CHARACTERISATION OF SUSPENSIONS IN SETTLING AND COMPRESSION

by

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PREFACE

I hereby declare that, except where due reference is made in the text, this thesis is solely my own original work, and is less than 100,000 words in length.

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To my supervisors David Boger in Chemical Engineering and Kerry Landman in Mathematics for their invaluable support and guidance throughout the project.

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ABSTRACT

The concentration of fine particle suspensions is a crucial step in many industrial processes. Two major processes that depend on this are the disposal of mine tailings as highly concentrated slurries, and the wet casting of ceramic components from highly concentrated suspensions. The thickening and filtration operations in these processes are still not completely understood. The successful design and operation of consolidation equipment must be based on the properties of the target suspension. The quantitative characterisation of suspensions in settling and compression was the prime objective of this thesis.

In a general consolidation model, the behaviour of suspensions in settling and compression is fully defined by two parameters; the compressive yield stress function and the hindered settling function. The compressive yield stress quantifies the strength of the suspension network in compression and determines the maximum concentration achievable for any given applied force. The hindered settling function quantifies the hydrodynamic drag forces experienced by consolidating particles in the suspension and determines the settling velocity and the time scale for the consolidation process.

These suspension consolidation parameters were determined using a variety of techniques. For measurement of the compressive yield stress, two centrifuge based techniques and a pressure filtration technique were evaluated both independently and with each other - with good results. It was thus verified that the compressive yield stress is a material property of suspensions in compression. For measurement of the hindered settling function, two pressure filtration techniques were developed using a custom built apparatus. Measurements were successfully made using these techniques for the first time.

The materials used in the study were three aqueous metal oxide suspensions systems; ZrO₂, TiO₂ and Al₂O₃. The shear and compression rheology of these systems is fully controlled by manipulation of the particle surface chemistry which changes the suspension micro-structure. The validity of the general consolidation model was systematically studied using suspensions prepared under various conditions. Factors
studied were the effects of flocculation state, initial concentration, steric stabilisation, suspension preparation methods and prior shear and compression history. These factors affected the compression rheology to varying degrees and were quantified. The conditions for maximum consolidation were determined. A correlation between shear and compression rheology also generated a useful empirical relationship that can be used in design and operation of consolidation equipment.

Finally, the measurement of the compressive yield stress and hindered settling function of a suspension was applied to the prediction of the concentration profile and sediment height in an operating continuous thickener. With some refinement, the model and techniques used in this study are a viable means for design and optimisation of continuous thickeners based on the material properties of the suspension.
PUBLICATIONS

The following papers have been published in support of the work in this thesis:


The following papers have been published as preliminary supplementary material from the works of de Guingand and Nguyen from whose works this thesis was inspired:


# TABLE OF CONTENTS

PREFACE ........................................................................iii

ACKNOWLEDGMENTS..................................................iii

ABSTRACT .....................................................................v

PUBLICATIONS ..........................................................vii

LIST OF FIGURES ......................................................xv

LIST OF TABLES ........................................................xxi

NOMENCLATURE .........................................................xxiii

Chapter 1  
**INTRODUCTION** ......................................................1  
1.1 BACKGROUND AND INDUSTRIAL APPLICATION ..............1  
1.2 RESEARCH APPROACH ..........................................4

Chapter 2  
**INTRODUCTORY THEORY** ........................................5  
2.1 INTRODUCTION ......................................................5  
2.2 SUSPENSION CONSOLIDATION ..................................6  
  2.2.1 BASIC MECHANISMS ....................................6  
  2.2.2 GENERAL CONSOLIDATION MODEL .................8  
2.3 COMPRESSION RHEOLOGY .......................................12  
  2.3.1 PREVIOUS WORK .........................................13  
  2.3.2 MULTIPLE SPEED EQUILIBRIUM SEDIMENT HEIGHT  
    TECHNIQUE ..................................................14  
    2.3.2.1 Iterative solution ....................................15  
    2.3.2.2 Approximate solution ..............................17  
2.3.3 CONCENTRATION PROFILE TECHNIQUE .................20  
  2.3.3.1 Theory ................................................20  
  2.3.3.2 Concentration profile measurement ................21  
2.3.4 INITIAL SETTLING RATE TECHNIQUE .....................22  
2.3.5 PRESSURE FILTRATION TECHNIQUE .......................24  
2.3.6 HIGH FREQUENCY SHEAR MODULUS TECHNIQUE .......26  
2.3.7 CONSOLIDATION CYLINDER TECHNIQUES .................27  
  2.3.8 SUMMARY ................................................29  
2.4 CONSOLIDATION RATE ..........................................29  
  2.4.1 PREVIOUS WORK .........................................30  
  2.4.2 HINDERED SETTLING FUNCTION, \( r(\phi) \) .............31  
2.4.3 INITIAL SETTLING RATE TECHNIQUE ..................33  
  2.4.4 CONTINUOUS VACUUM FILTRATION TECHNIQUE ....33
2.4.5 PACKED BED FORMATION TECHNIQUE ................................................. 35
2.4.6 PACKED BED FILTRATION TECHNIQUE ........................................... 37
2.4.7 SUMMARY ..................................................................................... 38
2.5 COLLOIDAL SURFACE CHEMISTRY ...................................................... 39
  2.5.1 INTER-PARTICLE INTERACTIONS ................................................... 39
    2.5.1.1 Van der Waals attraction .......................................................... 39
    2.5.1.2 Electric double layer repulsion ................................................. 40
    2.5.1.3 Steric stabilisation ..................................................................... 42
    2.5.1.4 Bridging flocculation ............................................................... 42
    2.5.1.5 Overall interaction (D.L.V.O. theory) .......................................... 42
  2.5.2 MANIPULATION OF SURFACE CHEMISTRY .................................... 44
  2.5.3 SUMMARY ..................................................................................... 46
2.6 CONTINUOUS THICKENER MODEL ..................................................... 48
  2.6.1 PREVIOUS WORK .......................................................................... 48
  2.6.2 THEORY ....................................................................................... 49
  2.6.3 SUMMARY ..................................................................................... 54
2.7 SUMMARY AND DETAILED OBJECTIVES ............................................. 55

Chapter 3
EXPERIMENTAL MATERIALS, SAMPLE PREPARATION AND SHEAR
YIELD STRESS MEASUREMENT ................................................................. 57
  3.1 INTRODUCTION .............................................................................. 57
  3.2 EXPERIMENTAL MATERIALS ............................................................ 57
    3.2.1 ZIRCONIA, ZrO₂ ......................................................................... 58
    3.2.2 TITANIA, TiO₂ ............................................................................ 62
    3.2.3 ALUMINA, Al₂O₃ ........................................................................ 62
  3.3 SAMPLE PREPARATION ..................................................................... 64
  3.4 SHEAR YIELD STRESS MEASUREMENT .......................................... 66
    3.4.1 DEFINITION AND VANE TECHNIQUE ....................................... 66
    3.4.2 EXPERIMENTAL APPARATUS AND METHOD .............................. 69

Chapter 4
COMPRESSION YIELD STRESS MEASUREMENT .................................... 71
  4.1 INTRODUCTION .............................................................................. 71
  4.2 MULTIPLE SPEED EQUILIBRIUM SEDIMENT HEIGHT TECHNIQUE .... 71
    4.2.1 EXPERIMENTAL EQUIPMENT ...................................................... 72
    4.2.2 EXPERIMENTAL PROCEDURE ...................................................... 72
    4.2.3 APPROXIMATE SOLUTION FOR Pₓ(ϕ) ........................................ 75
    4.2.4 ITERATIVE SOLUTION FOR Pₓ(ϕ) ................................................ 75
    4.2.5 EVALUATION OF APPROXIMATE AND ITERATIVE SOLUTIONS .. 80
  4.2.6 SUMMARY ..................................................................................... 88
  4.3 CONCENTRATION PROFILE TECHNIQUE ........................................... 91
    4.3.1 SECTIONING MEASUREMENT OF CONCENTRATION PROFILE 91
    4.3.2 DETERMINATION OF Pₓ(ϕ) FROM CONCENTRATION PROFILE .... 94
    4.3.3 VALIDATION ............................................................................... 96
    4.3.4 OPTIMUM CENTRIFUGE SPEED .................................................. 98
  4.3.5 SUMMARY ..................................................................................... 102
  4.4 PRESSURE FILTRATION TECHNIQUE ................................................ 102
    4.4.1 EXPERIMENTAL EQUIPMENT ...................................................... 103
Chapter 5
HINDERED SETTLING FUNCTION MEASUREMENT........................................... 119
5.1 INTRODUCTION .................................................................................. 119
5.2 MEASUREMENT OF $r(\phi)$ BY THE PACKED BED FORMATION
TECHNIQUE................................................................................................. 119
5.2.1 EXPERIMENTAL PROCEDURE......................................................... 120
5.2.2 CALCULATION OF $r(\phi)$............................................................ 123
5.2.3 VALIDATION .................................................................................... 124
5.2.3.1 Fresh samples versus re-slurried sample ..................................... 124
5.2.3.2 Filtration cylinder diameter effect ............................................. 126
5.2.4 UNUSUAL FILTRATION RATE BEHAVIOUR.................................... 127
5.3 MEASUREMENT OF $r(\phi)$ BY THE PACKED BED FILTRATION
TECHNIQUE................................................................................................. 128
5.3.1 EXPERIMENTAL PROCEDURE......................................................... 129
5.3.2 CALCULATION OF $r(\phi)$............................................................ 130
5.4 COMPARISON OF MEASUREMENT TECHNIQUES.............................. 132
5.4.1 TYPICAL RESULTS FOR COMPARISON.......................................... 132
5.4.2 ADVANTAGES AND DISADVANTAGES OF EACH TECHNIQUE....... 133
5.5 CURVE FITTING AND PARTICLE SIZE ESTIMATION.......................... 134
5.5.1 CURVE FITTING............................................................................... 134
5.5.2 PARTICLE SIZE ESTIMATION........................................................ 136
5.6 CONCLUSIONS..................................................................................... 137

