STUDIES OF ALKALI VAPOUR REMOVAL FROM HOT GASES AT 650°C BY ALUMINOSILICATE SORBENTS

by

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Στους γονείς μου, Νίκο και Κατε Χρυσοχοίδη,
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who devoted their lives to the proper education of their children.
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ABSTRACT

New advanced combined cycle coal-fired power generation systems are dependent on improvements in gas turbine technology and the development of hot gas cleaning techniques. These techniques are not only necessary to meet environmentally accepted emission limits for SO\textsubscript{x} and NO\textsubscript{x} but also to prevent downstream equipment from corrosion and erosion. Volatile alkali vapours in the exhaust gases produced by either coal gasification or combustion lead to corrosion of the gas turbine blades resulting in reduced operating life. Consequently, alkali removal systems which can operate upstream of the gas turbine have been incorporated into the development of the clean coal technologies.

A number of studies on alkali removal systems have been performed in the temperature range of 800°C - 1000°C. Solid aluminosilicates, such as emathlite, activated bauxite, kaolinite and Fuller's Earth, react with alkali vapours at high temperatures and therefore have been characterised as suitable alkali sorbents. Fuller's Earth was identified as potentially the most suitable sorbent for use in the UK at the specified operating temperatures. This material was studied in detail by McLaughlin (1990) for use in a fixed bed configuration within the British Coal Air-Blown Gasification Cycle.

Recently, it has been recognised that if ceramic filters are used for the removal of fine particulates, operating temperatures for alkali sorption will have to drop to 400°C-600°C, since these filters fail mechanically at higher temperatures. Much of the alkali will condense under these conditions and be removed by the filtration stages. However, the residual alkali levels may still exceed the revised turbine inlet specification of 24 ppb wt. Hence further studies of alkali sorption are required in this lower temperature region.

During this work, it proved difficult to obtain accurate results at temperatures as low as 600°C, because of the low level of vapour phase alkali. However, experiments were performed successfully at 650°C and atmospheric pressure, on the fixed bed sorption rig used previously for tests at 827°C and 927°C. Tests comparing Fuller's Earth and kaolin, showed kaolin to have a higher sorption capacity at this temperature. Fixed bed tests with sodium and potassium were performed with Fuller's Earth pellets. The runs were of 200-600 hrs duration, with 4.58 ppm wt NaCl (1.8 ppm wt Na), 5 %vol H\textsubscript{2}O and up to 160 ppmv HCl in the inlet
gas stream. Alkali uptake profiles were generated from chemical analysis of precise layers of pellets removed from the bed. Extensive modifications and improvements in analytical procedures enabled a closure of the mass balance of >99% to be achieved for a 600 hr run. Alkali exit levels measured using alumina wool filter pads in the exit gas were of the order of 5-6 ppb wt. Fuller's Earth pellets which had been pre-treated in gasifier gas and which were therefore contaminated with carbon, were tested and no difference was observed in their Na characteristics.

Element mapping techniques based on Scanning Electron Microscopy, confirmed that a shrinking core model for Fuller's Earth grains and kaolin pellets was appropriate. The 'two-reaction' mechanism proposed by McLaughlin (1990), was used to fit the experimental results at 650°C. Albite was identified by X-ray diffraction studies as the reaction product under high-acid conditions and nepheline under non-acid conditions. Exit gas analysis studies with an on-line monitor for HCl, showed the production of HCl to be directly connected with the presence of NaCl vapour and to increase significantly with the presence of water vapour in the system. However, the detailed reaction mechanism has not been identified yet.

The theoretical model developed for the high temperature studies (McLaughlin, 1990), using the pellet-grain model and the 'tank-in-series' method of solution has been applied successfully at 650°C. Parameters were extracted by curve fitting theoretical to experimental Na uptake concentration bed profiles. To test the numerical methods and the Szekely assumptions used in the McLaughlin program, two new computer programs were developed. The first, tested the pellet-grain model for a single pellet and the second was developed to solve the model more rigorously with a variable-order, variable-time-step numerical method. The new fixed bed model also incorporates the effects of temperature and pressure on selected parameters. It was used to predict the performance of a full-scale unit operating at 650°C and 24 bara. The results indicate that a bed of Fuller's Earth pellets, 3-10 mm in diameter, 4 m long and 4 m wide can achieve exit alkali levels below 20 ppb wt in continuous operation for up to 24,000 hrs.
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<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A</td>
<td>frequency factor in Arrhenius equation [cm s(^{-1})]</td>
</tr>
<tr>
<td>A(_g)</td>
<td>surface area of a grain [cm(^2)]</td>
</tr>
<tr>
<td>A(_{int})</td>
<td>reaction interfacial area per unit volume of grains [cm(^2) cm(^{-3})]</td>
</tr>
<tr>
<td>A(_m)</td>
<td>area occupied by adsorbate molecule [m(^2)]</td>
</tr>
<tr>
<td>A(_p)</td>
<td>surface area of a pellet [cm(^2)]</td>
</tr>
<tr>
<td>A(_r)</td>
<td>cross sectional area of the full-scale reactor [cm(^2)]</td>
</tr>
<tr>
<td>b</td>
<td>stoichiometric coefficient [dimensionless]</td>
</tr>
<tr>
<td>c</td>
<td>constant in Eq. 4.40 [cm(^2) s(^{-1}) K(^{-1.75})]</td>
</tr>
<tr>
<td>C(_{feed,i})</td>
<td>feed concentration of component i [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{i,0})</td>
<td>gas concentration of component i in the bed voidage [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{i,0,n})</td>
<td>gas concentration of component i in the bed voidage in tank n [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_i)</td>
<td>concentration of sorbate i in the solid per unit weight of initial solid [mol g(^{-1})]</td>
</tr>
<tr>
<td>C(_{i,0,n,j})</td>
<td>concentration of component i in the solid in tank n due to reaction j [mol g(^{-1})]</td>
</tr>
<tr>
<td>C(_{HCl,p})</td>
<td>gas concentration of HCl in the pores of a pellet [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{H_2O})</td>
<td>gas concentration of H(_2)O vapour at the surface of the unreacted core in a grain [mole cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{NaCl})</td>
<td>gas concentration of NaCl in a pellet [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{NaCl,p})</td>
<td>gas concentration of NaCl in the pores of a pellet [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{NaCl,s})</td>
<td>gas NaCl concentration at the exterior surface of a pellet [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{uc,NaCl})</td>
<td>reactant gas concentration at the surface of the unreacted core in a grain [mole cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{sol,r})</td>
<td>concentration of the solid reactant [mol cm(^{-3})]</td>
</tr>
<tr>
<td>C(_{sol,p})</td>
<td>concentration of the solid product [mol cm(^{-3})]</td>
</tr>
<tr>
<td>d</td>
<td>the perpendicular distance between adjacent planes in a crystal [Å]</td>
</tr>
<tr>
<td>D(_0)</td>
<td>frequency factor in Eq. 4.39 [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_{ax,i})</td>
<td>axial dispersion coefficient of component i [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_g)</td>
<td>diffusivity through the product layer in a grain (intragrain diffusivity) [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_{ij})</td>
<td>molecular diffusivity of component i into component j [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_m)</td>
<td>molecular diffusivity at the temperature and pressure of interest [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_{m,0})</td>
<td>known molecular diffusivity at T(_0), P(_0) [cm(^2) s(^{-1})]</td>
</tr>
<tr>
<td>D(_p)</td>
<td>intrapellet diffusivity [cm(^2) s(^{-1})]</td>
</tr>
</tbody>
</table>
\( e_i \) difference between measured and theoretical values (error)
\( E \) activation energy [J mol\(^{-1}\)]
\( E_{1-a} \) sum of squares error for a 1-\( a \) confidence interval [dimensionless]
\( E_{opt} \) sum of squares error at the optimum [dimensionless]
\( f \) friction factor [dimensionless]
\( F_g \) shape factor for the grain [dimensionless]
\( F_p \) shape factor for the pellet [dimensionless]
\( F_{p,a,p,1-a} \) value of the F-distribution at the 1-\( a \) level [dimensionless]
\( g(X) \) conversion function
\( k \) Boltzmann constant [JK\(^{-1}\)]
\( K_j \) weight of Na in the solid at saturation due to reaction \( j \) per unit weight of unreacted solid (reaction \( j \))
\( K_c \) equilibrium constant based on concentrations [(mol cm\(^{-3}\))\(^{1/2}\)]
\( K_e \) equilibrium group [dimensionless]
\( k_g \) gas film mass transfer coefficient [cm s\(^{-1}\)]
\( K_p \) equilibrium constant based on partial pressures [bar\(^{-1/2}\)]
\( k_s \) reaction rate constant group based on unit area of reaction interface [cm s\(^{-1}\)] (Eq. 4.11)
\( K_s, K_a \) intrinsic forward and backwards reaction rate constants [(cm s\(^{-1}\)) (cm\(^3\) mol\(^{-1}\))\(^{3/2}\)] or (cm [(cm s\(^{-1}\)) (cm\(^2\) mol\(^{-1}\))])
\( k', k_a \) forward and backwards reaction rate constant groups based on Eq. 4.11
\( L \) length of the fixed bed [cm]
\( L_r \) length of the full-scale reactor [cm]
\( m \) weight of Na in the solid per unit weight of unreacted solid
\( m_i \) theoretical value (alkali uptake value at position \( i \) in the bed)
\( M_i \) molecular weight of \( i \) [g mol\(^{-1}\)]
\( M_v \) gram molecular volume (22.4x10\(^{-3}\) m\(^3\) mol\(^{-1}\))
\( m_{sat} \) alkali concentration in the solid at saturation [dimensionless]
\( n \) exponent of the temperature ratio in the evaluation of \( D_m \)
\( n_i \) population of grains with radius \( i \)
\( N \) number of tanks
\( N_A \) Avogadro's number [molecules mol\(^{-1}\)]
\( p_l \) partial pressure of component \( i \) [bar]
\( P \) pressure [bar]
P_{atm} atmospheric pressure [bar]
P_0 pressure for the known molecular diffusivity [bar]
P_c critical pressure [atm]
P_{eL} axial Peclet number [dimensionless]
P_{eP} particle Peclet number [dimensionless]
p(X) conversion function
q_i concentration of sorbate i in the sorbent per unit volume of sorbent [mol cm\(^{-3}\)]
q(ς) function that describes the progress of reaction of a grain under product layer diffusion influence [Eq. 4.18]
R spatial coordinate measured from the center of the pellet [cm] or weight percentage that corresponds to each grain size for the Rosin-Rammler distribution
R_{Gas} ideal-gas law constant [J mol\(^{-1}\)K\(^{-1}\)]
r_c radius of the unreacted core in a grain [cm]
Re Reynolds number [dimensionless]
r_g grain radius [cm]
r_{HCl} local rate of generation of the gaseous product (HCl) based on unit volume of a pellet [mol cm\(^{-3}\) s\(^{-1}\)]
r_{NaCl} local rate of consumption of the gaseous reactant (NaCl) per unit volume of a pellet [mol cm\(^{-3}\) s\(^{-1}\)]
R_p pellet radius [cm]
SA sorbent surface area [m\(^2\) g\(^{-1}\)]
Sc Schmidt number [dimensionless]
Sh Sherwood number [dimensionless]
Sh* modified Sherwood number [dimensionless]
T temperature [K]
T_0 temperature for the known molecular diffusivity [K]
T’ temperature based on Eq. 4.27 [dimensionless]
T_b normal boiling point [K]
T_c critical temperature [K]
t time [s]
t’ time based on Eq. 4.19 [dimensionless]
u interstitial velocity [cm s\(^{-1}\)]
u superficial velocity [cm s\(^{-1}\)]
\( V_b \) liquid molar volume \([\text{cm}^3\text{mol}^{-1}]\)

\( V_F \) volumetric flow rate of the flue gases \([\text{cm}^3\text{s}^{-1}]\)

\( V_g \) volume of a grain \([\text{cm}^3]\)

\( V_m \) volume of monolayer \([\text{m}^3]\)

\( V_p \) volume of a pellet \([\text{cm}^3]\)

\( x_i \) experimental value (alkali uptake value at position \( i \) in the bed)

\( x_{np} \) percentage of pellets with radius \( R_p \), in a fixed bed

\( x_{wi} \) weight fraction of grains with radius \( r_g \) in a pellet

\( X_{gj} \) fractional conversion of the solid pellet due to reaction \( j \) = weight of Na reacted per unit weight of Na in the solid at saturation

\( X_{G_{r,g}} \) fractional conversion of the solid pellet due to reaction \( i \) and grains of radius \( r_g \)

\( y_i \) mole fraction of component \( i \) in the vapour

\( z \) axial position along the fixed bed \([\text{cm}]\)

**GREEK SYMBOLS**

\( \Delta H_0 \) enthalpy change \([\text{J mol}^{-1}]\)

\( \Delta G \) total Gibbs free energy \([\text{J mol}^{-1}]\)

\( \Delta p \) pressure drop \([\text{g cm}^{-1}\text{s}^{-2}]\)

\( \Delta t \) time step \([\text{s}]\)

\( \varepsilon_i \) characteristic energy (where the forces of attraction and repulsion between the molecules are balanced) \([\text{J}]\)

\( \varepsilon_p \) intrapellet porosity \([\text{dimensionless}]\)

\( \varepsilon_b \) interpellet porosity (bed voidage) \([\text{dimensionless}]\)

\( \eta \) position in the pellet based on Eq. 4.14 \([\text{dimensionless}]\)

\( \theta \) fraction of the surface used for adsorption or Bragg angle \([\text{rad}]\)

\( \lambda \) X-ray wavelength \([\text{Å}]\)

\( \mu \) bulk gas viscosity at the temperature and pressure of interest \([\text{g cm}^{-1}\text{s}^{-1}]\)

\( \xi_j \) local extent of reaction for the solid reactant based on Eq. 4.13 \([\text{dimensionless}]\)

\( \rho \) bulk gas density at the temperature and pressure of interest \([\text{g cm}^{-3}]\)

\( \rho_s \) sorbent density \([\text{mol cm}^{-3}]\)

\( \rho_T \) bulk gas density at 650°C and atmospheric pressure \([\text{g cm}^{-3}]\)

\( \sigma^*, \sigma \) dimensionless generalised gas-solid reaction groups, which incorporate both kinetic and
structural properties

\( \sigma_g \) dimensionless group, which incorporates chemical reaction and diffusion through the product layer effects

\( \sigma_i \) collision diameter (distance between molecules when the potential energy of interaction is zero) [K atm\(^{-1}\)]

\( \sum \nu \) atomic and structural diffusion volume increments [cm\(^3\)mol\(^{-1}\)]

\( \sum e^2 \) sum of squares of errors by comparing the experimental profile with the theoretically generated, when a parameter is perturbed by per\%

per\% percentage of perturbation

\( \sum e^2_{\text{opt}} \) sum of squares of errors by comparing the experimental profile with the optimum theoretical profile, and

\( \tau \) tortuosity factor [dimensionless]

\( \psi \) concentration driving force for reaction based on Eq. 4.12 [dimensionless]

\( \omega \) bulk density of the solid [g cm\(^{-3}\)]

\( \omega_{N_2} \) acentric factor for N\(_2\) [dimensionless]

\( \Omega_D \) diffusion collision integral [dimensionless]

\( \Omega_o \) collision integral [dimensionless]

**SUBSCRIPTS**

1 for reaction 1

2 for reaction 2

\( g \) for gas state

\( s \) for solid state

**ABBREVIATIONS**

AAS = Atomic Absorption Spectrophotometry

ABGC = Air-Blown Gasification Cycle

ACFBC = Atmospheric Circulating Fluidised Bed Combustor

BET = Brunauer Emmett Teller

CRE = Coal Research Establishment

CRT = Cathode Ray Tube
CHAPTER 1

INTRODUCTION

1.1 COAL - AN IMPORTANT ENERGY RESOURCE

Coal is one of the world’s most important and abundant fossil fuels. It accounts for approximately 30% of all the energy currently being used worldwide, the balance comprising oil, natural gas, nuclear and renewable energy sources (Figure 1.1). Only oil provides a greater share of world energy requirements than coal. However, two-thirds of the world’s oil and gas reserves are located in the Middle East, former USSR and Africa, while the geographical occurrence and production of coal is much more widespread (Figure 1.2). It is present in every continent and occurs in significant or potentially significant quantities in at least 60 countries. Even for countries with no fossil fuel, imported coal is inherently more secure than imported oil or gas, because of its much wider supply base. Although there was a progressive switching of the energy and chemical industries to natural gas, due to high efficiencies, low investments and minimum impact on the environment, this growing overdependence on one energy source, which is concentrated in regions that are politically unstable (Biggs, 1995), is not a desirable long term strategy. Besides, at the end of 1990, proven world resources of coal, were estimated to be sufficient for more than 200 years at 1990 production rates (IEA, 1993). These reserves are significantly greater than those for oil and natural gas (Figure 1.3).

The International Energy Agency (IEA), an autonomous body within the framework of the Organisation for Economic Co-operation and Development (OECD), is responsible for a comprehensive programme of energy co-operation among IEA participating countries to reduce excessive dependence on oil through energy conservation, development of alternative energy sources and energy research and development.

About one fourth of all energy used in the United States is derived from coal. The largest portion (86%) of that coal is used for electricity generation (Chriswell et al, 1995). In UK,
Figure 1.1: World energy use, 1990 (IEA, 1993).

Figure 1.2: World coal and oil reserves (IEA, 1993)
coal-fired power generation accounts for about 51% of the fuel used in electricity generation (Digest of United Kingdom, 1994). World-wide demand for electricity is forecast to grow at a considerable rate as the less developed countries industrialise (Daniel, 1991). For example, according to the long term plan of Korea's electric power requirement, total amount of electricity is expected to be more than doubled from 1992 to 2006. Coal usage in the electric power generation sector in Korea has been planned to steadily increase from 11% in 1992 to 20.2% and 28.3% in 1995 and 2006, respectively (Yun et al, 1995).

1.2 ADVANCED CLEAN COAL TECHNOLOGIES

Over many years, the most frequently used technology for the production of electricity from coal was pulverised fuel (pf)-fired boilers with a conventional steam cycle. Considering that the average operating thermal efficiency of the coal-fired power plants is approximately 33%, with the best plants achieving 40%, an increase of this efficiency towards 50% by the use of modern high efficiency systems can significantly reduce the coal consumption per year while maintaining the same electric power output (Quimby et al, 1995).
The combustion of any fossil fuel gives rise to emissions of gases, solids and liquids. Concern over the environmental consequences of fossil fuel combustion has encouraged many of the more developed countries to impose national or plant-specific limits on the emissions associated with coal use; primarily dust, sulphur dioxide ($SO_2$) and oxides of nitrogen ($NO_x$). Pressure has been increasing for international limitation agreements for acid rain emissions ($SO_2$ and $NO_x$), and also for carbon dioxide ($CO_2$) because of its association with the greenhouse effect. Approximately 70% of $SO_2$ emissions and 30% of $NO_x$ emissions come from power generation (DoE, 1994; ARIC, 1995). Recent calculations suggest that carbon dioxide emissions from the coal, account for between 17% and 23% of the man-made greenhouse effect. Ammonia also creates a problem because if unabated, it can be converted into high levels of $NO_x$ under certain conditions and thus contribute to the increase of nitrogen oxides' emissions. Trace metals in coal (<100 ppm wt) (Raask, 1985) such as barium, beryllium, chrome, lead, cobalt, strontium, cesium and uranium may also be vaporised and subsequently emitted to the atmosphere with the coal exhaust gases. Many of these metals are known to be harmful to humans and animals. Growth in total coal consumption in the long term, could therefore produce significant environmental problems if only conventional, inefficient and outdated power generation technologies are employed.

To meet the emission restrictions, modifications to the existing conventional plants, such as retrofitting of low $NO_x$ burners and introduction of flue gas desulphurisation (FGD) equipment, were necessary (Figure 1.4). These modifications lead to increases in the capital and operating costs, with loss in cycle efficiency when FGD is fitted, because large quantities of electric power are consumed for flue gas scrubbing due to the very large volumes of the exhaust gas (Minchener and Fantom, 1993). These effects have increased the need for alternative coal-fired power generation systems. These clean coal technologies are at the forefront of energy research and development, because their successful application will ensure that coal can continue to play a significant role in meeting the world's energy requirements into the 21st century.

The main criteria for advanced coal-fired technology have been identified as:
- Higher efficiency;
- Compliance with environmental standards;
- Minimum investment and operating cost.

Figure 1.4: Typical coal-fired power station with flue gas desulphurisation

1.3 DEVELOPMENT OF ADVANCED CLEAN COAL TECHNOLOGIES

There are several types of advanced coal technologies, based on coal combustion and/or gasification, that are currently approaching commercialisation or the advanced demonstration stage, whilst others are little more than theoretical concepts.

Fluidised bed technology has been extensively used by these clean coal power schemes, because it offers a number of advantages over conventional systems:

- the temperature window, around 900°C, at which the fluidised bed operates, greatly reduces the likelihood of NOx production and it is below the temperature at which ash melts to form slag
- sulphur emissions released during coal combustion or gasification can be reduced significantly by the addition of limestone in the fluidised bed
Advanced clean coal technologies based on coal combustion using fluidised beds are divided into two categories; Atmospheric Circulating (ACFBC) and Pressurised (PFBC) Fluidised Bed Combustors. In the ACFBC, steam is produced from the heat recovered from the combustor exhaust gas, whereas in PFBC the exhaust gas is also used to drive a gas turbine. This scheme combines the high temperature operation of the gas turbine with good heat recovery for the operation of the steam turbine. Fluidised bed coal gasification is used in the so-called Integrated Gasification Combined Cycle Systems, developed in recent years in an effort to significantly increase power generation efficiency. Such Combined Cycle Systems already operate with natural gas and can already achieve efficiencies in excess of 45%. Coal gas can be used in these systems in place of natural gas. Opportunities also exist for developing combined cycle designs which use coal in only part of the system. These systems that combine both natural gas and coal combustion offer considerable potential and are usually designed so that the gas turbine exhaust, from burning natural gas, provides pre-heated air for coal combustion in the steam turbine cycle. Such systems are particularly appropriate where it is not yet economically attractive to use coal-derived gas and where natural gas is available but is costly or limited in supply. A plant of this type has been in operation in Germany for several years (IEA, 1993). A further improvement, where the best features of coal gasification and combustion are combined in one system, are the Hybrid Combined Cycles. In these schemes, the gases produced by the pressurised fluidised bed gasification of coal drive a gas turbine for the production of electricity and the unburnt coal from the gasifier can be used in a separate atmospheric circulating fluidised bed combustion unit to produce heat for the steam turbine.

1.3.1 Atmospheric Circulating Fluidised Bed Combustion (ACFBC)

In a ACFBC system (Figure 1.5), the coal is burned in a fluidised bed, where air and limestone, for sulphur retention, are introduced at the base of the bed. Combustion air, at a temperature of ~900°C, carries away the solids into a high efficiency cyclone. The solids
collected there are recycled to the combustor via an external low velocity fluidised bed heat exchanger. The partially cleaned gas is cooled in a convective boiler, where heat recovery is obtained for the steam cycle. The cooled flue gas is filtered before being discharged to the atmosphere. As with conventional power plants, the thermal efficiency of the atmospheric circulating FBCs, when used for power generation, is a function of the steam cycle, under best conditions reaching 40%.

Figure 1.5: Power generation using Atmospheric Circulating Fluidised Bed Combustion (Minchener and Fantom, 1993).

By 1991, a number of plants were in operation in both Europe (Germany, France, Sweden) and North America (Canada). In the UK at present, there are two ACFBC plants operating on a commercial basis to produce steam for industrial use. The first is at ICI Dumfries and the second one is at Caledonian Paper plc in Scotland. With the support of the United States Department of Energy (USDoE) and the Morgantown Energy Technology Center (METC) in 1994, DONLEE Technologies Inc. performed a test at its pilot CFBC, which aimed to the use
of a lower cost CFBC in remote areas, where demand for heating and electric power has steadily increased and the use of locally available fuel to achieve self-sufficiency has become an important objective (Stuart et al, 1995).

1.3.2 Pressurised Fluidised Bed Combustion (PFBC)

The more advanced design of PFBCs encloses the entire bed and cyclone system within a pressurised vessel. Operating temperatures are similar to those maintained in the atmospheric systems. PFBCs offer two distinct advantages compared with atmospheric systems:
- the potential for combined cycle application
- a smaller unit size

Because the system operates under pressure, a PFBC unit can be physically substantially smaller than an atmospheric FBC. However, because the heat transfer tubes are immersed within the bed, the extent of size reduction will be determined by the total heat transfer requirements of the system.

Approximately 75-80% of the power is generated by the steam turbine. The discharge from the steam cycle is only slightly above ambient temperature and pressure. The gases leaving the combustor are under pressure and are cleaned of entrained particulates in a series of cyclones or in a single cyclone by a hot gas filter. Finally, the gases expand through a gas turbine, which generates more electricity. This system is shown in Figure 1.6 (IEA, 1993). This form of combined cycle application can increase the thermal efficiency of the process to between 42% and 44%.

PFBC technology has been under development in the UK for over 20 years, initially at the British Coal Utilisation Research Laboratory (CURL) at Leatherhead and later at the Grimethorpe Pressurised Fluidised Bed Combustion Establishment (GPFBCE) and the Coal Research Establishment (CRE). The commercial potential for the process has been established by successful tests on the bed fluidisation conditions, tubebank materials and design, combustion efficiencies, sulphur retention, NOx emissions, hot gas cleaning, gas turbine blade materials, coal feeding methods, instrumentation, turndown and control methods, ash disposal
and utilisation. This project was jointly funded in 1975, by the governents of the Federal Republic of Germany, the UK and the USA, under the auspices of the IEA. The potential of advanced power systems was recognised and additional jointed funding has been continuously contributed by the British Coal Corporation, the UK National Power, the UK Department of Trade and Industry, the US Department of Energy (USDoE), the US Electric Power Research Institute (EPRI) and Power Gen.

PFBC research in Finland started in the middle of 1980s with theoretical studies and literature reviews. The Otaniemi test rig for PFBC combustion and gasification was designed and constructed within the joint project of Helsinki University of Technology (HUT) and the Technical Research Center of Finland (VTT). The first tests took place in the autumn of 1987.
The research project is a part of the national LIEKKI combustion research programme financed by the Ministry of Trade and Industry of Finland (Hippinen et al, 1992).

A study was also completed for a PFBC power plant for electrical and process heat production in a remote Alaskan application, where an Alaskan coal, local limestone and municipal solid waste will be co-fired in an advanced fluidised bed combustor. This study was performed because in the near future rural village utilities will be faced with increased cost of electricity due to transportation, handling and storage costs of fuels (Phillips et al, 1995). Commercial application of PFBC plants has also taken place in Sweden (Vartan), Spain (Escatron), USA (Tidd, Ohio). Units under construction are in Japan (Wakamatsu) and in USA (pleasant Hill, Iowa) (IEA, 1993).

1.3.3 Integrated Gasification Combined Cycle (IGCC)

In IGCC systems, coal gasification is involved using air or oxygen and steam, to produce a fuel gas whose principal combustible components are carbon monoxide and hydrogen. The main characteristic is that the fuel gas produced from coal gasification is cleaned to remove dust, sulphur and other impurities, then is burned in the combustor chamber of the gas turbine and the hot combustion products are expanded through a gas turbine. The combustion gases are at a temperature of 1380°C, which corresponds to a turbine inlet temperature of 1260°C (the turbine's full potential working temperature) and therefore to a high thermodynamic efficiency. Waste heat from the gas turbine, combined with heat recovered from the gasification and gas cleaning processes is used to raise high pressure steam. This steam is directed to a turbo-alternator, which produces 30-40% of the total plant electricity output. The system is shown in Figure 1.7 (IEA, 1993). Net efficiencies of approximately 43% can be achieved, higher than with most advanced pf plants (40%).

A number of demonstration plants are planned or under construction throughout the world, notably in the USA. The US Department of Energy has been and continues to be a major player in the development of IGCC with the Clean Coal Program. Several IGCC projects have been announced. The ones closer to realization are: Tampa Electric (Florida), PSI-Wabash
River (Indiana) and Piñon Pine (Nevada) (USDoE, 1995). The US Department of Energy has established the IGCC performance goals for 2010 to 52% efficiency, with cost of electricity equal to 75% of that of pulverised coal plants and SO\textsubscript{x}/NO\textsubscript{x} emissions less than the existing limits (Harrison, 1995). In Europe, IGCC technology has also attracted great attention, but is seen as a technology able to serve two purposes: eliminate the excess carbon rejected from the Refining Industry and generate power from a product, fuel oil, which is progressively less demanded by the market. In Holland, a coal-based IGCC for Demkolec in Buggenum, started up at the end of 1993. A second IGCC is in construction at Puertollano in Spain. This second plant has received a substantial financial contribution by the European Community Joule program. Similar projects are being considered in Finland and other European countries (Farina, 1995). Since 1988, the Korea Electric Power Corporation has also been involved in introducing IGCC to the Korean Electric Sector (Ahn et al, 1995).

1.3.4 Hybrid Combined Cycles - British Coal Air-Blown Gasification Cycle

In the UK, a collaborative research and development programme, including PowerGen, Babcock Energy Ltd., the Coal Technology Development Division (CTDD) of British Coal Corporation, GEC ALSTHOM, the UK Department of Trade and Industry (DTI) and the European Commision, has been established to provide the basis for the demonstration of a
Hybrid Combined Cycle technology known as the Air-Blown Gasification Cycle (ABGC). This process, known formerly as the British Coal Topping Cycle, involves partial gasification of coal with combustion of the fuel gas in an industrial gas turbine and residual char burned in an atmospheric circulating fluidised bed combustor (ACFBC) (Cahill et al., 1995). This technology exhibits particular promise mainly due to the potential for exploitation of its constituent components in other advanced power generation cycles.

In detail, coal is partly gasified in an air-blown gasifier, which operates at around 1000°C and 25 bar (Minchener and Fantom, 1993). Using air rather than oxygen decreases the capital and operational costs of the plant. Sorbent (lime or dolomite) is also fed in the gasifier to obtain sulphur retention. The coal, sorbent, air and steam are introduced through a vertical spout at the base of the gasifier with additional air and steam being introduced through nozzles set in the wall of the conical base. Leaving the gasifier, the fuel gas passes from a cyclone for the particulates and the ash to be removed. A critical requirement is to ensure that the fuel gas is free of dust in order to avoid damage to the gas turbine. In commercial plants, cyclones are used as the only particulate removal equipment, since they operate reliably at high temperature and pressure (HTHP) conditions. However, the efficiency of cyclones is not satisfactory enough to protect the gas turbines from the erosivity of the particulates emitted. Much effort in recent years, has been devoted to the development of a more efficient clean-up system, using rigid ceramic elements as the filtration media. The testing of candle filters in British Coal's Grimethorpe facility (Burnard et al, 1993), over the temperature range of 780-850°C, showed that although the collection efficiency of candle filters was very promising, internal inspection of pressure vessel revealed many failures, like high temperature effects of thermal expansion and material creep. Microcracks identified at the binder medium and silicon carbide granular surfaces, suggest thermal shock effects resulting from cold air impingement during pulse jet cleaning cycles.

Work on hot gas filtration at lower temperatures, 400-600°C, has been carried out at the Coal Technology Development Division at Cheltenham. Temperature appears to have little effect on filter operation within this range and the results raised confidence in hot gas filtration. During the tests no element breakages occurred during operation, strength loss was acceptable.
and the permeability reached a constant level (Cahill et al, 1995). As a result, after the cyclone, gas temperature was reduced to 400-600°C in a boiler, which generates high pressure saturated steam. After the boiler, further particulate removal is obtained in the ceramic candle filter. The clean gas is then burned in the turbine combustor, where the combustion products are at a temperature of around 1380°C corresponding to a turbine entry temperature of 1260°C. The gaseous products are then expanded, driving the turbine compressor and the electric power generator. The exhaust gases pass to a waste heat boiler and then via a stack to atmosphere at 125°C. Air for the gasifier is provided via the gas turbine compressor, heat exchangers, a motor driven booster compressor and an air reheater.

Between 70 and 80% of the coal is converted in a low calorific value fuel gas (4 MJ/m³) due to the use of air instead of oxygen in the gasifier. A high calorific value fuel gas is undesirable since this will give a rise in the flame temperature in the gas turbine combustor, leading to higher NOx emissions. To avoid this problem in oxygen-blown gasifiers, the fuel gas produced is diluted with N₂ prior to the gas turbine combustor. The remaining unconverted coal (char) is cooled, depressurised and transferred to an atmospheric CFBC either directly from the base of the gasifier or from the cyclone and hot gas filters. This material is then burned to raise heat for the steam turbine cycle, which also produces power. The already sulphided sorbent in this material is converted to CaSO₄. Additional sorbent can be fed in the combustor to complete the sulphur retention process. The solids in the ACFBC are carried away by the combustion air and into high efficiency cyclones, where they are recycled to the combustor vessel, either directly or via external low velocity fluidised bed heat exchangers. After the cyclones, the partially cleaned gas is cooled in a waste heat boiler followed by combustion air preheaters. The cooled flue gas is passed through a bag filter and induced draught fan before being discarded to atmosphere. This system is shown in Figure 1.8 (Minchener and Fantom, 1993) and it is still under development.

The clear motivation for the advanced power systems was the increase of efficiency to the 50% level. The reported predicted efficiency of a commercial power plant based on British Coal's ABGC is around 46-47%. This is based on an European Gas Turbine, Frame 9F, with an inlet temperature of 1260°C. Cooling of the fuel gas down to 400 - 600°C does not affect
the efficiency of the cycle, as the heat recovered from the gas cooler before the ceramic filter is used in the steam cycle, where the steam turbine equally contributes (50%) to the power generation. Compared with the other technologies, this is the highest efficiency that has been reported (Table 1.1).

Table 1.1: Comparison of efficiencies achieved by clean coal technologies compared to pulverised coal-fired with desulphurisation unit technology

<table>
<thead>
<tr>
<th>Technology</th>
<th>PF+FGD</th>
<th>ACFBC</th>
<th>PFBC</th>
<th>IGCC</th>
<th>ABGC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>40%</td>
<td>40%</td>
<td>42-44%</td>
<td>43%</td>
<td>46-47%</td>
</tr>
</tbody>
</table>
The main advantages of the ABGC are:
(a) it can exploit the potential of high inlet temperature gas turbines while minimising the energy losses incurred in the production of fuel gas
(b) it predicts the lowest CO$_2$ emission due to its higher efficiency
(c) it is expected to be operated easier than the ACFBC, PFBC or IGCC plants, since it is able to continue operation even when some subsystems are out of service.

1.4 ASSOCIATED TECHNOLOGY IMPROVEMENTS

The future implementation of the advanced clean coal technologies will be influenced by improvements in gas turbine technology and by the development of hot gas cleaning techniques.

1.4.1 Gas Turbines

The major turbine manufacturers are continuing to design and develop more efficient gas turbines. Much of the current research is based on aircraft turbine technology and on the development of ceramic or ceramic/metal materials for use in component manufacture. Such advances will allow significant increases in turbine gas inlet temperatures, possibly to more than 1370°C by the beginning of the 21st century.

Gas turbines are widely used in the industrial sector as prime movers for oil and gas production. The description 'coal-fired turbine' is used solely for a turbine operating directly on the high temperature combustion products of coal as a substitute for oil or gas (Meadowcroft and Stringer, 1987). The reliability and availability of gas turbines is of major concern in production operations (Byworth, 1987). Limitations are frequently imposed by the premature degradation of critical hot gas path components such as rotor blades and nozzle guide vanes. These components operate under complex and demanding combinations of stress and temperature in a high-velocity gas stream which may contain aggressive species arising from impurities in the fuel and intake air.
Impurities can damage turbine components by a combination of erosion, corrosion and deposition. These three complications can result in increased maintenance costs and/or losses in cycle efficiency due to either deposit buildup on the airfoils or the need for filtration equipment. If the problems related to erosion, corrosion and deposition can be solved, coal-based plants with gas-turbines can have a competitive price relative to alternatives such as oil or natural gas.

Materials used for component fabrication must therefore possess the appropriate mechanical and physical properties to suit the individual requirements for specific areas of the turbine. Suitable materials include a range of nickel- and cobalt-base alloys known through their superior high-temperature performance as superalloys. Nickel-base superalloys are favoured for rotating components because of their enhanced strength, whereas cobalt-base superalloys are more generally preferred for static components. These materials resist corrosion through a strongly bonded chrome oxide layer (Cr$_2$O$_3$) over their surface (Cutler, 1987). This oxide layer presents a barrier between the elements in the metal and those in the environment. However, at temperatures ~850-900°C, there is a limitation in the protection provided by chromia in that it oxidises further to form the gaseous chromium trioxide, CrO$_3$ (Radcliff, 1987). Breakdown of the protective layer by aggressive species can lead to accelerated attack of the underlying metal.

The cost of the hot gas path components fabricated from these superalloys is relatively high and represents a significant proportion of the overall costs of turbine ownership. For instance, the price of a set of blades for a heavy-duty industrial gas turbine can be as high as £150,000 (Radcliff, 1987). Frequent replacement of these components during the total life of a turbine (~25,000 hrs) adds considerably to the running costs for that engine. However, the highest cost is incurred through premature and unexpected failure where not only is a major rebuild required, but the cost of down-time and associated lost production can override all other considerations.
1.4.1a Gas Turbine Alkali Corrosion Mechanisms

The chemical analysis of a typical UK power station coal and the component distribution in the ash are given in Table 1.2 (Meadowcroft and Stringer, 1987) and show that many of the elements involved in the corrosion processes are present in coal or chemically bound in aluminosilicates which primarily comprise ash.

<table>
<thead>
<tr>
<th></th>
<th>Ash</th>
<th>S</th>
<th>Cl</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO₂</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>16</td>
<td>1.5-2</td>
<td>0.1-0.5</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Ash</td>
<td>...</td>
<td>...</td>
<td>50</td>
<td>30</td>
<td>3.5</td>
<td>10</td>
<td>2</td>
<td>1.5</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

British coals formed directly in marine swamp areas and therefore they are rich in chlorine and alkalis, as these elements exist in high concentrations in seawater. Their concentration in these coals is usually above 1000 ppm (0.1%) (Raask, 1985). It is known that chlorine is rapidly released from coal as HCl. The HCl then releases alkali chlorides, which are volatile at bed temperatures. If the sulphur compounds are not effectively removed, the chlorides will react downstream with the sulphur oxides, generated in the gas turbine combustor, to give sulphates either in the combustion flame or close to the blade surface (Ferguson, 1980):

\[
2NaCl(g) + SO₃(g) + H₂O(g) → Na₂SO₄(s) + 2HCl(g)
\] (1.1)

These can then deposit onto the turbine's component surfaces, chemically interact with the protective oxide layers and cause hot corrosion.

Basically, there are two alkali sulphate corrosion processes: a high-temperature form (type I) with peak corrosion rates at about 850-900°C, and a low-temperature form (type II) with peak corrosion rates at about 700-750°C. Type I hot corrosion results from sodium sulphate fluxing the protective oxide layer, allowing access to sulphur onto the underlying metal. Sulphur then reacts with the chromium, which is responsible for the protection. Localised depletion of the
protective elements and progressive internal attack are produced. Type I hot corrosion produces a characteristic pattern of attack which includes a porous oxide scale, an irregular metal/scale interface and internal attack with preceding metal sulphides.

Type II hot corrosion requires sodium sulphate and sufficient sulphur trioxide to maintain a low melting deposit which readily fluxes the surface oxide. Thermodynamics favour high local $\text{SO}_3$ concentrations in the lower temperature range. Sodium sulphate forms a complex salt, which involves one of the base metals of the alloy; Co, or Ni. The attack is normally localised, producing pits with a scale rich in sulphur through the progressive fluxing of the deposits. There is little internal sulphidation of the alloy with this type of attack (Radcliff, 1987).

The release of alkali is very dependent on combustion and gasification temperature and it was found (Meadowcroft and Stringer, 1987), that the maximum permissible bed temperature, under which the alkali levels could be controlled for high chlorine coals, must not be more than 900°C. A reduction of 50-100°C (from 950 to 900-850°C) can mean the difference between catastrophic metal loss rates and acceptable corrosion on gas turbine blades. However, if the coal combustion or gasification temperature is limited to less than 900°C, a significant fraction ($\geq$10%) of the sulphur oxides can be present as $\text{SO}_3$, the fraction increasing as the temperature decreases and the pressure increases. Even with dolomite/limestone in the bed to absorb the sulphur emissions, levels of $\text{SO}_3$ of 10-50 ppm have been reported (Meadowcroft and Stringer, 1987). This will help the formation of low melting point sulphates and the occurrence of low temperature (type II) hot corrosion. As there will always be a temperature drop between the turbine combustor and the turbine, type II corrosion might be expected to be more prevalent than type I hot corrosion. Consequently, alkali chloride removal is important for the protection of the gas turbines. The high temperature corrosion problems of superalloys can also be associated with chlorides present in the exhaust gas. It is generally agreed that chlorides can produce breakdown of the normally protective surface oxide scales and can act as initiators of the hot corrosion reaction (Radcliff, 1987; Hancock, 1987; Smeggil et al, 1977). The rapid influence of chlorides is suggested to occur via gaseous diffusion through defects in the surface scale.
At 900°C where theoretical predictions of alkali concentrations are in the range of 1 to 10 ppm wt (Scandrett and Clift, 1984; Singh and Clift, 1986), experimentally reported alkali levels in coal-derived gases can vary over a wide range depending on the experimental conditions (Chapter 2). However, the target specification for the turbine expansion gas is 24 ppb wt (Na+K) (USDoE, 1986) and therefore alkali suppression would be necessary.

1.4.1b Corrosion-Erosion-Deposition Interactions

Whenever erosion and corrosion occur together there must be concern that there will be a synergistic effect resulting in a total loss rate greater than the sum of the losses from the two processes acting independently. An example (Barkalow et. al, 1980; Barkalow, 1984; Meadowcroft and Stringer, 1987) obtained in a high-velocity laboratory simulator where erosion was caused by 2.5 μm alumina particles at 180 ms\(^{-1}\) and corrosion by Na\(_2\)SO\(_4\)-K\(_2\)SO\(_4\) deposits is illustrated in Figure 1.9 (Meadowcroft and Stringer, 1987). In this example, the erosive damage rate was much worse than the corrosive damage rate, but together the damage rate became three times that of erosion alone. Deposition can significantly affect corrosion rates by building up locally aggressive environments or by capturing the alkali-containing species. Hot corrosion itself requires the deposition of alkali sulphates. In the example mentioned above, Figure 1.9, it was shown that in the high velocity gas, the extent of hot corrosion without erodent, varied around the target because of the effect of aerodynamics on deposition rate. Industrial combustion turbine research has shown that if the gas stream particle size is kept below 10 μm, then deposition and corrosion, not erosion, are responsible for limiting the useful lifetime of a gas turbine (Ross et al., 1988).

1.4.2 Hot Gas Cleaning

Although emission levels for SO\(_2\), NO\(_x\) and CO\(_2\) from the advanced clean coal technologies can be 20-25% lower than for most pulverised coal plants, hot gas cleaning techniques are not only developed to meet environmentally accepted emission limits for dust, SO\(_2\), NO\(_x\), NH\(_3\) and trace metals but also to prevent downstream equipment corrosion and erosion. Emissions like HCl, apart from having deleterious effects when are released into the atmosphere,
can cause acidic corrosion of downstream equipment such as turbine blades and heat exchangers. The presence of alkali species in the coal gas streams can also cause corrosion to the gas turbines and alkali low-melting compounds can provide the "glue" for forming deposits on turbine and heat exchanger surfaces. Dust emissions should be eliminated not only for environmental purposes but also because they can cause erosion to the gas turbines.

Appropriate hot gas cleaning technologies for dust removal, desulphurisation, elimination of NH₃, HCl, alkali and trace metal compounds, are being developed to enhance system efficiency. The importance of an effective gas filtration process lies on the fact that it can provide the requested clean-up of the exhaust gas before it is released to the atmosphere and can also protect downstream equipment, like the gas turbine. This is significant as regulations governing i.e. dust emissions to the environment are often much more stringent than those suggested for the protection of gas turbines. The dust emission limits required by environmental legislation vary from country to country, but a figure of less than 20 ppmw is a reasonable guideline (Burnard et al, 1993).

Figure 1.9: High velocity erosion-corrosion interactions for IN 738 at 870°C (Meadowcroft et al, 1987)
The techniques that appear to offer the greatest potential for dust removal include ceramic-based filters (Burnard et al, 1993; Cahill et al, 1995) and moving-bed granular collectors (Gäng et al, 1993; McDaniel, 1995). It was found, as was already explained in detail in Section 1.3.4, that in order to avoid thermal expansion and material creep of the ceramic filters, it was necessary to cool down the gasifier exhaust gas to 400-600°C. Much work on hot gas filtration was carried out in conjunction with the development of combined cycle processes. For gasification, the range of conditions of interest for filter operation, range from 250 to 700°C (Cahill et al, 1995). The lower temperature was set at 250°C, because any further cooling could cause NH₄Cl to form and deposit on downstream equipment (Schreurs, 1995). However, the decrease of gas stream temperature down to 250 or 400°C, would also influence the system’s efficiency. Taking the Buggenum plant (Schreurs, 1995), it was implied that each 100°C temperature drop in the exhaust gas, represented 1% loss of the chemical combustion energy of the coal that could have been converted to chemical combustion energy of the gas.

The other option for dust removal, the moving granular bed filter, could offer the advantage of efficient operation within the range of 300-800°C (Gäng et al, 1993). Application of granular bed filters opens the possibility of collecting both gaseous emissions and solid dust particles in one filter unit by using chemically reactive filter media. Under the sponsorship of the U.S. Department of Energy, a laboratory test program is underway at the Research Triangle Institute (RTI), in order to develop a moving granular-bed filter for multi-contaminant control (McDaniel, 1995).

To eliminate sulphur emissions from the exhaust gases, limestone is added in the gasifier and the process effectiveness was reported to vary from 50% (Tatar et al, 1995) to 90% (IEA, 1993). The wide range in the effectiveness is attributed to Ca/S ratios since the reaction is equilibrium limited under the gasifier conditions (Tatar et al, 1995; Fantom et al, 1995). Consequently, additional hot dry desulphurisation techniques are also being explored and attention is currently focusing on the development of a metal oxide which can react with H₂S and produce a metal sulphide. The sulphide can then be regenerated using an appropriate oxidant to produce a concentrated sulphur dioxide stream from which sulphur can be
recovered using conventional techniques (Fantom et al, 1995). Nickel oxide catalysts with zinc ferrite appear to be capable of meeting these requirements at 500-600°C. These compounds are proposed for the Piñon Pine IGCC system under development (Tatar et al, 1995), where the sulphur in the gas should be reduced to less than 30 ppmv for a low-sulphur coal. However, copper chromite appeared as the new suggestion for higher temperatures (650-750°C), since zinc was shown to suffer from volatilisation at elevated temperatures (Abbasian et al, 1995). Zinc titanate as a mixture of ZnO and TiO₂, it seems to stabilize the zinc and prevent its vaporisation, exhibiting good sulphur retention capacity and stability even at temperatures up to 735°C (Gäng et al, 1993).

Whilst additional removal of sulphur, from the fuel gas after the in-bed retention in the gasifier of ABGC, is not required to meet current emission targets (400 mg m⁻³ @ 1 atm, 273 K), it was considered essential to include a secondary sulphur retention unit in this cycle. This will allow the ABGC to compete with other technologies such as IGCC and PFBC, to be an appropriate technology for application worldwide where more stringent emission targets may apply and to meet likely future emission targets in the European Union. For the ABGC, the operating temperatures for hot gas cleaning is 400-600°C and at this temperature zinc titanate was found to react too slowly, making it unsuitable for use. A candidate sorbent, based on iron and molybdenum, is under development in the Netherlands (Fantom, 1995).

The formation of NOₓ during coal combustion or gasification depends on the availability of oxygen and the combustion or gasification temperatures. To modify these conditions and make them less favourable for NOₓ formation, the air-blown fluidised bed was chosen as the appropriate technology due to the lower operational temperatures (~1000°C) and the reduced oxygen usage. When the NOₓ limits (650 mg m⁻³, Department of the Environment, 1990) cannot be met by the above method, decrease of NOₓ levels can be achieved with low NOₓ gas turbine combustors, selective (SCR) and non-selective catalytic reduction (SNCR) prior to the gas turbine combustor or if this is inadequate, after the gas turbine to the exhaust gas. SCR involves mixing ammonia with the exhaust gases in the presence of titanium oxide as a catalyst, to produce nitrogen and water. The optimum performance temperature for these catalysts is 370-400°C, since at higher temperatures they begin to degrade. This technology
can achieve NO\textsubscript{x} reduction rates of 80-90%. In SNCR, an amine-based chemical, such as urea or ammonia, is injected into the exhaust gas stream where it reacts with NO\textsubscript{x} to produce nitrogen and water. This reaction takes place over a relatively narrow temperature range - between 900°C and 1100°C and can achieve 40-50\% NO\textsubscript{x} reduction.

Nitrogen bound in coal is partly released as NH\textsubscript{3} and HCN, which might enhance the formation of NO\textsubscript{x} in the gas turbine combustor. Although NO\textsubscript{x} can be controlled during combustion, additional measures might be necessary to reduce high levels of NH\textsubscript{3} and HCN. It was suggested that ammonia could decompose by contact with iron based minerals above 900°C or with dolomite above 1000°C. Dolomite and limestone above 800°C was also suggested to reduce HCN concentration (Gång et al, 1993). Research on the use of NH\textsubscript{3} decomposition catalyst in conjunction with the H\textsubscript{2}S sorbent, zinc titanate, already started at RTI. At temperatures below 800°C, none of the catalysts investigated were effective in a high H\textsubscript{2}S environment (McDaniel et al, 1995). To avoid deactivation of nickel catalysts caused by H\textsubscript{2}S, Simell et al, (1996) suggested that temperatures over 900°C should be used. This effect, in addition to the increase in the cycle efficiency, could be indicative of a longer term shift to higher temperatures for hot gas cleaning.

Emissions of chlorine from a coal-fired power plant can range from 50 to several thousand ppmv, depending on the chlorine content of the coal and the coal processing technique. It has been proposed that sodium minerals and especially nahcolite (NaHCO\textsubscript{3}) can effectively remove HCl from hot gases forming NaCl, CO\textsubscript{2} and H\textsubscript{2}O (Krishnan et al, 1995; McDaniel et al, 1995). However, the NaCl produced, will exacerbate the alkali removal problem (Gång et al, 1993). Without an efficient alkali removal unit in the system to reduce the alkali loading, limestone would be the preferred HCl sorbent in a temperature range of 400-800°C (Peukert et al, 1993).

Several researchers also investigated the removal of alkali compounds from hot gases, which helps preventing blade corrosion and prolongs the life of the gas turbine. They reported successful alkali removal from high temperature gas streams (800-1000°C) with aluminosilicate materials. These so-called "getters" which react irreversibly with alkalis, were
emathlite (Mulik et al, 1986), kaolin (Punjak et al, 1988) and calcium montmorillonite (McLaughlin, 1990). Alumino-silicates and silicates were reported (McDaniel et al, 1995; Helble et al, 1995) to also remove trace metals from exhaust gases. Under the program for the development of the British Coal Air-Blown Gasification Cycle, McLaughlin showed that alkalis could be efficiently removed at 827°C and 927°C, but in view of the reduced operating temperatures now being used, this technology must be re-evaluated at lower temperatures (400°C-600°C). Although at these temperatures, most of the alkali in the flue gases is expected to condense onto particulates and be removed by filtration, further studies could verify the performance of an alkali removal system over the temperature range of 600-927°C.

1.5 GENERAL REVIEW

The advanced clean coal technologies, based on fluidised bed combustion and/or gasification, appear to offer a more efficient, less polluting and cheaper method of coal-fired power generation when compared to the conventional pulverised fuel systems, currently in use. However, the efficiency of these technologies will be influenced by the development of gas cleaning techniques that can eliminate dust, sulphur compounds, NOₓ, NH₃, HCN, HCl, trace metals and alkali compounds, either because there are environmental consequences or because these compounds can corrode or erode the downstream equipment, especially the gas turbines used for combined cycle power generation.

Methods for particulate removal being developed include ceramic-based filters and moving-bed granular collectors. Ceramic filters can perform effectively, without mechanical failure, in the temperature range of 400-600°C, however, cooling of the fuel gases is required, which can result in lower cycle efficiency. Multi-contaminant control at high temperatures (~800°C), with a chemically reactive filter media in a moving-bed granular collector is a promising alternative technology, which is currently under study.

As part of the Contaminant Control Research programme for the development of the British Coal Air-Blown Gasification Cycle, the removal of the particularly corrosive alkali chloride
vapours at high temperatures (827 and 927°C), was studied experimentally and achieved by McLaughlin (1990), using calcium montmorillonite (Fuller's Earth), as the alkali sorbent. Although, in ABGC gas filtration temperatures have been reduced to 400-600°C, where most of the alkali vapours are expected to condense onto particulates, further studies are necessary to complete the development of an efficient alkali removal system for applications in the temperature range of 600-927°C, which could be used as an integral part of ABGC and also as a basis for multi-contaminant control systems. In the following Chapter, a detailed review of alkali vapour removal sorbents and systems is presented.
CHAPTER 2

LITERATURE SURVEY AND OBJECTIVES

The realization of advanced clean coal technologies for power generation, is very much dependent on the development of an efficient hot gas cleaning, including alkali removal, in order to reduce pollution and avoid corrosion of the gas turbine blades. This chapter reviews the experimental and theoretical studies reported in the literature, which have attempted to identify the form and concentration of alkali species present in coal-derived gases, assess potential sorbents for the removal of alkalies and study the mechanism of alkali sorption. The objectives of this work have been formulated on the basis of these studies and the need to address the technological challenges of new industrial processes.

