + W \quad \text{ (3.17)} \]

and

\[ F_Y_f = P_Y_P + W_Y_W \quad \text{ (3.18)} \]

where \( F, P \) and \( W \) are the air feed, product and net waste amounts per part cycle.

However, when recycling waste gas the mass balance over the bed is altered and the following conditions must be satisfied,

\[ F' = F + R \quad \text{ (n)} = P + W + R \quad \text{ (n+1)} \]

and

\[ F_Y_f' = F_Y_f + (R_Y_W) \quad \text{ (n)} = P_Y_P + [(W + R)_Y_W] \quad \text{ (n+1)} \]

where \( n \) denotes the nth part cycle.

The net amount of waste, \( W \), is fixed when the program is initiated. The model then assumes a value for the bed feed composition, which as a first approximation is taken as the feed composition from the previous cycle. Within the subroutine which determines the mass balance for each step, MASBAL, a new bed feed composition is calculated and compared to its original value. When these values are sufficiently close together \( F', y_f', \) and \( F \) are fixed, then the model continues as before.

3.5.2 Purge Snatching

Purge snatching refers to a modified purge step, in which the waste gas produced during purge could be selectively recycled into the feed line. The model was modified so that a fraction of purge waste gas could be recycled. The fraction was taken starting from the end of the purge step, when gas containing proportionally more of the least adsorbable component leaves the bed, (section 5.4).
Figure 3.4 describes the cycle in which the purge snatching time, $PS_t$, could be varied from zero to the purge step time, $PU_t$.

**Figure 3.4  Purge Snatching Process Cycle**

```
PS_t
|<->|
```

<table>
<thead>
<tr>
<th>BED1</th>
<th>DP</th>
<th>PU</th>
<th>PS</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
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<table>
<thead>
<tr>
<th>BED2</th>
<th>PD</th>
<th>DP</th>
<th>PU</th>
<th>PS</th>
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</table>

**Figure 3.5  Purge Snatching Operation**

This case differs from that for BWR, because all the waste gas is no longer mixed before recycling, so $Y_B$ and $Y_W$ are not equal. Essentially the model operates two successive purge steps of times $(PU_t - PS_t)$ and $PS_t$. The waste gases produced from these steps are collected separately, with that from the second purge step being recycled and mixed with the air feed.
Average values for $y_R$ and $y_w$ were found from the concentration of the gas leaving the bottom of the bed during purge and depressurization. The overall mass balance equation when recycling is as for BWR (equation 3.19), but the component mass balance is now,

$$F' y_f' = F y_f + (R y_R) \big|_n = P y_p + W y_w + (R y_w) \big|_{n+1} \quad (3.21)$$

3.5.3 Direct Purging from Another Bed

Normally purge gas is supplied either from the product reservoir, or directly from the top of a pressurized bed. Other models always consider the former case, as it is then reasonable to assume a constant composition purge gas for each purge step, which is easier to simulate. In this work the ILE model was extended to make direct purging available as an option. The model had to cope with a variable concentration purge gas, obtained from the second product release step shown in figure 3.6. The addition of direct purge meant that during one part cycle time significantly different product release velocities would be used.

Figure 3.6 The Normal Purge Cycle Used for Both Simulations and Experiments.

<table>
<thead>
<tr>
<th>BED1</th>
<th>DP</th>
<th>PU</th>
<th>PR</th>
<th>PD</th>
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<table>
<thead>
<tr>
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<th>PD</th>
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<th>PU</th>
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</table>

product release step: 1st, 2nd, 3rd

superficial velocity: v1, v2, v3
In the product release steps 1 and 3 only product gas is being removed from the pressurized bed, but in step 2 the pressurized bed is supplying both product and purge gas, so the product superficial velocity is greater.

\[ v_1 = v_3 \quad \text{and} \quad v_4 = v_2 - v_1 \]

\[ \frac{v_4}{A_{PU}} \cdot \frac{PH}{RT} \]

where \( \frac{v_4}{A_{PU}} \cdot \frac{PH}{RT} \) is the purge amount per purge step.

Initially the model was altered so as to handle multiple product release steps, and then subsequently to cope with direct purging.

Transferring purge from one bed directly to another greatly complicates the simulations. If shock waves move out of a bed in the second product release step, then they must be handled as they re-enter a bed in the next purge step. Coping with this was not a trivial problem and resulted in many modifications to CHARCL and FILLUP in particular. The simulations reported in this work used the product amount per part cycle as the controlled variable, so the creation of different product superficial velocities caused some additional complications for the control and mass balance routines, (appendix 2).

(Waste recycling was not investigated with the direct purge simulations).
Table 3.1 Boundary Conditions Summary

<table>
<thead>
<tr>
<th>Step</th>
<th>Known conditions</th>
<th>Characteristic Equations</th>
</tr>
</thead>
</table>
| PRESSURIZATION | \( v_L = 0 \)    | \[
\begin{align*}
\frac{dz}{dt} &= k_A k_B p'(L - z) \\
\frac{dY}{dt} &= \frac{(Y - k_A)(Y - k_B)p'}{Y}
\end{align*}
\] |
|              | \( p' > 0 \) & known |                           |
| PRODUCT RELEASE | \( v_o \) & \( Y_o \) known | \[
\begin{align*}
\frac{dz}{dt} &= v_o Y_o \\
\frac{dY}{dt} &= 0
\end{align*}
\] |
|              | \( p' = 0 \) |                           |
| DEPRESSURIZATION | initial values, \( v_L = 0 \) | As pressurization above |
|              | \( p' < 0 \) |                           |
| PURGE         | \( p' = 0 \) | \[
\begin{align*}
\frac{dz}{dt} &= v_L Y_L \\
\frac{dY}{dt} &= 0
\end{align*}
\] |
|              | \( v_L \) and \( Y_L \) known |                           |
| BACKFILL      | \( p' < 0 \) & known | \[
\begin{align*}
\frac{dz}{dt} &= k_A k_B p' z \\
\frac{dY}{dt} &= \frac{(Y - k_A)(Y - k_B)p'}{Y}
\end{align*}
\] |
|              | \( v_o = 0 \) |                           |

Modifications in this project

BWR and purge snatching both result in a changing feed composition, \( Y_o \), between cycles. This in turn changes the characteristic velocities during the product release steps.

The direct purge option produces a variable composition purge gas, \( Y_L(t) \), so the velocities of the characteristics produced during each purge step vary with time.

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3.6 General Comments on PSA Modelling

3.6.1 Introduction

To describe fully PSA processes models must allow for the combined influences of hydrodynamics, equilibria, kinetics as well as momentum effects. The models must also incorporate several process assumptions regarding, for example, variations in adsorbent properties and the non symmetrical adsorbent packing, plant designs and operations.

The aim of this section is to present a broader picture of PSA modelling and compare the simplified assumptions made in formulating the ILE model with some more advanced theories. The assumptions made in PSA models were discussed in section 2.7 with respect to models in the literature. They are discussed further below, but with emphasis placed on the mathematical expressions that may result from different assumptions.

3.6.2 Ideal Gas Law

The ideal gas law states that, \( PV = nRT \)

It assumes that the fugacity of a species is equal to its partial pressure, and this is known to be a good assumption for low pressures. Myers (1988), suggests that in most cases vapour phase imperfections can be safely ignored unless the pressure is greater than 500 kPa and the experimental error is less than a few percent.

The ideal gas law is assumed in all PSA models. It is not as good an assumption at low temperatures and it depends on the nature of the species. For this work with air at ambient temperature and pressures up to 644 kPa (80 psig) it is a good assumption.

(Note that deviations from ideality in the gas phase will also affect the amount and composition of the adsorbed phase).
3.6.3 Equilibrium

Accurate prediction of the pure gas equilibrium behaviour is an essential step towards the prediction of the multicomponent behaviour.

Microporous adsorbents, such as zeolites, where the pore sizes are not much larger than the molecular diameters of the sorbate molecules normally produce type I isotherms. This is further encouraged if there are relatively weak interactions between the sorbate molecules and the adsorbent. Since the Langmuir isotherm is of the correct qualitative form to represent type I isotherms it provides a reasonable fit for experimental data over quite a wide range. As many workers adopt the Langmuir isotherm its use and expansion is discussed below.

![Langmuir Isotherm Equation](image)

\[ \theta = \frac{q}{q_b} = \frac{bP}{1 + bP} \]  

(3.22)

where, \( b = \frac{k_a}{k_d} \)

= Coef't for the rate of adsorption

= Coef't for the rate of desorption

The Langmuir isotherm is derived from the assumptions that the rate of adsorption equals the rate of desorption, the molecules are adsorbed at a fixed number of well defined sites, each site can hold one adsorbate molecule, all the sites are energetically equivalent and no interactions occur between molecules adsorbed on neighbouring sites.

More complicated equilibrium theories account for multilayer adsorption (BET isotherm) and differences between adsorption sites. The subject of energetic heterogeneity was approached by Myers, (1988), who expanded the Langmuir isotherm, allowing for different distributions of energy for the adsorption sites.
Zeolites have a very narrow pore size distribution, but other adsorbents have sufficient variation in pore size that the partial exclusion of molecules from the total pore volume is realistic. Myers presents an Exclusion Theory to account for this phenomenon.

Some PSA models include theories for predicting the equilibrium behaviour of gas mixtures. Notably, Liow (1986) and Beaman (1985), used the ideal adsorbed solution theory (IAST) for their models, which simulated oxygen production on a 5A zeolite. A statistical thermodynamic model, [Ruthven, (1984)] has also been used to predict co-adsorption effects.

The model used in this work assumes the simplest case of linear independent isotherms, (equations 3.1 and 3.2). For the pressures and temperatures considered the pure gas oxygen and nitrogen isotherms are well approximated by straight lines, (figure 1.2). (The oxygen isotherms are better approximated by straight lines than the nitrogen isotherms). Improving the fit to the equilibrium data by using, say Langmuir isotherms, would have prevented Kirkby's model from being developed in the simple way described in section 3.2.

3.6.4 Mass Transfer

According to LeVan, (1988), five mechanisms are associated with the spreading of a concentration wave in a fixed bed, namely; axial dispersion, external mass transfer, pore diffusion, surface diffusion and reaction kinetics.

Transport rates have almost exclusively been modelled using diffusion theories based on Fick's Law.

\[ J = - D \frac{\delta C}{\delta x} \]  

(3.23)

(The true driving force for mass transfer is the chemical potential, but it is more convenient to use differences in concentrations).

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In PSA modelling rigorous solutions to diffusion equations are possible, but the normal approach has been to use an overall mass transfer coefficient, \( K_G \), and assume a linear driving force (LDF) between the bulk gas and the adsorbed phase.

LDF gives,
\[
\frac{\delta C_A}{\delta t} = K_G a (C_A^* - C_A)
\]

(3.24)

where \( C_A^* = C_{A0} + K_{ApA} \), the gas phase concentration in equilibrium with the adsorbed phase.

One approach to obtain the the overall mass transfer coefficient is to use a combined resistance theory, accounting for both film resistances and resistances through the particle.

\[
\frac{1}{K_G} = \frac{1}{K_g'} + \frac{1}{K_g''}
\]

(3.25)

where \( K_G \) = the overall mass transfer coefficient,
\( K_g' \) = the film mass transfer coefficient (Whitman film theory)
and \( K_g'' \) = the mass transfer coefficient for resistance in the particle (Gleuckauf theory).

PSA is dynamic and a constant concentration gradient is not always maintained while molecules move between the adsorbed and gas phases. Nakao and Suzuki (1983) showed that the mass transfer rate was dependent on the cycle times used and suggested empirical cyclic correction factors to the mass transfer coefficients.

The main limitation of the ILE model stem from its assumption of infinite mass transfer rates. Although at equilibrium more nitrogen is adsorbed on the 5A zeolite than oxygen, the rate of adsorption of oxygen is faster than that of nitrogen. Neglecting mass transfer effects is probably the main single reason why the ILE model over predicted product...
concentrations, [Kirkby, (1984)]. Liow's model (see section 3.6.3) accounted for mass transfer resistances in the particles, but not film mass transfer resistances between the bulk gas phase and the particle. Liow compared Kirkby's model with his own for simple, purge and backfill cycles. His model improved on Kirkby's qualitative and quantitative agreement with experimental results and Liow claims his model required moderate computer resources. Unfortunately neither Kirkby nor Liow give typical CPU times for their models, so the computational penalty of adding mass transfer resistances, axial dispersion (section 3.6.5) and co-adsorption effects to the assumptions made in the ILE model can not be assessed.

Many models that account for mass transfer consider kinetically controlled systems, for which accurate representation of the mass transfer resistances is more important. Most of these models assume the mass transfer resistances to be totally diffusion controlled. A notable exception is the work of LaCava et al, (1988). They showed that diffusion alone was inadequate to predict the uptake of some gases on particular CMS. Instead they proposed a mechanism where the molecules had to first surmount an energy barrier on entering the micropore cavity before following the classical Langmuir adsorption rate. A modified Langmuir kinetic expression was found to be a good approximation to their experiments for some conditions.

\[ R_i = P_i k_{a'} (1 - \Theta_i) - k_{d'} \Theta_i \]  

(3.26)

where \( k_{a'} \) and \( k_{d'} \) are related to the activation energies by Arrhenius type equations.

\[ k_{a'} = k_{a0} \exp\left(-\frac{E_{act}}{RT}\right) \quad \text{and} \quad k_{d'} = k_{d0} \exp\left(-\frac{E_{act} + H_{ads}}{RT}\right) \]

Note that at equilibrium \( k_{a'}/k_{d'} = b = k_a/k_d \) so consistency with the Langmuir isotherm is maintained.
3.6.5 Flow Properties

There is an abundance of theories describing flow in packed beds. PSA models generally assume plug flow, axial dispersion may be included, but to date radial dispersion is neglected.

A general mass balance over an element in the bed produces,

\[
\text{INPUT} = \text{OUTPUT} + \text{ACCUMULATION} + \text{ADSORBED} + \left[ \begin{array}{c}
\text{DISPERSION} \\
\text{TERM}
\end{array} \right]
\]

Having defined an ideal gas system, equilibria relationships, and mass transfer equations, the above mass balance may be developed.

The ILE model does not account for axial dispersion which again contributes to the over prediction of product concentration. Including dispersion terms makes the concentration fronts less sharp so lower product concentrations would be predicted.

3.6.6 Temperature

Relatively few PSA models include an energy balance in their solution, but as equilibria and mass transfer coefficients are often heavily temperature dependent this is likely to change.

The inclusion of an energy balance is more important for large plants where the greatest temperature variations (up to 100 K) are observed, (see section 2.4.2). For this project where moderate temperature variations occurred (25 K) there were no obvious trends in plant performance with changing process temperatures, (appendix 5). However, figure 1.2 illustrates the large temperature dependence for the oxygen and nitrogen pure gas equilibrium loadings on the 5A zeolite used experimentally in this work. So over a limited range of temperatures the benefit of decreasing temperature (greater adsorbent capacity) may be approximately balanced by the benefit of increasing temperature (faster mass transfer).
A typical heat balance would include the following terms.

\[
\begin{align*}
\text{ACCUMULATION IN ELEMENT} \Delta z &= \text{HEAT CAPACITY} \\
&= \text{GAS OUT} - \text{GAS IN} - \text{ENERGY OF EXPANSION OR COMPRESSION} \\
&+ \text{HEAT OF ADSORPTION} - \text{HEAT EXCHANGE WITH THE ENVIRONMENT}
\end{align*}
\]

Those PSA models that do include energy balances make further simplifications, for example they may assume a constant specific heat capacity for the particles, neglected temperature gradients in the particles or between the particles and the gas phase and assumes no radial gradients in the beds. No PSA model as yet includes the heat effects due to expansion and compression, [Psaras et al, (1988)]. For many PSA processes, including air separation with a 5A zeolite where the heats of adsorption are high, this term is relatively small and could reasonably be neglected. Indeed, in appendix 5, evidence is presented that the temperature variations observed in the beds during the experimental work presented in chapter 5, were caused mainly by adsorption and desorption rather than the pressure changes.

### 3.6.7 Momentum and Pressure Drop

For many systems it is reasonable to assume the bed pressures are functions of time only, (see for example section 5.9.4). Where pressure drops in the bed are accounted for, they are described by a number of theories including Darcy's Law, Ergun, Carman-Kozeny and Blake-Kozeny equations, [Bird, Stewart & Lightfoot, (1960)].

Realistically the gas superficial velocities are far from constant over each process step and so a momentum balance, as well as mass and
energy balances, is needed to accurately describe the processes. Although equations such as the Ergun equation are steady state momentum balances, they apply to flow around non porous, non adsorbing particles. No PSA model includes a complete momentum balance and problems such as the calculation of drag coefficients in transient flows have yet to be solved.

3.6.8 Process Assumptions

In addition to the relationships discussed above there are many other constraints and assumptions placed on PSA models which depend on the individual systems. Some of these are listed below.

1. The pressure profiles during the pressure changing steps are normally taken as linear, but an exponential decay has been used for depressurization. Very few models account for the valve characteristics.

2. Other simplifying assumptions regarding pressure are often made. For example, models consider the bed pressure to be constant during the purge and product release steps.

3. Perfect mixing of all regeneration and equalization gas is assumed.

4. Gas entering the beds is always assumed to be perfectly distributed over the bed cross sectional area.

5. Wall effects on flow and temperature are normally ignored.

6. The voidages at the ends of the beds are neglected.

7. Constant ambient conditions are assumed.

8. The models generally use average process flow rates over the different cycle steps.

9. The adsorbent is considered to be uniformly distributed in the bed.

10. Each adsorbent particle is assumed identical. The particles are treated as spheres and variations in particle size are ignored.
11. The models often have simplifying assumptions regarding the composition of the feed gas. For example, impurities in the feed are generally neglected.

12. All models assume complete symmetry for the plant operation.

3.7 Conclusions

The simplicity, availability and proven record of comparison with experimental results all made the ILE model suitable for use in this project. Novel waste recycling modes and the direct purge option were both successfully added to the model and the simulation results are presented in chapter 6. Although most commercial PSA processes include cycle steps which transfer variable composition gas from one bed to another, this is the first attempt to include transfer of variable composition gas between beds in a PSA model. The model has now been developed to a stage where it can already simulate a wide range of process cycles, and where the addition of new steps such as BPE should be easier, (chapter 7).

Many recent models account for mass and heat transfer effects, and they give improved agreements with experimental results compared to the ILE model, but at the cost of additional computer resources. As computers improve, further algorithms are developed and more experimental data becomes available, these complicated models will become more practical.
CHAPTER 4

EXPERIMENTAL APPARATUS

AND

PLANT PERFORMANCE REVIEW

4.1 Introduction

This chapter describes the apparatus used to obtain the experimental results presented in chapter 5.

The first stages of this project required the design, equipment selection and construction of a PSA plant to separate oxygen from air. In common with many industrial and most experimental research plants the design was based on a two bed process, using a 5A zeolite and operating a superatmospheric cycle. Other requirements were that the plant should have the flexibility to incorporate novel waste recycle modes into conventional cycles and a high degree of instrumentation and automation to enable the main process temperatures, pressures, flow rates and compositions to be continually monitored. All the equipment, including the compressor, was selected to be compatible with oxygen enriched environments and safe with pressures up to 120 psig, (928 kPa).

This chapter describes the plant design and the computer system used for data logging and control. It also assesses the overall plant performance. The information presented here is supplemented by appendix 3, which includes detailed specifications on the items of equipment, plant performance data, calibration procedures and further aspects regarding the plant construction and commissioning stages.
4.2 Plant Description

The plant description is split up into the following sections; feed line, adsorber beds, product line, regeneration lines, waste line and waste recycle line. These sections are now discussed with reference to figure 4.1.

4.2.1 Feed Line

Air entered the plant through a filter and two inch check valve (CV1). (The check valve was required for when the plant was recycling the waste stream and gas of different compositions to air could enter the suction line of the compressor). The feed gas was then compressed to 100 psig (780 kPa) using an oil free, air cooled, reciprocating compressor. (The compressor was remotely located to reduce the noise level in the main laboratory). The compressed gas passed into the feed reservoir and subsequently a refrigerant drier and filter arrangement, which delivered gas saturated in water vapour at 275 K. The gas then passed through a pressure regulator (PR1), a mass flowmeter, a diaphragm valve (DV2) and unlagged pipework before entering the adsorber beds at near ambient temperature. The pressure regulator was used to control the upper bed operating pressure and the diaphragm valve was used to alter the feed rate. A relief valve (PR2) was placed after the refrigerant drier so that in normal operation the compressor discharge pressure would be controlled at 100 psig. Any pressurized gas not required by the adsorber beds was recycled into the compressor suction line. Again, this was necessary to ensure a closed loop for the waste recycling case.

4.2.2 Adsorber Beds

Two adsorber beds 1 m long with internal diameters of 0.1 m were used. Initially each bed was filled with 5.77 kg of 1-2.5 mm particles of Bayer 5A zeolite. However, under these conditions the plant
performance was observed to deteriorate steadily. This was traced to water contamination of the zeolite, see section 4.4.1, and resulted in the beds having to be refilled. As the refrigerant drier alone had proved inadequate in removing water from the feed, 0.7 kg of 3 mm alumina particles was used to fill the bottom 0.1 m of each bed. The remainder of each bed was then filled with 5.04 kg of fresh zeolite of the same type. The adsorbent properties are summarized in table 4.1.

The adsorbents were secured in the beds by end plates, which consisted of fine gauze mesh secured to a brass ring around which was fitted an O-ring to produce a tight fit onto the vessel walls. Similar fittings were used to separate the alumina and zeolite sections in the beds. The top and bottom 0.0025 m of each bed represented excess gas volume of $3.93 \times 10^{-4}$ m$^3$ per bed. The total excess gas volume in the pipework surrounding the beds was estimated at $4.5 \times 10^{-4}$ m$^3$.

The beds were constructed with welded flanged ends. Two 1/4 inch (6.35 mm) fittings were added half way along the beds and they were normally connected to the pressure transducers. Five other 1/4 inch fittings were placed along each bed profile. They were added before the beds were hydraulically pressure tested, so that, if required, gas samples could be taken easily from different positions along the beds. These ports also enabled thermocouples to be fitted along one of the beds. The main dimensions and arrangement of fittings on the beds are shown in figure 4.2, and figure 4.3 shows the pipework layout around the beds.

4.2.3 Product line

Product gas was taken from the top of the beds and fed through a solenoid valve (SV5) into a product reservoir in which the pressure was regulated, (PR3). The solenoid valve controlled the product release step for those cycles which did not have continuous product release. It was
also used to restrict the product flow during initial cycles after start up, which had the benefit of reducing the number of cycles required to achieve steady state.

The mixed product gas leaving the product reservoir passed through a mass flowmeter before a sample was diverted through an oxygen analyser and the remainder was vented into an extractor duct. The reservoir pressure influenced the product flow rate, which was controlled using needle valves positioned after the reservoir, (NV1 & NV2).

4.2.4 Regeneration Lines

In normal operation the purge and backfill gases were supplied directly from the product stream leaving the top of the adjacent bed, (through NV3). This meant the regeneration gas used was of variable composition. Separate lines were used for the purge and backfill supplies, so that in combined cycles different regeneration gas flow rates were possible. The amount of regeneration gas to each bed, measured with a mass flowmeter, could be separately controlled using the needle valves installed on each line, (NV4, 5, 6 & 7). These were generally used to ensure symmetrical operation, but they also enabled some unsymmetrical purge cycle experiments to be conducted.

Towards the end of the experimental work the plant was modified, so that the regeneration gas could be supplied either directly from the adjacent bed, as before, or from the product reservoir, (through NV9). Some purge cycles were investigated to see which would be the more favourable source of purge gas. Figure 4.4 shows the piping arrangement at the top of the beds.
4.2.5 Waste Line

The normal path for waste gas was to leave the beds, enter the waste reservoir, and then pass through a mass flowmeter before entering the extractor duct. The rate of depressurization and the shape of the depressurization profiles could be altered by manipulating the diaphragm valves that were positioned on each side of the waste reservoir, (DV1 & DV3).

As the waste gas left the bottom of the beds a small fraction of it could be diverted through NV8 and an oxygen analyser. If the oxygen concentration in this stream was observed to be sufficiently high, such that it would be dangerous to recycle the gas to the compressor suction line, then SV10a would shut and SV10b would open. This action diverted the waste gas directly into the extractor duct. (SV10a and SV10b were wired in series with SV10a normally closed and SV10b normally open). The alternative waste gas route through SV10b could be used where rapid depressurization was required and it added to the plant flexibility by allowing different depressurization profiles to be investigated.

4.2.6 Waste Recycle Line

If the waste gas produced during either the depressurization or the purge step was to be recycled back into the feed line then the solenoid valves SV8 and SV9 would operate to close the normal waste path and divert the waste gas into the compressor suction line. By manipulating these solenoid valves the waste gas could be selectively recycled. The regulator in the recycle line (PR4) ensured that pressures above 2 psig (13.8 kPa) did not form in the compressor suction line. For some experiments the mass flowmeter on the net waste line was transferred to the waste recycle line.
Figure 4.1 Flow Diagram of the PSA Research Plant

- AIR INLET
- FILTER
- COMpressor
- FEED RESERVOIR
- DRIER
- MASTeR RESERVOIR
- MASTeR ANALYSER
- PRODUCT RESERVOIR
- PRODUCT ANALYSER
- OXYGEN PRODUCT
- BACKFILL LINES
- PRESSURE REGULATOR
- SOLENOID VALVE
- NEEDLE VALVE
- PRESSURE GAUGE
- MASS FLOWMETER
- THERMOCOUPLE
- PRESSURE TRANSFER
- PIPING
- CHECK VALVE

KEY:
- TT THERMOCOUPLE
- PT PRESSURE TRANSFER
- XXX MASS FLOWMETER
- PI PRESSURE REGULATOR
- GX NEEDLE VALVE
- DV DIACRAGM
- CHECK VALVE

FLOW PATHS:
- AIR INLET
- FILTER
- COMpressor
- FEED RESERVOIR
- DRIER
- MASTeR RESERVOIR
- MASTeR ANALYSER
- PRODUCT RESERVOIR
- PRODUCT ANALYSER
- OXYGEN PRODUCT
- BACKFILL LINES
- PRESSURE REGULATOR
- SOLENOID VALVE
- NEEDLE VALVE
- PRESSURE GAUGE
- MASS FLOWMETER
- THERMOCOUPLE
- PRESSURE TRANSFER
- PIPING
- CHECK VALVE
Figure 4.2  Diagram of an Adsorber Bed Showing the Positions of the Thermocouples along the Bed Profile

TT  THERMOCOUPLE
PT  PRESSURE TRANSDUCER
PI  PRESSURE GAUGE

PRODUCT STREAM

BED WALL

THERMOCOUPLE
GLOBE VALVE

alumina section

All dimensions in metres
Figure 4.3 Diagram of the Adsorber Beds and Surrounding Pipework
Figure 4.4 Diagram of the Pipework at the Top of the Beds

This diagram shows the separate lines used to supply the purge and backfill gas. It also illustrates the symmetry of the pipework at the top of the beds. As all the regeneration gas was supplied through the mass flowmeter shown below the purge and backfill amounts to each bed were recorded for each cycle. The manual valves on the purge and backfill lines were normally used to ensure symmetrical operation, but manipulating them allowed some unsymmetrical cycles to be investigated, (see section 5.9).
Table 4.1 Properties of the Adsorbents

1. Zeolite

Type 5A Bayer KEB054

Data supplied by Bayer, [Liow, (1986)]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, kg m(^{-3})</td>
<td>650</td>
</tr>
<tr>
<td>Bead density (Hg method at 100 kPa), kg m(^{-3})</td>
<td>1000</td>
</tr>
<tr>
<td>Crystal density (Benzene method at 100 kPa), kg m(^{-3})</td>
<td>1639</td>
</tr>
<tr>
<td>Solid density (Water method at 100 kPa), kg m(^{-3})</td>
<td>2534</td>
</tr>
<tr>
<td>Interparticle volume, m(^{3}) kg(^{-1})</td>
<td>0.526 x 10(^{-3})</td>
</tr>
<tr>
<td>Macropore volume, m(^{3}) kg(^{-1})</td>
<td>0.248 x 10(^{-3})</td>
</tr>
<tr>
<td>Micropore volume, m(^{3}) kg(^{-1})</td>
<td>0.225 x 10(^{-3})</td>
</tr>
<tr>
<td>Macropore porosity</td>
<td>0.29</td>
</tr>
<tr>
<td>Micropore porosity</td>
<td>0.25</td>
</tr>
<tr>
<td>Pore size (Mercury porosimetry), Angstrom</td>
<td>7980</td>
</tr>
</tbody>
</table>

Properties specific to this project

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size range, mm</td>
<td>1.0 - 2.7</td>
</tr>
<tr>
<td>Average particle size, mm</td>
<td>1.7</td>
</tr>
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</table>

2. Alumina

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size, mm</td>
<td>3.0</td>
</tr>
<tr>
<td>Bulk density, kg m(^{-3})</td>
<td>891</td>
</tr>
</tbody>
</table>

Additional Comments

i) Prior to filling the sieve lost less than 2% by weight when heated at a constant rate of about 50 K min\(^{-1}\) to 673 K.

ii) The presence on alumina in the bed has a negligible effect on the oxygen/nitrogen separation, [Bush, (1988)].