Chapter 6
COMPRESSION RHEOLOGY: RESULTS AND DISCUSSION............................ 139
6.1 INTRODUCTION .................................................................................. 139
6.2 RESULTS - EFFECT OF STRUCTURAL STATE..................................... 139
6.2.1 FLOCULATION STATE................................................................. 140
6.2.2 INITIAL CONCENTRATION........................................................... 146
6.2.3 STERIC STABILISATION................................................................. 151
6.2.4 SUSPENSION PREPARATION......................................................... 152
6.2.4.1 Sonication and high shear mixing ............................................. 152
6.2.4.2 Dilution effects........................................................................... 154
6.2.5 COMPRESSION HISTORY.............................................................. 158
6.3 DISCUSSION....................................................................................... 160
6.4 CORRELATION BETWEEN SHEAR AND COMpressive YIELD STRESSES................................................................. 167
6.5 CONCLUSIONS........................................................................................................................................... 171

Chapter 7
CONTINUOUS THICKENER MODELLING AND DESIGN............. 173
7.1 INTRODUCTION ........................................................................................................................................... 173
7.2 CONTINUOUS THICKENER CASE STUDY .............................................................................................. 174
7.3 SUSPENSION PROPERTIES ................................................................................................................ 175
7.4 THICKENER MODEL ............................................................................................................................. 178
7.5 CONTINUOUS THICKENER MODEL ..................................................................................................... 180
7.6 SENSITIVITY ANALYSIS ....................................................................................................................... 182
7.7 DISCUSSION ........................................................................................................................................... 188
7.8 CONCLUSIONS ....................................................................................................................................... 190

Chapter 8
CONCLUSIONS ................................................................................................................................................. 193

REFERENCES .................................................................................................................................................... 197

Appendix A
MULTIPLE SPEED TECHNIQUE: THEORY ......................................................... 211
A.1 INTRODUCTION ................................................................................................................................. 211
A.2 THEORY ............................................................................................................................................... 211

Appendix B
SEDIMENTATION CYLINDER TECHNIQUE: THEORY .................. 215
B.1 INTRODUCTION .................................................................................................................................. 215
B.2 THEORY ............................................................................................................................................... 215

Appendix C
MULTIPLE SPEED TECHNIQUE: APPROXIMATE SOLUTION ERROR ANALYSIS ................................................. 217
C.1 INTRODUCTION .................................................................................................................................. 217
C.2 ERROR THEORY .................................................................................................................................. 217
C.3 ERROR EVALUATION .......................................................................................................................... 219
C.4 REFERENCE .......................................................................................................................................... 220

Appendix D
SYNTHETIC DATA GENERATION ................................................................. 221
D.1 INTRODUCTION .................................................................................................................................. 221
D.2 GENERATION OF $H_{eq}(g)$ AND $\phi(z)$ DATA FROM A $P_y(\phi)$ CURVE ................. 221

Appendix E
DETERMINATION OF $P_y(\phi)$ FROM CONCENTRATION PROFILE ........ 225
E.1 INTRODUCTION .................................................................................................................................. 225
E.2 DISCRETE SOLUTION .......................................................................................................................... 225
E.3 NUMERICAL SOLUTION .................................................................................................................... 229
E.4 ERROR THEORY FOR DISCRETE SOLUTION .................................................................................. 232
Appendix F
GEL CONCENTRATION DETERMINATION FROM BATCH SETTLING
EXPERIMENTS ......................................................... 237
F.1 INTRODUCTION .................................................. 237
F.2 EXPERIMENTAL RESULTS ................................. 237

Appendix G
r(\phi) SAMPLE CALCULATIONS AND ERRORS ...................... 241
G.1 INTRODUCTION .................................................. 241
G.2 SAMPLE CALCULATION ......................................... 241
G.3 ERROR THEORY .................................................. 243
G.3.1 PACKED BED FORMATION .................................... 243
G.3.2 PACKED BED FILTRATION .................................... 244
G.4 ERROR EVALUATION ............................................ 244
G.5 REFERENCE ...................................................... 246
LIST OF FIGURES

Figure 2.1 Basic consolidation mechanisms showing driving forces and relative solid and liquid velocities (u and v respectively) for: a) batch filtration, b) batch gravity settling.................................6

Figure 2.2 Consolidation regions in a gravity thickener.............................................7

Figure 2.3 Schematic of multiple speed equilibrium sediment height technique.................................14

Figure 2.4 Numerical validation of the mean value theorem for the approximate solution; a) sample concentration profile from a synthetic function, \( P_y = 100 \left[ (\phi/0.18)^8 - 1 \right] \), for \( g = 5550 \text{ m/s}^2 \), showing the equivalent 'average' concentration \( \phi(\xi') \); b) comparison of the \( P(0)/\phi(0) \) areas as calculated by the algorithm and as by the mean value theorem (scaled units)........................................19

Figure 2.5 Schematic of initial settling rate technique for determination of consolidation parameters, \( P_y(\phi) \) and \( r(\phi) \); a) determination of initial slope for a single \( g \) value, b) determination of intercepts from initial slope versus \( 1/g \) plot.................................................................23

Figure 2.6 Schematic of pressure filtration technique for determination of \( P_y(\phi) \); a) initial state, b) equilibrium state.................................................25

Figure 2.7 Schematic of two sedimentation cylinder techniques to find \( P_y(\phi) \); a) find highest initial height \( H_0 \), for which no consolidation occurs for a range of \( \phi_0 > \phi_g \), b) measure \( H_{ci} \) for a range of initial heights \( H \).................................................................28

Figure 2.8 Prototype continuous vacuum filtration device to determine the hindered settling function, \( r(\phi) \).........................................................34

Figure 2.9 The two stages of filtration of an initially un-networked (\( \phi_0 < \phi_g \)) suspension; a) compact bed formation, b) compact bed consolidation [from Landman, et al. (1995)].........................................................36

Figure 2.10 a) Schematic of electric double layer repulsion for a negatively charged surface; b) corresponding schematic of electrostatic repulsion force versus distance from surface........................................41

Figure 2.11 Typical interaction energy versus particle separation curve.......................43

Figure 2.12 Effect of ionic strength on the shear yield stress-pH behaviour of a \( \text{ZrO}_2 \) suspension [from Leong, et al. (1993a)]...............................................45

Figure 2.13 Effect of polyacrylic acid (2000 Mw) on the shear yield stress-pH behaviour of a \( \text{ZrO}_2 \) suspension [from Leong (1994)].....................................................46

Figure 2.14 Comparison of the effect of steric stabilisation and bridging flocculation on the compressive yield stress for \( \text{ZrO}_2 \) suspensions [from Leong (1994)].....................................................47

Figure 2.15 Definition of variables for the modelling of a continuous gravity thickener for \( \phi_0 < \phi_g \).........................................................50

Figure 2.16 Concentration profiles in a steady state cylindrical thickener produced from synthetic data (\( m = 5 \) and \( n = 4.5 \) in Equations (2.47) and (2.48)) [corrected plots from Landman, et al. (1988)]...........52
Figure 2.17 Bed height versus underflow concentration in a steady state cylindrical thickener, from synthetic data (m = 5 and n = 4.5 in Equations (2.47) and (2.48)); a) scaled plots [corrected plots from Landman, et al. (1988)], b) unscaled plots for a typical mineral suspension.................................................................53

Figure 3.1 Particle size distribution for ZrO$_2$ as determined using a Coulter LS130 particle sizer; comparison of suspension preparation methods - sonication and high shear mixing.........................................................60

Figure 3.2 Particle size distribution for TiO$_2$ as determined using a Coulter LS130 particle sizer; suspension prepared by sonication, pH 3.5 (dispersed)........................................................................63

Figure 3.3 Particle size distribution for Al$_2$O$_3$ as determined using a Coulter LS130 particle sizer; suspension prepared by sonication, pH 4.0 (dispersed).........................................................65