2.1 LITERATURE SURVEY

2.1.1 Alkalis in Coal

Alkali metals contained in coal, are dispersed in the organic phase, as cations associated with carboxylic acids, and in the mineral phase. The mineral phase contains alkali metals in a soluble form or associated with aluminosilicates, such as albite (Na₂O·Al₂O₃·6SiO₂) (Raask, 1985; Srinivasachar et al, 1990). Almost all the sodium and 20% of the potassium, present in the mineral phase, are in a water-soluble form, while the remaining potassium is associated with aluminosilicates (Lee and Myles, 1986; Hodges and Richards, 1989). In coal, even though potassium salts are generally more volatile than analogous sodium salts, the problem with alkali metals is mainly related to sodium, because it is more available for release to the gas phase (Lee et al, 1992; Fantom, 1993). For example, during coal combustion the Na/K ratio, on a molar basis, of the volatile alkali species released in the flame is of the order of 3:1 or greater (Singh, 1986; Thambimuthu, 1993).

In coal combustion and gasification systems, as already mentioned in Chapter 1, the chlorine in coal is released rapidly as HCl, which then reacts with the sodium bound in the organic
coal lattice to release NaCl. The above process may be relevant to the mechanism of alkali release in British coals, which have an average chlorine content of 1.0 wt % compared to a world average of 0.1 wt% (Raask, 1985). However, Srinivasachar et al. (1990) suggest that the initial release of sodium, in the absence of chlorine, is in the form of NaOH at high temperatures or as Na₂O at temperatures below 1230°C.

### 2.1.2 Alkalis in the Combustion Environment

The principal gas phase alkali species in the combustion flue gases were estimated by Spacil and Luthra (1982) to be alkali chlorides, with hydroxide and sulphate partial pressures being no more than 20% of the total alkali chloride partial pressures. They also reported that the release of volatile alkali species depended on the coal chlorine content and increased for coals with a higher chlorine content. These predictions were based on computer calculations using data from JANAF tables (1971) and Barin and Knacke (1973) to minimise the system free energy, utilizing the chemical activities of all elements in the system as independent variables.

Theoretical calculations of this type, to determine the total vapour alkali concentrations, have also been conducted by other workers (Scandrett et al., 1984; Singh et al., 1986; Srinivasachar, 1990; Hald, 1994). In general, they are based on selected equilibrium reactions which are expected to take place in the coal combustor and result in correlations which predict alkali concentrations for various operating temperatures. Reactions forming condensed sulphates of the type:

\[
2\text{NaCl}_\text{(g)} + \text{H}_2\text{O}_\text{(g)} + \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{Na}_2\text{SO}_4\text{(s)} + 2\text{HCl}_\text{(g)}
\]  

result in higher residual alkali levels than those involving aluminosilicates contained in ash particles represented by:

\[
2\text{NaCl}_\text{(g)} + \text{H}_2\text{O}_\text{(g)} + \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2\text{(s)} \rightleftharpoons \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{Na}_2\text{O}_\text{(s)} + 2\text{HCl}_\text{(g)}
\]

In a specific combustion environment, the gaseous alkali level will depend on which reactions are predominant and the extent to which equilibrium is achieved. Predictions of the
equilibrium vapour alkali concentration in a PFBC environment for coals with 0.01 and 0.1 wt% chlorine content are shown by the solid lines in Figure 2.1 (Lee et al, 1984). These values indicate that even for the lower chlorine coal, the total vapour alkali concentrations at 800°C are likely to be at the limit of the 24 ppb wt, the target specification in the turbine expansion gas (USDoE, 1986). The corresponding experimental data are much higher than the theoretically calculated concentrations probably because the experimental data were obtained from PFBC units burning a wide variety of coals, with chlorine contents higher than the 0.01-0.1 wt% used in the calculations. However, it seems likely that for a coal with negligible or zero chlorine content, the condensation and removal of alkali as sulphates using particulate filtration alone, could in theory remove all alkali contaminants released during coal combustion (Thambimuthu, 1993).

![Figure 2.1](image_url)

**Figure 2.1:** Alkali vapour concentration in PFBC flue gas as a function of temperature (Lee et al, 1984)

### 2.1.3 Alkalis in the Gasifier Environment

In a gasifier (reducing) environment, with sulphur present as hydrogen sulphide rather than as oxides, the volatile chlorine species could persist as vapour right through to the combustion
stage of the gas turbine (Mojtahedi, 1987). Under these circumstances, if the alkali chlorides are not removed before combustion, then sulphates may form under the turbine oxidising environment. Although the turbine entry temperatures are sufficiently high to prevent condensation upstream, if the gas temperature in the boundary layers of the turbine blades drops to levels at which equilibrium favours condensed sulphate rather than vapour chloride, alkali deposition of \( \text{Na}_2\text{SO}_4 \) could be severe.

Mulik et al, (1983) used thermodynamic calculations to predict the form and concentration of alkali released during coal gasification in relation to their experimental work on alkali removal. Five different types of gasifiers (Westinghouse, Lurgi, Texaco, Shell Koppers and Winkler) were studied and alkali chlorides were identified as the predominant volatile species over alkali hydroxides and sulphates. Gas phase alkali concentration in the gasification flue gases was shown to increase with temperature and decrease with pressure. The total vapour concentrations of alkali chlorides also increase with an increasing coal chlorine content and hence an increasing HCl content in the fuel gas. Under these conditions the total vapour phase alkali concentrations could be at least one to three orders of magnitude higher than the 24 ppb wt limit for the safe operation of a gas turbine (Thambimuthu, 1993).

2.1.4 Thermodynamics of Alkali Removal

Alkali vapour can be effectively removed from process gas streams by solid sorbents, known as 'getters'. This concept evolved from observations that alkalis were irreversibly captured (gettered) by ash particles containing aluminosilicates, during coal combustion. Thermodynamic equilibrium calculations have been used to investigate a number of reaction schemes involving alkali salts and possible getter materials. From these results, reactions of vapour alkali chlorides with 'getter' materials are expected to be exothermic with their equilibrium extent of 'gettering' determined by temperature, pressure and gas composition (Singh et al, 1986).

Scandrett (1984) estimated the values of the equilibrium constants of candidate reactions using the JANAF thermochemical tables, in order to eliminate those which are unlikely to be thermodynamically feasible. However, this work was restricted to reactions for which thermodynamic data were available. Singh (1986) carried out calculations for individual
parallel gettering reaction systems, using a database and software support maintained at the National Physical Laboratory (NPL). The calculations were obtained by the minimisation of the total system Gibbs free energy subject to stoichiometric constraints. The assumptions for this analysis were that all gas mixtures were ideal (this was considered acceptable for the range of temperatures and pressures of interest) and that all condensed phases were pure single components. This latter assumption takes no account of the possibility of forming glasses, liquid mixtures, solid solutions or non-stoichiometric mixtures (Shand, 1958). Given the usual order-of-magnitude uncertainty with these theoretical calculations, the agreement between equilibrium constants ($K_p$) calculated by Scandrett and Singh is good.

Reactions with aluminosilicates were found to be thermodynamically favoured over reactions with silica alone (Scandrett et al, 1984; Singh et al, 1986). However, alkali removal with alumina as a 'getter' containing little or no silica and with no sulphur oxides present in the gases were not equilibrium favoured above about 527°C. These calculations therefore agree with Johnson and Lee's (1980) conclusion that the alkali removal with bauxite, which is mainly alumina, results primarily from physical adsorption.
For exothermic gettering reactions, the uptake was estimated to reach 99% at 727°C and to be well above 95% at 927°C, which means that alkali removal should be effective at the anticipated process temperatures. These calculations (Scandrett and Clift, 1984) were based on gases containing 3 %vol H₂O with no HCl present, apart from that formed by reaction (e.g. for North American coals) and for total system pressures of 1 and 10 atm. The basic reaction scheme used for alkali chlorides with aluminosilicate getters is shown in Equation 2.2, where it is clear that the reaction is favoured by increasing water vapour concentration but inhibited if HCl is present. Scandrett's work was extended to gas compositions with HCl present by Singh and Clift (1986) to account for the higher chlorine content of European coals. These results indicated that for high concentrations of HCl (160 - 320 ppmv), the gases must be cooled below 827°C if the sorbent gettering reaction is to reduce the volatile alkali concentration to a level below 0.1 ppm. As with other studies based on thermodynamic calculations, these predictions relate to equilibrium conditions for reactions which are assumed to take place during alkali capture, but which may not accurately represent the alkali sorption process.

2.1.5 Experimental Studies of Alkali Vapour Removal

Extensive experimental studies of alkali removal processes have been performed to investigate the capacity, reaction mechanism and rate of alkali capture of potential getter materials. Bench-scale reactor tests at high temperatures, with different carrier gas compositions and atmospheric or higher pressure have been used extensively for this work. Thermogravimetric (TG) tests under atmospheric pressure have also been used to characterise candidate materials.

For the systems of interest (PFBG and PFBC, Chapter 1), reactions were studied over a temperature range of 800-1000°C, at pressures up to 30 atm (Lee et al, 1980; Lee et al, 1986; Mulik et al, 1986; Punjak et al, 1990; McLaughlin, 1990). The carrier gases used varied from inert gases like N₂ and Ar to simulated combustion or gasification gases, depending on the process used. Combustion gases would typically contain O₂ and SO₂ (Lee et al, 1980; Lee et al, 1986; Punjak et al, 1990) whereas gasification gases contained H₂ and H₂S (Mulik et al, 1986). Depending on the type of coal burnt or gasified, the product gases would also contain various quantities of HCl, H₂O, CO₂, CO, CH₄ and N₂. Mulik et al (1983) found that the simulated gases did not interfere with the gettering process, but did produce a black carbon
coating on the reacted pellet. A similar deposition was observed with pellets tested in an atmospheric fluidised bed coal gasifier at CRE.

A wide range of alkali concentrations in combustion or gasification gases were measured or projected under different conditions. Lee et al (1992), showed that the time-averaged alkali vapour concentration (Na+K) present in PFBC flue gas from three Illinois coals at 900°C, with system pressure 9.2 atma, ranged from 67 ± 2 to 90 ± 3 ppb wt. A typical example is also presented in the Westinghouse reports (Mulik et al, 1986), where five different types of gasifiers (Westinghouse, Lurgi, Texaco, Shell Koppers and Winkler) studied and the estimated alkali concentrations released in the various systems is given in Table 2.1. It is not surprising therefore, to find that alkali concentrations used in experimental work have varied from 0.5 (Lee et al, 1986) to 200 - 300 ppmv (Punjak et al, 1990).

In addition, a hot gas with a fairly high alkali concentration may be required in laboratory experiments in order to obtain a detectable amount of alkali vapour within a reasonable period. For this reason, Lee and Johnson (1980) and Mulik et al, (1986) used 80 ppmv of NaCl, whereas McLaughlin (1990) used 40 ppmv NaCl.

2.1.5a Measurement of Gaseous Alkali Concentration

In order to assess the extent of alkali control required and to evaluate the performance of alkali control technology, accurate techniques for measuring the alkali concentration in a hot gas stream have had to be developed. Methods of alkali vapour measurement used, fall into two broad categories; 'batch' sampling techniques requiring typically several hours to obtain an alkali value off-line, and 'on-line' measurements producing instantaneous real-time alkali values. Batch sampling techniques require a fixed volume of gas to be drawn through an alkali collection device, which is then chemically analysed for alkali content. On-line methods giving instantaneous results have the advantage that time dependant changes and process perturbations can be quantified.

A batch-type sampling train based on condensation has been widely used for alkali measurement. Typically, this consisted of a quartz-lined stainless steel cold trap, three water bubblers, a pressure gauge, flow control and measurement devices (Lee and Myles, 1984).
At either end of the cold trap, Saffil fiber filters (95% Al₂O₃ and 5% SiO₂; 3 µm fiber diameter) were installed to serve as a particulate and condensed alkali aerosols filter. The alkali vapour passing through the upstream filter section was cooled and condensed in the cold trap and passed through three water bubblers for the final knockdown of the alkalis in the gas. At the end of each measuring period, the filter was collected, the cold trap rinsed with distilled water and the solutions collected from the bubblers. Each section was then analysed for alkali.

This condensation method was also used by British Coal and the Technical Research Centre of Finland. However, in order to avoid the alkali adsorption problems encountered with stainless steel, the British Coal system used a high-purity (>99.7% Al₂O₃) alumina lined air-cooled probe, followed by two bubblers and a Nextel (99% Al₂O₃) ultrafibre filter downstream. The system was used successfully on an atmospheric gasifier, after the ceramic filter. The sampling system developed at Technical Research Center of Finland, comprised a condenser and five bubblers. The gas sample was quenched by injection of distilled water after the reactor. Water vapour was condensed and captured by a cold trap and then the gas stream was led through washing bottles containing water. After the sampling the aqueous solutions were combined into one sample, which was analysed by an atomic absorption spectroscopy (AAS). No alkali metal was found in the condenser (Hokajarvi et al, 1991; Hippinen et al, 1992).

Hald (1994) also used a sampling probe, containing a high-purity alumina condenser, followed by bubblers. The bubblers were followed by a drying column, a gas meter and a pump. 94±6% of gaseous alkali metal chlorides were captured within the mole fraction ranges of 0.5 to 250 ppmv NaCl and 250 to 500 ppmv KCl. The problem experienced by all these systems was the formation of alkali aerosol particles during cooling. Such an aerosol can evade capture by bubblers and fiber filters. To test whether condensed alkalis, in the form of aerosols evaded the sampling system, Hald (1994) generated a known amount of vapour phase alkali metal from an aqueous solution and introduced it by a quartz nozzle into a furnace. A particle counter connected to the outlet gas, showed that some alkali particles escaped the test system and therefore could also possibly pass through the sampling system. McLaughlin (1990), also used the condensation method to measure the gaseous alkali concentration in exit gases, but the efficiency of the system was quite low (58%) and in the light of the problems
that other investigators met with this method, the idea was abandoned.

Cicero and Williams (1990) reviewed methods for measuring gaseous alkali and identified flame emission spectroscopy as the most appropriate on-line method for real time measurements. This system was used by Lee and Myles (1984), in the form of an Ames analyser for on-line sampling of the inlet and outlet gas streams from an alkali sorber vessel. Unfortunately, results obtained for sodium vapour concentration were <10 ppb wt, whereas the corresponding concentration measured by the batch-type sampling train was 70-140 ppbwt. This discrepancy is critical, because the Ames data would indicate that the alkali vapour concentration in the PFBC process stream should be low enough not to be considered a problem, while the sampling train data showed the opposite. One of the problems encountered with the Ames analyser was the capture of alkali by the stainless steel sampling tube when heated above 700°C. Trials on the Ames analyser were also conducted at CRE but the results were unsatisfactory.

Consequently, the on-line methods developed for measurement of alkali concentration in gas streams, are not sufficiently reliable to accurately determine low levels of alkali. Batch sampling techniques, which have been progressively developed are therefore likely to produce better results.

2.1.5b Material Selection for Experimental Apparatus

One of the major problems with the experimental studies of alkali vapour removal has been the selection of an alkali-resistant material for equipment which is in contact with salt vapour. This problem was encountered with the stainless steel sampling line used by Lee and Myles (1984). Alumina, Al$_2$O$_3$, is probably the most important and versatile of the high-grade oxide ceramics due to its favourable mechanical, thermal, electrical and chemical properties. High purity alumina ceramics show excellent overall resistance to chemical attack and are used in high-pressure sodium lamps, an application which needs a material to be inert to reactive hot sodium vapour (Lay, 1991). Silica-based materials are less resistant towards alkalis particularly at high temperatures and much lower temperatures in the presence of water. Beryllium oxide is one of the most resistant materials towards reactive alkali metals, but it is also very expensive and becomes volatile in the presence of water vapour.
The techniques used to characterise candidate sorbent materials were mainly thermogravimetric analysis (TG) and bench-scale reactors. In systems not connected to pilot-plant gasifiers or combustors, gaseous alkali was produced through evaporation of alkali solutions or by alkali sublimation (Lee et al, 1984; Mulik et al, 1986; Uberoi et al, 1990; McLaughlin, 1990; Lippert et al, 1993). The thermogravimetric method proved a quick and efficient way of verifying alkali uptake characteristics of the selected materials because only small quantities are required, thus avoiding the complications involved in a reactor system. Mulik et al, (1986) used a double balance thermogravimetric system (TG), which was designed to continuously monitor the weight loss of the alkali source and the weight gain of the candidate getter. McLaughlin (1990) used Simultaneous Thermal Analysis (STA) to screen candidate alkali sorbents. This method combines Differential Thermal Analysis (DTA) and Thermogravimetry (TG), which allowed the simultaneous measurement of energy and weight changes in a sample as a function of temperature. The samples used were mixtures of 10% by weight NaCl and 90% the candidate calcined sorbent, in order to avoid problems of using salt vapour. McLaughlin classified materials as suitable sorbents on the basis of the overall weight loss observed. Punjak et al, (1989) used a horizontal reactor tube to expose a flake of sorbent to alkali-containing hot gas and evaluated its gettering ability at the end of the experiment by chemically analysing the flake for sodium.

However, sorbents had also to be examined under conditions closer to those used in process applications in industry. Most of this experimental work has been done on laboratory or bench-scale rigs, involved fixed beds of solid sorbents. Other options under consideration include the entrained flow reactors, fluidised bed reactors, moving granular bed filters and the in-situ removal of alkalis using additives in the coal combustor or gasifier. Fixed packed bed sorbent systems are well characterised, and have been widely used because of their simplicity (Lee et al, 1980; Lee et al, 1986; Mulik et al, 1986; McLaughlin, 1990). Fluidised beds, although known for their good mass and heat transfer characteristics, have not been used because they were bound to increase the dust concentration in the process line due to attrition of the solid sorbent. In-situ removal of alkalis by using additives (Pintsch et al, 1991) was not reported as very successful, since kaolin tested by the Combustion Power Company (California/USA) could not adequately remove all the water soluble fraction of alkalis and...
bauxite tested by Westinghouse Electric Corporation (Pittsburgh/USA) was shown to release potassium and sodium even from the insoluble alkali fractions. Entrained flow reactors have been recently tested by Westinghouse (Lippert et al, 1993). Batch packed beds have the advantage over entrained flow reactors when the reaction rates of alkali sorption are low and long solids residence times are necessary. With entrained flow, the sorbent utilisation is far from complete because of the short residence times involved. The recent idea of moving granular bed filters for multicontaminant control, also allows almost complete exploitation of the sorbents due to the long sorbent residence times that can be achieved (McDaniel et al, 1995).

2.1.6 Alkali Getters

Since only a fraction of the water-soluble sodium contained in coal, appeared as a gaseous combustion product, the presence of materials that could capture sodium in a water-insoluble compound was indicated. It was demonstrated that the addition of an aluminosilicate clay to the combustion zone of a PFBC reduces the emission of alkali vapours (Lee et al, 1980). Mulik et al, (1983) from thermodynamic calculations on gasification of coal, predicted that condensation of volatile sodium would not be observed in the presence of ash constituents (1.2% Al, 2.4% Si), because of the formation of albite (Na₂O.Al₂O₃.6SiO₂). If kaolin, an aluminosilicate material (Al₂O₃.2SiO₂.5H₂O), was present the formation of both nepheléline (Na₂O.Al₂O₃.2SiO₂) and albite would be possible. Hodges and Richards (1988) found in the combustion products of coals with differing kaolin contents that sodium was in combination with aluminosilicates. These results suggested that aluminosilicates could be useful in reducing the gaseous alkali content in the flue gas.

Approximately 40 sorbent materials have been screened for alkali sorption processes by Lee et al, (1980), Mulik et al, (1986), McLaughlin (1990) and Gupta (1995). Materials which have been further studied in bench-scale reactors include activated bauxite, emathlite, kaolinite and calcium montmorillonite. The chemical composition of some of the materials studied is given in Table 2.2. Activated bauxite was studied by Lee and Johnson, Luthra and Leblanc, Lee and Myles, Mulik et al, Punjak et al and McLaughlin. It can be partly regenerated because it has been found to both physically and chemically adsorb alkali salt vapours. The NaCl vapour captured by physical adsorption was found to be easily removed by water leaching, while the
product formed by chemical fixation was water-insoluble. During thermal desorption, approximately 10% of the original activated bauxite weight gain was lost (Uoberoi et al, 1990), which indicated that this quantity of salt was physically adsorbed. The amount of adsorption has also been shown to decrease with increasing temperature (Lee and Johnson, 1980), which is another characteristic of physical adsorption. As a result, Mulik et al, were reluctant to use activated bauxite in process applications where changes in the conditions, such as temperature or gas composition, could cause desorption of the captured sodium.

Emathlite, kaolinite and calcium montmorillonite have been found to chemically adsorb alkali salt vapours and are therefore preferred to activated bauxite. Emathlite has been studied extensively by Mulik et al, as it was produced in Florida and provided a cheap solution for the US market. For similar reasons McLaughlin (1990) studied Fuller's Earth (calcium montmorillonite) as an appropriate material for the UK market.

2.1.6a Aluminosilicates as Getters

The most likely candidate alkali getter materials appear to be derived from layer aluminosilicates which contain two-dimensional tetrahedral sheets, with individual tetrahedra linked by sharing three corners (the basal oxygens) each forming a hexagonal mesh pattern of composition Si$_2$O$_5$. The fourth tetrahedral corner points in a direction normal to the sheet and forms part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally by sharing octahedral edges. Octahedral cations may be Mg$^{2+}$, Al$^{3+}$, Fe$^{2+}$, Fe$^{3+}$. Linking one octahedral sheet with one tetrahedral, produces a 1:1 clay mineral, such as kaolinite. A 2:1 clay mineral such as calcium montmorillonite and emathlite have two tetrahedral sheets sandwiching an octahedral sheet. If the 1:1 or 2:1 layers are not electrically neutral, for example via substitution of Mg$^{2+}$ for Al$^{3+}$ in montmorillonite, then the excess layer charge is neutralised by interlayer cations. The two structures are schematically shown in Figure 2.2. In activated bauxite, the functional unit structure of gibbsite [Al(OH)$_3$] consists of a layer of Al ions sandwiched between two closely packed layers of hydroxyl ions (Mulik et al, 1983).

The presence of water between the layers (often associated with the interlayer cations) is a characteristic of these materials. It has been suggested that the water molecules may be
Table 2.2: Approximate composition of candidate alkali getter materials (Lee et al, 1980; Mulik et al, 1986; Punjak et al, 1989; McLaughlin, 1990)

<table>
<thead>
<tr>
<th>Candidate getter material</th>
<th>Approximate composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Bauxite</td>
<td>11% SiO₂, 84.2% Al₂O₃, 4.8% Fe₂O₃</td>
</tr>
<tr>
<td>Emathlite</td>
<td>70.12% SiO₂, 13.29% Al₂O₃, 4.84% CaO, 3.2% Fe₂O₃, 2.47% MgO, 1.13% K₂O, 0.1% Na₂O, 0.36% TiO₂</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>52.1% SiO₂, 44.9% Al₂O₃, 0.8% Fe₂O₃, 2.2% TiO₂</td>
</tr>
<tr>
<td>Calcium Montmorillonite</td>
<td>55.2% SiO₂, 13.7% Al₂O₃, 8.1% Fe₂O₃, 0.7% TiO₂, 3.3% MgO, 6.3% CaO, 0.3% Na₂O, 0.6% K₂O</td>
</tr>
<tr>
<td>Vansil</td>
<td>46.1% CaO, 50.2% SiO₂, 0.21% Al₂O₃, 1.86% MgO, 0.15% Fe₂O₃, 0.22% Na₂O</td>
</tr>
<tr>
<td>Ebony Novacite</td>
<td>63.15% SiO₂, 3.24% C, 0.13% S, 19.16% Al₂O₃, 2.29% Fe₂O₃, 1.8% TiO₂, 0.25% CaO, 0.15% MgO</td>
</tr>
<tr>
<td>Zeolite 5A</td>
<td>molecular sieve Type 5A, aluminosilicate substrate with attached cations of Ca</td>
</tr>
<tr>
<td>Diatomaceous Earth</td>
<td>92% SiO₂, 5% Al₂O₃</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Burgess No. 10 pigment</td>
<td>44.8-45.3% SiO₂, 37.5-39.7% Al₂O₃</td>
</tr>
<tr>
<td>Attapulgus Clay</td>
<td>68% SiO₂, 12% Al₂O₃, 10.5% MgO</td>
</tr>
<tr>
<td>Barytes</td>
<td>mainly BaSO₄</td>
</tr>
<tr>
<td>Pumice</td>
<td>a naturally occurring volcanic rock formed by the rapid cooling of lava flows</td>
</tr>
<tr>
<td>Pyrophillite</td>
<td>Al₂Si₄O₁₀(OH)₂</td>
</tr>
</tbody>
</table>
arranged in a tetrahedral manner with respect to the oxygens of the 2:1 layers. For example, in calcium montmorillonite Mg$^{2+}$ can be substituted for some Al$^{3+}$ in the octahedral sheet. The resulting layer charge is balanced by interlayer cations (mainly Ca$^{2+}$ with small amounts of K$^+$ and Na$^+$). It was found that the Ca$^{2+}$ ions were located in the hexagonal cavities of the tetrahedra sheets in the anhydrous mineral, but entered the water layers in the hydrated mineral, whereas K$^+$ and Na$^+$ ions were located close to, or partially within the hexagonal cavities in the anhydrous and the hydrated phases. The interlayer cations tend to force the layers apart leading to a more open structure than the 1:1 layer silicate. Typical interlayer distances are 7.2 Å for 1:1 compared to 14.4-15.6 Å for 2:1 (Mineralogical Society, 1980). This may facilitate the ingress of alkali and/or water vapour and subsequent reaction.

All montmorillonites lose the majority of their interlayer water in the range 100-200°C giving a partially collapsed structure (Mineralogical Society, 1980). All this water appears to be lost by 450°C, and after heating to temperatures ≥450°C, most montmorillonites will not rehydrate. Continued heating beyond 450°C leads eventually to the loss of the structural hydroxyl groups. The loss of -OH groups takes place in two stages. A first loss at ~700°C,
with the original structure being essentially retained, followed by a second loss at 800-900°C associated with the collapse of the lattice. Removal of molecular water between layers will occur in kaolin at temperatures below 400°C. At temperatures between 400-700°C, all the lattice -OH groups are lost and kaolin undergoes a phase transformation to the quasi-stable metakaolin (Al₂O₃·₂SiO₂). At temperatures above 750°C, crystallisation processes include the formation of new phases, such as γ-alumina and/or silicon-spinel at 925°C and mullite (Al₂O₃·SiO₂) at 1100°C (Mulik et al, 1983; Atakül et al, 1990). Bauxite also undergoes a series of phase transformations, where gibbsite transforms to boehmite (Al₂O₃·H₂O) at ~300°C and then between 450°C and 1200°C to γ-, δ-, θ- and α-alumina (Mulik et al, 1983).

The presence of Ca, Mg and Fe in the solid sorbent will lead to a number of additional compounds in the calcined matrix which may enhance the uptake of sodium by the getter, through the formation of low-melting eutectics on stable reaction products. In particular, anorthite (CaO·Al₂O₃·₂SiO₂) has been identified in the calcined products of montmorillonite and the following reaction is possible:

\[
\text{SiO}_2 + 3(\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 2\text{NaCl}(g) + \text{H}_2\text{O}(g) = \\
2\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2 + 3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + 2\text{HCl}(g)
\]  

(2.3)

The reaction product (Na₂O·3CaO·6SiO₂) forms a low melting eutectic composition with SiO₂ and Na₂O·2SiO₂ (Schairer, 1957). The presence of Ca and Mg in the silica glass coverings of high pressure sodium lamps was found to accelerate the attack on silica by sodium vapour (Lay, 1983).

The typical composition of Fuller's Earth, is complex; 55.2% SiO₂, 13.7% Al₂O₃, 8.1% Fe₂O₃, 0.7% TiO₂, 3.3% MgO, 6.3% CaO, 0.3% Na₂O, 0.6% K₂O (McLaughlin, 1990). The general formula for a montmorillonite structure is (M⁺ₓ.nH₂O)(Alₙ₋ₓMgₓ)(Si₄O₁₀)(OH)₂, where M⁺ is the interlayer cation. For calcium montmorillonite the interlayer cation is Ca²⁺ and as a result its empirical formula is (Ca₀₂)(Al₁₆Mg₉₀₆)(Si₄O₁₀)(OH)₂. Its structure appears to be amorphous after calcination at 900°C, with some sanidine (KAlSi₃O₈), albite (Na₂O·Al₂O₃·6SiO₂), anorthite (CaO·Al₂O₃·2SiO₂), quartz and tridymite (SiO₂) present. These have been identified by X-Ray Diffraction by McLaughlin (1990). The calcined Fuller's Earth is a mixture of
oxides, which even though the effect of the minor constituents can be ignored, the variety of elements in the solid reactant composition implies that there may be a large number of reactions occurring at the same time being though impractical to consider all of them.

Emathlite's saturation capacity has been measured as 18 %wt, while bauxite gave an uptake of 5.6 %wt (Mulik et al, 1986). Kaolinite's alkali capacity was measured as 26.6 %wt by Punjak et al, (1990), but it was rejected by McLaughlin since it undergoes large exothermic phase transformations at temperatures above 900°C (Mulik et al, 1986; Atakül, 1990) and therefore its sorption characteristics may be affected. Instead, Fuller's Earth was used with an uptake of 12.6 %wt. Tests with emathlite, activated bauxite, kaolin and Fuller's Earth at the atmospheric pressure gasifier at CRE, performed at 950°C with alkali vapour levels being between 1 - 3 ppm wt Na and 0.6 - 1.3 ppm wt K (Fantom, 1993), identified Fuller's Earth to give the lowest outlet alkali value of 0.17 ppm wt Na and 0.06 ppm wt K. The total value of 0.23 ppm wt is still above the target range of 0.07 - 0.024 ppm wt but is predicted to be lower for a high pressure system.

2.1.6b Reaction Mechanism for Alkali Capture

The general equation (2.2) for alkali sorption by aluminosilicates used for thermodynamic calculations does not in itself provide verification of the reaction mechanism. One way of investigating the reaction mechanism, has been to examine the form of the gaseous reactants and the elements present in the solid sorbents after their exposure to alkali salt vapours.

Sodium chloride at the temperatures of interest (up to 1000°C) exists as a monomer and above ~1465°C it exists as (NaCl)_n, where n=2 or 3 (Holleman et al, 1985). Even if some dimers exist, these will be in equilibrium with the monomers (Datz et al, 1961). X-ray diffraction (XRD) studies were used to identify the solid reaction products. Mulik et al. (1986) studied the reaction mechanism of the sodium adsorption by emathlite and considered it as an initial surface reaction of sodium with silica. In the presence of alumina, sodium reacted with silica at localised regions within the substrate material, to form sodium feldspar (albite), Na_2O.Al_2O_3.6SiO_2, which has also been identified by XRD Analysis by Punjak et al, (1989). Nepheline Na_2O.Al_2O_3.2SiO_2, was identified as a reaction product with Fuller's Earth by McLaughlin (1990). After extended exposure of emathlite to the alkali chloride environment,
the production of a glass surface phase has been observed, which could be sodium di-silicate (Na$_2$O.2SiO$_2$) or a eutectic mixture (Eq. 2.3). The existence of a glassy product in saturated emathlite has also been indicated by X-ray Analysis by Punjak et al, (1989) and McLaughlin (1990). Punjak et al (1989) identified two reaction products in kaolinite and bauxite; nepheline, where the sodium cation is octahedrally coordinated, and carnegieite, where it is tetrahedrally coordinated, both with a composition of Na$_2$O.Al$_2$O$_3$.2SiO$_2$. These results are in agreement with the reaction schemes used for thermodynamic calculations. However, the formation of glasses at high alkali uptake, would indicate the presence of non-stoichiometric mixtures, which make the system more complex and as saturation is approached there may be a change in the reaction mechanism and the rate controlling step (McLaughlin, 1990).

Punjak et al, (1989) tested, after saturation, the reversibility of the alkali uptake for bauxite, kaolinite and emathlite. No desorption was observed for kaolinite and emathlite, but bauxite lost approximately 10% of its weight gain. This suggested that the mechanism of alkali sorption for bauxite involved both physical adsorption and chemical reaction, whereas for kaolinite and emathlite alkali capture occurred through irreversible reaction. Scanning Auger Analysis performed on treated kaolinite, emathlite and bauxite (Punjak et al, 1989), revealed no chlorine in the products of sorption for kaolinite and emathlite, whereas chlorine was partially retained by bauxite due to physical adsorption. Since chlorine (as HCl) should be released during the sorption reaction (Eq. 2.2), it was indicated that kaolin and emathlite reacted with sodium chloride to give gaseous HCl.

Mulik et al, (1986) also used X-ray diffraction, ion chromatography and atomic absorption analysis to compare the concentrations of sodium and chlorine in emathlite pellets. The results obtained have shown that the total chloride detected in the pellets was much less than the total sodium adsorbed (<0.01 %wt of the total chlorine compared to 3.3 %wt of the total sodium), indicating that HCl was liberated during the chemical adsorption as anticipated.

The experiments performed by Punjak (1988), showed that the maximum weight gain observed for kaolinite, was 5.2 %wt and 26.6 %wt under dry N$_2$ and simulated combustor flue gas (SFG) atmospheres, respectively. The dependence of capacity on the composition of the carrier gas, implied a difference between the mechanisms of adsorption under these two atmospheres. Most probably this difference was due to the presence of water in the SFG
atmosphere, which plays an important role in the alkali sorption reaction by attacking the silica lattice (Mulik et al, 1986). The presence of water vapour seemed to make chemical reaction the dominant sorption mechanism, while physisorption dominated the process in the absence of water vapour. McLaughlin (1990) demonstrated, using \( \text{N}_2 \) as a carrier gas which contained 5 \% vol water vapour, the inhibitory effect of the presence of HCl (160 ppmv HCl) in the feed. The observed Fuller's Earth sodium uptakes were \(-5 \%\) wt and 12.6 \%wt under 160 ppmv and 0 ppmv HCl respectively.

2.1.6c Effect of Water

The presence of water vapour has been shown to play a crucial role in the uptake of sodium by aluminosilicates. The rate and extent of corrosion of silica bricks by NaCl vapour is increased in the presence of water vapour and reaction with silicate glasses is a well established phenomenon. Water was demonstrated to enter glass structures (\( \text{Na}_2\text{O}.3\text{SiO}_2 \)) and effectively enhance the diffusivity of alkali ions into the glass (McVay and Farnum, 1974). TG studies on emathlite pellets showed (Figure 2.3) that a weight change was observed when both alkali and water vapour were present in the system, whereas there was no significant change when the pellet was exposed alternatively only to alkali or water vapour (Mulik et al, 1986).

![Figure 2.3](image)

**Figure 2.3** : Continuous Sodium Absorption Activity in Emathlite Pellet Under Various Operating Conditions (Mulik et al, 1986).
The fact that the uptake virtually stopped when emathlite was exposed to water vapour only, could imply that water is not incorporated into the lattice through either an adsorption or a reaction process. A detailed analysis of the effect of water vapour on Fuller’s Earth at elevated temperatures (600°C and 850°C) by Yadegarian (1992) showed little evidence to support an increase in Fuller’s Earth -OH population after water treatment of the sorbent at the temperatures of interest. Thus, there was no apparent explanation for the observed sodium uptake under dry conditions (McLaughlin, 1990; Uberoi, 1990). One option could be the inclusion of an alkali adsorption step in the mechanism. This has already been suggested (Mulik et al, 1986) and McLaughlin (1990) reported limited success with a mechanism incorporating these kinetics (L-H-H-W).

TG experiments (850°C and 1 atm) with 3 water concentrations (2.5, 4.6 and 6.2 %mol) were performed (Mulik et al, 1986) and the results suggested that water vapour enhanced the rate of reaction, although increase of water vapour beyond 4.6 %mol did not make much difference, since at this point the water was significantly in excess. Singh and Clift (1986) suggested that increasing water vapour should improve the getter efficiency because of the predictable effect on equilibrium. Punjak (1988) also found that the presence of water vapour increased the alkali loading capacity of kaolinite from 5.2 %wt under dry conditions to 26.6 %wt under the simulated flue gas conditions, which contained 2 %vol H₂O.

McLaughlin (1990) in the STA tests performed with 2-3 %vol water vapour in nitrogen, found that the addition of water vapour caused a decrease in the weight loss by the sample. This indicated that the rate of uptake increased. Fixed bed tests with calcium montmorillonite at 827°C, showed an increase in the maximum sodium uptake by the solid, from 5 to 12.6 %wt Na, when the water in the carrier gas increased from 0 to 5 %vol. Increasing the water vapour to 6-8 %vol did not produce any significant change confirming the trend observed by Mulik et. (1986).

2.1.6d Effect of Hydrogen Chloride

Since alkali capture by aluminosilicate getters is considered to proceed by reversible reactions which release HCl, the presence of HCl in the reaction environment could inhibit the capture of alkali by the solid sorbent. This would be significant for gases derived from coals of high
(1%) chlorine content, such as those of UK origin, with hydrogen chloride levels in the order of 300-800 ppmv, where much of the alkali would remain as vapour phase chlorides (Singh et al., 1986).

HCl was identified as a reaction product of kaolin and NaCl, with mass spectrometry by Gábor et al., (1986). McLaughlin performed a series of fixed bed tests by changing only the HCl concentration (0, 50, 160 ppmv). It was observed that by increasing the HCl concentration in the carrier gas, the sodium uptake by the solid sorbent would decrease (Table 2.3), indicating that HCl was inhibiting the gettering reactions. In a 200 hr high HCl test, where for the last 6 hrs of the experiment HCl was not added to the carrier gas, the sodium concentration profile showed an increase in uptake which demonstrated that the inhibitory effect of HCl could be easily reversed (Figure 2.4).

Table 2.3: Sodium levels in the top layer of Fuller's Earth pellets for different HCl concentrations. Experimental conditions: 40 ppmv NaCl, 5 %vol H₂O, N₂ as balance at 827°C (McLaughlin, 1990).

<table>
<thead>
<tr>
<th>HCl Concentration (ppmv)</th>
<th>Sodium Concentration (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.8 ± 0.3</td>
</tr>
<tr>
<td>55</td>
<td>6.5 ± 0.03</td>
</tr>
<tr>
<td>110</td>
<td>5.29 ± 0.05</td>
</tr>
<tr>
<td>160</td>
<td>4.95 ± 0.13</td>
</tr>
</tbody>
</table>

2.1.6e Potassium Chloride as the Alkali Salt

STA screening tests using KCl in place of NaCl (McLaughlin, 1990), indicated that the identified sorbents were equally effective with potassium. The similarity in uptake profiles also indicates that the capture mechanism could be similar. Mulik et al. (1986) observed that potassium was evolved during the reaction of sodium with emathlite, although previously a direct exchange of sodium for potassium was not observed as the principal mode of adsorption. However in fixed bed tests with NaCl capture (McLaughlin, 1990), the
concentration profiles for background potassium along the sorbent bed, indicated that sodium uptake promoted potassium release. About half of the potassium present in the sorbent was displaced down the bed upon retention of sodium, indicating that some element exchange may have occurred.

2.1.6f Effect of Temperature and Pressure

Tests performed by Mulik et al, (1986) at three different temperatures (775°C, 850°C and 900°C) have shown no significant difference in gettering activity of the emathlite pellets and concluded that this result helps in the adsorber bed design where the uncertainty associated with minor fluctuations in temperature may be safely neglected.

The equilibrium calculations obtained for the gettering reactions of vapour alkali chlorides with aluminosilicates (Scandrett and Clift, 1984), predicted that at the same temperature, the
extent of reaction is greater at 10 atm than at 1 atm and consequently, the getter efficiency was considered to improve as the pressure increased. The effect of temperature is of more interest, because the getter reaction is exothermic and therefore the equilibrium constant falls with increasing temperature (Singh and Clift, 1986). Both effects are obvious from the equilibrium constant equation for the gettering reaction

\[
K_p = \frac{[P_{HCl}]^2}{[P_{H_2O}] [P_{HCl}]^2} \Rightarrow Y_{HCl} = \frac{1}{P^{0.5}} \frac{1}{[K_p Y_{H_2O}^{0.5}]}
\]  

(2.4)

McLaughlin performed fixed bed experiments with Fuller’s Earth at 827°C and 927°C in the absence of HCl and obtained almost the same sodium uptake (12.6 and 12 %wt respectively). However, with 160 ppmv HCl present, the sodium uptake increased to 5.2 %wt at 927°C, instead of 4.5 %wt at 827°C. Although the difference is small, McLaughlin suggested that this effect may be due to a variable temperature dependence of the reactions used to describe the sorption process.

2.1.7 Mathematical Models for Non-catalytic Gas-solid Reactions

In order to formulate a theoretical description of the alkali sorption process, which would predict the behaviour of the process under various conditions of temperature, pressure and gas composition, a mathematical model has been developed based on non-catalytic gas-solid reactions of the form:

\[
A_{(g)} + bB_{(s)} = cC_{(s)} + dD_{(g)}
\]

(2.5)

where the (g) and (s) subscripts denote the gas and solid state of the reactants and products and b, c and d the stoichiometric coefficients. Water vapour may also be present as a second gaseous reactant.

The products of gas-solid reactions can either be only fluids or both fluids and solids. In this case, there are two products, one gaseous (HCl) and the other solid. The overall volume of solid may increase or decrease depending on the molar density of the solid product compared with that of the solid reactant. This is observed when HCl or SO₂ react with limestone CaCO₃.
or the calcined product CaO, and the solid products CaCl₂ and CaSO₄ respectively, occupy considerably more volume than the sorbent (Hartman & Coughlin, 1974; Peukert & Löffler, 1993). In most cases, including the present system, the change is small so that the overall solid reactant size may be regarded as constant.

The general principles used to formulate models for heterogeneous non-catalytic reactions involving a porous solid and a gas reactant, generally include the following steps:

1. external mass transport of gas reactant from the bulk gas to the outside surface of the porous solid
2. diffusion of the reactant gas within the pores of the solid
3. chemical reaction of the solid surface including the adsorption of reactants and the desorption of products
4. diffusion of the gaseous product through the porous solid
5. mass transfer of the gaseous product into the bulk gas stream

Depending on the structure of the solid, the nature of the solid product and the temperature of the process, one of the previous steps can be slower than the others and as a result will be rate controlling. Alternatively, when a step is very fast compared to the others, it could be ignored from the system's analysis without significant errors. However, it is often encountered that two or more steps could contribute in the rate of a process and should all be taken into account when the system is analysed mathematically.

When the solid is non-porous, the diffusion of the gaseous reactants is sufficiently slow to be rate-limiting (Ishida and Wen, 1968; Peukert and Löffler, 1993). Reaction between the gas and the solid is assumed to occur at a sharp interface between the solid product outer shell and the unreacted core of the solid, where the gaseous reactant concentration becomes zero or in the case of a reversible reaction, takes on its equilibrium value. The unreacted core shrinks in size as the reaction proceeds and diffusion through the product layer, which progressively thickens, becomes slower. This model is called the shrinking core model and has been incorporated into the general case of a porous solid. In a porous solid, there is a gradual change in the degree of conversion throughout the particle. The external layer will be completely reacted after a certain time and the thickness of this completely reacted layer will increase towards the interior of the particle. Under these conditions, in contrast to non-
porous solids, the reaction within the partially reacted zone occurs simultaneously with diffusion of fluid reactants in this zone.

When chemical reaction presents the major resistance to the overall progress of reaction, the concentration of the fluid reactant will be constant everywhere and the reaction will occur uniformly throughout the volume of the solid. If on the other hand, pore diffusion presents the major resistance, the reaction will occur in a narrow boundary between the unreacted and the completely reacted zones, where the gaseous reactant concentration becomes zero or takes its equilibrium value. This latter case is identical to the shrinking core system of a nonporous solid.

A widely used approach for the description of a gas-solid reaction in a porous solid, is the pellet-grain model (Szekely et al, 1976). This model postulates that the solid pellet consists of a number of small, non-porous particles or grains, which are surrounded by macropores through which the gas has to diffuse to reach the various grains. The reaction occurs in each grain according to the shrinking core model. A product layer will form with time around each grain and this will in turn offer some resistance to mass transfer. The advantage of the grain model over the older generalised shrinking core model is its explicit incorporation of structural parameters such as porosity and grain size and its correct prediction of the dependence of reaction rate on pellet size for porous pellets in the chemical or mixed control regimes. The pellet-grain model has been extensively studied and used to describe gas-solid reactions (Pigford and Sliger (1973), Wen and Ishida (1973), Hartman and Coughlin (1974), McLaughlin (1990), Duo et al (1993), Peukert and Löffler (1993)).

McLaughlin (1990) used the pellet-grain model to account for the alkali uptake by Fuller's Earth pellets in the convective mass balance for alkali in a fixed bed configuration. The pellets were made in a pan pelletiser by agglomerating fine, 30 μm diameter, nonporous grains with water. Although it was not easy to characterise the pellet structure, the pellet-grain model was used, assuming that the pellets had a spherical shape and were made up of individual, spherical grains of equal size. However, secondary electron images obtained by scanning electron microscopy showed that in reality the grains were of irregular shape and distributed in size.
In McLaughlin's system water was usually present in excess and consequently the reaction could be treated as zero order with respect to water. McLaughlin (1990) was unable to simulate the fixed bed profiles for sodium on Fuller's Earth, in the presence of water and HCl, by a single first-order reaction scheme. A three-step mechanism was also tried, where the adsorption of NaCl and the desorption of HCl were assumed to follow a Langmuir isotherm in which the surface reaction between the adsorbed NaCl and the hydrated silica lattice was the rate limiting step. This reaction scheme is based on Langmuir-Hinshelwood-Hougen-Watson (L-H-H-W) reaction kinetics and appeared to be applicable to moderate to high HCl concentrations for alkali uptake of less than 8% wt. With zero HCl concentration and higher alkali uptake, the assumption of a constant number of adsorption sites, was not valid since the top layers of pellets fused together forming a glass phase.

The failure of the above mechanisms to describe the reaction of NaCl with Fuller's Earth for this particular system, led to proposing a more complex mechanism, which was suggested by the shape of the experimental profiles obtained without HCl addition in the system. The profiles displayed a "knee" in the curve at ~6 %wt Na uptake, where the slope of the curve above 6 %wt appeared to be different from that below 6%wt, possibly indicating that two reactions were involved. The "two-reaction" scheme was based upon the assumption that the uptake of alkali by the sorbent occurred through two distinct, reversible reactions, which were first order, with respect to alkali (Figure 2.5).

The rate of one reaction was assumed to be sensitive to HCl concentration whereas the rate of the other was virtually independent of it. This was indicated experimentally by the fact that with no HCl in the feed an uptake of 12.6 %wt was observed, whereas under high HCl conditions (160 ppmv) the lower uptake of 5 %wt was obtained. This reaction scheme was successfully fitted to the fixed bed experimental data at 827°C and 927°C (Figures 2.6, 2.7).

2.2 OBJECTIVES

To complete the study of alkali removal in Combined Cycle Power Generation over the temperature range of interest for the development of hot gas cleaning techniques, 600-927°C, further experimental work is necessary at ~600°C. Fuller's Earth was identified as a potential
Figure 2.5: Combination of Two Simple Profiles to produce a Complex Final Curve. Both simple profiles were generated using a simple first order reaction model (McLaughlin, 1990).

Figure 2.6: Theoretical profiles generated using the two-reaction model, fitted to the high temperature (827°C) experimental data (McLaughlin, 1990)
alkali getter at 827-927°C by McLaughlin and to be consistent with this work within the British Coal Contaminant Control Program for the Air-Blown Gasification Cycle, this material was selected for further study. Kaolin was also reported as a very promising alkali getter, which needed further investigation at ~600°C. It was not used by McLaughlin, since it undergoes a large exothermic phase transformation to γ-alumina and/or silicon spinel and mullite (a non-getter) at about 925°C and 1100°C, very near the higher temperatures under investigation. Although, much work has been done in the area of alkali removal by aluminosilicate materials, it is still unclear as to the exact mechanism of reaction between the alkali salt, water vapour and the getter material, and the role played by HCl. Based on the above observations, the objectives of this project were primarily directed towards:

1) the evaluation of Fuller's Earth as a potential alkali sorbent at 600-650°C using sodium and potassium chloride as alkali salts.

2) the preliminary assessment of kaolin as an alternative getter to Fuller's Earth.

Figure 2.7: Theoretical profiles generated using the two-reaction model, fitted to the high temperature (927°C) experimental data (McLaughlin, 1990)
3) the study of the effect of HCl and H₂O on the alkali sorption reaction.

4) the revision, simplification and improvement of the McLaughlin fixed bed alkali sorption mathematical model, in order to predict the performance of a commercial alkali sorber.
EXPERIMENTAL METHODS AND RESULTS

The experimental programme of work completed in this research project, covers alkali sorption, sorbent characterisation and alkali uptake mechanism studies in the 600°C region. In this chapter, all the experimental techniques and apparatus used will be described and the results obtained will be presented.

3.1 EXPERIMENTAL METHODS

The experimental work consists of two main parts: the alkali sorption studies and the sorbent characterisation and analysis. The alkali sorption studies involve single-layer and fixed bed tests in a laboratory rig, whereas the sorbent characterisation and analysis involve chemical analysis of the solid sorbent, exit gas analysis, element mapping and X-ray diffraction studies of the untreated and treated solid sorbent, measurement of the specific surface area of the sorbent pellets and of the grain sizes that form the pellets.

3.1.1 Alkali sorption studies

3.1.1a Fixed Bed Rig

The fixed bed sorption rig used in this work, was originally built by McLaughlin (1990) for alkali sorption studies at high temperatures (827°C and 927°C) and under atmospheric pressure. The rig consisted of three main sections; Vapour Generation, Mixing and the Fixed Bed. In the Vapour Generation Section, a platinum crucible, containing NaCl crystals, was suspended by an R-type thermocouple from a microbalance (CI Electronics), in a high-purity sodium-resistant alumina tube. Hot N\textsubscript{2} gas passed down the alumina tube to evaporate NaCl. The concentrated NaCl gas stream was jet mixed through a 0.2 mm nozzle into the Mixing Section. The main gas stream of N\textsubscript{2} which could also contain H\textsubscript{2}O and HCl vapour, depending on the experimental conditions, was introduced into the Mixing Section through a heated side
arm ceramic tube. The sorbent bed of 0.5 mm pellets was packed onto a ceramic support plate in the Bed Section. Temperature was maintained by 7 individually controlled heating elements.

During the course of this work, the Fixed Bed Rig, which is fully described in Appendix I, was progressively upgraded to meet operational requirements at 650°C (Figure 3.1). Electrostatics, which were affecting the microbalance were reduced by screening and the crystal mounting was modified, so that a single NaCl crystal could be suspended directly on the thermocouple attached to the microbalance. A handling system was designed to facilitate its installation. The HCl injection system was fitted with teflon valves and modified to eliminate any release of acid vapour. A condenser, fitted to the exit of the reaction tube, effectively eliminated water and acid vapour prior to venting. Two new temperature programmers were installed to provide automatic control during start-up and close-down. A stable alkali rate of 0.3 mg/hr was maintained over the 200, 400 and 600 hrs run periods. The total weight loss recorded directly by the microbalance, was affected by zero drift (~0.4%) resulting from variations in room temperature and this had to be eliminated by enclosing the balance head in a temperature controlled box.

The gas composition for experiments performed at 650°C, was 4.58 ppm wt NaCl (2.2 ppmv Na), 5-6 %vol H$_2$O, 0-160 ppmv HCl with N$_2$ as balance. Water vapour was introduced into the main gas stream by two temperature controlled water bubblers. Concentrated hydrochloric acid could be injected into the main gas stream by a motorised syringe, depending on the experimental conditions. The fixed bed (10-15 mm) of aluminosilicate getter pellets was held by a fine Pt/Rh gauze or a perforated ceramic plate in the Bed Section. Under the sorbent bed, Nextel alumina wool filter pads were placed in the condensation zone to adsorb the exit gas alkali. At the end of each experiment, the fixed bed was sucked out of the rig in 0.5 mm layers. These layers were chemically analysed for alkali uptake by HF digestion and Atomic Absorption Spectrophotometry (AAS). The uptake alkali concentration values obtained, were plotted against their position in the bed, producing alkali concentration profiles (Figure 3.2).

Alkali exit gas analysis procedures were modified to improve accuracy. The Nextel alumina wool filter downstream of the bed was built up from a number of circular pads cut from the material. These pads form a series of 'layers' which can be easily removed for analysis.
Figure 3.1: Alkali Fixed Bed Sorption Rig
Figure 3.2: Alkali Uptake Profiles Generated from Bed Sections by Chemical Analysis of Pellets

without the need for further cutting. Work was done to optimise the number of pads used, the extent of compression and the location in the reaction tube.

3.1.1b Single-Layer Tests

As an alternative to the well established fixed bed method, a single-layer or 'thin bed' technique was used, since it has the advantage of providing direct information on sorption processes in the pellet without being affected by the bulk fluid dynamics in a fixed bed. This involved treating a single layer of pellets retained on a Pt/Rh gauze in place of the fixed bed.
The primary tests conducted in this series were of 200 hr duration with 6 %vol water. These mixed single layers of Fuller's Earth and kaolin pellets, covering a range of sizes, were treated with 0 and 50 ppmv (0 and 65 ppm wt) HCl respectively. Another single-layer test with 160 ppmv (208 ppm wt) HCl was completed with Fuller's Earth pellets pre-treated in an atmospheric gasifier at CRE. Reference pellets were included for comparative purposes. Table 3.1 presents in detail the single-layer operational conditions.