4.3 Control and Instrumentation

4.3.1 Instrumentation

The plant had two oxygen analysers, two pressure transducers, four mass flowmeters and twelve thermocouples. It also had twelve solenoid valves which were sequenced in time with the required cycle steps. The normal positions for these items on the plant are shown on figure 4.1. The specifications and calibration procedures for the instruments are discussed in appendix 3.
4.3.2 Computer Hardware

All the data logging and control for the plant was done from an IBM PC/AT. Figure 4.5 illustrates how it was integrated with the instrumentation and other items of computer hardware. The thermocouples were interfaced to an Amplicon A/D board which automatically performed cold end compensation calculations. The mass flowmeters, oxygen analysers and pressure transducers were interfaced to a Data Translation A/D board, which also sent the digital outputs to the solenoid valves and compressor.

During experiments, data could be sent to a printer, stored on disk, or both. Between experiments data could be transferred to the University of Surrey Prime Computer System, where it was analysed and plotted.

4.3.3 Computer Software

All the valve sequencing, safety checks, steady state checks and data logging were done within a single program using the IBM PC/AT. The software was written in Basic using a Microsoft Quickbasic Compiler, (version 2.0).

The advantage of having a single program which did all the data logging and control was that when the plant was observed to have reached steady state the required data could be recorded and the program could automatically alter the step times. This allowed continuous operation while assessing many different cycles and with minimum disturbance to the plant. At the end of each cycle the program calculated the average process temperatures and compositions, and produced a mass balance for each bed and every step in the cycle. The steady state bed temperature and pressure profiles were also recorded.

Several cycles were investigated, with and without various modes of waste recycling. The maximum memory was exceeded using the Microsoft
Quickbasic Compiler, so two programs were necessary to cover all the cycle options. Listings of these programs (PSA1.BAS and PSA2.BAS) are given on the enclosed microfiches. The program PSA1.BAS covered all the cycles investigated other than those for bulk waste recycling (section 3.5.1) for which PSA2.BAS was used. The programming logic for all cycles was the same and is summarized in figure 4.6.

4.3.3.1 Safety Checks

When recycling waste gas back into the feed line the oxygen concentration in the waste gas was monitored. If greater than 50% oxygen was detected the compressor would automatically shut down, and the solenoid valves would stop sequencing in such a manner that the adsorber beds would depressurize directly into the extractor duct.

As the plant ran unattended for many hours several checks were made to ensure that the main process flow rates and temperatures were within reasonable ranges. In the event of an abnormal reading, for example too high a compressor discharge temperature, the compressor would be automatically stopped and a controlled shut down initiated.

4.3.3.2 Mass Balance

The program almost continually scanned all the analogue inputs, the main interruptions occurring when the solenoid valves were being sequenced. The trapezium rule was used to calculate the amount of gas that passed each flowmeter for each cycle step. At the end of the cycles the overall mass balance to each bed was updated. (The time taken for one complete scan of all the analog inputs was approximately 0.8 s)

4.3.3.3 Steady State

PSA processes are dynamic, but they are said to have reached steady state, when within given limits successive cycles are identical.

The accumulation in the overall mass balance and the average
product oxygen concentration, which were calculated after each cycle, were used to check if the plant had reached steady state. The average product concentration was found to be the most effective parameter. In general, a minimum of 20 cycles was required before steady state was checked, and thereafter, if the average product concentration was constant to within 0.1% for five successive cycles and the mass balance accumulation was also constant to within 0.002 m³ (2 litres) at STP per cycle, then the plant was assumed to have reached steady state. Alternatively, an option was available so that if the plant did not satisfy these rules in an entered number of cycles (say 500) then steady state would be assumed.

Options for changing the steady state criteria were entered on initiating the programs. The programs would recognize that steady state had been achieved and would automatically save and print out the mass balance data, and the bed temperature and pressure profiles. All the cycles had to satisfy these criteria twice, before automatically proceeding to the next cycle configuration.

4.3.3.4 Automatic Operation of Successive Cycles

The plant could run automatically a number of different cycles by manipulating the times for the different cycle steps. However, there was no automatic way of altering the process flow rates, so the program generally required to be interrupted once every 1 to 2 days to manually adjust flow rates. If required the program could compare the performance of successive cycles and drive the plant towards an optimum operating position. For example, for purge cycles (section 5.4), the plant could automatically adjust the purge amount per part cycle for a fixed product amount per part cycle, until optimum operating conditions were achieved. The ability to remotely manipulate the flow rates using flow control valves would have made this a very powerful research tool indeed.
Figure 4.5  Block Diagram of the Instruments and Computer System

Both boards were accessed from a single program written in Basic using a Microsoft Quickbasic Compiler.

The built in timer was used for the valve sequencing.

PROGRAM FUNCTIONS

1. valve sequencing
2. data logging
3. steady state checks
4. safety checks
5. cycle optimization

This system was used for the theoretical modelling.
Figure 4.6 Functional Block Diagram for the Operating Programs

START

Input data for initial & subsequent automatic cycles

Initialize counters, timers arrays & constants

START new cycle

START new cycle step

Log data, safety checks & update the mass balance

Is the cycle finished?

Yes

Output the mass balance & average temperatures and compositions for the cycle.

No

Does the plant satisfy the steady state criteria?

Yes

Save & print cycle data

No

Is this the second time steady state has been satisfied?

Yes

Is a different cycle to be investigated automatically?

No

Should the plant be stopped?

Yes

Stop the compressor & isolate the beds

STOP

No

Continue cycling but with limited data logging

Program must be stopped manually

No

reset counters arrays, timers & constants

Yes

see options on next page

see data collection on next page
Figure 4.6 continued

1. Cycle options

Select the required cycle from menu

Input options for when steady state has been achieved
1. stop plant
2. continue cycling with less data collection
3. start a different cycle
at which stage all initial variables may be changed

Input 1. step times
2. steady state criteria
3. Ex No., date, etc.
4. No. of cycles before taking product from plant.

2. Data collection

Start new cycle step

Log analog values & update screen

Is the plant stable & operating safely ?

Yes

Update mass balance, average temperatures & compositions

Print fault & cycle data

No

Is there time for another analog scan ?

Yes

Round of step calculations

Shut down plant in appropriate manner

No

Is it time for the next step ?

Yes

Is the cycle finished ?

Continued on previous page
4.4 Plant Performance Review

4.4.1 Water Contamination

The plant was run initially without the alumina sections in the bottom of the beds, (section 4.2.2). This resulted in falling product concentrations and zeolite capacities for air. After this observation, samples of zeolite were taken from the beds and heated at a constant rate to 673 K and the weight loss was observed to be between 3 and 10 %. This confirmed that water had significantly contaminated the zeolite, that the beds would have to be refilled and that further drying of the feed air would be required. (Data illustrating these points is included in appendix 3, section A3.4).

After the alumina sections were added to the beds no further loss in performance was observed, (table A3.3). The alumina sections acted as a PSA drier, reducing the amount of water in the zeolite. For different cycles it is likely that the amount of water in the zeolite reaches a steady state and the alumina sections significantly decreased this residual amount of water.

For similar cycles producing the same oxygen concentration the amount of product removed from the plant per kg of zeolite was found to be marginally better after the beds had been refilled with alumina and zeolite. This showed that the alumina had a negligible effect on the oxygen nitrogen separation.

4.4.2 Particle Attrition

Care was taken when filling the beds to expel most of the dust produced. However, after many hours of operation a small amount of dust was collected on the filter protecting the mass flowmeter on the waste line. The relatively slow pressurization and depressurization rates resulted in no further observable dust formation.
The beds were not emptied after the alumina sections were added, but the observation that the performance did not deteriorate suggests that both the alumina and zeolite sections had not significantly deteriorated.

4.4.3 Equipment Reliability and Maintenance

The plant required very little routine maintenance other than the occasional cleaning of the air, water and compressor breather filters. Given the relative complexity some routine stoppages were required, to calibrate instruments and check that gas leaks had not developed.

With the exception of one failure, when the seal on a compressor piston disintegrated requiring the compressor to be replaced, all other equipment problems were of a minor nature.

Although the equipment proved satisfactory, several lessons and recommendations regarding both the plant design and the equipment selected are discussed in chapter 7.

4.5 Further Comments

During these experiments the plant ran for approximately 4100 hours, which for the normal cycle time used of 3 minutes, corresponds to 82,000 cycles. The analogue values were scanned every 0.7 seconds and each solenoid valve changed position up to 5 times per cycle. Given this record the plant was shown to be fairly reliable, and some very interesting and novel experimental results were obtained.
CHAPTER 5

EXPERIMENTAL METHODS AND RESULTS

5.1 Introduction

5.1.1 Experimental Aims

The main aims were to measure the product oxygen concentration and oxygen yield (defined in chapter 1) over a range of product amounts per part cycle for both conventional and novel process cycles. The novel cycles involved selectively recycling waste gas produced during the purge and depressurization steps back into the feed line. Computer simulations (chapter 6) on waste recycling showed that it could simultaneously increase the product oxygen concentration and yield, while reducing the oxygen content of the net waste gas.

Other aims were to produce an extensive range of experimental data for comparison with Kirkby’s ILE model and thereby to improve the understanding of the individual steps in PSA cycles.

The degrees of freedom in PSA processes were discussed in section 2.4. Of the operating variables, the ambient temperature, adsorbent type, particle size, feed composition and vessel dimensions cannot be manipulated easily. However, there still remains a number of independent operating variables such as the process pressures, flow rates and step times which can be altered at will and their importance to the performance of the cycles was considered in this project.
5.1.2 Process Cycles Investigated

The following process cycles, illustrated in figure 5.1, were investigated in the order shown below:

1. simple cycles,
2. purge cycles,
3. purge cycles with purge waste recycling, (Purge Snatching) *
4. backfill cycles,
5. combined purge with backfill cycles, and
6. purge cycles with purge and depressurization waste gas recycling, (Bulk Waste Recycling). *

* Purge snatching and bulk waste recycling were the novel methods used for selectively recycling the waste gas produced during depressurization and purge back into the feed line. Theories to describe these methods were discussed in section 3.5.

Some more detailed studies of certain cycles have also been conducted. For example, each time the plant reached steady state the bed temperature and pressure profiles were recorded. Typical pressure profiles are presented in sections 5.3 to 5.8 as the results from each cycle are discussed. The temperature effects, including sample bed temperature profiles, are reviewed separately in appendix 5.

Given the scope for research in PSA, the flexibility of the plant and its high degree of instrumentation there were many options for further studies on specific cycles. The eventual path chosen depended largely on the outcome of the initial cycle comparisons, but other options that were taken are now listed.

1. The effect of changing the shape of the depressurization profiles was investigated for purge cycles, (section 5.9).
2. The plant performance was examined for unsymmetrical operation of purge cycles, (section 5.9).

3. A comparison of the plant performance was made when taking purge gas either directly from another bed, or from the product reservoir, (section 5.9).

4. Axial pressure gradients were investigated for a range of pressurization and depressurization rates, (section 5.9).

5. A comparison of the plant performance was made with and without the beds and surrounding pipework thermally lagged, (appendix 5).

5.2 General Experimental Techniques

Chapter 4 and appendix 3 described the experimental apparatus and explained how many of the operating variables could be altered. They also described how the main process temperatures, pressures, flow rates and concentrations were measured.

5.2.1 Normal Operating Conditions

Unless otherwise stated all the experimental cycles were investigated with the following constant operating variables.

<table>
<thead>
<tr>
<th>Operating Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Operating Pressure (LOP)</td>
<td>2 psig (13.8 kPa)</td>
</tr>
<tr>
<td>Upper Operating Pressure (UOP)</td>
<td>60 psig (508 kPa)</td>
</tr>
<tr>
<td>Part Cycle Time</td>
<td>90 s</td>
</tr>
<tr>
<td>Average Pressurization Rate</td>
<td>2 psi s⁻¹ (13.8 kPa s⁻¹)</td>
</tr>
<tr>
<td>Average Depressurization Rate</td>
<td>2 psi s⁻¹ (13.8 kPa s⁻¹)</td>
</tr>
</tbody>
</table>

All the experiments described in this chapter, with the exception of the simple cycles were performed with each adsorber bed containing 5.04 kg of zeolite and 0.7 kg of alumina. For the simple cycle experiments no alumina was used but instead each bed contained 5.77 kg of zeolite. The reasons for modifying the plant to include the alumina sections are given in chapter 4.
Apart from the experiments that investigated different purge sources (section 5.9), all the regeneration gas used in the purge and backfill cycles was supplied directly from the top of the pressurized bed, and was therefore of variable composition.

The amount of gas entering and leaving each bed was monitored and if necessary manual valves were used to ensure that in normal running the plant was operated as symmetrically as possible.

5.2.2 Automatic Operation

The process flow rates could be altered using manual valves only, as described in section 4.2. To enable the plant to investigate automatically a number of different cycles a null step (or delay) was included in many of the cycles, (figure 5.1). The null step allows variables to be changed independently where in a commercial cycle they would normally be coupled. For example, including the null step in the purge cycle (figure 5.1b) uncoupled the purge amount and the purge flow rate. The null step was introduced directly after depressurization and involved the bed being isolated at both top and bottom. The null step time could be altered automatically as other step times were changed, so that single specific variables could be investigated while keeping all other variables including the part cycle time constant. The sequencing of the solenoid valves for the different cycles and steps studied is discussed in chapter 4.

The null step was positioned after depressurization to minimize its influence on the cycle performance. It was thought that when a bed depressurized, the concentration fronts within it would be destroyed, (see appendix 5). Other than altering the cycle times, the effect of including a null step was thought to be negligible, because the pressure in the depressurized bed increased at less than 0.03 psi s\(^{-1}\) indicating that very little further desorption occurs.
Figure 5.1 Experimental Cycles

DP = Depressurization  PR = Pressurization
PD = Product Release  NU = Null
PU = Purge  BF = Backfill
PS = Purge Snatching  WR = Bulk Waste Recycling

Figure 5.1a Simple Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>DP</th>
<th>NU</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PD</td>
<td></td>
<td></td>
<td>PD</td>
</tr>
</tbody>
</table>

Figure 5.1b Purge Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>DP</th>
<th>NU</th>
<th>PU</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PD</td>
<td></td>
<td></td>
<td></td>
<td>PD</td>
</tr>
</tbody>
</table>

Figure 5.1c Purge Snatching Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>DP</th>
<th>NU</th>
<th>PU</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td>PS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PD</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Figure 5.1d Backfill Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>DP</th>
<th>NU</th>
<th>BF</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PD</td>
<td></td>
<td></td>
<td></td>
<td>PD</td>
</tr>
</tbody>
</table>

Figure 5.1e Purge and Backfill Combined Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>DP</th>
<th>NU</th>
<th>PU</th>
<th>BF</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PD</td>
</tr>
</tbody>
</table>

Figure 5.1f Bulk Waste Recycle Cycle

<table>
<thead>
<tr>
<th>Bed</th>
<th>WR</th>
<th>DP</th>
<th>NU</th>
<th>PS</th>
<th>PR</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>PR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PD</td>
</tr>
</tbody>
</table>

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5.3 Simple Cycle Experiments

5.3.1 Introduction

The aim of these experiments was to assess some of the variables common to all the cycles investigated in this project. Simple cycles are of limited commercial significances in air separation as they are unable to produce the high oxygen concentrations (> 90%) which are normally required.

The simple cycles have the least number of degrees of freedom of the cycles investigated and as a base case were used to investigate the effects of changing the UOP, the cycle time and the rates of pressure change. Results from these experiments helped select the values of the variables that were fixed when the other process cycles were compared, (sections 5.4 to 5.8).

5.3.2 Methods

The simple cycle is described in figure 5.1a and table A4.1, in appendix 4, summarizes the cycle conditions for each experiment and also contains data obtained at steady state for the mass balances and average process variables.

The pressurization rate was altered using diaphragm valve DV2 and the depressurization rate was altered using DV1 and DV3, (see figure 4.1). The UOP was fixed using the pressure regulator on the feed line, (PR1) and the product flow rate was controlled using needle valves NV1 or NV2.

5.3.3 Simple Cycle Experiments

Ex1 For a fixed product amount the pressurization and depressurization rates were varied together. Equal pressurization and depressurization rates were used.

Ex2 For a fixed product amount the pressurization rate only was varied.
Ex3 For a fixed product amount the depressurization rate only was varied.

Ex4 For a fixed product amount the UOP was varied. The pressurization and depressurization rates were kept constant.

Ex5 The pressurization and depressurization rates, cycle time and UOP were kept constant while varying the product amount by changing the product release flow rate.

Ex6 The pressurization and depressurization rates and the UOP were kept constant, but a null step of between 0 and 100 seconds was introduced immediately after the depressurization so that the product amount per part cycle could be varied at fixed product flow rates.

5.3.4 Experimental Results

5.3.4.1 Pressurization and Depressurization Rates (Experiments 1 to 3)

Figure 5.2 shows a typical pressure-time profile for one simple cycle and illustrates the non-linearity of the pressure changes. Small changes in the LOP had significant effects on the plant performance. Hence, although during depressurization most of the gas left the bed in the first few seconds of the step, it was important to allow sufficient time for the bed pressure to approach atmospheric pressure.

Results shown in figures 5.3 and 5.4 suggested that it was advantageous to have a rapid depressurization, but for each cycle there appeared to be an optimum pressurization rate, (figure 5.5).
FIG 5.2 A Typical Simple Cycle Bed Pressure Profile

See Table A1.1, Ex 1 for cycle data

Figure 5.3 Vary PRESS & DEPRES Rates Simultaneously
Figure 5.4  Vary DEPRES Rate only for Simple Cycle

See Table A1.1, Ex 3 for cycle data

Figure 5.5  Vary PRESS Rate Only for Simple Cycle

See Table A1.1, Ex 2 for cycle data
DPT = 60 s
DPT = 10 s
5.3.4.2 The Upper Operating Pressure, (Experiment 4).

It was demonstrated that for air separation on this zeolite there is little advantage in using an UOP above 60 psig, (figure 5.6). This observation is consistent with the shape of the nitrogen gas isotherms, (figure 1.2). There were some advantages to the oxygen yield of operating at higher pressures, but these are likely to be offset against the additional compression costs. For example, table A4.1 shows that for 10 litres product per cycle, increasing the UOP from 60 to 80 psig only improved the oxygen yield from 27.4 % to 27.8 %, but the feed gas increased from 228 to 299 litres per cycle. (All amounts of gas in this chapter are given in litres at S.T.P. and 1 litre equals $1 \times 10^{-3}$ m$^3$).

Figure 5.6 Varying the UOP with Constant Pressure Changing Rates for Simple Cycles

![Graph showing varying UOP with oxygen concentration and flow rate](image-url)
5.3.4.3 Varying the Product Flow Rate and Product Amount Per Part Cycle, (Experiments 5 and 6)

Figure 5.7 shows the results of increasing the product flow rate for a given simple cycle. At very low flow rates, in this case less than 0.2 litres per second, changes in flow rate had little effect on product concentration. For higher product flow rates there was a steady decline in product concentration with increased flow rate. The average oxygen concentrations for the additional product removed between points on figure 5.7 (marginal oxygen concentrations) show that, for the cycle considered, increasing the product flow rate beyond 140 litres per cycle effectively resulted in air being added to the product.

If \( P \) litres of product are removed at an oxygen concentration of \( y \) and \((P + 5P)\) litres of product are removed with an oxygen concentration of \((y + 6y)\), then the marginal oxygen concentration \( y_m \) is calculated from the relationship shown below.

\[
\frac{Py + 5Py_m}{P + 5P} = y + 6y
\]

The effect of changing the product amount per part cycle is shown in figure 5.8. The shape of the graph is similar to figure 5.7 and again the marginal oxygen concentrations showed that removing more than 140 litres per cycle effectively results in air being added to the product.
Figure 5.7  Varying the Product Flow Rate for a Given Simple Cycle

See table A1.1, Ex 5 for cycle data

<table>
<thead>
<tr>
<th>Point</th>
<th>% Oxygen Concentration</th>
<th>Product Amount litres/cycle</th>
<th>Marginal % Oxygen Concentration Between Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>33.3</td>
<td>11.06</td>
<td>A-B 33.01</td>
</tr>
<tr>
<td>B</td>
<td>33.1</td>
<td>35.3</td>
<td>B-C 29.35</td>
</tr>
<tr>
<td>C</td>
<td>31.9</td>
<td>51.9</td>
<td>C-D 26.87</td>
</tr>
<tr>
<td>D</td>
<td>29.5</td>
<td>99.23</td>
<td>D-E 23.43</td>
</tr>
<tr>
<td>E</td>
<td>27.71</td>
<td>140.7</td>
<td>E-F 21.56</td>
</tr>
<tr>
<td>F</td>
<td>26.95</td>
<td>160.56</td>
<td>F-G 20.5</td>
</tr>
<tr>
<td>G</td>
<td>25.5</td>
<td>207.2</td>
<td>G-H 20.5</td>
</tr>
<tr>
<td>H</td>
<td>24.8</td>
<td>241.1</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 5.8 The Effect on the Product Oxygen Concentration of Changing the Product Amount Per Part Cycle

The diagram shows the relationship between the product oxygen concentration and the product amount per part cycle. The table below provides the oxygen concentration, product amount, and marginal concentration between points:

<table>
<thead>
<tr>
<th>Point</th>
<th>% Oxygen Concentration</th>
<th>Product Amount litres/cycle</th>
<th>Marginal % Oxygen Concentration Between Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>33.8</td>
<td>26.6</td>
<td>A-B 30.63</td>
</tr>
<tr>
<td>B</td>
<td>33.0</td>
<td>35.6</td>
<td>B-C 29.18</td>
</tr>
<tr>
<td>C</td>
<td>32.3</td>
<td>43.6</td>
<td>C-D 27.78</td>
</tr>
<tr>
<td>D</td>
<td>31.6</td>
<td>51.6</td>
<td>D-E 26.75</td>
</tr>
<tr>
<td>E</td>
<td>30.8</td>
<td>61.8</td>
<td>E-F 25.11</td>
</tr>
<tr>
<td>F</td>
<td>28.45</td>
<td>105.3</td>
<td>F-G 22.93</td>
</tr>
<tr>
<td>G</td>
<td>27.12</td>
<td>138.7</td>
<td>G-H 21.2</td>
</tr>
<tr>
<td>H</td>
<td>26.0</td>
<td>171.1</td>
<td>H-I 21.9</td>
</tr>
<tr>
<td>I</td>
<td>25.3</td>
<td>206.9</td>
<td>I-J 21.5</td>
</tr>
<tr>
<td>J</td>
<td>24.8</td>
<td>238.6</td>
<td></td>
</tr>
</tbody>
</table>

See Table A1.1, Ex 6 for cycle data.
5.3.5 Discussion

Many of the results presented in this section may be compared with the results of Kirkby (1984) and Liow (1986). They investigated simple cycles using similar plants and the same zeolite type as used in this work. However, Liow and Kirkby used larger adsorbent particles 3 - 5 mm in diameter compared to the 1 - 2.5 mm diameter particles used in this work.

Kirkby investigated the importance of the pressure changing rates and the UOP. He found no detectable effect on the product concentration of varying the average depressurization rate from 0.5 to 3.0 psi s\(^{-1}\). However, in this work increasing the average depressurization rate from 1 to 8 psi s\(^{-1}\) improved the oxygen concentration from 35.5 % to 39.6 % at 4 litres per part cycle product. Most of the improvement occurred between the depressurization rates of 4 and 8 psi s\(^{-1}\) which were not investigated by Kirkby. The effects of changing the pressurization rate were shown both in this work and by Kirkby to vary for different product flow rates, but they were found to be more significant in this work. The variations in performance with changing flow rates show that kinetic as well as equilibrium effects are important for this separation.

The pressure changes were not linear and only the significance of changing the average rates of pressure change may be compared. Figure 5.2, for example, shows that average pressurization and depressurization rates of 2 psi s\(^{-1}\) were used, but for the same cycle the peak depressurization rate was about 10 psi s\(^{-1}\) and the peak pressurization rate was about 4 psi s\(^{-1}\). The performance of some oxygen PSA plants has been improved by using flow controllers on the waste line (section 2.4.3) and this suggests that the shape of the pressure profile can affect the performances of the plants. Given that the plant designs and valve characteristics as well as the operating conditions alter the shape of the pressure profiles this highlights the difficulty in
comparing the experimental results of different workers. The effect of changing the shape of the pressure profiles was investigated for purge cycles, (see section 5.9).

Kirkby compared two upper operating pressures, UOPs, (40 and 60 psig) for different cycles at a constant product flow rate (0.873 litres s^{-1}), but for a wide range of product amounts per part cycle. He found that the cycles with 60 psig UOP consistently produced oxygen concentrations about 1 % above those obtained with the UOP set at 40 psig. In this work UOPs of 20, 40, 60 and 80 psig were investigated at two different product flow rates and the results showed that the importance of the UOP varied for different product flow rates. Figure 5.6 shows that the results obtained at 0.167 litres s^{-1} product are consistent with the finding of Kirkby, while the results obtained at 0.667 litres s^{-1} show no advantage in using an UOP of 60 psig rather that 40 psig.

Liow's simple cycle experiments included an investigation of different cycle configurations. He compared the performance of cycles with the null step positioned after the pressurization, product release or depressurization steps and concluded that that the position of the null step had no obvious effect for simple cycles. Liow states that his simple cycles came to steady state in 6 to 15 cycles which compares with the 10 to 30 cycles required in this work.

Both Kirkby and Liow investigated the effect on product oxygen concentration of increasing the product amount per part cycle and their result show similar trends to those observed in this work with one exception. Liow found that the oxygen concentration increased by 1 - 2 % as the product amount per part cycle was increased from 1 to about 6 litres and then as the product amount was further increased there was a steady decline in oxygen concentration. On no occasion in this work did an increase in product amount result in an improved oxygen
concentration.

The maximum oxygen concentration obtained with a simple cycle in this project was 39.6%. Liow managed to produce 29.3% oxygen using similar sized beds to those in this work and Kirkby produced 36% oxygen with larger beds. Kirkby's beds were not identical and while one of his beds contained 11.9 kg of adsorbent the other contained only 11.4 kg of adsorbent. (For the simple cycles in this work the beds contained 5.77 kg zeolite/bed). Liow and Kirkby did not include alumina sections in their beds and Liow does not disclose the mass of adsorbent per bed for his experiments. This is unfortunate as it means comparisons on the basis of product output per unit mass of adsorbent could not be made.

As oxygen PSA plants are generally required to produce over 90% oxygen an additional step or steps must be included in the cycles to further regenerate the beds.

5.4 Purge Cycle Experiments

5.4.1 Introduction

The main aim of these experiments was to investigate the effect of purge amounts per part cycle and purge flow rate on the oxygen concentration and oxygen yield for a range of product amounts per part cycle.