Figure 3.4 Schematic of vane technique for measurement of the shear yield stress of suspensions; a) dimensions of vane, b) experimental configuration using a Haake RV3 Rheometer.........................................................68

Figure 4.1 Typical (g, $H_{eq}$) raw data and slope, $dH_{eq}/dg$, from the multiple speed equilibrium sediment height technique (ZrO$_2$, pH 5.7, $\phi_0 = 0.151$); a) normal coordinates, b) logarithmic coordinates........74

Figure 4.2 Typical $P_y(\phi)$ data determined using the approximate solution for the multiple speed equilibrium sediment height technique; (g, $H_{eq}$) data from Figure 4.1 (ZrO$_2$, pH 5.7, $\phi_0 = 0.151$)........................................................76

Figure 4.3 Schematic of stopping criteria used in the iterative solution for the multiple speed equilibrium sediment height technique (scaled units)...........................................................................78

Figure 4.4 Schematic of techniques for extrapolation of $P_y(\phi)$ data to $P_y(\phi_0) = 0$..................................................................................80

Figure 4.5 Synthetic compressive yield stress functions used for validation of the multiple speed equilibrium sediment height technique. Shown are the exponents for power law and exponential functions..............81

Figure 4.6 Typical synthetic raw data generated from an 8$^{th}$ order power law function for $P_y(\phi)$..........................................................82

Figure 4.7 Comparison of the exact solution (8$^{th}$ order power law) with that generated from the iterative solution; a) 2$^{nd}$ and 3$^{rd}$ order fits, b) and c) the % difference from the exact curve for $P_y$ and $\phi$ respectively (also shown are the mean differences and the 99% confidence intervals)............................................................84

Figure 4.8 Comparison of the exact solution (8$^{th}$ order power law) with that generated from the approximate solution; a) 2$^{nd}$ and 3$^{rd}$ order fits, b) and c) the % difference from the exact curve for $P_y$ and $\phi$ respectively (also shown are the mean differences and the 99% confidence intervals)............................................................84

Figure 4.9 Examples of the effect of 2% noise in $H_{eq}$ data on the iterative solution compared with the exact solution (8$^{th}$ order power law)............87

Figure 4.10 Comparison of theoretical and calculated concentration profiles (8$^{th}$ order power law) for a selected number of g values; 1) 76 m/s$^2$, 
2) 520 m/s², 3) 1,076 m/s², 4) 2,187 m/s², 5) 3,298 m/s²,
6) 4,964 m/s², 7) 5,520 m/s².................................................................89

Figure 4.11 Typical behaviour of $H_{eq}$ and $z$ with g (generated from a synthetic
$P_y(\phi)$ function - $8^{th}$ order power law)...................................................90

Figure 4.12 Sectioning measurement technique to determine the concentration
profile of a sediment in a centrifuge tube; a) set sectioning depth of
spatula, b) scrape 3 layer of sediment, c) transfer sediment layer
to weighing tin.........................................................92

Figure 4.13 a) Example of the concentration profile of a consolidated
suspension measured by sectioning - error bars are smaller than the
symbols (ZrO$_2$, pH 5.4, $\phi_0 = 0.178$); b) corresponding $P_y(\phi)$
determined from data in a) using two solution methods.........................95

Figure 4.14 Validation of the concentration profile technique for determination
of $P_y(\phi)$; a) $\phi(z)$ profiles determined from a synthetic $P_y(\phi)$ function
for two particular g values, b) comparison of numerical integration
of data in a) with the original $P_y(\phi)$ function........................................97

Figure 4.15 Effect of centrifuge speed on; a) concentration profile, and
b) compressive yield stress (ZrO$_2$, pH 4.9, $\phi_0 = 0.150$).......................99

Figure 4.16 Effect of centrifuge speed on; a) concentration profile, and
b) compressive yield stress (TiO$_2$, pH 5.7, $\phi_0 = 0.291$).......................100

Figure 4.17 Scaled concentration profiles from Figure 4.15 and Figure 4.16;
a) ZrO$_2$, pH 4.9, $\phi_0 = 0.150$, b) TiO$_2$, pH 5.7, $\phi_0 = 0.291$..............101

Figure 4.18 Schematic of filtration device at the University of Melbourne for
measurement of $P_y(\phi)$ and $r(\phi)$.........................................................104

Figure 4.19 Typical concentration profiles of packed beds formed by constant
pressure filtration; device at University of Melbourne, cylinder
diameter = 40.20 mm (ZrO$_2$, pH 5.2, $\phi_0 = 0.052-0.055$)......................107

Figure 4.20 Comparison of pressure filtration devices at the University of
Illinois and at the University of Melbourne for determination of
$P_y(\phi)$ for similar ZrO$_2$ suspensions.....................................................108

Figure 4.21 Effect of centrifuge diameter on $P_y(\phi)$ determined by the multiple
speed technique; symbols - approximate solution, lines - iterative
solution (ZrO$_2$, pH 7.1, $\phi_0 = 0.150$).................................................110

Figure 4.22 Effect of centrifuge diameter on $P_y(\phi)$ determined by the multiple
speed technique; symbols - approximate solution, lines - iterative
solution (TiO$_2$, pH 6.9, $\phi_0 = 0.246$).................................................111

Figure 4.23 Schematic of postulated concentration profile of a suspension
centrifuged to equilibrium showing the effect of the centrifuge tube
walls; solid lines - constant concentration, dashed lines - zero shear
stress.................................................................112

Figure 4.24 Schematic showing greater gravitational acceleration at walls of
centrifuge tube due to greater distance from centre..................................114

Figure 4.25 Comparison of techniques for measurement of $P_y(\phi)$; LSC, MSC
and HSC correspond to low, medium and high speed centrifuges
respectively (ZrO$_2$, pH 7.6, $\phi_0 = 0.15$).............................................115

Figure 4.26 Comparison of techniques for measurement of $P_y(\phi)$; LSC, MSC
and HSC correspond to low, medium and high speed centrifuges
respectively (TiO$_2$, pH 6.9, $\phi_0 = 0.14-0.16$).......................................116
Figure 5.1  Typical filtration rate plot illustrating two different measurement methods on the device at the University of Melbourne (ZrO$_2$, pH 6.9, $\phi_0 = 0.050$, cylinder diameter = 40.20 mm); a) V versus t, b) V versus V ................................................................. 121

Figure 5.2  Filtration rate data determined using the device at the University of Illinois (ZrO$_2$, pH 7.6, $\phi_0 = 0.156$) .............................................................................................. 122

Figure 5.3  Typical r($\phi$) data for ZrO$_2$ determined by the packed bed formation technique using filtration devices at the University of Melbourne (pH 6.5-6.9, $\phi_0 = 0.046-0.050$), and at the University of Illinois (pH 7.6, $\phi_0 = 0.156$) ................................................................. 123

Figure 5.4  Effect on r($\phi$) determined by the packed bed formation technique using the same sample for each successive pressure by re-slurrying the packed bed, compared with using a fresh sample at each applied pressure (filtration device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 125

Figure 5.5  Effect of the filtration cylinder diameter on r($\phi$) determined by the packed bed formation technique for ZrO$_2$ suspensions (device at University of Melbourne) ........................................................................ 126

Figure 5.6  Filtration rate data showing unusual behaviour midway through the filtration (ZrO$_2$, pH 6.5-6.9, $\phi_0 = 0.047-0.050$, device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 128

Figure 5.7  Typical packed bed filtration behaviour at pressures less than the packed bed formation pressure, $\Delta P_{bed}$ (ZrO$_2$, pH 6.7-7.1, $\phi_0 = 0.082-0.085$, device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 130

Figure 5.8  Comparison of typical r($\phi$) data determined by the packed bed formation technique and the packed bed filtration technique (ZrO$_2$, pH 6.7-7.1, $\phi_0 = 0.082-0.085$, device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 131

Figure 5.9  Comparison of typical r($\phi$) data determined by the packed bed formation technique and the packed bed filtration technique (ZrO$_2$, pH 6.6-6.8, $\phi_0 = 0.050-0.052$, device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 133

Figure 5.10 Typical hindered settling function and curve fits determined by the packed bed formation technique (ZrO$_2$, pH 6.5-6.9, $\phi_0 = 0.046-0.050$, device at University of Melbourne, cylinder diameter = 40.20 mm) ...................................................................................... 135

Figure 6.1  Particle size distribution of ZrO$_2$ suspensions determined using a Coulter LS130 particle sizer for a range in flocculation states - dispersed (pH 3.5), weakly flocculated (pH 5.3) and strongly flocculated (pH 6.8). Samples were prepared by sonication........................................ 141

Figure 6.2  Effect of pH on $P_\phi$($\phi$); ZrO$_2$, $\phi_0 = 0.15$ (determined using the multiple speed technique) ...................................................................................... 142

Figure 6.3  Plot of $P_\phi$ versus pH for lines of constant concentration taken from Figure 6.2 plus additional data ...................................................................................... 143