3.1.1c Alkali Uptake Profiles at 650°C

Alkali uptake studies at 600°C were conducted on the modified fixed bed rig, with a fixed bed run for NaCl on Fuller's Earth over 240 hrs. The rest of the experimental work was obtained at 650°C with N₂ as a carrier gas containing 5-6 %vol H₂O vapour and 4.58 ppm wt NaCl (2.2 ppmv Na). 10 mm beds were used for alkali profile measurements with 0.425-0.500 mm Fuller's Earth pellets. 200 hrs tests with 160 ppmv (208 ppm wt) HCl were conducted for both sodium and potassium. Vaporization temperature had to be lowered by 40°C to maintain the 0.3 mg/hr rate for potassium because of its higher volatility. A 10 mm bed with 0.425-0.500 mm Fuller's Earth pellets was used for a 400 hr run with NaCl and 160 ppmv HCl. After the successful completion of the 400 hr run, a 600 hr run with NaCl was attempted. A 15 mm bed of 0.5-0.6 mm Fuller's Earth pellets was used for a 600 hr run with 160 ppmv HCl and 4.58 ppm wt NaCl, because all the 0.425-0.5 mm pellets were used by previous runs. A second 600 hr run, with NaCl and no HCl using the same pellets, was also performed successfully. Table 3.2 gives details of the fixed bed operational conditions.

3.1.2 Sorbent Characterisation and Analysis

3.1.2a Chemical Analysis

In this work the alkali uptake along the sorbent bed was determined by chemical analysis of the layers of pellets. The following method was developed by Totland et al. (1987) and modified by Oliver et al. (1989). Each layer was sucked out of the rig with a vacuum probe assembly, ground uniformly with a mortar and pestle and divided in three samples of 40-50 mg each. All the samples were placed in PTFE beakers and digested three times at 90-100°C with AnalAr Grade concentrated HNO₃ (70%) and AnalAr HF (48%) with a volume ratio of
Table 3.1: Experimental Conditions for Thin Bed Tests at 650°C

<table>
<thead>
<tr>
<th></th>
<th>Fuller's Earth &amp; kaolin</th>
<th>Fuller's Earth &amp; kaolin</th>
<th>Fuller's Earth &amp; CRE pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>650</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Duration (hrs)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Flow rate (ml/min)</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Gas Composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl (ppmv)</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>(ppm wt)</td>
<td>4.58</td>
<td>4.58</td>
<td>4.58</td>
</tr>
<tr>
<td>HCl (ppmv)</td>
<td>0</td>
<td>50</td>
<td>160</td>
</tr>
<tr>
<td>(ppm wt)</td>
<td>0</td>
<td>65</td>
<td>208</td>
</tr>
<tr>
<td>H₂O (% vol)</td>
<td>6</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>N₂</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuller's Earth</td>
<td>0.6-0.85</td>
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<td>0.6-0.85</td>
</tr>
<tr>
<td></td>
<td>0.425-0.5</td>
<td>(CRE &amp; FE)</td>
<td></td>
</tr>
<tr>
<td>kaolin</td>
<td>0.85-1</td>
<td>0.85-1</td>
<td></td>
</tr>
<tr>
<td>Height of the bed</td>
<td>1 layer</td>
<td>1 layer</td>
<td>1 layer</td>
</tr>
<tr>
<td></td>
<td>200 hr Run (Sodium)</td>
<td>200 hr Run (Potassium)</td>
<td>400 hr Run (Sodium)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------------</td>
<td>------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>650</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Duration (hrs)</td>
<td>200</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Flow Rate (ml/min)</td>
<td>950</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Gas Composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl (mg)</td>
<td>60±0.03</td>
<td>-</td>
<td>120±1</td>
</tr>
<tr>
<td>(ppmv)*</td>
<td>2.2</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td>(ppm wt)</td>
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<td>-</td>
<td>4.58</td>
</tr>
<tr>
<td>KCl (mg)</td>
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<td>60±0.7</td>
<td>-</td>
</tr>
<tr>
<td>(ppmv)**</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>(ppm wt)</td>
<td>-</td>
<td>4.58</td>
<td>-</td>
</tr>
<tr>
<td>HCl (ppmv)</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>(ppm wt)</td>
<td>208</td>
<td>208</td>
<td>208</td>
</tr>
<tr>
<td>H₂O (vol %)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>N₂</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>0.425-0.5</td>
<td>0.425 - 0.5</td>
<td>0.425 - 0.5</td>
</tr>
<tr>
<td>Height of the bed (mm)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

* 2.2 ppmv NaCl = 1.8 ppm wt Na
** 1.7 ppmv KCl = 2.4 ppm wt K
2:1. The solutions were evaporated to dryness between digestions. At the end of the digestion procedure, 8 ml of 12.5 % HNO₃ were added to each sample and this was made up with deionised water to 100 ml in polypropylene volumetric flasks. Blank samples of both the getter material and the reagents were included in each analysis. Atomic Absorption Spectrophotometry (AAS) was used to determine the concentration of alkali in the solutions.

A full review of the analytical procedure was undertaken and although the previously developed method was generally followed, improvements in safety and accuracy, were implemented (Appendix II). The optimum number of digestions was found to be 3 for the sorbent powder and 4 for alumina wool. The acid quantities were reduced and consequently the sample weights decreased to 30-40 mg. Analytical solutions of digested samples made up in polypropylene volumetric flasks for alkali analysis by AAS were not sufficiently accurate for results at 650°C because of the lower concentrations involved. More accurate flasks made from PolyMethylPentene (PMP) were substituted. The hot plate was replaced by a heating block with drilled beaker positions to improve the efficiency of the digestion steps. Lightweight aluminium sample containers were used for accurate weighing of samples.

3.1.2b Exit Gas Analysis

Alkali (Na or K) released in the exit gases from the reactor was captured by condensation in the alumina wool filter pads which were digested in HF. An electrochemical fuel cell for detecting HCl, which is described in detail in Appendix III, was initially selected as the most suitable method for a quantitative and specific detection of HCl in the rig exit gases. A three-week conditioning was necessary for the cell and as a short term measure, a simple analytical system based on Dräger tube HCl detection was employed. Gas was drawn through the tube, heated to 35°C to prevent condensation, at a constant rate (250 ml/min) for 5 minutes, by a constant vacuum system. This prevented pressure fluctuations which would occur with a Dräger gas detector pump. Flowrate was monitored by a calibrated electronic flowmeter throughout the test period. Tests were conducted with NaCl at a rate of approximately 0.3-0.7 mg/hr with a 10 mm Fuller's Earth getter bed, under wet (4-5 %vol water) and dry conditions. Unfortunately, this system was not satisfactory for continuous monitoring.

Fixed bed tests with Fuller's Earth pellets of 0.3 - 0.425 mm diameter, were performed with
the on-line electrochemical cell (3HL CiteL). During the experiments, an air flow of 10 cm³/min⁻¹ was passed through the cell, in order to maintain the electrochemical reaction. The air supply was established at this level in order not to dilute the gas coming from the rig and decrease the HCl concentration giving thus a false reading. The exit gas flowrate through the cell was ~650 cm³/min⁻¹ from a total flowrate of 950 cm³/min⁻¹. The cell was mounted in a box and insulated, so that its temperature will stay constant. HCl response was recorded to a Squirrel data logger and the output in mV (0.5 mV=1 ppmv HCl) was exported to a spreadsheet, where plots of output signal versus time were made.

To be able to perform experiments with and without water, a three-way valve was installed in the main line. With this valve, it was possible to add to the main N₂ line either another N₂ stream which was sparging through two small bubblers or an equivalent (20 cm³/min⁻¹) dry N₂ stream for the dry experiments. For the dry runs, the system was checked for possible water sources, which had to be eliminated.

HCl was monitored on-line in the exit from the fixed bed rig in experiments of few hours duration, which were performed by switching the salt in the feed on and off or by changing the salt weight loss rate from 0.3 to 0.5 and 0.7 mg/hr, in order to establish the role of the salt in the reaction mechanism. Water vapour temperature could be measured in the bubblers and the water vapour production could be controlled by heating or cooling the water bath containing the bubblers.

3.1.2c Element Mapping

Scanning Electron Microscopy (SEM) linked element mapping techniques provided a clearer image of the sorption process within pellets. These techniques are described in Appendix IV. The preparation of the pellets for the SEM analysis was done by vacuum mounting in a mixture of epofix resin and epofix hardener followed by careful grinding in non-aqueous media, such as glycol, and polishing with a methanol-based lubricant. The grinding papers used in sequence were 500, 1200 and 2400 µm. The polishing cloths used were 6µ DUR and 1µ MOL. The duration of grinding and polishing and the number of times that each cloth would be used was not standard, as at the end of each step the sample was checked under an optical microscope. The reason for that was that the pellets were very fragile and pieces could
easily be removed during the cutting procedure, leaving a rough sample surface.

Imaging of distribution patterns for selected elements, primarily sodium, potassium, aluminium, silicon and calcium, in Fuller's Earth and kaolin pellets was accomplished with both Energy Dispersive X-ray Analysis (EDS) and Wavelength Dispersive System (WDS) scanning methods. Data was collected simultaneously overnight on four elements, with WDS assigned to the primary alkali (Na/K) to achieve maximum image enhancement. Digital mapping was used to generate hard copies of the output through a colour video processor. The acquisition times used were 0.8 s for the EDS system and 0.5 s for the WDS system and the electron beam was accelerated to an energy of 10 keV. The intensity of these colour images gives an adequate representation of the relative surface concentration of an element across a section of the pellet.

3.1.2d Specific surface area measurements

The pellet surface area measurements were performed on a 100CX Omnisorp instrument. Pellet surface was evaluated by the Brunauer-Emmett-Teller (BET) equation. Static and the dynamic methods were both used for the measurements. The technique is described in Appendix V.

3.1.2e Grain size measurements

The initial grain size measurements were obtained under an optical microscope for the two pellet sizes, 0.425-0.5 and 0.5-0.6 mm, used in the fixed bed experiments. The pellets were mounted in resin and used for these measurements before they were used for SEM. The pellet sizes and a random number of grains per pellet were measured. Another method used was with the secondary electron images obtained by SEM, which were re-photographed and via OPTIMAS 5.2, a Digital Image Analysis package, the grain-size distribution in a pellet could be determined. Derived grain diameters were determined by measuring the major axis length of the grain projected area on the plane of the cut.
3.1.2f X-ray diffraction studies

X-ray powder diffraction is a fingerprint method which can give an indication of the phases present in a powder. X-ray powder diffraction studies were obtained on raw Fuller's Earth powder and on both calcined and treated Fuller's Earth pellets. Treated pellets from the high-acid and the non-acid 600 hr runs were used and for the non-acid run these were further divided into dark and light pellets for separate examination.

3.2 RESULTS

The results obtained from the above studies are presented in this section and will be discussed in Chapter 6.

3.2.1 Alkali Sorption Studies

3.2.1a The Fixed Bed Rig

 Modifications to the fixed bed rig proved highly effective. The stability of control of alkali vaporisation even for the 600 hr runs was excellent. The measured overall value for the rate was 0.299 mg hr$^{-1}$ compared to the required value of 0.3 mg hr$^{-1}$ and the calculated total weight loss agreed with the direct weighing of the crystal to within 0.05 mg. This was partly due to the technique of tare adjustment used to maintain the microbalance in its most stable operating range of 0-30 mg. Gas leaks were eliminated to give a N$_2$ material balance to ±0.5%. Mass balance was improved dramatically and more than 99% of sodium vaporised was accounted for by chemical analysis. The use of Nextel alumina wool pads for capturing alkali in the exit gas has significantly simplified analytical procedures in this respect. Temperature control of all heating elements is better than ±0.5°C, resulting in stable, reproducible operation over long periods. Temperature differences within the fixed bed were reduced and their values measured (radial and axial) in a 15 mm bed were of the order of 1.5°C. Revision of the computer control and data handling program considerably enhanced the overall performance.
3.2.1b Single-Layer Tests

A mixed single-layer test with Fuller's Earth and kaolin was performed in order to evaluate both sorbents simultaneously. The mixed single layer of Fuller's Earth and kaolin pellets treated with 50 ppmv (65 ppm wt) HCl, resulted in sodium uptakes of 3.48 %wt and 11.38 %wt respectively. This compares with 5 %wt and 9 %wt in the absence of acid. The high acid, single-layer test performed with CRE pre-treated Fuller's Earth pellets and reference pellets, gave uptake values of 5-6 % wt for both types of pellets. Further, the background level of sodium of the CRE pre-treated pellets is almost the same as that of the reference Fuller's Earth pellets (0.26 and 0.23 %wt respectively). All the single-layer results are presented in Table A.II.3.

3.2.1c Alkali Uptake Profiles at 650°C

The mass balance obtained from the first run at 600°C was poor. The maximum sodium gas phase concentration was limited to 0.82 ppm wt (or 1 ppmv, NaCl : 2.09 ppm wt) by the low operating temperature. At 650°C the 200 hr tests with 160 ppmv (208 ppm wt) HCl gave sodium uptake values at the top of the bed of 3.24 %wt for sodium and 2.75 %wt for potassium. Detailed results for the alkali uptake values along the fixed beds are given in Tables A.II.4 & A.II.5. The alkali concentration profiles are given in Figure 3.3. The 200 hr run with sodium gave a poor mass balance, which can be attributed mainly to inexperience in the experimental techniques. The results of the 400 hr run showed an uptake value of 4.3 %wt at the top of the bed. Detailed results are given in Table A.II.6 and the uptake profile is shown in Figure 3.4. The experimental outlet sodium concentration was estimated 5.5 ppb wt and the closure of the sodium mass balance was 95%. For the 600 hr run, a maximum uptake value of 3.7 % wt (Table A.II.7) was obtained and the sodium profile was better developed compared with the 200 and 400 hr profiles (Figure 3.4). The estimated outlet sodium concentration was 5.7 ppb wt, which was similar to the 400 hr result. The closure of the sodium mass balance was 99%. For the non-acid 600 hr run, a maximum uptake value of 14.6 %wt was obtained (Table A.II.8 and Figure 3.5), while an non-uniform colour change of Fuller's Earth pellets was observed at the first layers of the fixed bed. A stable alkali rate was maintained at 0.3 mg/hr over the 200, 400 and 600 runs and results show that the calculated total weight loss from run data agrees with direct measurements on the crystal to within approximately 0.1%.
Figure 3.3: Comparison of Experimental Results between Potassium and Sodium Uptake Profiles for 200 hr Runs.

Figure 3.4: Experimental Uptake Sodium Profiles for the 200, 400 and 600 hr High-acid Runs.
Figure 3.5: Experimental Uptake Sodium Profile for the Non-acid and High-acid 600 hr Runs.

3.2.2 Sorbent Characterisation and Analysis

3.2.2a Chemical Analysis

The polypropylene volumetric flasks initially used for alkali analysis by AAS, in some cases produced volumetric errors of up to 1%, whereas the new PMP flasks reduced this by a factor of 10. The new heating block improved the safety of the digestion procedure and the heat transfer to the teflon beakers. As a consequence, there was no deposition of the material on the walls of the beakers during the digestions. The use of aluminium boats as weighing devices, improved the weighing accuracy to ±0.02 mg by eliminating the electrostatic effects. By using the vacuum probe assembly and the traveling microscope, the accuracy of the layer depths measurements was improved to ±0.1 mm, a significant improvement compared to the distance from the layer weight and the measured mass of solid per unit length of bed (Table A.II.9). Due to the present analytical procedure and the better equipment used, very accurate results were obtained (Table A.II.2).
3.2.2b Exit Gas Analysis

The electrochemical cell appeared to be sensitive to water, but always followed a certain pattern. Whenever water was introduced in the system, the cell response was shifted from the 'No Water' baseline (Figures A.III.2-3). The same response was observed for different water vapour temperatures and with two different cells. In most of the experiments performed, the water baseline was first established and then the salt temperature was increased. Figures A.III.4 and 5 demonstrate the HCl cell response in the presence of both water and salt.

When the salt weight loss rate was decreased from 0.7 to 0.5 mg/hr, the corresponding HCl response decreased as well (Figure A.III.5). When salt vaporisation was stopped, the HCl response curve fell slowly until it reached the water baseline (Figure A.III.6). By increasing the water temperature, the HCl response curve was shifted (Figure A.III.5). The HCl response curve was almost flat when no water was introduced in the system and only salt was produced (Figure A.III.7).

Dräger tube tests have been performed simultaneously with the electrochemical cell tests. Although the Dräger tube tests can generally only give approximate results, they have confirmed the results obtained by the cell. Used Dräger tubes are shown in Figure 3.6. The scale values should be divided by 2 because the measuring range selected was 0.5 to 5 ppmv. A Dräger test tube (c) showed 1 ppmv HCl being produced, when the bed was exposed only to sodium for 9-10 hrs. When H₂O was introduced in the system after the bed was exposed only to NaCl (0.7 mg/hr) for 9-10 hrs, 4 ppmv of HCl were produced (tube (a)). Salt production of 0.3 mg/hr gave a result of 2 ppm HCl (tube (b)). The fourth tube (d) is a blank, presented only for comparison reasons. Water leaks were identified and eliminated from the system. One was found to be a heat exchanger water line, which was preheating the main gas line before it was entering the rig.

3.2.2c Element Mapping

Excellent results were obtained with SEM/EDS/WDS scanning methods. The secondary electron images of Fuller's Earth and kaolin pellets clearly illustrate the pellet structure and
the grain shapes and sizes (Figures A.IV.4-6). Although both were made on a pan pelletiser, the kaolin pellets have a layered structure unlike the agglomerated porous structure of Fuller's Earth pellets.

Element mapping of sodium, potassium, aluminium and silicon are evenly distributed in untreated pellets, but calcium is confined to discrete regions. Treated Fuller's Earth and kaolin pellets exhibit very different sorption patterns. In Fuller's Earth pellets, sodium has diffused throughout the pellet and then started reacting with the individual grains (Figures A.IV.7,9). In kaolin pellets, sodium reacted only at the periphery of the pellet and did not diffuse in the whole structure (Figures A.IV.8,10). Carbon mapping of CRE treated pellets was not successful because of the carbon containing mounting resin. However, results indicate that although the pellets are blackened on the surface, little carbon penetrates the interior of the grains and sorption of alkali proceeds satisfactorily through the surface barrier (Figure A.IV.15). The potassium treated Fuller's Earth pellets seem to follow the same sorption pattern.
as sodium (Figure A.IV.16). Sodium maps of Fuller's Earth pellets and grains from different layers of the sorbent bed, show the gradual decrease of sodium along the bed (Figures A.IV.9,14). No structural difference is observed between the dark and the light-coloured Fuller's Earth pellets after the 600 hr non-acid run (Figures A.IV.19,20). Linescans, that were performed across Fuller's Earth grains, can also give information on the alkali sorption pattern (Figures A.IV.12,18).

3.2.2d Specific surface area measurements

The surface area of calcined Fuller's Earth pellets, with diameter 0.5-0.6 mm and after calcination, was found to be 0.54 m$^2$g$^{-1}$. The static method result was used because it is more sensitive, thus it can give more accurate results for low surface areas.

3.2.2e Grain size measurements

The pellet and grain sizes measured under the optical microscope are presented in detail in Table A.VI.1. The measured mean pellet diameters were 0.400-0.525 mm for a nominal size of 0.425-0.5 mm, and 0.575-0.625 mm for a nominal size of 0.5-0.6 mm. The corresponding measured mean grain diameters were 0.030±0.003 mm and 0.044±0.010 mm. An example of the preliminary grain size distribution measurements for a 0.5-0.6 mm pellet is also presented in Figure A.VI.2.

3.2.2f X-ray diffraction studies

From X-ray powder diffraction studies, calcium montmorillonite, as expected, was identified in the raw Fuller's Earth powder. The calcined Fuller's Earth appeared to be mostly amorphous. In the high-acid treated Fuller's Earth, albite (Na$_2$O.Al$_2$O$_3$.6SiO$_2$) and quartz were identified. More characteristic, identical fingerprints were obtained from the dark- and light-coloured pellets, indicating the presence of nepheline (Na$_2$O.Al$_2$O$_3$.2SiO$_2$) and quartz. The values of the d-spacings measured for the identification of the phases present, are given in Tables A.VII.1-3.
3.3 SUMMARY

The experimental work completed in this project included single-layer and packed bed tests performed in the fixed bed rig, originally built by McLaughlin and subsequently modified for experiments at 650°C. The getter materials tested in the single-layer tests were Fuller's Earth, kaolin and gasifier pre-treated Fuller's Earth pellets, whereas packed bed tests were performed only with Fuller's Earth. The gas composition used was 4.58 ppm wt NaCl (1.8 ppm wt Na), 5 %vol H\textsubscript{2}O, 0-160 ppmv HCl and N\textsubscript{2} as the carrier gas. One packed bed test was also performed with KCl as the alkali salt at a concentration of 4.58 ppm wt.

Due to improvements obtained in the chemical analysis for the captured Na in the getter material and the great care taken to avoid leaks and to establish a stable rate of salt production in the rig, very accurate experimental results were obtained. The 600 hr high-acid run was the most accurately analysed with a 99% Na mass balance being achieved. The gasifier pre-treated, carbon-coated Fuller's Earth pellets exhibited the same Na uptake as the calcined Fuller's Earth pellets, while kaolin seemed a very promising getter for use at 650°C.

Dräger tubes and an electrochemical cell were used for monitoring HCl concentration in a series of preliminary exit gas analysis tests. The results confirmed that the HCl production was directly connected with the presence of NaCl vapour in the system and that its rate of production was enhanced by H\textsubscript{2}O vapour. SEM/EDS/WDS analysis was used to give a better idea of the getter pellet structure and the alkali distribution in the reacted material. From the pellet structure images, via an image analysis package, preliminary grain size distribution studies were obtained. Specific surface area measurements showed that calcined Fuller's Earth pellets have a low surface area. X-ray studies indicated albite to be the most likely solid product for high-acid conditions and nepheline for non-acid conditions.
THEORY AND PARAMETER ESTIMATION

A theoretical description of the physical and chemical processes is necessary in order to be able to extrapolate with confidence, the process performance under conditions other than the experimental ones. The basis on which a theory will be accepted as appropriate, taken from a comparison of experimental results with theoretical predictions. The equations involved in the theoretical description of a fixed bed sorber and in the alkali retention by the solid sorbent, are presented in this chapter. The same general theoretical approach for the alkali sorption process has also been used by McLaughlin (1990). The estimation of the parameters used in the theoretical description, is also presented at the end of this chapter.

4.1 THEORY

4.1.1 Fixed Bed Model

The alkali sorption model for a fixed bed is based on the following convective mass balance over the interparticle gas phase of a bed section (Figure 4.1), which can be expressed in the form:

\[
D_{ax} \frac{\partial^2 C \partial \partial z^2}{\partial t^2} - \frac{u \partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\partial C_s}{\partial t} 
\]

and is based on the principle that:

(in - out) + (in - out) = accumulation + loss through
due to due to in gas phase accumulation
axial dispersion convection in solid getter

72
where \( C_{i0} \) = gas concentration of component \( i \) in the bed voidage [mol cm\(^{-3}\)]
\( C_i^* \) = concentration of sorbate \( i \) in the solid per unit weight of initial solid [mol g\(^{-1}\)]
\( t \) = time [s]
\( z \) = axial position along the fixed bed [cm]
\( D_{ax,i} \) = axial dispersion coefficient of component \( i \) [cm\(^2\)s\(^{-1}\)]
\( u \) = superficial velocity [cm s\(^{-1}\)]
\( \omega \) = bulk density of the solid [g cm\(^{-3}\)]
\( \varepsilon_b \) = interpellet porosity (bed voidage) [dimensionless]
\( \varepsilon_p \) = intrapellet porosity [dimensionless]

The assumptions used for the convective mass balance are
1) Isothermal operation
2) No wall effects or radial dispersion
3) Negligible pressure drop across the sorbent bed

The validity of the above assumptions for the case examined in this study will be discussed later in Chapter 6.

The initial and boundary conditions of the above mass balance are

at \( t = 0 \) and \( z \geq 0 \) : \( C_{i0} = 0 \) \hspace{1cm} (4.1a)

at \( z = 0 \) and \( t > 0 \) : \( C_{i0} = C_{\text{feed},i} \) \hspace{1cm} (4.1b), and

\[
u(C_{i0} - C_{\text{feed},i}) = - \varepsilon_b D_{ax,i} \frac{\partial C_{i0}}{\partial z} \hspace{1cm} (4.1c)
\]

where \( C_{\text{feed},i} \) = feed concentration of component \( i \) [mol cm\(^{-3}\)]
\( L \) = length of the fixed bed [cm]

The alkali sorption process has been described (McLaughlin, 1990) to occur by a two-reaction scheme, where both reactions are reversible and first order with respect to NaCl. This scheme is adopted here for modelling the process and the two reactions are given by

\[
\text{NaCl}_\text{(g)} + \frac{1}{2} \text{H}_2\text{O}_\text{(g)} + b_1 \text{Reactant}_1, \text{(s)} = \text{Product}_1, \text{(s)} + \text{HCl}_\text{(g)} \hspace{1cm} (4.2)
\]
\[ \text{NaCl}_\text{(g)} + \frac{1}{2} \text{H}_2\text{O}_\text{(g)} + b_1 \text{Reactant}_2, \text{(s)} = \text{Product}_2, \text{(s)} + \text{HCl}_\text{(g)} \]  

(4.3)

where \( (g) \) and \( (s) \) denote gas and solid state respectively, and

\[ b_1 \text{ and } b_2 = \text{stoichiometric coefficients} \]

Figure 4.1: Flow of Gas Component \( i \) through a Bed Section of Length \( \delta z \) (Levenspiel, 1972)

Thus, the gas components of the present system are NaCl, H\(_2\)O and HCl, where NaCl and H\(_2\)O are the reactants and HCl is the product. The accumulation of alkali (Na or K) in the sorbent is due to the two reactions and will be calculated from the pellet-grain model (Szekely et al, 1976; Levenspiel, 1972) described subsequently, while the accumulation of alkali in the gas phase is due to the bed voidage (\( \varepsilon_b \)) and will be calculated from the convective mass balance for the fixed bed, which is solved with the "tanks-in-series" method. The "tanks-in-series" method of solution will be described in Chapter 5.
4.1.2 Pellet-Grain Model

The reaction between a porous solid and a gas, leaving a porous solid product, is an important problem that is frequently encountered in many chemical and metallurgical processes. One of the models used for the description of reaction systems, is the pellet-grain model, originally described by Sohn and Szekely et al (1972), where the grains are located in the pellet pore structure and reactants diffuse from the bulk gas across a surface film, through the pores, into the grains and through to the reaction interface. Gaseous reaction products diffuse out in the reverse direction. The model is described diagramatically in Figure 4.2 and it deals with the capture of alkali by getter particles.

The extent of reaction within a solid pellet for this system is described by a modification of the pellet-grain model for a gas-solid reversible reaction which is first order with respect to the gaseous reactant. This model was extended by McLaughlin (1990) to two simultaneous, first order, reversible reactions.

4.1.2a Assumptions

The assumptions that were made by Szekely et al. (1976) for the derivation of this model, which are open to criticism, are the following:

1) The system is isothermal.
2) The pseudo-steady state approximation is appropriate for describing the concentration of the gaseous reactants within the pellet.
3) The solid structure is macroscopically uniform and is unaffected by the reaction.
4) Diffusion within the pellet is either equimolar counterdiffusion or at low concentration of the diffusing species, and the effective diffusivities of gaseous reactant and product are equal and uniform throughout the pellet.
5) Convective mass transfer within the pellet can be considered negligible.
6) The reaction is first order with respect to the gaseous reactant, NaCl, and independent of local conversion of solid so long as there remains some unreacted solid.
Figure 4.2: The Pellet-Grain Model for a Fixed Bed Sorber
The next two assumptions were made initially by Szekely et al (1976) for simplicity, in order to derive the equations describing the process, but were relaxed later:

7) The resistance due to external mass transport is negligible.
8) Diffusion of the gaseous reactants through the product layer of the individual grains is not rate-limiting.

The above assumptions will be discussed further in conjunction with the experimental work in Chapter 6.

4.1.2b Model Equations

To find the accumulation of sodium in the solid, the equations for the conservation of the gaseous reactant and product in a pellet were combined with a mass balance for the solid reactant for each reaction. For the conservation of the solid reactant, it was assumed that within each grain the reaction front retains its original geometrical shape (assumed spherical) for successive times. When the intrinsic chemical reaction rate is controlling, the concentration of the fluid reactant will be constant everywhere and the reaction will occur uniformly throughout the volume of the solid (Figure 4.3). Then the local rate of a reversible reaction at a solid surface, first order with respect to gaseous species, when chemical reaction controls, may be expressed as:

\[-\rho_s \frac{dr_c}{dt} = b k_s (C_{NaCl,0} - \frac{C_{HCl,0}}{K_e})\]  \hspace{1cm} (4.4)

where \( r_c \) = radius of the unreacted core in a grain [cm]
\( k_s \) = reaction rate constant group based on unit area of reaction interface [cm s\(^{-1}\)]
\( K_e \) = equilibrium group [dimensionless]
\( \rho_s \) = sorbent density [mol cm\(^{-3}\)]

The local (position-dependent) rate of consumption of gaseous reactant in a unit volume of
pellet is proportional to the local rate of consumption of solid reactant per unit volume of pellet.

\[
P_{p} = \frac{1}{V} \frac{dR}{dt}
\]

where \( D_p \) = intrapellet diffusivity [cm s\(^{-1}\)]

\( R \) = spatial coordinate measured from the center of the pellet [cm]

\( R_p \) = pellet radius [cm]

When diffusion through the product layer in the grains controls, the rate of consumption of the reactant gas at any instant is given by its rate of diffusion to the reaction surface.
where $D_g = \text{diffusivity through the product layer in a grain (intragrain diffusivity)} \ [\text{cm}^2\text{s}^{-1}]$

$r_g = \text{grain radius [cm]}

The derivation of this equation comprises two parts. In the first part, the unreacted core was stationary when considering the concentration gradient of the reactant gas at any time, while in the second part of the analysis, the size of unreacted core could change with time and the concentration gradient of the reactant gas remains constant (Levenspiel, 1972).

\[
-\rho_s \left( \frac{1}{r_c} - \frac{1}{r_g} \right) r_c^2 \frac{dC_c}{dt} = \frac{D_g}{r_c} \left( C_{\text{HCl}_0} - \frac{C_{\text{HCl}_0}}{K_e} \right) \left( \frac{K_e}{1 + K_e} \right)
\]

\[
(4.6)
\]

Figure 4.4: The Pellet-grain Model for a Solid undergoing Reaction under Conditions of Pore Diffusion Control

Assuming that the concentration driving force is constant at all times during the reaction of the pellet, when diffusion through the external gas film controls, the rate of reaction is given by

\[
-\rho_s \frac{R^2}{R_p^2} \frac{dR}{dt} = bk_g \left( C_{\text{NaCl}_0} - \frac{C_{\text{HCl}_0}}{K_e} \right) \left( \frac{K_e}{1 + K_e} \right)
\]

\[
(4.7)
\]

where $k_g = \text{gas film mass transfer coefficient [cm s}^{-1}]$
The above conversion-time expressions assume that a single resistance controls throughout the reaction of a pellet. However, the relative importance of the gas film, product layer, pore of the pellet and reaction steps will vary as conversion progresses. For example, for a constant size particle the gas film resistance remains unchanged, the resistance to reaction increases as the surface area of unreacted core decreases, while the product layer resistance is nonexistent at the start because no product is present, but becomes progressively more and more important as the product layer builds up. In general, then, it may not be reasonable to consider that just one step controls throughout reaction.

The conservation equations of the gaseous reactants and products in the pores of a pellet (pore fluid balance) were written as (Szekely et al, 1976):

\[ \frac{1}{R^2} D_p \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_{\text{NaCl}}}{\partial R} \right) - x_{1, \text{NaCl}} = 0 \] (4.8)

\[ \frac{1}{R^2} D_p \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_{\text{HCl}}}{\partial R} \right) + x_{1, \text{HCl}} = 0 \] (4.9)

where \( r_{\text{LNaCl}} \) = local rate of consumption of the gaseous reactant (NaCl) per unit volume of a pellet [mol cm\(^{-3}\) s\(^{-1}\)]

\( r_{\text{LHCl}} \) = local rate of generation of the gaseous product (HCl) based on unit volume of a pellet = \( r_{\text{LNaCl}} \) [mol cm\(^{-3}\) s\(^{-1}\)]

\( C_{\text{NaCl}} \) 
\( C_{\text{HCl}} \) = gas concentrations of NaCl and HCl in the pores of a pellet [mol cm\(^{-3}\)]

The boundary conditions for the above equations, written only for NaCl, are the following

at \( t = 0 \) : \( C_{\text{NaCl}} = 0 \) \hspace{1cm} (4.8a)

at \( R = 0 \) : \( \frac{\partial C_{\text{NaCl}}}{\partial R} = 0 \) \hspace{1cm} (4.8b)

at \( R = R_p \) : \( C_{\text{NaCl}} = C_{\text{NaCl}} \) and \( D_p \frac{\partial C_{\text{NaCl}}}{\partial R} = k_c [C_{\text{NaCl}} - C_{\text{NaCl}}] \) \hspace{1cm} (4.8c)

where \( C_{\text{NaCl}} \) = gas NaCl concentration at the exterior surface of a pellet [mol cm\(^{-3}\)]
The local, position-dependent rate of consumption of gaseous reactant in a unit volume of pellet is given for first order kinetics (Szekely et al, 1976):

\[ \dot{X}_{1,\text{NaCl}} = A_{\text{intf}} \left[ K_s C_{\text{uc}, \text{NaCl}} C_{\text{sol}, l} r C_{\text{H}_2\text{O}}^{1/2} - K_b C_{\text{uc}, \text{HCl}} C_{\text{sol}, pr} \right] \]  

(4.10)

Considering \( C_{\text{sol}, l}, C_{\text{sol}, pr} \) and \( C_{\text{H}_2\text{O}} \) as constant

\[ X_{1,\text{NaCl}} = 3 (1 - \epsilon_p) \frac{r^2}{r_s} K_s (C_{\text{uc}, \text{NaCl}} - \frac{C_{\text{uc}, \text{HCl}}}{K_s}) \]  

(4.11)

where \( k_s \) = reaction rate constant group based on unit area of reaction interface = \( K_s C_{\text{sol}} C_{\text{H}_2\text{O}}^{1/2} \)

\[ K_s = \text{intrinsic forward reaction rate constant} \left[ (\text{cm}^{-1} \text{s}^{-1})(\text{cm}^3 \text{mol}^{-1})^{3/2} \right] \]

\[ K_b = \text{intrinsic backward reaction rate constant} \left[ (\text{cm}^{-1} \text{s}^{-1})(\text{cm}^3 \text{mol}^{-1}) \right] \]

\[ K_e = \text{equilibrium constant based on concentrations} = \left( \frac{K_s C_{\text{sol}, l}}{K_b C_{\text{sol}, pr}} \right) = k_s/k_b \]

\[ [(\text{mol cm}^{-3})^{-1/2}] \]

\( C_{\text{sol}, l} \) = concentration of the solid reactant [mol cm\(^{-3}\)]

\( C_{\text{sol}, pr} \) = concentration of the solid product [mol cm\(^{-3}\)]

\( K_e \) = equilibrium group = \( K_e [C_{\text{H}_2\text{O}}]^{1/2} \) [dimensionless]

\( C_{\text{uc}, \text{NaCl}} \) = reactant gas concentration at the surface of the unreacted core in a grain [mol cm\(^{-3}\)]

\( C_{\text{uc}, \text{HCl}} \) = product gas concentration at the surface of the unreacted core in a grain [mol cm\(^{-3}\)]

\( C_{\text{H}_2\text{O}} \) = concentration of water vapour at the surface of the unreacted core in a grain [mole cm\(^{-3}\)]

\( A_{\text{intf}} \) = reaction interfacial area per unit volume of grains = \( 3 (1 - \epsilon_p) r_e^2 / r_s^3 \) [cm\(^2\) cm\(^{-3}\)]

The mathematical representation of these systems led to a set of simultaneous differential equations which had to be solved numerically. In complicated systems, it is quite often desirable to work with dimensionless groups because such treatment provides both
an overview of the interaction of the various parameters and a convenient framework for the interpretation of the dimensionless groups' values. Consequently, Szekely et al. in order to recast the pellet-grain model in a dimensionless form, defined initially a dimensionless concentration driving force for reaction, \( \psi \), a dimensionless local extent of reaction for the solid reactant, \( \xi \), and a dimensionless position in the pellet, \( \eta \), as follows when spherical geometry is assumed:

\[
\psi = \left( C_{\text{NaCl}, \rho} - \frac{C_{\text{HCl}, \rho}}{K_\rho} \right) / \left( C_{\text{NaCl}, 0} - \frac{C_{\text{HCl}, 0}}{K_\rho} \right) \tag{4.12}
\]

\[
\xi = (A_g \tau_c) / (3 V_g) \tag{4.13}
\]

\[
\eta = A_p R / 3 V_p \tag{4.14}
\]

where \( C_{\text{NaCl}}, C_{\text{HCl}} = \) concentrations of the gaseous reactant and product in the bed voidage \([\text{mol cm}^{-3}]\)

\( A_g \) & \( A_p = \) surface area of a grain and a pellet respectively \([\text{cm}^2]\)

\( V_g \) & \( V_p = \) volume of a grain and a pellet respectively \([\text{cm}^3]\)

The assumption that the diffusion of the gaseous reactant through the product layer around the individual grains, is very fast compared with the rate of interfacial chemical reaction, is valid when the grain size is very small. However, for a system with large grains or fast reactions, the effect of intragrain diffusion may be significant (Pigford et al., 1973; Szekely et al., 1973). When the effect of intragrain diffusion is taken into account, the conservation equation of the gaseous reactant within the pellet in a dimensionless form is:

\[
\frac{\partial^2 \psi}{\partial \eta^2} - 18 \sigma^2 (\xi^2 / [1 - \sigma_g^2 \eta'/\xi]) \psi = 0 \tag{4.15}
\]
where

\[ \sigma^2 = \frac{\sigma^*}{18} = \frac{x_p^2 (1 - \epsilon_p) k_p}{6 D_p x_g} \left(1 + \frac{1}{K_e}\right) \]  \hspace{1cm} (4.16) \]

\[ \sigma^* = \frac{3 V_p}{A_p} \sqrt{\frac{(1 - \epsilon_p) k_s A_g}{D_p V_g}} \left(1 + \frac{1}{K_e}\right) \]  \hspace{1cm} (4.17) \]

and,

\[ \sigma_g^2 = \frac{k_g x_g}{6 D_g} \left(1 + \frac{1}{K_e}\right) \]  \hspace{1cm} (4.18) \]

where \( \sigma_g \) = dimensionless group, which incorporates chemical reaction and diffusion through the product layer effects,

\( \sigma^*, \sigma = \) dimensionless generalised gas-solid reaction groups, which incorporate both kinetic and structural properties, and

\[ q(\xi) = 1 - 3\xi^2 + 2\xi^3 \]

The function \( q(\xi) \) describes the progress of reaction of a grain under product layer diffusion influence.

The rate of movement of the reaction interface within a grain can be written for the first order reaction as follows

\[ \frac{\partial \xi}{\partial t^*} = -\Psi \left[1 - \sigma_g^2 q'(\xi)\right]^{-1} \]  \hspace{1cm} (4.19) \]

The boundary conditions associated with the conservation equations of the gaseous and solid reactants, assume that all the grains are initially unreacted, the reactant concentration at the outer surface of the pellet is determined by mass transfer across the gas film surrounding the pellet and that the concentration profile of reacted alkali is symmetrical about the center of
the pellet. The boundary conditions, expressed mathematically in a dimensionless form are

\[
\begin{align*}
\text{for all } \eta \text{ and } t^* = 0 & : \xi = 1 \\
\text{for } \eta = 1 \text{ and } t^* \geq 0 & : \frac{\partial \psi}{\partial \eta} = Sh^*(1-\psi) \\
\text{for } \eta = 0 \text{ and } t^* \geq 0 & : \frac{\partial \psi}{\partial \eta} = 0
\end{align*}
\]

(4.19)

where \( Sh^* = \) modified Sherwood number = \( \frac{k_s x R_p}{D_p} \)

The second boundary condition is used when external mass transport is taken into account; otherwise when the reactant concentration at the outer surface of the pellet is maintained at the bulk gas reactant concentration, then

\[
\eta = 1 \text{ and } t^* \geq 0 : \psi = 1
\]

(4.19)

In Equation (4.19):

\[
t^* = \frac{b k_e}{\rho_e} \left( \frac{A_g}{3 V_g} \right) \left( \frac{C_{NaCl,0} - C_{HCl,0}}{k_e} \right) t
\]

(4.20)

The dimensionless representation of the governing equations shows that the concentration driving force for reaction, \( \psi \), and the local extent of reaction of the solid reactant, \( \xi \), are related to the position in the pellet, \( \eta \), and time \( t^* \) through a single parameter \( \sigma^* \). This parameter \( \sigma^* \) incorporates both kinetic and structural properties and is a measure of the relative magnitude of chemical reaction and diffusion rates. As \( \sigma^* \) approaches zero (\( \sigma^* < 0.3 \)), the process is reaction controlled and as it approaches infinity (\( \sigma^* > 3.0 \)), the process is pore diffusion controlled (Evans et al, 1973; Szekely, 1976). \( \sigma^* \) can be interpreted as a dimensionless pellet size (Evans et al, 1974). Pellets with a small value of \( \sigma^* \) (<0.3) might be expected to react rapidly compared with pellets of large \( \sigma^* \) due to less hindrance of reaction from intrapellet diffusion in the smaller pellets. This behaviour was seen in the entrance regions of a fixed bed (Fig. 4.5, 4.6, 4.7). The extent of reaction at the entrance of the bed and e.g. for \( t^* = 1 \) is highest for \( \sigma^* = 0.3 \) and lowest for \( \sigma^* = 3 \). Deep within the bed, however, the situation is reversed and for the same time and at the same position, the extent of reaction is highest for \( \sigma^* = 3 \) and lowest for \( \sigma^* = 0.3 \). This could be explained on the grounds that for a bed made up of the smaller, more reactive pellets, the gaseous reactant is depleted close to gas inlet. Consequently, pellets remote from the gas inlet have no opportunity to react.
until the pellets closer to the inlet are almost completely reacted.

Figure 4.5 : Fixed Bed Reactor : Extent of Reaction vs. Position in Bed for Reaction Modulus = 0.3 (Evans et al, 1974).

Another important dimensionless parameter in the model is $\sigma_{g2}$, which represents the ratio of the capacities for chemical reaction and for diffusion of the gaseous reactants and products through the product layer formed around the grains. This ratio is a special form of Damköhler number II (chemical reaction generation to molecular diffusion mass transfer). When its value is bigger than 10, then the sorption process is expected to be controlled by the intragrain diffusion. When it is smaller than 0.1, then the effect of intragrain diffusion is negligible (Szekely et al, 1976).

In order to avoid the computational burden of solving the partial differential equations numerically, a useful approximation was developed (Sohn et al, (1974); Szekely et al (1976); Sohn, (1978)) based on the idea that:

\[
\text{time required to attain a certain conversion} = \text{time required to attain the same conversion under reaction control} + \text{time required to attain the same conversion under intragrain diffusion control} + \text{time required to attain the same conversion under intrapellet diffusion control} + \text{time required to attain the same conversion under gas film mass transfer control}
\]

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In this approximation each term is considered linear in concentration and all the resistances act in series. By introducing the dimensionless groups, the following equation can be used with an iterative procedure to calculate the pellet fractional conversion, $X_g$ (Szekely, 1976; Evans and Ranade, 1980).
\[ t^* = g(Xg) + \alpha_g^2 p(Xg) + \sigma^2 [p(Xg) + (2Xg/Sh^*)] + (0.21Xg - 0.31Xg^2) \]

\[ \times (1 + \sigma^2) \exp\{-0.9 [\ln (\sigma/1.08)]^2\} \]  \hspace{1cm} (4.21)

The terms on the right are the asymptotic expressions which can be related to conversion through simple relationships, the mathematical forms of which are given subsequently

(i) when chemical reaction controls

\[ t^* = g(Xg) = 1 - (1 - Xg)^{1/3} \]  \hspace{1cm} (4.22)

(ii) when intrapellet diffusion controls

\[ t^* = \sigma^2 p(Xg) = \sigma^2 [1 - 3 (1 - Xg)^{2/3} + 2 (1 - Xg)] \]  \hspace{1cm} (4.23)

(iii) when intragrain diffusion controls

\[ t^* = \sigma_g^2 p(Xg) = \sigma_g^2 [1 - 3 (1 - Xg)^{2/3} + 2 (1 - Xg)] \]  \hspace{1cm} (4.24)

(iv) when external mass transport controls

\[ t^* = 2\sigma^2 Xg/Sh^* \]  \hspace{1cm} (4.25)

The expressions for \( g(Xg) \) and \( p(Xg) \) have also been derived for a single non-porous, spherical particle in Levenspiel (1972). In these expressions, the fractional time for complete conversion \( (t/T) \) in terms of the unreacted core radius \( (r_c) \) or the fractional conversion \( (Xg) \), is given by (i) above when chemical reaction controls, by (iii) above when intragrain diffusion controls and by (iv) when external mass transfer controls.

The last term in the expression of additive times, i.e.

\[ (0.21Xg - 0.31Xg^2) (1 + \sigma^2) \exp\{-0.9 [\ln (\sigma/1.08)]^2\} \]  \hspace{1cm} (4.26)
intermediate values of \( \sigma^* \) (0.3<\( \sigma^* \)<3.0). This approximation for the \( X_g \) calculation agrees well with the analytical solution under the limiting conditions where only chemical reaction or diffusion controls. The asymptotic behaviour of the system has been examined (Sohn and Szekely, 1972) and provided useful guidelines, both for the range to be covered by computation and for the most convenient form in which the results may be presented.

The bulk gas concentration surrounding a pellet was assumed in Szekely's study to be constant. However, in a fixed bed the gaseous reactant and product concentrations are changing with time and position in the bed. A study on the time-dependent gaseous reactant concentration external to the pellet, has been performed by Evans and Song (1974).

4.2 PARAMETER ESTIMATION

The parameters used by the above mathematical expressions can be either measured by experiment, derived from literature or through fitting of the theory to the experimental results. It was also in the scope of this research project to examine the effect of temperature and pressure on the performance of alkali sorption since McLaughlin (1990) performed experiments at high temperatures, 827 and 927°C and his values could be of use at 650°C, where the present experiments have taken place. Specifications for an approximate design of the process at 600°C is of interest for industrial applications. As a result, including temperature and pressure in the model equations was necessary. The effects of temperature and pressure on parameters, that can be evaluated through theoretical correlations, can be easily assessed, whereas generally for measured parameters experiments are necessary at different temperatures and pressures.

4.2.1 Measured Parameters

The molar density of calcium montmorillonite, \( \rho_s \), was calculated by McLaughlin (1990) by using the molecular weight of its general chemical formula, \( \text{Ca}_{0.2}\text{Al}_{1.6}\text{Mg}_{0.4}\text{Si}_4\text{O}_{10} \), and the supplier's measurement of its actual density. The calculated value was \( 4.12 \times 10^{-3} \) moles cm\(^{-3} \).
The measured mass of solid per unit length of bed, \( \omega A_r \) (where \( A_r = \) cross-sectional area of the reactor), was experimentally measured for each run in g of solid/mm length of bed. The values measured were 0.4067, 0.3563, 0.3663 and 0.3561 for the 200, 400, 600 (high-acid) and 600 (non-acid) hr runs, respectively (Table A.II.1). The superficial velocity was set to 10 cm s\(^{-1}\) by industrial interest. The NaCl vapour production rate was held constant and measured to be 0.3 mg hr\(^{-1}\), which for a volumetric flowrate of 950 ml min\(^{-1}\), corresponds to 4.58 ppm wt (2.2 ppmv) inlet NaCl concentration. The HCl inlet concentration was varied from 0-160 ppmv. The Fuller's Earth Na uptake capacity was measured by McLaughlin and found to be 12.6 %wt under non-acid conditions and 4.5 %wt under high-acid conditions. The pellet porosity was measured by mercury porosimetry and the value found was 0.2 (McLaughlin, 1990). Since these pellets were already fragile, it was not desirable to have more porous pellets since this would affect their crushing strength.

The pellet sizes used for experiments in this work, were a mixture of particles in the ranges 0.425-0.5 mm and 0.5-0.6 mm diameter. In reality, in a fixed bed reactor it is unlikely that the pellets will be of the same size. Preliminary theoretical calculations were attempted by introducing two pellet sizes in the convective mass balance, in order to investigate the effect of a pellet-size distribution in a fixed bed reactor. These calculations are presented in Appendix VI. The grain diameter used by McLaughlin (1990) for pellets of 0.425-0.5 mm diameter, was 30 \( \mu \)m. This was confirmed in this work since grain diameters were measured for the same pellets, under an optical microscope and found to be 30±3 \( \mu \)m. For bigger pellets of 0.5-0.6 mm diameter, the grain diameter was 44±10 \( \mu \)m. In the pellet-grain model, it was assumed that the sorbent pellets consist of spherical grains of equal size, in order to simplify the model. However, in commercial pellets the above assumption may be poor and it could be necessary to make allowance for a grain size distribution. In Appendix VI, preliminary theoretical calculations for a grain-size distribution are also presented.

### 4.2.2 Literature-derived Parameters

Parameters calculated from correlations in literature are the viscosity and density of the carrier gas, the molecular and the intrapellet diffusivity of the gaseous reactants and products in the
carrier gas, the gas film mass transfer coefficient and the Re, Sc and Sh numbers.

The bed voidage used was 0.35, as this seems to be quite a common value in the literature for randomly packed beds (Ruthven, 1984). The viscosity of the bulk gas, $N_2$, is independent of pressure at low pressures, whereas its value for different temperatures can be found either by interpolation from existing tables in the literature (Perry's, 1984; Handbook of Chemistry and Physics, 1974; Gas Encyclopaedia, 1976) or by the Chapman-Enskog relationship (Reid et al, 1977)

$$
\mu = \frac{5}{16} \frac{(\pi M_{N_2} RT)^{1/2}}{(\pi \sigma_{N_2}^2) \Omega_v} = 26.69 \frac{\sqrt{M_{N_2} T}}{\sigma_{N_2}^2 \Omega_v} \tag{4.27}
$$

where $M_{N_2}$ = molecular weight of $N_2 = 28.0134$ g mol$^{-1}$

$T$ = temperature (K) = 923 K

$\Omega_v$ = collision integral = $f(T^*) = 0.8358$ [dimensionless]

$T^* = kT/\epsilon_{N_2} = 9.1623$ [dimensionless]

$k$ = Boltzmann constant = $1.3805 \times 10^{-23}$ JK$^{-1}$

$\epsilon_{N_2}$ = characteristic energy (where the forces of attraction and repulsion between the molecules are balanced) = $f(T_c, \omega_{N_2}) = 1.3907 \times 10^{-21}$ J

$\sigma_{N_2}$ = collision diameter (distance between molecules when the potential energy of interaction is zero) = $f(T_c, P_c, \omega_{N_2}) = 3.659$ K atm$^{-1}$

$T_c, P_c$ = critical temperature and pressure for $N_2 = 126.2$ K and 33.5 atm

$\omega_{N_2}$ = acentric factor for $N_2 = 0.04$ [dimensionless]

The viscosity values of $N_2$ found from interpolation and by the previous expression are $376.47 \times 10^{-6}$ and $383.53 \times 10^{-6}$ g cm$^{-1}$ s$^{-1}$, respectively at 650°C.

The temperature and pressure dependence of the bulk gas ($N_2$) density is taken from the ideal-gas law and is expressed as
\[
\rho = \rho_{273} \frac{P}{P_{\text{atm}}} \frac{273}{T}
\]  
(4.28)

where \( \rho \) = bulk gas density at the temperature and pressure of interest [g cm\(^{-3}\)]

\( \rho_{273} \) = bulk gas density at 273 K and atmospheric pressure = 1.2507 \times 10^{-3} [g cm\(^{-3}\)]

\( P, T \) = pressure and temperature of interest

\( P_{\text{atm}} \) = the laboratory working pressure (1 atm)

The density of nitrogen at 650°C calculated from the above expression, was found to be 0.3699 \times 10^{-3} g cm\(^{-3}\).

The molecular diffusivity of NaCl in N\(_2\) in the temperature and pressure of interest can be calculated from the Chapman-Enskog relationship (Reid et al, 1977)

\[
D_{\text{NaCl-N}_2} = 1.858 \times 10^{-3} T^{3/2} \left[ \frac{(M_{\text{NaCl}} + M_{\text{N}_2})}{M_{\text{NaCl}} M_{\text{N}_2}} \right]^{1/2}
\]

(4.29)

where \( M_{\text{NaCl}} \) = molecular weight of NaCl = 58.44 [g mol\(^{-1}\)]

\( \epsilon_{\text{NaCl-N}_2} = (\epsilon_{\text{NaCl}} \epsilon_{\text{N}_2})^{1/2} = 5.725 \times 10^{-21} \) J, where \( \epsilon_i / k = 1.15 T_b \)

\( T_b \) = normal boiling point [K] (for NaCl : 1686 K and for N\(_2\) : 77.2 K)

\( T' = kT / \epsilon_{\text{NaCl-N}_2} = 2.828 \) [dimensionless]

\( \sigma_{\text{NaCl-N}_2} = (\sigma_{\text{NaCl}} + \sigma_{\text{N}_2}) / 2 = 3.6969 \) K atm\(^{-1}\), where \( \sigma_i = 1.18 V_b^{1/3} \)

\( V_b \) = liquid molar volume [cm\(^3\)mol\(^{-1}\)] (for NaCl : 27.098 cm\(^3\)mol\(^{-1}\) and for N\(_2\) : 34.722 cm\(^3\)mol\(^{-1}\))

\( \Omega_D \) = diffusion collision integral (dimensionless) = 0.9654

The molecular diffusivity calculated from the above relationship is 0.9 cm\(^2\)s\(^{-1}\) for the NaCl-N\(_2\) system.