The optimum purge amount with respect to the oxygen concentration, is the purge amount which gives the highest obtainable oxygen concentration for a fixed product amount per part cycle. Similarly, the optimum purge amount with respect to oxygen yield is that amount which gives the highest obtainable oxygen yield.

More experiments were completed using purge cycles than any other cycle. Most of the results are presented in this section although some miscellaneous purge cycle experiments, such as those that investigated
unsymmetrical plant operation and those that compared supplying the purge from different sources, are included in section 5.9.

5.4.2 Method

The purge cycle used for these experiments is shown in figure 5.1b. All the experiments had a cycle time of 180 s. This was split up into 90 s product release, 30 s each for pressurization and depressurization with a maximum possible 30 s for purge. If less than 30 s was required for purging then a null step was used before the purge step and the sum of the null and purge step times equalled 30 s.

For a typical set of experiments the product and purge flow rates were first fixed manually, (section 4.2). Then the controlling program was set up to operate a number of cycles where the purge time would gradually decrease from 30 to 0 s, in steps of 2, 3 or 5 s, while the null step would be increased from 0 to 30 s in compensation. In this way the effect of changing the purge amount per part cycle for a fixed product amount per part cycle was investigated. (Alternatively, the purge step time could be increased while the null step time was decreased, but this made no difference to the results).

Before looking at many product amounts per part cycle the effect of changing the purge flow rate was investigated. This was done by selecting a fixed product flow rate and repeating the above set of experiments, but for different purge flow rates. Results from these experiments showed that the plant performance deteriorated when the purge flow rate became too large, so suitably low purge flow rates were used for all the remaining experiments.

The oxygen concentration in the waste gas was observed during these experiments to investigate how it might change for different purge amounts.
5.4.3 Results

5.4.3.1 Purge Flow Rate

Figure 5.9 shows that the maximum obtainable oxygen concentration fell with increased purge flow rate, once the purge flow rate exceeded a critical value. This critical value corresponded to an average particle Reynolds number of about 20 for the purge gas in the bed being regenerated. (The calculation of the particle Reynolds number is included in appendix 4). Typically the peak particle Reynolds numbers for the purge gas were a factor of ten greater than the average values.

Two trends were observed when the critical purge flow rate was exceeded: the amount of purge required to produce the maximum obtainable oxygen concentration fell, and the oxygen concentration in the waste gas during purge increased.

Figure 5.9 The Maximum Obtainable Product Oxygen Concentration versus the Average Purge Flow Rate for a Given Purge Cycle
5.4.3.2 Product Yield and Concentration versus the Purge Amount Per Part Cycle

Figure 5.10 presents typical sets of results for three different product amounts per part cycle. It shows that the maximum yield is obtained at lower purge amounts than the maximum concentration. Ten different product amounts per part cycle were investigated and for each of these a minimum of seven different purge amounts per part cycle were used.

From results such as those in figure 5.10, oxygen concentration and yield contour plots were constructed in the purge amount per part cycle and the product amount per part cycle plane, (figures 5.11 & 5.12). These plots show the performance of the cycle for product amounts of 1 to 12 litres per part cycle over a wide range of purge amounts per part cycle. Also plotted is the optimum loci for oxygen concentration and yield at different product amounts per part cycle. The loci diverged as the product amount per part cycle decreased, so that at low product amounts there were significant differences in the amounts of purge required to optimize the oxygen concentration or yield. The optimum purge amount was between 15 to 25 % of the feed amount and the purge to feed ratio increased as the product amount was increased. Both contour plots show how sensitive the plant was to changes in the product amount per part cycle at the low product amounts necessary to produce 90 to 95 % oxygen. Small changes in the purge amount per part cycle for these conditions made little difference to either the oxygen concentration or yield. At higher product amounts per part cycle small changes in the purge amount could make major differences to the oxygen concentration and yield.

The optima loci have been used to plot figure 5.13, which shows the best possible oxygen concentrations and the best possible oxygen yields obtainable using this purge cycle, for a range of product amounts.
per part cycle. Although these best results are not simultaneously achieved they are a good basis for comparing the performances of the purge cycle with other cycles.

Figure 5.10 Typical Sets of Purge Cycle Data at Different Product Amounts Per Part Cycle

See table A4.2, Ex 144 for cycle data
PRODUCT = 1 litre/part cycle
% OXYGEN CONCENTRATION
% OXYGEN YIELD

See table A4.2, Ex 136 for cycle data
PRODUCT = 2.385 litres/part cycle
% OXYGEN CONCENTRATION
% OXYGEN YIELD

See table A4.2, Ex 137 for cycle data
Product = 3.73 litres/part cycle
% OXYGEN CONCENTRATION
% OXYGEN YIELD

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Figure 5.11 Oxygen Concentration Contour Plot for the Purge Cycles

PRODUCT PER PART CYCLE litres

PURGE PER PART CYCLE litres

- 95 % OXYGEN
- 90 % OXYGEN
- 80 % OXYGEN
- 70 % OXYGEN
- 60 % OXYGEN
- 50 % OXYGEN
- 40 % OXYGEN
- OPTIMA LOCUS
Figure 5.12 Oxygen Yield Contour Plots for the Purge Cycles

![Graph showing Oxygen Yield Contour Plots for the Purge Cycles](image)

- **PRODUCT PER PART CYCLE**: litres
- **PURGE PER PART CYCLE**: litres
- Symbols represent oxygen yield percentages:
  - △ 4% Oxygen Yield
  - ▽ 6% Oxygen Yield
  - ★ 8% Oxygen Yield
  - ▼ 10% Oxygen Yield
  - ● 12% Oxygen Yield
  - ▲ 14% Oxygen Yield
  - ○ 16% Oxygen Yield
  - ▲ 18% Oxygen Yield
  - ▼ 20% Oxygen Yield
  - △ 22% Oxygen Yield
  - Dashed line represents optimum purge amounts
Figure 5.13 Best Plant Performances for Purge Cycles

Figure 5.14 Waste Gas Oxygen Concentration Profiles
5.4.3.3 Waste Gas Concentrations

Figure 5.14 shows the waste gas oxygen concentrations for two cycles. One where less than the optimum purge amounts was used, (underpurged) and the other where more than the optimum purge amounts was used, (overpurged). The figure shows that gas containing more oxygen than air is lost in the waste stream for the overpurged case.

There was no waste gas flow during the pressurization step and the reading on the analyser is a result of gas from the end of the purge step remaining in the analyser cell. This explains partially the high oxygen concentrations observed at the start of the depressurization step.

It is interesting to note the oxygen concentration at the end of the purge step as this can give a good indication of the plant performance. It is often considered that the optimum purge amount is that amount such that 21 % oxygen (or the equivalent feed gas composition) is just observed in the waste gas stream at the end of the purge step. In practice, cycles that were optimized for oxygen yield showed maximum waste gas concentrations very close to 21 % oxygen, but where the plant was optimized for oxygen concentration, which is normal in industry, then the maximum waste gas oxygen content was often higher, (21 to 25 % oxygen).

5.4.3.4 Bed Pressure Profiles

During the purge steps the bed being regenerated increased in pressure, while the bed supplying the regeneration gas decreased in pressure. Figure 5.15 illustrates the largest observed changes in pressure and also shows how the pressure profiles varied for a set of purge cycle experiments as the purge and null times were altered.
Figure 5.15  Bed Pressure Profiles for the Purge Cycle Experiments

The profiles below show the largest variations in pressure observed during the null and product release steps, for all the purge cycle experiments.
5.4.4 Discussion

Product of up to 95.7% oxygen was obtained with the purge cycles. Generally 40 to 70 cycles were required to reach steady state compared to the 10 to 30 cycles required by the simple cycles. However, in some cases where a sharp concentration front might just be breaking through the bed at the end of a step, the steady state criteria were not satisfied after 500 cycles. Gradual changes in the ambient conditions could also hinder the attainment of steady state.

The existence of a critical purge flow rate has not previously been reported. It's presence may explain why in similar previous work, Kirkby (1984) and Liow (1986), their purge cycles failed to produce greater than 70% oxygen. For the cycle used to investigate purge flow rates in this work the critical purge flow rate corresponded to an average particle Reynolds number of 20. This was obtained at a constant product amount of 0.8 litres per part cycle and using smaller adsorbent particles to those used by Kirkby and Liow.

Kirkby investigated purge cycles over a range of purge amounts from 0 to 150 litres per part cycle which means that most of his purge cycle experiments (those with purge amounts greater than 35 litres per part cycle) produced average particle Reynolds numbers above the critical value found in this work. At 50 litres purge per part cycle Kirkby's average particle Reynolds number was calculated to be 29 and this increased to 88 at 150 litres per part cycle, (see appendix 4). Kirkby discovered that lowering his purge flow rate increased the product oxygen concentration but due to mechanical difficulties only a limited range of purge flow rates were investigated. Liow also found the purge flow rate to be an important variable. Although he used similar sized beds to those used in this work the adsorbent particles he used were significantly bigger (3 - 5 mm diameter compared to 1 - 2.5 mm) and he had difficulty in setting the purge flow rate low enough to prevent
breakthrough at the bottom of the bed before the end of the purge step. Significantly Liow's experiments produced optimum purge amounts between 10 and 15 litres per part cycle. This compares with optimum purge amounts of 20 to 25 litres per part cycle for this work over a similar range of product amounts per part cycle.

Clearly, further work is required to investigate the importance of purge flow rates for different product amounts, bed dimensions and particle sizes. Flow rates which are too high give insufficient time for local equilibrium to be approached, so the kinetic separation becomes more significant and decreases the product oxygen concentration. The higher purge flow rates produce longer concentration profiles in the bed, which start to break through the bottom of the bed at lower purge amounts.

The construction of the contour plots was time intensive, but they gave a thorough description of the plant performance for these purge cycles. Once constructed they were used both for comparing the performance of other cycles to purge cycles and for comparing the performance of purge cycles over a range of product and purge amounts.

Ideally the regenerating bed should have been purged at the lower operating pressure and there should have been no change in pressure during product release. In practice the regenerating bed pressure increased by up to 4 psig during purge and pressurized bed dropped by about 5 psig when required to supply both purge and product gas. Possibilities for reducing these effects by improving the plant design are discussed in chapter 7.

It was observed in many of the purge cycle experiments that greater than 21% oxygen could be lost in the waste gas produced during the purge step, (figure 5.14). This was particularly evident for high product purities when more than the optimum amount of purge gas was used. It certainly represents a loss in product yield and possibly also
concentration, so possibilities for selectively recycling some of the waste gas produced during this step back into the suction line of the compressor were investigated.

5.5 Purge Waste Recycle Experiments (Purge Snatching)

5.5.1 Introduction

This section describes the experiments in which the waste gas produced during the purge step was selectively recycled back into the feed line.

5.5.2 Method

The modified purge cycle used for these experiments is shown in figure 5.1c. All the experiments had a 30 s purge step and the purge amount was varied by changing the flow rate. Care was taken to ensure that the flow rate remained below the critical value reported in section 5.4.3.1. Figure 5.1c shows that the purge waste recycling (purge snatching) time was measured from the end of the purge step. This resulted from the previous observation that better quality waste gas was produced at the end of the purge step.

For fixed product amounts of 2 and 4 litres per part cycle the effect of selectively recycling waste gas produced during the purge step was investigated for different purge amounts. For each set of experiments the product and purge flow rates were fixed and the purge snatching time was automatically varied between 0 and 30 s, in steps of 5 s. A purge snatching time of zero produced a conventional purge cycle, while a purge snatching time of 30 s represented total purge waste recycle.
5.5.3 Results

5.5.3.1 Oxygen Concentration and Yield

Figures 5.16a to 5.16d present typical results showing how the product oxygen concentration and yield were affected by changing the purge snatching time, for different fixed purge amounts per part cycle. The inaccuracies of the waste gas flow measurements (appendix 3) produced errors in calculating the amount of recycled gas, which was required for calculating the net air feed and hence the oxygen yield. For this reason the figures display two values for oxygen yield at each purge snatching time. These values have been calculated from the data presented in table A4.3 and define boundaries within which the true oxygen yields should lie, (see appendix 4 for sample calculations). The errors in the yield calculations increased with both increasing purge amount and increasing purge snatching time.

Given the definition of oxygen yield it is not surprising that any amount of recycling improved the yield. However, the significant advantage of purge snatching is illustrated in figures 5.16a and 5.16b, where the oxygen concentration and yield are both improved simultaneously above the best capabilities of the purge cycles.

In general, the higher the purge flow rate the more purge waste gas was produced and the higher its average oxygen concentration. Hence, the overpurged cycles benefited most from purge snatching. However, while figure 5.16a presents results from a slightly overpurged cycle, which produced a better oxygen concentration than was capable using the normal purge cycle, figure 5.16d illustrates that if too much purge is used then any amount of purge snatching fails to improve on the purge cycle results.

Figure 5.16b, which presents data from a cycle which had a purge amount close to the optimum purge amounts for no recycling, still showed an improvement in the oxygen concentration with purge snatching. As the
purge amount was decreased both the amount of purge waste gas and its average oxygen concentration decreased. This is reflected in figure 5.16d, an underpurged cycle, which showed a decrease in oxygen concentration with increasing purge snatching.

5.5.3.2 Waste Gas Concentration

In all cases investigated waste recycling reduced the average oxygen concentration of the waste stream. This is reflected in the improved yields and is best illustrated in figure 5.17 which compares the waste gas oxygen profiles for an overpurged cycle with different purge snatching times. It is interesting to note that although the oxygen amount in the net waste was reduced by recycling, the minimum oxygen content in the waste remained roughly constant.

5.5.4 Discussion

Typical industrial plants might have a purge to feed ratio between 1 and 5, so a considerable amount of gas can be lost in the waste stream during the purge step. These experiments showed how easily purge waste gas can be recycled and that by selective recycling of waste gas plant performances can be achieved which are better than those obtained with conventional purge cycles. Figure 16a shows that purge snatching increased the product concentration from 75.3 to 81.3 % oxygen while at the same time improving the oxygen yield from 11.9 % to at least 15.7 %. The best possible purge cycle results at the same product amount of 4 litres per part cycle are 79 % oxygen concentration at 13 % oxygen yield. Hence although the purge snatching cycles were not optimized they did show in this example an increase in product concentration of 2.3 % and an increase in oxygen yield of 2.7 % compared with the best purge cycle results.

At near optima purge conditions the purge waste gas amount is approximately 20 % of the total waste gas. Recycling all the purge waste...
gas did not greatly reduce the waste gas oxygen concentration, but the theoretical simulations (chapter 6) predicted that waste recycling would have most effect on the waste gas concentration when greater than 70% of the waste gas was recycled, (see also the bulk waste recycling results in section 5.8).

An effect of purge snatching, that was not foreseen, was the increase in pressure it produced for the bed being regenerated. This was due to a higher pressure drop in the recycle lines compared to the normal waste lines. This effect was most evident for overpurged cycles, where figure 5.18 illustrates that purge snatching could increase the bed pressure by up to 3 psi. These changes in pressure introduced additional errors to the mass balance calculations, but should be accounted for within the ranges of yields shown on figures 5.16a to 5.16d.

Selectively recycling gas of a higher oxygen content than air has the added advantage of lowering the compression costs, by reducing the fraction of the more adsorbable component in the feed and thereby reducing the amount of feed gas required to pressurize the bed. Table A4.3 illustrates that purge snatching significantly reduced the feed amount per cycle, but it was not possible to establish how much of the reduction was due to the change in bed feed composition and how much was due to the increase in bed pressure both of which were effects of purge snatching.

It would be interesting to assess the potential of purge snatching by including it in other cycles and also to compare the results obtained in this section with results obtained from other conventional cycles. In the next section the best purge snatching results are compared with the best purge cycle results and some backfill cycle results. Also, possible advantages of waste recycling for other separations are discussed in chapter 7.
Figure 5.16 The Effects of Purge Snatching on Product Oxygen Concentration and Yield for Different Purge Amounts Per Part Cycle.

Figure 5.16a

Figure 5.16b

See Table A4.3, Ex 157 for cycle data
PRODUCT = 4 litres/part cycle
PURGE = 38 litres/part cycle

- % OXYGEN CONCENTRATION
- % OXYGEN YIELD
- Purge cycle optimum Conc
- Purge cycle optimum yield

See Table A4.3, Ex 165 for cycle data
PRODUCT = 2.1 litres/part cycle
PURGE = 23 litres/part cycle

- % OXYGEN CONCENTRATION
- % OXYGEN YIELD
- Purge cycle optimum concn
- Purge cycle optimum yield
Figure 5.16c  Purge Snatching for a Highly Overpurged Cycle

See table A.1.3, Ex 156 for cycle data
PRODUCT = 4 litres/part cycle
PURGE = 30 litres/part cycle

% OXYGEN CONCENTRATION
% OXYGEN YIELD
Purge cycle optimum concn
Purge cycle optimum yield

Figure 5.16d  Purge Snatching for an Underpurged Cycle

See table A.1.3, Ex 158 for cycle data
PRODUCT = 4 litres/part cycle
PURGE = 17 litres/part cycle

% OXYGEN CONCENTRATION
% OXYGEN YIELD
Purge cycle optimum concn
Purge cycle optimum yield
Figure 5.17  Purge Snatching Effects on the Waste Gas Conc.

Purge snatching time = 30 s
Purge snatching time = 20 s
Purge snatching time = 10 s
Purge snatching time = 0 s

NOTE
1. This is an overpurged cycle.
2. There was no waste flow during the pressurization (PR) steps

Figure 5.18  Purge Snatching Bed Pressure Profiles

See table A1.3, Ex 156 for cycle data

An overpurged cycle
See table A1.3, Ex 157 for cycle data

Purge Snatching Time = 20 s
Purge Snatching Time = 10 s
Purge Snatching Time = 0 s
5.6 Backfill Experiments

5.6.1 Introduction

The aim of these experiments was to investigate the performance of backfill cycles at different backfill rates and backfill pressures for a range of product amounts per part cycle. (The backfill pressure is the pressure of the bed being regenerated at the end of the backfill step).

5.6.2 Method

The cycle used is shown in figure 5.1d. The same cycle constraints placed on the purge cycle experiments, as detailed in section 5.2.1, were used for these experiments. Within the 180 s cycle time, 90 s was allocated for product release and 30 s for depressurization. This left a possible 60 s for backfill and pressurization, but the pressurization rate was fixed at 2 psi s\(^{-1}\). The null step time was therefore manipulated so that for each cycle the sum of the null, backfill and pressurization times was 60 s.

Initially the product amount per part cycle was fixed and the effects of changing the average backfill rate between 1 and 2 psi s\(^{-1}\) was observed. The product and backfill flow rates were fixed with manual valves as described in section 4.2. Then the controlling program was set up to run successive cycles from zero to total backfill pressure by changing the null, backfill and pressurization times whenever steady state had been satisfied and to collect the cycle data. The actual timer changes between cycles depended on the backfill rate chosen, but typically seven different backfill pressures were investigated for each set of flow rates.

Having established that the backfill flow rate was an important operating variable an average backfill rate of 2 psi s\(^{-1}\) was selected and the effect of changing the backfill pressure on the oxygen
concentration and oxygen yield was investigated over a range of product amounts per part cycle. For these experiments the product flow rate was first fixed and the controlling program increased the backfill time from 0 to 30 s in steps of 5 s, while decreasing the pressurization time from 30 to 0 s. As the backfill rate and pressurization rates were the same a constant 30 s null step was used throughout.

5.6.3 Results

5.6.3.1 Backfill Rate

Four backfill rates between 2 and 1 psi s\(^{-1}\) were investigated and each time the backfill rate was decreased there was an improvement in the plant performance. This is illustrated in figure 5.19 which, for 1.2 litres product per part cycle, compares the changes in the product oxygen concentrations with backfill pressure at backfill rates of 1 psi s\(^{-1}\) and 2 psi s\(^{-1}\).

Figure 5.19 The Effects on Product Oxygen Concentration of Changing the Backfill Rate.

![Graph showing product oxygen concentration vs. backfill pressure for different backfill rates.](image)
5.6.3.2 Oxygen Concentration and Yield

Typical results at 2 psi s\(^{-1}\) backfill rate, but different product amounts per part cycle are shown in figure 5.20. The low product amounts per part cycle repeatedly showed a distinct optimum backfill pressure with respect to oxygen concentration, (see results obtained at 2 litres per part cycle product). The optimum backfill pressure with respect to oxygen concentration decreased with increased product amount per part cycle, but the optimum backfill pressure with respect to oxygen yield did not vary greatly. Loci through these optima have been plotted in figure 5.21a, where they are compared to the corresponding optimum loci for the purge cycles, (figure 5.21b).

5.6.3.3 Pressure Profiles

Figures 5.22 and 5.23 present typical backfill cycle pressure profiles obtained at 1 and 2 psi s\(^{-1}\) backfill rates respectively. They illustrate the consistency in the shape of the depressurization profiles and the negligible pressure increase during the null steps. They also show that the backfill rates remained fairly constant for different backfill pressures, while the pressurization rates became slower as the backfill pressure increased. These variations are specific to the plant, but could be reduced by a flow controller on the feed line.

These graphs also show that while the pressurized bed was required to supply backfill gas it was unable to maintain its UOP, which could temporarily fall below 50 psig. The fall in pressure for the bed supplying regeneration gas was also observed for the purge cycles (section 5.4.3.4). Despite a greater fall in bed pressure for the backfill cycles they still performed better than the purge cycles. It is possible that the cocurrent partial depressurization effect (defined in section 1.4.1) could be enhancing the performance. Figure 5.22 and 5.23 show that the UOP was not always obtained at the end of the
pressurization step and that the bed pressure was still increasing at the beginning of product release. Commercial plants sometimes start to remove product before the UOP has been reached (see section 1.4.1.3), but the significance of doing this requires further research. The recommendations for future work are given in section 7.2.

Figure 5.20 Typical Oxygen Concentrations and Yields Obtained for Backfill Cycles at Different Product Amounts Per Part Cycle
Figure 5.21 Comparison of the Optima Loci for Oxygen Concentration and Yield Between Purge and Backfill Cycles

**Figure 5.21a** Optima Backfill Pressures for Backfill Cycles

**Figure 5.21b** Optima Purge Amounts for Purge Cycles
See table A1.4, Ex 231 for cycle data
Average backfill rate = 1 psi/s
Average pressurization rate = 2 psi/s

Figure 5.22 BackFill Pressure Profiles at 1 psi/s

See table A1.4, Ex 252 for cycle data
Average BackFill Rate = 2 psi/s
Average Pressurization Rate = 2 psi/s

Figure 5.23 BackFill Pressure Profiles at 2 psi/s
5.6.4 Discussion

The results from figure 5.19 were compared with the best purge cycle results at 1.2 litres per part cycle product, figure 5.13.

<table>
<thead>
<tr>
<th></th>
<th>% O2 Concentration</th>
<th>% O2 Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average backfill rate 1 psi s^{-1}</td>
<td>94.6</td>
<td>7.37</td>
</tr>
<tr>
<td>Average backfill rate 2 psi s^{-1}</td>
<td>90.1</td>
<td>7.36</td>
</tr>
<tr>
<td>Normal purge cycle</td>
<td>94.2</td>
<td>7.2</td>
</tr>
</tbody>
</table>

(Note that the best oxygen concentrations and yields were not obtained simultaneously).

The backfill cycle with a backfill rate of 1 psi s^{-1} produced higher oxygen concentrations and yields than the purge cycles. However, at a backfill rate of 2 psi s^{-1} the product oxygen concentrations obtainable from backfill cycles were less than the best purge cycle results. All the backfill cycles produced oxygen yields above the yields obtained with the corresponding purge cycles. A direct comparison, at a fixed product amount per part cycle, between the backfill cycle results and the purge snatching results was not available, but both results are compared again with the best purge cycle results in figure 5.24. (Note that the calculations of the oxygen yield may not be reflected in improved power consumption, but the backfill cycles required less compressed feed gas than either the purge or purge snatching cycles. This point is illustrated in appendix 4, which contains mass balance data for each cycle configuration).

Figure 5.24 shows that the best oxygen yields obtained using backfill cycles were 2 to 3 % above the best values obtained using purge cycles.

As with the purge cycle results many of the backfill cycle results presented in this section may be compared with the previous similar works of Liow (1986) and Kirkby (1984). Liow investigated the
importance of changing the backfill pressure and backfill rate on the oxygen concentration and his results are in good agreement with the findings from this work. He compared backfill cycle performances at average backfill rates of 0.6 and 1 psi s\(^{-1}\) and found that higher oxygen concentrations were obtained using the slower backfill rate. The best oxygen concentrations obtained using these average backfill rates were slightly above the best results Liow observed using purge cycles, which agrees with the findings of this work. Liow also compared the performance of several different backfill cycle configurations and used two zeolite types.

Kirkby's backfill cycle experiments again showed similar trends for oxygen concentrations at different backfill pressures, but due to mechanical problems his plant was difficult to operate at backfill pressures above 50 psig.

Kirkby and Liow supplied their backfill gas directly from the pressurized bed and as with this work they found that the pressure in the donating bed decreased during the backfill step. Kirkby and Liow did not observe differences in optimizing for oxygen yield and oxygen concentration and do not comment on changes in the optimum backfill pressure with changing product amount per part cycle. The backfill cycles in this work produced up to 95.7% oxygen, but neither Kirkby or Liow were able to produce greater than 70% oxygen from their backfill experiments.

Not as many backfill cycles were investigated as purge cycles, but nevertheless it did appear that the optima loci produced for the backfill cycles were in complete contrast to those produced for the purge cycles. Specifically, the optimum backfill pressure locus, with respect to oxygen yield, lay above that for oxygen concentration and both loci appeared to diverge as the product amount per part cycle was increased. (figure 5.21a). For the purge cycles the optima purge amount
locus, with respect to oxygen yield, lay below that for oxygen concentration and the loci converged with increasing product amount per part cycle, (figure 5.21b). This observation may help to explain why cycles having both purge and backfill regeneration often produce better plant performances than cycles having only one of these steps, [Kirkby, (1984)]. Combined purge and backfill cycles are investigated in the next section.

Figure 5.24 Comparison of the Best Purge Cycle Performances with the Highest Oxygen Concentrations and Yields Obtained for the Purge Snatching and Backfill Experiments
5.7 Purge and Backfill Combined Experiments.

5.7.1 Introduction

Many commercial plants operate cycles having both purge and backfill steps. The main aim of these experiments was to confirm that the performance of the plant could be improved by having both steps present in the same cycle. Kirkby (1984) showed that the combined cycle produced higher oxygen concentrations than either purge or backfill cycles, but he only investigated the combined cycles for a single product amount per part cycle and the maximum oxygen concentration he obtained was 74%.

5.7.2 Method

As for the purge and backfill experiments a cycle time of 180 s was selected, with a product release time of 90 s and a depressurization time of 30 s. A purge time of 30 s was used and the backfill rate was set to 2 psi s\(^{-1}\). Then for fixed product and purge amounts per part cycle the controlling program was set up to run successive cycles by increasing the backfill time from 0 to 30 s, while reducing the pressurization time from 30 to 0 s. Three product amounts were investigated (1.2, 2.5 and 4.2 litres per part cycle) and, for each case, sets of experiments were repeated for several purge amounts per part cycle. A total of 70 different cycles were investigated.

5.7.3 Results

The results showed that the cycles with purge and backfill could produce higher oxygen concentrations and yields than either the best purge cycle results, or the backfill cycles for a backfill rate of 2 psi s\(^{-1}\). The improved performance was greatest for the highest product amount investigated (4.2 litres per part cycle). Figures 5.25 and 5.26, present sets of results at this product amount for purge amounts of 25 and 12 litres per part cycle. The optimum purge amount with respect
to oxygen concentration for a purge cycle at 4.2 litres per part cycle, product was previously found to be 25 litres per part cycle, (figure 5.13).

Figures 5.25 and 5.26 show that both the maximum oxygen yield and concentration were improved by reducing the purge amount from 25 to 12 litres per part cycle. This demonstrates that if backfill is used with purge then the required amount of purge to optimize the plant performance is reduced.