Figure 6.4  Shear yield stress versus pH for ZrO$_2$ of various concentrations ......................................................... 144

Figure 6.5  Effect of flocculation state on a) r($\phi$), and b) $P_\phi$($\phi$), for ZrO$_2$ suspensions; measured using the packed bed formation technique
Figure 6.6 Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for strongly flocculated $\text{Al}_2\text{O}_3$ (pH 9.3-9.4) determined by the multiple speed technique. ................................. 145

Figure 6.7 Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for strongly flocculated $\text{ZrO}_2$ (pH 6.8-7.2) determined by the multiple speed technique. ................................. 147

Figure 6.8 Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for weakly flocculated $\text{ZrO}_2$ (pH 5.6-5.7) determined by the multiple speed technique. ................................. 148

Figure 6.9 Effect of initial concentration on $P_y(\phi)$ for weakly flocculated $\text{ZrO}_2$ (pH 5.2-5.4) determined by the concentration profile technique. ................................. 149

Figure 6.10 a) Effect of initial concentration, $\phi_0$, on $r(\phi)$ for strongly flocculated $\text{ZrO}_2$ suspensions (packed bed formation technique using fresh samples at each pressure, device at University of Melbourne, cylinder diameter 40.20 mm).  b) Corresponding $P_y(\phi)$ data determined with the $r(\phi)$ data in a). ................................................................. 150

Figure 6.11 Effect of pH on $P_y(\phi)$ for $\text{ZrO}_2$ with and without 2000 Mw polyacrylic acid, $\phi_0 = 0.176$ (multiple speed technique, curves taken at constant concentration). ................................................................. 151

Figure 6.12 Effect of preparation method on $P_y(\phi)$ for weakly flocculated $\text{ZrO}_2$ (pH 5.5-5.7, $\phi_0 = 0.100-0.104$) determined by the concentration profile technique. ................................................................. 153

Figure 6.13 Effect of preparation method on $P_y(\phi)$ for weakly flocculated $\text{ZrO}_2$ sterically stabilised with 1.0dwb% 2000 Mw PAA (pH 6.0, $\phi_0 = 0.262$) determined by the multiple speed technique. ................................. 154

Figure 6.14 Effect of dilution on $P_y(\phi)$ for weakly flocculated $\text{ZrO}_2$ sterically stabilised with 1.0dwb% 2000 Mw PAA as determined by the multiple speed technique; ● base suspension, high shear 5 min, ○ diluted just by stirring in water, □ diluted then sonicated for 2 min ................................................................. 156

Figure 6.15 Effect of dilution on $P_y(\phi)$ for strongly flocculated $\text{ZrO}_2$ sterically stabilised with 1.0dwb% 2000 Mw PAA as determined by the multiple speed technique; ● base suspension, high shear 5 min, ○ diluted just by stirring in water, □ diluted then sonicated for 20 s ................................................................. 157

Figure 6.16 Effect of compression history on $P_y(\phi)$ for strongly flocculated $\text{ZrO}_2$ (pH 7.0-7.1, $\phi_0 = 0.190-0.197$) as determined by the concentration profile technique ................................................................. 159

Figure 6.17 a) Plot of normalised $P_y$ versus pH for data from Figure 6.3.  b) Plot of normalised $\tau_y$ versus pH for data from Figure 6.4 ................................................................. 161

Figure 6.18 Plot of $P_y$ versus $\phi_0$ for lines of constant concentration taken from Figure 6.7 and Figure 6.8 for strongly and weakly flocculated $\text{ZrO}_2$; filled symbols - strongly flocculated (pH 6.8-7.2), unfilled symbols - weakly flocculated (pH 5.6-5.7) ................................................................. 162

Figure 6.19 Schematic of two possible microstructures of a flocculated suspension; a) aggregated structure, b) interlinked chain-like structure (the number of flocs in each drawing is the same) ................................................................. 164
Figure 6.20  a) Compressive and shear yield stresses as a function of concentration for both weakly and strongly flocculated ZrO₂.
  b) Compressive yield stress prediction from shear yield stress using data in a). ................................................................. 168

Figure 6.21  a) Compressive and shear yield stresses as a function of concentration for both weakly and strongly flocculated TiO₂.
  b) Compressive yield stress prediction from shear yield stress using data in a). ........................................................................... 170

Figure 7.1  Approximate scale drawing of the red mud continuous thickener at Wagerup, Western Australia. ................................................................. 174

Figure 7.2  Measured continuous thickener concentration profile at Wagerup, 18.9 m from the thickener centre. ................................. 175

Figure 7.3  Compressive yield stress of red mud thickener underflow. ........... 177

Figure 7.4  Hindered settling function for red mud thickener underflow measured by the packed bed formation technique (device at University of Melbourne, cylinder diameter = 28.40 mm, \( \phi_b = 0.176-0.182 \)). ................................................................. 178

Figure 7.5  a) Comparison of the measured red mud continuous thickener concentration profile at Wagerup, with that predicted from the model using measured suspension parameters.  b) Corresponding bed height versus underflow concentration plot (the dashed curve indicates where the solution diverged for that range in \( \phi_u \)). ................................................................. 181

Figure 7.6  a) Compressive yield stress functions for determination of the concentration profiles in a red mud continuous thickener; including curve fits of the raw data, and curve fits using a range of the exponent m to form bed heights of 8.70 m.  b) Corresponding concentration profiles predicted for the continuous thickener at Wagerup using the \( P_y(\phi) \) functions in a). ................................................................. 183

Figure 7.7  a) Compressive yield stress functions for determination of the concentration profiles in a red mud continuous thickener; including curve fits of the raw data, and curve fits using a constant exponent m and a range of pre-exponential factor A.  b) Corresponding concentration profiles predicted for the continuous thickener at Wagerup using the \( P_y(\phi) \) functions in a). ................................................................. 185

Figure 7.8  Effect of variation in the hindered settling function on the predicted concentration profile of the red mud thickener at Wagerup. ................................................................. 186

Figure 7.9  Effect of variation in the feed concentration on the predicted bed height of the red mud continuous thickener at Wagerup. ................................................................. 188

Figure D.1  Geometry of centrifuge tube for generation of synthetic data. .......... 222

Figure E.1  Schematic of trapezoidal rule for calculation of \( P_y(\phi) \) from sectioning analysis of concentration profile. ................................. 227

Figure E.2  Schematic of coordinate transformations for numerical determination of \( P_y(\phi) \) from concentration profile measurements; a) centrifuge tube layout, b) \( \phi(H) \) coordinate system, c) \( \phi(s) \) coordinate system, d) \( \Phi(x) \) coordinate system. ................................................................. 230

Figure F.1  Typical settling curve to determine the gel concentration of a ZrO₂ suspension (pH 6.9, \( \phi_0 = 0.021 \)). ................................................................. 239

Figure F.2  Gel concentration \( \phi_g \) versus pH for ZrO₂ suspensions of various \( \phi_0 \). ................................................................. 240
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Chemical analysis of the zirconia as determined by the manufacturer.</td>
<td>59</td>
</tr>
<tr>
<td>3.2</td>
<td>Particle size analysis of the ZrO₂ as determined using a Coulter LS130 and as supplied by the manufacturer using a Leeds and Northrup Microtrac (the d₁₀ size range means 10% of the particles by volume lie below this size, etc).</td>
<td>60</td>
</tr>
<tr>
<td>3.3</td>
<td>Other properties of the zirconia used in this thesis, as determined by the manufacturer.</td>
<td>61</td>
</tr>
<tr>
<td>3.4</td>
<td>Properties of the titania used in this thesis [from Liddell (1996)].</td>
<td>62</td>
</tr>
<tr>
<td>3.5</td>
<td>Particle size distribution by volume for TiO₂ as determined using a Coulter LS130.</td>
<td>63</td>
</tr>
<tr>
<td>3.6</td>
<td>Particle size distribution by volume for Al₂O₃ as determined using a Coulter LS130.</td>
<td>65</td>
</tr>
<tr>
<td>4.1</td>
<td>Comparison of ( P_γ(\phi) ) measurement techniques; 1. Dependent on centrifuge size. 2. Per sample. 3. Minimum number of data points required - greater accuracy is achieved with more points, but times increase proportionally.</td>
<td>117</td>
</tr>
<tr>
<td>5.1</td>
<td>Particle diameter calculation from intercept of hindered settling function, C.</td>
<td>136</td>
</tr>
<tr>
<td>6.1</td>
<td>Grid of experiments performed to determine the effect of preparation and dilution on ( P_γ(\phi) ) for both weakly and strongly flocculated ZrO₂ suspensions (Runs 1 and 2 respectively).</td>
<td>155</td>
</tr>
<tr>
<td>6.2</td>
<td>Grid of ZrO₂ suspensions prepared for compression history experiments listed in Table 6.3 (400 mL samples prepared using high shear Ultra-Turrax mixer).</td>
<td>158</td>
</tr>
<tr>
<td>6.3</td>
<td>Compression history cycles imposed on samples of each suspension in Table 6.2.</td>
<td>158</td>
</tr>
<tr>
<td>6.4</td>
<td>Power law constants for fit of ZrO₂ data in Figure 6.20a.</td>
<td>167</td>
</tr>
<tr>
<td>6.5</td>
<td>Power law constants for fit of TiO₂ data in Figure 6.21a.</td>
<td>169</td>
</tr>
<tr>
<td>7.1</td>
<td>Particle size distribution by volume for red mud at Wagerup as determined using a Coulter LS130 [from Pashias (1997)].</td>
<td>176</td>
</tr>
<tr>
<td>7.2</td>
<td>Effect of variation in gel concentration on the predicted bed height of the continuous thickener at Wagerup.</td>
<td>187</td>
</tr>
<tr>
<td>C.1</td>
<td>Typical measurement errors for parameters in the approximate solution of ( P_γ(\phi) ) from the multiple speed equilibrium sediment height technique.</td>
<td>220</td>
</tr>
<tr>
<td>E.1</td>
<td>Typical measurement errors for parameters in the discrete solution of ( P_γ(\phi) ) from the concentration profile technique.</td>
<td>235</td>
</tr>
<tr>
<td>F.1</td>
<td>Summary of settling experiments to estimate the gel concentration, ( \phi_g ), for the determination of ( r(\phi) ).</td>
<td>238</td>
</tr>
<tr>
<td>G.1</td>
<td>Typical calculation of ( (\lambda/V_p)r(\phi) ) for the packed bed formation technique and the packed bed filtration technique (data in Figure 5.9).</td>
<td>242</td>
</tr>
</tbody>
</table>
Table G.2  Typical measurement errors for parameters in the determination of 
r(\phi) by either the packed bed formation technique or the packed bed 
filtration technique for the device at the University of Melbourne........245