The molecular diffusivity, \( D_m \), or specifically for the diffusion of NaCl in N\(_2\), \( D_{\text{NaCl-N}_2} \), can be also calculated at the temperature and pressure of interest when it is already known at other conditions from the expression (Brodkey and Hershey, 1988):
where \( D_m \) = molecular diffusivity at the temperature and pressure of interest \([\text{cm}^2 \text{s}^{-1}]\)

\( D_{m,0} \) = known molecular diffusivity at \( T_0 \) and \( P_0 \) \([\text{cm}^2 \text{s}^{-1}]\)

\( T, P \) = temperature and pressure of interest

\( T_0, P_0 \) = temperature and pressure for the known molecular diffusivity

\( n = 1.75-2.0 \) (the value used in the model is 1.75)

The molecular diffusivity of NaCl in \( \text{N}_2 \) at 650°C has been calculated as 1.0 cm²s⁻¹ from the value used by Punjak (1988) at 800°C, and as 0.9 cm²s⁻¹ from the value that Mulik et al (1986) used at 900°C. These values are very close to the calculation obtained by the Chapman-Enskog relationship.

The molecular diffusivity of HCl in \( \text{N}_2 \) has been calculated by using the empirical correlation derived by Fuller et al (1966)

\[
D_{\text{HCl-N}_2} = \frac{10^{-3} T^{1.75} \left[ \frac{(M_{\text{HCl}}+M_{\text{N}_2})}{M_{\text{HCl}} M_{\text{N}_2}} \right]^{1/2}}{p \left[ \left( \sum \nu_i \right)_{\text{HCl}}^{1/3} + \left( \sum \nu_i \right)_{\text{N}_2}^{1/3} \right]^{2}} \tag{4.31}
\]

where \( \sum \nu_i \) = atomic and structural diffusion volume increments (Table 11-1 in Reid et al, 1977) \([\text{cm}^3 \text{mol}^{-1}]\)

The molecular diffusivity of HCl in \( \text{N}_2 \), calculated from the above empirical equation at 650°C, is 1.334 cm²s⁻¹.

The effective diffusivity in the porous pellet, \( D_p \), should be independent of the grain size, if diffusion within the pellet is in the molecular regime. If diffusion however, is in the transition or the Knudsen regime, the intrapellet diffusivity may be markedly affected by the grain size (Szekely and Evans, 1971). McLaughlin (1990) measured the mean pore radius to be 3.8 µm. At these relatively large pore diameters Knudsen diffusion can be considered negligible.

The temperature and pressure effect on the intrapellet diffusivity, \( D_p \), is effectively calculated
through the molecular diffusivity (Ruthven, 1984) from the expression:

\[ D_p = \frac{D_m}{\tau} \]  

(4.32)

where \( \tau \) = tortuosity factor

The tortuosity is defined as the relative average length of the flow path of a fluid particle; the length of the path to the length of the porous media and allows for both varying direction of diffusion and varying pore cross section. Since the tortuosity is essentially a geometric factor, it should be independent of either temperature or the nature of the diffusing species. There is a general correlation between tortuosity and porosity (tortuosity varies inversely with porosity) and the higher tortuosity factors or low effective macropore diffusivities are generally found for highly compacted low-porosity pellets (Ruthven, 1984). Values of \( \tau \) were taken from the literature (Satterfield, 1970; Ruthven, 1984) and for alumino-silicates \( \tau \) takes values of 2-6. In this model, the mean value of 4 has been used. As a result, the intrapellet, effective diffusivities of NaCl, H\(_2\)O and HCl at 650°C are respectively 0.25, 0.47 and 0.33 cm\(^2\)s\(^{-1}\).

For the estimation of the gas film mass transfer coefficient, \( k_p \), Reynolds, Schmidt and Sherwood numbers are calculated from the equations (Wakao and Funazkri, 1978)

\[ Sh = 2.0 + 1.1 Sc^{1/3} Re^{0.6} \]  

(4.33)

\[ Re = \frac{2R_e \rho u}{\mu} \]  

(4.34)

\[ Sc = \frac{\mu}{\rho D_m} \]  

(4.35)
where $Re = \text{Reynolds number}$

$Sc = \text{Schmidt number}$

$Sh = \text{Sherwood number}$

The temperature and pressure effects are taken into account through the known relationships for the density, viscosity and molecular diffusivity. At 650°C, the dimensionless numbers and the gas film mass transfer coefficients calculated for the two particle sizes used, are given in the Table 4.1.

4.2.3 Fitted Parameters

The stoichiometric coefficients, $b_1$ and $b_2$, used for the two-reaction mechanism were both set to 1.0 (McLaughlin, 1990). The reaction rate constant, $k_s$, the equilibrium group, $K_e$ and the intragrain diffusivity, $D_g$, are parameters that cannot be set a priori and as a result they have to be estimated by fitting the theoretical model to the experimental results. Values were

Table 4.1: $Sc$, $Re$, $Sh$, $Sh^*$ and $k_s$ for the two pellet sizes, 0.425-0.5 mm and 0.5-0.6 mm, at 650°C.

<table>
<thead>
<tr>
<th>Pellet size (mm) →</th>
<th>0.425 - 0.5</th>
<th>0.5 - 0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Sc$</td>
<td>1.018</td>
<td>1.018</td>
</tr>
<tr>
<td>$Re$</td>
<td>0.454</td>
<td>0.540</td>
</tr>
<tr>
<td>$Sh$</td>
<td>2.689</td>
<td>2.764</td>
</tr>
<tr>
<td>$Sh^*$</td>
<td>5.374</td>
<td>5.528</td>
</tr>
<tr>
<td>$k_s$</td>
<td>58.1</td>
<td>50.26</td>
</tr>
</tbody>
</table>
obtained by McLaughlin (1990) at 827 and 927°C and by extrapolation could be used as initial estimates for the curve fitting at 650°C. Assuming that the reactions are elementary and can achieve dynamic equilibrium, extrapolation could be obtained by using the Arrhenius equation for \( k_s \) (Smith, 1987),

\[
k_s = A e^\frac{-E}{R_{gas}T}
\]  

(4.37)

the Van't Hoff Equilibrium relationship for \( K_e \)

\[
\frac{d\ln K_e}{dT} = \frac{\Delta H^0}{R_{gas}T^2}
\]  

(4.38)

and since intragrain diffusion is an activated process, the Arrhenius equation for \( D_g \) (Ruthven, 1984)

\[
D_g = D_0 e^\frac{-E}{R_{gas}T}
\]  

(4.39)

or a correlation from Perry's (1984)

\[
D_g = C T^{1.75}
\]  

(4.40)

where

- \( A \) = frequency factor [cm s\(^{-1}\)]
- \( D_0 \) = frequency factor [cm\(^2\) s\(^{-1}\)]
- \( E \) = activation energy [J mol\(^{-1}\)]
- \( c \) = constant [cm\(^2\)s\(^{-1}\)K\(^{-1.75}\)]
- \( R_{gas} \) = ideal-gas law constant [J mol\(^{-1}\)K\(^{-1}\)]
- \( \Delta H_0 \) = enthalpy change (is assumed constant with temperature) [J mol\(^{-1}\)]

This procedure for the parameter extrapolation can be considered only as very approximate, because of the very wide range of temperatures involved and the poor quality of data at the higher temperatures of 827°C and 927°C (McLaughlin, 1990), due to poor mass balances compared to the 650°C results.
4.3 SCALE-UP

In large-scale power plant pressure drops must be minimised because they represent irreversible losses which reduce the overall efficiency of the plant. In scale-up calculations, the pressure drop can be found from the Ergun equation for a certain Reynolds number (Ruthven, 1984). A dimensionless friction factor, \( f \), is calculated as follows,

\[
f = \frac{(1 - \varepsilon_b)}{\varepsilon_b^2} \left[ \frac{150 (1 - \varepsilon_b)}{R \varepsilon + 1.75} \right]
\]  

where \( \varepsilon_b = \text{bed voidage} = 0.35 \)

Reynolds number is based on pellet diameter, superficial gas velocity and the bulk density and viscosity of \( \text{N}_2 \). The temperature and pressure effects on \( \text{N}_2 \) bulk density and viscosity were discussed in Section 4.2. Pressure drop in flow through packed columns is correlated to \( f \) with the following equation (Ruthven, 1984)

\[
f = \left( 2 \frac{R_p}{L_r} \right) \left( \frac{\Delta p}{\rho u^2} \right)
\]  

where \( \Delta p = \text{pressure drop} \ [\text{g cm}^{-1} \text{ s}^2] \)

\( L_r = \text{length of the reactor} \ [\text{cm}] \)

\( R_p = \text{pellet radius} \ [\text{cm}] \)

\( u = \text{superficial velocity} \ [\text{cm s}^{-1}] \)

\( \rho = \text{bulk gas density at the temperature and pressure of interest} \ [\text{g cm}^{-3}] \)

and

\[
u = \frac{V_F}{A_x}
\]  

where \( A_x = \text{cross sectional area of the reactor} \ [\text{cm}^2] \)

\( V_F = \text{volumetric flow rate of the flue gases} \ [\text{cm}^3 \text{s}^{-1}] \)
4.4 SUMMARY

The theoretical description of the alkali sorption model has been based on the convective mass balances for the gaseous reactants and products over the interparticle gas phase of a bed section. To solve the convective mass balance, a model that could describe the alkali retention by the aluminosilicate sorbent pellet was necessary.

The pellet-grain model, originally derived by Sohn and Szekely (1972), was used to describe the sorbent pellet conversion due to the alkali capture for two simultaneous, reversible reactions that contribute to the sorption process. To avoid the computational burden of partial differential equations describing the intraparticle processes, the law of additive times was used.

Most of the parameter values used in the model were assigned from published data or direct measurements. The rest of the parameters must be derived by curve fitting theoretical predictions with the experimental results. The temperature and pressure dependence of the parameters was also presented to enable the extrapolation of the model parameters to other desirable conditions.

In the pellet-grain model used, the pellet and the grain sizes were assumed uniform and their shape as spherical. To evaluate in future, the effect of the pellet and grain-size distributions, preliminary theoretical calculations are presented in Appendix VI. In addition to the fixed bed model presented, the pressure drop concept is introduced for the scale-up calculations.
CHAPTER 5

NUMERICAL METHODS AND RESULTS

In this chapter, the numerical methods used to solve the system of equations that describe the alkali sorption process for a fixed bed and the computer programs developed are presented. All possible validation and checking of both the model and the solution technique are required to help ensure that the final, full-scale process will work as expected.

Initially, the original program, written by McLaughlin (1990) is described together with the modifications and improvements made in this work. Secondly, an attempt to use a dynamic modelling environment, gPROMS, is described because, despite being only partially successful, the attempt illustrates the care required to implement a robust and accurate solution of the model. Thirdly, a new computer program is presented, based on the same theory used by McLaughlin but utilising different numerical methods to solve the model equations. The results are presented and compared with respect to the numerical methods used.

Fourthly, the experimental uptake concentration profiles of Na along the fixed bed act as a basis for the extraction of values for parameters such as reaction rate constants, intragrain diffusivities and equilibrium group constants by comparison with the theoretical profiles. Fifthly, a sensitivity analysis is presented which shows which parameters have the most effect on the fitting process. Finally, some results from scale-up calculations using the new model are described.

5.1 NUMERICAL METHODS

5.1.1 The McLaughlin program

McLaughlin (1990) wrote a computer program in Fortran77, which by combining the pellet-grain model and the "tanks-in-series" approximation for the fixed bed (Figure 4.2) can
simulate the alkali sorption process under study. In the pellet-grain model, the Szekely approximation (Eq. 4.21) is solved for the pellet conversion, \( X_g \), by the Newton-Raphson method. As the present model involves two simultaneous reactions (Eq. 4.2 and 4.3), this procedure is repeated twice and each pellet conversion term, multiplied with the experimentally measured capacity for each reaction, gives the uptake of Na by the sorbent for each reaction (Punjak, 1988). These values are added to give the overall amount of Na captured per unit weight of unreacted solid for a section of the fixed bed:

\[
m = \sum_{j=1}^{n} K_j X_{gj}
\]  

where \( m \) = weight of Na in the solid per unit weight of unreacted solid

\( K_j \) = weight of Na in the solid at saturation due to reaction \( j \) per unit weight of unreacted solid (reaction \( j \))

\( X_{gj} \) = fractional conversion of the solid pellet due to reaction \( j \) = weight of Na reacted per unit weight of Na in the solid at saturation

The "tanks-in-series" solution, which is described in detail in the next paragraph, was used to solve the sodium convective mass balance over a bed section and a time interval.

The secant method is used to solve the convective sodium mass balance over a tank and calculate the tank exit gas concentration \( (C_{out}) \). When the material balance closes, the next tank is considered over the same time interval, with the exit gas from the current tank becoming the inlet concentration for the next tank downstream. Once the mass balance for each stage has been solved, another step is made in time and the process is repeated, starting from the gas inlet end of the bed again. Thus, the program generates a profile of solid sodium uptake concentration against the cumulative solid weight in the bed.

The program has been developed in this work to include an optimisation mode, where the model profile is fitted to one or more experimental profiles supplied by the user. When in optimisation mode, model predictions of concentrations are compared with measured values and an optimiser routine (NAG Library, E04JAF) minimises the sum of squares of errors. This is achieved by adjusting the values assigned to selected parameters e.g. \( k_{sl} \) and \( K_{el} \) for reaction 1 and \( D_{g2} \) for reaction 2. The optimiser requires initial estimates of the selected parameters and the result obtained is checked to ensure it is not dependent on the initial estimates, this helps avoid the routine converging on local minima. In simulation mode, a
theoretical sodium uptake profile along the fixed bed will be generated based on the parameter values specified by the user.

5.1.1a Tanks-In-Series Solution

The convective sodium mass balance over the interparticle gas phase of a bed section (Eq. 4.1), is solved with the "tanks-in-series" method of solution, derived from Deans and Lapidus (1960). The fixed bed is visualised as a series of finite elements (Figure 4.2), with each element represented by a well stirred tank. Thus each element has a uniform gas composition.

In the "tanks-in-series" approximation, the fluid is flowing through a series of equal-size ideal stirred tanks, and the number of tanks in this series is an additional parameter (Levenspiel, 1972). For a large number of tanks, N, the deviation from plug flow is small. This can be shown by a system of N equal-size mixed reactors connected in series. Though the concentration is uniform in each reactor, there is nevertheless a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, suggests that the larger the number of units in series the closer should the behaviour of the system approach plug flow. The convective mass balance for a component i over a tank n, in a fixed bed of length L, is given by:

$$\frac{u}{(L/N)\epsilon_b} (C_{i,n} - C_{i,n-1}) + \frac{dC_{i,p,n}}{dt} + \frac{\omega}{\epsilon_b \sum_{j=1}^{2}} \frac{dC_{i,s,n,j}}{dt} = 0 \quad (5.2)$$

where $C_{i,n} = \text{gas concentration of component } i \text{ in the bed voidage in tank } n \text{ [mol cm}^{-3}\text{]}$

$j = \text{index indicating the number of reaction}$

$C_{i,s,n,j} = \text{concentration of component } i \text{ in the solid and in tank } n \text{ due to reaction } j \text{ [mol g}^{-1}\text{]}$

The "tanks-in-series" approximation was chosen by McLaughlin, to solve the sodium convective mass balance along the sorbent bed, as it reduces the second order partial differential equations of the convective mass balance (Eq. 4.1), to ordinary differential equations and the axial dispersion term is eliminated.
McLaughlin solved the convective mass balance for sodium (Eq. 5.2) by applying the finite difference approximation in time to the accumulation terms, thus making the mass balance an algebraic equation:

\[
\frac{dC_{j,0,n}}{dt} = C_{j,0,n}(t+\Delta t) - C_{j,0,n}(t) \quad \text{(5.3)}
\]

\[
\frac{dC^a_{j,0,n,i}}{dt} = C^a_{j,0,n,i}(t+\Delta t) - C^a_{j,0,n,i}(t) \quad \text{(5.4)}
\]

Generally, to determine the number of tanks, \( N \), from the tanks-in-series solution, and the axial Peclet number, \( \text{Pe}_L \), from the dispersed plug flow model, comparison of the residence time distribution (RTD) curves (E and C) available in the literature (Levenspiel, 1972), should be performed. These curves are obtained by these models, when an ideal pulse input was introduced in a fixed bed reactor (E = C) (Figure 5.1).

![Figure 5.1: RTD Curves as predicted by the Dispersed Plug Flow and the Tanks-in-series Approximation (Levenspiel, 1972)](image)

The axial Peclet number is defined as \( \text{Pe}_L = \nu L / D_{ax} = (\nu R_p / D_{ax})(L/R_p) \), with \( R_p \) as the particle
diameter and \( \nu \) the interstitial velocity. Since \( \nu R_p/D_{ax} \), the particle Peclet number, \( \text{Pe}_p \), is of the order of 0.5 - 2.0 (Ruthven, 1984), \( \text{Pe}_L \) will be of the order of \( L/R_p \) and more specifically \( 0.5(L/R_p) < \text{Pe}_L < 2(L/R_p) \). The bigger the \( \text{Pe}_L \), the smaller the axial dispersion coefficient, \( D_{ax} \), will be and consequently, the smaller the effect of the axial dispersion term will be in the convective mass balance of Eq. 4.1. As a result, the relative influence of axial dispersion diminishes with increasing column length.

In the present work, the length of the bed was 10-15 mm, the pellet diameter 0.4-0.6 mm and the interstitial velocity \( \sim 30 \text{ cm/s} \). The axial Peclet number for this system, estimated from correlations given by Langer et al (1978) and by Edwards and Richardson (1968), was approximately \( \sim 50 \), which is in the region of values calculated from the definition of \( \text{Pe}_L \), approximately 12.5-50. This \( \text{Pe}_L \) corresponds to intermediate amount of axial dispersion (Figure 5.1) and comparison with the "tanks-in-series" method gives approximately 20 tanks \( (N=20) \) to account for this amount of axial dispersion.

For long industrial columns, ideal plug flow is often closely approached, since the particle size is rarely below 1 mm and the bed length/particle diameter ratio is usually well in excess of 1000, which means that \( 500<\text{Pe}_L<2000 \) and \( D_{ax} \rightarrow 0 \) (Bono, 1989). Axial dispersion in a packed bed for gases, generally appears to have negligible effect on performance as long as the bed depth is greater than about 50 particle diameters (Carberry and Wendel, 1963; Rase, 1990). Evidently, unless the column is short, the contribution of axial dispersion to overall performance is small. Care needs to be exercised however, with short laboratory columns to ensure axial dispersion is accounted for adequately.

5.1.1b Review of McLaughlin's Program

During the revision of McLaughlin's program, a number of uncertainties over the assumptions made in the pellet-grain model and the approximations used in the computer program were revealed. The points that required further investigation, were the following:

1) The choice of time step: the finite difference approximation in time, used to solve the Na convective mass balance (Eq. 5.3 and 5.4), provided only a first order accurate solution, as it is really valid only when the time step used is very small \( (\Delta t \rightarrow 0) \). This discretisation in
time combined with the tanks-in-series approximation for the position in the bed, has turned the Na convective mass balance to algebraic equations, which were solved with the secant method.

2) The HCl convective mass balance, which was simply based on the stoichiometry of the reaction, one mole of NaCl reacts and gives one mole of HCl and was written for a tank, n, as an algebraic equation of the form

\[ C(HCl, n, 0) = C(NaCl, n-1, 0) - C(NaCl, n, 0) + C(HCl, feed) \]  

(5.5)

instead of a differential convective mass balance. However, this equation cannot be used if NaCl consumption/HCl production is not 1:1.

3) In the pellet-grain model, the concentrations of gaseous reactants and products around a pellet were assumed constant. However, in a fixed bed these concentrations change with time. To be able to use the pellet-grain model in a fixed bed sorber, the time step should be small enough not to violate the assumption of constant concentration around a pellet.

4) In order to ensure that both conversions increase monotonically, the Szekely formula (Eq. 4.21) was solved in the following manner. The pellet-grain algorithm recalled the conversion \( X_{old} \) attained for the current tank at the end of the previous time step. It then calculated the time \( t_{old} \) to reach that conversion with gas concentration constant at its present level. Finally, it calculated the new conversion, \( X \), at the new time, \( t_{old} + \Delta t \). Consequently, whenever the pellet-grain model was called, \( t_{old} \) would represent from time zero, how long it would take for a pellet to reach \( X_{old} \) at the present constant gas concentration. Therefore, this procedure ensures that while \( t^* \) is positive, \( Xg \) increases. If the reaction is required to reverse this procedure is not valid, as will be discussed below.

5) The model assumes that the local conversion rate is independent of the local average solid concentration so long as there remains some unreacted solid. This assumption is implicit in the shrinking core model, which deals with non-porous grains which form the pellets. The concentration of the solid reactants at the reaction front have been assumed constant and have been incorporated into the values of \( k_s \) and \( K_c \) (Eq. 4.10).
5.1.1c Modifications and Improvements

During this work, the McLaughlin program was modified and improved. One of the improvements accomplished, is that the structure is now based on a main program which calls subroutines for specific calculations. Data are entered via windows which appear before the execution of the calculations. In the windows, the user can specify the necessary data, the temperature (927, 827, 650 or 600°C) and pressure of interest, the estimates of the optimised parameters and whether simulation or optimisation calculations will be performed.

Data on the density and viscosity of the bulk gas (Perry, 1984), which is N₂ in laboratory conditions, are listed in the programme for the three temperatures at which experiments were conducted, 650°C, 827°C and 927°C, and for 600°C, which was the current temperature of interest for scale-up. To use the programme at any other temperature, the density and viscosity of N₂ at this temperature, have to be entered by the user. The pressure effects on the model parameters are directly introduced in the mathematical equations. Consequently, the programme can be used for any pressure (in bar). The optimised parameters can be extrapolated from 827°C and 927°C down to 650°C and 600°C through the Arrhenius equation (Eq. 4.37), the Van't Hoff equilibrium relationship (Eq. 4.38) and the temperature dependence equation for Dᵔ (Eq. 4.40).

To improve the stability of the convergence of the optimisation procedure, the optimised parameters were normalised so that the range of values used would be between 0 and 1.

Several other minor errors were corrected in the original program, e.g.
1) the axial position values ascribed to the concentrations calculated for each tank were corrected, and
2) a similar correction was made to the calculation of the axial positions of the experimental concentrations.

5.1.2 Modelling in the gPROMS environment

To obtain an independent solution to the alkali sorption model, gPROMS, a modelling environment for dynamic processes, under development at Imperial College (Barton and
Pantelides, 1993) was used. This exercise was intended to help check the solutions attained from the existing code.

Equations 5.2 and 4.21 together with the appropriate initial conditions and boundary values were solved by a gPROMS program as shown in Appendix VIII. The results from this gPROMS program did not correspond exactly to the results from the McLaughlin program and it was essential to understand why there were differences.

The first check was to use gPROMS to solve the original partial differential equation (Equation 4.1) without the tanks-in-series approximation. The method of Orthogonal Collocation on Finite Elements was used and the results were identical to the gPROMS solution to the tanks-in-series approximation.

It was then suspected that the Szekely approximation (Equation 4.21) might have multiple roots and gPROMS was selecting the wrong root. The Szekely approximation was discovered to have multiple roots when solved for Xg under some, but not all, conditions (see Figure 5.2).

![Figure 5.2](image)

**Figure 5.2**: Pellet Conversion versus Dimensionless Time, $t^*$, using the parameters presented in Table 5.1 and evaluated initially by McLaughlin's program, for the 600 hr high-acid run.
At this point it was decided that gPROMS would not be used further because gPROMS provides the user with very little control over its internal numerical procedures.

5.1.3 Pellet-grain model for a single pellet

In view of the difficulties encountered above, it was decided to write a complete new program in which the solution to the Szekely approximation could be checked thoroughly. The first stage in the development of this program was to code a solution for a single pellet.

Szekely's approximation was solved with the Newton-Raphson method to calculate the fractional conversion of a Fuller's Earth pellet. This approach is the same as that incorporated in McLaughlin's program. Initially, the program was written for a single reaction, but subsequently it was developed for two simultaneous reactions.

This computer program (Appendix VIII) can be used for different sets of parameters and different solids. The user can specify in the beginning, the Newton-Raphson search parameters: the maximum number of iterations and the accuracy required. System parameters such as the pellet and grain radius, intrapellet diffusivity, gas film mass transfer coefficient, stoichiometric coefficients, molar solid density, pellet porosity and inlet concentration terms should also be specified and by changing the values of the equilibrium constant, the reaction rate constant and the intragrain diffusivity, experimental conditions can be simulated.

The conversion due to each reaction, as well as the total pellet conversion can both be predicted with time (Figures 5.6, 5.7). At the pellet-grain level, no negative conversions (false roots) appeared and the Newton-Raphson routine converged without any problems.

The next check in this study, was a comparison between the numerical evaluation of the reaction rate, dXg/dt, with the analytical expression derived from the differentiation of the $t^*$ expressions (Eq. 4.21) with time:

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\[
\frac{dXg1}{dt} \left[ \frac{(1-Xg1)^{-2/3}}{3} + a_1^2 (2 (1-Xg1)^{-1/3} - 2 + 2/NSh^*) + a_{g1}^2 (2 (1-Xg1)^{-1/3} - 2) + \frac{0.21 - 0.62Xg1} {1 + a_1} \exp (-0.9 (\log (\sqrt{a_1} / 1.08))^2) \right] =
\]

\[
\frac{b_1 k_{g1}}{\rho g x_g} (C_{Na,0,n} - C_{HCl,0,n} / K_{a1}) + \frac{b_1 k_{g1} t}{\rho g x_g} \frac{dC_{Na,0,n}}{dt} - \frac{b_1 k_{g1} t}{\rho g x_g K_{a1}} \frac{dC_{HCl,0,n}}{dt}
\]

(5.6)

where the concentration of component i in the above expression is assumed constant over the specified time interval, following Szekely's approximation for a constant gaseous concentration around a pellet. This check was conducted because the value of \( dXg/dt \) is the term in the convective mass balance which is calculated from the Szekely approximation.

This comparison was performed to check the robustness, and cross-check the accuracy of the coding. No significant errors or discrepancies were discovered. Simulations of the pellet-grain model for a single pellet and results from the comparison of the numerical and analytical estimation of the reaction rates, are presented in Section 5.2.1 (e.g. see Figure 5.9).

### 5.1.4 Alkali Fixed Bed Sorption Solution by Gear's Method

Once the single pellet solution had been studied and tested extensively, it was incorporated in a simulation of a fixed bed sorber. The gaseous Na concentration was normalised with respect to the Na feed concentration, whereas for the HCl the base for normalisation was the arbitrary very small value of 0.001 ppmv, since in non-acid runs division by zero needed to be avoided. The convective mass balances for Na and HCl were written as ordinary differential equations according to the "tanks-in-series" method of solution (Eq. 5.2), whereas both reaction rates were calculated analytically (Eq. 5.6) by the pellet-grain subroutines. A further improvement over previous programs was that the new program can conduct simulations at any temperature or pressure specified by the user (The McLaughlin program had restricted the user to the particular values of temperature).

The system of 4N ODEs derived, was solved in time and position in the bed, simultaneously for the gaseous Na and HCl concentrations and the two-pellet conversions. However, the system proved to be stiff and therefore could not be solved with a simple integration method, such as fourth-order Runge-Kutta. This stiffness arises from the fact that the accumulation in the gas phase is much smaller than the accumulation in the solid phase and, as a result, it is
extremely difficult to solve simultaneously for both quantities. Evans and Song (1974), being probably mostly interested in the solid conversion, overcame this problem by assuming that when the system pressure is low, the accumulation in the gas phase was much smaller than the accumulation in the solid phase, and therefore can be neglected in the convective mass balance. However, the general aim of modelling the Na sorption process, is the ability to use the models derived from laboratory data, to predict what will happen at full scale. Commercial plants will work with pressures higher than atmospheric and the assumption of negligible gas accumulation is not valid. Furthermore, the exact prediction of the Na concentration in the outlet gas is the primary objective of the alkali removal process.

Consequently, a robust integration method that can solve accurately in time should be used. The method chosen was the variable-time-step, variable order Gear’s method with a maximum accuracy of 6th order (Gear, 1971; Schiesser, 1976). An advantage of the variable-step numerical methods is that they incorporate a quality control decision routine, which may reject the result, set a smaller steps size and solve again, until compatibility with a predetermined accuracy criterion has been achieved, with minimum computational effort (Press, 1992). This is quite important, especially in the beginning of the process, where the gaseous concentrations of the reactants and products in the bed voidage are very small because the fresh solid reacts quickly and thus the stiffness of the problem is more pronounced. As time progresses, the local rate of reaction decreases and hence the stiffness becomes less important.

Towards the end of the run time, the time step will approach the value of the maximum time step set by the user. At this point, the choice of the maximum time step proved very important. If big maximum time steps (e.g. 100 hrs) are chosen, the Na mass balance will not close as the assumption of the constant gas concentration around the pellet in the Szekely’s model, is valid over small times only. A maximum time step of 5 hrs was found to give the best compromise between accuracy and run time.

The new program requires substantial computational effort. For example, a simulation for the high-acid 600 hr run using 5 tanks would finish in 1/2 hr with a Sun Workstation or 1 hr with a 166 MHz Intel Pentium. Thus, neither an optimisation subroutine was added to it yet nor a pellet- or grain-size distribution. The stiffness of the problem could probably be avoided if
the accumulation terms in the gas and the solid could be solved in separate steps by keeping one constant while solving for the other. The Fortran code of the new computer program is presented in Appendix VIII.

It should be noted that the two computer programs, the modified McLaughlin program and the new program using Gear's method, under the same conditions gave the same results, which are presented in the next sections.

In writing and testing the new program it was realised that the Szekely approximation must be used with extreme caution when the reaction is required to change direction. In reality if external conditions change so much that forward reaction would cease, the back reaction would commence with a new shrinking core that would start at the surface of the grain and would convert the product shell back to the original material. If the conditions which caused this reversal of the reaction applied for long enough, the new reaction front would reach the original front and the grain would be returned to its original state.

None of the programs in this chapter can simulate this reaction reversal; they all contain the assumption that there is only ever one reaction front in its grain. Therefore, there are situations which the programs cannot simulate and which could arise in practice. One example is if the bed inlet conditions are not constant, and there is a change from high to low sodium concentrations.

### 5.2 RESULTS

#### 5.2.1 Fitting and Optimisation

The new computer program derived in this work, like McLaughlin's program, enables six parameters related to the two-reaction alkali sorption process; the rate constants \(k_{s1} \& k_{s2}\), the equilibrium groups \(K_{e1} \& K_{e2}\) and the intragrain diffusivities \(D_{g1} \& D_{g2}\), to be evaluated by curve fitting experimentally derived data to simulated profiles calculated for selected values of these parameters. All other parameters used by the model are assigned from published data or direct measurements listed in Chapter 4. In order to simplify the
optimisation procedure, McLaughlin assumed a $K_{e2}$ value of 5000, to make the second reaction independent of HCl concentration and far from equilibrium, and assumed a large $k_{s2}$ (1000 cms$^{-1}$) and a large $D_{g1}$ (10 cm$^2$s$^{-1}$), inspired by the convex shape of the high-acid profiles, obtained under diffusion limitation conditions and by the concave shape of the non-acid profiles, obtained under reaction limitation conditions (Moriyama, 1971). Consequently, the optimisation subroutine in the McLaughlin model can adjust the remaining three parameters, $k_{s1}$, $K_{e1}$ and $D_{g2}$, until the sum of squares of errors between the experimental and calculated points is minimised. In this work, the values of all six parameters were estimated from both computer programs, by using trial and error to fit theoretical to experimental profiles. The parameter values obtained initially at 650°C with McLaughlin's program, before the problem of negative pellet conversions was realised, are given in Table 5.1. These parameters give a generally good fit despite the convergence problem. For comparison, in the same table, the new optimum set of parameters, derived by both computer programs to give positive conversions for both reactions, is also presented. McLaughlin's optimisation subroutine used in just estimating the sum of squares of errors, $\Sigma e_{opt}^2$, between the experimental and the optimum theoretical uptake profile. The fitting of the experimental and the theoretical Na uptake profiles drawn along the fixed bed are presented in Figures 5.3, 5.4.

Table 5.1: Fitted parameters for the two-reaction model at 650°C. Experimental details:

4.58 ppm wt NaCl, 5 %vol H$_2$O in N$_2$ and 0-160 ppmv HCl

<table>
<thead>
<tr>
<th>Runs</th>
<th>$k_{s1}$ (cm/s$^1$)</th>
<th>$K_{e1}$ (cm$^2$s$^{-1}$)</th>
<th>$D_{g1}$ (cm$^2$s$^{-1}$)</th>
<th>$k_{s2}$ (cm/s$^1$)</th>
<th>$K_{e2}$</th>
<th>$D_{g2}$ (cm/s$^1$)</th>
<th>$\Sigma e_{opt}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(initial values)</td>
<td>0.2</td>
<td>76</td>
<td>0.001</td>
<td>0.7</td>
<td>5000</td>
<td>3.8x10$^{-5}$</td>
<td>1.63 &amp; 0.8</td>
</tr>
<tr>
<td>200 &amp; 400 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 hrs :</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) non-acid</td>
<td>0.0002</td>
<td>5000</td>
<td>0.001</td>
<td>0.7</td>
<td>5000</td>
<td>2.0x10$^{-5}$</td>
<td>2.6747</td>
</tr>
<tr>
<td>b) high-acid</td>
<td>0.0002</td>
<td>5000</td>
<td>0.001</td>
<td>0.7</td>
<td>5000</td>
<td>0.15x10$^{-6}$</td>
<td>2.36e-6</td>
</tr>
<tr>
<td>200 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 hrs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600 hrs</td>
<td>0.0002</td>
<td>5000</td>
<td>0.001</td>
<td>0.7</td>
<td>5000</td>
<td>2.0x10$^{-5}$</td>
<td>0.15e-6</td>
</tr>
<tr>
<td>600 hrs (non-acid)</td>
<td>0.2</td>
<td>5000</td>
<td>0.001</td>
<td>0.7</td>
<td>5000</td>
<td>2.0x10$^{-5}$</td>
<td>2.6737</td>
</tr>
</tbody>
</table>
Figure 5.3 : Theoretical Profiles generated using the Two-reaction Model, fitted to the 200 and 400 Experimental data at 650°C (20 tanks and max time step=15 min).

Figure 5.4 : Theoretical Profiles generated using the Two-reaction Model, fitted to the 600 hr Experimental data at 650°C (20 tanks and max time step=15 min).
Fitting the experimental profiles obtained by McLaughlin, i.e. at 827°C, with both computer programs, the parameters derived for a high-acid and a non-acid run, are given in Table 5.2 and the simulated profiles are presented in Figure 5.5. The discussion of the curve fitting and parameter values obtained will be presented in Chapter 6.

Table 5.2: Fitted Parameters for the Two-reaction Model at 827°C. Experimental details: 83.55 ppm wt (40 ppmv) NaCl, 5 %vol H2O in N2 and 0-160 ppmv HCl

<table>
<thead>
<tr>
<th>Runs</th>
<th>$k_{s1}$ (cms$^{-1}$)</th>
<th>$K_{s1}$ (cmV$^{-1}$)</th>
<th>$D_{g1}$ (cmV$^{-1}$)</th>
<th>$k_{s2}$ (cmV$^{-1}$)</th>
<th>$K_{s2}$</th>
<th>$D_{g2}$ (cmV$^{-1}$)</th>
<th>$\Sigma e^2_{opt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>McLaughlin's values for both 827°C runs</td>
<td>1.87x10$^{-2}$</td>
<td>3.33</td>
<td>10</td>
<td>1000</td>
<td>5000</td>
<td>3.03x10$^{-5}$</td>
<td>2.06</td>
</tr>
<tr>
<td>73 hrs (high-acid)</td>
<td>2.114x10$^{-5}$</td>
<td>10000</td>
<td>0.001</td>
<td>1000</td>
<td>10000</td>
<td>1.643x10$^{-5}$</td>
<td>1.11</td>
</tr>
<tr>
<td>97.7 hrs (non-acid)</td>
<td>2.114x10$^{-2}$</td>
<td>10000</td>
<td>0.001</td>
<td>1000</td>
<td>10000</td>
<td>1.643x10$^{-5}$</td>
<td>2.49</td>
</tr>
</tbody>
</table>

Figure 5.5: Theoretical Profiles generated using the Two-reaction Model, fitted to the 827°C McLaughlin's Experimental data (20 tanks and max time step=15 min).
Using the parameters derived by fitting theoretical uptake profiles with the fixed bed experimental data at 650°C, simulations were obtained for a single pellet under high-acid and non-acid runs. For a 600 hr non-acid simulation (Figure 5.6), reaction 1 seems to reach equilibrium, whereas reaction 2 reaches only 80% of its theoretical saturation capacity value. The total conversion is predicted to reach 95%, where 95% corresponds to the experimentally measured value of 14.5 %wt. This could mean that the overall measured saturation capacity for Na sorption could possibly be marginally underestimated. Similar simulations for a 600 hr high-acid run with a single pellet (Figure 5.7), present the same result for reaction 2 as the non-acid run. For reaction 1, it is predicted that it would reach only 10% of its capacity, which could be expected as under high-acid conditions the first reaction almost ceases. The overall conversion reaches only 30%, which can be all attributed to the second reaction.

The rates of the two reactions, $dX_{g1}/dt$ and $dX_{g2}/dt$, were plotted versus time and it was noticed that $dX_{g2}/dt$ would change rapidly at early times, which could be justified as this reaction was considered fast (Figure 5.8). Consequently, the numerical evaluation of $dX_{g2}/dt$ deviates from the analytical solution (Eq. 5.6) at the beginning of the run (Figure 5.10). Under
Figure 5.7: Pellet-grain, Two-reaction Model for predicting the Pellet Conversion under High-acid Conditions after a 600 hr Run

Figure 5.8: Rates of Reaction 1 and 2 using the 600 hr High-acid Run Parameters
these conditions, the Newton-Raphson routine can become slow to converge. However, for the first reaction which is reaction rate controlled, the analytical and numerical values of $dX_{g1}/dt$ coincide at all times (Figure 5.9).

### 5.2.2 Sensitivity analysis

To examine the dependency of the alkali sorption model performance on the parameters, each one was perturbed in turn ±10%, in order to identify and focus on the most significant ones. Since the two computer programs perform in the same way under the same conditions and McLaughlin's modified program had incorporated the sum of squares of errors, it was used for the sensitivity analysis. The sensitivity of the model with each of its parameters was calculated from:

$$
\left( \frac{\sum e^2}{\sum e^2_{opt}} \right) \times 100\% \quad \text{per}\% \quad (5.7)
$$
Figure 5.10: Comparison of Numerical and Analytical Calculation of $dXg2/dt$ using the 600 hr High-acid Run Parameters

where $\sum e^2 = \text{sum of squares of errors by comparing the experimental profile with the theoretically generated, when a parameter is perturbed by per\%}$

$\text{per\%} = \text{percentage of perturbation}$

$\sum e^2_{\text{opt}} = \text{sum of squares of errors by comparing the experimental profile with the optimum theoretical profile, and}$

$e_i = x_i - m_i = \text{error = difference between measured and theoretical values}$

$x_i = \text{experimental alkali uptake value at position i in the bed}$

$m_i = \text{theoretical alkali uptake value at position i in the bed}$

$N = \text{number of experimental values}$

All the parameters were perturbed by the same fractional amount, in order to compare them on the same basis. The parameters estimated from literature, i.e. the molecular diffusivity, the external gas film mass transfer coefficient and the bed porosity could be subjected justifiably to bigger changes than $\pm10\%$, since they are calculated from empirical correlations. However, the measured values such as pellet and grain radius, volumetric gas flowrate, NaCl and HCl concentration and sorbent capacity usually are subjected to much smaller experimental errors. The results are presented in Table 5.3.
Table 5.3: The effect of perturbing the model parameters in turn on the sum of squares of errors when the theoretically generated profiles are compared with a standard experimental profile (600 hrs, high-acid run unless otherwise stated)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Perturbation</th>
<th>Sensitivity (Eq. 5.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas film mass transfer coef ($k_g$)</td>
<td>+10%</td>
<td>-0.27</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.43</td>
</tr>
<tr>
<td>intrapellet diffusivity ($D_p$)</td>
<td>+10%</td>
<td>-0.34</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.53</td>
</tr>
<tr>
<td>pellet porosity ($\varepsilon_p$)</td>
<td>+10%</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.18</td>
</tr>
<tr>
<td>bed voidage ($\varepsilon_b$)</td>
<td>+10%</td>
<td>-0.03</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>-0.05</td>
</tr>
<tr>
<td>superficial velocity ($u$)</td>
<td>+10%</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>230</td>
</tr>
<tr>
<td>mass of solid per unit length of bed ($\omega A_c$)</td>
<td>+10%</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>182</td>
</tr>
<tr>
<td>sorbent molar density ($\rho_s$)</td>
<td>+10%</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>12.1</td>
</tr>
<tr>
<td>pellet radius ($R_p$)</td>
<td>+10%</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>-2.1</td>
</tr>
<tr>
<td>grain radius ($r_g$)</td>
<td>+10%</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>75</td>
</tr>
<tr>
<td>No. of time steps</td>
<td>+10%</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.01</td>
</tr>
<tr>
<td>No. of tanks</td>
<td>+10%</td>
<td>-3.1</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>1.24</td>
</tr>
</tbody>
</table>
Table 5.3 (Cont.)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Perturbation</th>
<th>Sensitivity (Eq. 5.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>High-acid conditions</td>
</tr>
<tr>
<td>stoichiometric coefficient ($b_1$)</td>
<td>+10%</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.19</td>
</tr>
<tr>
<td>stoichiometric coefficient ($b_2$)</td>
<td>+10%</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>55</td>
</tr>
<tr>
<td>sorbent saturation capacity ($K_1$)</td>
<td>+10%</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.29</td>
</tr>
<tr>
<td>sorbent saturation capacity ($K_2$)</td>
<td>+10%</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>246</td>
</tr>
<tr>
<td>HCl inlet concentration ($C_{HCl, feed}$)</td>
<td>+10%</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>-0.63</td>
</tr>
<tr>
<td>NaCl inlet concentration ($C_{NaCl,feed}$)</td>
<td>+10%</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>252</td>
</tr>
<tr>
<td>equilibrium group ($K_{eq1}$)</td>
<td>+10%</td>
<td>-0.015</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.012</td>
</tr>
<tr>
<td>equilibrium group ($K_{eq2}$)</td>
<td>+10%</td>
<td>-0.53</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>1.01</td>
</tr>
<tr>
<td>reaction rate constant for reaction 1 ($k_{r1}$)</td>
<td>+10%</td>
<td>-0.2</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>0.25</td>
</tr>
<tr>
<td>reaction rate constant for reaction 1 ($k_{r2}$)</td>
<td>+10%</td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>3.4</td>
</tr>
<tr>
<td>intragrain diffusivity for reaction 1 ($D_{g1}$)</td>
<td>+10%</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>-0.003</td>
</tr>
<tr>
<td>intragrain diffusivity for reaction 2 ($D_{g2}$)</td>
<td>+10%</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>-10%</td>
<td>44</td>
</tr>
</tbody>
</table>
Since the sensitivity is normalised, values bigger than unity indicate that the model is sensitive to a specific parameter. The results indicate that the model appears to be most sensitive to the mass of solid per unit length of bed, the solid molar density, the superficial velocity, the grain radius, the Na saturation capacities of Fuller's Earth and the inlet NaCl concentration, whereas from the fitted parameters the most significant appear to be the stoichiometric coefficients \(b_1\) and \(b_2\), the intragrain diffusivity and the rate constant for reaction 2. These results agree with McLaughlin's sensitivity analysis at 827°C. Figure 5.11 presents the change in the Na uptake profile by perturbing the grain radius by ±10% from its 20 μm value at the 600 hr runs. A detailed discussion of the sensitivity analysis results is presented in Chapter 6.

![Figure 5.11: Effect of Perturbing the Grain Radius ±10% on the Optimum Theoretical Profile for the High-acid 600 hr Run](image)

5.2.3 Scale-Up

When Eq. 4.41, 4.42 and 4.43 are combined, a relationship between the length and the cross sectional area, thus diameter of the reactor, is obtained. By trial and error, a series of reasonable combinations were established and investigated further. To obtain geometrical
similarity, the bulk density (g of solid per cm$^3$ of bed) was considered independent of scale-up. The exit gas alkali level can be calculated by the computer programs for the obtained combinations of the reactor's dimensions. In this work, the reactor diameter has been specified by CRE as 4 m, as calculated to satisfy the volumetric flow rate and superficial velocity demands.

Based on experimental results on Fuller's Earth capacity for alkali sorption, the volume of the bed required to adsorb a given amount of alkali over a certain operating period, can be estimated. From the 600 hr high-acid experiment, it was calculated from the sodium uptake and mass balance that 0.0127 g Na can be retained per g of bed. For a design margin, the estimated bed volume will be divided by 0.75. Consequently, the estimated bed volume should be safe to operate over the proposed times.

The approximate pellet diameters that are reasonable for scale-up, can be determined by the requirement to minimise the wall effects and the axial and radial dispersion. The ratios of pellet and reactor diameters for reasonable wall effect factors, can be estimated from Figure 7.2 in Ruthven (1984). In estimating the pellet dimensions, wall effects (Ruthven, 1984) can be considered insignificant for a 4 m vessel.

The evaluation of the reactor length was based on an inlet gas composition, provided by CRE, with a total alkali concentration of 129.4 ppbv, 942 ppmv HCl (dry gas) and 15 %vol water vapour. The superficial velocity of 30 cm/s was specified, at 24 bara pressure and 650°C. The pressure drop should not be more than 1 bar (CRE). The reactor length has been estimated in order to satisfy geometric similarity and the sorbent consumption for 8000, 16000 and 24000 hrs operation and corresponding values are given in Table 5.4. In this table, the estimated pressure drop is also given for various pellet diameters.

The biggest Reynolds number, based on pellet diameter, calculated for the scale-up conditions, roughly 700, indicates that the flow is just laminar. The smallest axial Peclet number calculated for the above combinations is 300, for the smallest bed length (1.5 m) and the biggest pellet (10 mm), and corresponds to a small amount of dispersion. From Figure 5.1, the number of tanks that can account for this axial dispersion is approximately 20 - 30. The equilibrium group ($K_e$) and the rate reaction constant ($k_r$) include the effect of water vapour
and system pressure. Therefore the values used for scale-up, are calculated for the new water concentration (15 %vol) and the operational pressure (24 bara) from the relationships resulting for these parameters from equation 4.10. The scale-up calculations are performed at 650°C, therefore both parameters are not temperature affected. The bigger the pellets, the more the diffusion in the pellet dominates the process. This effect can be illustrated in Figure 5.12. Also, the parameters of the first reaction do not affect the process as the first reaction is inactive at an acid concentration of 942 ppmv HCl (dry basis)/800 ppmv HCl (wet basis).

Table 5.4: Proposed Dimensions for the Fixed Bed Reactor, the Sorbent Pellets and the Estimated Pressure Drop for the Required Operational Conditions and Different Operating Times

<table>
<thead>
<tr>
<th>Operational Time</th>
<th>8000 hrs</th>
<th>16000 hrs</th>
<th>24000 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Diameter (m)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Bed Length (m)</td>
<td>1.5</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Pellet Diameter = 3 mm

| Pressure Drop (bar) | 0.13 | 0.25 | 0.35 |

Pellet Diameter = 5 mm

| Pressure Drop (bar) | 0.08 | 0.15 | 0.20 |

Pellet Diameter = 7 mm

| Pressure Drop (bar) | 0.05 | 0.10 | 0.13 |

Pellet Diameter = 10 mm

| Pressure Drop (bar) | 0.03 | 0.07 | 0.09 |

Table 5.5 presents the effect on the outlet alkali concentration for different values of $K_{e1}$ and $K_{e2}$, whereas the appropriate calculated value for 15 %vol H$_2$O and 24 bara is 42500, if the 5000 value is used for 5 %vol H$_2$O and atmospheric pressure. For 15 %vol H$_2$O, the calculated $k_{s1}$ and $k_{s2}$ values are 0.0017 cm s$^{-1}$ and 5.95 cm s$^{-1}$ respectively. The highest outlet alkali concentration calculated at the end of the cycle, is approximately 18 ppb wt for 942
ppmv inlet HCl concentration and for 8000, 16000 and 24000 hrs. The effect of HCl inlet concentration on the alkali capture by the sorbent bed is shown in Table 5.6 and it suggests that HCl removal will improve alkali removal.

![Figure 5.12: Effect of Pellet Diameter on the Na Uptake Concentration Profile for 8000 hrs and Bed Length 1.5 m](image)

**Figure 5.12**: Effect of Pellet Diameter on the Na Uptake Concentration Profile for 8000 hrs and Bed Length 1.5 m

**Table 5.5**: Effect of $K_e$ on Alkali Outlet Concentrations in Scaled-Up Reactor with Inlet HCl Concentration of 942 ppmv (8000 hrs)

<table>
<thead>
<tr>
<th>$K_{el}$ = $K_{e2}$ values $\rightarrow$</th>
<th>10000</th>
<th>30000</th>
<th>42500</th>
<th>50000</th>
<th>60000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet Alkali Concentration (Na+K) (ppb wt)</td>
<td>84</td>
<td>26</td>
<td>18</td>
<td>15</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 5.6: Effect of HCl Inlet Concentration on the Outlet Alkali Concentrations in Scaled-Up Reactor ($K_{e1} \& K_{e2} = 42500$)

<table>
<thead>
<tr>
<th>ppmv HCl $\rightarrow$</th>
<th>942</th>
<th>800</th>
<th>600</th>
<th>400</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet Alkali Concentration (Na+K) (ppb wt)</td>
<td>18</td>
<td>15</td>
<td>11</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

5.3 SUMMARY

Computer simulation of chemical processes is a well established feature of process design for scale-up from laboratory experiments. The model developed by McLaughlin, was formulated from data collected on a laboratory-scale fixed bed rig at high temperatures ($827^\circ$C-$927^\circ$C) under simulated operating conditions, where $N_2$ as the carrier gas contained 10-40 ppmv NaCl, 5 %vol $H_2O$ and 0-160 ppmv HCl. In the model, expressions derived for the thermodynamics and kinetics of the sorption process were combined with the mass transfer properties of a fixed bed. At best, this model can only approximate the 'real' alkali sorption process since inevitably, many assumptions are made and experimental constraints impose limitations on laboratory derived data.

In the present research project, the McLaughlin program was revised in order to be used with more confidence in developing a commercial plant-scale process. In addition, temperature and pressure effects were investigated, to make it possible to predict the alkali removal performance at $927^\circ$C, $827^\circ$C, $650^\circ$C and $600^\circ$C and various pressures in the required range (up to 25 bar), especially for scale-up calculations.

The tanks-in-series solution was written in gPROMS and the results did not agree with McLaughlin's program. The original PDEs for the bed were then solved in gPROMS and the two gPROMS solutions agreed exactly. This study led to the discovery that the Szekely approximation has a false root under some conditions. It was suspected that this false root was being selected by gPROMS and this could account for the difference between the McLaughlin and gPROMS programs. The gPROMS simulations were discontinued because gPROMS does not presently provide direct control over the internal numerical procedures.
To resolve the above issues, a new computer program was written and checked extensively against the theory. Initially this program solved the equations for a single pellet only. This program was then incorporated in the development of a fixed bed model, where the system of equations was solved simultaneously and rigorously in time and position in the fixed bed, with a variable-time-step, variable-order integration method. The concentration profiles derived for the same set of parameters, agreed with the existing model and suggested that although this is a very approximate representation of the process, it is still valid under the set of conditions used.

The McLaughlin program has not been modified to cope with a situation which could arise in reality where the conversion inside the bed first rises but subsequently falls when higher concentrations of HCl arrive. A much more detailed model of the reaction kinetics would be required to describe the advancing front of stripped grain as the reverse reaction takes place.

A sensitivity analysis was also performed on the parameters of the model to identify a number of measured and fitted parameters that affect significantly the theoretical Na uptake profiles. Scale-up calculations based on interest for industrial applications were also performed in order to give an approximate design specification of an alkali removal unit that could possibly be installed after the ceramic filter in the gasification line of the British Coal Air-Blown Gasification Cycle. The recommended length of a 4 m diameter commercial sorber is 1.5, 3 and 4 m in order to replace the sorbent bed after 8000, 16000 and 24000 hrs of operation respectively.
CHAPTER 6

DISCUSSION OF EXPERIMENTAL AND THEORETICAL RESULTS

In this chapter both the experimental results obtained during this work and the theoretical predictions of the model, will be discussed. The assumptions made in the theory will also be reviewed in the light of the experimental results. Finally, a discussion of the sensitivity analysis of the model on the parameters used will be presented.

6.1 EXPERIMENTAL RESULTS

Modifications to the original fixed bed rig were considered necessary to obtain stable, reproducible and accurate experimental results at 650°C, in order to form a reliable basis for the estimation of the parameter values for the model, by fitting the theoretical results to the experimental profiles.