Figure 5.27 presents the worst variations in pressure profiles obtained with these experiments. This figure illustrates the difficulty experienced in maintaining a constant backfill rate. It also shows that significant cocurrent depressurization occurred and that in most cases the product release step began before the UOP had been reached. These points were previously discussed in section 5.6.3.3.

5.7.4 Discussion

The results presented in this section are consistent with those of Kirkby (1984). Both sets of results showed that the combined cycles could produce higher oxygen concentrations than were obtainable using either purge or backfill cycles. They also agree in showing that the optimum purge amount was decreased if a backfill step was also included in the cycle. Kirkby found that at any given backfill pressure there was a clearly defined optimum purge amount, but an insufficient number of experiments were completed to confirm this finding.

At the product amount of 1.2 litres per part cycle where a comparison was also available with the backfill cycle for a backfill rate of 1 psi s⁻¹, the purge, backfill and combined cycles could all produce between 94 and 95.7 % oxygen. Comparisons under these conditions are difficult to make because of changes in ambient conditions, the difficulty of exactly reproducing cycle condition and experimental
errors become significant.

The number of cycles required to satisfy the steady state criteria were not significantly different for these experiments to the purge and backfill cycles.

It would have been interesting to have tried different purge step times and backfill rates and also to have assessed the cycles over a wider range of product amounts, but the scope for experimental work with these cycles is so vast that only a selection of possibilities was investigated. It would also have been interesting to include a purge snatching step in the combined cycle and to have observed if this further improved the performance of the plant. These options are included in the recommendations for future experimental work, (section 7.2.2).
Figure 5.25 Product Oxygen Concentrations Obtained from Purge and Backfill Combined Cycles Compared to Those Obtained With Cycles Having Only One Regeneration Step

- **PRODUCT** = 4.2 litres/part cycle
- **BEST PURGE ONLY RESULT**
- **BACKFILL** = 2 psi/s
- **NO PURGE**
- **BACKFILL** = 2 psi/s
  - **PURGE** = 25 litres/part cycle
- **BACKFILL** = 2 psi/s
  - **PURGE** = 12 litres/part cycle

BACKFILL PRESSURE psig
Figure 5.26 Oxygen Yields Obtained from Purge and Backfill Combined Cycles Compared to Those Obtained With Cycles Having Only One Regeneration Step

- PRODUCT = 4.2 litres/part cycle
- BEST PURGE ONLY RESULT
- BACKFILL = 2 psi/s
- NO PURGE
- BACKFILL = 2 psi/s
- PURGE = 25 litres/part cycle
- BACKFILL = 2 psi/s
- PURGE = 12 litres/part cycle

BACKFILL PRESSURE psig

PRODUCT = 4.2 litres/part cycle
BEST PURGE ONLY RESULT
BACKFILL = 2 psi/s
NO PURGE
BACKFILL = 2 psi/s
PURGE = 25 litres/part cycle
BACKFILL = 2 psi/s
PURGE = 12 litres/part cycle
Figure 5.27  Pressure Profiles for Combined Purge and Backfill Cycles

See table A4.5, Ex 256 for cycle data
Purge = 25 litres/part cycle
Product = 4.2 litres/part cycle
Average backfill rate = 2 psi/s

- BKT = 30 s, PRT = 0 s
- BKT = 20 s, PRT = 10 s
- BKT = 10 s, PRT = 20 s
- BKT = 0 s, PRT = 30 s
5.8 Bulk Waste Recycling Experiments

5.8.1 Introduction

In these experiments the waste gas produced during both the depressurization and purge steps was recycled back into the feed line. It was hoped that as the waste recycle ratio (defined below) was increased that the net waste gas leaving the plant would be sufficiently pure in nitrogen to be of use. Computer simulations (section 6.2) had indicated that it might be possible to recycle large amounts of waste gas, thereby improving the oxygen yield, without any detrimental effect to the product oxygen concentration.

\[
\text{recycle ratio} = \frac{\text{the amount of waste recycled}}{\text{the total amount of waste}}
\]

The purge, backfill and combined cycles had continuous product release and 30 s depressurization steps. Unfortunately the regulator on the recycle line limited the rate at which the waste gas could be recycled and from an UOP of 60 psi only 50 % of the waste gas could be recycled in 30 s. A larger waste reservoir would have allowed greater temporary storage of waste gas between successive depressurization and pressurization steps. However, in order to be able to investigate higher than 50 % waste recycle ratios a cycle was devised where one bed was pressurized while the other bed was being depressurized, (figure 5.1f). The cycle included a purge step, with the option of purge snatching, but there was no longer a continuous product release step. As the pressurization and depressurization steps were simultaneous it was not possible to supply backfill gas directly from one bed to another so bulk waste recycling with backfill cycles was not investigated. (At a later stage the plant was modified to allow the regeneration gas to be supplied from the product reservoir, but no further waste recycle experiments were completed using this option).
The waste gas oxygen concentration profiles from purge cycles, (figure 5.14), indicated that the waste gas produced at the beginning of the depressurization step contained relatively more oxygen than that produced toward the end of the depressurization. Figure 5.1f therefore shows that the waste recycle time was varied from the start of depressurization.

5.8.2 Method

A cycle time of 180 s was selected again with 30 s for product release and 30 s for purge during which all the purge waste gas was recycled, (total purge snatching). This left 60 s each for pressurization and depressurization.

A number of sets of experiments were completed at different product amounts per part cycle and for each set the controlling program increased the waste recycle time from 0 to 60 s in steps of 10 s as each successive cycle satisfied the steady state criteria. A waste recycle time of 60 s combined with a 30 s purge snatching time should have resulted in no net waste gas being produced from the plant. This assumes that no gas other than product escaped from the plant. In reality some gas is likely to have been lost through gas leaks and also through the compressor breathers.

Unfortunately, significant quantities of the gas that was recycled into the compressor suction line escaped from the plant through the 2 inch check valve on the air inlet line. Rather than operating on a spring loading this check valve had an open and shut flap that was slow to close when the pressure in the suction line rose above atmospheric pressure. It was not possible to replace this valve with a spring loaded one as the additional pressure drop in the suction line could then have damaged the compressor. The waste losses were estimated for the total recycle experiments and figure 5.28 was extrapolated to a
true 100 % waste recycle ratio. This allowed the experimental waste recycle ratios to be corrected.

The experiments were all performed for the optimum purge amounts with respect to oxygen concentration as reported in section 5.4.

5.8.3 Results

Figure 5.28 shows the effect on the product oxygen concentration of bulk waste recycling (BWR) for several product amounts per part cycle. In most cases, as expected, the effect of recycling gas containing less oxygen than is present in the feed air produced a drop in the product oxygen concentration. However, for the lowest product amount investigated, 1.6 litres per part cycle, BWR initially produced a simultaneous increase in the oxygen content of the product and a decrease in the oxygen content of the waste.

Figure 5.28 shows that for 1.6 litres per part cycle product over 70% of the waste gas could be recycled before any decrease in the product oxygen concentration was observed, which corresponds to an improvement in oxygen yield from approximately 6% to 50%. (table A4.6).

Figure 5.29 illustrates some waste gas oxygen concentration profiles, produced at a constant product amount, but different recycle ratios. They show that as the recycle ratio increased, both the average and minimum oxygen content of the waste gas decreased. The purge snatching experiments lowered the average, but not the minimum, oxygen concentration in the waste gas, (see figure 5.17). The minimum oxygen content observed in the waste gas with the BWR cycles was 12 %.

Figure 5.30 shows bed pressure profiles for the BWR experiments, showing that a higher lower operating pressure of 8 psig was used. This was necessary for total waste recycle into the compressor suction line.
5.8.4 Discussion

It was unfortunate that the design limitations required a complete change of cycle type before high waste recycle ratios could be investigated. This made comparisons with previous cycles difficult. It was also unfortunate that the losses in the compressor suction line prevented even higher recycle ratios from being observed, as then the waste gas oxygen concentration may have dropped sharply giving a secondary nitrogen product. Despite these set backs, the results obtained at 1.6 litres per part cycle product were very encouraging. They agreed with the initial modelling predictions (section 6.2) that it was possible, for some cycles, to recycle large amounts of waste gas while simultaneously increasing the product oxygen concentration and yield as well as reducing the oxygen content of the waste gas.

The most efficient oxygen PSA plants can produce over 90% oxygen product at oxygen yields around 50 to 60%, and to obtain such a yield with the conditions used for this research project suggests that there is still scope for improvement with commercial plants.

Selective waste recycling has many effects including altering the compression costs through varying the feed gas composition and hence the capacity of the beds. It may also have uses for other separations where the waste gas may be required in a purer form. For other separations an oil free compressor may not be necessary and with greater choice of compressors one could be selected to operate over a wider range of suction pressures. Possibilities for improving the design and equipment selected for future waste recycle work are given in chapter 7.
Figure 5.28  BWR at Different Product Amounts Per Part Cycle

All experiments had complete purge waste recycle

See table A4.6, Ex 316-319 for cycle data

- Product = 1.6 litres/part cycle
- Product = 2.2 litres/part cycle
- Product = 1.1 litres/part cycle
- Product = 8.1 litres/part cycle
Figure 5.29 Waste Gas Oxygen Concentration Profiles for Different BWR Times

See table A4.6, Ex 317 for cycle data
WRT = Bulk Waste Recycle Time
PRODUCT = 2.2 litres/part cycle
PURGE = 21 litres/part cycle

WRT = 60 s
WRT = 40 s
WRT = 20 s
WRT = 0 s
Figure 5.30  Typical Bed Pressure Profiles for the BWR Experiments

See table A4.6, Ex 319 for cycle data

- WRT = 60 s
- WRT = 40 s
- WRT = 20 s
- WRT = 0 s
5.9 Miscellaneous Experiments

This section presents results from some miscellaneous experiments, completed after the cycle comparisons reported in sections 5.3 to 5.8.

5.9.1 Comparison of Purge Sources

The plant was modified so that the purge gas could be supplied either directly from the pressurized bed (as before), or from the product reservoir. The purge cycle shown in figure 5b was used. Then for different fixed product amounts per part cycle, the purge amounts per part cycle were varied by changing the null and purge step times as described in section 5.4.2. Before each set of experiments the purge flow rate and required source were selected with manual valves, (section 4.2).

The differences between using a direct variable composition purge, or a mixed purge supply were often small, and figure 5.31 represents the largest differences observed. The results show that a higher product oxygen concentration could be obtained when constant composition purge was supplied from the product reservoir. The improved oxygen concentrations are reflected in better oxygen yields, (table A4.7). Figure 5.31 shows that, for overpurged cycles, the fall in oxygen concentration with increased purge amount was greater for the case where the purge gas was supplied directly from the pressurized bed. Hence, for industrial plants which have limited instrumentation, optimizing the purge amount is less critical if the purge gas is supplied from the product reservoir rather than directly from another bed.

An insufficient number of experiments were completed to draw conclusions as to whether changing the purge source also changes the required amounts of purge to optimize the oxygen concentration and
yield, but any reduction in the required purge amount reduces compression costs.

No other published experimental work considers the differences between these purge sources, and apart from the simulation results presented in section 6.6, all theoretical models assume a fully mixed purge supply.

Figure 5.31 Comparison of Product Oxygen Concentrations Obtained Using Different Purge Sources
5.9.2 Comparison of Cycles With and Without Continuous Product Release

By using the cycles shown in figures 5.1b and 5.1f, but having no waste recycle, purge cycles were compared where the product amount per part cycle was kept constant, but the product superficial velocity varied. The aims of these experiments were to investigate whether one cycle configuration performed better than another and to assess if changes in the product superficial velocity affected the performance of the plant.

Results are presented in table A4.8 for three different sets of experiments, all at the same product amount per part cycle, but for a range of purge amounts per part cycle. Experiment 605 used cycle 5.1b and the purge gas was supplied from the product reservoir. Experiment 606 also used cycle 5.1b, but the purge was supplied directly from the pressurized bed. Results from these experiments were compared with experiment 607, for which cycle 5.1f was used with the purge supplied from the pressurized bed, but this time a higher product superficial velocity was necessary as there was no longer continuous product release.

Comparing experiments 607 with experiment 606 showed that the cycle with the higher product superficial velocity produced marginally better product oxygen concentrations. This was surprising and suggests that the arrangement of cycle steps in figure 5.1f may be superior to the continuous product release cycle of figure 5.1b. However, using cycle 5.1b, but supplying purge gas from the product reservoir even better oxygen concentrations were obtained.

The results illustrated how the arrangement of steps in cycles affects their performance and also showed that over the range of product amounts per part cycle investigated variations in the product flow rate did not greatly affect plant performance.
5.9.3 The Shape of the Depressurization Profiles

The shape of the depressurization profiles could be altered by manipulating the manual valves on either side of the waste reservoir, or by venting directly into the extractor duct through solenoid valve SV10b, (figure 4.1). A number of sets of purge cycle experiments similar to those reported in section 5.4 were done, where the only variable should have been the shape of the depressurization profile. Unfortunately it proved very difficult to ensure that the lower operating pressure (LOP) was exactly the same in each case.

Figure 5.32a shows three sets of results for the oxygen concentrations obtained at different purge amounts per part cycle. Figure 5.32b shows the three depressurization profiles corresponding to the sets of results presented in figure 5.32a. The results show that as the depressurization profile became more linear the product concentrations improved, (figures 5.32a & 5.32b). Of special relevance is the comparison between experiments 176 with 178, where although the LOP for experiment 176 was 2 psi above that for experiment 178 it still produced similar if not marginally better oxygen concentrations.

Note that the maximum rate of pressure change for experiment 176 was about 17 psi s⁻¹ compared with the maximum rate of pressure change for experiment 178 which was about 40 psi s⁻¹.

5.9.4 Axial Pressure Gradients

The simple cycle pressure profiles were studied for a wide range of flow rates. For each set of flow rates the pressure transducers where moved from their normal position at the centre of the beds to the other ports along the bed profiles.

In every case no change in the bed pressure profiles was observed by moving the pressure transducers, so it was concluded that for the conditions used axial pressure gradients were negligible. The results
also showed that even the peak flow rates were controlled by the pipework surrounding the beds and not the pressure drop across the bed. Assuming a bed was 1 m long and regularly packed with identical solid spherical particles 1.7 mm in diameter, then the flow required at S.T.P. to produce a 1 bar pressure drop across such a bed would be in excess of 50 litres s\(^{-1}\). (The Carmen Kozeny equation was used to predict the pressure drop across a packed bed and the calculation is included in appendix 4).

Figure 5.32 Variations in Product Oxygen Concentration Produced by Changing the Shape of the Depressurization Profile.
5.9.5 Unsymmetrical Purge Cycle Operation

The importance of symmetrical operation was mentioned in chapters 1 and 2. The aim of these experiments was to observe just how significant symmetry is by operating some unsymmetrical purge cycles. Using the cycle described in figure 5.1b, the product amount per part cycle was fixed and the purge flow rate to one of the beds was also fixed. Different purge flow rates, below the critical value reported in section 5.4.3.1, were selected for the other bed (using NV5, see figure 4.1). In each case the purge and null step times were varied (as described in section 5.4) to obtain the product oxygen concentrations for ranges of purge amounts per part cycle.

The results are presented in figure 5.33 and they indicate clearly the fall in performance observed when operating unsymmetrically. This emphasizes the importance of symmetry both of operation and design. Kirkby (1984) also investigated unsymmetrical operation, but as one of his beds contained significantly more adsorbent than the other he found that the highest oxygen concentrations were produced when the amount of purge gas supplied to the bed containing more adsorbent was greater than the amount of purge supplied to the other bed. The difference in adsorbent capacity for the beds used by Kirkby would have certainly contributed to the lower oxygen concentrations he observed compared to those obtained in this work.

5.9.6 Discussion

In formulating the ILE model (see chapter 3) many assumptions were made. It was assumed that the bed pressures were a function of time only and that the operation was perfectly symmetrical. The experimental results presented in this chapter suggest these are good assumptions for theoretical comparisons with the experimental results. The ILE model does not distinguish between different pressure profiles, so for
simplicity linear pressure profiles were assumed. This study has shown that the pressure changes were far from linear and that changing the shape of the pressure-time profiles can alter the performance of the plant. A further assumption made in Kirkby's ILE model is that the product gas is perfectly mixed and that the purge gas is supplied from the product reservoir. In most of the experiments using purge cycles in this work and all the purge cycles investigated experimentally by Kirkby the purge gas was supplied directly from the pressurized bed and was therefore of variable composition. However, this work has shown experimentally that the product oxygen concentrations obtained are affected by altering the source of purge gas. This observation prompted the development of the ILE model so as to give the option of simulating purge supply from a product reservoir as before or directly from another bed, (see section 6.6).

Relatively few experiments were done to illustrate some of the points made in this section. However the section does show comparisons in performance previously neglected, and it also illustrates possibilities for greater optimization of PSA processes.
Figure 5.33 Unsymmetrical Purge Cycle Oxygen Concentrations

Constant average purge flow rate to bed A of 1 litre/s

PUa = PURGE TO BED A
PUb = PURGE TO BED B

PUb/PUa = 1.00
PUb/PUa = 0.69
PUb/PUa = 0.83
PUb/PUa = 1.14
5.10 Conclusions

Despite the rapid growth in applications of PSA since 1960 and the large volume of associated published literature, there have been relatively few publications of experimental results for bulk gas separations using a range of operating cycles. This work helps to fill that gap for oxygen separation from air. It also serves as a useful set of experimental results against which mathematical models may be compared. Many of the experimental results have been compared with other experimental results, [Kirkby. (1984) & Liow, (1986)]. However, the experimental results from this work are especially valuable because unlike other publications, many of these experiments involved producing gas of greater than 90% oxygen which is necessary to satisfy the commercial demand.

The reproducibility of results from many sets of experiments at various product amounts per part cycle was found to be good. The largest experimental errors occurred in determining the mass balance over the beds. Here the mass flow meters gave absolute errors of up to 10%, (appendix 3).

The main experimental conclusions are summarized below.

1. The simple cycles failed to produce more than 40% oxygen, whereas the other cycles could all produce 95% oxygen. For the product amounts per part cycle investigated, the combined purge with backfill cycle produced the highest obtainable oxygen concentrations and yields. Provided the backfill rate was sufficiently low, then backfill on its own produced a higher oxygen concentration than purge on its own, (see point 4 on the next page). The yields obtained from the backfill cycles were better than those obtained with purge cycles. Some of these points are illustrated on the next page, where the best obtainable results are summarized for different cycles, but all for a product amount of 4.2 litres per part cycle.
<table>
<thead>
<tr>
<th>Cycle Purge</th>
<th>Backfill psi s⁻¹</th>
<th>Highest Obtainable Results % Oxygen Concentration</th>
<th>% Oxygen Yield</th>
</tr>
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<tr>
<td>25.0</td>
<td>None</td>
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<td>13.00</td>
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<td>12.0</td>
<td>2.0</td>
<td>82.5</td>
<td>16.55</td>
</tr>
</tbody>
</table>

2. The experiments showed that the optimum purge to feed ratio is not constant, and that there are differences between optimizing for oxygen yield and oxygen concentration.

3. A critical purge velocity was found, such that if the purge velocity was increased beyond this value, then the maximum obtainable oxygen concentration decreased sharply irrespective of purge amount.

4. The performance of the backfill cycles was improved by using a slower backfill rate. For example, at a product amount of 1.2 litres per part cycle, the maximum obtainable oxygen concentration was improved from 90.1% to 94.6% oxygen by slowing the average backfill rate from 2 to 1 psi s⁻¹.

5. Points 3 and 4 illustrate that, although oxygen separation on zeolites is essentially equilibrium controlled, changing the process flow rates can greatly affect the plant's performance. It is not clear to what degree the mass transfer resistances contributes to the changes in performance with flow rates, but the results emphasize the importance of both kinetics and hydrodynamic considerations for PSA plants.

6. The product oxygen concentration and oxygen yield were both improved beyond the capabilities of a normal purge cycle by the selective recycling of purge waste gas.
7. For the lowest product amount per part cycle investigated, over 70% of the waste gas was recycled before any decrease in the product oxygen concentration was observed. This represents an improvement in oxygen yield from 6% to 50%. For this case bulk waste recycling initially produced a simultaneous increase in the oxygen content of the product and a decrease in the oxygen content of the waste.

8. The pressure and waste gas concentration profiles were shown to vary greatly for different cycles and changing operating conditions. The optimum operating conditions for purge cycles occurred when the maximum observed oxygen concentration in the waste gas was approximately equal to that in air. The plant performance was improved by making the pressure changes as linear as possible and hence reducing the maximum superficial velocities in the beds.

9. The importance of symmetrical operation for PSA processes was illustrated.

10. It was found, for purge cycles, to be more advantageous to the product concentration to supply purge gas from the product reservoir, rather than directly from another bed. At a product amount of 2.4 litres per part cycle, supplying purge from the product reservoir improved the maximum obtainable oxygen concentration from 85.5 % to 88.8 %.

In the course of the experimental work many areas for further research have been identified and some valuable experience regarding plant designs and equipment selections have been gained. These aspects are discussed in chapter 7. The experimental results are compared to the modelling results in the next chapter.
Model Simulations and Their Comparison

With the Experimental Results

6.1 Introduction

Prior to the experimental work the ILE model had been used to assess the potential for waste recycling. Initial results, section 6.2, showed that it was possible in some cases to recycle large amounts of waste gas while simultaneously improving the product oxygen concentration and yield. This surprising discovery instigated the experimental work on waste recycling, from which evolved the separate modes of purge snatching and bulk waste recycling.

The ILE model has proven qualitative agreement with experiments, Kirkby (1984), although it over predicted product oxygen concentrations. An aim of this project was to see if the qualitative agreement could be extended for a wider range of cycles and if the quantitative agreement between theory and experiments could be improved. The model used by Kirkby and its development to the version used for this work were described in chapter 3 and appendix 2.

The main model assumptions are;

(a) instantaneous local equilibrium,
(b) linear independent isotherms,
(c) air is considered a binary mixture of oxygen and nitrogen,
(d) isothermal operation,
(e) plug flow with no dispersion,
(f) linear pressure changes and no pressure drop over the beds.

The model also includes the process assumptions of perfect symmetry and product mixing.
The following simulation work was completed:

1. purge and backfill contour plots similar to the experimental ones produced in sections 5.4 and 5.5 were constructed,
2. further waste recycle simulations were done for bulk waste recycling with both purge and backfill cycles,
3. an attempt was made to model the purge snatching mode, and
4. the model was used to compare the performance of purge cycles when the purge gas was supplied fully mixed or directly from one bed to another.

Results from the above simulations are presented in sections 6.3 to 6.7, where they are also compared with the experimental work. To keep the theoretical results directly comparable with experimental results the bed dimensions, inlet velocities and step times were the same as those used for the experiments. The physical constants and operating parameters used for the simulations are summarized in appendix 6.

The construction of the characteristics and the boundary values used by the model for each cycle step were discussed in chapter 3. Also, typical characteristic plots for purge and backfill cycles were previously presented by Kirkby, (1984). The inclusion of waste recycling did not make any fundamental changes to the characteristic plots other than by changing characteristic velocities during the product release step. However, the direct purge simulations required three different product release steps to account for the different product superficial velocities, produced in the experimental cycles. Therefore, examples of the characteristic plots for the direct purge simulations are included in section 6.7.

The model considers air to be a mixture of 21.88 % oxygen and 78.12 % nitrogen. Argon is treated as oxygen. The oxygen concentrations shown in the simulation results refer to the argon/oxygen mixture.
6.2 Initial Waste Recycle Simulations

Prior to the construction of the plant described in chapter 4, a number of simulations using backfill cycles were completed to assess the potential of selectively recycling waste gas. The fraction of waste gas to be recycled was selected at the beginning of each simulation. The model allowed all the waste gas to be perfectly mixed, so the recycled and net waste gas streams were the same composition. However, changing the fraction of waste gas to be recycled altered the net air feed amount, and the bed feed, product and waste compositions.

Recycling depressurization waste gas was called bulk waste recycling (BWR) and the development of the model to include this option was described in section 3.5.1. For product amounts per part cycle of 9 and 18 litres and for backfill pressures between 0 and 80 psig, waste recycle ratios from 0 to 1 were investigated. (See appendix 6 for other simulation parameters).

\[
\text{waste recycle ratio} = \frac{\text{waste recycled}}{\text{total amount of waste}}
\]

Most simulations showed that increasing the waste recycle ratio caused a decrease in the product and waste oxygen concentrations, but an increase in the oxygen yield. Figure 6.1 presents typical results for 9 litres per part cycle product at 20 psig backfill pressure. Occasionally, waste recycling caused a simultaneous increase in the product oxygen concentration and yield. This was most evident at 9 litres per part cycle product and 10 psig backfill pressure, where figure 6.2 shows that 70% of the waste gas could be recycled before the product oxygen concentration fell below its value for no waste recycling. This corresponded to a 22% improvement in oxygen yield.

Results for the 9 and 18 litres per part cycle simulations are summarized in figures 6.3 and 6.4 respectively. (These figures were
produced from a total of 126 simulations). At the higher product amount per part cycle waste recycling always produced a decrease in product oxygen concentration. In both cases the product oxygen concentration and yield contours became closer together for higher waste recycle ratios and very steep changes in product oxygen concentration and yield occurred when the waste recycle ratio was increased above 70%.

Figure 6.1 Typical Results for BWR with Backfill Cycles

![Graph showing typical results for BWR with backfill cycles.]

Backfill Pressure = 20 psig

\( \text{\% product oxygen concn} \)
\( \text{\% product oxygen yield} \)
\( \text{\% waste nitrogen yield} \)

Figure 6.2 Special Case Results for BWR with Backfill Cycles

![Graph showing special case results for BWR with backfill cycles.]

Backfill Pressure = 10 psig

\( \text{\% product oxygen concn} \)
\( \text{\% product oxygen yield} \)
\( \text{\% waste nitrogen yield} \)

\( \text{waste nitrogen yield} = \text{the amount of nitrogen in the net waste gas} \)
\( \text{the amount of nitrogen in the air feed} \)
Figure 6.3 Contour Plot for Backfill Cycle With Bulk Waste Recycling, (9 litres per part cycle product)

Figure 6.4 Contour Plot for Backfill Cycle With Bulk Waste Recycling, (18 litres per part cycle product)

**KEY**

- - - product concn
--- product yield

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>x</td>
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</tr>
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<td>○</td>
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<td>▽</td>
<td>60%</td>
</tr>
<tr>
<td>◇</td>
<td>70%</td>
</tr>
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</table>

\[
\text{product yield} = \frac{02 \text{ in Product}}{02 \text{ in waste}}
\]

\[
\text{waste recycle ratio} = \frac{\text{waste recycled}}{\text{total waste}}
\]
6.3 Conventional Purge and Backfill Cycles

This section presents the results for the two conventional cycles examined. Both purge and backfill cycles were previously studied by Kirkby, (1984). He showed that there were optima purge amounts and backfill pressures, but did not distinguish between optimizing for oxygen yield or concentration and also did not comment on how these optima might vary with changing product amounts per part cycle.

6.3.1 Purge Cycle Simulations

Figure 6.5 presents typical simulation results, showing how the product oxygen concentration and yield varied with purge amount per part cycle for different product amounts per part cycle. The figure shows that there are differences in optimizing for oxygen yield and concentration and that the optima purge amounts vary with product amount per part cycle.

From graphs, such as figure 6.5, and for similar ranges of product and purge amounts per part cycle to those used in the experimental work, contour plots of oxygen concentration and yield were produced, figures 6.6 and 6.7. The contour plots illustrate the predicted behaviour of the purge cycles over a wide range of conditions.