Table G.3  Typical measurement errors for parameters in the determination of 
r(\phi) by the packed bed formation technique for the device at the 
University of Illinois.............................................245

Table G.4  Error ranges for r(\phi) determined by the packed bed formation 
technique and the packed bed filtration technique for devices at the 
University of Melbourne and at the University of Illinois..............246
## NOMENCLATURE

**Arabic**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_p$</td>
<td>particle radius (m)</td>
</tr>
<tr>
<td>$A$</td>
<td>pre-exponential factor for compressive yield stress function curve fits (Pa)</td>
</tr>
<tr>
<td>$b$</td>
<td>intercept of $t/V$ versus $V$ plot (s/m)</td>
</tr>
<tr>
<td>$B$</td>
<td>scaled drag function, Equation (2.54) (-)</td>
</tr>
<tr>
<td>$c$</td>
<td>effective solids mass concentration in filter feed (kg/m$^3$)</td>
</tr>
<tr>
<td>$C$</td>
<td>pre-exponential factor for hindered settling function curve fits (Pa.s/m$^2$)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle diameter (m)</td>
</tr>
<tr>
<td>$d_x$</td>
<td>particle diameter below which are ‘x’ % by volume of the particles (m)</td>
</tr>
<tr>
<td>$D$</td>
<td>pre-exponential factor for shear yield stress function curve fits (Pa)</td>
</tr>
<tr>
<td>$D_v$</td>
<td>vane diameter (m)</td>
</tr>
<tr>
<td>$f(\phi)$</td>
<td>scaled compressive yield stress function, Equation (2.49) (-)</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration (m/s$^2$)</td>
</tr>
<tr>
<td>$g_0$</td>
<td>gravitational acceleration at sea level (9.81 m/s$^2$)</td>
</tr>
<tr>
<td>$G_{so}$</td>
<td>high frequency limit of the shear modulus (Pa)</td>
</tr>
<tr>
<td>$h_0$</td>
<td>container size (m)</td>
</tr>
<tr>
<td>$H$</td>
<td>suspension or thickener bed height (m)</td>
</tr>
<tr>
<td>$H_{avg}$</td>
<td>average height of section (m)</td>
</tr>
<tr>
<td>$H_b$</td>
<td>centrifuge tube base height (m)</td>
</tr>
<tr>
<td>$H_d$</td>
<td>section depth from top of centrifuge tube (m)</td>
</tr>
<tr>
<td>$H_{eq}$</td>
<td>equilibrium sediment height (m)</td>
</tr>
<tr>
<td>$H_f$</td>
<td>final packed bed height (m)</td>
</tr>
<tr>
<td>$H_i$</td>
<td>height of bottom of section from base of bed (m)</td>
</tr>
<tr>
<td>$H_t$</td>
<td>centrifuge tube height (m)</td>
</tr>
<tr>
<td>$H_v$</td>
<td>vane height (m)</td>
</tr>
<tr>
<td>$H_0$</td>
<td>initial suspension height (m)</td>
</tr>
</tbody>
</table>
k permeability ($m^2$)
kT thermal energy ($J$)
$K(\phi)$ compressional modulus (Pa)
l(t) height of compact bed interface (m)
L scaled continuous thickener bed height (-)
m exponential factor for compressive yield stress curve fits (-)
$m_1$ slope of $t/V$ versus $V$ plot ($s/m^2$)
$M$ cumulative concentration of solids (volume fraction.m)
$M_b$ mass of packed bed (g)
$M_c$ mass of empty centrifuge tube + lid (g)
$M_f$ final mass of weighing tin + sample (g)
$M_i$ initial mass of weighing tin + sample (g)
$M_{ns}$ mass of filled centrifuge tube + lid - supernatant (g)
$M_s$ mass of filled centrifuge tube + lid (g)
$M_t$ mass of empty weighing tin (g)
n exponential factor for hindered settling function curve fits (-)
N number of data points (-)
p exponential factor for shear yield stress curve fits (-)
P network pressure (Pa)
$P_f$ fluid pressure (Pa)
$P_{os}$ osmotic pressure (Pa)
$P_s$ particle pressure (Pa)
$P_{y}(\phi)$ compressive yield stress function (Pa)
$\Delta P$ applied pressure difference (Pa)
q fluid flux in vacuum filter ($m^3/s$)
$Q_p$ total particle volumetric flowrate through thickener ($m^3/s$)
r(\phi) hindered settling function (-)
R centrifuge radius (m)
$R_m$ membrane hydraulic resistance ($m^{-1}$)
R(\dot{\phi}) \quad \text{scaled hindered settling function, Equation (2.50) (-)}

R_0 \quad \text{radius of thickener at feed input point (m)}

s \quad \text{distance from top of bed (m)}

S \quad \text{centrifuge speed (rpm)}

t \quad \text{time (s)}

\text{t}_{cf} \quad \text{compact formation time (s)}

T_{\text{max}} \quad \text{maximum torque at the yielding point in the vane technique (N.m)}

u \quad \text{particle settling velocity (m/s)}

u_0 \quad \text{Stokes settling velocity for a single particle in infinite media (m/s)}

v \quad \text{liquid velocity (m/s)}

V \quad \text{volume of fluid expressed per unit area of membrane (m}^4\text{)}

V_A \quad \text{attractive interaction energy (J)}

V_{\text{Max}} \quad \text{energy barrier to coagulation (J)}

V_p \quad \text{particle volume (m}^3\text{)}

V_R \quad \text{repulsive interaction energy (J)}

x \quad \text{distance from centre of centrifuge (m)}

Y \quad \text{scaled vertical distance from bottom of thickener, Equation (2.45) (-)}

Y_w \quad \text{scaled } z_w (-)

z \quad \text{vertical spatial coordinate (m)}

z_{\text{avg}} \quad \text{average height of section measured from centre of centrifuge (m)}

z_c \quad \text{critical height (m)}

z_w \quad \text{vertical height of conical section of thickener (m)}

Z \quad \text{function of } z, \text{ Equation (A6) (m)}

\textbf{Greek}

\alpha \quad \text{compact bed hydraulic resistance per unit mass of bed (m/kg)}

\alpha(Y) \quad \text{scaled cross-sectional area of a thickener, Equation (2.46) (-)}

\beta \quad \text{scaled particle flux in a thickener, Equation (2.52) (-)}
\( \Delta \) correction factor in the calculation of \( P \), Equation (2.19) (-)

\( \Delta' \) correction factor in the calculation of \( P \), Equation (2.15) (-)

\( \varepsilon \) correction factor in the calculation of \( \phi \), Equation (2.18) (-)

\( \varepsilon' \) correction factor in the calculation of \( \phi \), Equation (2.14) (-)

\( \eta \) fluid viscosity \((\text{Pa.s})\)

\( \kappa \) dynamic compressibility \((\text{Pa}^{-1}\text{s}^{-1})\)

\( 1/\kappa \) inverse Debye or decay length \((\text{m})\)

\( \lambda \) drag coefficient for a single particle in infinite media \((\text{Pa.s.m})\)

\( \xi \) mean value theorem height \((\text{m})\)