The stable alkali vapour production of 0.3 mg hr⁻¹ in the laboratory rig, even after 600 hrs, and the control of gas leaks during each experiment, made a significant contribution to the dramatic improvement in the sodium mass balance. The Na mass balance, which reached very high levels of accuracy, 99% at the 600 hr high-acid run, coupled with the very low outlet Na concentration (5-6 ppb wt), measured by chemical analysis of the alumina wool pads downstream of the bed, formed very strong evidence for the effectiveness of the alkali removal process at 650°C.

Alkali aerosol formation has not been considered a problem, since a highly accurate sodium mass balance was obtained, the alumina wool filter pads were placed in the alkali condensation zone of the rig and all of the exit gas alkali was captured in the first pad under the fixed bed. The three pad alumina wool filter was preferred for the capture of the exit gas alkali instead of a sampling train, with a condenser and bubblers, since the latter system would create a larger back pressure in the packed bed.
Results obtained from a thin bed test with no filter, showed that salt crystals grow out from the tube wall as fine needles when the temperature of the wall has dropped to 400-500°C. On this evidence, the filter was extended into this zone in order to provide a matrix of condensation nuclei within the gas path, although with a full bed in place alkali levels would be much lower and condensation characteristics may change. These changes improved the collection efficiency of the filter and provided a better assessment of the exit gas concentration.

Other improvements to the experimental procedure included the replacement of the polypropylene volumetric flasks used for alkali analysis by AAS with new polymethylpentene ones, the new heating block, teflon beakers used for the acid digestion step and the elimination of the electrostatics affecting the weighing of Fuller's Earth samples. These measures reduced significantly the analytical errors involved in the chemical analysis of the solid sorbent and further improved the closure of the mass balance. Very accurate experimental uptake values, with standard deviations of less than 2.5% (Table A.II.2) were achieved. The position of each layer in the bed was also measured very accurately by the travelling microscope technique. The improvement in the quality of these experimental results is indicated by the small magnitude of the error bars (±0.01 cm) corresponding to the position in the bed (Table A.II.9).

6.1.1 Single-Layer Tests

Single-layer studies, being free from packed bed effects, can give direct information on the sorption characteristics of a pellet. In order to be consistent with the previous work (McLaughlin, 1990) and since Fuller's Earth performed very well as an alkali sorbent at the high temperatures of 827°C and 927°C, it was also chosen for examination as a potential sorbent at 650°C. The other aluminosilicate material that has been extensively suggested by literature as a potential getter is kaolin. At 650°C it is not expected to undergo any phase transformation and as a result, it was examined as an alternative to Fuller's Earth.

The mixed single-layer tests performed with two candidate sorbent materials simultaneously had the advantage of evaluating both sorbents at the same time and under the same
conditions. Kaolin, when examined with Fuller's Earth in a mixed layer under non-acid conditions (Table A.II.3), showed an enhanced uptake (9 %wt in kaolin and 5 %wt in Fuller's Earth), while in the presence of acid Fuller's Earth exhibited a characteristically reduced uptake (3.48 %wt) and kaolin did not seem to be affected (11.38 %wt). Since kaolin appears to be a promising getter at the intermediate temperature of 650°C, fixed bed tests will be necessary to confirm the above results.

Carbon deposition on Fuller's Earth pellets, pre-treated at the CRE atmospheric gasifier, did not seem to affect the sorption of sodium. Treated and untreated, calcined Fuller's Earth pellets, in a single-layer test under high-acid conditions (Table A.II.3) achieved the same sodium uptake (5-6 %wt). This may indicate that the evaluation of Fuller's Earth in N₂, could possibly be approximately valid for a coal-derived gas environment.

N₂ was used as a carrier gas for the experiments on the fixed bed rig. This made the procedure practicable, because N₂ is an inert, non-toxic gas. However, it was unlikely to interfere with or distort the alkali sorption process (McLaughlin, 1990) in the same way that real flue or gasifier gases might. It was reported by Mulik et al (1986) and Punjak (1988) that the simulated flue gas did not affect the alkali sorption process. As a result, there was no need to add further complications to the system at this stage by using hazardous gases such as CO, H₂, CO₂, CH₄ and H₂S. However, since the alkali sorption process in an N₂ environment has been proved efficient, the effect of these gases on the alkali sorption process should be evaluated more precisely.

6.1.2 Fixed Bed Tests

In order to ensure that the fixed bed of pellets was effectively isothermal during an experiment, two independently controlled heater windings were used for the upper and the lower part of the bed. Axial and radial temperature differences of 1-2°C were measured, indicating that the system could be considered isothermal. Since the pellets used were small in size (~0.5 mm in diameter), heat should be quickly transferred and evenly distributed (Froment and Bischoff, 1979; Rase, 1990).
Pellets of 0.4 to 0.6 mm diameter were used in order to minimise the gas channelling near the walls. Under these conditions, where 40-60 pellets correspond to a tube diameter, the wall effects should be insignificant, especially when the pellets are distributed in shape and size.

The pressure drop across the bed was monitored continuously at 50-60 mm H₂O (~5.8x10⁻³ atm). Volumetric flow rates were checked at the beginning and at the end of each experiment to confirm that leaks had not developed. Extensive care was taken so that the temperature of the high precision flow controllers and the supply pressure regulator used, were kept stable in order to minimise the fluctuation in the gas flow rate caused by ambient temperature changes. Temperature control was also applied to the microbalance head for the elimination of fluctuations in the rate of loss of salt.

A fixed bed test at 600°C, with NaCl and Fuller's Earth over 240 hrs clearly illustrated the difficulties associated with sorption runs at this temperature. The maximum sodium gas phase concentration was very low, 0.82 ppm wt Na (1 ppmv), and the amount of Na entering the bed would be at least a factor of 10 lower than that for higher temperature runs (827°C and 927°C). The poor mass balance obtained from this first run may be due to operating errors and further runs would have been necessary to determine the getter performance at this temperature. However, it was unlikely that bed profile modelling would be effective using these results and higher temperatures were used to increase the sodium content of the gas entering the bed and hence reduce the run times to acceptable values. It was decided to conduct experiments at 650°C, where the sodium gas phase concentration was more suitable for experimental work.

To investigate the sorption of sodium and potassium by Fuller's Earth, two 200 hr, high-acid runs were completed, one with NaCl and the other with KCl. The uptake values for potassium and sodium, 2.751 %wt and 3.244 %wt respectively, showed that Fuller's Earth can retain K as well as Na, although the two alkali concentration profiles were not identical (Figure 3.3).

The 200 hr run with NaCl did not give a good mass balance (Table A.II.5) and since a more fully developed profile would provide more precise parameter values obtained by curve fitting, longer runs, should be performed. A 400 hr run was attempted first, as all the previous runs were of much shorter duration. In the 400 hr run, the closure of the sodium mass balance was
95% (Table A.II.6) and the outlet gas sodium concentration was 5.5 ppb wt. Next, a 600 hr, high acid run was performed and this was the most successful with a sodium mass balance of 99% (Table A.II.7) and an average outlet gas sodium concentration of 5.7 ppb wt. The agreement of the effluent gas sodium concentrations from the 400 and 600 hr runs was a very positive sign of the excellent performance of the fixed bed rig and of Fuller's Earth as a potential alkali sorbent. The 600 hr sodium uptake profile along the fixed bed was better developed than for the previous experiments but was not the same general shape as the 200 and 400 hr profiles. Furthermore, the maximum sodium uptake was 3.68 %wt, less than the 4.35 %wt that obtained at the 400 hr run. The profiles for the 200 and 400 hr runs were the same general shape.

One difference with the 600 hr run was the size of Fuller's Earth pellets used, 0.5-0.6 mm, instead of 0.425-0.5 mm since all the smaller pellets available had been used for previous runs. Since the 600 hr duration run seemed to give a well developed Na uptake profile at these low Na concentrations, a 600 hr, non-acid run was also performed to examine the effect of HCl on Fuller's Earth sorptive performance at 650°C. The combination of these runs was considered adequate for curve fitting and estimation of the model parameters.

Kaolin fixed bed studies could not be completed during this work because of the very long runs involved for the evaluation of Fuller's Earth. However, since kaolin proved to be a potential getter at the temperature of 650°C, it needs further investigation. Apart from the fixed bed tests and the rate of uptake that needs to be measured, the reaction mechanism and the product of the reaction needs to be determined and the effect of carbon deposition on the uptake reaction requires further investigation.

6.1.3 Element Mapping

In order to gain more information on the pellet structure and the alkali distribution in the pellets and grains, scanning electron microscopy and a combination of the energy and wavelength dispersive systems were used to obtain secondary electron and X-ray images of the sorbent pellets and grains.
The pellets used for SEM measurements had to be mounted in resin and then cut and polished to reveal the structure of the pellets and the grains. The spatial sodium distribution could also be measured. The problem is that the depth of the sample cut is unknown due to the fragility of the pellets.

The secondary electron images (Figures A.IV.4,5,6) clearly show the pellet structure for Fuller's Earth and kaolin, which appear to be very different. Fuller's Earth pellets are formed from grains of irregular shape and non-uniform size, interconnected with a random channel structure. Kaolin pellets contain very fine grains in an essentially uniform concentrically layered structure. Both materials contain regions of agglomeration.

Kaolin and Fuller's Earth pellets exhibit very different sorption patterns. Within grains, the 'shrinking core' mechanism is clearly evident for Fuller's Earth, whereas the shrinking core is more obvious with kaolin for the whole pellet (Figures A.IV.7-10). Linescans, performed across Fuller's Earth grains, also support the shrinking core model for grains (Figures A.IV.11,12,17,18), as sodium levels are higher at the outer edge of grains than in the middle. Pellets and grains taken from different depths of the fixed bed and consequently exposed to different alkali concentrations, still exhibit the same behaviour (Figures A.IV.9,14), although the unreacted core of the grains is bigger as the alkali concentration decreases deep in the bed. For the 600 hr non-acid run, it was observed that in the first layers of the bed some pellets became lighter in colour. This could be attributed to either impurities in the pellets or to radial Na concentration gradients in the laboratory rig. To separate the light from the dark pellets for chemical analysis was considered impractical since the resulting quantities would be too small to give accurate analytical results. However, X-ray images obtained from dark and light pellets (A.IV.19,20) did not indicate a significant difference in the alkali sorption pattern. McLaughlin also observed a pellet colour change at uptake levels slightly below saturation and attributed it to possible inherent inhomogeneity in Fuller's Earth.

Fuller's Earth pellets treated with potassium seemed to follow the same sorption pattern as sodium (Figures A.IV.16,18). X-ray images of Fuller's Earth pellets pre-treated in the CRE atmospheric gasifier for ~100 hrs, indicated that carbon did not penetrate the interior of the grains and sorption of alkali proceeded as normal through the external surface of the carbon barrier on the grains (Figure A.IV.15). The results indicate that even under real conditions
(carbon-coated pellets) and for two different alkalis, the pellet-grain model can be used safely to represent the alkali sorption with Fuller's Earth as a getter.

Significant work on the existing models has been reported to account for structural changes during a gas-solid reaction (Szekely and Evans, 1971; Hartman and Coughlin, 1974; Ranade and Harrison, 1979; Georgakis et al, 1979; Duo et al, 1993; Peukert and Löffler, 1993). However, in this work no structural changes were noticed in the pellets, even after they had been exposed to alkali vapour for 600 hrs. This can be confirmed by secondary electron images of unexposed and exposed Fuller's Earth pellets for experiments at 650°C (Figures A.IV.4,5) and also for exposed pellets (non-acid run) that underwent a colour change during the experiment (Figures A.IV.19,20).

McLaughlin (1990) reported no major structural changes to sorbent pellets even at high alkali concentrations (40 ppmv NaCl) and high temperatures (827°C and 927°C), unless the alkali uptake was above 8.5 %wt, when the sorbent appeared to become amorphous, forming a glassy phase. The possible formation of sodium di-silicate \( \text{Na}_2\text{O.2SiO}_2 \) or a eutectic (Eq. 2.3) at 767°C was suggested either could explain the glassy phase observed in the experiments at 827°C and 927°C and the absence of such phase in the 650°C runs. Unfortunately no other measurement, such as the specific surface area, could be made on the treated sorbent since the quantities used were small and most of it was destroyed by the chemical analysis used to determine the alkali uptake. However, the specific surface area of calcined pellets was measured at 0.54 m\(^2\)g\(^{-1}\), which is comparable with McLaughlin's value of 2.9 m\(^2\)g\(^{-1}\) for calcined Fuller's Earth pellets, in the sense that both values indicate small specific surface areas.

### 6.1.4 Alkali Sorption Mechanism

The gas-solid reactions are generally quite complex and scaling-up a process has to be approached with caution unless there is a clear understanding of the reaction mechanism. Ideally the model for a process should be based as closely as possible on the actual reaction mechanism, because extrapolation to different operating conditions can then be carried out with much more confidence.
The two-reaction scheme proposed by McLaughlin because the experimental data could not be fitted with one reaction was also adopted in this work. The two reactions were formulated as follows:

\[
\text{NaCl} \text{(g)} + \frac{1}{2} \text{H}_2\text{O} + b_1 \text{Reactant}_1, (a) \rightarrow \text{Product}_1, (a) + \text{HCl} \text{(g)} \tag{6.1}
\]

\[
\text{NaCl} \text{(g)} + \frac{1}{2} \text{H}_2\text{O} + b_2 \text{Reactant}_2, (a) \rightarrow \text{Product}_2, (a) + \text{HCl} \text{(g)} \tag{6.2}
\]

The inhibitory effect of HCl on the reaction scheme was shown by McLaughlin, when at 827°C and 927°C the alkali uptake decreased from 14.4 %wt to 4.7 %wt (based on g of Na per g of initial solid) by increasing the inlet HCl concentration from 0 to 160 ppmv. During this work, a similar decrease, from 14.6 %wt to 3.68 %wt, in the Na uptake was observed at 650°C. To justify the effect of HCl and the difference in the Na capture, McLaughlin assumed that only the first reaction is dependent on the presence of HCl in the system, whereas the second reaction will proceed even with HCl introduced into the system. X-ray studies obtained during this work identified nepheline (a sodium feldspathoid: \( \text{Na}_2\text{O}.\text{Al}_2\text{O}_3.2\text{SiO}_2 \)) under non-acid conditions (Product 1) for both light and dark-coloured pellets (Table A.VII.3) and albite (sodium feldspar: \( \text{Na}_2\text{O}.\text{Al}_2\text{O}_3.6\text{SiO}_2 \)) as the solid product under high-acid conditions (Product 2) (Table A.VII.2).

Feldspars are framework silicates formed by tetrahedral groups, usually \( \text{SiO}_4 \) and \( \text{AlO}_4 \), linked in three dimensions by sharing all the oxygens with adjacent tetrahedral groups (Mineralogical Society, 1980). Feldspathoids are chemically similar to feldspars, in that they are aluminosilicates of chiefly potassium, sodium and calcium. The main difference is their silica content; feldspathoids usually contain about two-thirds as much silica as feldspars. Although generally this is the case, nepheline contains one-third of the silica of albite. This is also roughly the ratio of the Na uptake observed under non-acid and high-acid conditions. It is also worthwhile mentioning that nepheline takes its name from a Greek word meaning cloud, because when immersed in acid it becomes cloudy (Cornelius et al, 1971). The fact that nepheline was identified as the reaction product in both the light- and dark-coloured pellets, is further evidence that the difference in colour does not imply a difference in alkali uptake.
Albite and nepheline were also identified as solid reaction products at 827°C and 927°C by McLaughlin (1990). Mulik et al (1986) and Uberoi et al (1990) made similar observations for alkali capture by emathlite. Fuller's Earth should be expected to react like emathlite as they are both 2:1 layered aluminosilicates.

A literal interpretation of the two-reaction scheme assumes that there are two distinct species that react with sodium and produce two different solid products. Under high-acid conditions, reaction 2 is assumed to dominate and therefore the identification of albite only as a reaction product agrees with the reaction scheme. However, under non-acid conditions, two reaction products would be expected, both albite and nepheline. Since only nepheline was identified, this could be attributed to the higher uptake value of the first reaction (9.9 %wt), which means that nepheline would be formed in larger amounts than albite and therefore give a stronger X-ray fingerprint. At this point, it could be argued that only one reaction is taking place with two products, depending on the presence of HCl, albite or nepheline. Since there is no evidence, either from previous work on alkali sorption by aluminosilicates or from this work as to the exact reaction mechanism and the interaction between NaCl and HCl, the two-reaction scheme will be temporarily accepted since it can adequately simulate the alkali sorption experiments across the full temperature range of 650-927°C (Chapter 5). However, further work is necessary to specify the exact role of HCl in the alkali sorption process.

Another area that needs further experimental investigation is the reversibility of the reaction, which is relevant to the way the Szekely pellet-grain model deals with reversible reactions. Consequently, checks should be carried out on whether the alkali sorption reactions are really reversible and this can be achieved by exposing fixed beds already treated with Na to high feed HCl concentrations. This information could be very useful and relevant in the real process conditions where the HCl concentration could fluctuate during operation.

6.1.4a Effect of NaCl and H₂O vapour on the reaction mechanism

Experiments to identify the HCl production as a result of the sorption of alkali by Fuller's Earth, to explore the effect of water on the process and possibly define the order of reaction with respect to this reactant, are described in detail in Chapter 3 and the results obtained are presented in Appendix III. The following summarises the main results and conclusions:
1) HCl was produced when both NaCl and H2O were present in the system. When NaCl was introduced in the feed, the HCl response was initially quite slow and it would take at least 10-15 min before the system could reach a stable HCl concentration (Figures A.III.4,5). The measured HCl followed the increase or decrease of the NaCl feed, e.g. Figure A.III.5, where the NaCl in the feed was reduced from 0.7 to 0.5 mg/hr and then increased back to the initial value. The observed HCl response for 0.7 mg/hr (~5.1 ppmv) NaCl in the feed was ~3 ppmv HCl, (Figure A.III.6), although from the assumed reaction scheme, a response of ~5 ppmv was expected. This result could be interpreted in several ways:

a) NaCl is initially physically adsorbed by the sorbent and reacts slowly to produce HCl and therefore the rate of NaCl arrival at the sorbent does not equal the rate of HCl production. This scheme is supported by other workers in the absence of water vapour (Uberoi et al, 1990), but is not the case here;

b) both physical adsorption of NaCl on the solid and chemical reaction of NaCl with the sorbent occur in parallel. Consequently not all the NaCl in the feed reacts to produce HCl;

c) HCl is produced instantly by chemical reaction, but it cannot diffuse quickly out of the sorbent pellets;

d) NaCl reacting with the sorbent produces HCl but not in a 1:1 stoichiometry, as is assumed in the present two-reaction scheme.

However, the definite connection of the production of HCl with the presence of NaCl in the system was also confirmed when the response curve fell slowly back to the baseline (Figure A.III.6) as NaCl was eliminated from the system.

2) Under dry conditions, HCl was still produced but in small quantities (0.5-1.0 ppmv HCl) (Figure A.III.7). The idea of attributing the HCl produced only to residual -OH in the calcined sorbent was rejected, because the concentration of these residual -OH groups was measured by Yadegarian (1992) and they should have been exhausted early in this experiment. Every possible source of water in the system was also checked and eliminated. This slow Na uptake under dry conditions has been reported by a number of other researchers, Mulik et al (1986), Uberoi et al (1990) and McLaughlin (1990), but has not been explained.
If water vapour is absent, then the proposed mechanism would require hydroxyl groups to be retained in the calcined montmorillonite pellets. Total loss of hydroxyl groups and the collapse of the montmorillonite structure does not occur until 900°C. The pellets used, have been calcined at 850°C by McLaughlin (1990) and residual -OH groups may still exist in the sorbent's structure. Although, in the presence of water vapour at high temperatures, hydroxyl groups could possibly be readily regenerated in the silica lattice, a number of experiments on water treatment of Fuller's Earth at 600°C and 850°C (Yadegarian, 1992), did not confirm an increase of =SiOH and =AlOH groups.

Water retention by the bed seemed to be likely in the presence of alkali salt. The evidence, for this is that the increase in the production of HCl in the beginning of the experiments was slow (60 min) (Figure A.III.5), whereas later in the experiment it was quicker (10 min) for the same NaCl concentration in the system (Figure A.III.6). This observation was also reported by Mulik et al. (1986), who suggested that water was not retained by the sorbent bed through either an adsorption or reaction step in the absence of alkali. This seems unlikely since most aluminosilicates are strongly hydrophilic.

3) The physical adsorption of NaCl by the sorbent bed was indicated when after a dry run, the salt being introduced in the feed stopped and H₂O was introduced in the system (Figure A.III.7). The HCl response was quite high for ~10 min (4 ppmv HCl from a Drager tube test) (normal water peak at 30°C was ~0.9 mV and in this experiment it was ~1.1 mV) and then it dropped gradually as the physically adsorbed NaCl was exhausted by reacting with H₂O. Uberoi et al., (1990) also reported that physisorption dominated the sorption process in the absence of water vapour.

Drager tube tests were performed simultaneously with the measurements of HCl using the online monitor (Figure 3.6). Although generally the Drager tube tests can only give approximate results, they confirmed the results taken from the cell. When the bed was exposed only to alkali for 9-10 hrs, a Drager test tube showed 1 ppmv HCl being produced. The 4 ppmv HCl result, was produced when H₂O was introduced in the system after the bed was pre-treated with NaCl (0.7 mg/hr) for 9-10 hrs. Continuous exposure to water and decrease of the salt production to 0.3 mg/hr gave a result of 2 ppmv HCl. This value was expected for this alkali concentration.
A quick answer to the water concentration effect was expected with the exit gas analysis tests performed with the HCl on-line monitor (electrochemical cell). Unfortunately, since the cell was found to be quite sensitive to water (Figures A.III.2,3) despite its specifications, the only conclusion that could be drawn from these tests with respect to water, was that NaCl will react with the sorbent material quicker in the presence of water vapour and much slower in its absence, producing HCl in both cases. The HCl produced in the absence of water (~1 ppmv), is much less than when water is present (~3 ppmv).

The presence of water is playing a crucial role in the uptake of sodium by Fuller's Earth and is one of the areas that needs further investigation. To find the real order of reaction with respect to water vapour, fixed bed tests with different water concentrations have to be performed. The comparison of these results should give the order of reaction with respect to water vapour. Since it was not clear from the above results, the same approach should be taken to establish the order of reaction with respect to NaCl and to gain further understanding of the reaction mechanism.

In summary, the HCl production is directly connected with the presence of NaCl in the system. In the absence of H₂O vapour, physical adsorption of NaCl is likely to dominate the process, whereas in its presence the production of HCl is significantly enhanced. The positive role of water vapour in the capture of sodium is fortunate since water is unavoidably present in all the gases currently under consideration in the industrial applications of this work.

6.1.4b Sodium Uptake Capacity

The Na saturation capacity of Fuller's Earth should be independent of temperature since it depends only on the stoichiometry of the reactions. A close examination of the maximum uptake values obtained at 650°C, 827°C and 927°C, gives a total approximate value of 14 %wt (Table 6.1). From the measurements under high-acid conditions, it seems that the uptake due to the second reaction increases with increasing temperature. Apart from the fact that the 827°C and 927°C results are not very accurate, according to the two-reaction scheme, the first reaction is reaction rate limited, whereas the second is intragrain diffusion limited. Consequently, the first reaction will be more temperature dependent than the second.
Table 6.1: Maximum Na uptake values (%wt) obtained from experiments performed at the indicated temperatures

<table>
<thead>
<tr>
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<th>650°C</th>
<th>827°C</th>
<th>927°C</th>
</tr>
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<tbody>
<tr>
<td>1st reaction</td>
<td>9.9</td>
<td>9.7</td>
<td>8.2</td>
</tr>
<tr>
<td>2nd reaction</td>
<td>4.7</td>
<td>4.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Total</td>
<td>14.6</td>
<td>14.4</td>
<td>13.6</td>
</tr>
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As a result, the increase in the uptake at 927°C under high HCl conditions can probably be attributed to the first reaction. Unfortunately, no conclusions can be drawn as to the effect of temperature on the two reaction uptakes since their performance cannot be separated, and further investigation is necessary. Furthermore, Figures 5.6 and 5.7, from the pellet-grain model, suggest that reaction 2 reaches only 80% of its capacity after 600 hrs of experiment. Since the Na saturation capacity of potential sorbents is a very important parameter for scale-up calculations, long runs, perhaps of 1000 hrs, and at different temperatures, should also be performed with Fuller's Earth and kaolin in order to measure this parameter with confidence. However, if the chosen ultimate capacities for Fuller's Earth are low, the estimated sorber bed, from the scale-up calculations, will be safely oversized.

6.2 PELLET-GRAIN MODEL

The assumptions that were made for the Szekely approximation of the pellet-grain model presented in Chapter 4, are discussed here in more detail and comparison with the experimental conditions and results obtained:

1) The system is isothermal. The model assumes the process to be isothermal and this is confirmed by measurements, described in Chapter 3, where the maximum temperature difference within the bed was less than 2°C.

2) The pseudo-steady state approximation for the bulk concentration of the gaseous reactants and products in the pellet can be considered appropriate in the case where these concentrations are constant, but the concentration at the reaction interface of the shrinking
core varies as the core shrinks. In this case as the product layer thickens, diffusion through it presents a bigger resistance to mass transfer. However, if transport through the product layer is fast, the concentration at the reaction interface will be very close to the bulk concentration. If the external concentration fluctuates then the concentration at the shrinking core will also fluctuate, a condition which is not accounted for in the pellet-grain model. To approximate to a constant external concentration, small time steps were used when solving for a fixed bed.

3) The solid structure is macroscopically uniform and is unaffected by the reaction. The secondary electron images of the unreacted and the reacted solid pellets (Figures A.IV.4,5) show that there are no differences in the pellet structure. The structural changes to the sorbent (Fuller's Earth) were only apparent at sodium loadings in excess of about 8.5% wt at temperatures of 827°C and 927°C (McLaughlin, 1990), but they were not observed at 650°C, even with Na uptakes of 14.6 %wt (Figures A.IV.19,20).

4) The molecular diffusivities of NaCl and HCl in N₂ have been calculated as 0.9 and 1.3 cm²s⁻¹ at 650°C. Consequently these and the intrapellet macropore diffusivities, Dₚ, can be considered equal. Furthermore, as the diffusing species are at low concentration (4.58 ppm wt Na and 0-208 ppm wt HCl), the diffusivities of the gaseous reactant and product can be considered uniform throughout the pellet and independent of concentration.

5) Convective mass transfer within the pellet can be considered negligible. The pressure drop across the sorbent bed was monitored continuously during the experiments and was shown to be small, 50-60 mm H₂O (~5.8*10⁻³ atm). As a result, the pressure drop across a single pellet should also be negligible.

6) The reactions are first order with respect to the gaseous reactant, NaCl, and independent of local conversion of solid so long as there remains some unreacted solid. Since the order of reaction with respect to NaCl was not revealed by the HCl exit gas analysis, and other experiments with different NaCl concentrations were not performed, first order reactions were chosen as the simplest scheme that could fit the experimental data. This assumption is frequently made for mathematical convenience, in the absence of direct experimental proof. If this assumption needs to be relaxed, Evans and Szekely (1972) have already considered the effect of reaction order in non-catalytic gas-solid reactions.
The next two assumptions were made initially by Szekely et al. (1976) for simplicity, in order to derive the equations describing the process, but were relaxed later:

7) The resistance due to external mass transport is negligible. In laboratory scale experimental studies, this could be valid by using sufficiently high gas velocities. However, in practical systems involving packed beds of solid particles, external mass transport may be fully or partially rate controlling. The external gas film mass transfer coefficient, $k_g$, was calculated to be 58.1 and 50.26 cm/s for pellet diameters of 0.46 and 0.55 mm. For the 600 hr high-acid run, the contribution of external mass transport to $t^*$ for the second reaction, was calculated to be 9.9% for short times (i.e. $X_g = 0.01$) and 0.9% towards the end of the experiment ($X_g = 0.8$). For the 600 hr non-acid run, the corresponding contributions to $t^*$ for the first reaction have been calculated as 3.9% and 2.5% respectively. Consequently, the pellet-grain model predicts that the effect of external gas film mass transfer in the experimental reactor can be significant for short times, but diminishes as time progresses. This effect was not examined experimentally since measurements were made at superficial velocity of 10 cm/s to comply with industrial specifications.

8) Diffusion of the gaseous reactants through the product layer of the individual grains is not rate-limiting. In the development of the pellet-grain model, Szekely et al (1972) initially neglected the effect of diffusion through the product layer because of the small size of the grains. However, for a system with large grains or fast reactions, the effect of intragrain diffusion may be significant (Sohn and Szekely, 1974). Punjak et al (1989) found from their experiments with kaolinite, emathlite and bauxite, with sorbent particles larger than 80 μm, that both interphase and intraphase diffusional resistances influence the observed kinetics for all three sorbents. For the 600 hr non-acid run, the contribution of intragrain diffusion resistance to $t^*$ for the first reaction, was 0.06% at short times ($X_g = 0.01$) and it increased towards the end of the experiment ($X_g = 0.8$) to 5.4%. This increase is expected as the product layer builds up with time. For the 600 hr high-acid run, the intragrain diffusion contributes even more to $t^*$ with 7.66% in the beginning of the run and 90% close to the end. These contributions clearly show that the diffusion of the gaseous reactants and products through the product layer of the grains had to be taken into account.
6.3 PARAMETER EVALUATION AND DISCUSSION

Fitting of the theoretical to the experimental profiles obtained during this work was successful. The fit with the 600 hr high-acid run, which was the most accurate experiment is especially good (Figure 6.1). For the high-acid runs, the first reaction equilibrium group, \( K_{s1} \), was set to 5000 in order to overcome the problem of negative conversions obtained due to the reversibility of the reaction. The rate constant, \( k_{s1} \), was estimated to have a value of 0.0002 cm s\(^{-1}\), instead of the initial value of 0.2 cm s\(^{-1}\) (Table 5.1) and this low value was used in experiments where the first reaction seems to stop earlier in the experiments. For the non-acid run, \( k_{s1} \) was found to fit the experimental curve with the value of 0.2 cm s\(^{-1}\). This high value ensures that under non-acid conditions reaction 1 proceeds, without being hindered by the HCl concentration. Both curves would be fitted with a \( D_g \) value of \( 10^{-4} \) cm\(^2\) s\(^{-1}\). Although intragrain diffusivity values are generally in the order of \( 10^{-6} - 10^{-8} \) cm\(^2\) s\(^{-1}\), it has been accepted by Duo et al (1993), that derived values can vary by orders of magnitude. Thus, the above value of \( D_g \) could be generally accepted. In fitting the 827°C experimental results, the \( D_g \) value of 10 cm\(^2\) s\(^{-1}\) used by McLaughlin, was rejected as an unreasonable figure, being even bigger than the intrapellet diffusivity, \( D_p = 0.34 \) cm\(^2\) s\(^{-1}\). Re-evaluating McLaughlin’s parameters to fit the experimental data at 827°C and in order to avoid negative conversions, \( K_{s1} \) was assigned the value of 10000, instead of the value of 3.33 assigned by McLaughlin. \( k_{s1} \) for the high-acid run, could best fit the experimental profile with a value of 2.11x10\(^{-5}\), whereas for the non-acid run it was 2.11x10\(^{-2}\) cm s\(^{-1}\), comparable to McLaughlin's value, 1.87x10\(^{-2}\) cm s\(^{-1}\) (Table 5.2).

\( K_{e2} \) for the 600 hr high-acid run, can take any value greater than 2000 and the theoretical profile will fit the experimental curves within the experimental error bars (Figure 6.2). This implies that under these conditions reaction 2 is not limited by equilibrium. The curves generated for values 5000 - 20000 were considered better fits compared to the 2000 fit. \( k_{s2} \) seems to be important in fitting the tail of the experimental alkali uptake curves, and the best value estimated was 0.7 cm s\(^{-1}\). Fitting the 827°C results, the same \( k_{s2} \) value with McLaughlin (1000 cm s\(^{-1}\)) was used, whereas the \( K_{s2} \) was given the value of 10000, as negative conversions were obtained for the second reaction at this temperature for the value of 5000 suggested by McLaughlin.
Figure 6.1: Computer Generated Sodium Bed Profile from the Alkali Sorption Model fitted to Experimental Data from the 600 hr Fixed Bed Run.
The most important parameter of all, appears to be $D_{g2}$. As the same solid sorbent (Fuller's Earth) was used, the solid product and effectively the intragrain diffusivity were expected to be the same for all the runs. The optimum $D_{g2}$ value established for the 200 and 400 hr runs was $3.8 \times 10^{-5}$ cm$^2$s$^{-1}$, whereas for the 600 hr run it was $2.0 \times 10^{-5}$ cm$^2$s$^{-1}$. The result from the 600 hr run in terms of the characteristic dimensionless groups used in the model (Chapter 4), can possibly show that diffusion in the grain product layer starts controlling the overall process ($\sigma_g^2 = 11.66 \approx 12$ and $\sigma = 0.37$). For the 200 and 400 hr runs, although the diffusion in the grain product layer seems to contribute to the overall process, the reaction kinetics and the diffusion in the pellet play a more important role ($\sigma_g^2 = 8.75$ and $\sigma = 0.36$).

However, if the intragrain diffusivity estimated from the 400 hr run had been used to predict the 600 hr run profile (Figure 6.3), the theoretical profile would have been steeper than the experimental one. This could be a problem for scale-up calculations. The difference observed could be attributed to the different size pellets used for the runs. The two sets of pellets used
were also found to differ in their grain radius. The time for a conversion or complete conversion, which is measured in the experiments, is directly connected to $r_g^2/D_{g2}$ and not $D_{g2}$ alone. Consequently, if the grain radius measurement is in error, the $D_{g2}$ prediction would also appear to vary as well. However, it seems likely that the value of $D_{g2}$, which best fits all the experimental data, will be in the range $3.0 \times 10^5 \pm 1.0 \times 10^5 \text{ cm}^2\text{s}^{-1}$. The intragrain diffusivity value used for the 827°C results, $1.64 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, is in the same range as the value that McLaughlin suggested, i.e. $1.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$.

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**Figure 6.3:** Effect of using the $D_{g2}$ value of the 400 hr run and $r_g = 20 \text{ μm}$ to predict the sodium concentration profile of the 600 hr high-acid run.

The parameter values extracted by curve fitting should be used with caution as for example, the model would fit equally well the experimental data with two different sets of parameters, initially with $K_{el}=76$ and $k_{el}=0.2 \text{ cm s}^{-1}$ and later with $K_{el}=5000$ and $k_{el}=0.0002 \text{ cm s}^{-1}$. This clearly illustrates the problems of modelling complex processes and could have an impact on the interpretation of the optimum fitted parameter values. For reaction 1, the initial set of parameters would make the reaction equilibrium limited, whereas the latter set would make it reaction-rate limited. With the latter set of parameters, both reactions have equal equilibrium.
constant groups ($K_{s1}=K_{s2}=5000$) and under non-acid conditions, comparable reaction rate groups ($k_{s1}=0.2$ and $k_{s2}=0.7$ cm s$^{-1}$). $k_{s1}$ under high-acid conditions, is low, 0.0002 cm s$^{-1}$, indicating that the reaction rate group could be affected by HCl concentration. However, the intragrain diffusivity values through the product layers, albite and nepheline, seem to differ by two orders of magnitude, $D_{g1}=0.001$ cm$^2$s$^{-1}$ and $D_{g2}=2.0\times10^{-5}$ cm$^2$s$^{-1}$, which could mean that intragrain diffusion could be more significant in albite than nepheline.

Although extrapolation of the fitted parameters was considered initially, it should be kept in mind that the alkali sorption system is quite complex and as it is represented by two simultaneous reactions, it would be expected that simple extrapolation for the evaluation of each reaction's parameters separately could be quite unreliable. Besides, the optimum fitted parameter values obtained during this work for McLaughlin's runs at 827°C and 927°C were not the same with McLaughlin's best fit, and since the experimental data at high temperatures were not very accurate, extrapolation is not recommended with these data.

### 6.4 Sensitivity Analysis of the Model Parameters

**a) Effect of gas film mass transfer coefficient ($k_g$)**

The gas film mass transfer coefficient, $k_g$, is a function of the Sherwood number, the molecular diffusivity and the pellet radius (Eq. 4.36). As $Sh$ has been calculated from the Wakao & Funazkri correlation (Eq. 4.33) and the molecular diffusivity from the published data, an error of 10% could be involved in the prediction of $k_g$.

From Table 5.3, it is shown that the model is not very sensitive to $k_g$, which was expected, as $k_g$ has already a significant value under the experimental conditions of this work and its contribution to $t'$ was earlier shown not to be significant, apart from short times during an experiment.

**b) Effect of Molecular Diffusivity ($D_m$)**

The method of calculating molecular diffusivities using parameters obtained directly from
experimental diffusion data (Fuller et al, 1966) probably has a higher accuracy than methods using parameters obtained by independent means (where errors with experimental data can reach ~22%). However, it should be pointed out that accurate experimental diffusion measurements are difficult to make and that most observations are subject to a fair amount of experimental uncertainty. The typical error is probably of the order of 5% (Fuller et al, 1966). It is obvious that if the above diffusivity values are susceptible to errors, the model's sensitivity to these values should be evaluated.

By changing the molecular diffusivity, \(D_m\), or the intrapellet diffusivity, \(D_p\), by ±10% of the calculated value, the sensitivity is very small indicating that the model is not very sensitive to these parameters. This means that even the Fuller's Earth pellets are not quite porous, the reactants do not encounter difficulties in diffusing and reaching the grains.

c) Effect of pellet size \((R_p)\)

For the laboratory conditions, it was shown above that the intrapellet diffusivity would not affect the theoretical results for the porous pellets used. Consequently, the model should be insensitive to perturbations of ±10% in the pellet size. This is confirmed by the small independent sensitivity of the model to this parameter. It should be noted that the group of parameters, \(k_g\), \(D_m\) and \(R_p\), are all interconnected in the modified Sherwood number and consequently perturbing each one separately will have a similar effect on the model's performance. Also, even though under the specific experimental conditions their effect may be insignificant, they are incorporated in the model, since under other conditions, e.g. scale-up calculations, they may be important. One example is Figure 5.12, where the Na uptake profiles are affected when the pellet size changes from 3 to 10 mm. This could be expected because the pellets are getting big enough for intrapellet diffusion to start dominating the performance of the process.

d) Effect of grain size \((r_g)\)

The effect of the grain size on the results of the simulations was pronounced when the same optimised parameter values were used for fitting the 200, 400 and 600 hr experimental uptake profiles. The optimum intragrain diffusivity value obtained for the 200 and 400 hr runs would
not fit the 600 hr run (Figure 6.3) unless the grain radius was given a value of 27 µm, bigger than the 20 µm measured value and bigger than the 15 µm, value used for the 200 and 400 hr runs. The sensitivity of the model to the grain radius is apparent as sensitivities of ~130 and 75 are obtained with a perturbation of ±10% respectively from the measured value of 20 µm.

The fixed bed results showed that the uptake of the first layer for the 400 hr run (4.35 % wt) was more than the corresponding uptake for the 600 hr run (3.68 % wt). This could be attributed to the different grain radii used in the two runs and the grain radius is incorporated in the reaction rate expression. Daoudi et al. (1991) also found that conversion levels increased as grain size decreased in experiments performed on the reaction of HCl with fully calcined commercial limestone particles.

A Coulter Counter measurement of Fuller's Earth powder has given a rough idea of the grain sizes that should be expected. Almost 50% by volume of the powder particles were smaller than 25 µm and 80% smaller than 45 µm. However, the grain size distribution could change once the grains are agglomerated and calcined to form pellets. Grain sizes in pellets could be measured accurately from the secondary electron images obtained by SEM. Electron microscopy is a particle-sizing technique in which individual particles are observed and measured, but in this case the instrument was found to be incorrectly calibrated and the images were of no direct use.

However, the secondary electron images of Fuller's Earth pellets obtained by SEM have been examined using an image analysis package to measure the grain radius, and hence the distribution of grain sizes in the pellets. These measurements were based on the convention of taking the major axis to represent the grain diameter. This is an arbitrary convention which may result in some systematic errors. The distribution illustrates the non-uniform grain sizes in Fuller's Earth pellets (Figure A.VI.2), which is also illustrated in the SEM digital maps i.e. for the 200 hr run, where the smaller grains are completely converted, whereas the big grains are only partially converted. This implies that the mean effective grain size would increase with time. The size distribution obtained by the image analysis package could be represented by the Rosin-Rammler or log-normal distribution (Allen, 1981) (Figure A.VI.3). Szekely and Proster (1975) have shown that the rate of conversion for pellets produced with grains having a log-normal size distribution is not significantly different from that of pellets.
produced from grains of the same size. However, for this system the grain-size distribution has to be incorporated in the model and further examined in order to give a definite answer on the effect of the non-uniform grain size on the process.

The grain sizes of the resin-mounted pellets used for SEM were also measured by an optical microscope. The measurements of grain sizes of the two pellet sizes used showed that the smaller pellets have a grain diameter of 30±3 μm (200 & 400 hrs), and the bigger ones a grain diameter of 44±10 μm (600 hr runs) (Table A.VI.1). Although this method cannot be very accurate, because the selection of the grains measured was random and the number of measurements was small, it can still give some idea of the grain size.

e) Effect of water vapour

McLaughlin (1990), using the Szekely approximation for the pellet-grain model, has effectively incorporated the water vapour concentration term in $K_e$ and $k_s$. As a result, the $K_e$ and $k_s$ values estimated, are characteristic of the water concentration in the system. The water vapour concentration used at 827 and 927°C experiments as well as the 650°C runs, was 5 %vol. This value was used throughout the experimental work because it was of industrial interest. For this reason and due to the long duration of the fixed bed tests, especially at 650°C, no fixed bed tests without water or with different water concentrations were performed.

Under the low Na concentrations of the 650°C runs, the rate of reaction could be safely considered as zero order in H₂O, because this was in such abundant supply that its concentration was nearly constant throughout the experiment. However, experiments are required to determine the effect of water on the reaction and the equilibrium constants.

f) Effect of superficial velocity (u)

The superficial velocity determines the volumetric flow rate of the inlet gas and consequently the quantity of NaCl that enters the fixed bed reactor. The volumetric flow rate was always measured before and after the experiments, to ensure that the maximum error did not exceed ±1%. In addition, as mentioned in Section 6.1.2, the temperature of the high precision flow
controllers and supply pressure regulator was kept stable in order to minimise the fluctuation in the gas flow rate caused by ambient temperature changes. The closure of the sodium mass balance also indicates that the superficial velocity has been determined accurately. From the sensitivity analysis it is shown that if the error is large (±10%), e.g. a major leak in the system has occurred, the fitting of the experimental and theoretical concentration profiles is going to be seriously affected.

g) Effect of interpellet (ε_i) and intrapellet (ε_p) porosity

Perturbing the bed voidage by ±10% does not affect the model's performance very much under the laboratory conditions but it will affect the pressure drop in full-scale fixed beds. Changing the pellet porosity by ±10% does not have a significant effect on the theoretical Na concentration profiles. This result agrees with the model insensitivity to the intrapellet diffusivity, because diffusion through the pellet does not present a significant resistance to the sorption process under the experimental conditions.

h) Effect of mass of solid per unit length of bed (\( \omega_{A_s} \)) and sorbent molar density (\( \rho_s \))

The mass of solid per unit length of bed can be determined accurately by experiment. This is confirmed in Table A.II.9, where the experimentally measured distances with a travelling microscope are compared with the distances calculated from the measured mass of solid per unit length of bed and these values agree to within ±0.01 cm. The sorbent molar density is less certain and could vary by ±10% since the value used was supplied by the manufacturers. The sensitivity analysis (Table 5.3) showed that such a big change in this parameter would affect the concentration profile significantly, since this quantity represents the amount of sorbent in the bed.

i) Effect of stoichiometric coefficients (b_1 & b_2) and sorbent saturation capacities (K_1 & K_2)

As the reactions are written, the stoichiometric coefficients of the solid reactants, b_1 and b_2, were taken as 1.0, although for the solid product of reaction 1, nepheline (Na_2O.Al_2O_3.2SiO_2), the sodium content is three times higher than for albite (Na_2O.Al_2O_3.6SiO_2), which is the solid product of reaction 2. Perturbing the stoichiometric coefficients by ±10%, showed a
significant effect of \( b_2 \) on the high-acid results, where the second reaction is taking place. This agrees with the above observation that albite has a lower sodium content compared with nepheline, and may indicate that \( b_2 \) could be different from unity; a point which should be borne in mind.

The sorbent saturation capacity for Na was experimentally measured by McLaughlin but it needs further investigation across the experimental range of temperature (650 - 927°C), since it is an important parameter for scale-up and process economics. The total capacities measured at 827°C from McLaughlin, 12.5 %wt, based on reacted solid material, or 14.5 %wt, based on initial solid, generally agrees with the value obtained from fixed bed tests at 650°C, 14.6%wt, which is based on initial solid. However, the capacity of the second reaction, 4.7 %wt, still seems to be under question as already discussed taking into account Figures 5.6,5.7.

j) Effect of NaCl inlet concentration

Increasing the NaCl inlet concentration, a faster uptake would be expected. Eventually at high NaCl concentrations, a plateau should start to form as the Na uptake reaches the saturation capacity of the solid. These effects as predicted from the present theory are shown in Figure 6.4. The NaCl inlet concentration is a measured value and great care was taken so that the experimental error would not be more than ±2%.

k) Effect of number of tanks and time steps

In this work, the effect of axial dispersion has been taken into account by the selection of the number of tanks used in the numerical solution. Ideal plug flow is approached and the effective axial dispersion decreases as the number of tanks increases. As a result, a sharper concentration profile and stiffer equations are expected as the number of stages increases. The smaller the number of tanks, the more the concentration profile flattens because the effect of axial dispersion increases.

In making the tanks-in-series approximation, a Taylor's series expansion has been truncated before the second order term, which can be considered as an "apparent axial dispersion" term, which simulates the actual axial dispersion (Nagaev, 1974).
As a result, when the number of tanks is small, e.g. \( N = 5 \), the second order term becomes significant and effective axial dispersion becomes more pronounced (Figure 6.5). The model appears to be unaffected by the size of time steps used, at least in the scale of \( \pm 10\% \). For very big time steps, it was observed that the Na mass balance would not close.

![Graph showing NaCl concentration in the bed](image)

**Figure 6.4**: Effect of changing the NaCl feed concentration to the 600 hr high-acid run

1) **Effect of pressure**

All the experiments were performed at atmospheric pressure because this makes the apparatus simpler, since leaks in the system should be limited to a minimum. Minimisation of leaks is quite important as an incorrect alkali mass balance can lead to false conclusions about the sorptive capacity of the getter. As pressure was incorporated in the model, a theoretical concentration profile was obtained for the laboratory reactor at 24 bara with the same superficial velocity, 10 cm s\(^{-1}\), used in the experiments (Figure 6.6). This prediction will again be sensitive to all the assumptions concerning the reaction kinetics and equilibria.
Changing the equilibrium groups \( (K_1 \text{ and } K_2) \) values ±10\% (Table 5.3), did not seem to make much difference as the value of 5000 seems to be high enough to keep the two reactions far from equilibrium. The reaction rate group \( (k_{s1}) \) for reaction 1 slightly affects the tail of the concentration profile for the non-acid run, while it does not affect the high-acid results. This was expected as the first reaction does not take place to any significant extent under high-acid conditions, where the second reaction parameters should be more significant. The reaction rate group \( (k_{s2}) \) for reaction 2 only affects the tail of the profile of the high-acid run, while it does not seem to affect the non-acid results, since the first reaction is more pronounced under these conditions. Perturbing the intragrain diffusivity for reaction 1 by ±10\% does not affect the concentration profile of the non-acid run as the first reaction, indicated by the shape of the profile, is reaction-rate limited, while the same diffusivity for reaction 2 affects the profile of the high-acid run quite significantly, indicating that the process is diffusion limited under these conditions.
6.5 SCALE-UP

The scale-up calculations for the reactor dimensions were performed on the basis of constraints set by the required bed pressure drop (<1 bar), the appropriate bed length/pellet diameter ratio to minimise the effect of axial dispersion, the appropriate bed/pellet diameter ratio to minimise radial dispersion, the superficial velocity (30 cm s\(^{-1}\)), the inlet alkali concentration (129.4 ppb wt Na+K), the required outlet alkali level (70-100 ppb wt Na+K) and the proposed operating times for the commercial sorbers (8000, 16000 and 24000 hrs) (Fantom, 1993).

The scale-up of the alkali removal process at 600-650°C and 24 bara, was based on the fixed bed sorption model, which assumes that the system is isothermal and there are no significant radial concentration and velocity gradients. The significance of the axial dispersion decreases
generally as the superficial velocity and the length of the reactor increase, and it increases with the pellet diameter. In most cases, axial dispersion can be considered negligible. The smallest axial Peclet number calculated for this system is 300, which corresponds to an intermediate amount of axial dispersion. N₂ was considered as the bulk, carrier gas for scale-up, since it was used throughout the experimental work. Fuel gas contaminants (Mulik et al, 1986), in particular tar components, do not apparently affect the sorbent's alkali performance on the basis of the results with the Fuller's Earth pellets that have been carbon-coated.

For a 4 m diameter sorber, the proposed reactor lengths are 1.5 m for 8000 hrs of operation, 3 m for 16000 hrs and 4 m for 24000 hrs (Table 5.4). The highest outlet alkali concentration would be highly affected by the HCl concentration and the water vapour content in the coal-derived gases (Tables 5.5, 5.6). For the proposed 129.4 ppb wt alkali feed concentration, 942 ppmv HCl feed concentration and \( K_{s1}, K_{s2}, k_{s1}, k_{s2} \) calculated by the laboratory optimum values and the 15 %vol \( H_2O \) vapour feed concentration in the full-scale reactor, the highest outlet alkali concentration predicted is ~18 ppb wt.

### 6.6 SUMMARY

The results indicate clearly that the modifications to the fixed bed rig proved successful and the care taken during the experiments for the determination of sodium uptake was worthwhile. Since the accuracy achieved for the experimental results was very high, they provided a strong basis for testing the theory. The single-layer tests gave a strong indication of the relative gettering capacities between Fuller's Earth, kaolin and gasifier-pretreated Fuller's Earth pellets, while the fixed bed tests with Fuller's Earth were used for the extraction of the parameter values that describe the process.

SEM images strongly supported the idea of representing the alkali uptake by Fuller's Earth with the pellet-grain model, since the porous pellet structure was formed by grains of irregular shape and non-uniform size. These images also show the alkali sorption to follow the shrinking core pattern within the grains. Exit gas analysis measurements proved that the HCl production was directly connected to the alkali concentration in the system, while the presence
of water significantly increases the rate of uptake. However, the exact role of water in these reactions remains uncertain and more experiments with different concentrations of water and NaCl are necessary in order to specify the order of reaction with respect to these reactants. X-ray studies identified albite to be the solid product of reaction 2 and nepheline as the solid product of reaction 1, which generally agrees with the observations of other researchers on the solid reaction products of the alkali retention process by aluminosilicates. At 650°C it would appear that either reaction 1 occurs under non-acid conditions or reaction 2 occurs at high-acid conditions. Further experiments at intermediate HCl concentrations are required to show if these reactions are really in parallel or in series.

The fixed bed alkali sorption model, which incorporates the pellet-grain model and the tanks-in-series method of solution for the Na and HCl convective mass balances in the fixed bed, proved capable of fitting the experimental profiles at the temperature range of 650-927°C. To reveal the possible uncertainties involved in the pellet-grain model and the numerical methods used in McLaughlin's computer program, a new program was developed using the Gear's method, a variable-time-step, variable order numerical method to solve the stiff system of the differential equations that describe the bed and pellet performance. The optimum model parameter values were used as a basis for the scale-up calculations. The sensitivity analysis performed on the model parameters showed a number of parameters that can significantly affect the model's performance. The sensitivity to measured parameters such as superficial velocity, mass of solid per unit length of bed and NaCl inlet concentration justifies the effort during this work to reduce the experimental errors. Measured parameters that still need further investigation are the Na saturation capacities and the grain size, where the mean grain size used in the model should possibly be introduced as a grain size distribution, in order to represent reality more accurately. From the fitted parameters, the model is more sensitive to the stoichiometric coefficient and the intragrain diffusivity for reaction 2 under high-acid conditions.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The application of the advanced clean coal technologies is critically dependent on improvements in gas turbine technology and the development of hot gas cleaning techniques. Studies on alkali salt vapour removal at high temperatures, 827 - 927°C, were carried out by McLaughlin (1990) under the Contaminant Control Programme for the development of the British Coal Air-Blown Gasification Cycle, since alkali salt vapours were found to seriously corrode the gas turbine components. Fuller's Earth, an aluminosilicate proved to be an efficient sorbent for the removal of alkali vapours from hot gases with packed beds. However, the development of hot gas cleaning techniques with ceramic filters for the removal of the fine particulate matter, have now focused on the temperature range of 400 - 600°C because of equipment failure at higher temperatures. At these temperatures, most of the alkali chloride vapour, which is the predominant alkali species in gasifier product gas would be expected to condense on the particulate matter and be removed by filtration.

However, since gas cleaning techniques are under development, a complete alkali vapour removal study in the temperature range of interest, 600-927°C, was necessary and further work at the lower temperature of ~600°C needed to be performed. As a result, at the temperature of 600°C, the application of the fixed bed sorption method and the suitability of Fuller's Earth and kaolin as alkali getters, needed to be checked. The alkali sorption model should be revised and confirmed and the uptake mechanism should also be investigated by detecting the HCl concentration in the fixed bed effluent.