6.3.2 Comparison of Theory with Experiment for the Purge Cycles

More data for comparing theory with experiment was produced for the purge cycles than any other cycle. Comparing the experimental purge contour plots, figures 5.11 and 5.12, with figures 6.6 and 6.7 demonstrates the good qualitative agreement between the model and experiments. They show that, at low product amounts per part cycle, changing the purge amount per part cycle had little effect, but as the product amount increased the purge amounts selected could greatly affect the oxygen concentration and yield. The experimental and simulated results also agree in showing that more purge is required to optimize
the oxygen concentration than oxygen yield and that the purge amount optima increase with increasing product amount per part cycle. However, the differences in purge amount optima were greater for the experimental results, (figure 6.8).

The model continued to over predict the product oxygen concentrations, (figure 6.9). However, whereas Kirkby had been unable to produce greater than 70% oxygen using purge cycles, the experimental purge cycles in this project could produced 95% oxygen which contributed to the improved quantitative agreement for oxygen concentrations achieved in this work, (see section 5.4).

The oxygen yields for the same experiments and simulations used to plot figure 6.9 are compared on figure 6.10. The quantitative agreements for oxygen yields were better than those for the oxygen concentrations. At 4 litres per part cycle product, the optimum oxygen yields showed excellent quantitative agreement. However, normally the model under predicted oxygen yields, which given that it also over predicted oxygen concentrations, highlights the difference in adsorbent capacity between the model and experiments. Generally for similar purge cycles the model predicted 5 to 10% more feed gas than was measured experimentally. Although the mass flowmeters showed good reproducibility there were absolute errors in their readings and experimentally the overall errors in the mass balance were estimated at 10%, (appendix 3).

Figures 6.8 to 6.10 show that the quantitative agreement between the simulations and experiments varied with changing purge and product amounts per part cycle. This demonstrates the need to test models against a wide range of experimental results.
Figure 6.5  Simulated Product Oxygen Concentrations and Yields for Purge Cycles

% OXYGEN CONCENTRATION

% OXYGEN YIELD

PURGE AMOUNT  litres/part cycle

yield 0 to 25 %]

% concentration  2 l/part cycle
% concentration  4 l/part cycle
% concentration  8 l/part cycle
% concentration  12 l/part cycle
% yield  2 l/part cycle
% yield  4 l/part cycle
% yield  8 l/part cycle
% yield  12 l/part cycle
Figure 6.6  Theoretical Purge Cycle Product Oxygen Concentration Contour Plot

Theoretical Purge Cycle Product Oxygen Concentration Contour Plot

PRODUCT AMOUNT litres/part cycle

100 % OXYGEN CONCENTRATION
95 % OXYGEN CONCENTRATION
90 % OXYGEN CONCENTRATION
80 % OXYGEN CONCENTRATION
70 % OXYGEN CONCENTRATION
60 % OXYGEN CONCENTRATION
50 % OXYGEN CONCENTRATION
40 % OXYGEN CONCENTRATION
NB. The purge was fully mixed

168
Figure 6.7 Theoretical Purge Cycle Oxygen Yield Contour Plot

NB. The purge was fully mixed
This figure illustrates that the experiments produced greater differences between the purge amounts required to optimize the oxygen concentration and yield than was observed with the simulations. At low product amounts per part cycle it was difficult to obtain the optima purge amounts from the simulation results as for these conditions the model frequently predicted a product concentration of 100% oxygen and the simulations were particularly insensitive to the purge amount.
Figure 6.9 Comparison of Simulated and Experimental Oxygen Concentrations for Purge Cycles at Different Product Amounts Per Part Cycle

Figure 6.10 Comparison of Simulated and Experimental Oxygen Yields for Purge Cycles at Different Product Amounts Per Part Cycle
6.3.3 Backfill Simulations

The effects of changing the backfill pressure on the product oxygen concentration and yield were investigated over the same range of product amounts per part cycle as the purge cycles. Figure 6.11 shows some typical results and figures 6.12 and 6.13 present the contour plots for product oxygen concentrations and yields in the product amount per part cycle and backfill pressure plane. These figures illustrate that the backfill pressures became more critical as the product amount per part cycle was increased. Also they show that, for the lower product amounts per part cycle, variations in backfill pressure above 20 psig had very little affect on either the product oxygen concentration or yield.

6.3.4 Comparison of Theory with Experiment for the Backfill Cycles

An insufficient number of backfill experiments were done to complete backfill contour plots. However comparisons of experimental and simulated results are presented in figures 6.14 and 6.15. They show that the model over predicted the product oxygen concentration, while the same experiments produced excellent agreement with the simulations for oxygen yields. The oxygen concentrations produced experimentally were shown to increase significantly with decreasing backfill rate, (figure 5.19). The experimental results presented in figure 6.14 were for the fastest backfill rate examined and consequently produced the greatest difference in oxygen concentration when compared with simulation results. The ILE model takes no account of the effects of changing the backfill rate.

The experiments showed that higher backfill pressures were required to optimize the oxygen yield rather than product oxygen concentration. This was also true for the simulation results although their differences in optima backfill pressures were much less. Below
product amounts of 6 litres per part cycle the product concentration and yield were so insensitive to changing backfill pressure that trends in the optima backfill pressures could not be identified.

Figure 6.11 Typical Oxygen Concentrations and Yields Simulated with Backfill Cycles
**Figure 6.12** Theoretical Oxygen Conc'n Backfill Contours

**Figure 6.13** Theoretical % Oxygen Yield Backfill Contours

NB. The purge was fully mixed.
Figure 6.14 Comparisons for Backfill Oxygen Concentration

Figure 6.15 Comparisons for Backfill Oxygen Yields
6.4 Bulk Waste Recycling for Purge and Backfill Cycles

The initial bulk waste recycling (BWR) simulations using backfill cycles were encouraging. This was illustrated in figure 6.2, but those results were produced at a backfill pressure of 10 psig, well below optimum backfill pressures and using different cycle parameters to those used experimentally. This section presents further BWR simulations for both purge and backfill cycles, but using model parameters which agree more exactly with the experimental work, (appendix 6).

6.4.1 BWR with Backfill Cycles

For fixed product amounts of 8 and 4 litres per part cycle, the backfill pressure was varied from 0 to 60 psig and, for each backfill pressure, waste recycle ratios between 0 and 1 were investigated. Figure 6.16 presents the results for the 8 litres per part cycle simulations. For each backfill pressure investigated increasing the waste recycle ratio caused a fall in product oxygen concentration and an increase in oxygen yield. However up to waste recycle ratios of about 70% the fall in product concentrations were small compared to the increases in oxygen yields. Figure 6.17 presents results for the 4 litres per part cycle simulations. At this product amount the model predicted 100% oxygen concentration over a wide range of backfill pressures, but it also showed that, where 100% oxygen was simulated with a conventional backfill cycle, then waste recycle ratios of 60 to 70% could be used before the product concentration fell. Hence, 20% improvements in oxygen yield and a reduction in the waste oxygen content from about 19% to 12% could be obtained without loss in product concentration.
BFP = BackFill Pressure
Concentration, BFP = 0.0 psig
Concentration, BFP = 14.7 psig
Concentration, BFP = 29.4 psig
Concentration, BFP = 44.1 psig
Concentration, BFP = 58.9 psig
Yield, BFP = 0.0 psig
Yield, BFP = 14.7 psig
Yield, BFP = 29.4 psig
Yield, BFP = 44.1 psig
Yield, BFP = 58.9 psig

Figure 6.16 BWR for a BackFill Cycle: 8 l/part cycle

Figure 6.17 BWR for BackFill Cycle: 4 l/part cycle
6.4.2 BWR with Purge Cycles

Some simulations were completed using purge cycles to see what effect bulk waste recycling would have and to allow comparison with the experimental work. For a product amount per part cycle of 4 litres, different purge amounts were fixed, then as before the waste recycle ratio was varied from 0 to 1. The data collected from these simulations is summarized in figure 6.18. Interestingly, at near the optima purge amounts, waste recycling caused an initial increase in product oxygen concentration, before it then fell. All other purge amounts showed a continuous fall in product oxygen concentration with increased waste recycling. Table 6.1 contains mass balance data for the special case, where an increase in product concentration was produced by waste recycling. This table illustrates another effect of waste recycling in that by changing the composition of the bed feed gas, the amount of gas required to pressurize the beds could be altered. In general, bulk waste recycling returned gas enriched in nitrogen (the more adsorbable component) into the feed line, which increased slightly the amount of gas required to pressurize the beds, resulting in higher compression costs. Table 6.1 shows that increasing the waste recycle ratio from 0 to 90 % resulted in a 1.5 % increase in the amount of gas required to pressurize the beds.

Figure 6.19 shows the effects of BWR on other purge cycles at different higher product amounts and all at near their optima purge amounts per part cycle. However, no further cases of increases in product oxygen concentration were observed by increasing the recycle ratio.
6.4.3 Comparison of BWR Simulations and Experiments

Experimentally BWR was only investigated for purge cycles, (section 5.8). Figure 6.19 compares simulated product oxygen concentrations with the experimental results, (section 5.8). All these cycles had purge amounts that were close to their optima amounts for no recycling. Figure 6.19 again demonstrates that the theoretical predictions had good qualitative agreement with experimental results. Both experiments and theory showed that recycling waste gas generally decreased the product oxygen concentration, but for the highest product concentrations examined, waste recycling caused an initial increase in product oxygen concentration. The main difference between these results is that the experiments showed that significantly more waste gas could be recycled, than theoretically predicted, before the product oxygen concentration fell below its value for no recycling. Therefore the experiments showed a greater increase in oxygen yield, and hence potential energy saving from waste recycling, than was predicted by the simulations.

The highest waste recycle ratio that could be achieved experimentally was 70 %, but the experiments showed that most change in the product and waste oxygen concentrations would have occurred at waste recycle ratios above 70 % and this is also predicted by the simulation results.
Table 6.1 Simulation Results for BWR with Purge Cycles.

The results below are for the special case where some waste recycling simultaneously increased the product oxygen concentration and decreased the waste oxygen concentration.

(Product = 4 l/part cycle, Purge = 22 l/part cycle purge).

<table>
<thead>
<tr>
<th>waste recycle ratio</th>
<th>volumes at STT.P.</th>
<th>product oxygen concn % O2</th>
<th>waste oxygen concn % O2</th>
<th>product oxygen yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>air feed</td>
<td>waste recy'd bed feed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>153.58</td>
<td>153.58</td>
<td>98.89</td>
<td>19.68</td>
</tr>
<tr>
<td>0.1174</td>
<td>136.21</td>
<td>17.59</td>
<td>153.80</td>
<td>99.50</td>
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<tr>
<td>0.1979</td>
<td>124.19</td>
<td>29.66</td>
<td>153.85</td>
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<td>0.2785</td>
<td>112.17</td>
<td>41.75</td>
<td>153.92</td>
<td>97.70</td>
</tr>
<tr>
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<td>100.14</td>
<td>53.86</td>
<td>154.00</td>
<td>96.52</td>
</tr>
<tr>
<td>0.4395</td>
<td>88.11</td>
<td>65.97</td>
<td>154.09</td>
<td>94.84</td>
</tr>
<tr>
<td>0.5199</td>
<td>76.09</td>
<td>78.12</td>
<td>154.20</td>
<td>92.77</td>
</tr>
<tr>
<td>0.6003</td>
<td>64.06</td>
<td>90.28</td>
<td>154.34</td>
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<tr>
<td>0.6807</td>
<td>52.03</td>
<td>102.51</td>
<td>154.54</td>
<td>86.24</td>
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<td>40.00</td>
<td>114.82</td>
<td>154.83</td>
<td>80.68</td>
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<td>27.97</td>
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<td>139.95</td>
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</tr>
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<td>------</td>
<td>21.88</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 6.19 Theory vs Experiments For BWR with Purge Cycles

All experiments had complete purge waste recycle.

<table>
<thead>
<tr>
<th>Experiment, Product</th>
<th>Waste conc</th>
<th>1 l/part cycle</th>
<th>2 l/part cycle</th>
<th>4 l/part cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment, Product</td>
<td>Waste conc</td>
<td>1.6 l/part cycle</td>
<td>2.2 l/part cycle</td>
<td>4.4 l/part cycle</td>
</tr>
<tr>
<td>Experiment, Product</td>
<td>Waste conc</td>
<td>8 l/part cycle</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.19 BWR For Purge Cycles: 4 l/part cycle

% WASTE RECYCLE RATIO (RR)

100
80
60
40
20
0

100
80
60
40
20
0

CONCENTRATION OR YIELD
6.5 Purge Snatching

The ILE model was developed to simulate purge cycles where only the purge waste gas was recycled, (purge snatching). Experimentally it was shown that purge snatching could, in some cases, produce simultaneously both oxygen concentrations and yields above those possible from conventional purge cycles. The development of the model to include purge snatching is described in section 3.5.2 and the process cycle on which these simulations were based is shown in figure 5.1c.

The cycles had a 30 s purge step and the purge snatching time was altered from 0 to 30 s, which corresponded from no purge waste recycle to total purge waste recycle. As with the experiments, the purge snatching time occurred during the latter part of the purge step during which experimentally higher oxygen concentrations in the waste gas were observed, (see section 5.5). Figure 6.22, discussed in section 6.6, includes a waste gas oxygen concentration profile for a purge step for an over purged cycle. It shows that the simulations predicted that the highest oxygen concentrations in the waste gas occurred at the end of the purge step and that for over purged cycles the waste gas could have oxygen concentrations higher than air.

6.5.1 Simulation Results

Three sets of results are presented, all had a product amount of 8 litres per part cycle, but the purge amount was varied. Figure 6.20 shows the product oxygen concentrations obtained for an over purged, an under purged and a near optima purged cycle for different purge snatching times. Figure 6.21 presents the corresponding oxygen yields for the same simulations. In both figures the purge snatching results are compared with the best possible oxygen concentration and yield obtained from the simulated conventional purge cycles.
The results showed that, at near optima purge conditions, purge snatching could produce oxygen concentrations and yields above those capable from conventional purge cycles. However, the model did not converge to steady state for all the simulations run and those that did converge proved particularly sensitive to changes in the number of time intervals or points selected along each characteristic curve. Increasing the number of points along the characteristics increased the computer time required, but improved the accuracy of the simulations and generally produced an increase in the steady state oxygen concentration and yield. This effect was most pronounced for the over purged cycles, where the maximum observed increase in oxygen concentration due to changing the number of points was 2.9%. Figures 6.20 and 6.21 contain results obtained with the lowest number of points used (11), but for the over purged cycles results are also included where the number of points for each step was increased to 31. Increasing the number of points from 11 to 31 resulted in a 5.5 fold increase in the CPU time required.

Changing the number of points did not correct the scatter in the results which is evident in figures 6.20 and 6.21. Instead, the lack of consistency for the purge snatching results was caused by relatively few characteristics leaving the bed during the purge or purge snatching steps, which affected the accuracy of the waste gas concentration predictions with time. Correcting this difficulty requires changes to the way the program develops its characteristic plots and this is a recommendation for future work, (see section 7.2.3.).

Table 6.1 showed that BWR increased the volume of gas required to pressurize the beds and therefore increased compression costs. For the purge snatching simulations, where the recycled gas could contain proportionally more oxygen (the least adsorbable component) than air, waste recycling decreased the volume of gas required to pressurize the beds. Hence, at its best purge snatching increased the product oxygen
concentration and yield, while simultaneously reducing the waste oxygen concentration and compression costs.

Table 6.2 illustrates the predicted effects on the bed feed amount of changing the purge snatch time for the over purged results presented in figures 6.20 and 6.21. It shows that increasing the recycle ratio from 5.24% to 18.1% reduced the gas to be compressed by 0.8%.

<table>
<thead>
<tr>
<th>purge snatching time s</th>
<th>waste recycle ratio</th>
<th>volumes at S.T.P.</th>
<th>product oxygen concn</th>
<th>product oxygen yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>litres per part cycle</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>air feed</td>
<td>waste recy'd</td>
<td>total bed feed</td>
</tr>
<tr>
<td>5</td>
<td>0.0524</td>
<td>155.84</td>
<td>6.76</td>
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<td>0.0890</td>
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<td>162.49</td>
</tr>
<tr>
<td>15</td>
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<td>16.63</td>
<td>161.75</td>
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<td>161.73</td>
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<tr>
<td>25</td>
<td>0.1810</td>
<td>134.69</td>
<td>26.57</td>
<td>161.26</td>
</tr>
</tbody>
</table>

6.5.2 Comparison of Theory with Experiment for Purge Snatching

Relatively few experiments and simulations were done for purge snatching and as described above the accuracy of the simulations could be improved. Nevertheless, both experiments (section 5.5) and theory showed that purge snatching could improve the oxygen concentrations and yields above values possible with ordinary purge cycles for cycles close to optimum purge conditions. They also showed that recycling purge waste caused most benefit to the oxygen concentration for the over purged cycles, which produce the most purge waste gas. Purge snatching produced a small fall in oxygen concentration for the under purged cycles, where relatively small amounts of nitrogen enriched gas were recycled.

The simulations predicted a small saving of power when purge snatching at close to or above optima purge amounts. The experiments also showed a decrease in bed feed amount with increased purge snatching time, but experimentally this could have been caused by the increase in bed pressure when purge snatching, (figure 5.18).
Figure 6.20 Theoretical Prediction of the Effect of Purge Snatching on the Product Oxygen Concentration for Cycles Having Different Purge Amounts Per Part Cycle. (Product = 8 litres/part cycle).

Figure 6.21 Theoretical Prediction of the Effect of Purge Snatching on the Oxygen Yield for Cycles Having Different Purge Amounts Per Part Cycle. (Product = 8 litres/part cycle).
6.6 Direct Purging

In section 6.3 comparisons were made between experimental and simulated results for purge cycles and backfill cycles. However, experimentally the regeneration gas was supplied directly from the pressurized bed, while the model simulated the regeneration gas being supplied from a perfectly mixed product reservoir. Previous workers have ignored these differences and that was the approach taken for the comparisons made in section 6.3. However, the experimental results presented in section 5.9 showed a small but significant difference in performance when purge gas was supplied from the product reservoir compared to when it was supplied directly from the pressurized bed. The ILE model was extended so as to be able to simulate direct transfer of purge gas from one bed to another, (section 3.5.3). This section presents the results from the direct purge cycles and compares them with the mixed purge cycle results.

6.6.1 Direct Purge Simulations

Transferring variable composition purge gas from one bed to another is significantly harder to simulate than the alternative of assuming a perfectly mixed purge source. Direct purging required the model to handle variable composition gas entering a bed, including shock waves moving between beds. It meant that during product release different product superficial velocities were used to model just product release or simultaneous product release and purge supply to another bed. As the purge was supplied in the middle of the product release step (figure 5.1b), the model ran three successive product release steps with the middle one removing both product and purge gas from the pressurized bed. This arrangement corresponded closely to the experimental purge cycles discussed in section 5.4.
Characteristic plots for a mixed purge cycle were fully discussed by Kirkby, (1984). Figure 6.22 contains characteristic plots, bed concentration profiles and concentration versus time plots for gas leaving the beds for a direct purge cycle. The example shown in figure 6.22 is for an over purged cycle and may be used to highlight some of the differences between the mixed purge and direct purge options.

The bed concentration profile at the end of the pressurization step shows that high oxygen concentration gas has been produced in the upper section of the bed, but a small amount of much lower oxygen concentration (poor quality) gas has collected at the top of the bed. This plot also shows that the bed contains a shock wave at approximately 0.7 m up the bed. (The zeolite bed length was 0.85 m). Three successive 30 s product release steps followed the pressurization step, but during the second product release step significantly more gas was removed from the bed to supply purge gas as well as product gas. In the first product release step the poor quality gas from the top of the bed entered the product stream. In the third product release step the gas that entered the product stream was also of poor quality because a shock wave left the bed at the end of the second product release step leaving no high oxygen concentration gas remaining in the bed.

If all the product and regeneration gas had been mixed the average oxygen concentration of the product gas would have been improved. Also the direct purge option meant that the shock wave entered the bed being regenerated, so although most of the purge gas had been of high oxygen concentration, the last portion of the purge gas was of low oxygen concentration.

If a fully mixed purge source had been used the effect of the shock wave leaving the bed on the product concentration would have been dampened. This explains why the model showed that the mixed purge supply
was superior for over purged cycles and why the product concentration decreased sharply for the direct purge option when the purge amount was increased above the optimum value.

In industry, where it may not be easy to optimize exactly the purge amount, it may be advantageous to select a mixed purge source because the penalty for over purging would be less severe than for a direct purge source.

The direct purge characteristic plots differ to the mixed purge plots because the direct purge option required three product release steps having different characteristic velocities. A further difference to the mixed purge characteristic plots is that the variable composition purge gas produced different characteristic velocities for those characteristics entering the bed during the purge step, so that adjacent characteristics were no longer parallel.

6.6.2 Direct Purge Versus Mixed Purge Simulations

Figures 6.23 and 6.24 compare the product oxygen concentrations and yields obtained for 8 litres per part cycle product over a range of purge amounts. The figures show that at more than optima purge amounts the mixed purge cycles produced higher oxygen concentrations and yields. These figures also shows that less purge was required to optimize the cycle having direct purge compared to the cycle with the mixed purge source. However, as both purge sources produced similar maximum oxygen concentrations (figure 6.23), the model predicted that it is more energy efficient to supply purge gas directly. This is reflected in figure 6.24, where the direct purge option produced a higher oxygen yield than was obtainable with the mixed purged source.
Figure 6.22  Characteristic Plots for a Directly Purged Cycle

Pressurization Step

The First Product Release Step
Figure 6.22 continued

The Second Product Release Step

PRODUCT RELEASE CHARACTERISTICS

PRODUCT CONCENTRATION PROFILE

BED CONCENTRATION PROFILE

The Third Product Release Step

PRODUCT RELEASE CHARACTERISTICS

PRODUCT CONCENTRATION PROFILE

BED CONCENTRATION PROFILE
**Figure 6.22 continued**

**Depressurization Step**

**Depressurisation Characteristics**

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<td>2</td>
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<tr>
<td>3</td>
<td>6</td>
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**Bed Concentration Profile**

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<th>Distance (m)</th>
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**Purge Step**

**Purge Characteristics**

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**Bed Concentration Profile**

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<th>Composition (mol. %)</th>
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</thead>
<tbody>
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**Waste Concentration Profile**

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</thead>
<tbody>
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<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 6.23 Simulated Direct Purge vs Mixed Purge Concentrations

Figure 6.24 Simulated Direct Purge vs Mixed Purge Yields
6.6.3 Comparing Theory with Experiment for Different Purge Sources

The experimental and theoretical comparisons both illustrated interesting but conflicting differences between supplying the purge gas fully mixed (from a product reservoir), or directly from another bed. The experiments showed that higher oxygen concentrations could be obtained by using a mixed purge, but for both purge sources the optima purge amounts were very similar, (figure 5.31). The simulations predicted that both purge sources produced similar maximum oxygen concentrations, but that by using a direct purge supply less purge would be required for optima conditions. The theory and experiments agreed in showing that at more than optima conditions the mixed purge source was superior.

6.6.4 Discussion

Due to the difficulties encountered in extending the model to cope with supplying purge directly between beds, relatively few direct purge simulations were completed. Further work comparing direct purge with mixed purge is recommended. Also given that the model now has the ability to transfer variable composition gas between beds it would be relatively simple to further extend the model to compare, for example, direct backfill with fully mixed backfill cycles, (see section 7.2.3).

6.7 Computer Resources

The ILE model was modest in CPU time. Typically, the purge cycles (with the mixed purge source) required 15 to 20 seconds per cycle of CPU time and normally took 30 to 70 cycles to reach steady state. These times were obtained using a Prime 9750 system operating primos revision 21 and include the time occupied by the system as well as that directly used to run the model. Increasing the number of points calculated on each characteristics produced increased CPU times, but only produced
small changes in predicted plant performances. This was illustrated for the purge snatching simulations which were most sensitive to variations in the number of characteristic points. During this work several modifications were made to the model, including changes to the way in which the characteristics were developed and they resulted in CPU time saving of up to 20\%, (see appendix 2).

6.7 Conclusions

The qualitative agreement between the model and experiment was extended to cover a wider range of conventional purge and backfill cycles. It was also extended to cover bulk waste recycling, purge snatching and direct purge supply, although relatively few purge snatching and direct purge simulations were completed. This is the first time either waste recycling or direct purging have been included in a PSA model. It is also the first time that transfer of variable composition gas between beds has been included in a PSA model.

The model continued to over predict product oxygen concentration, but generally gave good quantitative agreement for oxygen yields. However, comparing the simulations with the experimental results showed that the quantitative agreement varied with the cycle parameters used. This highlights the need for models to be tested for many different cycle configurations.

The simulations confirmed the experimental finding that backfill cycles could produce higher oxygen concentrations and yields than purge cycles, but could not account for the variations in the experimental results due to changing the purge or backfill flow rates.

The BWR and purge snatching simulations showed the same advantages of waste recycling that were observed experimentally and illustrated the value of the ILE model in predicting the location of optimum operating conditions.
CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This dissertation describes both experimental and theoretical studies for the separation of oxygen from air using a zeolite adsorbent and a two bed PSA process.

Effort was concentrated on the experimental work which investigated conventional simple, purge, backfill and combined cycles as well as two novel cycles for selectively recycling waste gas back into the feed line. Theoretical modelling predicted that waste recycling could improve product oxygen concentrations and yields. The experimental approach for the cycles investigated was to optimize the oxygen concentration and yield for a range of operating conditions, while observing the importance of the main process variables.

The theoretical work involved developing Kirkby's ILE model (1984), to simulate selective recycling of purge and depressurization waste gas. The model assumed perfectly mixed product and regeneration gas, but it was extended to give the option of supplying variable composition purge gas directly from one bed to another.

The range of experimental work provided further data for assessing the qualitative and quantitative predictive capabilities of the model.
7.1.1 Experimental

Despite the increased industrial importance of PSA, there have been relatively few publications covering bulk gas separations using several cycles and a range of operating conditions. This work helps fill that gap, for oxygen separation from air using a 5A zeolite and it should serves as a useful set of results with which future mathematical models may be compared.

The simple cycles produced up to 39% oxygen, while the purge, backfill and combined cycles could all produce 95% oxygen. For the product amounts per part cycle investigated, the combined purge with backfill cycles produced the highest obtainable oxygen concentrations and yields. Provided the backfill rate was sufficiently low, then backfill on its own produced a higher oxygen concentration than purge on its own. The yields obtained from the backfill cycles were always better than those obtained from purge cycles.

Both forms of waste recycling, namely purge snatching and bulk waste recycling (BWR), showed for different cycles that they were able to increase simultaneously the product oxygen concentration, reduce the waste oxygen concentration and improve the oxygen yield. The purge snatching cycles produced oxygen concentrations and yields above the best possible results from the conventional purge cycles. The best BWR results showed that 70% of the waste gas could be recycled without a significant fall in the product oxygen concentration, but while producing a nine fold improvement in oxygen yield. Generally purge snatching reduced compression costs and BWR increased compression costs, but these effects were small. Unfortunately the full potential of waste recycling was not investigated as design limitations meant that complete waste recycling could not be obtained, (section 7.2.1).

The discovery of a critical purge velocity may explain why in previous similar work, Kirkby (1984) and Liow (1986), purge cycles had
failed to produce greater than 70% oxygen. The backfill experiments showed that the rate of backfilling had a large effect on the plant performance. The importance of flow rates was again illustrated by the experiments which investigated the pressure changing steps. Clearly, although oxygen separation on zeolites is essentially equilibrium controlled, kinetics are important. If the flow rates are too high such that insufficient time is available for local equilibrium in the beds to be obtained, then the kinetic separation becomes more significant which decreases the product oxygen concentration. Also, changes in flow rates will affect the influence on the separation of temperature variations within the bed.

The purge cycle experiments showed that the optimum purge to product ratio is not constant as product amount varies and that there were differences between optimizing for oxygen yield and oxygen concentration. Similarly, the backfill cycle experiments showed that the backfill pressures required to optimize oxygen concentration and yield were different. However, while more purge was required to optimize the oxygen concentration rather than the yield, it was the other way round for the backfill cycles, for which less backfill was required to optimize the oxygen concentration rather than the yield. The relationships between these optima were investigated for a range of product amounts per part cycle and may help explain why the combined purge and backfill cycles produced the best performances.