\( \xi' \) mean value theorem height \((\text{m})\)

\( \rho_f \) fluid density \((\text{kg/m}^3)\)

\( \rho_s \) solids density \((\text{kg/m}^3)\)

\( \Delta \rho \) density difference between solids and fluid in suspension \((\text{kg/m}^3)\)

\( \tau_y \) shear yield stress \((\text{Pa})\)

\( \nu \) Poisson's ratio (-)

\( \phi \) suspension solids concentration (volume fraction)

\( \phi_b \) bottom concentration at equilibrium in a batch thickener (volume fraction)

\( \phi_{cp} \) close packing concentration limit of suspension (volume fraction)

\( \phi_f \) final suspension concentration (volume fraction)

\( \phi_g \) gel concentration (volume fraction)

\( \phi_m \) mean concentration (volume fraction)

or, mass concentration (mass fraction)

\( \phi_u \) underflow concentration in a continuous thickener (volume fraction)

\( \phi_0 \) initial suspension concentration (volume fraction)

\( \Phi(x) \) concentration function measured from centre of centrifuge (volume fraction)

\( \omega \) angular speed \((\text{rad/s})\)
Chapter 1

INTRODUCTION

1.1 BACKGROUND AND INDUSTRIAL APPLICATION

The concentration of fine particle suspensions is a crucial step in many industrial processes. Two major processes that depend on this step are the disposal of mine tailings as highly concentrated slurries, and the wet casting of ceramic components from highly concentrated suspensions. A brief background to these processes now follow.

Mining operations produce vast quantities of tailings. Commercial yields of precious metals extracted from mined ore are often of order grams per tonne. Yields also decline as mines approach the end of their working life and as global resources are exhausted. The quantity of waste tailings produced from mining operations is thus enormous and is growing [e.g. Glenister and Abbott (1989)]. This is a world wide problem.

The extraction of precious metals from ore typically requires that the ore be finely crushed and mixed with large quantities of water. Extraction chemicals are added such as cyanide for gold extraction, concentrated sulphuric acid for copper and concentrated caustic soda for alumina. The waste stream from the extraction plant thus consists of a dilute mixture of mineral particles in aqueous suspension, together with chemicals that are potentially harmful should they enter the environment. A waste treatment plant is necessary. It usually has three objectives: to recover the process water, to recover the extraction chemicals, and to produce a waste that can be safely disposed. Process water and extraction chemicals are often major operating costs in mining operations; their
maximum recovery is thus a high priority. The safe disposal of mine tailings, however, is often not fully achieved, but with proper consideration the first two objectives can usually also be solved.

Efficient recovery of process water requires fast and effective separation of the particulate solids from the waste stream. Traditionally, process water is recovered by adding flocculant to the waste stream to agglomerate particles that then quickly settle in clarifiers or thickeners leaving a clear supernatant. The tailings are then pumped into large settling ponds from which the supernatant is recycled back into the process and the solids slowly settle and eventually fill the pond. Given the huge volumes of waste produced by mining operations, this disposal technique has numerous environmental and economic problems [Cooling (1985); Nguyen and Boger (1986); Ritzey (1989)].

An increasingly viable disposal technique is to highly concentrate the mine tailings in a large thickener, then pump the slurry to the disposal area in a ‘semi-dry’ state [Robinsky (1975, 1978); Wood and McDonald (1986); Glenister and Abbott (1989); Cooling and Glenister (1992); Pashias, et al. (1996)]. There are several compelling reasons for this trend in tailings disposal. Semi-dry tailings can be discharged from a central position in the disposal area to form a conical mound. Central discharge dramatically reduces the landfill area required compared with a conventional tailings dam. Pumping energy requirements are reduced due to the smaller volume of tailings. The enhanced recovery of process water also increases the recovery of the extraction chemicals. Any extraction chemicals not recovered are bound in the suspension matrix and are less likely to leach into the environment and become a future problem. The tailings dry fast; thus revegetation of the tailings disposal area can begin relatively quickly. A potential problem with semi-dry disposal is dusting; that is, the surface layer may loosen and become airborne in wind. Dusting is minimised by careful position of the tailings area with respect to prevailing winds and natural wind barriers. Overall, these arguments support the adoption in certain instances of a semi-dry disposal strategy in which mine tailings are concentrated and pumped as a thick slurry or paste to the disposal area.

Another important application of highly concentrated mineral suspensions is in the rapidly expanding ceramics industry where the wet processing of concentrated
suspensions has recently become more prevalent [Lange (1989); Horn (1990); Rice (1990); Ulrich (1990); Haerle and Haber (1996)]. Traditional methods press the dry powder in a mould, then sinter the particles to form the ceramic object. In wet processing, the mould is filled with a suspension at the highest possible concentration. Alternatively, a porous mould is filled with a suspension at a lower concentration, then a pressure is applied and a high packing is achieved. When the wet ceramic is fired, shrinkage is minimised which is the major cause of ceramic cracking and strength reduction. The objective then is to produce a suspension that can be concentrated to the required level. This can be achieved by precisely controlling the surface chemistry of the particles [Horn (1990); Leong (1994)] and by applying the correct compressive pressure until the suspension is sufficiently consolidated.

The problems of interest for the concentration of both mine tailings and ceramic suspensions, are the selection, design and operation of the consolidation equipment. To achieve high concentrations, the equipment must compress the suspensions. Compressive forces can be applied in several ways. In a deep thickener, the weight of the overlying sediment acts to compress the layers of sediment underneath. Centrifugation operates on the same principle but gravitational acceleration is enhanced by the centrifugal motion. In filtration, pressure can be applied by capillary forces through a porous medium, by direct external pressure, by vacuum pressure, or even centrifugal pressure. Mine tailings are typically concentrated in large thickeners as filtration or centrifugation is usually impractical due to the large treatment volumes. Ceramic suspensions are filtered either mechanically or pneumatically.

Consolidation equipment design and operation must be based on the properties of the target suspension. The strength of the suspension in compression determines the magnitude of the compressive force required for consolidation. The sediment height in a thickener or centrifuge to produce a given underflow concentration, or the applied pressure to produce a given filtration cake density, is thus determined. The time scale for settling and consolidation of the suspension also determines the throughput of thickeners or centrifuges, or the filtration time for filters. Therefore, compression strength and the settling or consolidation rate are the suspension properties that must be measured for design.
The aim of this research is to quantitatively characterise particulate suspensions in settling and compression.

Given that the relevant properties of the suspension can be measured, the goal then is to model the processes to enable prediction of consolidation behaviour based on these properties. Using a model, consolidation performance is easily evaluated for changing properties of the suspension; for example, surface properties of the particles in suspension can be manipulated. Many more conditions and variables may then be evaluated in the laboratory without the costly interruption of an operating plant. This information can be used to design processes or optimise existing processes for the concentration of mineral suspensions.

1.2 RESEARCH APPROACH

To achieve the aim, theory for consolidation of suspensions is described in Chapter 2 including techniques for characterisation and measurement of relevant suspension properties. Fundamental surface chemistry is also included to introduce how properties of consolidating suspensions may be manipulated.

In Chapter 3, experimental details of the materials used in this study, the preparation method of the suspensions and basic measurement techniques are described.

In Chapters 4 and 5, techniques for characterisation of the compressive behaviour and consolidation rate of suspensions are described, compared and evaluated.

In Chapter 6, parameters influencing the compression rheology of suspensions are presented and discussed.

In Chapter 7, the application of these measurements and results to the design and operation of a real consolidation process is described.

Finally, in Chapter 8, major conclusions and recommendations for future work are presented.
Chapter 2

INTRODUCTORY THEORY

2.1 INTRODUCTION

The objective of this chapter is to overview theories for the characterisation and measurement of the fundamental properties of consolidating suspensions. Areas requiring investigation are identified. The overall direction of the thesis is thus defined.

Introduced in the first section of the chapter is a background to the process of consolidation. A comprehensive fundamental model to describe the consolidation process is developed. The model uses two parameters to describe the dynamics of a consolidating suspension; a compressive yield stress and a hindered settling function. The theory and techniques for measurement of these parameters are described in detail. Introduced next are the essentials of colloidal surface chemistry relevant to this thesis. Manipulation of the surface chemistry can result in vast changes in the bulk and structural properties of colloidal suspensions. The consolidation model can thus be investigated under a range of suspension conditions by using such control. Application of the model to the design of a consolidation process is then possible. As a test of the model, the theory and procedure for the design of a continuous gravity thickener is explained.
2.2 SUSPENSION CONSOLIDATION

2.2.1 BASIC MECHANISMS

Particulate suspensions consolidate by two basic processes; by filtration and by gravity settling. In filtration (both pressure and vacuum), an external pressure difference applied across the suspension forces the liquid through a permeable membrane leaving the solids to form a packed cake or bed. The effect of gravity is negligible. In gravity settling, solids fall due to the influence of gravity thus displacing liquid upwards. The weight of overlying sediment acts as an additional force to compress the layers of sediment below. In Figure 2.1, the driving forces and the relative solid and liquid velocities ($u$ and $v$ respectively) are shown for batch filtration and for batch gravity settling. Note that the solid and liquid velocities are in the same direction for filtration but are opposite in direction for gravity settling. In filtration, the liquid drag on particles, which transport the solids to the membrane, enhance the consolidation rate. In contrast, the liquid drag in gravity settling acts to hinder the rate of consolidation of

![Diagram](image)

**Figure 2.1** Basic consolidation mechanisms showing driving forces and relative solid and liquid velocities ($u$ and $v$ respectively) for: a) batch filtration, b) batch gravity settling.
particles. At equilibrium, liquid drag is zero in both cases. For a similar applied force, a similar maximum concentration is thus expected from both filtration and gravity settling. The hydrodynamics though are very different in each process and the gravity settling process is expected to take longer to reach equilibrium for the same applied force.