A fixed bed run for NaCl on Fuller's Earth over 240 hrs at 600°C clearly illustrated the difficulties of working at this temperature. The amount of NaCl entering the bed was very low 0.82 ppm wt Na. Consequently, it was unlikely that bed profile modelling could be effective using these results. Increasing the temperature to 650°C increased the sodium concentration at the inlet to the bed to 1.8 ppm wt Na making the system experimentally practicable, although run times had to be eventually extended to 600 hrs. The combination of the above
two modifications allowed accurately measurable sodium profiles to develop within the bed of Fuller's Earth pellets.

The fixed bed rig has proved capable of stable operation for up to 600 hrs at 650°C with a constant alkali vaporisation rate of 0.3 mg hr⁻¹. Operating conditions can be adjusted to virtually eliminate temperature gradients for a getter bed depth of 10-15 mm. The accuracy of sampling the bed has been improved to ±0.1 mm. Alumina wool filter pads downstream of the bed are effective exit gas alkali traps and sodium mass balances have been closed to better than 99%. The analytical method for quantitative determination of alkalis in getter pellets has been substantially modified to meet current safety standards without loss of accuracy. The resulting alkali uptake profiles derived from analysis of the fixed getter bed are consequently of very high quality.

Single-layer and packed bed experiments lasting up to 600 hrs were performed at 650°C, under atmospheric pressure and a gas inlet composition of 4.58 ppm wt (2.2 ppmv) NaCl, 5 %vol H₂O and 0 - 160 ppmv (0-208 ppm wt) HCl with nitrogen as the carrier gas. In addition, single-layer tests of 200 hrs, provided a simple way of avoiding the complications of a fixed bed, to evaluate the sorbent's capacity for sodium vapours at 650°C and for evaluating two sorbents simultaneously by using a mixed layer. While Fuller's Earth exhibits a characteristically reduced uptake in the presence of acid, kaolin does not seem to be seriously affected. Fuller's Earth pellets which had been pre-treated in a gasifier and which were therefore coated in carbon were also tested. These pellets showed the same sodium uptake values as clean Fuller's Earth pellets used for all the other runs. This indicated that the carbon deposition in the gasifier may not affect the sorption capacity.

Fixed bed tests of 200, 400 and 600 hrs performed with 10-15 mm beds of Fuller's Earth pellets exhibited well developed profiles for the non-acid and high-acid 600 hr runs. A maximum uptake value of 14.6 %wt was obtained without acid, whereas a 3.8 %wt uptake was obtained with 160 ppmv HCl. These uptake values are similar to the values obtained by McLaughlin under similar conditions. The reduced uptake under high-acid conditions confirmed that the previously observed inhibitory effect of HCl was also present at the intermediate temperature of 650°C. The experimental outlet sodium concentration obtained from the chemical analysis of the alumina wool pads downstream of the fixed bed, was found to be 5.5 ppb wt. A KCl high-acid, fixed bed run exhibited a maximum uptake value of
2.75%wt and a concentration profile along the bed not identical to the corresponding NaCl one.

SEM/EDS/WDS digital element mapping proved to be a highly effective technique for the study of alkali uptake within pellets. Shrinking core behaviour is evident in the grain structure of Fuller's Earth, but not for the overall pellet. The reverse is true for kaolin. Linescans performed across Fuller's Earth grains, also support the shrinking core model for grains. X-ray images obtained on the light- and dark-coloured pellets observed at the 600 hr non-acid run, did not indicate any difference in the alkali sorption pattern. Consequently, the difference in colour was attributed to impurities in the pellets. Carbon deposited on pellets pretreated in the CRE gasifier did not inhibit alkali sorption. The shrinking core behaviour is also evident for potassium sorption by Fuller's Earth. Comparing the secondary electron images of untreated and treated pellets, a structural change was not obvious at the temperature of 650°C, even after pellets were exposed to alkali vapour for 600 hrs. Unfortunately, no measurement of the specific surface area was obtained on the treated sorbent since the required quantities were bigger than the available sorbent after the chemical analysis for the determination of the alkali uptake.

The two-reaction scheme suggested by McLaughlin (1990), has been applied to the alkali sorption process at 650°C and the theoretical profiles could fit the experimental results at both non-acid and high-acid conditions. However, the 650°C profiles did not show the characteristic 'knee' shape of the non-acid profiles at 827 and 927°C. X-ray studies have indicated the formation of albite under high-acid conditions and of nepheline under non-acid conditions. It is possible that both nepheline and albite were produced in the absence of HCl, but that only nepheline could be detected because the nepheline effectively masked the presence of albite using the current methods. However, there is evidence from this work that one reaction applies in the absence of acid leading to the production of nepheline and a second reaction applies in the presence of HCl which has a greatly reduced sodium capacity and leads to the production of albite. At 650°C, there is no direct evidence that both reactions occur either in parallel or series. The bed profiles do not show the 'knee' at 650°C which led to the development of the two-reaction theory at 827°C and 927°C.

The reaction mechanism was studied with fixed bed runs, where the HCl concentration was
measured approximately at the bed exit with an on-line HCl monitor. It has been confirmed that HCl is produced when both NaCl and H₂O vapour are present in the system. However, the HCl concentration measured was lower (~3 ppmv) than the expected (~5 ppmv) value calculated from the NaCl feed concentration (~5 ppmv).

NaCl seems to be physisorbed on Fuller's Earth under dry conditions. Although the presence of water vapour in the system was found to increase significantly the rate of uptake, the detailed mechanism of the reaction has not been investigated. The uptake under dry conditions cannot be attributed to hydroxyl groups that have not been lost during calcination alone. A study in which the calcined Fuller's Earth was rehydroxylated with water and then exposed to NaCl in dry gas was conducted. The resultant sorption of NaCl exceeded the capacity of the hydroxyl groups created. This study indicates that NaCl and water must be present simultaneously for the effective sorption of sodium.

The alkali sorption model, which combines the tanks-in-series approximation for the convective mass balance in the fixed bed, with a pellet-grain model for the gas-solid reaction occurring within each sorbent pellet, originally derived by McLaughlin from high temperature studies, has been revised and modified to take account of pressure and temperature effects. It can work now for any pressure and for temperatures where experimental work has been done; at 650, 827 and 927°C, and at 600°C, where there is industrial interest for gas cleaning in the Air-Blown Gasification Cycle.

During the revision of McLaughlin's model, a number of uncertainties over the assumptions made and the numerical methods used, were revealed. The most important issue, which was revealed through experimenting in gPROMS, a dynamic simulation environment, was over the reaction reversibility. In the Szekely approximation for a reversible gas-solid reaction, equilibrium can be approached only from one side and if conditions subsequently change to reverse the reaction, the model can erroneously predict negative conversions. Therefore, if a reaction is required to be fully reversible, the Szekely approximation would not be appropriate for predicting the pellet conversion.

A new computer program has been written using the variable-time-step, variable order, Gear's method, to solve the system of 4N equations that account for the Na and HCl convective mass
balances in the N tanks of the fixed bed and for the alkali uptake by the sorbent pellets with the two-reaction mechanism. Temperature and pressure effects were incorporated in the program, so that it can work for any temperature and pressure. The only problem with the new program is that the quantities to be solved, the gaseous reactant and product concentrations and the pellet uptake concentrations, constitute a stiff system. Stiffness will increase even more when the system approaches plug flow and this will increase the computational time required for solution. However, since under the conditions checked, the two programs can give the same answer, the McLaughlin program can be considered a valid approximation of the alkali sorption process under most circumstances.

The pellet-grain model has been independently checked in simulating in time a single pellet alkali uptake. The Szekely approximation for the pellet conversion was solved using the Newton-Raphson method as in McLaughlin's program. The comparison of the analytical and the numerical estimation of the rate of reaction has shown that while the analytical value would be sensitive to a fast reaction, like the second reaction whose rate is changing quite rapidly in short times, the numerical value would be insensitive. This proves that the Newton-Raphson method can be safely used for a single pellet simulation where the gaseous reactant concentrations are assumed constant around a pellet. In order to minimise the errors arising from this assumption for a fixed bed, small time steps have to be used. The Na mass balance would not close for large time steps (e.g. 100 hrs).

An optimum set of equilibrium constants, reaction rate constants and intragrain diffusivities ($K_e$, $k_s$ and $D_g$) for the two-reaction scheme has been obtained by fitting the experimental with the theoretically produced Na concentration uptake profiles. A sensitivity analysis of the model parameters has revealed that the model predictions are most sensitive to parameters such as the superficial gas velocity, the sorbent bulk and molar density, the grain radius, the saturation capacities of the two reactions, the feed NaCl concentration and from the fitted parameters, the stoichiometric coefficient and the intragrain diffusivity for reaction 2 under high-acid conditions. The high sensitivity of the model to these parameters justifies the efforts to minimise the experimental errors.

Secondary electron images of the grains in a pellet have indicated that the Fuller's Earth pellets are made of non-uniform size grains. A drawback of the grain model is that a uniform
grain size had to be postulated in order to express the governing equations in a readily soluble form. The effect of the grain size on the model was pronounced at high-acid conditions, where intragrain diffusion predominated and the intragrain diffusivity could not take the same value to match the 200, 400 and 600 hr runs. The grain radius required to simulate the 600 hr run was 27 μm for the same intragrain diffusivity, considerably larger than the corresponding 200 and 400 hr grain radius value, i.e. 15 μm. Pellet structure images obtained by SEM via an image analysis package, have given a grain-size distribution based on the number of grains measured on the cut plane of a pellet. The measured distribution seems to follow the Rosin-Rammler distribution.

Scale-up simulations have indicated that exit gas alkali levels of below 20 ppb wt should be obtained with a 4 m bed length of 3-10 mm diameter pellets in a 4 m diameter reactor at 25 bar operating continuously for up to 24000 hrs under the operating conditions specified by CRE. The main features of the operating conditions are a total alkali concentration of 129.4 ppbv, 15 %vol H₂O vapour and 942 ppmv HCl (dry basis). These predictions are based on data obtained at 650°C. In a full-scale reactor, bigger pellets compared with the laboratory conditions, are used and diffusion through the pellet could present a significant resistance. Hence, in the full-scale reactor, the idea of a pellet-size distribution would be relevant where it is not relevant in the laboratory test particles.

In summary, the fixed bed sorption has been proved to be an effective method of alkali vapour removal at the intermediate temperature of 650°C. The inhibitory effect of HCl has been observed at this temperature. The alkali sorption model derived from the high temperature experimental results, has been successfully applied at 650°C. A new computer program was developed to solve rigorously the McLaughlin model. The model parameters were evaluated by fitting the theoretical Na uptake profiles along the fixed bed with the corresponding experimental results. These values have been used for scale-up calculations. The two-reaction scheme seems to describe satisfactorily the alkali sorption process in the temperature range of 650-927°C.
7.2 RECOMMENDATIONS

According to the conclusions made from this research project, further investigation can be recommended on the following subjects:

1) As the single-layer tests indicated that kaolin appears to perform very well as an alkali getter at the temperature of 650°C, fixed bed tests are necessary to confirm these preliminary results. The product of the reaction with kaolin needs to be determined and the reaction equilibria and rates need to be measured. Further studies will be required to determine if real operating conditions preclude the use of kaolin. For instance, the effect of carbon deposition on the kaolin pellets needs to be investigated to ensure it does not inhibit the reaction with sodium.

2) The saturation capacity of Fuller's Earth for Na was measured by McLaughlin to be ~14.4%. Since these experimental results were not very accurate, the performance of the model seems to be sensitive to the saturation capacities of the two reactions and the sorbent's saturation capacity is an important parameter for scale-up, further investigation is necessary to measure accurately these quantities. These studies can be performed in a small laboratory reactor (possibly a simple batch reactor) but for very long run times (e.g. 1000 hrs).

3) The specific surface area (BET) should be measured from pellets before and after treatment in order to confirm that there is no loss of surface area during reaction. This again should be especially important to ensure there are no structural changes when pellets are exposed to sodium for very long periods of time.

4) Further experiments, at intermediate HCl concentrations are required to show if these reactions are really in parallel or in series, since under non-acid conditions only nepheline was identified, instead of the combination of both nepheline and albite that was expected.

5) Experiments to investigate the reversibility of the uptake reactions, when fixed beds that have already been exposed to sodium are exposed to a high feed HCl concentration. This would be an important observation since the Szekely approximation cannot be applied simply if the reactions are truely reversible.
6) Further investigation of the role of water in the reaction scheme and the order of reaction with respect to water vapour and NaCl is necessary. In order to find the order of reaction, TGA or fixed bed tests with different water and NaCl inlet concentrations have to be performed.

7) To improve the speed of the new computer program, an investigation should be conducted where the concentration gradients of the gaseous reactants and products are kept constant when solving for the pellet fractional conversion and then vice versa. This might eliminate some problems caused by the stiffness of the system of equations, since these phenomena occur on quite different time scale.

8) Size distributions for the pellet and the grains should be incorporated into the model. In the laboratory scale studies described in this work, the pellets were too small to represent a significant resistance to mass transfer, but in commercial units the requirement to minimise the pressure drops will ensure much larger and less uniformly sized pellets will be used.
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APPENDIX I

DESCRIPTION OF THE FIXED BED SORPTION RIG

A.I.1 Description of the main parts of the rig

The Fixed Bed Rig, Figure A.I.1, used for the evaluation of alkali sorption characteristics of aluminosilicates like Fuller's Earth and kaolin, consists of the following parts:

- The microbalance head is mounted in a temperature controlled enclosure containing a heating element and fan in order to eliminate the effects of variations in room temperature. The operating temperature is 35±0.5°C.

- The Vapour Generator: an ultra-pure (>99.95%) alumina tube of 17 cm length and 1.2 cm i.d., in which a NaCl crystal is suspended in a N₂ gas stream (110 cm³·min⁻¹) by an R-type thermocouple from a 5 g capacity microbalance (CI Electronics). The crystal temperature is recorded via 0.001" wires connected to the thermocouples used to suspend the crystal from the microbalance. These thin wires are required to minimise any effect on balance performance. The crystal temperature is determined by the heater outside the alumina tube. The heater's temperature is controlled by a programmable CRL temperature controller.

The crystal is drilled at the bottom to fit over the thermocouple junction and at the top for a Pt wire to keep it in position. This way, the crystal temperature can be directly measured. The weight of the crystal used, depends on the duration of the run. For a 600 hr run, the crystal weight should be not less than 200 mg, as the experiment requires 180 mg NaCl vapour to be produced. The alumina tube ends to a nozzle of 5 cm length and 0.23 mm diameter, which is required for jet mixing of the gas streams (McLaughlin, 1990). The nozzle is also made from ultra-pure alumina.

To cut down heat transfer to the balance head from the heaters below, a water cooled heat exchanger connects the alumina tube to the microbalance with "Viton" neoprene O-rings, providing a seal between the tube and the heat exchanger. An internal heater coil preheats the
Figure A.I.1: Schematic Diagram of the Fixed Bed Alkali Sorption Rig
gas entering the vapour generator.

- The Mixing Section: an alumina (96%) tube of 17.5 cm length, between the Vapour Generator and the Bed Section. The two ceramic tubes are of the same diameter and are connected with a polished spring compression butt joint. In this tube, the NaCl vapour stream is mixed with the main gas stream, N\textsubscript{2} (carrier gas) with 5 %vol H\textsubscript{2}O vapour, which enters the system from a heated side arm ceramic tube. Jet mixing occurs at the nozzle.

The main gas stream passes through two bubblers, which are kept submerged in a water bath at 34°C. The bath's temperature determines the percentage of water in the main gas stream. Liquid concentrated hydrochloric acid can also be injected after the bubblers’ assembly. The acid is supplied to the system by a syringe which is filled in by a small acid reservoir. Teflon valves were used throughout. The syringe is mechanically driven and injects acid into a heated gas line at a fixed flow rate. The flow rate depends on the required HCl concentration.

- The Bed Section: an alumina (96%) tube, of 20 cm length and 2.5 cm i.d., in which a fine Pt/Rh gauze supported on a ceramic disc drilled with 15 mm holes, holds the randomly packed sorbent bed. Alumina wool pads are inserted under the fixed bed to capture condensed alkali in outlet gas. The best arrangement, was three compressed pads close to the bed (85 mm from the exit of the ceramic tube) and one at the bottom of the tube, before the exit.

- a condenser system, which is fitted at the exit of the fixed bed ceramic tube, to collect the water and HCl introduced and generated into the system.

A.1.2 Control

At the ultra-pure alumina tube, there is an external heating coil, made by 1.5 mm wire, which maintains the crystal's temperature. Heating was performed by Thermocoax (Philips Scientific) mineraly insulated heater wire, sheathed with Inconel. An internal coil using 1 mm diameter wire is used to preheat the nitrogen flowing in the Vapour Generation section. The crystal's weight is monitored by a balance control unit via the CI microbalance. The weight loss rate is calculated by an Isis IBM-compatible computer, which is finally connected to the CRL
controller through an RS-232 connection. A proportional-integral control algorithm determines the appropriate temperature of the Vapour Generator to keep the weight loss rate as constant as possible.

External heating coils of 2.5 mm Thermocoax wire, are used to heat to the required temperature the mixing section and the fixed bed section. A secondary coil of 1.5 mm wire was added to the bottom of the bed section to reduce the gradient across the sorbent bed. All the heaters are connected to programmable PID controllers (West 3400 & 3750) and via them their temperature is monitored and controlled by the computer. At the 650°C experiments, the temperatures for the different parts of the rig are specified as set-points for the controllers and are given in Table A.I.1. The Vapour Generator, the Gas Inlet, the Mixing Section and the Fixed Bed Section are all well insulated with strips of alumina wool. The main gas stream coming out from the bubblers, is first preheated with warm water being circulated in a concentric to the main gas stream tube and is coming from a water bath held at ~50°C. Before it enters the side arm ceramic tube, it is trace heated with externally wound heating coil. The tubes used are made by PTFE.

A.I.3 Power Supply

The power supply to the heater coils is via two Slidup B-20 Variac transformers, set at 110V and 40V, and a Stanton-Redcroft ZUSM 207B transformer supplying 75V, 20V and 18V. A RS Variac supplies 17V to the trace heater on the gas inlet and HCl injection point.

A.I.4 Gas Supply

Nitrogen at 15 ml/min NTP is flushing the balance head and at 90-120 ml/min NTP enters through the water-cooled top. The main gas stream is 835 ml/min NTP. Gas flow control is performed by Negretti M2545 flow controllers temperature controlled. The gas composition in the system for the 650°C experiments, is 4.58 ppm wt NaCl, 5 %vol H₂O, 0, 50 or 160 ppmv HCl and N₂ as balance. The actual superficial velocity is 10 cm s⁻¹.
Table A.I.1: Temperature controller set-points for the heating elements in the rig

<table>
<thead>
<tr>
<th>Coil</th>
<th>Temperature controller set-points (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal</td>
<td>650</td>
</tr>
<tr>
<td>Salt Vapour Generator</td>
<td>640 - 660</td>
</tr>
<tr>
<td>Gas Inlet</td>
<td>600</td>
</tr>
<tr>
<td>Trace Heater</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Mixing Section</td>
<td>595 - 610</td>
</tr>
<tr>
<td>Mixing Section-Nozzle</td>
<td>670 - 710</td>
</tr>
<tr>
<td>Bed Section</td>
<td>630 - 640</td>
</tr>
<tr>
<td>Lower Bed Section-secondary</td>
<td>680 - 683</td>
</tr>
</tbody>
</table>

A.I.5 Safety

Most of the experiments have a duration of some days which requires a safety system for long term, unattended operation. The gas pressure in the balance head is monitored continuously and the gas supply will be vented to the atmosphere if the pressure exceeds 750 mm H₂O. The bed pressure drop is also monitored continuously. The temperature controllers have alarm limits, which when exceeded, shut off and lock out all the power supplies. This will also occur if the flow monitor on the outlet of the water cooling loop detected "NO FLOW" or if the mains power supply failed temporarily. All power supplies are fitted with 30 μA earth current trip.

A.I.6 Data Handling

An Isis 8086 computer logs the salt crystal weight loss rate, the temperatures of the vapour generator, NaCl crystal, gas inlet, mixing section, nozzle, fixed bed top and bottom section and microbalance head, the gas pressure inside the microbalance and the bed pressure drop, the elapsed time from the beginning of the experiment and the number of control steps made by CRL controller in order to control salt vaporisation rate. These readings can be extracted on floppy disk throughout an experiment.

One of the more serious problems of the system is to maintain gas tight seals at ceramic-
ceramic joints. A four-spring system is used to keep the joint tightly sealed and also let the two ceramic tubes be freely aligned. The gas flow rates were always checked before and after an experiment with a bubble flowmeter and the results were very satisfactory (95 - 99% sodium mass balance).

A.I.7 Performance

The consistency of the experimental apparatus and method were checked by the 200, 400 and 600 hr experiments at 650°C (923 K) with 4.58 ppm wt NaCl, 5 %vol H2O and 160 ppmv HCl. The almost parallel profiles of 200 and 400 hr, Figure 3.4, show the same system behaviour, where their only difference is the amount of sodium adsorbed, which in 400 hr run is double the 200 hr amount. Also, the same outlet alkali concentration of the 400 and 600 hr, 5-6 ppb wt, was another proof of the system's reproducibility.

A.I.9 Experimental Procedure

A detailed experimental procedure was developed for the operation of the fixed bed rig at 650°C, during the start-up, run time and shut-down of an experiment. The NaCl crystal is cut and drilled in order to be held in vertical position by the thermocouple and the rig is lowered to enable the crystal to be fitted to the balance hangdown. To protect the microbalance the hangdown is clamped, while the crystal is positioned on the hangdown. The rig is raised and sealed to the balance head.

The sorbent bed is prepared by fitting the alumina wool pads in the bed section and by pouring weighed calcined pellets into the bed section to a depth of 10-15 mm. This is then shaken to settle the pellets. The top is leveled by sucking layers of pellets until the required bed height obtained. The pellets are then taken out of the bed, weighed and poured back again. The bed section is manipulated into place and the heater raised around it. The bed section is hanged by a four-spring system and the ceramic-ceramic joint is sealed by the strength of the springs. The springs are holding the metal base on which the bed section is placed. The main gas stream, without H2O, is turned on and the total flowrate is checked. The settings for the flow controller are given in Table A.I.2.
The HCl injection system is prepared. The acid reservoir is filled in order to supply the acid syringe till the end of the experiment. The bubblers are filled with deionised water and the water bath with tap water. The nitrogen cylinders should be checked so that they would last till the end of the experiment. The transfer of nitrogen cylinders is avoided during an experiment because it is causing disturbances to the microbalance and eventually fluctuations to the temperature of the vapour generator if the CRL is not turned OFF. The water flowing in the heat exchanger, between the ultra-pure alumina tube and the microbalance, should also be checked to be always ON. The outlet of the gases is connected to the condenser. The liquid HCl collected there, is disposed two or three times till the end of an experiment, depending on its duration.

Finally, all the connections are checked, the power and the computer are turned on and the temperature of the rig is slowly raised (~5°C min⁻¹) till 100°C and then quicker (~10°C min⁻¹) till 650°C. The final temperatures and the ramping rates of the internal coil in the vapour generator, the gas inlet, the mixing, the nozzle and the bed section and the secondary heater of the lower bed section are set via the computer and for the external heater of the vapour generator the temperature is ramped via the programmable controller. The vapour generator temperature remains at 580°C till the whole system reaches the final temperature (~15 min). This is done in order not to have NaCl vapour in the system before the required temperature is reached. At this point and before the main gas stream starts passing through the bubblers and HCl starts being injected, a flowrate measurement is taken to make sure that the system is not leaking. The experiment starts by quickly ramping the temperature of the vapour generator from its holding temperature of 580°C to the operating temperature of 650°C.

### Table A.I.2: Flow Controller Settings

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the experiment</td>
<td>650°C</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>10 cm s⁻¹</td>
</tr>
<tr>
<td>Temperature of the Flow Controller</td>
<td>32°C</td>
</tr>
<tr>
<td>Pressure of the Flow Controller</td>
<td>2 bar</td>
</tr>
<tr>
<td>Total Flow Rate (STP)</td>
<td>950±5 ml min⁻¹</td>
</tr>
<tr>
<td>Settings for Head Section</td>
<td>11</td>
</tr>
<tr>
<td>Salt Section</td>
<td>18.19</td>
</tr>
<tr>
<td>Bed Section</td>
<td>13.15 - 13.285</td>
</tr>
</tbody>
</table>

A.I.7
at this temperature, the data starts logging and the cascade control system is turned on, regulating the temperature to maintain a constant gas concentration. Before turning the control system on, it is necessary to set up the CRL controller via the computer. The set up values are given in Table A.I.3.

Table A.I.3: CRL Controller Set up Values

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt Weight Loss Rate</td>
<td>0.3 mg hr⁻¹</td>
</tr>
<tr>
<td>Integral Value*</td>
<td>20 - 50</td>
</tr>
<tr>
<td>Temperature Set-point**</td>
<td>640 - 660°C</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>700°C</td>
</tr>
</tbody>
</table>

* The integral value depends on how strictly the salt temperature needs to be controlled. When the integral value is exceeded, the CRL controller makes a temperature change to maintain the salt weight loss rate at 0.3 mg hr⁻¹.

** The temperature set-point should be set at the temperature value that the vapour generator displays at that instant.

Throughout the experiment, certain things need to be checked. These are the water level (in the bubblers and the bath), the acid level, the nitrogen cylinders, all the temperatures and pressures, the liquid level (acid and water) in the condenser, the crystal weight loss and the loss rate. When the balance reaches 30 mg, it should be re-tared because it is working better in this region. Before re-taring or adding water to the bubblers, the CRL control and the data logging should be stopped. The loss rate has to re-stabilise for the control and logging to start again.

At the end of the run, the temperatures decrease by 10°C min⁻¹ until 580°C, where it stays for 15 min. At this temperature the salt vapour production stops and the acid and water that enter the main gas stream, are switched off. A flow rate measurement is performed again, to check if there is any leak in the system and to compare the final flowrate with the initial measured at the same temperature. Finally, the system is cooled down to 25°C. When the system’s temperature is ~200°C, the power is shut off and the whole system is left to cool down at a natural rate. When the whole system has cooled down, the main gas stream is shut off and the bed section is removed from the rig, ready to be sucked in layers and analysed chemically.
APPENDIX II

MEASUREMENT OF ALKALI CONCENTRATION PROFILES

At the end of each experiment, the getter material was chemically analysed to evaluate its sorptive capacity and define the alkali uptake concentration profile along the fixed sorbent bed. The main steps of this procedure are as follows:

A.II.1 Sectioning of the fixed bed

In order to produce an accurate alkali uptake concentration profile along the sorbent fixed bed, it was considered necessary to measure accurately the height of each layer that the bed was divided into (Figure 3.2). The sectioning of the fixed bed was done by a vacuum probe assembly. This assembly consists of a thin metal tube connected to a vacuum pump enabling the pellets to be sucked from one end and collected at the other end in a small glass bottle, an adjustable ruler which moves the metal tube up or down to the required length, and a perspex piece which holds the whole assembly together. During the bed sectioning, the ceramic tube was kept in a vertical position. A flat teflon ring at the top of this tube was necessary to keep the vacuum assembly aligned. The suction actually starts when the metal tube is 1 mm above the bed of pellets.

At the 600 hr runs, the accuracy of the vacuum probe assembly was checked by a travelling microscope, which measured the height of the bed after each suction. The length of the vacuum assembly's thin metal tube was measured by a Vernier Caliper before each suction. The accuracy of the layer lengths' measurements was ±0.1 mm. The experimentally measured distance in the bed was compared with the distance estimated from the layers' weight and the mass of solid per unit length of bed and it was found that these values agreed to ±0.1 mm, which is a remarkably good result (Table A.II.9).

The removal of the alumina wool pads from the bottom of the ceramic tube was carried out with a pair of tongs.
A.II.2 Chemical Analysis of the Fixed Bed Samples

After the sorbent samples were taken out of the rig they had to be chemically analysed in order to specify their Na content, which was necessary for plotting the alkali uptake concentration profiles along the fixed bed. The procedure that had to be followed consists of the following steps:

a) grinding each layer using pestle and mortar. The grinding was done very carefully because a uniform powder was required to obtain a uniform sodium concentration.

b) dividing each layer in three samples of 30-40 mg each. The weight of the samples was reduced by 10-20 mg in comparison with the previous work because the acid proportions at the digestion step were also reduced. Electrostatic problems during weighing were overcome by using aluminium boats as weighing devices. As a result, the weighing accuracy was improved to ±0.02 mg. After weighing, the samples were transferred to the teflon beakers used for the digestion step. Due to electrostatics, the powder tended to stick on the beaker walls. Deionised water was used to carry away the powder from the beaker walls. To eliminate the effect of water in the analysis, three samples with the same quantity of water and without any powder were analysed as well. These samples are known as the "reagent blanks".

c) digesting the samples with HNO₃ (70%, Analytical Reagent, Fisons) and HF (48%, Analar Grade, Merck). The system that was used previously, a hot plate with 50 ml teflon beakers standing on it each containing 8 ml HNO₃ and 4 ml HF per digestion, had to be changed due to safety restrictions (Safety Policy: SP/04/93, University of Surrey). A new safe heating block with 21 drilled beaker positions was made. The advantage of the drilled positions was that it kept the beakers at the same temperature throughout the digestions, which prevented the fume condensation at the top part of the beaker walls. The beakers, specially designed for this heating block, were smaller than the previous ones. Therefore, the acid quantities used had to be reduced. This also complied with the safety restrictions for the HF concentration in the effluent fumes, which is 2.5 mg/m³ for 10 min (COSHH, OES).
In the past, the samples were digested three times, but now as the whole set up was changed, it was necessary to find out the optimum number of digestions and acid proportions. The digestions tried per sample were 2 to 6 and the optimum found to be 3 times for the sorbent powder and 4 times for the alumina wool as the wool's weight was greater. The acid proportions tried were 2 ml HNO₃/1 ml HF, 4 ml HNO₃/4 ml HF and 4 ml HNO₃/2 ml HF. The last acid proportion was found to be the most appropriate and in connection with the safety restrictions for the HF concentration in the effluent fumes, only six samples could digest simultaneously.

The final digestion procedure, which was obtained at 95°C, was the following:

1) heating up the wet samples to bring them to dryness
2) addition of 4 ml HNO₃
3) after 10 min, addition of 2 ml HF
4) drying of the samples
5) repeating the acid addition as many times as required for each material
6) at the end of all the digestions, addition of 8 ml of 12.5% HNO₃ in each sample
7) after 10 min, removal of the samples from heating
8) cooling of the samples
9) making up the samples to 100 ml solutions with deionised water

New PMP flasks, whose calibration error was <0.1%, were bought to improve accuracy in making the 100 ml solutions. In the fume cupboard, the new set-up was separate closed bottles and separate syringes for each acid. Complying with the safety regulations, the personal protective equipment used was a laboratory coat, ideally with press stud fastening, a plastic apron, safety spectacles, a full face visor and two pairs of gloves, with the external being HF resistant. The HF resistant gloves had to be neutralised before their removal from the fume cupboard. The neutralising agent used for sodium analysis was KOH and for potassium analysis was NaHCO₃. An important point was that the neutralising agent should not contain the alkali of analytical interest because the measured alkali concentrations were very small and easily subject to errors if there was another source of the same alkali in the vicinity.

A.II.3
analysing the samples with Atomic Absorption Spectrophotometry (Perkin Elmer Spectrophotometer, Chemistry Department). The best performance of the instrument is at a sodium concentration of 1 ppm and therefore the standard solutions used for the estimation of the calibration line had concentrations of 0.5, 1, 1.5 and 2 ppm Na. The standards were made from a "Spectrosol" sodium standard solution of 1000 ppm. A standard blank solution, which contained no sodium, was used to autozero the instrument. The instrument's accuracy in the absorbance readings was ±0.003. The absorbance values of the standards were taken at the beginning and at the end of the sample measurements and their mean used for estimating the equation of the calibration line. The first layers of the fixed beds showed a sodium concentration well above 1 ppm, which made dilution of the samples necessary. Using less material, in order to eliminate the error introduced by dilution, was rejected because of the errors introduced by using very small quantities of material. The idea of using standards with higher sodium concentrations was also rejected because the instrument was more sensitive in the area of 0.5-2 ppm Na.

A.II.3 Processing of the AAS Results

Lotus package was used for the calculation of the alkali concentration in the sorbent at certain positions in the fixed bed. The calculation sequence was the following:

- the average of the AAS readings for each standard solution was found and from the five values calculated (four standard solutions and a standard blank), the equation of the calibration curve could be specified with regression analysis. It may be better to consider concentrations up to 1.5 ppm, because at 2 ppm the calibration curve starts deviating from linearity

- the average of a sample's AAS readings was found and its sodium concentration, in ppm, was calculated from the equation of the calibration line. If the sample was diluted, the sodium concentration was multiplied by the number of dilutions

- the sodium concentration of the reagent blank solution was subtracted from each sample's
sodium concentration

- untreated solid material was also analysed in order to find its background level of sodium

- to subtract the background level of sodium from the sample's concentration, both concentrations had to be calculated on the same basis, which was g Na/g of clean solid

- the g of clean solid for each reacted sample were calculated by subtracting the total sodium concentration from the sample's weight

- from the g Na/g of clean solid for the control material, each sample's background g of sodium could be found and subtracted from its total sodium concentration

- as a result, the samples' net sodium uptake could be calculated in terms of g of Na/g of solid, where solid = clean solid + background sodium

- the sodium concentration that was finally used for a layer was the mean of the sodium concentrations calculated from its three analysed samples

- the layers' lengths in the bed were evaluated by the layers' weights and the mass of solid per unit length of bed

- to evaluate the weight of each layer in terms of g of solid, the same procedure had to be followed but on a layer level, which required the mean of the g of Na/g of reacted solid of the layer's three samples, where reacted solid = clean solid + background sodium + adsorbed sodium. This was because the layers were weighed after the experiment, which means that they also contained the adsorbed Na.

A.II.4 Measurement of mass of solid per unit length of bed

One of the experimentally measured quantities was the mass of solid per unit length of bed
expressed in g of unreacted solid/mm of the fixed bed, with the initial solid including its background alkali. As a result, this value had to be estimated before the beginning of an experiment. The unreacted sorbent pellets were tipped into the lower ceramic tube of the rig, which retains the fixed bed on a Pt/Rh gauze. The bed was shaken to obtain a better pellet packing. A thick metal tube, which ended to a flat metal piece with diameter almost equal to the internal diameter of the ceramic tube, was used to flatten the bed surface. The height of the bed was then measured with a Vernier Caliper and if it was more than required, layers of the bed were sucked out until the desired height was measured. At the end, the bed was weighed and effectively the mass of solid per unit length of bed could be estimated. The measured values for the fixed bed runs obtained are as follows:

Table A.II.1 : Measured mass of solid per unit length of bed for the fixed bed runs obtained in this work

<table>
<thead>
<tr>
<th></th>
<th>200 hr (NaCl)</th>
<th>400 hr (high-acid)</th>
<th>600 hr (non-acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of solid per unit length of bed (g/mm of bed)</td>
<td>0.4067</td>
<td>0.3563</td>
<td>0.3663</td>
</tr>
</tbody>
</table>

A.II.6
The tables with the analytical results of the single-layer and fixed bed alkali sorption tests are presented below:

Table A.II.2: Summary of the high-acid 600 hr run analytical results

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorb</th>
<th>Std.Dev.</th>
<th>Dilution (times)</th>
<th>Weight of sample (g)</th>
<th>g Na/g solid*</th>
<th>Mean±Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1A(a)</td>
<td>0.116</td>
<td>0.003</td>
<td>25</td>
<td>0.03777</td>
<td>0.03729</td>
<td>0.03684±0.0006</td>
</tr>
<tr>
<td></td>
<td>0.117</td>
<td>0.001</td>
<td>25</td>
<td>0.03766</td>
<td>0.03777</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.112</td>
<td>0.001</td>
<td>25</td>
<td>0.03696</td>
<td>0.03673</td>
<td></td>
</tr>
<tr>
<td>Layer 1B(a)</td>
<td>0.091</td>
<td>0.001</td>
<td>25</td>
<td>0.03037</td>
<td>0.03261</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.214</td>
<td>0.002</td>
<td>10</td>
<td>0.02866</td>
<td>0.03623</td>
<td></td>
</tr>
<tr>
<td>Layer 2(a)</td>
<td>0.113</td>
<td>0.001</td>
<td>25</td>
<td>0.03874</td>
<td>0.03522</td>
<td>0.03561±0.00036</td>
</tr>
<tr>
<td></td>
<td>0.115</td>
<td>0.001</td>
<td>25</td>
<td>0.03871</td>
<td>0.03594</td>
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</tr>
<tr>
<td></td>
<td>0.113</td>
<td>0.001</td>
<td>25</td>
<td>0.03869</td>
<td>0.03527</td>
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</tr>
<tr>
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<td>0.113</td>
<td>0.002</td>
<td>25</td>
<td>0.03799</td>
<td>0.03599</td>
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<td>Layer 3(a)</td>
<td>0.108</td>
<td>0.001</td>
<td>25</td>
<td>0.03800</td>
<td>0.03421</td>
<td>0.03405±0.00019</td>
</tr>
<tr>
<td></td>
<td>0.105</td>
<td>0.002</td>
<td>25</td>
<td>0.03736</td>
<td>0.03378</td>
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<td>0.107</td>
<td>0.001</td>
<td>25</td>
<td>0.03770</td>
<td>0.03415</td>
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<td>0.101</td>
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<td>25</td>
<td>0.03839</td>
<td>0.03138</td>
<td>0.03178±0.00047</td>
</tr>
<tr>
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<td>0.104</td>
<td>0.001</td>
<td>25</td>
<td>0.03837</td>
<td>0.03245</td>
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<td>0.100</td>
<td>0.001</td>
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<td>0.03788</td>
<td>0.03150</td>
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<td>Layer 5(a)</td>
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<td>0.002</td>
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<td>0.03858</td>
<td>0.02963</td>
<td>0.02963±0.00075</td>
</tr>
<tr>
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<td>0.02735±0.00078</td>
</tr>
<tr>
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<td>10</td>
<td>0.03795</td>
<td>0.02663</td>
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</tr>
<tr>
<td></td>
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<td>0.001</td>
<td>10</td>
<td>0.03828</td>
<td>0.02705</td>
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<td>Layer 7(a)</td>
<td>0.257</td>
<td>0.003</td>
<td>8</td>
<td>0.03394</td>
<td>0.02823</td>
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</tr>
<tr>
<td></td>
<td>0.270</td>
<td>0.002</td>
<td>8</td>
<td>0.03555</td>
<td>0.02834</td>
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<tr>
<td>Layer 7(a)</td>
<td>0.256</td>
<td>0.001</td>
<td>8</td>
<td>0.03777</td>
<td>0.02462</td>
<td>0.02514±0.00070</td>
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<tr>
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<td>0.03840</td>
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<td>0.002</td>
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<td>0.03839</td>
<td>0.02514</td>
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<tr>
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<td>0.02628</td>
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<td>Samples</td>
<td>Absorb</td>
<td>Std.Dev.</td>
<td>Dilution (times)</td>
<td>Weight of sample (g)</td>
<td>g Na/g solid*</td>
<td>Mean± Std.Dev.</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>----------</td>
<td>------------------</td>
<td>----------------------</td>
<td>---------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Layer 8(a)</td>
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<td>0.001</td>
<td>8</td>
<td>0.03787</td>
<td>0.02405</td>
<td>0.02356±0.00026</td>
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<tr>
<td>(b)</td>
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<td>8</td>
<td>0.03846</td>
<td>0.02352</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
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<td>0.001</td>
<td>8</td>
<td>0.03811</td>
<td>0.02351</td>
<td></td>
</tr>
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<td>1st Analysis</td>
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<td></td>
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</tr>
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<td>Layer 8(a)</td>
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<td>5</td>
<td>0.03597</td>
<td>0.02328</td>
<td></td>
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<tr>
<td>(b)</td>
<td>0.347</td>
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<td>5</td>
<td>0.03395</td>
<td>0.02343</td>
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</tr>
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<td>2nd Analysis</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Layer 9(a)</td>
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<td>8</td>
<td>0.03857</td>
<td>0.02126</td>
<td>0.02120±0.00005</td>
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<td>(b)</td>
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<tr>
<td>(c)</td>
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<td>8</td>
<td>0.03825</td>
<td>0.02121</td>
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<td>Layer 10(a)</td>
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<td>5</td>
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<td>0.01817</td>
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<tr>
<td>(b)</td>
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<td>5</td>
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<td>(c)</td>
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<td>5</td>
<td>0.03816</td>
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<td>5</td>
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<td>0.01638</td>
<td>0.01631±0.00007</td>
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<tr>
<td>(b)</td>
<td>0.254</td>
<td>0.002</td>
<td>5</td>
<td>0.03807</td>
<td>0.01634</td>
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<td>0.002</td>
<td>5</td>
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<td>0.01621</td>
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<td>5</td>
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<td>5</td>
<td>0.03806</td>
<td>0.01264</td>
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<td>4</td>
<td>0.03774</td>
<td>0.00797</td>
<td>0.00800±0.00004</td>
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<tr>
<td>(b)</td>
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<td>0.001</td>
<td>4</td>
<td>0.03866</td>
<td>0.00807</td>
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</tr>
<tr>
<td>(c)</td>
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<td>0.001</td>
<td>4</td>
<td>0.03778</td>
<td>0.00796</td>
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<td>0.001</td>
<td>2</td>
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<td>0.00385</td>
<td>0.00385±0.00001</td>
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<tr>
<td>(b)</td>
<td>0.220</td>
<td>0.001</td>
<td>2</td>
<td>0.03785</td>
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<td>0.001</td>
<td>2</td>
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<td>0.00384</td>
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<td>1</td>
<td>0.03793</td>
<td>0.00177</td>
<td>0.00176±0.00001</td>
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<tr>
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<td>1</td>
<td>0.03795</td>
<td>0.00175</td>
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<td>(c)</td>
<td>0.317</td>
<td>0.002</td>
<td>1</td>
<td>0.03796</td>
<td>0.00177</td>
<td></td>
</tr>
<tr>
<td>Layer 16(a)</td>
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<td>1</td>
<td>0.03866</td>
<td>0.00055</td>
<td>0.00054±0.00001</td>
</tr>
<tr>
<td>(b)</td>
<td>0.226</td>
<td>0.002</td>
<td>1</td>
<td>0.03862</td>
<td>0.00052</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>0.225</td>
<td>0.001</td>
<td>1</td>
<td>0.03827</td>
<td>0.00054</td>
<td></td>
</tr>
<tr>
<td>Layer 17(a)</td>
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<td>1</td>
<td>0.03791</td>
<td>0.00022</td>
<td>0.00022±0.00002</td>
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<tr>
<td>(b)</td>
<td>0.200</td>
<td>0.003</td>
<td>1</td>
<td>0.03765</td>
<td>0.00025</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>0.200</td>
<td>0.001</td>
<td>1</td>
<td>0.03854</td>
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<tr>
<td>Layer 20(a)</td>
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<td>0.001</td>
<td>1</td>
<td>0.03767</td>
<td>0.00008</td>
<td>0.00008±0.00000</td>
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<tr>
<td>(b)</td>
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<td>0.001</td>
<td>1</td>
<td>0.03851</td>
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<tr>
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<td>1</td>
<td>0.03878</td>
<td>0.00005</td>
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</table>
### Table (cont.)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorb</th>
<th>Std.Dev.</th>
<th>Dilution (times)</th>
<th>Weight of sample (g)</th>
<th>g Na/g solid*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Wool</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) top</td>
<td>0.370</td>
<td>0.003</td>
<td>1</td>
<td>0.1018</td>
<td>0.00152</td>
</tr>
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<td>(b) middle</td>
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<td>0.001</td>
<td>1</td>
<td>0.0837</td>
<td>0.00000</td>
</tr>
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<td>(c) bottom2</td>
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<td>0.001</td>
<td>1</td>
<td>0.1076</td>
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</tr>
<tr>
<td>(d) bottom1</td>
<td>0.057</td>
<td>0.001</td>
<td>1</td>
<td>0.0772</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

* Solid = initial solid which contains the sorbent and the background Na

### Table

<table>
<thead>
<tr>
<th>Samples</th>
<th>Abs</th>
<th>Std.Dev.</th>
<th>Dilution (times)</th>
<th>Weight of sample (g)</th>
<th>g Na/g solid*</th>
<th>Mean± Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated (a)</td>
<td>0.186</td>
<td>0.002</td>
<td>1</td>
<td>0.03781</td>
<td>0.00239</td>
<td>0.00233±0.00004</td>
</tr>
<tr>
<td>Fuller's (b)</td>
<td>0.181</td>
<td>0.001</td>
<td>1</td>
<td>0.03817</td>
<td>0.00231</td>
<td>0.00000</td>
</tr>
<tr>
<td>Earth (c)</td>
<td>0.182</td>
<td>0.001</td>
<td>1</td>
<td>0.03854</td>
<td>0.00230</td>
<td>±0.00002</td>
</tr>
<tr>
<td>Untreated (a)</td>
<td>0.069</td>
<td>0.001</td>
<td>1</td>
<td>0.0757</td>
<td>0.00043</td>
<td>0.00040±0.00002</td>
</tr>
<tr>
<td>Alumina (b)</td>
<td>0.062</td>
<td>0.001</td>
<td>1</td>
<td>0.0752</td>
<td>0.00038</td>
<td>0.00000</td>
</tr>
<tr>
<td>Wool (c)</td>
<td>0.067</td>
<td>0.001</td>
<td>1</td>
<td>0.0810</td>
<td>0.00039</td>
<td></td>
</tr>
<tr>
<td>Reagent Blank</td>
<td>0.005</td>
<td>0.001</td>
<td>1</td>
<td>-</td>
<td>0.015-0.02 ppm</td>
<td></td>
</tr>
<tr>
<td>Tube + gauze</td>
<td>0.131</td>
<td>0.001</td>
<td>1</td>
<td>-</td>
<td>0.693 ppm</td>
<td></td>
</tr>
</tbody>
</table>

* Solid = initial solid which contains the sorbent and the background Na

A.II.9
Table A.II.3: Experimental Results for the Single-Layer Tests at 650°C

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sodium uptake (%wt)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Pellets</td>
<td></td>
</tr>
<tr>
<td>Fuller’s Earth (Surrey Tests)</td>
<td>0.23</td>
</tr>
<tr>
<td>Fuller’s Earth (CRE Treated)</td>
<td>0.26</td>
</tr>
<tr>
<td>Kaolin</td>
<td>0.1</td>
</tr>
<tr>
<td>Fuller’s Earth and Kaolin Non-Acid Run</td>
<td></td>
</tr>
<tr>
<td>Fuller’s Earth</td>
<td>5.0</td>
</tr>
<tr>
<td>Kaolin</td>
<td>9.0</td>
</tr>
<tr>
<td>Fuller’s Earth and Kaolin Acid Run</td>
<td></td>
</tr>
<tr>
<td>Fuller’s Earth</td>
<td>3.5</td>
</tr>
<tr>
<td>Kaolin</td>
<td>11.4</td>
</tr>
<tr>
<td>Fuller’s Earth and CRE Pellet Acid Run</td>
<td></td>
</tr>
<tr>
<td>Fuller’s Earth</td>
<td>5.6</td>
</tr>
<tr>
<td>CRE Treated Pellets**</td>
<td>6.3</td>
</tr>
<tr>
<td>Reagent Blank</td>
<td>0.018 ppm</td>
</tr>
</tbody>
</table>

* The sodium uptake is based on g Na/g solid (Solid = initial solid which contains the sorbent and the background Na)

** The CRE treated pellets are from Layer 5 of CRE fixed bed
# Table A.II.4: Experimental Values for high-acid 200 hr Potassium Run

<table>
<thead>
<tr>
<th>Samples</th>
<th>Potassium (%wt)*</th>
<th>Potassium (mg)</th>
<th>% of Total K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>2.751</td>
<td>4.739</td>
<td>15.30</td>
</tr>
<tr>
<td>Layer 2</td>
<td>2.485</td>
<td>3.723</td>
<td>12.02</td>
</tr>
<tr>
<td>Layer 3</td>
<td>2.267</td>
<td>4.476</td>
<td>14.45</td>
</tr>
<tr>
<td>Layer 4</td>
<td>2.048</td>
<td>3.797</td>
<td>12.25</td>
</tr>
<tr>
<td>Layer 5</td>
<td>1.663</td>
<td>3.329</td>
<td>10.74</td>
</tr>
<tr>
<td>Layer 6</td>
<td>1.206</td>
<td>2.432</td>
<td>7.85</td>
</tr>
<tr>
<td>Layer 7</td>
<td>0.753</td>
<td>1.345</td>
<td>4.34</td>
</tr>
<tr>
<td>Layer 8</td>
<td>0.394</td>
<td>0.759</td>
<td>2.45</td>
</tr>
<tr>
<td>Layer 9</td>
<td>0.295</td>
<td>0.494</td>
<td>1.59</td>
</tr>
<tr>
<td>Layer 10</td>
<td>0.168</td>
<td>0.307</td>
<td>0.99</td>
</tr>
<tr>
<td>Layer 12</td>
<td>0.027</td>
<td>0.092</td>
<td>0.30</td>
</tr>
<tr>
<td>Layer 14</td>
<td>0.062</td>
<td>0.050</td>
<td>0.16</td>
</tr>
<tr>
<td>Alumina Wool</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) top1</td>
<td>0.019</td>
<td>0.025</td>
<td>0.08</td>
</tr>
<tr>
<td>(b) top2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(c) middle</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(d) bottom2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(e) bottom1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(f) plug wool</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
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<tr>
<td>Ceramic tube,</td>
<td></td>
<td>0.032</td>
<td>0.10</td>
</tr>
<tr>
<td>base,Pt/Rh gauze</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>Total potassium</td>
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<td>Total potassium</td>
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<td>30.981</td>
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<tr>
<td>Unaccounted for</td>
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<td>5.381**</td>
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</tr>
<tr>
<td>Untreated Fuller's</td>
<td>0.565</td>
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<td>-</td>
</tr>
<tr>
<td>Earth</td>
<td></td>
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</tr>
<tr>
<td>Untreated Alumina</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wool</td>
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</tr>
<tr>
<td>Reagent Blank</td>
<td>-</td>
<td>0.0 ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

* The weight percentage is based on g K/g solid (Solid = initial solid which contains the sorbent and the background K).
** Layers 11 & 13 have not been analysed.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Sodium (%wt)*</th>
<th>Sodium (mg)</th>
<th>% of Total Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>3.244</td>
<td>10.608</td>
<td>45.00</td>
</tr>
<tr>
<td>Layer 2</td>
<td>2.530</td>
<td>4.329</td>
<td>18.36</td>
</tr>
<tr>
<td>Layer 3</td>
<td>2.041</td>
<td>4.072</td>
<td>17.27</td>
</tr>
<tr>
<td>Layer 4</td>
<td>1.507</td>
<td>2.258</td>
<td>9.58</td>
</tr>
<tr>
<td>Layer 5</td>
<td>1.035</td>
<td>2.139</td>
<td>9.07</td>
</tr>
<tr>
<td>Layer 6</td>
<td>0.557</td>
<td>1.150</td>
<td>4.88</td>
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<tr>
<td>Layer 7</td>
<td>0.313</td>
<td>0.437</td>
<td>1.85</td>
</tr>
<tr>
<td>Layer 8</td>
<td>0.144</td>
<td>0.245</td>
<td>1.04</td>
</tr>
<tr>
<td>Layer 9</td>
<td>0.133</td>
<td>0.258</td>
<td>1.09</td>
</tr>
<tr>
<td>Layer 10</td>
<td>0.061</td>
<td>0.113</td>
<td>0.48</td>
</tr>
<tr>
<td>Layer 11</td>
<td>0.031</td>
<td>0.103</td>
<td>0.44</td>
</tr>
<tr>
<td>Layer 12</td>
<td>0.005</td>
<td>0.018</td>
<td>0.07</td>
</tr>
<tr>
<td>Layer 13</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Layer 14</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Layer 15</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Alumina Wool</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) top1</td>
<td>0.024</td>
<td>0.032</td>
<td>0.13</td>
</tr>
<tr>
<td>(b) top2</td>
<td>0.000</td>
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<td>0.00</td>
</tr>
<tr>
<td>(c) middle</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(d) bottom1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(e) bottom2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Ceramic tube,</td>
<td></td>
<td>0.14</td>
<td>0.59</td>
</tr>
<tr>
<td>base,Pt/Rh gauze</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Sodium out</td>
<td>25.90</td>
<td>109.85</td>
<td></td>
</tr>
<tr>
<td>Total Sodium in</td>
<td>23.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unaccounted for</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated Fuller's Earth</td>
<td>0.241</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated Alumina Wool</td>
<td>0.036</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reagent Blank</td>
<td></td>
<td>0.015-0.02ppm</td>
<td></td>
</tr>
</tbody>
</table>

* The percentage is based on g Na/g solid (Solid = initial solid which contains the sorbent and the background Na)