Studying the temperature profiles (appendix 5) gave an interesting insight into the operation of the cycles and if a unique relationship between the thermal and concentration waves in the bed exists, then it is possible that the bed temperatures could be used for plant optimization.
Some of the miscellaneous work presents experimental comparisons not previously published. They showed, for purge cycles, that it was more advantageous to the product concentration to supply purge gas from the product reservoir, rather than directly from another bed and that unsymmetrical operation was detrimental to the plant performance. Also the product oxygen concentrations were improved by making the depressurization pressure profiles as linear as possible and hence reducing the maximum superficial velocities during depressurization.

7.1.2 Theoretical

Recently, by accounting for a greater number of effects such as mass transfer, coadsorption and axial dispersion as well as equilibrium effects mathematical models have produced improved agreement between theories and experiments, [Beaman, (1985); Liow, (1986)]. However, no model as yet is able to qualitatively and quantitatively predict the behaviour of PSA plants for many different cycles and operating conditions.

Given the effort necessary to produce the experimental results, the development of a completely new model to supersede current ones was unrealistic for this project. Instead the theoretical aims were to improve the efficiency of Kirkby's ILE model, to extend the model to cover other cycle options and to assess its agreement with experimental results over a wider range of operating conditions. In comparison to other more complicated models the ILE model is modest on CPU time, had already some proven qualitative agreement with purge and backfill cycles and had predicted that waste recycling may be of benefit. The main disadvantage of the ILE model is its inability to account for finite rates of mass transfer. The model was successfully developed to allow selective recycling of just the purge waste gas (purge snatching), or recycling of both the purge and depressurization waste gases (BWR) for
both purge and backfill cycles. It was also altered to allow the option of supplying the purge gas from the product reservoir, as before, or directly from another bed. The direct purge option is more difficult to simulate and has previously been avoided in PSA modelling despite its widespread use in industry. It required the model to handle variable composition gas and shock waves entering the beds. It also meant that product release had to be modelled as three consecutive steps.

The model proved very robust in producing results for the purge and backfill contour plots and also the BWR simulations. However, modelling purge snatching and direct purging was more difficult and in both these modes the model occasionally had difficulty in attaining steady state. Relatively few direct purge cycles were simulated, but it was predicted that less purge would be required to optimize the product concentration or yield if the purge gas was supplied directly from the another bed, rather than from a product reservoir. The purge snatching simulations relied heavily on the accurate prediction of concentration versus time for streams leaving the bed and they were most sensitive to changes in the number of characteristics starting in the bed at the beginning of each step. Although, the model was able to fill gaps between the characteristics there were cycle steps, particularly at low product velocities, where relatively few characteristics left the bed. In these situations accurate prediction of gas concentrations leaving the bed was more difficult and they produced a certain amount of scatter in the results.

Typically the improvements to the model (appendix 2) produced savings in CPU time of up to 20% for similar purge cycles. Although the efficiency of the program was improved, the fundamental equations and method of solution were not changed.
7.1.3 Comparison Between Theory and Experiment

The model's qualitative agreement with experimental results for the purge and backfill cycles was demonstrated for a wide range of conditions. The model agreed with the experimental results by illustrating the differences in optimizing for product oxygen concentration and yield. They also agreed in showing how the optima purge and backfill amounts changed for different product amounts, but the experimental difference was greater. The model continued to over predict product concentration although the quantitative agreement improved in some cases due to the higher concentrations obtained experimentally. Generally, the quantitative agreement for oxygen yields was good.

Comparisons of the experimental and theoretical contour plots showed that the differences between the experimental and theoretical oxygen concentrations and yields varied as the product amount per part cycle was altered. This meant that the quantitative agreement of oxygen concentrations and yields could appear good at certain product amounts, whereas a comparison over a range of product amounts showed much greater differences. This illustrates the need to test models over wide ranges of conditions.

The BWR simulations for the purge cycles extended the model's qualitative agreement with experiment. Both theory and experiment showed, for certain cycles, that recycling waste gas could improve the oxygen concentration. Theory and experiment agreed in showing that the largest change in product and waste concentrations occurred at high waste recycle ratios. It was also shown that most benefit from BWR was achieved at product concentrations above 90% oxygen.

Relatively few experiments and simulations were completed to compare plant performances for either different purge sources or for purge snatching with different cycles. The purge snatching simulations
agreed with the experiments in predicting higher oxygen concentrations and yields than were possible from conventional purge cycles. The model also agreed with the experiments in showing that, where more than the optima purge amounts were used, a mixed purge source was better. The simulations did not show as obvious a difference in the maximum obtainable oxygen concentrations obtained by changing the purge source, but they did show that direct purging achieves optima conditions using less purge gas. The purge snatching and direct purge simulations would both benefit from further work on the model. A purge step is included in most commercial PSA processes so improvements to the step by selection of the purge source or by modifications to the step (for example purge snatching) are important to industry.

7.2 Recommendations

The preceding text has already identified many areas for future theoretical and experimental research into PSA. This section lists improvements to the experimental apparatus which may help future similar projects and then summarizes the main recommendations for further experimental and theoretical research.

7.2.1 Plant Design

Overall the plant performed well, and required little maintenance. It did however have some limitations and there were certain aspects of the design which, with hindsight, could be improved.

(a) The use of mass flow controllers, as opposed to mass flowmeters, should prove extremely useful. They should reduce the small variations in the mass balances observed for similar cycles, enable the flow rates to be controlled automatically and also give greater opportunity for investigating the importance of average and peak flow rates on plant performance. (It should be possible to integrate mass flow controllers
with the existing Data Translation A/D board).

(b) A number of improvements could be made for future investigations of waste recycling. Both a larger waste reservoir and a larger pressure relief valve on the recycle line should give greater flexibility to the experiments. (The maximum rate of recycling was less than $\frac{1}{6}$ of the maximum rate of depressurization and the waste reservoir had only enough capacity to hold 50% of the gas from each depressurization step).

The main fault with the plant design came from the loss of recycled gas through the air inlet, flap operated, check valve. This will not be easily rectified without causing additional pressure drop in the compressor suction line, which could damage the compressor. However, under other circumstances a spring loaded inlet check valve should prove more effective and the volume of the suction line could be increased to reduce the pressure fluctuations within it.

(c) The use of finer thermocouples will probably result in greater temperature differences being observed in the adsorber beds. Their use is strongly recommended for further studies of bed temperature profiles or the effects of bed lagging.

(d) The loss of pressure in the bed donating the regeneration gas was not ideal for the purposes of comparing cycle performances with each other and with the theoretical model. This effect could be reduced by either increasing the bed pressurization rate, decreasing the regeneration flow rate or by using a back pressure regulator at the top of the beds.

Alternatively, the signals from the bed pressure transducers could be used to operate the solenoid valve on the product line. This would enable the importance of cocurrent partial depressurization to be investigated.
(e) The choice of pipe fittings should be made so as to reduce the number of possible sources for gas leaks. In general, soldered fittings should be used wherever possible.

(f) The alumina sections proved very effective in protecting the zeolite from moisture vapour and their inclusion in future plant designs is recommended.

7.2.2 Future Experimental Work

The scope for PSA research is vast. This project has considered only one application, oxygen separation from air with a zeolite adsorbent. There are other applications for which there is a severe lack of publications. The increased popularity of PSA with industry is largely a result of improved plant design and adsorbents and there are certainly improvements still to be made in these areas. On a more fundamental level, techniques need to be developed for measuring reliably the physical properties of the adsorbents, namely equilibria, heat of adsorption and kinetic data. Some recommendations for continued experimental research on PSA processes are given below.

(a) Many industrial PSA plants include BPE steps, but there is a complete absence of published experimental work considering the optimization of these steps and comparing the different forms of BPE. The waste recycle experiments showed how selective use of the waste gas can prove advantageous. Other experiments illustrated the importance of the rates of pressurization, depressurization and regeneration. Improved use of the waste gases, which may include both BPE and waste recycling, could have a large influence on plant performances.

(b) Novel selective waste recycling was able, for some cycles, to increase the product oxygen concentration and yield, while simultaneously decreasing the waste oxygen concentration and compression
costs, for a relatively small increase in capital costs. It should be assessed for use in other plants. It may also prove useful in other separations where a purer waste gas is desirable.

(c) To further improve the understanding of the steps in PSA cycles a combined study of the bed temperature and concentration profiles should prove useful. While the bed temperatures are relatively simple to record, measuring the bed concentration profiles is much harder, (a mass spectrometer would be required). Theoretical models are able to predict bed temperature and concentration profiles, but few if any studies have compared these models with experimental results.

(d) The importance of the process temperatures should be further investigated. The bed feed line from the refrigerant drier could be lagged and a small heater could be installed on this line so that the plant performance could be observed for different bed feed temperatures. The comparison of the plant performance with and without the beds lagged was inconclusive (appendix 5). However, if finer thermocouples and mass flow controllers were installed on the plant the significance of lagging the beds and surrounding pipework should be reassessed.

(e) Most of the results presented in this work were for a fixed part cycle time. It would be interesting to observed the changes in product concentration and yield for a range of cycles times and to have compared for example the purge contour plots for different cycle times.

(f) Relatively few experiments were done for the miscellaneous results presented in section 5.9. However, the investigations of different purge sources, different cycle configurations, unsymmetrical operation and the effects of changing the shape of the bed pressure profiles all merit further research.
There is still a need for published experimental work to investigate other cycle steps common in industry; namely, second cut and cocurrent partial depressurization.

7.2.3 Future Theoretical Work

PSA modelling may be advanced in a number of directions. There is a need to increase the variables accounted for within the models and significant progress in this area has been made in recent years, (section 2.7). Currently, models may be formulated to account for the combined influences of hydrodynamics, equilibria, kinetic and momentum effects. They must also include a number of process assumptions. However, the accuracy of these models is limited by the accuracies with which the model parameters may be measured. These more complicated models should continue to be developed and they will become more useful as computers improve and more reliable experimental data are produced.

There is also a need to extend models to cover a greater range of operating cycles. Several commonly used cycle steps namely, BPE, cocurrent partial depressurization and second cuts have been neglected in theoretical work. Their inclusion in existing models, many of which have reasonable qualitative agreement with experimental results, would enable theoretical comparisons of many different cycles which may lead to improved plant performances. Currently, the modelling of many operating cycles is best suited to those models which use relatively low computer times, such as the ILE model used in this work.

Specific recommendations for further development of the ILE model are now given. Many of these recommendations apply equally well to the development of other models. Liow (1986), for example, included mass transfer, axial dispersion and coadsorption in his model for oxygen enrichment from air. He claimed improved agreement with experimental results in comparison to the ILE model, but his model still over
predicted product concentrations and the computational requirements of both models were not compared.

(a) The ILE model has reasonable qualitative agreement over many types of cycles, it is modest on CPU time and it now has the ability to transfer variable composition gas from one bed to another. It could relatively easily be further developed to include cocurrent partial depressurization, second cuts, direct backfill supply, different BPE modes and unsymmetrical operation. No other model simulating equilibrium dominated separations includes these options.

The inclusion of BPE is especially overdue. It has been included in certain models which simulate kinetically dominated separations, where greatly simplifying assumptions are made that the adsorbed phase remains unchanged during equalization and the gas phase in each bed becomes perfectly mixed. These "frozen solid" assumptions would not be satisfactory for bulk gas equilibrium separations, such as oxygen separation from air with a 5A zeolite, where significant adsorption and desorption occur during the pressure changing steps. Instead the models need to simulate transferring variable composition gas from one bed to another and to account for the separation during the pressure changes. The ability to do this would allow the different forms of BPE to be compared.

(b) Currently, the ILE model is efficient in filling gaps in the characteristic plane within the bed, but for short cycle step times or low gas velocities relatively few characteristics cross the end of the bed. The accuracy of the model in predicting the concentrations of gases as they leave the bed could be improved by modifications to the way in which the characteristics are produced so that more characteristics cross these important boundaries. This modification would have particular benefit to the direct purge and purge snatching results presented in chapter 6.
Most of the simplifying assumptions made in the ILE model contribute to its over prediction of the product oxygen concentration. Its quantitative agreement with experiments varies with product amount per part cycle, but if the quantitative agreement could be improved using simple correction factors then the significance of the model to industry would be enhanced. As it is the qualitative agreements can help to predict optimum operating conditions, as shown in this work by its waste recycling predictions.

PSA processes are already widely used in industry and, given that the efficiency of these processes is almost certain to improve in future years, the importance of PSA technology should increase.
REFERENCES

Espitalier-Noel P.M. & Kirkby N.F., 1988, Oxygen Enrichment from Air using a Zeolite Adsorbent and a Two-Bed Pressure Swing Adsorption Unit, paper presented at A.I.Ch.E. meeting in Denver, Colorado. (soon to be published).
Flores-Fernandez G., 1978, Ph.D. Diss., Uni. of Cambridge, U.K.


Kahle, 1942, German Patent 871,886.


Kirkby N. F., 1984, Ph.D. Diss., Uni. of Cambridge, U.K.


Liow J-L., 1986, PhD. Diss, Uni. of Cambridge, U.K.


Null, 1979, German Patent 2,847,310.


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## Appendix 1

### PATENT REVIEW

This appendix contains a selection of the main patents granted to those companies which have been influential in the development of PSA.

**Patent Origins**

<table>
<thead>
<tr>
<th>GB</th>
<th>DE</th>
<th>EP</th>
<th>FR</th>
</tr>
</thead>
<tbody>
<tr>
<td>British</td>
<td>German</td>
<td>European</td>
<td>French</td>
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</tbody>
</table>

**1. Air Products and Chemicals, Inc.**

Air Products (AP) entered the PSA market fairly late, but now have patents for many different gas separations.

<table>
<thead>
<tr>
<th>Patent</th>
<th>Date</th>
<th>Country</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BISKIS</td>
<td>1967</td>
<td>US</td>
<td>Hydrogen purification by fractionation with alternate regenerative adsorption.</td>
</tr>
<tr>
<td>BLIGH</td>
<td>1974</td>
<td>DE</td>
<td>Separation of the rare gases using PSA.</td>
</tr>
<tr>
<td>DRISSEL &amp; SIRCAR</td>
<td>1975</td>
<td>DE</td>
<td>PSA process which operated at sub atmospheric pressure yielding a 90% O2 product.</td>
</tr>
<tr>
<td>SIRCAR &amp; ZONDLO</td>
<td>1977</td>
<td>US</td>
<td>First major PSA patent by AP giving 95% O2 &amp; 99.7% N2 simultaneously as products. Vacuum desorption was used in an eight minute cycle.</td>
</tr>
<tr>
<td>SIRCAR</td>
<td>1979</td>
<td>US</td>
<td>DESCRIBES METHODS TO SEPARATE 3 OR MORE COMPONENT MIXTURES, ONE OF WHICH IS HYDROGEN.</td>
</tr>
<tr>
<td>BLIGH</td>
<td>1980</td>
<td>GB</td>
<td>O2 plant with an 8 vessel configuration using a rotary valve with vacuum desorption.</td>
</tr>
<tr>
<td>SIRCAR</td>
<td>1980</td>
<td>EP</td>
<td>Two products recovered from a 3 or more component feed.</td>
</tr>
<tr>
<td>KRATZ &amp; SIRCAR</td>
<td>1984</td>
<td>US</td>
<td>DESCRIBES A MEDICAL O2 GENERATOR FOR DOMICILLARY PURPOSES WHICH GENERATES A 90% O2 PRODUCT.</td>
</tr>
<tr>
<td>SIRCAR</td>
<td>1984</td>
<td>US</td>
<td>DESCRIBES A PROCESS FOR ARGON-PURIFICATION.</td>
</tr>
<tr>
<td>ANON</td>
<td>1984</td>
<td>EP</td>
<td>EXCHANGED FAUXITE ADSORBENT WITH POLY VALENT IONS TO OBTAIN A HIGHER ADSORBENT SELECTIVITY AND CAPACITY FOR AIR SEPARATION.</td>
</tr>
</tbody>
</table>

**2. Bergbau-Forschung GmbH**

Bergbau-Forschung began work on CMS in the 1960's. Their main interest is in nitrogen enrichment from air.

<table>
<thead>
<tr>
<th>Patent</th>
<th>Date</th>
<th>Country</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WERNER &amp; MUNZNER</td>
<td>1969</td>
<td>GB</td>
<td>BF began its research into carbon molecular sieves in the 1960's and produced a no. of patents dealing with the manufacture of these sieves.</td>
</tr>
<tr>
<td>JUNGEN &amp; KARWART</td>
<td>1970</td>
<td>GB</td>
<td>One of many patents discussing batch air separation.</td>
</tr>
<tr>
<td>MUNZNER et al.</td>
<td>1971</td>
<td>ZA</td>
<td>BF's first continuous air separator for up to 95% O2. Vacuum desorption for 93-99.5% nitrogen with a low dew point and CO2 concentration.</td>
</tr>
<tr>
<td>MUNZNER et al.</td>
<td>1972</td>
<td>ZA</td>
<td>Separation of hydrocarbons.</td>
</tr>
<tr>
<td>PETERS et al.</td>
<td>1975</td>
<td>DE</td>
<td>Hydrogen recovery units.</td>
</tr>
<tr>
<td>BORSE &amp; al.</td>
<td>1976</td>
<td>DE</td>
<td>PSA for treating coke oven gas.</td>
</tr>
<tr>
<td>SCHROETER et al.</td>
<td>1978</td>
<td>DE</td>
<td>USED ACTIVATED CARBON OF 2 DIFFERENT POROSITIES IN RECOVERY OF N2 FROM COKE OVEN GAS TO FULLY UTILIZE THEIR PROPERTIES.</td>
</tr>
<tr>
<td>JUNGEN</td>
<td>1978</td>
<td>GB</td>
<td>Nitrogen recovery.</td>
</tr>
<tr>
<td>JUNGEN et al.</td>
<td>1978</td>
<td>DE</td>
<td>Popular commercial plant operating from super to subatmospheric pressure for air separation.</td>
</tr>
<tr>
<td>KNOBLAUCH &amp; HEINHACK</td>
<td>1981</td>
<td>DE</td>
<td>TREATING HIGHER HYDROCARBONS. THE EFFORT WAS MADE TO INCREASE THE YIELD AND REDUCE REGENERATION FOR DEALING WITH DIFFICULT MATERIALS.</td>
</tr>
<tr>
<td>KNOBLAUCH et al.</td>
<td>1982</td>
<td>DE</td>
<td>TREATING HYDROGEN SULPHIDE STREAMS.</td>
</tr>
<tr>
<td>HENNING et al.</td>
<td>1982</td>
<td>EP</td>
<td>POPULAR COMMERCIAL PLANT OPERATING FROM SUPER TO SUBATMOSPERIC PRESSURE FOR AIR SEPARATION.</td>
</tr>
<tr>
<td>RICHTER et al.</td>
<td>1983</td>
<td>DE</td>
<td>TREATMENT OF CO2 AND METHANE.</td>
</tr>
<tr>
<td>KNOBLAUCH et al.</td>
<td>1984</td>
<td>DE</td>
<td>IN DECREASING THE PRESSURE EQUALIZATION TIME IT HAS BEEN POSSIBLE TO PRODUCE NITROGEN WITH ONLY 10 TO 1000 ppm OF OXYGEN.</td>
</tr>
<tr>
<td>KNOBLAUCH</td>
<td>1984</td>
<td>DE</td>
<td>NOX PURIFICATION OF AIR. (WITH THERMAL REGENERATION)</td>
</tr>
</tbody>
</table>

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3. BOC Group PLC

BOC concentrated their early efforts on PSA as a means of air separation. The table below does not include patents from the Japanese companies.

<table>
<thead>
<tr>
<th>Inventor</th>
<th>Year</th>
<th>Country</th>
<th>Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARMOND &amp; CARNE</td>
<td>1962</td>
<td>US</td>
<td>3,063,217</td>
<td>A moving bed apparatus, operating at 90 K, incorporating adsorption and temperature swing to separate Kr and Xe from an oxygen-rich feed. The adsorbent was silica gel.</td>
</tr>
<tr>
<td>SMITH &amp; ARMOND</td>
<td>1974</td>
<td>ZA</td>
<td>74 1399</td>
<td>Enriched air to a product of 55-60% O2 at cryogenic temperatures.</td>
</tr>
<tr>
<td>ARMOND</td>
<td>1975</td>
<td>ZA</td>
<td>74 2002</td>
<td>Extended the lower operating pressure to subatmospheric for CO/N2 and CO2/fuel mixtures. Used partial backfill and second cut steps in a PSA air separator where molecular sieve cakes were used as an oxygen adsorbent.</td>
</tr>
<tr>
<td>WEBBER</td>
<td>1975</td>
<td>ZA</td>
<td>74 6791</td>
<td>Describes an electric powered compact PSA apparatus using zeolite molecular sieve to generate breathing air for medical use. PSA using SA zeolite was used to produce N2 of 99.9% purity with 67.5% recovery. 4 beds, 1 bed system in which the waste stream is utilized.</td>
</tr>
<tr>
<td>SMITH</td>
<td>1976</td>
<td>DE</td>
<td>2,559,120</td>
<td>Suggests a procedure where the product is withdrawn at a lower pressure than the feed.</td>
</tr>
<tr>
<td>ARMOND &amp; WEBBER</td>
<td>1976</td>
<td>ZA</td>
<td>74 3280</td>
<td>Used a coupled CMS/ZMS system to remove both nitrogen and argon producing 99.7% oxygen.</td>
</tr>
<tr>
<td>ARMOND &amp; RAY</td>
<td>1977</td>
<td>DE</td>
<td>2,707,245</td>
<td>Describes an adsorption column coupled to a rectifier to recover argon from an O2 stream.</td>
</tr>
<tr>
<td>SMITH &amp; WEBBER &amp;</td>
<td>1979</td>
<td>DE</td>
<td>2,855,426</td>
<td>Oxygen production using two adsorbents.</td>
</tr>
<tr>
<td>ARMOND &amp; SMITH</td>
<td>1982</td>
<td>GB</td>
<td>2,086,258</td>
<td>The particle size was reduced and it was claimed that this allowed decreased power consumption, bed size and cycle times. N2 PSA plant. Claims that the plant reached steady state very quickly when restarted.</td>
</tr>
<tr>
<td>ARMOND &amp; DEVERELL</td>
<td>1982</td>
<td>GB</td>
<td>2,091,121</td>
<td>PSA using magnetic moving beds.</td>
</tr>
</tbody>
</table>

4. Exxon

Exxon were especially influential in the early stages of PSA development and many people consider Skarstrom to have invented PSA.

<table>
<thead>
<tr>
<th>Inventor</th>
<th>Year</th>
<th>Country</th>
<th>Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKARSTROM</td>
<td>1960</td>
<td>US</td>
<td>2,964,627</td>
<td>Early work on gaseous adsorption process.</td>
</tr>
<tr>
<td>SKARSTROM</td>
<td>1963</td>
<td>US</td>
<td>3,082,166</td>
<td>Drying of gases leading to their recovery.</td>
</tr>
<tr>
<td>JEVAYEKARAN et al</td>
<td>1979</td>
<td>GB</td>
<td>2,003,742</td>
<td>Describes the first use of a buffer tank in the purge step of PSA.</td>
</tr>
<tr>
<td>SMITH</td>
<td>1980</td>
<td>DE</td>
<td>3,007,427</td>
<td>PSA using magnetic moving beds.</td>
</tr>
<tr>
<td>ARMOND &amp; SMITH</td>
<td>1982</td>
<td>GB</td>
<td>2,086,258</td>
<td>PSA using magnetic moving beds.</td>
</tr>
<tr>
<td>ARMOND &amp; DEVERELL</td>
<td>1982</td>
<td>GB</td>
<td>2,091,121</td>
<td>PSA using magnetic moving beds.</td>
</tr>
<tr>
<td>MAHON &amp; PHILLIPS</td>
<td>1985</td>
<td>US</td>
<td>3,212,236</td>
<td>PSA using magnetic moving beds.</td>
</tr>
<tr>
<td>SKARSTROM et al.</td>
<td>1966</td>
<td>US</td>
<td>3,237,377</td>
<td>Initial PSA process using 13X zeolite in a 2 bed process and BPE to give an O2-rich product.</td>
</tr>
<tr>
<td>SKARSTROM et al.</td>
<td>1966</td>
<td>US</td>
<td>3,282,647</td>
<td>The early patents by Skarstrom are considered by many to signify the first invention of PSA. Describes a two bed O2 PSA for which the idea of BPE was introduced.</td>
</tr>
<tr>
<td>WAGONSKE et al.</td>
<td>1982</td>
<td>US</td>
<td>4,319,892</td>
<td>PSA using magnetic moving beds.</td>
</tr>
<tr>
<td>HATCH et al.</td>
<td>1982</td>
<td>US</td>
<td>4,319,893</td>
<td>PSA using magnetic moving beds.</td>
</tr>
</tbody>
</table>

5. Grace

Grace started to patented PSA processes in 1973. Their main interests were in air separation and air drying.

<table>
<thead>
<tr>
<th>Inventor</th>
<th>Year</th>
<th>Country</th>
<th>Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAUGHAN</td>
<td>1974</td>
<td>DE</td>
<td>2,147,574</td>
<td>Describes the zeolite used by Grace.</td>
</tr>
<tr>
<td>LEE &amp; STAIRL</td>
<td>1974</td>
<td>US</td>
<td>2,788,036</td>
<td>Describes their first PSA unit for O2 production using BPE and purging in a twin bed process.</td>
</tr>
</tbody>
</table>

214
6. L’Air Liquide

L’Air Liquide were one of the pioneers of gas separations by adsorption.

<table>
<thead>
<tr>
<th>Inventor/Inventors</th>
<th>Year</th>
<th>Country</th>
<th>Document</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOMINE &amp; GUERIN</td>
<td>1961</td>
<td>FR</td>
<td>1,117,918</td>
<td>Process incorporating BPE to separate nitrogen and argon from air.</td>
</tr>
<tr>
<td>de MONTGAREUIL</td>
<td>1964</td>
<td>US</td>
<td>1,155,468</td>
<td>Describes a very versatile PSA plant, which could operate with many adsorbents using up to 6 adsorbent beds. For air separation the productivities varied from 322-1930 g absorbent per litre oxygen product. Study of separating oxygen and argon mixtures.</td>
</tr>
<tr>
<td>DOMINE &amp; QUOEX</td>
<td>1967</td>
<td>FR</td>
<td>1,477,542</td>
<td>PSA process for oxygen production.</td>
</tr>
<tr>
<td>ELUARD</td>
<td>1968</td>
<td>FR</td>
<td>1,601,126</td>
<td>Describe cycles for purifying hydrogen.</td>
</tr>
<tr>
<td>ELUARD</td>
<td>1969</td>
<td>FR</td>
<td>1,552,064</td>
<td>Hydrogen separation from carbon oxides.</td>
</tr>
<tr>
<td>ELUARD</td>
<td>1970</td>
<td>FR</td>
<td>1,601,126</td>
<td>Multi-column plant in which product is fed to the beds to give an intermediate pressure before feed takes beds to U.O.P.</td>
</tr>
<tr>
<td>DOMINE &amp; HAY</td>
<td>1970</td>
<td>DE</td>
<td>1,939,701</td>
<td>PSA to remove water and CO2 from air.</td>
</tr>
<tr>
<td>HUBERT et al.</td>
<td>1972</td>
<td>FR</td>
<td>2,130,897</td>
<td>Series of process designs including control systems for processes. One design had different materials so gas streams with impurities could be purified with one of the many different cycle configurations. The plant is suitable for air separation.</td>
</tr>
<tr>
<td>BAUDOIN et al.</td>
<td>1973</td>
<td>FR</td>
<td>2,157,053-9</td>
<td>Air separation PSA plant with many BPE steps.</td>
</tr>
</tbody>
</table>

7. Linde

Linde have been involved in gas separation and adsorption since 1940. They produced several processes using TSA and first used PSA for hydrogen purifications.