The process of suspension consolidation by gravity settling can be separated into four regions, as illustrated in Figure 2.2. This distinction was first made by Coe and Clevenger (1916) who investigated the design of sludge thickeners, and refined by Fitch (1962). The first uppermost region is clear liquid or supernatant. The second region is the hindered settling region in which the concentration is relatively constant with height and particles or flocs influence each other as they fall under gravity. The third region is a transition region where particles decelerate due to contact with other particles from the concentrated region below. The transition region can be very narrow with a sharp concentration gradient and is considered as a discontinuity or shock wave in thickener models by several workers [Auzerais, et al. (1988); Howells, et al. (1990)]. Finally, the fourth region is a compression region where a concentration gradient exists in which each floc is in mutual contact and compression of the structure occurs due to the weight of the overlying sediment. The precise nature of the mechanism of compression in this region is discussed in the next section.

![Diagram of Consolidation Regions](chart.png)

**Figure 2.2** Consolidation regions in a gravity thickener.
The above picture for gravity settling is applicable when the initial suspension concentration, $\phi_0$, is less than the gel concentration or gel point, $\phi_g$. Throughout this thesis, concentration is measured by volume fraction of solids in suspension. When $\phi_0 < \phi_g$, the system consists of separated particles or flocs and is considered to be un-networked. If particles or flocs are touching, forming a contiguous space-filling networked structure ($\phi_0 > \phi_g$), then only a constant concentration region (at concentration, $\phi_0$) and a compression region are present.

The process of consolidation by filtration is similarly subdivided [Landman and White (1994)]. If the suspension is initially un-networked ($\phi_0 < \phi_g$), then the filtration process consists of two stages. First, a compact bed builds up on the membrane. The bed increases in height with time, and has a changing concentration profile with $\phi_g$ at the top of the bed. After a certain time, the bed reaches the piston and consolidation of the fully networked bed begins - the second stage of filtration (sometimes called expression). If $\phi_0 \geq \phi_g$, then only the second stage of filtration will occur. Buttersack (1994) has further developed a theory that removes this distinction between the two stages of filtration. Filtration is discussed in more detail later in the chapter.

A general model to describe the developing concentration profiles in filtration and in batch and continuous thickening for all initial suspension conditions is required. With such a model, prediction of the performance of consolidation operations is possible.

2.2.2 GENERAL CONSOLIDATION MODEL

An excellent review of the development of early thickening and compression theory has been compiled in the thesis of de Guingand (1986). This background is not repeated here; instead, the current widely accepted general consolidation model is discussed.

General equations describing the fundamental dynamics of consolidating suspensions are clearly stated in the review paper of Landman and White (1994). These equations were first compiled by Buscall and White (1987) and are applicable to batch and continuous thickening and to filtration. A one-dimensional force balance in the vertical
downward ($z$) direction (i.e., in the direction of $g$) on a volume element of suspension, concentration $\phi$, is derived for the solid phase. As usual [Bergström (1992); Landman, et al. (1988)], inertial forces, bulk and wall shear forces are assumed negligible.

$$\frac{-\lambda}{V_p} r(\phi) (u - v) + \frac{\partial P}{\partial z} + \phi \frac{\partial P}{\partial z} + \rho_s \phi g = 0. \quad (2.1)$$

The first term is the hydrodynamic resistance where $\lambda$ is the drag coefficient for a single particle in infinite media, $V_p$ is the particle volume, $(u - v)$ is the velocity of the particle relative to the local fluid in the direction of $g$, and $r(\phi)$ is a hindered settling function which accounts for hydrodynamic interactions between the particles (discussed further in Section 2.4.2). The second and third terms are the particle and fluid pressure gradients in the suspension network. The fourth term is the net centrifugal force exerted on the suspension where $\rho_s$ is the density of the solid phase, and $g$ is the gravitational acceleration. A similar equation is written for the fluid phase;

$$\frac{\lambda}{V_p} \frac{\phi r(\phi)}{(1 - \phi)} (u - v) + \frac{\partial P}{\partial z} + \rho_f g = 0, \quad (2.2)$$

where $\rho_f$ is the fluid density. Combining Equations (2.1) and (2.2) gives

$$\frac{-\lambda}{V_p} \frac{\phi r(\phi)}{(1 - \phi)} (u - v) + \frac{\partial P}{\partial z} + \Delta \rho \phi g = 0, \quad (2.3)$$

where $\Delta \rho = \rho_s - \rho_f$. Conservation of particle and fluid mass give the continuity equations

$$\frac{\partial \phi}{\partial t} - \frac{\partial (\phi u)}{\partial z} = 0, \quad (2.4)$$

and

$$\frac{\partial (1 - \phi)}{\partial t} - \frac{\partial ((1 - \phi) v)}{\partial z} = 0. \quad (2.5)$$

Combining and integrating Equations (2.4) and (2.5) gives

$$\phi u + (1 - \phi) v = \begin{cases} 0, \text{ for batch settling} \\ \text{operating flux, for continuous thickening} \\ \frac{dH}{dt}, \text{ for pressure filtration.} \end{cases} \quad (2.6)$$
Equation (2.6) is used to eliminate the liquid velocity, \( v \), in Equation (2.3) which together with Equation (2.4) are two equations in three unknowns, \( \phi \), \( u \) and \( P_s \). A constitutive equation relating the particle pressure, \( P_s \), to \( \phi \) and \( u \) is required to completely define problem.

The particle pressure arises due to interactions between neighbouring particles. For fully dispersed or stable suspensions, the particle pressure is equivalent to the osmotic pressure, \( P_{os}(\phi) \) [Buscall and White (1987)]

\[
P_s = P_{os}(\phi)
\]

which can be measured [Cairns, et al. (1976, 1981); Miller and Zukoski (1994)]. Stable suspensions consolidate to form dense beds with concentrations approaching the close packing limit, \( \phi_{cp} \).

For flocculated suspensions, a continuous networked structure forms when the average concentration exceeds the gel concentration or gel point, \( \phi_g \). In a settling suspension of dilute particles or flocs, \( \phi_g \) is the mean concentration at which particles or flocs just come in contact. Compressive forces are transmitted by the resulting networked structure which can then support itself. If the applied compressive force is sufficiently small, the network will resist compression elastically. As the applied compressive force is increased, a point is reached where the network will yield and irreversibly consolidate. Yielding is due to the breaking or rearrangement of bonds between particles and/or the formation of more contact points between particles. This process is modelled by introducing the concept of the network possessing a compressive yield stress, \( P_y \), an explicit function of the local concentration, \( \phi \) [Buscall and White (1987)]. The network thus resists compression until \( P_s \) exceeds the local compressive yield stress, \( P_y(\phi) \). The \( P_y(\phi) \) function depends implicitly on the properties of the suspension network structure, that is, the number, strength and arrangement of inter-particle bonds.

The structure is determined by the flocculation state, any surface active additives, and any previous shear or compression history of the suspension. \( P_y(\phi) \) is expected to be an increasing function of \( \phi \), is zero for \( \phi < \phi_g \), and is very large for \( \phi \rightarrow \phi_{cp} \).
For flocculated suspensions the following constitutive equation was proposed by Buscall and White (1987) to describe the dynamics of consolidation:

\[
\frac{D\phi}{Dt} = \begin{cases} 
0 & , \quad P_s < P_y(\phi) \\
\kappa(\phi)[P_s - P_y(\phi)] & , \quad P_s > P_y(\phi)
\end{cases}
\]  

(2.8)

where \(D\phi/Dt\) is the material derivative of the local concentration, and \(\kappa(\phi)\) is a rate constant called the dynamic compressibility. Equation (2.8) says that the network resists compression if \(P_s < P_y(\phi)\), but collapses if \(P_s > P_y(\phi)\).