A.II.12
Table A.II.6: Experimental Values for high-acid 400 hr Sodium Run

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sodium (% wt)*</th>
<th>Sodium (mg)</th>
<th>% of Total Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>4.354</td>
<td>9.597</td>
<td>20.17</td>
</tr>
<tr>
<td>Layer 2</td>
<td>4.166</td>
<td>9.530</td>
<td>20.03</td>
</tr>
<tr>
<td>Layer 3</td>
<td>3.444</td>
<td>8.161</td>
<td>17.15</td>
</tr>
<tr>
<td>Layer 4</td>
<td>2.922</td>
<td>4.740</td>
<td>9.96</td>
</tr>
<tr>
<td>Layer 5</td>
<td>2.368</td>
<td>5.219</td>
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</tr>
<tr>
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<td>2.812</td>
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</tr>
<tr>
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<td>1.379</td>
<td>2.639</td>
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</tr>
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<td>Layer 8</td>
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</tr>
<tr>
<td>Layer 9</td>
<td>0.371</td>
<td>0.674</td>
<td>1.42</td>
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<tr>
<td>Layer 10</td>
<td>0.101</td>
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<td>0.36</td>
</tr>
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<td>Layer 11</td>
<td>0.009</td>
<td>0.016</td>
<td>0.03</td>
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<td>Layer 12</td>
<td>0.000</td>
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<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Layer 14</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Layer 15</td>
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<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Alumina Wool</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) top</td>
<td>0.131</td>
<td>0.111</td>
<td>0.23</td>
</tr>
<tr>
<td>(b) middle</td>
<td>0.002</td>
<td>0.002</td>
<td>0.00</td>
</tr>
<tr>
<td>(c) bottom</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(d) plug</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Ceramic tube,</td>
<td></td>
<td>0.034</td>
<td>0.07</td>
</tr>
<tr>
<td>base, Pt/Rh gauze</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Sodium out</td>
<td>-</td>
<td>45.227</td>
<td>95.05</td>
</tr>
<tr>
<td>Total Sodium in</td>
<td>-</td>
<td>47.572</td>
<td>-</td>
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<tr>
<td>Un accounted for</td>
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<td>2.345</td>
<td>4.95</td>
</tr>
<tr>
<td>Untreated Fuller's Earth</td>
<td>0.231</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Untreated Alumina Wool</td>
<td>0.037</td>
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<td>-</td>
</tr>
<tr>
<td>Reagent Blank</td>
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<td>0.11 ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

* The weight percentage is based on g Na/g solid (Solid = initial solid which contains the sorbent and the background Na)

A.II.13
Table A.II.7 : Summary of the Results for the high-acid 600 hr Sodium Run

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sodium (%wt)*</th>
<th>Sodium(mg)</th>
<th>% of Total Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>3.684</td>
<td>7.397</td>
<td>10.48</td>
</tr>
<tr>
<td>Layer 2</td>
<td>3.561</td>
<td>10.125</td>
<td>14.34</td>
</tr>
<tr>
<td>Layer 3</td>
<td>3.405</td>
<td>5.002</td>
<td>7.09</td>
</tr>
<tr>
<td>Layer 4</td>
<td>3.178</td>
<td>7.450</td>
<td>10.55</td>
</tr>
<tr>
<td>Layer 5</td>
<td>2.963</td>
<td>6.188</td>
<td>8.77</td>
</tr>
<tr>
<td>Layer 6</td>
<td>2.735</td>
<td>5.052</td>
<td>7.16</td>
</tr>
<tr>
<td>Layer 7</td>
<td>2.514</td>
<td>4.324</td>
<td>6.13</td>
</tr>
<tr>
<td>Layer 8</td>
<td>2.356</td>
<td>4.364</td>
<td>6.18</td>
</tr>
<tr>
<td>Layer 9</td>
<td>2.120</td>
<td>3.724</td>
<td>5.27</td>
</tr>
<tr>
<td>Layer 10</td>
<td>1.866</td>
<td>3.350</td>
<td>4.74</td>
</tr>
<tr>
<td>Layer 11</td>
<td>1.631</td>
<td>2.944</td>
<td>4.17</td>
</tr>
<tr>
<td>Layer 12</td>
<td>1.234</td>
<td>4.726</td>
<td>6.70</td>
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<tr>
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<td>0.800</td>
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<td>4.17</td>
</tr>
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<td>Layer 14</td>
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<td>Layer 17</td>
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<td>0.11</td>
</tr>
<tr>
<td>Layer 20</td>
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</tr>
<tr>
<td>Alumina Wool</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(a) top</td>
<td>0.152</td>
<td>0.155</td>
<td>0.22</td>
</tr>
<tr>
<td>(b) middle</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(c) bottom2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>(d) bottom1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Ceramic tube,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>base, Pt/Rh gauze</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.067</td>
<td>0.09</td>
</tr>
<tr>
<td>Total Sodium out</td>
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<td>70.107</td>
<td>99.31</td>
</tr>
<tr>
<td>Total Sodium in</td>
<td></td>
<td>70.576</td>
<td>-</td>
</tr>
<tr>
<td>Unaccounted for</td>
<td></td>
<td>0.469</td>
<td>0.69**</td>
</tr>
<tr>
<td>Untreated Fuller's Earth</td>
<td>0.233</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Untreated Alumina Wool</td>
<td>0.040</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reagent Blank</td>
<td></td>
<td>0.015-0.02 ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

* The percentages are based on g Na/g solid (Solid = initial solid which contains the sorbent and the background Na)
** Layers 18 & 19 have not been analysed

A.II.14
Table A.II.8: Experimental Values for the non-acid 600 hr Sodium Run (The analysis has been performed by AEA Technology, Analytical Services)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sodium (%wt)*</th>
<th>Sodium (mg)</th>
<th>% of Total Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>14.61</td>
<td>19.096</td>
<td>27.16</td>
</tr>
<tr>
<td>Layer 2</td>
<td>10.839</td>
<td>26.314</td>
<td>37.43</td>
</tr>
<tr>
<td>Layer 3</td>
<td>6.406</td>
<td>10.768</td>
<td>15.32</td>
</tr>
<tr>
<td>Layer 4</td>
<td>2.688</td>
<td>5.207</td>
<td>7.41</td>
</tr>
<tr>
<td>Layer 5</td>
<td>1.023</td>
<td>1.76</td>
<td>2.5</td>
</tr>
<tr>
<td>Layer 6</td>
<td>0.247</td>
<td>0.414</td>
<td>0.59</td>
</tr>
<tr>
<td>Layer 7</td>
<td>0.146</td>
<td>0.252</td>
<td>0.36</td>
</tr>
<tr>
<td>Layer 8</td>
<td>0.048</td>
<td>0.088</td>
<td>0.12</td>
</tr>
<tr>
<td>Layer 9</td>
<td>0.025</td>
<td>0.044</td>
<td>0.06</td>
</tr>
<tr>
<td>Layer 10</td>
<td>0.028</td>
<td>0.048</td>
<td>0.07</td>
</tr>
<tr>
<td>Layer 11</td>
<td>0.029</td>
<td>0.052</td>
<td>0.07</td>
</tr>
<tr>
<td>Layer 12</td>
<td>0.029</td>
<td>0.053</td>
<td>0.07</td>
</tr>
<tr>
<td>Layer 13</td>
<td>0.026</td>
<td>0.047</td>
<td>0.07</td>
</tr>
<tr>
<td>Layer 14</td>
<td>0.018</td>
<td>0.032</td>
<td>0.04</td>
</tr>
<tr>
<td>Layer 15</td>
<td>0.017</td>
<td>0.054</td>
<td>0.08</td>
</tr>
<tr>
<td>Layer 16</td>
<td>0.025</td>
<td>0.091</td>
<td>0.13</td>
</tr>
<tr>
<td>Layer 17</td>
<td>0.035</td>
<td>0.122</td>
<td>0.17</td>
</tr>
<tr>
<td>Layer 18</td>
<td>0.029</td>
<td>0.099</td>
<td>0.14</td>
</tr>
<tr>
<td>Layer 20</td>
<td>0.036</td>
<td>0.123</td>
<td>0.17</td>
</tr>
<tr>
<td>Layer 22</td>
<td>0.023</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>Alumina Wool (a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total top</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Sodium Out</td>
<td>-</td>
<td>64.745</td>
<td>92.07</td>
</tr>
<tr>
<td>Total Sodium In</td>
<td>-</td>
<td>70.297</td>
<td></td>
</tr>
<tr>
<td>Unaccounted for</td>
<td>-</td>
<td>5.552</td>
<td>7.93**</td>
</tr>
<tr>
<td>Untreated Fuller's Earth</td>
<td>0.175</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Untreated Alumina Wool***</td>
<td>0.040</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reagent Blank</td>
<td>-</td>
<td>~0.062 ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

* The percentages are based on g Na/g solid (Solid = initial solid which contains the sorbent and the background Na)
** Layers 19, 21, 23 and the rest of the alumina wool have not been analysed
*** The untreated alumina wool value has been taken from the high-acid 600 hr run
Table A.II.9: Comparison of the weight derived and the experimentally measured distances

<table>
<thead>
<tr>
<th>Layers</th>
<th>Weight of layer (g)*</th>
<th>Weight derived distance (cm)**</th>
<th>Experimentally measured distance (cm)**</th>
<th>Mean distance (± 0.01 cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(A+B)</td>
<td>0.20101</td>
<td>0.027</td>
<td>0.023</td>
<td>0.025</td>
</tr>
<tr>
<td>2</td>
<td>0.28470</td>
<td>0.094</td>
<td>0.083</td>
<td>0.088</td>
</tr>
<tr>
<td>3</td>
<td>0.14691</td>
<td>0.152</td>
<td>0.137</td>
<td>0.144</td>
</tr>
<tr>
<td>4</td>
<td>0.23693</td>
<td>0.205</td>
<td>0.195</td>
<td>0.200</td>
</tr>
<tr>
<td>5</td>
<td>0.20886</td>
<td>0.266</td>
<td>0.262</td>
<td>0.264</td>
</tr>
<tr>
<td>6</td>
<td>0.18265</td>
<td>0.319</td>
<td>0.315</td>
<td>0.317</td>
</tr>
<tr>
<td>7</td>
<td>0.17198</td>
<td>0.368</td>
<td>0.362</td>
<td>0.365</td>
</tr>
<tr>
<td>8</td>
<td>0.18522</td>
<td>0.416</td>
<td>0.411</td>
<td>0.413</td>
</tr>
<tr>
<td>9</td>
<td>0.17566</td>
<td>0.466</td>
<td>0.461</td>
<td>0.463</td>
</tr>
<tr>
<td>10</td>
<td>0.17951</td>
<td>0.514</td>
<td>0.510</td>
<td>0.512</td>
</tr>
<tr>
<td>11</td>
<td>0.18050</td>
<td>0.563</td>
<td>0.560</td>
<td>0.561</td>
</tr>
<tr>
<td>12</td>
<td>0.38300</td>
<td>0.640</td>
<td>0.635</td>
<td>0.637</td>
</tr>
<tr>
<td>13</td>
<td>0.36782</td>
<td>0.743</td>
<td>0.735</td>
<td>0.739</td>
</tr>
<tr>
<td>14</td>
<td>0.35191</td>
<td>0.841</td>
<td>0.835</td>
<td>0.838</td>
</tr>
<tr>
<td>15</td>
<td>0.35549</td>
<td>0.938</td>
<td>0.935</td>
<td>0.936</td>
</tr>
<tr>
<td>16</td>
<td>0.38155</td>
<td>1.038</td>
<td>1.035</td>
<td>1.036</td>
</tr>
<tr>
<td>17</td>
<td>0.35024</td>
<td>1.138</td>
<td>1.135</td>
<td>1.136</td>
</tr>
<tr>
<td>20</td>
<td>0.44523</td>
<td>1.455</td>
<td>1.455</td>
<td>1.455</td>
</tr>
</tbody>
</table>

* Weight of the layer = initial solid which contains the sorbent and the background Na

** The distances are taken in the middle of the layers.
APPENDIX III

EXIT GAS ANALYSIS

A.III.1 Dräger HCl Detection Tubes

- Application Range
  Determination of hydrochloric-acid gas in air or technical gases.

- Mode of Operation
  The tube contains two layers: a white pre-layer and a blue indicating layer. When air or a gas sample are sucked through the tube, the indicating layer changes colour to yellow in the presence of hydrochloric acid.

- Principle of Reaction
  HCl + bromphenol blue → yellow reaction product

- Ambient Conditions
  Temperature: 5°C to 40°C

- Measurement and Evaluation
  The measuring range used was:
  
  1 to 10 ppm (10 strokes, scale n=10)
  0.5 to 5 ppm (20 strokes, scale n=10, divide scale values by 2).

  The suction volume of the Dräger gas detector pump during one stroke was measured experimentally and found to be 60 ml for 12 s, which corresponds to ~300 ml/min. The specific gas detector pump was found to leak and a different pump system was used for the measurement, which could involve errors according to the Dräger specifications. The HCl quantity was expected in the range 0.5 - 5 ppmv and as a result 20 strokes or an equivalent volume of gas (1.2 lt for 240 s) should be obtained each time for a proper measurement.
A.III.2 Electrochemical Cell - On-line HCl monitor

The electrochemical cell used as an on-line monitor of HCl concentration in the exit gases from the fixed bed rig is a three electrode toxic gas CiTiceL. The cells are manufactured by City Technology (City Technology Ltd, 1990). They are micro-fuel cells designed to be maintenance free and stable over long periods of time. They use the gaseous diffusion barrier technology which has proved quite successful. A high reserve of electrochemical activity ensures that each CiTiceL has a long life and excellent temperature stability.

The three electrode toxic gas CiTiceL consists of a sensing electrode, a counter and a reference electrode separated by a thin layer of electrolyte as shown in Figure A.III.1. The central feature is the gaseous diffusion barrier. This limits the flow of gas to the sensing electrode and ensures that the electrochemical activity of the electrode is far in excess of the amount of gas with which it has to deal.

![Figure A.III.1: Toxic Gas CiTiceL Schematic (City Technology Ltd, 1990)](image)

Gas diffusing to the sensing electrode reacts at the surface of the electrode either by oxidation (e.g. CO, H₂S, SO₂, NO, H₂, HCN, HCl), or reduction (NO₂ and Cl₂). Reactions are catalysed
by electrode materials specially developed by City Technology and designed to be specific to the gas being sensed. A specific reaction for HCl was not given by City Technology Ltd. Three electrode CiTiceLs are designed to be operated in such a way that the change in potential of the sensing electrode as a result of exposure is used as the measure of concentration.

- Performance Characteristics of CiTiceL 3HL (HCl)

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min Range (ppmv)</td>
<td>0 - 5</td>
</tr>
<tr>
<td>Max Range (ppmv)</td>
<td>0 - 100</td>
</tr>
<tr>
<td>Temperature Range (°C)</td>
<td>-5 to +40</td>
</tr>
<tr>
<td>Baseline (Pure Air at STP-ppmv equiv.)</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Maximum Baseline Shift (ppmv 20-40°C)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

- Humidity

The performance of toxic gas CiTiceLs is relatively unaffected by humidity, provided conditions are non-condensing and the CiTiceLs will simply follow the change in concentration of the measured gas due to a change in humidity. CiTiceLs are based on the use of aqueous electrolytes, which in conjunction with the porous diffusion barrier, permit water vapour to be absorbed into the electrolyte under conditions of high water vapour pressure and allows the electrolyte to dry out at very low ambient water vapour pressures. Continuous operation is possible between 15% and 90% RH over the full temperature range as the electrolyte will reach an equilibrium balance with the external water vapour pressure, at a volume and concentration which does not affect the life or the performance of the cells.

Two cells were used during the experiments performed in this research project, both showing a specific response to the presence of water vapour in the gas analysed, indicating that the cell is sensitive to water, despite its specifications. When only water vapour was introduced into the system, the signal would increase and stabilise at a new baseline which was 0.5 - 1 mV above the No Water baseline. When the water was turned off again, the signal decreased and would stabilise at the original No Water baseline (Figures A.III.2,3).
Temperature Effects
Both the span signal and the baseline (zero current) are slightly affected by temperature. In this work, the cell was kept under the constant temperature of ~25°C.

Pressure Effects
CiTiceLs can give a transient response when exposed to a sudden change in pressure in the presence of the measured gas. The peak signal decays in only a few seconds. This response was also observed in this work.

Calibration
For maximum accuracy, CiTiceLs should be calibrated using a gas mixture in the range where most measurements are to be made. Where this is not possible, a mixture towards the top of the cell range should be chosen. Calibration gases exceeding the range of the cell must not be used. A gas concentration of 20 ppmv HCl is recommended for calibration. However, the HCl concentrations expected here are in the range 0 - 4 ppmv, and as a result a 20 ppmv calibration gas cannot be used. No reliable calibration gas was available in the range of 0 - 4 ppmv, because this concentration is very small and HCl can be easily adsorbed on the surface of the container.

Sampling Systems
The sensor should be suitably protected by appropriate filtration to remove highly corrosive constituents and particulate matter. The usual protection takes the form of a porous PTFE membrane which can be sealed to the cell by an O-ring arrangement.

The active gas component of a gas stream may adsorb on to the surfaces of the materials used in the gas supply system. This will deplete the concentration of the adsorbed gas in the supply stream until the material is saturated. Gases such as CO, H₂ and NO do not usually show any problems with adsorption. Adsorption problems become increasingly significant in the order

SO₂ < H₂S < NO₂ < Cl₂ < HCl

These adsorption effects are minimised by employing suitable materials in contact with the gas, together with high flow rates and short gas lines. Fluoropolymers such as PTFE (polytetrafluoroethylene), TFE (trifluorinatedethylene) and FEP (fluorinated ethylene propylene) have very low gas adsorption properties and are suitable for use in gas handling.
systems. The exit gas from the fixed bed sorption rig does not contain particulate matter and the tube used to connect the exit of the rig with the cell is made by PTFE.

- Operation

CiTiceLs require a small supply of oxygen to the counter and reference electrodes to allow correct operation. The oxygen is normally provided in the sample stream or by air diffusing to the front of the sensor or by diffusion through the sides and rear of the sensor—a few thousand ppm is normally sufficient. Continuous exposure to anaerobic sample gas may cause the sensor to malfunction in spite of the rear oxygen access paths. A continuous air supply of ~10 ml/min was provided to the electrochemical cell throughout the duration of the experiments performed.

- Outputs

Toxic gas CiTiceLs are available with the standard µA output signal or with a circuit board attached to provide either a 0 to 1V output (calibrated to 1 or 10 mV ppm⁻¹) or a 4 to 20 mA output. The output signal in mV was recorded in a Squirrel Data Logger. The data were then transferred to a spreadsheet where the output signal versus time was plotted.

A.III.3 Figures of Exit Gas Analysis Measurements

In this appendix, measurements of HCl concentration in the effluent gas of fixed bed runs with Fuller’s Earth, gaseous NaCl and H₂O (if used) versus time are presented. The cell was connected to the fixed bed rig and the response was recorded on a Squirrel data logger and the output was exported to a spreadsheet.
Figure A.III.2 : Direct Water Response of the New Electrochemical Cell
\( (T_{\text{water}} = 30.7^\circ C) \)

Figure A.III.3 : Water Response of the New Electrochemical Cell connected to the outlet of the Fixed Bed Rig \( (T_{\text{water}} = 30.7^\circ C) \)
Figure A.III.4: HCl Response with Salt and Water ON and OFF during the experiment

Figure A.III.5: HCl Response with Salt and Water ON and OFF during the experiment
Figure A.III.6: HCl Response with Salt and Water ON and OFF during the experiment (continued from Figure A.III.5)

Figure A.III.7: Consumption by water of Physically Adsorbed Salt
APPENDIX IV

ELEMENT MAPPING TECHNIQUES

Scanning Electron Microscopy (SEM) is used primarily to study the surface or near surface structure of bulk specimens (Goodhew, 1988).

A.IV.1 Scanning Electron Microscope

An electron gun produces electrons and accelerates them to an energy between about 2 keV and 40 keV. Two or three condenser lenses then demagnify the electron beam until, when it hits the specimen, it may have a diameter of only 2-10 nm. The electron beam is scanned in a similar way to a television receiver in a rectangular set of straight lines. As the electron beam hits the specimen secondary electrons, backscattered electrons and X-rays are generated.

The volume of the specimen that is penetrated by the electrons is called the interaction volume and the volume from which the detected X-rays originate is called the sampling volume. It is difficult to make the interaction volume much smaller than 1 μm³ without reducing the energy of the electron beam so much that no useful X-rays are emitted. X-rays are not easily absorbed and most will escape from the specimen. X-rays are used for chemical analysis rather than imaging. Electrons will not be backscattered out of the specimen if they have penetrated more than a fraction of a micron, so the backscattered signal originates from very near the surface. Secondary electrons are generated by the primary electrons, which hit the atoms at the surface of the specimen. The secondary electron signal originates from a region which is little larger than the diameter of the incident beam and is produced by secondary and backscattered electrons.

The imaging data for the SEM comes from the detector as an electrical signal, which is amplified. The simplest on-line processing involves the adjustment of image brightness and contrast using a linear amplifier. In normal operation, as the beam scans the specimen, the corresponding pixels on the cathode ray tube (CRT) are illuminated for a very small period of time. It is possible to transfer this reading to a computer, and after a complete scan, an image is digitally recorded. A framestore is used to transfer the data to a monitor screen.
(VDU), so that the stored pixel data are represented as points of the appropriate intensity on
the VDU. The scan can be controlled with a computer, so that instead of moving the beam
in a raster scan, it is moved directly to the required pixel points and is allowed to dwell on
each point for a predetermined time (the acquisition times used are 0.8s for the Energy
Dispersive System and 0.5s for the Wavelength Dispersive System). At the same time all the
available signals are collected, including several different types of X-ray signal.

A.IV.2 Methods of detection and counting of X-rays

Two different methods are used for detection and counting of X-rays: the EDS and the WDS.

Energy Dispersive Analysis

The detector is a small piece of semiconducting silicon which must be in the line of sight of
the specimen to collect as many as possible of the X-rays emitted. Each X-ray arriving at the
detector excites a number of electrons into the conduction band of the silicon making the
same number of positively charged holes in the outer electron shells (Figure A.IV.1). For each
of these excitations, an energy of 3.8eV is required. The number of electron-hole pairs
generated is proportional to the energy of the X-ray photon being detected. If a voltage is
applied across the semiconductor, a current will flow as each X-ray is absorbed in the detector
and the magnitude of the current will be proportional to the X-ray energy. The resultant
current is amplified and then stored in the appropriate channel of a Multichannel Analyser
(MCA). Each channel corresponds to a different X-ray energy. As a result, a histogram of
the energies of all the X-rays arriving at the detector, is collected (Figure A.IV.2). The EDS
system is controlled by a computer which also stores the characteristic X-ray energies from
all chemical elements. By comparing the data collected with the characteristic energies, the
elements in the sample are identified.

Advantage: with an EDS a complete spectrum can be acquired in a few minutes.
Disadvantages: 1) the energy resolution of the detector is poor, which means that each
X-ray line is not detected as a sharp line but as a broad peak
2) there can be a large amount of electronic noise in the system

A.IV.2
Both of these factors will affect the limit of detectability of the analyser and its use for quantitative analysis.

Figure A.IV.1: A silicon energy-dispersive X-ray detector.
Note: The beryllium window and gold contact layers are grossly exaggerated in thickness; typical thicknesses would be 7-8 \( \mu \text{m} \) for the Be, and 10-20 nm for the Au (Goodhew, 1988).

Figure A.IV.2: A simplified energy-dispersive analysis system.
Note: Pulses from the detector are amplified and then stored in the appropriate channel of a multi-channel analyser. In reality, the MCA would contain perhaps 1000 channels instead of the 24 shown here (Goodhew, 1988).

Wavelength Dispersive Analysis

The X-rays emitted from the specimen are diffracted by a curved crystal and then focused on to the detector. The curved crystal acts as a filter, so that only X-rays of a chosen wavelength
are allowed to fall on the detector. To cover a wide X-ray spectrum, a range of crystals, normally four, is required. The specimen, crystal and detector must all be aligned carefully (Figure A.IV.3). The detector used for WDS is a much simpler one than that one used for EDS.

Figure A.IV.3: A crystal X-ray spectrometer.

Note: X-rays emitted from the specimen are collimated by two slits S1 and S2, diffracted by the curved crystal, and then focused on to the detector. For the maximum efficiency the specimen, crystal and detector must all lie on the Rowland circle of radius R (Goodhew, 1988).

Advantage: the resolving power and the sensitivity of a crystal spectrometer are excellent
Disadvantage: as each X-ray wavelength is detected separately, a scan of all the required wavelengths can take a considerable time

This disadvantage of an X-ray spectrometer restricts its applications to the detection of low concentrations, detection of light elements and quantitative measurements of peak heights.

In summary, the EDS is better suited to rapid qualitative analysis, while WDS may give more accurate quantitative results.
A.IV.3 Digital X-Ray Mapping

In order to examine the variation of chemical composition within a sample, many analyses must be carried out over the area of interest. An alternative is to select the X-ray signal from an element of interest and to display its intensity as the specimen is scanned.

A great improvement is obtained by using digital X-ray mapping to display information about the distribution of an element. In this method the beam is controlled by a computer to move to a grid of points on the specimen. The beam remains at each of these points for a preset time, while an analysis is carried out. The data are stored in the computer memory and may be displayed on a grey level or colour scale. Each analysis point then becomes a pixel in the displayed image.

One of the advantages of X-ray mapping is that, with an EDS system, data from several elements may be collected at the same time by directing the counts from specified channels of the spectrum into different computer stores. An electron image may be acquired at the same time. In obtaining an X-ray map the spatial resolution is limited to around 1 μm³ and there is no point in working at high magnifications. Having acquired a digital X-ray map, the data may be subsequently manipulated.

A.IV.4 Problems of Qualitative Analysis

Before being examined in an SEM, the specimens must be coated with a thin conducting layer of gold or carbon. Gold can absorb X-rays emitted from the specimen and emit its own characteristic X-rays. In this work all the specimens were carbon coated. An alternative approach to the problem of specimen charging is to operate the microscope at a lower accelerating voltage.

As X-rays travel in straight lines from the specimen to the detector, X-rays from regions of the specimen which are not in the line of sight of the detector will not be detected. Rough specimens can give rise to anomalous X-ray emissions. In this work all samples were polished very carefully.
Some X-rays originate deep from within the specimen, from regions which are not visible in the electron image.

A.IV.5. Problems of Quantitative Analysis

The quantitative analysis in an electron microscope depends on:

- where the X-rays are generated
- how strongly the X-rays are absorbed by the specimen on the way up to the surface
- the analysis may not be uniformly representative of the whole sampling volume, because more of the X-rays emitted on average could have come from near the surface than from deeper inside the specimen.

A.IV.6 Instrument Description

The instrument that was used for X-ray mapping is a JEOL JXA 8600 Superprobe, which possesses:

- four computer controlled crystal spectrometers (WDS), containing a range of crystals such that a wide spectrum can be covered
- an EDS system for obtaining preliminary qualitative analysis
- a fixed focus microscope, not only for examination of the specimen, but more importantly for ensuring that the specimen height may be adjusted until it is correctly aligned with the detectors
- a motorised specimen stage, the position of which is computer controlled. Thus, areas of interest may be selected by the operator and the instrument may then be left to carry out the analysis, perhaps running for several hours automatically.
A.IV.7 Secondary Electron and X-ray Images of Fuller's Earth and kaolin pellets and grains

The secondary electron images and the digital X-ray maps of sodium and potassium distribution in Fuller's Earth and kaolin pellets, performed during this work, are presented below.

Figure A.IV.4: Secondary Electron Image (Video Map) of an untreated Fuller's Earth Pellet
Figure A.IV.5: Secondary Electron Image (Video map) of a treated Fuller's Earth Pellet (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol, fixed bed test)

Figure A.IV.6: Secondary electron Image (Video map) of a treated Kaolin Pellet (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, single-layer test)
Figure A.IV.7: Digital X-ray Map of Sodium Distribution in a Treated Fuller's earth Pellet (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol fixed bed test)

Figure A.IV.8: Digital X-ray Map of Sodium Distribution in a Treated Kaolin Pellet (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, single-layer test)
Figure A.IV.9: Digital X-ray Map of Sodium Distribution in a Treated Fuller's Earth Grain (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, single-layer test)

Figure A.IV.10: Digital X-ray Map of Sodium Distribution in a Treated Kaolin Grain (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, single-layer test)
Figure A.IV.11: Secondary Electron Image (Video Map) of a Fuller's Earth Pellet showing the grain across which a linescan was obtained (650°C, 200 hrs, Na:1.8 ppmwt, HCl:160 ppmv, H₂O:5%vol, fixed bed test, layer 5)

Figure A.IV.12: Linescan across the above indicated Fuller's Earth Grain representing the Sodium Distribution
Figure A.IV.13: Secondary Electron Image (Video Map) of a Fuller's Earth Grain (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol, fixed bed test, layer 5)

Figure A.IV.14: Digital X-ray Map of Sodium Distribution in the above Fuller's Earth Grain
Figure A.IV.15: Digital X-ray Map of Sodium Distribution in a Grain from a CRE-treated Fuller's Earth Pellet (650°C, 200 hrs, Na: 1.8 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol, single-layer test)

Figure A.IV.16: Digital X-ray Map of Potassium Distribution in a treated Fuller's Earth Grain (650°C, 200 hrs, K: 2.4 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol, fixed bed test, layer 1)
Figure A.IV.17: Secondary Electron Image (Video Map) of a treated Fuller's Earth Pellet (650°C, 200 hrs, K: 2.4 ppm wt, HCl: 160 ppmv, H₂O: 5 %vol, fixed bed test, layer 1)

Figure A.IV.18: Linescan across the above indicated Fuller's Earth Grain representing the Potassium Distribution
Figure A.IV.19 : Digital X-ray Map of Sodium Distribution in a Treated Light-coloured Fuller's Earth Pellet (650°C, 600 hrs, Na:1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, fixed bed test)

Figure A.IV.20 : Digital X-ray Map of Sodium Distribution in a Treated Dark-coloured Fuller's Earth Pellet (650°C, 600 hrs, Na:1.8 ppm wt, HCl: 0 ppmv, H₂O: 5 %vol, fixed bed test)
APPENDIX V

MEASUREMENT OF THE SPECIFIC SURFACE AREA OF THE SORBENT PELLETS

The evaluation of the specific surface area of a sorbent is based on the adsorption of a gas on its solid surface. Nitrogen at its boiling point (-195.8°C) is usually used as the adsorbate during the measurement. For different pressures, lower than atmospheric, different values of adsorbed gas volumes are estimated. If these data are presented on a diagram, isotherm curves are taken. If the adsorbed gas formed a monolayer film over the surface of the adsorbent, it would be very easy to calculate the surface area from the adsorbed gas volume. However, the physically adsorbed molecules form a multilayer film over the sorbent surface and, as a result, the measured adsorbed volume does not represent the right value of the surface area. The chemisorption process is pictured as leading ultimately to a monolayer film over the surface of the adsorbent. After analysis of data, it was observed that the lower part of the linear area of the isotherms represents the formation of a monolayer film. If this can be determined with accuracy, the monolayer volume and thus the specific surface area, can be calculated.

A.V.1 Langmuir Adsorption Isotherm

The derived adsorption isotherm results from an investigation of the equilibrium that is set up between the gas phase and the partially formed monolayer. The equilibrium state can be interpreted in terms of the dynamic equilibrium that results from an equal rate of evaporation of the adsorbed material and of condensation of the gas-phase molecules (Barrow, 1979).

The rate of evaporation can be taken to be proportional to the fraction of the surface used for adsorption (θ) and can be written as \( k_1 \theta \), where \( k_1 \) is the proportionality constant. The rate of condensation furthermore is taken to be proportional both to the gas pressure \( P \), and to the fraction of the surface that has not been covered by adsorbed molecules \((1-\theta)\).

At equilibrium, the rate of evaporation is equal to the rate of condensation
\[ k_1 \theta = k_2 P (1 - \theta) \]  \hspace{1cm} (A.V.1)

where \( k_2 \) = proportionality constant for the condensation. Rearrangement gives

\[ \theta = \frac{k_2 P}{(k_1 + k_2 P)} \]  \hspace{1cm} (A.V.2)

and introduction of \( a = \frac{k_1}{k_2} \) allows the result to be written

\[ \theta = \frac{P}{(a + P)} \]  \hspace{1cm} (A.V.3)

For adsorption up to a monolayer, the amount of gas \( V \) adsorbed at some pressure \( P \) and the amount of gas \( V_m \) needed to form a monolayer are related to \( \theta \) according to

\[ \frac{V}{V_m} = \theta \]  \hspace{1cm} (A.V.4)

From the previous equations

\[ V = (V_m P)/(a + P) \]  \hspace{1cm} (A.V.5)

and after rearrangement

\[ P/V = (a/V_m) + (P/V_m) \]  \hspace{1cm} (A.V.6)

The surface area may then be calculated from

\[ SA = \frac{(N_A V_m)}{M_v} \]  \hspace{1cm} (A.V.7)

where \( N_A \) = Avogadro's number (molecules / mol)  
\( A_m \) = area occupied by adsorbate molecule (m\(^2\) / molecule)  
\( V_m \) = volume of monolayer (m\(^3\))  
\( M_v \) = gram molecular volume (22.4x10\(^{-3}\) m\(^3\) / mol)  
\( SA \) = sorbent surface area (m\(^2\))

**A.V.2 BET Surface Area**

This multilayer adsorption theory may be used to calculate the surface area of a sample. The detail of the theory is not explained here but some of the assumptions made in the theory are listed (Gregg, 1967):
1) Within each layer, dynamic equilibrium is assumed to prevail; in layer i, the number of molecules evaporating per second is equated to the number condensing on it per second from the layer immediately above, the (i+1)th layer.

2) The latent heat of adsorption in all layers above the first is equal to the latent heat of condensation \( L : E_2 = E_3 = \ldots = E_i = L \)

3) The evaporation-condensation constants in all layers above the first are identical.

4) When pressure \( P \) becomes equal to the saturated vapour pressure, the adsorbate vapour condenses as an ordinary liquid on to the adsorbed film, so that the number of molecular layers become infinite on the surface, which is postulated to be freely exposed to the vapour phase.

The linear BET equation in its most common form is given by:

\[
P/[V(P_0-P)] = 1/(V_mC) + (C-1)/(V_mC) \times P/P_0
\]

(A.V.8)

where \( V_m \) = volume of the monolayer (m\(^3\) g\(^{-1}\))

\( V \) = volume adsorbed

\( P \) = sample pressure

\( P_0 \) = saturation vapour pressure

A plot of \( P/V(P_0-P) \) against \( P/P_0 \) should give a straight line having a slope \((C-1)/V_mC\) and an intercept \(1/V_mC\). The BET surface area is then calculated from the equation (A.V.7). For nitrogen, a value of 16.2 Å\(^2\) for \( A_m \) is used as default value, and after applying the appropriate conversion factors, the equation is simplified to:

\[
SA = 4.35 \times V_m
\]

(A.V.9)

A.V.3 100CX Omnisorp Instrument

The adsorption measurements are based on the pressure drop that is observed in a space where a material has been placed capable of adsorbing a significant quantity of gas. Thus, the
measured quantity is the pressure in the sample bulb when equilibrium has been reached.

The 100CX Omnisorp Instrument is used for the measurement of the surface area of Fuller's Earth pellets. The instrument has a calibrated manifold volume and a mass flow controller, which is used to provide a known flow rate of adsorbate or to dose the manifold for subsequent equilibration with the sample. Nitrogen is used as the adsorbate for the surface area measurements. The instrument should achieve very high vacuum in the order of $10^{-5}$ torr or lower before it is used for a measurement. For the determination of low surface areas because the low volume of gas adsorbed minimises the pressure reduction during the dosing procedure and very small pressure changes can not be accurately determined with the 1,000 torr transducer, a low value absolute pressure range allows the use of a 10 torr transducer, which is able to measure small pressure differences accurately. The two measurement methods used by the instrument are the Static and the Continuous Flow Method.

**Static Flow Method**

In the Static Flow Method, the mass flow controller doses the calibrated manifold with adsorbate and once the target pressure has been reached, the controller is turned off. When the pressure is equilibrated in the manifold, the sample valve is turned on and the adsorbent is subjected to the adsorbate till the pressure is again equilibrated. The volume of gas adsorbed is calculated from the difference of the two equilibrated pressures. The volume of the sample bulb (dead volume), where no adsorption can take place, is subtracted from the calculated volume to provide the volume of the gas adsorbed. The dead space evaluation is performed with He, which is a non adsorbing gas at the temperature used for the measurement.

**Continuous Flow Method**

In the Continuous Flow Method, the mass flow controller doses the adsorbate gas continuously and directly to the sample. This method is insensitive to the measurement of low surface areas and as a result, it was considered inappropriate for Fuller's Earth pellets.
APPENDIX VI

PELLET- AND GRAIN-SIZE DISTRIBUTION

A.VI.1 Pellet-size Distribution

In reality, in a fixed bed reactor it is unlikely that the pellets will be all the same size. The investigation of the effect of a pellet size distribution in the reactor was attempted by introducing two pellet sizes in the convective mass balance. The sorbent bed was considered to consist of $x_{rpi}\%$ of pellet size 1 and $x_{rpi}\%$ of pellet size 2, where $x_{rpi} + x_{rpi} = 100$. To achieve this distribution, the bulk density of the fixed bed, $\omega$, was multiplied for each pellet size with its percentage. As a result, the 'accumulation in the solid' term becomes

\[ \frac{\omega}{\varepsilon_b} \sum_{i=1}^{N_R} K_i \sum_{rpi=1}^{2} x_{rpi} \frac{\partial XG_{rpi}}{\partial t} \]  

(A.VI.1)

A.VI.2 Grain-size Distribution

In the pellet-grain model, it has been assumed that the sorbent pellets consist of grains of equal size. Generally, a pellet is usually formed by compacting fine grains of particle with or without binding agents and the grains are usually of irregular shape and are distributed in size. However to facilitate the presentation of the model, the overall shape of a grain may be approximated by that of a sphere. In the following it is assumed that the real grain size distribution can be approximated by a number of discrete grain sizes. To substitute the mean grain size used in the convective mass balance with two or three grain sizes, the grain size distribution had to be translated to weight fractions of each grain size.

The accumulation in the solid getter in the convective mass balance (4.1) for a multiple reaction scheme is written as

A.VI.1
where \( K_n \) and \( XG_n \) = the sorbent capacity and the solid conversion respectively for reaction 1

\( (K_n) \) and reaction 2 \( (K_n) \)

\( N_R = \) total number of reactions

For more than one grain size, this term is written

\[
\frac{\omega}{\varepsilon_{p, r_i}} \sum_{r_i=1}^{N_R} \sum_{r_{gi}=1}^{N_g} K_{r_i} x_{r_{gi}} \frac{\partial XG_{r_{gi}}}{\partial t}
\]

(A.VI.3)

where \( x_{r_{gi}} = \) the weight fraction of the grains with \( r_{gi} \) radius

\( N_g = \) total number of grain sizes used

\( XG_{r_{gi}} = \) solid conversion for reaction \( r_i \) and grain radius \( r_{gi} \)

If a pellet consists of \( N \) grain sizes then the volume of solid in the pellet equals the sum of

the volumes of the grains inside the pellet

\[
\frac{4}{3} \pi R_p^3 (1 - \varepsilon_p) = \sum_{i=1}^{N} n_i \frac{4}{3} \pi r_{si}^3
\]

(A.VI.4)

where \( n_i = \) the number of particles in each grain size

Multiplying by the solid density, \( \rho_s \), the volumes are converted to weights and the weight

fractions of the grains with different grain sizes, can be calculated by

\[
x_{r_{si}} = \frac{n_i r_{si}^3}{R_p^3 (1 - \varepsilon_p) \sum_{i=1}^{N} n_i r_{si}^3}
\]

(A.VI.5)

The number of grains for each grain size, can be found from the number fraction which is

A.VI.2
known already from the analysis for two grain sizes with populations $n_1$ and $n_2$. If $k_1$ is the number fraction of grains with radius $r_g$, then

$$\frac{n_1}{n_1 + n_2} = k_1 = n_4 = \left(\frac{k_1}{1 - k_1}\right)n_2 \quad \text{(A.VI.6)}$$

and consequently from the previous equations

$$n_2 = \frac{(1 - \epsilon_p)R_p^3}{k_1 \left(\frac{r_1^3}{1 - k_1} + r_2^3\right)} \quad \text{(A.VI.7)}$$

For three grain sizes with populations $n_1$, $n_2$ and $n_3$

$$\frac{n_1}{n_1 + n_2 + n_3} = k_1 = n_4 = \left(\frac{k_1}{1 - k_1}\right)(n_2 + n_3) \quad \text{(A.VI.8)}$$

$$\frac{n_3}{n_1 + n_2 + n_3} = k_3 = n_5 = \frac{k_3}{k_2}n_2 \quad \text{(A.VI.9)}$$

and in combination with the previous equations

$$n_2 = \frac{R_p^3(1 - \epsilon_p)}{r_2^3 + \frac{k_1}{1 - k_1}r_2^3} \quad \text{(A.VI.10)}$$

$$A = \frac{(\frac{k_1}{1 - k_1}r_2^3 + r_3^3)k_3}{(r_2^3 + \frac{k_1}{1 - k_1}r_2^3)(k_2 + k_3 + k_4)} \quad \text{(A.VI.11)}$$
### A.VI.3 Results

#### Table A.VI.1: Measured pellet & grain diameters (measurements made with an optical microscope)

<table>
<thead>
<tr>
<th>Nominal Pellet Diameter (mm)</th>
<th>Measured Pellet Diameter (mm)</th>
<th>Measured Mean Grain Diameter ±Std.Dev.(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.425-0.500</td>
<td>0.525</td>
<td>0.030±0.008 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.400</td>
<td>0.030±0.000 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.525</td>
<td>0.033±0.005 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.525</td>
<td>0.030±0.000 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.450</td>
<td>0.030±0.007 (4 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.400</td>
<td>0.033±0.005 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.475</td>
<td>0.036±0.005 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.475</td>
<td>0.030±0.000 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.500</td>
<td>0.027±0.005 (3 grains)</td>
</tr>
<tr>
<td>0.425-0.500</td>
<td>0.475</td>
<td>0.027±0.004 (4 grains)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.400-0.525</td>
<td>0.030±0.003</td>
</tr>
<tr>
<td>0.500-0.600</td>
<td>0.600</td>
<td>0.032±0.009 (5 grains)</td>
</tr>
<tr>
<td>0.500-0.600</td>
<td>0.625</td>
<td>0.037±0.003 (5 grains)</td>
</tr>
<tr>
<td>0.500-0.600</td>
<td>0.625</td>
<td>0.053±0.025 (5 grains)</td>
</tr>
<tr>
<td>0.500-0.600</td>
<td>0.575</td>
<td>0.054±0.021 (8 grains)</td>
</tr>
<tr>
<td>Mean</td>
<td>0.575-0.625</td>
<td>0.044±0.010</td>
</tr>
</tbody>
</table>
Determination of the grain limits in a Fuller's Earth pellet, using a secondary electron image for the estimation of the grain size distribution.

Histogram of the major axis grain length as representative of the grain diameter, based on the number of grains measured in the above pellet.
Figure A.VI.3: Grain diameter versus 100/R, where R is the weight percentage that corresponds to each grain size for the Rosin-Rammler distribution, based on the histogram of Figure A.VI.2.
APPENDIX VII

X-RAY DIFFRACTION STUDIES

A.VII.1 Bragg’s Law

By analogy with the diffraction of light, crystals with their regularly repeating structures should be capable of diffracting radiation that has a wavelength similar to the interatomic separation, ~1 Å. Three types of radiation are used for crystal diffraction studies: X-rays, electrons and neutrons. X-rays are by far the most useful. The X-ray wavelength commonly employed is the characteristic Kα radiation, λ=1.5418 Å, emitted by copper. When crystals diffract X-rays, it is the atoms or ions which act as secondary point sources and scatter the X-rays.

The Bragg approach to diffraction is to regard crystals as built up in layers or planes such that each acts as a semi-transparent mirror. Some of the X-rays are reflected off a plane with the angle of reflection equal to the angle of incidence, but the rest are transmitted to be subsequently reflected by succeeding planes. When two X-ray beams are reflected from adjacent planes within the crystal (Figure A.VII.1), the perpendicular distance between the planes, the d-spacing, d, and the angle of incidence, or Bragg angle, θ, are related by Bragg’s law:

\[ 2dsin\theta = n\lambda \]  

(A.VII.1)

where \( n \) = order of diffraction

Figure A.VII.1: Derivation of Bragg’s law for X-ray diffraction (West, 1984)
When Bragg's law is satisfied, the reflected beams are in phase and interfere constructively. At angles of incidence other than the Bragg angle, reflected beams are out of phase and destructive interference or cancellation occurs. In real crystals, which contain thousands of planes and not just two, Bragg's law imposes a stringent condition on the angles at which reflection may occur.

A.VII.2 The Powder Method

When reduced to basic essentials, the X-ray diffraction experiment requires an X-ray source, the sample under investigation and a detector to peak up the diffracted X-rays. Within this broad framework, there are three variables which govern the different X-ray techniques: (a) radiation (monochromatic or of variable $\lambda$), (b) sample (single crystal, powder or a solid piece), and (c) detector (radiation counter or photographic film).

In the powder method, a monochromatic beam of X-rays strikes a finely powdered sample that ideally has crystals randomly arranged in every possible orientation. In such a powder sample, the various lattice planes are also present in every possible orientation. For each set of planes therefore, at least some crystals must be oriented at the Bragg angle, $\theta$, to the incident beam and thus, diffraction occurs for these crystals and planes. The diffracted beams may be detected either by surrounding the sample with a strip of photographic film (Debye-Scherrer focusing methods) or by using a movable detector, such as a Geiger counter, connected to a chart recorder (diffractometer). During this work, a photographic film was used. The principles of the powder method are shown in Figure A.VII.2.

![Figure A.VII.2](image_url)  
*Figure A.VII.2 : The powder method (West, 1984)*
The original powder method, the Debye-Scherre, is little used nowadays but it is simple and instructive to consider its mode of operation. For any sets of lattice planes, the diffracted radiation forms the surface of a cone, as is shown in Figure A.VII.3. The only requirement for diffraction is that the planes be at angle $\theta$ to the incident beam; no restriction is placed on the angular orientation of the planes about the axis of the incident beam. In a finely powdered sample, crystals are present at every possible angular position about the incident beam and the diffracted beams that result appear to be emitted from the sample as cones of radiation. If the Bragg angle is $\theta$, then the angle between diffracted and undiffracted beam is $2\theta$ and the angle of the cone is $4\theta$. Each set of planes gives its own cone of radiation. The cones are detected by a thin strip of film wrapped around the sample. Each cone intersects the film as two short arcs (Figure A.VII.4), which are symmetrical about the two holes in the film. These allow entry and exit of incident and undiffracted beams. In a well powdered sample, each arc appears as a continuous line, but in coarser samples the arcs may be spotty due to the relatively small number of crystals present.

![Diagram](image.png)

**Figure A.VII.3**: The formation of a cone of diffracted radiation in the powder method (West, 1984)

**Figure A.VII.4**: Schematic Debye-Scherrer photograph (West, 1984)
To obtain d-spacings from the Debye-Scherrer film, the separation, S, between pairs of corresponding arcs is measured. If the film (camera) radius, R, is known, then \( S/2\pi R = 40/360 \), from which \( 2\theta \) and therefore \( d \) may be obtained for each pair of arcs. In this work, the camera diameter was 114.86 mm, which means that \( 40 = 1 \) mm. The disadvantages of this method are that exposure times are long and that closely spaced arcs are not well resolved. This is because, although the incident beam enters the camera through a pinhole slit and collimator tube, the beam is somewhat divergent and the spread increases in the diffracted beams. If in an effort to increase the resolution, a finer collimator is used, the resulting diffracted beams have much less intensity and longer exposure times are needed. Apart from considerations of the extra time involved, the amount of background radiation detected by the film increases with exposure time and weak lines may be lost altogether in the background.

The other modern powder technique is diffractometry, which gives a series of peaks on a strip of chart paper. A convergent incident beam is obtained by placing a bent single crystal of quartz or graphite between the X-ray source and the sample. The orientation of this bent crystal is adjusted so that it diffracts the incident beam and converts it from a divergent beam into a convergent one. The beam then strikes the sample and the diffracted beams are arranged to give fairly good resolution of peaks. Both peak positions and intensities (peak heights) are readily obtained from the chart to make this a very useful and rapid method of phase analysis.

The most important use of the powder method is in the qualitative identification of crystalline phases or compounds. While most chemical methods of analysis give information about the elements present in a sample, powder diffraction is very different and perhaps unique in that it tells what crystalline compounds or phases are present but gives no direct information about their chemical constitution.

Each crystalline phase has a characteristic powder pattern which can be used as a fingerprint for identification purposes. The two variables in a powder pattern are peak position, i.e. d-spacing, which can be measured very accurately if necessary, and intensity, which can be measured either qualitatively or quantitatively. It is rare but not unknown that two materials have identical powder patterns. More often, two materials have one or two lines with common
d-spacings, but on comparing the whole patterns which may contain between 5 and 100 observed lines, the two are found to be quite different. In more extreme cases, two substances may happen to have the same unit cell parameters and therefore, the same d-spacings, but since different elements are probably present in the two, their intensities are quite different. The normal practice in using powder patterns for identification purposes is to pay more attention to the d-spacings but, at the same time, check that the intensities are roughly correct.

For the identification of unknown crystalline materials, an invaluable reference source is the Powder Diffraction File (Joint committee on Powder Diffraction Standards) previously known as the ASTM file, which contains the powder patterns of about 35000 materials. In the search indices, materials are classified either according to their most intense peaks or according to the first eight lines in the powder pattern in order of decreasing d-spacing. Problems arise if the material is not included in the file or if it is not pure but contains lines from more than one phase.
### A.VII.3 Results on the d-spacings measurements

Table A.VII.1: d-spacings obtained from X-ray diffraction studies on raw Fuller's Earth powder. These values are compared with the characteristic d-spacings of Calcium Montmorillonite

<table>
<thead>
<tr>
<th>d-spacings (Raw Fuller's Earth)</th>
<th>Intensity</th>
<th>d-spacings (Calcium Montmorillonite)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.6</td>
<td>high</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>4.93</td>
<td>very low</td>
<td>5.01</td>
<td>60</td>
</tr>
<tr>
<td>4.44</td>
<td>high</td>
<td>4.50</td>
<td>80</td>
</tr>
<tr>
<td>3.33</td>
<td>low</td>
<td>3.30</td>
<td>10</td>
</tr>
<tr>
<td>3.24</td>
<td>very low</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.003</td>
<td>medium</td>
<td>3.02</td>
<td>60</td>
</tr>
<tr>
<td>2.54</td>
<td>medium</td>
<td>(2.58) - (2.50)</td>
<td>40</td>
</tr>
<tr>
<td>2.28</td>
<td>very low</td>
<td>2.26</td>
<td>10</td>
</tr>
<tr>
<td>2.08</td>
<td>very low</td>
<td>2.15</td>
<td>10</td>
</tr>
<tr>
<td>1.88</td>
<td>very low</td>
<td>1.88</td>
<td>10</td>
</tr>
<tr>
<td>1.69</td>
<td>very low</td>
<td>1.70</td>
<td>30</td>
</tr>
<tr>
<td>1.497</td>
<td>medium</td>
<td>1.493</td>
<td>50</td>
</tr>
<tr>
<td>1.288</td>
<td>low</td>
<td>1.285</td>
<td>20</td>
</tr>
</tbody>
</table>
Table A.VII.2: d-spacings obtained from X-ray diffraction studies on calcined and treated Fuller's Earth pellets under high-acid conditions. These values are compared with the characteristic d-spacings of Albite and Quartz.