<table>
<thead>
<tr>
<th>Inventor/Inventors</th>
<th>Year</th>
<th>Country</th>
<th>Document</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>STRIECH &amp; JAKOB</td>
<td>1976</td>
<td>DE</td>
<td>2,460,513</td>
<td>Hydrogen recovery units with multi-bed operation.</td>
</tr>
<tr>
<td>BENKNANN</td>
<td>1977</td>
<td>DE</td>
<td>2,604,305</td>
<td>9 column H2 plant treating 30,000 m3/hr of crude gas.</td>
</tr>
<tr>
<td>LEITZEB</td>
<td>1978</td>
<td>DE</td>
<td>2,702,784,5</td>
<td>Used Bergbau-Forschung’s CMS to formulate cycles for H2 generation from air where the amount of O2 in the product could be varied by the pressure of the regeneration step.</td>
</tr>
<tr>
<td>BENKHANN</td>
<td>1980</td>
<td>DE</td>
<td>2,916,585</td>
<td>Equalized pressure on suction and delivery side of a vacuum pump when no equalization was taking place to save energy.</td>
</tr>
<tr>
<td>LEITZEB</td>
<td>1982</td>
<td>DE</td>
<td>3,030,081</td>
<td>Reduced the start up period for a PSA process from 8 to 2 cycles.</td>
</tr>
</tbody>
</table>

8. Union Carbide Corporation

Union Carbide Corporation hold more patents on PSA than any other company. They were first to exploit hydrogen PSA on a large scale.

<table>
<thead>
<tr>
<th>Inventor/Inventors</th>
<th>Year</th>
<th>Country</th>
<th>Document</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>McROBBIE</td>
<td>1964</td>
<td>USP</td>
<td>3,140,931</td>
<td>Specified a zeolite (of 14.6 Angstroms) at 223-243 K for O2 PSA plants.</td>
</tr>
<tr>
<td>KIYONAGA &amp; PREDERGAST</td>
<td>1968</td>
<td>DE</td>
<td>1,272,891</td>
<td>Looked at product purity for He purification to see when the product release step ended and when regeneration should begin. Extended PSA air purification to a wider range of organic and inorganic with ammonia modified molecular sieves.</td>
</tr>
<tr>
<td>LEE &amp; SCHOOPS</td>
<td>1969</td>
<td>DE</td>
<td>1,911,678</td>
<td>4-5 bed O2 plant using BPE and backfill for a better product recovery.</td>
</tr>
<tr>
<td>WAGNER</td>
<td>1969</td>
<td>USP</td>
<td>3,438,418</td>
<td>Air separation plant with 4-5 beds, using multiple BPE steps to improve O2 recovery.</td>
</tr>
<tr>
<td>GAFFI</td>
<td>1971</td>
<td>USP</td>
<td>3,586,816</td>
<td>Described a versatile PSA plant using BPE and backfill for a better product recovery.</td>
</tr>
</tbody>
</table>
Union Carbide Corporation patent continued

Batta 1972 US 3,636,679 3 bed air separation plant. Similar recovery to his 1971 plant but less hardware. Used series of beds operating at different pressures in O₂ production for sewage treatment.

Batta 1972 DE 2,153,808 Used two or more adsorptive zones and depressurized before equilibrium was achieved. N₂/N₂ system.

McCombs 1973 DE 2,153,807 Used upper bed pressure to control H₂/CÖ₂ PSA plant. Batta suggests purge/feeding ratio for O₂ must be at least 4 for high performance plants.

Wagner 1973 US 3,703,068

Batta 1973 US 3,717,974

Collins 1973 US 3,751,878 PSA to remove carbon dioxide from natural gas.

Rudelstoffer & Fuderer 1976 US 3,986,849 A polybed process for H₂ purification taking up to 1.7 million cubic feet of of feed per day.

Collins 1976 US 3,973,931 The air feed was heated to about 318 K improving O₂ recovery from 39.8% to 46.4%.

Doshi 1978 US 4,077,780 Describes a process for H₂ and N₂ recovery from ammonia purge gas. N₂ Argon is concentrated in this process and could be further purified.


Keller & Kuo 1982 US 4,354,859 O₂ PSA plant. Productivity increased by imposing cyclic gas flow and pressure variations on the gas mixture in the adsorption column from opposite ends.

Wilson 1982 US 4,359,328 Showed that inverted PSA was possible. i.e. N₂ from air using a zeolite adsorbent.

Fuderer 1982 US 4,333,744 Claimed to enhance H₂ recovery from CO₂ by firstly using a pre-heated and partially purified feed steam followed by the untreated feed stream.

Fuderer 1982 US 4,340,398 Describes a cycle using both BPE and equalization with a buffer vessel.

Doshi & Kishore 1982 US 4,381,189 PSA process where concurrent depressurization was terminated at a relatively high intermediate pressure level, followed by BPE to the other beds.

Fuderer 1983 US 4,398,926 Coupled PSA with a membrane separation system and a power turbine to recover high pressure hydrogen.

Doshi 1983 US 4,398,926 Suggested a longer purge step for enhanced product recovery and a multi-valve surge drum which could collect counter current depressurization gas and provide purge gas simultaneously.

Cassidy & Doshi 1984 US 4,461,630 Sequence of direct and indirect pressure equalization steps for systems with at least 5 adsorption beds to improve product recovery and purity.

Fuderer 1984 US 4,468,237 Used concurrent purge step at the adsorption pressure before a concurrent depressurization.

Fuderer 1984 US 4,475,929 4 bed process with purge and pressure changing steps. PSA drying process.

Fuderer 1984 EP 115,752 Gives a flow sheet for an H₂ PSA system coupled with a power turbine which compressed air for an air separation unit. The O₂ produced is used in the H₂ generation system which feeds the PSA plant.

CONTRACTING FIRMS

1) Aerojet General Corporation

Milton 1965 USP 3,144,654 Used a SA zeolite to produce an O₂ rich product using heat or vacuum regeneration for a tonnage to portable size design.

2) Barrett Corporation

Ruder & Isles 1975 USP 3,922,149 A PSA unit designed to produce enriched air for use on board jet aircraft.

3) Deutsche Babcock & Wilcox

Meyer 1974 DE 2,268,672 N₂ PSA plant.

216
4) Howe-Baker Engineers Inc.

BRAZZEL 1973 US 3,775,964 Aspects of PSA control.
SHELL, TAMER & BRAZZEL 1974 US 3,788,037 Describes various PSA designs.
BRAZZEL 1978 DE 2,309,197 H₂ purification units.

5) Petrocarbon Development Ltd.

BIRD 1976 US 3,944,400) PSA systems for many gases.
GB 1,444,321

6) Foster Wheeler Energy Corporation

ANON 1979 DE 2,844,274 PSA process.

7) Green & Kellogg Inc.

McCOMBS & VRANA 1978 DE 2,752,801 PSA to produce high quality O₂. Modular design.
McCOMBS 1983 US 4,373,938 Illustrated the modular concept for PSA plants.

Other Patents of Interest

1) British Celanese Ltd.

FINLAYSON & SHARP 1932 GB 365,092 Gas mixture was fed into a pressure vessel of activated carbon or silica gel where certain gases were adsorbed more strongly than others. This was a batch process but the first to use the principles of PSA.

2) Bendix Corporation

ANON 1975 DE 2,454,801 PSA device for the production of respiratory air.
GARDNER 1978 DE 2,559,120 Describes a design where a piston filled adsorbent moves within a cylinder to produce oxygen rich air.

3) Normalair - Garrett Holding Ltd.

HAMLIN & TAYLOR 1982 EP 46,169 Used a microprocessor to control the operation of a separation system generating breathing air for a life support system.

4) Farbenfabriken Bayer A.G.

HEINZE 1962 Bel 613,267 First to integrate pre-treatment beds in PSA.

Japanese Companies

1) Osaka Oxygen Industries LTD.

MAGIWARA et al. 1974 JP 49 54289 Their first O₂ plant giving 90 % product and 53 % yield.
MAGIWARA et al. 1978 JP 53 96987 Improved their previous O₂ plant by using vacuum desorption.
MAGIWARA et al. 1978 JP 53 99891 O₂ purity improved by using vacuum desorption.
MAGIWARA et al. 1982 JP 58 135186 They managed to improve their yield from their O₂ plant by using a three bed process.

217
2) Toray

INOGUE & TSUNOI 1977 JP 52 135106 A N2 PSA unit giving a product containing only 0.06 % O2.

MIVAO & TSUNOI 1977 JP 52 54681 N2 PSA unit using 4 beds to reduce the amount of N2 to be recycled.

MIVATER et al. 1977 JP 52 99977 Air separation PSA unit demonstrating the use of buffer vessels to obtain a steady flow of product. Synthetic zeolite manufacture.

ANON 1980 JP 55 17614 Air separation PSA in which the adsorption stage is split.

3) Nokusan

MAEDA 1977 JP 52 68893 Describes their first O2 PSA plant. A conventional two bed process. Similar plant to previous patent but with improved pipework.

MAEDA et al. 1977 JP 52 80294 Improved O2 recovery by up to 20% on previous design.

YAGISHI & MAEDA 1979 JP 54 61091.2 PSA plant for the production of argon.


ANON 1982 JP 57 54443 Air separation PSA process. 4 bed system with 12 stages in each cycle.

4) Japan Oxygen Company

KATSUKI et al. 1977 JP 52 81092 Describes their first O2 PSA plant.

OKADA & WAKAZUMI 1978 JP 53 37583.4 PSA unit coupled to an expansion apparatus to recover pressure power by conversion to mechanical energy.

ANON 1982 JP 57 43289 A PSA unit composed of two concentric columns packed with adsorbent between them and several heat transfer plates in the outer column to increase efficiency. Product oxygen from the PSA process was purified further by a membrane unit and the final product was used for regeneration to reduce the regeneration time.

ANON 1983 JP 58 151304

5) Hitachi

ANON 1981 JP 55 152518 Describes their first two bed O2 PSA plant.

ANON 1981 JP 56 45804 N2 PSA unit with pressure equalization using buffer vessels.

ANON 1982 JP 56 54208 Air separation PSA in which the beds were 75% filled with 5Å zeolite and 25% filled with 4Å zeolite to improve O2 yield. In this design a pressure control valve is used to control the exhaust gas from the beds and this was said to have improved the O2 yield.

ANON 1982 JP 57 7802 Zeolite manufacture for air separation.

ANON 1984 JP 57 136935 Zeolite manufacture for air separation.

6) Seiitetsu Kagahi Co Ltd.

Anon 1984 JP 59 92907 Argon recovery from a zeolite / CMS route.

7) Mitsubishi Heavy Industries

AKITANI et al. 1979 JP 54 62994 Describes their first O2 PSA plant which only produced low purity product.

AKITANI et al. 1979 JP 54 79775 N2 PSA process for M2 generation.

AKITANI et al. 1979 JP 54 122677N N2 PSA process in which internal and external heat exchangers are used to promote efficient operation.

MISHIMOTO et al. 1980 JP 55 24517 This describes a different rotor stator design in which it is claimed the adsorbent is used more efficiently.

ANON 1981 JP 57 78922 In this PSA process to separate CO2 from N2 microwave irradiation was used to regenerate the column.

ANON 1982 JP 57 107221.2 In this design an expansion turbine is coupled to the column so that the expanded nitrogen can be used as a coolant for the feed.

ANON 1983 JP 58 223613 Zeolite manufacture for air separation.
Appendix 2  The Subprograms of the ILE Model

A2.1 Introduction

This appendix summarizes the functions of each subprogram in the ILE model and illustrates their arrangement in a block diagram, (figure A2.1). In addition, the major modifications made to the model in this project are discussed.

A2.2 The Subprogram Functions

CPL (command programming language) PROGRAMS

- **RUNPSA.CPL**: controls and gives access to the following functions.
- **COMPILE.CPL**: compiles all the subprograms.
- **DEBUG.CPL**: enables the model to run with a debugger mode.
- **BUILD.CPL**: creates a segment file of all subprograms.
- **PREPSA.CPL**: creates and edits the data file for the main program.

FORTRAN PROGRAMS

Creating and Editing Input Files

- **ASKPAR**: editing data files, includes HELP information.
- **MENU**: menu for creating data files.
- **GETPAR**: loads default parameters.
- **MODPAR**: modifies default parameters.
- **FILPAR**: creates data in a file.

Utility Programs

- **PROFIN**: stores the initial bed concentration profile.
- **PROFOU**: contains the final profile in the bed, or may be used to dump the bed profile at the end of each step. This information is useful when simulations need to be restarted from their final position.

Utility Files

- **RLFIN**: stores the initial concentrations and times for characteristics leaving the top of the bed during the last product release step. This may be used for the initial purge step.
- **RLFOU**: stores the characteristics that left the product end of the bed in the previous product release step.
Routine to Initialize the Simulation

MAIN reads the input files and checks that sensible data has been fed to the program. It notes which graphs, tables, and messages are required to be printed, at different stages of the simulation. It prints a table summarizing this information, and finally sets the program in motion by calling CNSTEP.

Utility Programs

CNSTEP stores the cycle configuration, sequences the cycle steps, dictates the number of time steps and counts the number of complete cycles. The model can start on any step.

MASBAL prepares and outputs the mass balances for every step at the end of each cycle. It files information for re-starting simulations, and where required data is stored for plotting. It also calculates the feed compositions for those cycles which include waste recycling.

CONTRL is called from MASBAL. This routine manipulates the product superficial velocity to the set point.

ITERM If steady state has been reached, or the model has run the required number of cycles, then this routine terminates the simulation.

Cycle Steps

All the cycle steps are called from within CNSTEP. They establish the boundary conditions, the step times and the intervals for calculating the characteristics. CHARCL is the main routine for calculating the characteristics and is called from these routines, (see figure A2.1).

PRESSN is a pressurization step.

PRODR is a product release step.

PRODRP is a pseudo-step. It is used where more than one product release step is required, such as for the direct purge simulations. This routine will change the value for the product superficial velocity before itself calling PRODR.

DEPRES is a depressurization step.

PURGE covers both fully mixed purge and direct purge.

BACKFL is a backfill step.

LOADAI creates an array (AI) of initial compositions versus position in the correct order from the output of the previous step (RDr array). LOADAI is called from all the cycle step programs.

Characteristic Handling

CHARCL produces a characteristic map in the distance time plane for each process step. It must cope with the formation and propagation of both shock and simple waves and must also identify and amend arrays when characteristics leave the bed. The operation of this routine is summarized in figure A2.2.
CLEARO deletes any characteristics that are effectively superimposed on each other. It also limits the total number of characteristics in the bed at any one time.

FILLUP is called at the end of CHARCL. It identifies gaps in the characteristic maps and fills them. In correcting the gaps FILLUP must accurately determine the type of gaps to be filled. They may be for example, adjacent to shock waves, or at the end of the beds. When adding new characteristics it must ensure that they do not cross existing ones. It must also correctly insert data into the boundary and characteristic point arrays. The operation is summarized in figure A2.3.

FILLEM handles the case where FILLUP is called, but there are less than two characteristics left in the bed. If this routine is called then something may be seriously wrong and the messages printed are helpful for tracking the source of the problem.

Error Handling

PMORTC takes advantage of the PRIMOS option for calling a user supplied routine when a run time error occurs. This is used to print data helpful in tracking the source of the error.

FAILCK contains writing routines for various failures.

ISSCHK writes out the working arrays in the event of a controlled failure.

ISSCAL checks that the values of the current characteristic points array (the ISS working array) are legal. If they are not then the program is terminated with an appropriate message.

CHPROF This routine checks that the characteristics are in strictly correct order and that no characteristics have crossed a shock wave.

ICMF checks mole fractions are in the range 0 to 1.

Equation Solving

DO2BASF (is not a source file). It is the NAG Library program which contains the relevant routine for solving the ordinary differential equations. (Runge Kutta Merson 4th order).

VOYO | Contains the main boundary equations for calculating the change in composition with time along each characteristic.

VLYL | characteristic velocities and the change in composition.

AUX |

PDASH |

Shock Wave Tracking

ISORT deletes unwanted characteristics from the working arrays.

ISHFT adds characteristics to the bottom of working arrays.

ICSW Counts the number of shock waves and gives a code to each new shock wave.

SHKCRS is fed the position of characteristics that have crossed and calculates the shock wave position and composition.

SHOCKX finds where in the distance/time plane the current and previous characteristics have crossed.
Miscellaneous Routines

INFILE opens and closes files. Much of the work performed by this routine was previously done outside the fortran programs.

HPRINT summarizes the model printing options.

AILENG character handling for file names.

Graphics and Tables

MASPLT is a routine to plot the product oxygen concentration and yield against the cycle number.

GPLTCH plots characteristic map.

GPLTBV plots boundary values and the final bed profile.

BMMSGS writes out values that have been dumped into boundary arrays.

SKMSGS writes out shock wave data.

CHMSGS prints the array containing the characteristic points in the bed.

Service Routines to all the above

AUG/ converts between ordinary mole fractions and augmented mole fractions.

DAUG calls a NAG routine for sorting numbers into ascending order. It is used to satisfy the requirements for complete arrays.

ASCEND as above, but sorts into descending order.

DESCEN

STLINE interpolates between two points, \((X_1,Y_1)\) and \((X_2,Y_2)\) to calculate values of \(Y\) for given values of \(X\).

LSHIFT manipulate file names.

RSHIFT

A2.3 Program Alterations made in this Project

Many superficial modifications to the model made it more versatile, more efficient, improved its layout and in some cases improved its accuracy. Some novel modes of operation were added, namely: bulk waste recycling, purge snatching and direct purging. These cycle options resulted in more complicated simulations, as observed in the characteristic plots presented in chapter 6. The robustness of the model was improved and many extra messages were added to help track the simulations through the numerous subprograms.

Relatively few routines escaped without alterations, but many of them were of a trivial nature and do not merit further comment. This section describes the main changes.

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A2.3.1 Modifications to Existing Routines

1. CHARCL

The main changes to CHARCL resulted from the direct purge option. This meant the model had to cope with not only a variable composition purge gas, but also the occurrence of shock waves entering the bed in the boundary values. Dealing with these problems, while maintaining a robust model, proved a considerable challenge and produced several additional clauses in the program logic.

2. FILLUP

As with CHARCL several modifications to FILLUP were required as a result of the direct purge option and other changes were made to improve programming efficiency.

Previously when FILLUP detected a significant gap at an end of a bed it would place characteristics very close to the nearest characteristic in the bed until the gap criteria was satisfied. A similar technique was used for filling gaps adjacent to shock waves. These routines often resulted in large numbers of redundant characteristics lying very close to each other. An alternative mechanism for filling these gaps was devised whereby the program inserted characteristics that began halfway between the end of the bed and the characteristic nearest it. If the gap criterion remained unsatisfied a further characteristic would begin halfway between the starting points for the new gap. A similar logic was used to fill gaps close to shock waves. These improved mechanisms for filling gaps reduced the computational load and reduced the need for the routine CLEARO.

3. CONTRL

The control options needed additional clauses to cope with those cycles having more than one product superficial velocity.
4. PRODR

This routine was modified so that if direct purge was required the characteristics leaving the bed during the product release step supplying the purge gas would be stored in a separate array to the other product release steps.

5. PURGE

This routine was modified for the purge snatching option. When purge snatching, effectively each purge step was split in two and two different purge waste gas compositions were obtained. The second waste gas composition corresponds to recycled gas.

6. MASBAL

The mass balance calculations and summary tables had to be altered depending on the waste recycle mode selected. In addition, when waste recycling the feed gas composition was calculated within MASBAL.

7. CNSTEP

The subprogram was made more versatile, allowing for up to 10 cycle steps in any order, (including multiple occurrence of the same step).

A2.3.2 New Program Routines

1. The Creation and Editing of Data Files

Previously the data files were created manually. This was replaced by a number of Fortran programs, (ASKPAR, MODPAR, FILPAR, GETPAR & MENU), and a small CPL program, (PREPSA.CPL). These new programs resulted in friendlier (HELP information included) and more efficient creation and editing of data files.

The new simulation options were built into the data preparation programs.
2. PRODRP

The pseudo cycle step PRODRP was called from CNSTEP and used to change the product superficial velocity where required. The product release step would then continue as before by calling PRODR. This routine also indirectly ensures that the product is not mixed so that variable composition purge gas is used in subsequent purge steps.

3. CHPROF

This routine (called from CHARCL) is a debugging tool which checks the bed profiles to ensure that the distance co-ordinates of characteristics occur in strictly ascending or descending order. If an error occurred, for example a characteristic may have wrongly crossed a shock wave, then this routine is helpful in isolating the exact cycle step where the simulation may have started to go wrong.
Figure A2.1  Structural Diagram of Model Subroutines

PREPSA.CPL  ASKPAR  MODPAR  MENU  FILPAR  GETPAR

WORKING DATA FILE

PROFIN  PROFOU  RLFIN  RLFOU

MAIN

MASTL

MASBAL  CONTRL  ITERN

CNSTEP

PRESSN  PRODR  DEPRES  PURGE  BACKFL

PRODRP

CLEAR

LOADA1

FILLUP

FILLEM

Boundary Values

AUX  VOYO  VLYL  PDASH

Shock Wave Tracking

ISORT  ISHFT  ICSW  SHKCRS  SHOCKX

Graphics & Tables

GPLTCH  GPLTBV  BVMSGS  SKMSSG  CHMSSG

Plotting Facilities

Error Handling

ICMF  ISSCAL  FAILCK  ISSCHK  CHPROF  PMORTC

Equation Solving

DO2BAF

NAG LIBRARY

Service Routines to all the above:

AUG  DAUG  ASCEND  DESCEN  STLINE  LSHIFT  RSHIFT
Figure A2.2 Block Diagram of CHARCL Operation

CLEARO deletes any unwanted characteristics

Initialize counters and arrays

Select next time step

NO

Select next charn in bed

YES

Next boundary value characteristic?

Enter index into pointer array

NO

DO2BAF

Calculate characteristic

SHKCRS

Check for shock wave

Has characteristic crossed a boundary?

YES

Enter into boundary array

Delete characteristic pointer

NO

Next characteristic

YES

Step complete

NO

FILLUP

Check for gaps

Store graphics

Load return arrays

EXIT

YES

227
Figure A2.3 Block Diagram of FILLUP Operation

1. Enter
2. FILLEM if required
3. Set gap criteria:
   1) distance between adjacent characteristics
   2) concn change between adjacent chars
4. Initialise counters
5. Inspect final bed profile
6. Does gap violate 1) or 2)?
   - YES: Locate origin of gap
   - NO: Next characteristic
7. Is gap adjacent to a shock wave?
   - NO: Interpolate into origin of gap
   - YES: locate the initial gap
8. Calculate new characteristic
9. Has gap been filled?
   - NO: Raise error
   - YES: Load array with new characteristics, rearrange pointers
10. Output message if required
Appendix 3  Experimental Apparatus and Plant Performance

A3.1 Introduction

This appendix contains information to supplement chapter 4. Specifically details on the individual items of equipment are given. A summary of the calibration procedures and data showing the variations in plant performance with operating time are also presented.

Table A3.1 Equipment Specifications

<table>
<thead>
<tr>
<th>Item</th>
<th>Manufacturer/Part No.</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor</td>
<td>HPC Ltd OFB1000</td>
<td>capacity 25.5 m³ hr⁻¹</td>
</tr>
<tr>
<td>Refrigerant Drier</td>
<td>HPC Ltd SRD30</td>
<td>motor 5.5 KW, 530 rpm</td>
</tr>
<tr>
<td>Water filter</td>
<td>HPC Ltd AA0011G</td>
<td></td>
</tr>
<tr>
<td>Feed reservoir</td>
<td>HPC Ltd</td>
<td>50 litres</td>
</tr>
<tr>
<td>Product reservoir</td>
<td>HPC Ltd</td>
<td>20 litres</td>
</tr>
<tr>
<td>Waste reservoir</td>
<td>HPC Ltd</td>
<td>30 litres</td>
</tr>
<tr>
<td>Pressure safety valves</td>
<td>HPC Ltd</td>
<td>110 psig rating</td>
</tr>
<tr>
<td>Air filter Inlet NRV</td>
<td>HPC Ltd</td>
<td></td>
</tr>
<tr>
<td>Computer Equipment</td>
<td>IBM PC/AT</td>
<td></td>
</tr>
<tr>
<td>Printer</td>
<td>Northumber NEC-P3</td>
<td></td>
</tr>
<tr>
<td>12 bit A/D card</td>
<td>Data Trans DY2801/A</td>
<td></td>
</tr>
<tr>
<td>Thermocouple A/D card</td>
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<td>1 &quot; BSP</td>
<td>Alcon Ltd OACP/S4/7V</td>
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</tr>
<tr>
<td>1 &quot; BSP n.o.</td>
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<td>Bents Ltd Wescol P.L.O-8.SE</td>
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<tr>
<td>Diaphragm relief valve</td>
<td>Stephen Wells C.20</td>
<td>compressor recycle</td>
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</table>

OTHER SPECIFICATIONS

Degreasing solvent           | Horgan Chemical Fluorisor |
Sealants                     | Rocol Ltd Oxyseal and Sealogen |
Adsorber Beds x 2            | 1 m long, 0.1 m internal diameter |
Piping & fittings            | Mainly copper piping with brass compression fittings, although some mild steel was used. |
Compressor suction line 2    |                                 |
Compressor discharge and feed lines 28 mm |                     |
Product and regeneration lines 3/8 " |
A3.2 Plant Construction and Commissioning

Careful consideration was given to the safety aspect of the project, and this resulted in modifications to the plant layout, pressure tests on the beds, as well as additional pressure safety valves and shut down equipment. All the equipment was selected so as to be compatible with enriched oxygen environments and the pipework was degreased using the solvent Fluorisol during construction. The items of equipment are listed in table A3.1.

A major task during the commissioning stage was the elimination of gas leaks. This resulted in many of the fittings being soldered. Other leaks were removed using either Oxyseal or Sealogen, both oxygen compatible sealants manufactured by Rocal Limited.

A3.3 Calibration

Once the plant was built, but before the adsorber beds were filled the calibration of all the instruments was checked. The pressure transducers and mass flowmeters were calibrated by the manufacturers for the operating conditions used, but their outputs were verified.

Pressure Measurements

The pressure transducers were checked against the plant's six pressure gauges and three pressure regulators, all of which were checked against each other. There was no means of adjusting the output from the transducers other than returning them to the manufacturers. However, their outputs were automatically temperature compensated and they did not noticeably stray throughout the experiments.

Temperature Measurement

The copper constantan thermocouples were all accurate to within +/- 0.8 K at 273 K. This was shown to be true both at the beginning and end of the experimental work.
Flow Measurement

The process flow rates were measured using mass flowmeters, which measured the thermal capacity of the gas stream. The pipework was constructed so that the gas flow could be diverted through just one flowmeter, or each flowmeter in turn before passing through previously calibrated rotameters. (For simplicity these calibration lines are not shown on figure 4.1). The manufacturers claim the flowmeters have a long term error of less than 1% per year. Over the 15 month period of experimental work their calibration was checked four times. These included once at the beginning and once at the end of the experimental work, but the flowmeters did not require adjustment at any stage. However, they did require a warm up period before use of about 15 minutes. The transient behaviour of the flowmeters was observed by depressurizing the empty pressure vessels (of known volume) through them.

At steady flows the flowmeters were found to be very accurate, with the accumulation in the mass balance being consistently less than 5% of the feed gas. Also the mass balance results from successive cycles showed excellent reproducibility. The manufacturers quote accuracy and linearity errors of less than 1% and reproducibility errors of less than 0.2%. However, the time constant for the flowmeters was 0.7 seconds and there were absolute errors in the flow measurements when the flow rates varied rapidly. This was observed to be especially relevant for the waste gas amount measured during depressurization, where a larger waste reservoir would have reduced the errors. This is illustrated in the plant performance data of tables A3.2 and A3.3, where all other flow amounts were fairly steady, but the waste amounts for similar cycles varied by as much as 40 litres (0.04 m³) per cycle. As the measurements of the feed and product amounts were more consistent it was sometimes necessary to assume zero accumulation in the mass balance.
over the beds and then to interpolate the waste amount. This approach rendered the mass flowmeter on the waste line redundant, other than as a check, so it was eventually moved onto the waste recycle line.