<table>
<thead>
<tr>
<th>d-spacings (calcined pellets)</th>
<th>d-spacings (treated pellets)</th>
<th>Intensity</th>
<th>d-spacings (albite)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.439</td>
<td>4.34 (quartz)</td>
<td>very low</td>
<td>4.033</td>
<td>84</td>
</tr>
<tr>
<td>4.04</td>
<td>3.427</td>
<td>medium</td>
<td>3.399 (quartz)</td>
<td>100</td>
</tr>
<tr>
<td>3.42</td>
<td>3.332</td>
<td>high</td>
<td>3.204</td>
<td>100</td>
</tr>
<tr>
<td>3.35</td>
<td>3.186</td>
<td>low</td>
<td>3.178</td>
<td>88</td>
</tr>
<tr>
<td>2.675</td>
<td>2.675</td>
<td>very low</td>
<td>2.5 (quartz)</td>
<td>2</td>
</tr>
<tr>
<td>1.85</td>
<td>1.859</td>
<td>low</td>
<td>1.85 (quartz)</td>
<td>8</td>
</tr>
</tbody>
</table>
Table A.VII.3: d-spacings obtained from X-ray diffraction studies on treated Fuller’s Earth dark- and light-coloured pellets under non-acid conditions. These values are compared with the characteristic d-spacings of Nepheline and Quartz

<table>
<thead>
<tr>
<th>d-spacings (dark pellets)</th>
<th>d-spacings (light pellets)</th>
<th>Intensity</th>
<th>d-spacings (nepheline)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.28</td>
<td>4.28</td>
<td>high</td>
<td>4.32</td>
<td>35</td>
</tr>
<tr>
<td>4.181</td>
<td>4.18</td>
<td>high</td>
<td>4.165</td>
<td>80</td>
</tr>
<tr>
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<td>3.78</td>
<td>high</td>
<td>3.834</td>
<td>100</td>
</tr>
<tr>
<td>3.243</td>
<td>3.24</td>
<td>high</td>
<td>3.266</td>
<td>70</td>
</tr>
<tr>
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<td>2.98</td>
<td>high</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>2.88</td>
<td>2.88</td>
<td>very low</td>
<td>2.88</td>
<td>35</td>
</tr>
<tr>
<td>2.58</td>
<td>-</td>
<td>very low</td>
<td>2.57</td>
<td>50</td>
</tr>
<tr>
<td>2.34</td>
<td>2.32</td>
<td>medium</td>
<td>2.336</td>
<td>35</td>
</tr>
<tr>
<td>2.08</td>
<td>2.06</td>
<td>very low</td>
<td>2.083</td>
<td>16</td>
</tr>
<tr>
<td>1.914</td>
<td>1.6</td>
<td>very low</td>
<td>1.82 (quartz)</td>
<td>14</td>
</tr>
<tr>
<td>1.55</td>
<td>1.55</td>
<td>low</td>
<td>1.54 (quartz)</td>
<td>9</td>
</tr>
<tr>
<td>1.387</td>
<td>1.39</td>
<td>low</td>
<td>1.37 (quartz)</td>
<td>8</td>
</tr>
</tbody>
</table>
APPENDIX VIII

COMPUTER PROGRAMS

A.VIII.1 PELLET-GRAIN MODEL FOR A SINGLE PELLET

```fortran
C Extension of the pellet-grain model, for a single pellet and with two
C simultaneous reactions taking place, that returns the numerical and
C analytical estimation of the reaction rate (dXg/dt) and compares them
C The numerical evaluation is estimated from the Newton-Raphson
C solutions over a time step, whereas the analytical value is estimated
C from the Szekely approximation

IMPLICIT DOUBLE PRECISION (A-H,0-Z)
EXTERNAL RAPHSON1,RAPHSON2
INTRINSIC ABS

REAL*8 XACC,relaxf,RP,RG,DGAS,KG,B1,B2,BTAP,RHO,F1,F2,
1 XLAST1,TIME,DELTI,TI,CNACL,CNA,NCNA,CHCLIN,CHCL,
2 NCHCL,KSI,KSI1,DE1,KE2,KS2,DE2,XLAST2,XF,FTOT,MNA,
3 TOL,DG1,DXGDT1,DG2,DXGDT2

INTEGER JMAX,L,TINT

OPEN(UNIT=8,FILE='deriv7.OUT1')
OPEN(UNIT=9,FILE='deriv8.OUT')
OPEN(UNIT=10,FILE='deriv9.OUT')

JMAX=50 /* maximum number of iterations
XACC=1.0D-12 /* accuracy required by the Newton-Raphson
relaxf=0.5d0 /* relaxation factor to be used if needed

/* initialise system parameters

TI=2160000.0D0 /* real time [s]
TINT = 100.0
DELTI = TI/TINT /* TIME STEP

c delti=1800.0

c delti=1.0d0

TIME=0.0D0 /* initialise time
XLAST1=0.0D0 /* initial value for conversion for reaction 1
XLAST2=0.0D0 /* initial value for conversion for reaction 2
DG1=0.0D0 /* initialise derivatives
DG2=0.0D0 /* initialise derivatives

MNA=0.0D0 /* total pellet Na uptake [g Na/g SOLID]
XF=0.0D0 /* overall pellet conversion
F1=9.9D0/100.0D0 /* Na uptake due to reaction 1 [g Na/g initial
solid]
F2=4.7D0/100.0D0 /* Na uptake due to reaction 2 [g Na/g initial
solid]

FTOT=14.61D0/100.0D0 /* total Na uptake [g Na/g initial solid]
TOL=1.0D-04 /* tolerance for checking whether the Xg

A.VIII.1
```
value close to 1 can be accepted or not

\[ RP = 0.055/2.0D0 \] /* pellet radius [cm] \\
\[ RG = 20.0D-4 \] /* grain radius (20 microm) [cm] \\
\[ DGAS = 0.25D0 \] /* intrapellet diffusivity [cm^2/s] \\
\[ KG = 50.26D0 \] /* gas film mass transfer coefficient [cm/s] \\
\[ RH0 = 4.1200D-3 \] /* moles sorbent/cm for Fuller's Earth \\
\[ B1 = 1.0D0 \] /* stoichiometric ratio for reaction 1 \\
\[ B2 = 1.0D0 \] /* stoichiometric ratio for reaction 2 \\
\[ ETAP = 0.20D0 \] /* intrapellet porosity \\

Concentration terms for NaCl and HCl

\[ CNACL = 2.2 \text{ ppmv} \] and \[ CHCLIN = 160 \text{ ppmv} \]

Parameters that can be optimised

\[ KE1 = 5000.0D0 \] /* reaction equilibrium constant \\
\[ KS1 = 0.0002D0 \] /* reaction rate constant [cm/s] \\
\[ DE1 = 10.0D-02 \] /* intragrain diffusivity [cm^2/s] \\
\[ KE2 = 5000.0D0 \] \\
\[ KS2 = 0.7D0 \] \\
\[ DE2 = 2.0D-05 \]

DO 13 L=1,TINT \\
TIME = TIME + DELTI \\
CALL RAPHSON1(L,TINT,TIME,XLAST1,JMAX,RP,DELT1,DGAS,KG, \\
1 RG,RHO,B1,ETAP,CNACL,CNA,NCNA,CHCLIN,CHCL, \\
2 NCHCL,KE1,KS1,DE1,XACC,TOL,DXG1,DXGDT1) \\
WRITE(8,1000) XLAST1,TIME,DXG1,DXGDT1 \\
1000 FORMAT(1X,4(1X,E13.6)) \\
CALL RAPHSON2(L,TINT,TIME,XLAST2,JMAX,RP,DELT2,DGAS,KG, \\
1 RG,RHO,B2,ETAP,CNACL,CNA,NCNA,CHCLIN,CHCL, \\
2 NCHCL,KE2,KS2,DE2,XACC,TOL,DXG2,DXGDT2) \\
WRITE(9,1010) XLAST2,TIME,DXG2,DXGDT2 \\
1010 FORMAT(1X,4(1X,E13.6)) \\
MNA = (F1*XLAST1+F2*XLAST2) /* total pellet Na uptake \\
XF = MNA/FTOT /* [g Na/g clean sorbent] \\
WRITE(10,1020) XF,MNA,TIME \\
1020 FORMAT(1X,3(1X,E13.6)) \\
13 CONTINUE \\
END \\

A.VIII.2
SUBROUTINE RAPHSON1(L,TINT,TIME,XLAST1,JMAX,RP,DELT1,DGAS,KG,
1 RG,RHO,B1,ETAP,CNACL,CNA,NCNA,CHLIN,CHCL,
2 NCHCL,KE1,KS1,DE1,XACC,TOL,DXG1,DXGDT1)

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
EXTERNAL GRAIN1
INTRINSIC ABS,DABS
REAL* 8 TIME,XLAST1,RP,DELT1,DGAS,KG,NCHCL,KE1,KS1,DE1,FUN,DFUN,
1 RG,RHO,B1,ETAP,CNACL,CNA,NCNA,CHLIN,CHCL,XGUESS,DX,XACC,
2 TOL,DXG1,DXGDT1
INTEGER L,TINT,JMAX,J2

XGUESS = XLAST1

PROGRAM FOR NEWTON-RAPHSON METHOD FOR FINDING ROOTS

DO 11 J2=1,JMAX
  TIME=TIME
  CALL GRAIN1(XGUESS,FUN,DFUN,RP,DELT1,J2,TIME,DGAS,KG,
1 RG,RHO,B1,ETAP,CNACL,CNA,NCNA,CHLIN,CHCL,
2 NCHCL,KE1,KS1,DE1,TOL,DXGDT1)

C Condition for the pellet that has been saturated before the end of
C experiment time

IF(XGUESS.GE.1.0D0.AND. (XGUESS-1.0D0 ).LT.TOL) THEN
  XGUESS=1.0D0
  WRITE(1,'(IX,''XGUESS1 = '',E12.4,''TIME='',D12.4,''J2='',
1 14)') XGUESS,TIME,J2
  GOTO 12
ENDIF

C Condition for a much bigger Xg than 1

IF((XGUESS-1.0D0 ).GE.TOL) THEN
  PRINT *, ''XG1 BIGGER THAN 1''
  WRITE(1,'(1X,''XGUESS1 = '',E12.4,''TIME='',D12.4,''J2='',
1 14)') XGUESS,TIME,J2
  GOTO 12
ENDIF

DX=FUN/DFUN
XGUESS=XGUESS-DX

Or we could use a relaxation factor

Xguess = Xguess - Relaxf*DX

XGUESS=XGUESS-relaxf*DX

The WRITE statement can appear immediately after this comment and give
the real value of XGUESS (negative or positive), or
it can be written later as 0 or 1 or its normal value depending on the
conditions

WRITE(1,'(1X,''XGUESS1 = '',E12.4,''TIME='',D12.4,''J2='',
1 14)') XGUESS,TIME,J2

A.VIII.3
C Condition for a really negative Xg

IF(XGUESS.LT.0.0D0.AND.DABS(XGUESS).GT.1.D-14) THEN
  XGUESS=0.DO
  IF(J2.GE.JMAX) THEN
    WRITE(1,'(1X,'XGUESS1 = ',E12.4,'TIME=','D12.4,'J2=','
         I4)') XGUESS,TIME,J2
    GOTO 12
  ENDIF
ENDIF

C Condition for the negative Xg, which is smaller than the computer's accuracy and therefore can be considered really as zero

ELSEIF(DABS(XGUESS).LT.1.D-14) THEN
  XGUESS=0.DO
  IF(J2.GE.JMAX) THEN
    WRITE(1,'(1X,''XGUESS1 = ',E12.4,'TIME=','D12.4,'J2=','
         I4)') XGUESS,TIME,J2
    GOTO 12
  ENDIF
ENDIF

WRITE(1,'(1X,''XGUESS1 = '',E12.4,'TIME=',D12.4,'J2='',
         I4)') XGUESS,TIME,J2

IF(ABS(DX).LT.XACC) THEN /* convergence
  GOTO 12
ENDIF

11 CONTINUE
PAUSE 'XGUESS EXCEEDING MAXIMUM ITERATIONS'

C XGUESS IS THE SOLUTION FROM THE GRAIN MODEL FOUND BY NEWTON-RAPHSON METHOD AND USED TO FIND THE OVERALL SOLID'S CONTENT

12 DXG1=(XGUESS-XLAST1)/DELT1 /* numerical evaluation of dXgl/dt

XLAST1=XGUESS /* this is the new value that will be used later

END

SUBROUTINE GRAIN1 (XGUESS,FUN,DFUN,RP,DELT1,J2,TIME,DGAS,KG,
1          RG,RHO,B1,ETAP,CNACL,CNA,NCNA,CHCLIN,CHCL,
2          NCHCL,KE1,KS1,DE1,TOL,DXGDT1)

C #################################################################
C #
C GRAIN1: PROVIDES VALUE AND DERIVATIVE OF MODEL EQUATION AT XGUESS
C #
C SZEKELY, EVANS AND SOHN "PELLET-GAS-SOLID REACTIONS"
C ACADEMIC PRESS, NEW YORK, 1976
C #
C #################################################################

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTRINSIC ABS,EXP,LOG

REAL*8 XGUESS,FUN,DFUN,XG,PHI2,SHERW,PHIG,DGAS,KG,CHCL,
1     EQN1,EQN2,EQN3,DEQN1,DEQN2,DEQN3,DELT1,CNA,NCNA,
2     TSTAR,TIME,CIN2,RP,RG,RHO,B1,ETAP,CNACL,CHCLIN,
3     NCHCL,KE1,KS1,DE1,TOL,TSTAR1,DXGDT1

A.VIII.4
INTEGER J2
XG=XGUESS

Condition if the value of XGUESS is so close to 1, that it has reached saturation and should not proceed any more

IF(XGUESS.GE.1.0D0.AND.(XGUESS-1.0D0).LT.TOL) THEN
  XGUESS=1.0D0
  GOTO 10
ENDIF

Condition if XGUESS is much bigger than 1

IF((XGUESS-1.0D0).GE.TOL) GOTO 10

INTRINSIC REACTION RATE, 1ST ORDER
CIN2 = PRESENT GAS NA CONC IN THE TANK
KE = KC * CH2O^0.5 = CHCL/CNACL => CNACL = CHCL/KE
CIN2 = CNA - CHCL/KE

CIN2=(CNA-CHCL/KE)

Normalised Expression of concentration driving force

CIN2=(NCNA*CNACL-NCHL*CHCLIN/KE)

Calculation of modified Sherwood number and the dimensionless groups sigma and sigmag for Szekely approximation

PHI2=RP**2*(1.0D0-ETAP)*KS1/(6.0D0*DGAS*RG)*(1.0D0+1.0D0/KE1)
SHERW=KG*RP/DGAS
PHIG=KS1*RG/(6.0D0*DE1)*(1.0D0+1.0D0/KE1)

WRITE(1, '  (  1  '' GRAIN1 HERE!''/ 1  '' PHI2 = ''E12.4/
  2  '' SHERW = ''E12.4/
  3  '' PHIG = ''E12.4)') PHI2,SHERW,PHIG

TSTAR1=1.0D0+PHIG+PHI2*(1.0D0+2.0D0/SHERW)+(0.21D0-0.31D0)*
(1.0D0+PHI2)*EXP(-0.9D0*(LOG((PHI2**(1.0d0/2.Od0))/
2 1.08D0)))**2)

TSTAR=BI*KS1*CIN2*TIME/(RHO*RG)

WRITE(1, ('tstar1=','d12.4, 'tstar=','d12.4')) tstar1,tstar

Condition if tstar1=time for complete conversion is a criterion whether Xg should stop proceeding to bigger values than 1

IF((TSTAR1-TSTAR).LT.0.005D0) THEN
  XGUESS=1.0D0
  GOTO 10
ENDIF

A.VIII.5
EQN1 = g(XG)
EQN2 = p(XG)
EQN3 = LAST TERM OF THE TSTAR EQUATION FOR XG

EQN1=1.0D0-(1.0D0-XG)**(1.0D0/3.0D0)
EQN2=1.0D0-3.0D0*(1.0D0-XG)**(2.0D0/3.0D0)+2.0D0*(1.0D0-XG)
EQN3=(0.21D0*XG-0.31D0*XG**2)*(1.0D0+PHI2)*EXP(-0.9D0*
1 (LOG((PHI2**(1.0D0/2.0D0))/1.08D0))**2)

FUN = VALUE OF FUNCTION AT XGUESS

FUN=EQN1+EQN2*PHIG+PHI2*(EQN2+2.0D0*XG/SHERW)+EQN3-TSTAR

CALCULATE DERIVATE OF FUNCTION W.R.T. XG

DEQN1 = (1.0D0-XG)**(-2.0D0/3.0D0)/3.0D0
DEQN2 = 2.0D0*(1-XG)**(-1.0D0/3.0D0)-2.0D0
DEQN3 = (0.21D0-0.62D0*XG)*(1.0D0+PHI2)*EXP(-0.9D0*
1 (LOG((PHI2**(1.0D0/2.0D0))/1.08D0))**2)

DFUN IS VALUE OF DERIVATIVE AT XGUESS

DFUN = DEQN1+PHI2*(DEQN2+2.0D0/SHERW)+PHIG*DEQN2+DEQN3

Analytical calculation of dXgl/dt

DXGDT1=((B1*KS1*CIN2)/(RHO*RG))/DFUN

RETURN

END

SUBROUTINE RAPHSON2(L,TINT,TIME,XLAST2,JMAX,RP,DELTI,DGAS,KG,
1 RG,RHO,B2,ETAP,CNACL,CNA,NCNA,CHCLIN,CHCL,
2 NCHCL,KE2,KS2,DE2,XACC,TOL,DXG2,DXGDT2)

PROGRAM FOR NEWTON-RAPHSON METHOD FOR FINDING ROOTS

DO 11 J2=1,JMAX
10 CALL GRAIN2(XGUESS,FUN,QFUN,RP,DELTI,J2,TIME,DGAS,KG,
1 RG,RHO,B2,ETAP,CNACL,CNA,NCNA,CHCLIN,CHCL,
2 NCHCL,KE2,KS2,DE2,TOL,DXG2,DXGDT2)

Condition for the pellet that has been saturated before the end of experiment time

A.VIII.6
IF(XGUESS.GE.1.0D0.AND.(XGUESS-1.0D0).LT.TOL) THEN
   XGUESS=1.0D0
   WRITE(1,'(IX,''XGUESS2 = '''E12.4,'''TIME='',D12.4,'''J2=''',''
      I4)') XGUESS,TIME,J2
   GOTO 12
ENDIF

Condition for a much bigger Xg than 1

IF((XGUESS-1.0D0).GE.TOL) THEN
   XGUESS=1.0D0+TOL
   IF(J2.GE.JMAX) THEN
      PRINT *, 'XG2 BIGGER THAN 1'
      WRITE(1,'(IX,''XGUESS2 = 1'',E12.4,'''TIME='',D12.4,'''J2=''',''
         I4)') XGUESS,TIME,J2
      GOTO 12
   ENDIF
ENDIF

DX=FUN/DFUN
XGUESS=XGUESS-DX

Or we could use a relaxation factor
Xgues = Xgues - Relaxf*DX
XGUESS=XGUESS-relaxf*DX

The WRITE statement can appear immediately after this comment and give
the real value of XGUESS (negative or positive), or
it can be written later as 0 or 1 or its normal value depending on the
conditions

WRITE(1,'(IX,''XGUESS2 = '''E12.4,'''TIME='',D12.4,'''J2=''',''
       I4)') XGUESS,TIME,J2

Condition for a really negative Xg

IF(XGUESS.LT.0.0D0.AND.DABS(XGUESS).GT.1.D-14) THEN
   XGUESS=0.DO
   IF(J2.GE.JMAX) THEN
      PRINT *, 'NEGATIVE XG2 ENCOUNTERED RESET TO ZERO'
      WRITE(1,'(IX,''XGUESS2 = '''E12.4,'''TIME='',D12.4,'''J2=''',''
         I4)') XGUESS,TIME,J2
      GOTO 12
   ENDIF
ENDIF

Condition for the negative Xg, which is smaller than the computer's
accuracy and therefore can be considered really as zero

ELSIF(DABS(XGUESS).LT.1.D-14) THEN
   XGUESS=0.DO
   IF(J2.GE.JMAX) THEN
      WRITE(1,'(IX,''XGUESS2 = '''E12.4,'''TIME='',D12.4,'''J2=''',''
         I4)') XGUESS,TIME,J2
      GOTO 12
ENDIF

A.VIII.7
ENDIF

WRITE(1,'(1X,'""XGUESS2 = ",E12.4,'""TIME= ",D12.4,'""J2= ",
1 I4)') XGUESS,TIME,J2

IF(ABS(DX).LT.XACC) THEN /* CONVERGENCE
  GOTO 12
ENDIF

11 CONTINUE

PAUSE 'XGUESS EXCEEDING MAXIMUM ITERATIONS'

XGUESS IS THE SOLUTION FROM THE GRAIN MODEL FOUND BY
NEWTON-RAPHSON METHOD AND USED TO FIND THE OVERALL SOLID'S
NA CONTENT

12 DXG2=(XGUESS-XLAST2)/DELTI /* numerical evaluation of dXg2/dt

XLAST2=XGUESS /* this is the new value that will be used later
END

SUBROUTINE GRAIN2 (XGUESS, FUN, DFUN, RP, DELTI, J2, TIME, DGAS, KG, 
1 RG, RHO, B2, ETAP, CNACL, CNA, NCNA, CHCLIN, CHCL, 
2 NCHCL, KE2, KS2, DE2, TOL, DXGDT2)

C #################################################################
C #
C GRAIN1: PROVIDES VALUE AND DERIVATIVE OF MODEL #
C EQUATION AT XGUESS #
C #
C SZEKELY, EVANS AND SOHN "PELLET-GAS-SOLID REACTIONS" #
C ACADEMIC PRESS, NEW YORK, 1976
C #
C #################################################################

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTRINSIC ABS, EXP, LOG

REAL*8 XGUESS, FUN, DFUN, XG, PHI2, SHERW, PHIG, DGAS, KG, 
1 EQN1, EQN2, EQN3, DEQN1, DEQN2, DEQN3, DELTI, CNA, NCNA, 
2 TSTAR, TIME, CIN2, RP, RHO, B2, ETAP, CNACL, CHCLIN, CHCL, 
3 NCHCL, KE2, KS2, DE2, TOL, TSTAR2, DXGDT2

INTEGER J2

XG=XGUESS

C Condition if the value of XGUESS is so close to 1, that it 
C has reached saturation and should not proceed any more
C
IF(XGUESS.GE.1.0D0.AND.(XGUESS-1.0D0).LT.TOL) THEN
  XGUESS=1.0D0
  GOTO 10
ENDIF

C Condition if XGUESS is much bigger than 1
C
IF((XGUESS-1.0D0).GE.TOL) GOTO 10
XGUESS=1.0+TOL 
GOTO 10
ENDIF

C INTRINSIC REACTION RATE, 1ST ORDER
C CIN2 = PRESENT GAS NA CONC IN THE TANK
C KE = KC * CH2O^0.5 = CHCL/CNACL => CNACL = CHCL/KE

A.VIII.8
CIN2 = CNA - CHCL/KE

CIN2=(CNA-CHCL/KE2)

Normalised Expression of concentration driving force

CIN2=(NCNA*CNACL-NCHCL*CHCLIN/KE2)

Calculation of modified Sherwood number and the dimensionless groups sigma and sigmag for Szekely approximation

PHI2=RP**2*(1.0DO-ETAP)*KS2/(6.0DO*DGAS*RG)*(1.0DO+1.0DO/KE2)

SHERW=KG*RP/DGAS

PHIG=KS2*RG/(6.0DO*DE2)*(1.0DO+1.0DO/KE2)

WRITE(1,('GRAIN2 HERE!'/
1 ' PHII2 = ,E12.4/
2 ' SHERW = ',E12.4/
3 ' PHIG = ',E12.4') PHI2,SHERW,PHIG

TSTAR2=1.0DO+PHIG+PHII2*(1.0DO+2.0DO/SHERW)+(0.21DO-0.31DO)*
1 (1.0DO+PHII2)*EXP(-0.9DO*(LOG((PHII2**<1.OdO/2.OdO))/
2 1.08DO)**2)

TSTAR=B2*KS2*CIN2*TIME/(RHO*RG)

WRITE(1,('tstar2=',d12.4, 'tstar=',d12.4') tstar2,tstar

Condition if tstar2=time for complete conversion is a criterion whether

Xg should stop proceeding to bigger values than 1

IF((TSTAR2-TSTAR).LT.0.005D0) THEN
XGUESS=1.0DO
GOTO 10
ENDIF

EQN1 = g(XG)
EQN2 = p (XG)
EQN3 = LAST TERM OF THE TSTAR EQUATION FOR XG

EQN1=1.0DO-(1.0DO-XG)**(1.0DO/3.0DO)
EQN2=1.0DO-3.0DO*(1.0DO-XG)**(2.0DO/3.0DO)+2.0DO*(1.0DO-XG)
EQN3=(0.21DO*XG-0.31DO*XG**2)*(1.0DO+PHII2)*EXP(-0.9DO*
1 (LOG((PHII2**(1.0DO/2.0DO))/1.08DO)**2)

FUN = VALUE OF FUNCTION AT XGUESS

FUN=EQN1+EQN2*PHIG+PHII2*(EQN2+2.0DO*XG/SHERW)+EQN3-TSTAR

CALCULATE DERIVATE OF FUNCTION W.R.T. XG

DEQN1 = (1.0DO-XG)**(-2.0DO/3.0DO)
DEQN2 = 2.0D0*(1-XG)**(-1.0D0/3.0D0)-2.0D0
DEQN3 = (0.21D0-0.62D0*XG)*(1.0D0+PHI2)*EXP(-0.9D0*
1  (LOG((PHI2**(1.0D0/2.0D0))/1.08D0))**2)

DFUN IS VALUE OF DERIVATIVE AT XGUESS
DFUN = DEQN1+PHI2*(DEQN2+2.0D0/SHERW)+PHIG*DEQN2+DEQN3

DFUN = DEQN1+PHI2*(DEQN2+2.0D0/SHERW)+PHIG*DEQN2+DEQN3

C Analytical evaluation of dXg2/dt
DXGDT2=((B2*KS2*CIN2)/(RHO*RG))/DFUN
10 RETURN
END

A.VIII.2 FIXED BED SORPTION PROGRAM

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C ALKALI FIXED BED SORPTION MODEL SOLVED BY GEAR'S METHOD
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C Main program:
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
EXTERNAL FCT
INTEGER*4 NMAX, NDIM, I, IHLF, IREC, ISTEP, IEND, ITEST, J, IMOD,
1 NTANKS
INTEGER*4 TT
parameter (ntanks=20)
parameter (nmax=4*NTANKS, k1=12*nmax, k2=nmax*nmax)
DIMENSION Y(8,Nmax),  DERY(Nmax),  AUX(8,Nmax),  PRMT(5)
DIMENSION save(12,nmax), error(nmax), pw(k2),  ymax(nmax)
REAL * 8 PRMT, AUX, DERY, Y, A, B, C, X, XEND, H ,AJ ,BJ, CJ, R1, R2,
1 DELT, DABS
REAL*8 TEMPERATURE, PRESSURE, VISC, DENS, WU,
1 REYNOLDS, SCHMIDT, VEL, DIA
common /param/ kel, ke2, ksl, ks2, del, de2,
common /tempre/ temperature, pressure, vise,
1 reynolds, schmidt,vel, dia, sherwm
common /conc/ cnac1, chclin
c
NDIM no of equations
Y(NDIM) array of dependent variables
DERY(NDIM) array of derivatives (right hand sides)
NDIM=4*ntanks

TEMPERATURE=923.0D0  ! temperature of interest (K)
PRESSURE=1.01325    ! pressure of interest (bar)
TEM=1.3805D-23*TEMPERATURE/1.3907D-21
WU = (1.16145/(TEM**0.14874))+(0.52487/EXP(0.77320*TEM)+
(2.16178/EXP(2.43787*TEM))

VISC=26.69D0*SQR(28.013D0*TEMPERATURE)*10.0D-06/
(3.659D0**2.0D0*WU)

DENS=1.2507*10.0D-03*273.0D0*PRESSURE/(TEMPERATURE*1.01325)

CNACL=2.2D-06*PRESSURE/(83.138*TEMPERATURE)

CHCLIN=160.0D-06*PRESSURE/(83.1384*TEMPERATURE)

DIA=0.055D0 ! pellet diameter [cm]
VEL=10.0D0 ! superficial velocity [cm/s]
DM = 1.3D0*(1.01325D0/PRESSURE)*((TEMPERATURE/1173.0D0)**0.75D0

DENS=1.2507*10.0D-03*273.0D0*PRESSURE/(TEMPERATURE*1.01325)

CNACL=2.2D-06*PRESSURE/(83.138*TEMPERATURE)

CHCLIN=160.0D-06*PRESSURE/(83.138*TEMPERATURE)

DIA=0.055D0 ! pellet diameter [cm]
VEL=10.0D0 ! superficial velocity [cm/s]
DM = 1.3D0*(1.01325D0/PRESSURE)*((TEMPERATURE/1173.0D0)**0.75D0

REYNOLDS = (DENS*VEL*DIA)/VISC
SCHMIDT=VISC/(DENS*DM)
SHERWM=2.0D0+1.1D0*(SCHMIDT**(1.0D0/3.0D0)*REYNOLDS**0.6)
KG=(SHERWM*DM)/DIA

DGAS = DM / 4.0D0 ! intrapellet diffusivity

REYNOLDS = (DENS*VEL*DIA)/VISC
SCHMIDT=VISC/(DENS*DM)
SHERWM=2.0D0+1.1D0*(SCHMIDT**(1.0D0/3.0D0)*REYNOLDS**0.6)
KG=(SHERWM*DM)/DIA ! gas film mass transfer coefficient [cm/s]

RG=20.0D-4
RHO=4.1200D-3
B1=1.0D0
B2=1.0D0
ETAP=0.055D0/2.0D0
KE1=5000.0D0
KS1=0.0002D0
DE1=0.001
KE2=5000.0D0
KS2=0.7D0
DE2=2.0D-05

*** set the initial values for Y
DO I=1,NMAX
Y(I,1)=0.D0
ENDDO

*** Define the error weights (use equal weights for all variables)
DO I=1,NDIM
ymax(I)=1.D0/NDIM
ENDDO

C set variables for integration
C
hmin=1.4-14 ! min time step [s]
hmax=900.0D0 ! max time step [s]
jstart=0
mf=2
maxder=6
eps=1.0D-3 ! accuracy
ml=8
mu=8

C
h=hmin
x=-h
TT = 0
10000 continue
C

A.VIII.11
call DIFSUB_NEW(Ndim,x,Y,derY,SAVE,H,HMIN,HMAX,EPS,WF,K1,K2,FCT)

\[ TT = TT + 1 \]

IF(MOD(TT, 1) .EQ . 0) then
    write(6,1234) jstart,x/3600.d0,h,(y(1,j),j=1,4)
ENDIF

1234 format(1x,i3,1x,f10.6,1x,5(1pe11.4,1x))
1235 format(1x,15x,12x,4(1pe11.4,1x))
1236 format(1x,i3,10(1pe13.6,1x))

if(x/3600.d0.gt.600.0d0) go to 20000
! for a 600 hr run
if(kflag.eq.1) then
go to 10000
else
    write(8,1234) jstart,x/3600.d0,h,(y(1,j),j=1,4)
do itank=2,ntanks
        write(8,1235) (y(1,(itank-1)*4+j) , j = 1,4)
    enddo
    stop
endif
C20000 continue
    write(8,1234) jstart,x/3600.d0,h,(y(1,j),j=1,4)
do itank=2,ntanks
        write(8,1235) (y(1,(itank-1)*4+j) , j = 1,4)
    enddo
    STOP
END

C

Subroutine FCT(ndim, X, Y, DERY)
implicit real*8 (a-h,o-z)
INTEGER NDIM, I, ntanks, TINT, jmax, L, J2, TSTAR_FLAG1
PARAMETER(ntanks=20)
dimension Y(8,NDIM), DERY(NDIM), NCNA(ntanks), NCHCL(ntanks),
1     XLAST1(ntanks), XLAST2(ntanks), DXG1(NTANKS), DXG2(NTANKS),
2     XXLAST1(NTANKS), XXLAST2(NTANKS), DXGDT1(NTANKS),
3     DXGDT2(NTANKS), CIN1(NTANKS), CIN2(NTANKS), MNA(NTANKS),
4     BEdPOS(NTANKS)
REAL*8 BITA2, BITA3, BITA4, BEDDEN, BEdLEN, TIME, DFUn1,
1     F1, F2, RP, DERY, X, FRMT, DELZ, ETA, AREA, BEdDIa, VFL0,
2     WSORB, Y, NCNA, NCHCL, XLAST1, XLAST2, DXG1, DXG2,
3     MNA, relaxf, xacc, xf, xguess, FTOT, RG, RHO, B1, B2, DFUn2,
4     ETAP, XXLAST1, XXLAST2, DXGDT1, DXGDT2, CIN2, CIN1,
5     Fun, BEdPOS
REAL*8 TEMPERATURE, PRESSURE, VISC, DENS, WU, TEM, DM,
1     REYNOLDS, SCHMIDT, SHERWM

common /param/ ke1, ke2, ks1, ks2, del, de2, rp, etap, rg, rho, bl,
1     b2
common /tempre/ temperature, pressure, visc, dens, wu, tem, dm,
1     reynolds, schmidt,vel, dla, sherwm
common /diff/ dgas, kg
common /conc/ cnac1, chclin

EXTERNAL GRAIN1, GRAIN2
INTRINSIC EXP, LOG
SAVE XLAST1,XLAST2

C

TIME=X
! REAL TIME [S]

A.VIII.12
BEDLEN = 1.516D0       ! BED LENGTH [CM]
DELTZ = BEDLEN / ntanks ! TANK LENGTH [CM]
ETA  = 0.35D0          ! BED VOIDAGE
BEDDIA = 2.5D0          ! BED DIAMETER [CM]
AREA = (BEDDIA / 2.0D0)**2 * 3.1416D0 ! BED X-SECTIONAL AREA [CM^2]
VFLO = AREA * VEL      ! VOLUMETRIC FLOW RATE [CM^3/S]
BEDDEN = 0.3663D0      ! [G SORBENT/CM OF BED HEIGHT]
WSORB = BEDDEN * 10.0 / AREA ! [G SORBENT/CM^3 OF BED]
F1 = 9.9D0 / 100.0D0   ! Na uptake due to reaction 1 [g Na/g initial sorbent]
F2 = 4.7D0 / 100.0D0   ! Na uptake due to reaction 2 [g Na/g initial sorbent]

C \- CONVECTIVE MASS BALANCE CONSTANTS
BITA2 = VEL / (DELTZ * ETA)
BITA3 = (WSORB * F1) / (ETA * 23.0)
BITA4 = (WSORB * F2) / (ETA * 23.0)

C \- Initialise system parameters

DXGL (NTANKS) = 0.0D0       ! initialise derivatives
DXG2 (NTANKS) = 0.0D0       ! initialise derivatives
DXGT1 (NTANKS) = 0.0D0
DXGT2 (NTANKS) = 0.0D0
MNA (NTANKS) = 0.0D0        ! total pellet Na uptake [g Na/g initial sorbent]
XF = 0.0D0
XGUESS = 0.0D0

FTOT = 14.61D0 / 100.0D0   ! total Na uptake [g Na/g initial sorbent]

DO 1010 \- I = 1, NTANKS
NCNA(I) = Y(1, (I-1) * 4 + 1)
NCHC1(I) = Y(1, (I-1) * 4 + 2)
XLAST1(I) = Y(1, (I-1) * 4 + 3)
XLAST2(I) = Y(1, (I-1) * 4 + 4)
1010 CONTINUE

C \- ENTER THE TESTED ANALYTICAL FORMULA FOR DXG1 AND DXG2

C \- DERY (3) = DXGL (NTANKS)
C \- DERY (4) = DXG2 (NTANKS)

DO 20 \- I = 1, NTANKS
    CALL GRAIN1(XLAST1, FUN, DFUN1, RP, J2, TIME, DGAS, KG, I, RG, 1
                RHO, B1, ETAP, CNACL, NCNA, CHCLIN, NCHCL, KE1, KS1, DE1, CIN1)
20 CONTINUE

C \- Analytical calculation of dxgl/dt

DXGT1 (I) = ((B1 * KS1 * CIN1(I)) / (RHO * RG)) / DFUN1
    CALL GRAIN2(XLAST2, FUN, DFUN2, RP, J2, TIME, DGAS, KG, I, RG, 1
                RHO, B2, ETAP, CNACL, NCNA, CHCLIN, NCHCL, KE2, KS2, DE2, CIN2)

C \- Analytical evaluation of dxg2/dt

DXGT2 (I) = ((B2 * KS2 * CIN2(I)) / (RHO * RG)) / DFUN2
    IF (I.EQ.1) THEN
        DERY((I-1) * 4 + 3) = (DXGT1(I))
    END
DERY((I-1)^4+1) = (DXGDT2(I))
DERY((I-1)^4+1) = (-BITA2*(NCNA(I)-1.0*D0)-
1 (BITA3/CNACL)*DERY((I-1)^4+3)-(BITA4/CNACL)*
2 DERY((I-1)^4+4))
DERY((I-1)^4+2) = (-BITA2*(NCHCL(I)-1.0*D0)+
1 (BITA3/CHCLIN)*DERY((I-1)^4+3)+(BITA4/CHCLIN)*
2 DERY((I-1)^4+4)) ELSE
DERY((I-1)^4+3) = DXGDT1(I)
DERY((I-1)^4+4) = DXGDT2(I)
DERY((I-1)^4+1) = -BITA2*(NCNA(I)-NCNA(I-1)) -
1 (BITA3/CNACL)*DERY((I-1)^4+3)-(BITA4/CNACL)*
2 DERY((I-1)^4+4)
DERY((I-1)^4+2) = -BITA2*(NCHCL(I)-NCHCL(I-1)) +
1 (BITA3/CHCLIN)*DERY((I-1)^4+3)+(BITA4/CHCLIN)*
2 DERY((I-1)^4+4)) ENDIF

MNA(I)=F1*Y(1,(I-1)^4+3)+F2*Y(1,(I-1)^4+4) total Na uptake (% wt)
BEDPOS(I)=DELZ*(1-0.5) ! position in the bed (in the middle of each tank) [cm]

CONTINUE
RETURN
END

SUBROUTINE GRAIN1 (XLAST1, FUN, DFUN1, RP, J2, TIME, DGAS, KG, I, 1 RG, RHO, B1, ETA1, CNACL, NCNA, CHCLIN, NCHCL, KE1, KS1, DE1, 2 CIN1)
CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC
CCC GRAIN1: PROVIDES VALUE AND DERIVATIVE OF MODEL EQUATION AT XGUESS FOR REACTION 1
CCC PELLET-GRAIN MODEL / SZEKELY APPROXIMATION
CCC
CCC IMPLICIT DOUBLE PRECISION (A-H,O-Z)
INTEGRAL J2,NTANKS,I PARAMETER(ntanks=20)
DIMENSION NCNA(NTANKS), NCHCL(NTANKS), XLAST1(NTANKS), 1 CIN1(NTANKS)
REAL*8 XGUESS, FUN, DFUN1, XG, PHI2, SHERW, PHIG, DGAS, KG, EQN1, 1 EQN2, EQN3, DEQN1, DEQN2, DEQN3, NCNA, TSTAR, TIME, CIN1, RP, 2 RG, RHO, B1, ETA1, CNACL, CHCLIN, NCHCL, KE1, KS1, DE1, TOL, 3 XLAST1
REAL*8 TEMPERATURE, PRESSURE, VISC, DENs, WU, TEM, DM, 1 REYNOLDS, SCHMIDT, DIA, VEL, SHERWM common /tempre/ temperature, pressure, visc, dens, wu, tem, dm, 1 reynolds, schmidt,vel1, dia, sherwmx

XGUESS=XLAST1(I)
XG=XGUESS

REACTION RATE EXPRESSION FOR A 1ST ORDER REACTION
AT EQUILIBRIUM : KE = KC * CH2O^0.5 = CHCL/CNACL => CNACL = CHCL/KE
CIN2 = CNA - CHCL/KE = PRESENT GAS NA CONC IN THE TANK

Normalised Expression for the concentration driving force
CIN1(I)=CNACL*(NCNA(I)-NCHCL(I)*(CHCLIN/CNACL)/KE1)

CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

A.VIII.14
Calculation of modified Sherwood number and the dimensionless groups

\[
\begin{align*}
\Phi_2 &= R^2 \cdot (1.0D0 - ETAP) \cdot K S1 / (6.0D0 \cdot D G A S \cdot R G) \cdot (1.0D0 + 1.0D0 / KE1), \\
\text{sigma value} \\
\text{SHERW} &= K G \cdot R P / D G A S, \\
\text{modified Sherwood number} \\
\text{PHIG} &= K S1 \cdot R G / (6.0D0 \cdot DE1) \cdot (1.0D0 + 1.0D0 / KE1), \\
\text{sigmag value} \\
\end{align*}
\]

\[
TSTAR = B1 \cdot K S1 \cdot CIN1(I) \cdot TIME / (RHO * R G)
\]

\[
\begin{align*}
\text{E} & = g(XG) \\
\text{P} & = p(XG) \\
\text{EQN3} & = \text{LAST TERM OF THE TSTAR EQUATION FOR XG} \\
\text{EQN1} & = 1.0D0 - (1.0D0 - XG) ** (1.0D0 / 3.0D0) \\
\text{EQN2} & = 2.0D0 * (1.0D0 - XG) ** (2.0D0 / 3.0D0) - 2.0D0 \\
\text{EQN3} & = (0.21D0 * XG - 0.31D0 * XG ** 2) ** (1.0D0 + PHIG) * EXP(-0.9D0 * \\
& \log((PHI2 ** (1.0D0 / 2.0D0)) / 1.08D0) ** 2) \\
\end{align*}
\]

\[
\begin{align*}
\text{FUN} & = \text{VALUE OF FUNCTION AT XGUESS} \\
\text{FUN} & = \text{EQN1 + EQN2 * PHIG + PHI2 * (EQN2 + 2.0D0 * XG / SHERW + EQN3 - TSTAR} \\
\end{align*}
\]

\[
\begin{align*}
\text{DEQ1} & = (1.0D0 - XG) ** (-2.0D0 / 3.0D0) / 3.0D0 \\
\text{DEQ2} & = 2.0D0 * (1.0D0 - XG) ** (-1.0D0 / 3.0D0) - 2.0D0 \\
\text{DEQ3} & = (0.21D0 - 0.62D0 * XG) * (1.0D0 + PHI2) * EXP(-0.9D0 * \\
& \log((PHI2 ** (1.0D0 / 2.0D0)) / 1.08D0) ** 2) \\
\end{align*}
\]

\[
\begin{align*}
\text{DFUN} & = \text{VALUE OF DERIVATIVE AT XGUESS} \\
\text{DFUN} & = \text{DEQ1 + PHI2 * (DEQ2 + 2.0D0 / SHERW + PHIG * DEQ2 + DEQ3} \\
\end{align*}
\]

Analytical calculation of dXg1/dt

\[
\text{DXGDT1} = ((B1 * KS1 * CIN2) / (RHO * RG)) / \text{DFUN}
\]

RETURN

END

SUBROUTINE GRAIN2 (XLAST2, FUN, DFUN2, RP, J2, TIME, DGAS, KG, I, 1
RG, RHO, B2, ETAP, CNACL, NCNA, CHCLIN, NCHCL, KE2, KS2, 1
DE2, CIN2)

GRAIN2: PROVIDES VALUE AND DERIVATIVE OF MODEL 1
EQUATION AT XGUESS FOR REACTION 2

PELLET-GRAIN MODEL / SZEKELY APPROXIMATION

IMPLICIT DOUBLE PRECISION (A-H,0-Z) 1
INTRINSIC ABS, EXP, LOG 1
INTEGER J2, NTANKS, I 1
PARAMETER(ntanks=20)

A.VIII.15
DIMENSION NCNA(NTANKS), NCHCL(NTANKS), XLAST2(NTANKS),
CIN2(NTANKS),
REAL*8 XGUESS, FUN, DFUN2, XG, PHI2, SHERW, PHIG, DGAS, KG, EQA1,
EQA2, EQN3, DEQN1, DEQN2, DEQN3, NCNA, TSTAR, TIME, CIN2, RP,
REYNOLES, SCHMIDT, VEL, DIA, SHERWM

common /temprec/ temperature, pressure, visc, dens, wu, tem, dm,
reynolds, schmidt, vel, dia, sherwm

XGUESS=XLAST2(I)
XG=XGUESS

REACTION RATE EXPRESSION FOR A 1ST ORDER REACTION
AT EQUILIBRIUM : KE = KC * CH2O^0.5 = CHCL/CNACL => CNACL = CHCL/KE
CIN2 = CNA - CHCL/KE = PRESENT GAS NA CONC IN THE TANK

Normalised Expression of concentration driving force
CIN2(I)=CNACL*(NCNA(I)-NCHCL(I))*(CHCL/CNACL)/KE2

Calculation of modified Sherwood number and the dimensionless groups
sigma and sigmag for Szekely approximation

PHI2=RP**2*(1.0D0-ETAP)*KS2/(6.0D0*DGAS*RG)*(1.0D0+1.0D0/KE2)
sigma value

SHERW=KG*RP/DGAS
PHIG=KS2*RG/(6.0D0*DE2)*(1.0D0+1.0D0/KE2)

WRITE(1,('"GRAIN2 HERE!"'))
WRITE(1,('"PHI2 = '' ,E12.4/'))
WRITE(1,('"SHERW = '' ,E12.4/'))
WRITE(1,('"PHIG = '' ,E12.4/'))

TSTAR=B2*KS2*CIN2(I)*TIME/(RH0*RG)

EQN1 = g(XG)
EQN2 = p(XG)
EQN3 = LAST TERM OF THE TSTAR EQUATION FOR XG

EQN1=1.0D0-(1.0D0-XG)**2*(1.0D0/3.0D0)
EQN2=1.0D0-3.0D0*(1.0D0-XG)**2*(1.0D0/3.0D0)+2.0D0*(1.0D0-XG)
EQN3=(0.21D0*XG-0.31D0*XG**2)*(1.0D0+PHI2)*EXP(-0.9D0*
1 (LOG((PHI2**2(1.0D0/2.0D0))/1.08D0)**2)

FUN = VALUE OF FUNCTION AT XGUESS
FUN=EQN1+EQN2*PHIG+PHI2*(EQN2+2.0D0*XG/SHERW)+EQN3-TSTAR

CALCULATE DERIVATE OF FUNCTION W.R.T. XG

DEQN1 = (1.0D0-XG)**2*(-2.0D0/3.0D0)/3.0D0
DEQN2 = 2.0D0*(1-XG)**2*(-1.0D0/3.0D0)-2.0D0
DEQN3 = (0.21D0-0.62D0*XG)*(1.0D0+PHI2)*EXP(-0.9D0*
1 (LOG((PHI2**2(1.0D0/2.0D0))/1.08D0))**2)

DFUN IS VALUE OF DERIVATE AT XGUESS
A.VIII.3 gPROMS ALKALI FIXED BED SORPTION PROGRAM

DECLARE

TYPE
  gas_conc = 0: -0.1e-1: 10.0  UNIT = "moles/cm3"
  conversion = 0: -2e-1: 1.00051
# MASS_Na = 0: -1.0e10: 1.0e10  unit = 'g'
END

MODEL bed

PARAMETER
  u  AS REAL  # superficial velocity
  eb AS REAL  # inter-particle voidage
  ep AS REAL  # inter-grain particle voidage
  p AS REAL  # solid density
  w  AS REAL  # solid bulk density
  L  AS REAL  # length of the bed
  ntanks AS INTEGER # number of tanks
  dz AS REAL  # tank length
  Area AS REAL  # XSA of the bed
  ncomp AS INTEGER # no. of components
  kg AS REAL  # gas film mass transfer coefficient
  Rp AS REAL  # pellet radius
  ksi AS REAL  # reaction-rate constant
  k AS REAL  # reaction-rate constant
  Ke1 AS REAL  # equilibrium group
  Ke2 AS REAL  # equilibrium group
  rg AS REAL  # grain radius
  cap2 AS REAL  # Na sorption capacity
  cap1 AS REAL  # Na sorption capacity
  Dp AS REAL  # intra-pellet diffusion coefficient
  De1 AS REAL  # intra-grain diffusion coefficient
  De2 AS REAL  # stoichiometric coefficient for Szekely
  b1 AS REAL  # stoichiometric coefficient
  b2 AS REAL  # stoichiometric coefficient
  Nsh AS REAL  # modified Sherwood number
  sigmal AS REAL  # dummy
  sigma1 AS REAL  # dummy
  sigmag AS REAL  # dummy
  sigma2 AS REAL  # dummy
  sigma2 AS REAL  # dummy
  a AS ARRAY(ncomp) OF REAL  # stoichiometric coefficients
Cfeed AS ARRAY(ncomp) OF REAL  # feed concentrations [moles/cm³]
Dax AS ARRAY(ncomp) OF REAL  # axial dispersion coefficients

VARIABLE
C AS ARRAY(ncomp, ntanks) OF gas_conc
XG AS ARRAY(ntanks) OF conversion
XGG AS ARRAY(ntanks) OF conversion
# gNa_in AS mass_Na  # sodium entering the bed
# gNa_out AS mass_Na  # leaving
# gNa_bed_g AS mass_Na  # stored within the bed (g)
# gNa_bed_s AS mass_Na  # stored within the bed (s)
# gNa_err AS mass_Na  # mass balance error

SET
u := 10.0 ;  # superficial velocity [cm/s]
eb := 0.35 ;  # inter-particle voidage
ep := 0.2 ;  # inter-grain particle voidage
ps := 4.12e-3 ;  # solid density [moles/cm³]
L := 1.5 ;  # length of the bed [cm]
ntanks := 20 ;  # number of tanks
dz := L/ntanks ;  #
Area := 4.911 ;  # XSA of the bed [cm²] (2.5cm diameter)
kg := 50.26 ;  # gas film mass transfer coefficient [cm/s]
Rp := 0.55/20.0 ;  # pellet radius [cm]
ks1 := 10.0e-3 ;  # reaction-rate constant [cm/s]
ks2 := 0.7 ;  #
Ke1 := 76.0 ;  # equilibrium group
Ke2 := 5000.0 ;  #
rg := 20.0e-4 ;  # grain radius [cm]
cap2 := 0.047 ;  # FE capacity for 2nd reaction
# cap1 := (12.6/(100.0-12.6))-cap2 ;  # for JM
# cap1 := (14.61/100)-cap2 ;  #
# cap1 := (14.61/100)-cap2 ;  #
NSh := kg*Rp/Dp ;  # modified Sherwood number
# NSh := 5.9815 ;  #

sigma1 := Rp^2.0*(1.0-ep)*ks1/(6.0*Ds*rg)*(1.0+1.0/Ke1) ;  # sigmaA analogous to Thiele modulus
sigma1 := ks1*rg*(1.0+1.0/Ke1)/(6.0*De1) ;
sigma2 := Rp^2.0*(1.0-ep)*ks2/(6.0*Dp*rg)*(1.0+1.0/Ke2) ;
sigma2 := ks2*rg*(1.0+1.0/Ke2)/(6.0*De2) ;

# sigma1 := 0.2777e-4 ;  #
# sigma1 := 0.3377e-6 ;  #
# sigma2 := 0.1919 ;  #
# sigma2 := 0.1919 ;  #
# w := (1.0-eb)*(1.0-ep)*ps*332.9 ;  # solid bulk density [g/cm³]
w := 0.7459 ;  #
a := [1.0,0,-1.0] ;  #
Cfeed := [2.867e-11,0,2.085e-9] ;  # feed concentrations [moles/cm³]
Dax := [1.26,2.08,1.68] ;  # axial dispersion coefficients
# Dax := [1.26,0.0001,0.0001] ;

BOUNDARY

A.VIII.18
FOR i := 1 TO ncomp DO
  Dax(i)/dz*(C(i,2)-C(i,1))=u/eb*(C(i,1)-Cfeed(i))+dz*$C(i,1)+
  dz*w/eb*a(i)*(cap1/23.0)*$XG(1)+
  Dax(i)/dz*(C(i,20)-C(i,19))+u/eb*(C(i,20)-C(i,19))+dz*$C(i,20)+
  dz*w/eb*a(i)*(cap2/23.0)*$XGG(20)=0 ;
END # for i

EQUATION
FOR J := 1 TO ntanks DO
  # Szekely approximation
  b1*ksl/(ps*rg)*time*(C(1,J)-C(3,J)/Kel) =
  1.0-(1.0-XG(J))^(1.0/3.0)+
  sigma1*(1.0-3.0*(1.0-XG(J))^(2.0/3.0)+2.0*(1.0-XG(J)))+
  (0.21*XG(J)-0.31*XG(J)^2.0)*(1.0+sigma1)*
  exp(-0.9*(log(sigma1^(1.0/2.0)/1.08))^(2.0)) ;
  b2*ks2/(ps*rg)*time*(C(1,J)-C(3,J)/Ke2) =
  1.0-(1.0-XG(J))^(1.0/3.0)+
  sigma2*(1.0-3.0*(1.0-XG(J))^(2.0/3.0)+2.0*(1.0-XG(J)))+
  (0.21*XG(J)-0.31*XG(J)^2.0)*(1.0+sigma2)*
  exp(-0.9*(log(sigma2^(1.0/2.0)/1.08))^(2.0))
END # for J

FOR J := 2 TO (ntanks-1) DO # 0+ to avoid conflict with the BC
  FOR i := 1 TO ncomp DO
    # convective material balance with axial dispersion
    Dax(i)/dz*(C(i,(J+1))+C(i,(J-1))-2.0*C(i,J))=
    u/eb*(C(i,J)-C(i,(J-1)))+dz*$C(i,J)+
    dz*a(i)*w/eb*(cap1/23.0)*$XG(J)+dz*a(i)*w/eb*(cap2/23.0)*$XGG(J) ;
  END # for i
  END # for j

# Finally, the overall material balance.
# Ignore gas phase Na inside pellets - just gas outside, and solid
# assume 3.663g clean sorbent per axial cm of bed
# $gNa_in = Cfeed(1) * u * Area * 23.0 ;
# $gNa_out = C(1,ntanks) * u * Area * 23.0 ;
# gNa_bed_g = INTEGRAL( z := 0 : L ; C(1,z)*eb*Area*23.0 ) ;
# gNa_bed_s = INTEGRAL( z := 0 : L ; (XG(z)*cap1 + XGG(z)*cap2)*3.663 ) ;
# gNa_err = gNa_in - gNa_out - gNa_bed_s - gNa_bed_g ;
END # for model

#######################################################################

PROCESS novl3u
UNIT plant AS bed

MONITOR
  plant.XG(1); plant.XG(2); plant.XG(3); plant.XG(4); plant.XG(5);
  plant.XG(6); plant.XG(7); plant.XG(8); plant.XG(9); plant.XG(10);
  plant.XG(11); plant.XG(12); plant.XG(13); plant.XG(14); plant.XG(15);

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plant.XG(16); plant.XG(17); plant.XG(18); Plant.XG(19); plant.XG(20);
plant.XGG(1); plant.XGG(2); plant.XGG(3); plant.XGG(4); plant.XGG(5);
plant.XGG(6); plant.XGG(7); plant.XGG(8); plant.XGG(9); plant.XGG(10);
plant.XGG(11); plant.XGG(12); plant.XGG(13); plant.XGG(14); plant.XGG(15);
plant.XGG(16); plant.XGG(17); plant.XGG(18); Plant.XGG(19); plant.XGG(20);

# plant.gNa_in; plant.gNa_out; plant.gNa_bed_g; plant.gNa_bed_s;
plant.gNa_err;

INITIAL
  WITHIN plant DO
    FOR i := 1 TO ncomp DO
      FOR J := 1 TO ntanks DO
        C(i,J) = 0.0 
      END # for J
    END # for i
  END # for WITHIN

  FOR J := 1 TO ntanks DO
    XG(J) = 0.0 ; XGG(J) = 0.0 ;
  END # for J

# gNa_in = 0.0 ; # no sodium has been in or out at t = 0
# gNa_out = 0.0 ;

END # for WITHIN

SCHEDULE
  CONTINUE FOR 2160000 # i.e. 600hr in seconds
  CONTINUE FOR 2160000

END # PROCESS