The flowmeters measured the instantaneous flow rate and this was integrated over each step time using the trapezium rule to calculate the amount of gas passing each flowmeter for each step. Over these time intervals the initial and final flow rates were assumed equal to the first and last recorded outputs from the flowmeters.

Oxygen Concentration Measurement

The oxygen analysers required the most frequent calibration, which was done using cylinders of oxygen and nitrogen before most sets of experiments. They measured the volume paramagnetic susceptibility of the sample gas on a scale of pure nitrogen to pure oxygen, at the temperature and pressure at which the last calibration occurred.

A3.4 Plant Performance Versus Running Time

Initially the beds contained only zeolite, but for these conditions significant deteriorations in plant performance were observed with running time. The deteriorations were traced to water contamination of the zeolite, so the beds were refilled, but this time a section of alumina was placed in the bottom of the beds to act as a PSA drier and partially protect the zeolite, (see sections 4.2.2 & 4.4.1).

The majority of experiments done with the beds containing only zeolite investigated purge cycles. Some results from these experiments are shown in table A3.2 to illustrate the fall in plant performance. These results, for similar cycles, demonstrate the fall in product concentration with running time. Also during the 700 hour period between these experiments a 3.2% fall in the capacity of the zeolite for air was observed.
Note that with the exception of the simple cycle experiments, which produced low product concentrations, all the experimental results presented in chapter 5 were taken when the beds contained both alumina and zeolite.

Once the beds had been filled with alumina and zeolite no further fall in plant performance with running time was observed. Again, purge cycles were operated more than any other cycle so they were used to monitor the plant performance. Table A3.3 includes some similar purge cycle results taken during the first 1000 hours after the beds were refilled with the alumina section present. Unlike the results in table A3.2, these results show no obvious decline in product concentration or zeolite capacity with running time. Once the purge contour plots (figures 5.12 & 5.13) had been produced, fully describing the product concentration and yield for ranges of product amount and purge amount, they were used as the basis to check plant performance with time.

It was impossible to exactly reproduce cycles due to changing ambient conditions and the number of operating variables involved. This can be seen in tables A3.2 and A3.3, where the ambient and feed gas temperatures are included.

Water Content of the Feed Air

Gas left the refrigerant drier saturated in water at 275 K, containing about 0.0044 kg water per kg of dry air. For one bed pressurization per 180 s this translates to 2.7 kg of water passing through each bed after 10 days continuous operation. The capacity of 5A zeolite for water at ambient temperature and pressure is about 0.3 kg water per kg of adsorbent, [Breck, (1974)]. Given this information, potentially enough water passed through the beds to totally saturate them in only 6.5 days, (156 hours).
It is probable that even without the alumina sections in the beds the performance of the plant would have eventually stabilized as the moisture content in the zeolite reached a pseudo steady state. However, the presence of large amounts of water in the beds would have interfered with the experimental results so the decision was made to include the alumina sections. Alumina has a high affinity for water, but as the water is easily desorbed during depressurization to atmospheric pressure, the amount of water entering the zeolite sections was greatly reduced.

Table A3.2 Typical Results for Plant Performance Versus Running Time without the Alumina Sections Present

General cycle variables common to all cycles below

<table>
<thead>
<tr>
<th>Upper operating pressure</th>
<th>60 psig (508 kPa)</th>
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</thead>
<tbody>
<tr>
<td>Lower operating pressure</td>
<td>2 psig</td>
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<tr>
<td>Part cycle time</td>
<td>90 s</td>
</tr>
<tr>
<td>Average pressurization rate</td>
<td>2 psi s⁻¹</td>
</tr>
<tr>
<td>Average depressurization rate</td>
<td>2 psi s⁻¹</td>
</tr>
<tr>
<td>Null time</td>
<td>15 s</td>
</tr>
<tr>
<td>Purge time</td>
<td>15 s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ex No.</th>
<th>Prod Approx</th>
<th>Average Temperatures</th>
<th>Volume at STP per cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc % O₂ running hours</td>
<td>Ambient Feed K</td>
<td>Feed litres x 10⁻³ m³</td>
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<td>14</td>
<td>91.3</td>
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Table A3.3  Typical Results for Plant Performance Versus Running Time with the Alumina Sections Present

General cycle variables common to all cycles below

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<tr>
<td>Part cycle time</td>
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</tr>
<tr>
<td>Average pressurization rate</td>
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<tr>
<td>Average depressurization rate</td>
<td>2 psi s⁻¹</td>
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<td>Null time</td>
<td>15 s</td>
</tr>
<tr>
<td>Purge time</td>
<td>15 s</td>
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</tbody>
</table>

(The running hours now refer to the number of running hours since the beds were refilled)

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<thead>
<tr>
<th>Ex No.</th>
<th>Prod Conc % O2</th>
<th>Approx running hours</th>
<th>Average Temperatures</th>
<th>Volume at STP per cycle</th>
<th>Volume at STP per cycle</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Feed Ambient Feed</td>
<td>Feed Product Purge Waste</td>
<td>Feed Product Purge Waste</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>litres ( x 10⁻³ m³ )</td>
<td>litres ( x 10⁻³ m³ )</td>
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<td>295.8</td>
<td>222.2</td>
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<tr>
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<td>371.4</td>
<td>295.8</td>
<td>295.8</td>
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<td>296.9</td>
<td>222.8</td>
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### Appendix 4  Typical Data and Sample Calculations for the Experimental Results Reported in Chapter 5

#### Table A4.1  Simple Cycle Data, (section 5.3)

Data common to all cycles

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<th>Ex</th>
<th>UOP</th>
<th>PRT</th>
<th>NUT</th>
<th>DPT</th>
<th>Av</th>
<th>Av</th>
<th>TOTAL FLOW PER CYCLE (Litres at S.T.P.)</th>
<th>PRODUCT</th>
<th>Av</th>
<th>PROD</th>
<th>% O2</th>
<th>FLOW 1/S</th>
<th>CONCEN</th>
<th>YIELD</th>
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<tbody>
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<td>No. psig</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>Ambient</td>
<td>Feed</td>
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<td>K</td>
<td>Feed</td>
<td>PROD</td>
<td>WASTE</td>
<td>at S.T.P</td>
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Table A4.2  Purge Cycle Data, (section 5.4)

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Particle Reynolds Number Calculation

The average particle Reynolds number corresponding to the critical purge flow rate reported in section 5.4 is calculated below.

\[
\text{particle Reynolds number, } (Re)_p = \frac{\rho v dp}{\mu}
\]

where, \(\rho\) = the gas density \(= 1.35\, \text{kg m}^{-3}\) (288 K, 1 atm)
\(v\) = the superficial velocity \(= 0.17825\, \text{m s}^{-1}\)
\(dp\) = particle diameter \(= 1.7 \times 10^{-3}\, \text{m}\) (average size)
\(\mu\) = gas viscosity \(= 0.02 \times 10^{-3}\, \text{Ns m}^{-2}\)

Hence the average \((Re)_p = \frac{1.35 \times 0.17825 \times 10^{-1} \times 1.7 \times 10^{-3}}{0.02 \times 10^{-3}} = 20.5\)
Comparison with Kirkby's work

Kirkby, (1984), investigated purge amounts from 0 to 5 litres s\(^{-1}\)

Kirkby's data

- bed cross sectional area = 0.0153 m\(^2\)
- average particle size = \(4 \times 10^{-2}\)
- gas density = 1.35 kg m\(^{-3}\)
- viscosity = \(2.0 \times 10^{-5}\)

The average (Re)p at 5 litres s\(^{-1}\) purge = \(\frac{\rho v dp}{\mu}\)

\[
= \frac{1.35 \times (5 \times 10^{-3}/0.0135) \times 4 \times 10^{-3}}{2.0 \times 10^{-5}} = 88
\]

Although no information is available to compare the peak purge flow rates of this work with those used by Kirkby, the average purge flow rates used by Kirkby frequently produced Reynolds particle numbers above the critical value observed in this work.

Table A4.3  Purge Snatching Data, (section 5.5)

Operating parameters common to all cycles

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- UOP = 60 psig
- PRT = 30 s
- DPT = 30 s
- PUT = 30 s
- NUT = 30 s

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238
Table A4.3 continued

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</tr>
<tr>
<td>s</td>
<td>(LITRES AT S. T. P.)</td>
</tr>
<tr>
<td>FEED</td>
<td>PROD</td>
</tr>
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</table>

| | | | | | | |
| 158.0 | 30 | 214.5 | 7.89 | 33.8 | 240.9 | 69.39 | 28.1 | 14.0 | 13.5 |
| 158.1 | 25 | 215.4 | 7.76* | 33.9 | 246.7 | 69.81 | 22.3 | 13.4* | 13.0 |
| 158.2 | 20 | 216.8 | 8.04 | 34.0 | 253.8 | 70.43 | 25.2 | 14.1 | 13.7 |
| 158.3 | 15 | 218.2 | 8.21 | 34.0 | 251.1 | 71.01 | 17.8 | 13.9 | 13.6 |
| 158.4 | 10 | 219.4 | 8.12 | 34.0 | 258.3 | 71.32 | 10.7 | 13.2 | 13.0 |
| 158.5 | 5 | 220.9 | 8.19 | 33.9 | 263.7 | 71.74 | 5.3 | 13.0 | 12.9 |
| 158.6 | 0 | 221.0 | 8.09 | 34.0 | 267.0 | 71.89 | ----- | 12.5 | 12.5 |
| 165.0 | 30 | 227.8 | 4.26 | 46.1 | 266.3 | 93.75 | 50.5 | 10.7 | 10.1 |
| 165.1 | 25 | 228.5 | 4.26 | 46.2 | 272.4 | 93.81 | 44.4 | 10.3 | 9.8 |
| 165.2 | 20 | 233.2 | 4.27 | 46.1 | 281.2 | 93.68 | 35.6 | 9.7 | 9.3 |
| 165.3 | 15 | 235.0 | 4.34 | 46.1 | 291.2 | 93.60 | 25.6 | 9.2 | 9.0 |
| 165.4 | 10 | 238.0 | 4.51 | 46.2 | 301.9 | 93.11 | 14.9 | 8.9 | 8.8 |
| 165.5 | 5 | 240.9 | 4.54 | 46.3 | 310.3 | 92.63 | 6.5 | 8.5 | 8.4 |
| 165.6 | 0 | 242.7 | 4.34 | 46.2 | 316.8 | 92.38 | ----- | 7.8 | 7.8 |

* The low product amount for this cycle gave a lower than expected yield

REC = the amount of waste gas recycled per cycle

Y1 = % oxygen amount for no recycle - net waste amount

Y2 = % corrected yield for over predicted waste flows

In calculating the yield, the recycled gas must be subtracted from the feed amount, to obtain the net air inlet to the plant.

Sample calculations for Y1 and Y2, (see Ex 156.3)

\[
\text{Product amount} \times \text{Product concentration} \times \frac{100}{\text{Net air feed} \times \text{Air concentration}}
\]

\[
Y1 = \frac{8.81 \times 72.88}{[257.7 - (322.1 - 296.3)] \times 21.0} \times \frac{100}{1} = 13.2\%
\]

where, the recycled amount = waste (ex156.6) - waste (ex156.3).

The mass flowmeter on the waste line tended to over predict flows and calibration checks with rotameters suggested the true waste flow the measured value multiplied by 0.75.

\[
Y2 = \frac{8.81 \times 72.88}{[257.7 - (0.75 \times (322.1 - 296.3))] \times 21.0} \times \frac{100}{1} = 12.8\%
\]

239
Table A4.4  Backfill Cycle Data, (section 5.6)

Operating parameters common to all cycles
LOP = 2.5 psig  UOP = 60 psig
DPT = 30 s  PDT = 90 s  PUT = 0 s  PST = 0 s

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<th>BKT</th>
<th>PRT</th>
<th>TOTAL FLOW PER CYCLE (litres at S.T.P.)</th>
<th>Measured</th>
<th>Inferred</th>
</tr>
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<td></td>
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<td>PROD</td>
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<th>Measured</th>
<th>Inferred</th>
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240
### Table A4.5  Purge and Backfill Combined Cycles, (section 5.7)

Operating parameters common to all cycles

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### Table A4.6  Bulk Waste Recycle Data, (section 5.8)

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241
Table A4.6 continued

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</table>

WRR = waste recycle ratio
As some recycled waste gas escaped from the plant from the compressor suction line 100 % WRR above corresponded in practice to a WRR of only 70 %, (see section 5.8).

Table A4.7 Purge Source Data

PRT = 30 s DPT = 30 s PDT = 90 s PST = 0 s WRT = 0 s
Ex 602 Purge supplied directly from the pressurized bed
Ex 603 Purge supplied from the product reservoir

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<th>Av</th>
<th>LITRES PER CYCLE</th>
<th>Av</th>
<th>% O2</th>
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<td>s</td>
<td>Ambient</td>
<td>Feed</td>
<td>(LITRES AT S. T. P.)</td>
<td>PROD</td>
<td>YIELD</td>
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<td></td>
</tr>
<tr>
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Table A4.8  Product Superficial Velocity and Purge Source Data

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<th>Av</th>
<th>LITRES PER CYCLE</th>
<th>Av</th>
<th>% O2</th>
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<td>s</td>
<td>s</td>
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<td>Feed</td>
<td>(Litres at S.T.P.)</td>
<td>PROD</td>
<td>YIELD</td>
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Sample Pressure Drop Calculation

The pressure drop in a packed bed can be described by the Carman Kozeny equation. The calculation below assumes a bed of length 1 m is uniformly packed with solid spherical 1.7 mm particles.

Pressure Drop  =  $180 \mu L v \left[ \frac{(1 - \varepsilon)^2}{\varepsilon^3 dp^2} \right]$

where, $\mu$ = viscosity = $2 \times 10^{-5}$ Ns m$^{-2}$
$L$ = bed length = 1 m
$v$ = gas superficial velocity
$\varepsilon$ = voidage (say 1/3)
$dp$ = average particle diameter = 1.7 $\times$ $10^{-3}$ m

Hence, the gas superficial velocity required to produce 1 bar (1 $\times$ $10^5$ Pa) pressure drop over the bed is

$v = \frac{1 \times 10^5 \times 0.333^3 \times (1.7 \times 10^{-3})^2}{180 \times 2 \times 10^{-5} \times 1 \times 0.667^2} = 6.67$ m s$^{-1}$

The beds have a cross sectional area of 0.007854 m$^2$, so the required volumetric flow to produce a 1 bar pressure drop is about 52 litres s$^{-1}$.
Appendix 5  Process Temperature Effects

A5.1 Introduction

Each time the plant reached steady state (approximately 1500 times), the bed temperature profiles and other average process temperatures were recorded. This appendix contains sample temperature profiles and discusses the relevance of other temperature variations that were observed.

The temperatures were measured with thermocouples, which were placed axially along one of the beds and also on all the main process lines. Their positions on the plant are shown on figures 4.1 and 4.2.

A5.2 Radial Temperature Gradients

Initially the thermocouples positioned along bed 2 were only long enough for their ends to be about 0.005 m inside the bed wall. (The bed diameter was 0.1 m). When the beds were refilled to add the alumina sections (chapter 4), longer thermocouples were installed along the bed and their ends were 0.02 m inside the bed wall. This change immediately produced greater temperature variations for similar purge cycles, which suggests that significant radial gradients may have been present and that there were certainly wall effects. Typically the observed temperatures changes within the zeolite for similar purge cycles were increased from about 13 K to 20 K by using the longer thermocouples.

A5.3 Axial Temperature Profiles

Figures A5.1, A5.2, A5.3 and A5.4 show typical steady state temperature profiles for conventional simple, backfill, purge and combined cycles, all at approximately 4 litres per part cycle product. They illustrate how the temperatures at fixed positions in the bed varied between different cycles and the relationship of these
temperatures to the ambient and feed gas temperatures. The feed gas temperature decreased at the beginning of each pressurization step as the air expanded into the bed to be pressurized.

The lowest thermocouple in the bed (T8), entered the alumina section and showed relatively little variation in temperature compared to the thermocouples inserted in the zeolite. This point is illustrated in figure A5.1, a simple cycle temperature profile. The zeolite temperatures decreased during depressurization and increased during pressurization, while changes in the alumina section were very small. This suggests that the dominant factor in determining the zeolite bed temperatures are the strong heats of adsorption and desorption and not the changes in pressure. It also illustrates the importance of the pressure changing steps to this process.

The simple cycle temperature profiles showed consistently an increase in zeolite bed temperature moving up the bed, but for the more complicated cycles the coldest and hottest parts of the bed were at different positions along the bed profile and not necessarily at the ends of the beds. Also, although simple cycle temperature variations of up to 13.5 K could be observed over one cycle, at any given time the temperature span in the zeolite was no more than 4 K. The lack of variations in temperature during the product release step is a result of only small concentration profiles being produced during the simple cycles. It may also show, along with the lack of temperature variations during the null steps, that there were high resistances to heat transfer within the bed, (see figure A5.1).

Much greater temperature variations were observed for the higher oxygen concentrations produced with the purge, backfill and combined cycles. For example the combined purge and backfill cycle in figure A5.4 showed a temperature variation over one cycle of 23 K and at any given time the temperature differences in the zeolite were as high as 11 K.
Figures A5.2a to A5.2c show the effects of increasing the purge amount per part cycle. Figures A5.3a and A5.3b show the effects on bed temperature of increasing the backfill amount per part cycle. All these graphs contain examples of sudden changes in temperature, or thermal waves, which are produced as concentration waves move in the bed. For example, figure A5.2c shows that the thermocouple nearest the top of the bed (T12) recorded a sharp rise in temperature after 140 s of the cycle. This was caused by a concentration wave passing up the bed during product release. (The concentration and thermal waves do not travel in the bed at the same speed).

Some of these graphs show a sharp fall in the temperature recorded by the lowest placed thermocouple in the zeolite (T9), during product release. It is likely that this occurs due to significant desorption due to loss of pressure when the pressurized bed is required to donate product and regeneration gas simultaneously.

Interpretation of the temperature profiles gave an interesting insight into the operation of combined cycles. This is illustrated for figures A5.4a to A5.4d, which show the changing temperatures for a cycle having a constant purge amount per part cycle, but an increasing amount of backfill. Figure A5.4a has no backfill and during product release a thermal wave passes the top thermocouple, (T12). The effect of backfilling is to force oxygen rich gas down the bed. This is substantiated in figure A5.4b which had a small amount of backfill. Now a thermal wave passes the top two thermocouples in the bed during product release. Even more backfill, figure 5.4c, and the thermal wave was detected by the top three thermocouples in the bed, although it was most significant at the top. Figure A5.4d had total backfill, which produced a lower oxygen concentration than for figure A5.4c, which in turn resulted in less dramatic temperature changes. Figures A5.4b to A5.4d illustrate another interesting point: while the temperatures
recorded by the top three thermocouples were increasing, again during product release, the temperature recorded by the bottom thermocouple in the zeolite was decreasing. This indicates that significant adsorption and desorption were occurring simultaneously in different parts of the bed.

Many different patterns of temperature profiles were recorded and it is impossible to show examples from every cycle investigated. Purge snatching did not greatly change the temperature profiles that were observed with purge cycles, (figure A5.5). However the temperature profiles produced from the bulk waste recycling experiments were significantly different to those observed with other cycles, (figure A5.6).

A5.4 Other Process Temperatures

Although the feed and ambient temperature were monitored and variations in these values are given in appendix 4, it was difficult to draw conclusions as to their importance to the plant performance. It would be interesting to observe the plant performance for similar cycles by varying the feed gas temperature, which could be controlled using a heat exchanger on the feed line. This was not investigated in this project but is a recommendation for the future.

The maximum and minimum temperatures observed for each cycle were approximately equidistant from the ambient temperatures, but the variations in ambient temperature were too small to comment on their importance to the performance of the plant.

A5.5 The Effects of Lagging the Beds and Interconnecting Pipework

A final year undergraduate project, [Penrose, (1988), internal report], investigated the effect of thermal lagging. The aims were to run similar purge cycles at two fixed product amounts but varying purge
amounts per part cycle, to compare the plant performances with no lagging to that with only the beds lagged and then again with the beds and interconnecting pipework lagged. Specifically the product oxygen concentration, the bed heat loss or gain from the environment and the zeolite temperature profiles were compared.

The benefit or otherwise of lagging proved inconclusive as for one product amount lagging caused a small increase in oxygen concentration, while at the other product amount the reverse was true. Each additional stage of lagging did produce greater temperature variations over the cycles of about 1 to 3 K, which is considered detrimental to the process, (see section 2.4.3.2). The heat balance results illustrated the near adiabatic bed operation. The maximum heat losses or gains were about 200 J/cycle, or 5% of the feed gas enthalpy per cycle.

There were quite large errors in determining the heat balances over the beds. For example the enthalpies of the stream were calculated using average cycle temperatures and did not account for changing flow rates. Also, the kinetic energies of the streams were neglected and the lagging of the beds could have been more thorough. With these errors it was impossible to draw firm conclusions for the effect on plant performance. The work did highlight many improvements, particularly to the instrumentation, which would facilitate studies like this in the future. The main recommendations were the use of flow controllers and smaller diameter thermocouples, (chapter 7). If some of the errors could be eliminated then the effects of lagging should be re-assessed.

A5.6 Discussion

The effects of temperature on plant performances were discussed in chapter 2, where it was stated that large industrial oxygen PSA plants can produce temperature variations in the beds of up to 100 K.
This work showed that even the small PSA plants produce significant temperature differences. Figure 1.2 illustrates the dependence of the isotherms on temperature over a 20 K range similar to that observed in the beds. For example, it shows that at 60 psig increasing the temperature from 273 to 293 K reduced the zeolite capacity for oxygen and nitrogen by between 30 to 40%.

Although the thermocouples were inserted into the packed zeolite the temperatures they recorded do not necessarily represent the true temperature changes within the bed. In practice the temperatures inside the particles might show even greater changes.

The axial temperature profiles in the zeolite showed a number of thermal waves moving along the bed. Thermal waves generally lag behind concentration waves, but if the relationship between them is known then temperature measurements may be used to help optimize plant operation. Indeed temperatures at the top of beds have been used to control PSA processes, a sudden increase in temperature during product release indicating that a concentration front is about to break through the end of the bed at which stage the product release step should be terminated. In this manner the zeolite is used most efficiently.

The interpretation of the axial temperature profiles helped to explain the operation of some cycles. It would have been extremely interesting to have used the ports along the bed profiles to sample the gas concentrations and thereby relate the temperature changes to concentration changes. Unfortunately to do this, without significantly disturbing the cycles only very small amounts of gas could be removed which are insufficient for use with the Servomex analysers used. It therefore remains a strong recommendation for the future that a mass spectrometer be used in conjunction with thermocouples to study temperature and concentration waves in the beds, (see section 7.2.2).
**Figure A5.1 Simple Cycle Bed Temperature Profiles:**

- **Bed Feed Temperature**
  - T8: Alumina
  - T9: 0.3 m from bed bottom
  - T10: 0.5 m from bed bottom
  - T11: 0.7 m from bed bottom
  - T12: 0.9 m from bed bottom
  - Average Ambient Temperature

- **Purge - 12.5 litres per part cycle**

- **Product: 4 litres per cycle**

**Figure A5.2a Purge Cycle Bed Temperature Profiles:**

- **Bed Feed Temperature**
  - T8: Alumina
  - T9: 0.3 m from bed bottom
  - T10: 0.5 m from bed bottom
  - T11: 0.7 m from bed bottom
  - T12: 0.9 m from bed bottom
  - Average Ambient Temperature

- **Purge - 12.5 litres per part cycle**

- **Product: 4 litres per cycle**
Product = 4 litres/part cycle

Bed Feed Temperature
T8 alumina
T9 0.3 m from bed bottom
T10 0.5 m from bed bottom
T11 0.7 m from bed bottom
T12 0.9 m from bed bottom
Average Ambient Temperature

Purge = 23.3 litres per part cycle

Figure A5.2b  Purge Cycle Bed Temperature Profiles:  PUT = 20 s

Product = 4 litres/part cycle

Bed Feed Temperature
T8 alumina
T9 0.3 m from bed bottom
T10 0.5 m from bed bottom
T11 0.7 m from bed bottom
T12 0.9 m from bed bottom
Average Ambient Temperature

Purge = 35.5 litres per part cycle

Figure A5.2c  Purge Cycle Bed Temperature Profiles:  PUT = 30 s
Figure A5.3a Backfill Cycle Bed Temperature Profiles: BKT = 10 s

Product = 4 litres/part cycle
Bed Feed Temperature
T9 Alumina Temperature
T9 0.3 m from bed bottom
T10 0.5 m from bed bottom
T11 0.7 m from bed bottom
T12 0.9 m from bed bottom
Average Ambient Temperature

Backfill Pressure = 30 psig

Figure A5.3b Backfill Cycle Bed Temperature Profiles: BKT = 30 s

Product = 4 litres/part cycle
Bed Feed Temperature
T9 Alumina Temperature
T9 0.3 m from bed bottom
T10 0.5 m from bed bottom
T11 0.7 m from bed bottom
T12 0.9 m from bed bottom
Average Ambient Temperature

Backfill Pressure = 57 psig
Figure A5.4a  Combined Purge & Backfill Temperature Profiles

PUT = 30 s, Purge = 25 litres per part cycle
BKT = 0 s, Backfill Pressure = 0 psig

Figure A5.4b  Combined Purge & Backfill Temperature Profiles

PUT = 30 s, Purge = 25 litres per part cycle
BKT = 10 s, Backfill Pressure = 30 psig
Figure A5.4c Combined Purge & Backfill Temperature Profiles

Figure A5.4d Combined Purge & Backfill Temperature Profiles
Figure A5.6 Typical Bulk Waste Recycle Temperature Profiles

Figure A5.5 Typical Purge Switching Temperature Profiles
Appendix 6  Simulation Parameters

Initial Backfill BWR Simulations Reported, (section 6.2)

- Part cycle time = 38.5 s
- Pressurization time = 10 s
- Product release time = 30 s
- Depressurization time = 11 s
- Purge time = 12 s
- Backfill time = 14 s
- Upper operating pressure = 80 psig (652.6 kPa)
- Lower operating pressure = 0 psig (101.3 kPa)
- Oxygen Adsorption Parameter (ZKA) = 3.27
- Nitrogen adsorption parameter (ZKB) = 4.66
- Temperature = 293 K
- Bed length = 1.0 m
- Bed cross sectional area = 0.00785 m²
- Feed concentration = 21.88 % oxygen

The net waste amount, backfill pressure and product amount were all varied between simulations.

All Other Simulations, (section 6.3 to 6.7)

- Part cycle time = 90 s
- Pressurization time = 30 s
- Product release time = 90 s
- Depressurization time = 30 s
- Purge time = 0 - 30 s
- Backfill time = 0 - 30 s
- Upper operating pressure = 514.8 kPa
- Lower operating pressure = 101.3 kPa
- Oxygen adsorption parameter (ZKA) = 3.27
- Nitrogen adsorption parameter (ZKB) = 4.66
- Temperature = 293 K
- Bed length = 0.85 m
- Bed cross sectional area = 0.00811 m²
- Feed concentration = 21.88 % oxygen

The product amount, purge amount, backfill pressure, control mode and inlet superficial velocities were varied. For the BWR, the required net waste amount was entered and for the purge snatching experiments the purge snatching time was entered. The direct purge simulations used three successive product release steps, each of 30 seconds.

Note

The equilibrium constants used for this work are the same as those used by Kirkby (1984).
THE MICROFICHE FROM APPENDIX 7 ARE MISSING FROM THIS THESIS
Appendix 7 Experimental Operating Programs

The enclosed microfiches contain listings of the two programs used to control and log data from the PSA research plant, (see section 4.3.3). The programs were written in basic for use with a Microsoft Quickbasic Compiler.

PSA1.BAS covered all cycles investigated except bulk waste recycling. PSA2.BAS was used for the bulk waste recycling experiments.