It can be argued that \(P_s\) will always be close to \(P_y(\phi)\). If the drainage of the fluid is the rate determining step in the dynamics of collapse, then \(\kappa(\phi)\) is of order \(O(\phi/\eta)\), where \(\eta\) is the fluid viscosity [Dixon (1978); Buscall and White (1987)]. For this case, estimating the order of the terms in Equation (2.8) gives

\[
P_s = P_y(\phi)\left[1 - O(a_p^2/h_0^2)\right],
\]

(2.9)

where \(a_p\) is the particle size and \(h_0\) is the container size. Typically, \(O(a_p^2/h_0^2) \sim (10^{-12} - 10^{-8})\), and therefore Equation (2.8) can be replaced by

\[
P_s(z, t) = P_y[\phi(z, t)]
\]

(2.10)
in the compression region. The compressive yield stress is thus a direct measure of the particle pressure or of the strength of bonds between particles in a flocculated suspension under compression.

It is important to note that the use of Equation (2.10) assumes that compression is irreversible (since the pressure completely characterises the local concentration), which is particularly significant when viscoelastic systems are examined. This equation is also only strictly valid for strongly flocculated systems possessing a contiguous space-filling network structure. Bergström (1992) notes that for weakly flocculated systems in particular, the top portion of the sediment slowly increases with concentration, which is contrary to the model of Potanin and Russel (1996).

Equation (2.3), with \(v\) eliminated, and Equation (2.4) together with either Equation (2.7) or Equation (2.10) are the basis of a complete theory for the consolidation of
suspensions. Two parameters of the suspension are required; the compressive yield stress function, $P_y(\phi)$, and the hindered settling function, $r(\phi)$. A complete description of these parameters and their measurement is given later in the chapter.

Recently, a complementary theory applicable to both the sedimentation of suspensions and the consolidation of a sediment bed or saturated soil was developed by Toorman (1996). Toorman used a similar theoretical basis to that presented here and integrated soil mechanics with chemical engineering techniques. Models for the consolidation of soils, such as described by Gibson, et al. (1967), Been and Sills (1981), Lee and Sills (1981) and Schiffman, et al. (1985), have followed a parallel, but very different development to the general consolidation model presented here. Other general theories have been developed by Olson and Ladd (1979), Tiller, et al. (1987), and Tiller and Hsyung (1993).

### 2.3 COMPRESSION RHEOLOGY

Rheology is the science of the deformation and flow of matter. Rheology is normally associated with deformation and flow in shear fields. Compression rheology is a subset of rheology in which deformation and flow are due to compression fields acting on the material. The field of compression rheology is relatively new. Work characterising the compression rheology of suspensions is described in this section.

In the previous section, the compressive yield stress, $P_y(\phi)$, was postulated as a material property of flocculated suspensions. The compressive yield stress, $P_y$, quantifies the strength of the suspension, at concentration $\phi$, when subjected to an applied compressive load. In compression or centrifugal thickening, the sediment height required to produce a given underflow or bottoms concentration can be calculated from a measurement of $P_y(\phi)$ for the suspension. In filtration, the applied pressure required to produce a given filter cake concentration can be similarly determined. The compressive yield stress thus defines the scale of the consolidation equipment necessary to produce the required
output concentration. Theories for measurement techniques of the parameter, $P_y(\phi)$, are discussed in this section.

### 2.3.1 PREVIOUS WORK

The direct measurement of $P_y(\phi)$ for consolidating suspensions began in the last fifteen years. Interest has slowly increased with industry becoming more aware of its importance and usefulness in the design and optimisation of consolidation operations.

Dell and Keleghan (1973) and Shin and Dick (1975) first measured the compressive stress in a settling column for flocculated clay and inorganic sludge respectively. Lockyear and White (1979) used a low speed centrifugal technique to characterise the 'thickenability' of sewage sludge. They were able to predict the developing concentration profile with time in a batch thickener and used a simple model of $P_y(\phi)$ to verify the results. The first explicit measurement of $P_y(\phi)$ was made by Buscall (1983) who did some preliminary experiments using polystyrene latex. It was first used for an industrial application by de Guingand (1986) who studied the compression characteristics of bauxite residue or red mud. In that work, an optimum flocculant dosage significantly enhanced the compressibility of the red mud. The compressive yield stress has also been successfully used at the University of Melbourne in the design of several thickening operations for the Australian mining industry (unpublished work, 1992-1996). The compression de-watering of fine coal tailings containing a significant proportion of clay has been investigated by de Kretser (1995). The clay in these tailings was found to control the rheology and consolidation characteristics of the system, and precise manipulation of the suspension chemistry enabled improved compression. Recent work on cement pastes and alumina suspensions by Miller, et al. (1995) found a dependence of $P_y(\phi)$ on the initial concentration of the sample and only a weak dependence on the compressive history of the suspension. Miller, et al. (1996) focused on evaluating the measurement of $P_y(\phi)$ using alumina and zirconia suspensions. Their
work partially overlaps with this work. Finally, Eckert, et al. (1996) determined $P_y(\phi)$ for the consolidation of fine tailings from tar sands.

The above workers used several techniques for the determination of $P_y(\phi)$. All the currently available techniques are reviewed in the following sections.

### 2.3.2 MULTIPLE SPEED EQUILIBRIUM SEDIMENT HEIGHT TECHNIQUE

The compressive yield stress function for a suspension, $P_y(\phi)$, can be obtained from centrifuge experiments [Buscall and White (1987)]. The experiment is illustrated in Figure 2.3. Suspension samples are placed in cylindrical, transparent, flat bottomed, centrifuge tubes and the equilibrium sediment height, $H_{eq}$, is measured for various

![Diagram](image)

**Figure 2.3** Schematic of multiple speed equilibrium sediment height technique.
increasing values of the gravitational acceleration, \( g \), at the bottom of the tube. Initially, the volume fraction concentration of the flocculated suspension is uniform throughout at \( \phi_0 \). Also required for the calculations are the initial height of the suspension, \( H_0 \), the density difference between the solid and the fluid, \( \Delta \rho \), and the centrifuge radius from the centre to the internal base of the tube, \( R \). These raw data are the basis of the so called 'multiple speed equilibrium sediment height technique'.

Beginning with these raw \((g, H_{eq})\) data, the development of equations in the general consolidation model give a parameterisation in \( g \) for \( P(0) \) and \( \phi(0) \); the pressure or solid stress, and the volume fraction concentration at the bottom of the tube (at \( z = 0 \)). [For simplicity \( P_s(z, t) \), which at equilibrium is independent of \( t \), is now replaced by the notation \( P(z) \).] Using these equations, \( P(0) \) as a function of \( \phi(0) \) is calculated by either an iterative or an approximate solution procedure that are described in turn below. The application of Equation (2.10) thus means that this curve is equivalent to the compressive yield stress function, \( P_y(\phi) \).

### 2.3.2.1 Iterative solution

The underlying differential equation relating the pressure \( P(z) \) to \( g \) at equilibrium is determined from Equation (2.3):

\[
\frac{dP}{dz} = -\Delta \rho \phi g \left( 1 - \frac{z}{R} \right). \tag{2.11}
\]

This equation together with a mass conservation equation are manipulated in various ways, as detailed in Appendix A [White (1995)]. Functions for \( \phi(0) \) and \( P(0) \) are determined

\[
\phi(0) = \frac{\phi_0 H_0(1 - \varepsilon)}{\left( \frac{H_{eq}}{g} \frac{dH_{eq}}{dg} \right) \left( 1 - \frac{H_{eq}}{R} \right) + \frac{H_{eq}^2}{2R}}, \tag{2.12}
\]

\[
P(0) = \Delta \rho g \phi_0 H_0(1 - \Delta), \tag{2.13}
\]
where \( \varepsilon \) and \( \Delta \) are determined from associated differential equations

\[
\frac{d\varepsilon^*}{dz} = \frac{\phi \left[ Z(z) + \left( 1 - \frac{H_{eq}}{R} \right) g \frac{dH_{eq}}{dg} \right]}{\phi_0 H_0 R (1 - z/R)^2},
\]

(2.14)

\[
\frac{d\Delta^*}{dz} = \frac{P(z)}{\Delta \phi \phi_0 H_0 g R (1 - z/R)^2},
\]

(2.15)

\[
\varepsilon = \varepsilon^*(H_{eq}), \quad \Delta = \Delta^*(H_{eq}).
\]

(2.16)

where \( \varepsilon^*(0) = 0 \) and \( \Delta^*(0) = 0 \). Equations (2.12) and (2.13) explicitly show how the \( \varepsilon \) and \( \Delta \) functions act as corrections to \( \phi(0) \) and \( P(0) \) respectively. Note that when \( \Delta \) is ignored, \( P(0) \) represents the case when the applied force is constant throughout the sample (applicable to batch thickeners and to pressure filtration).

The \( \varepsilon^* \) and \( \Delta^* \) are integral functions of the concentration and pressure profiles in the centrifuge tube, and also involve \( H_{eq} \) and its derivative. These concentration and pressure profiles are unknown in the consolidating region, \( 0 < z < z_c \), thus these functions must be solved by numerical integration together with the main differential equation, Equation (2.11).

In the constant concentration region, \( z_c < z < H_{eq} \),

\[
\phi = \phi_0
\]

\[
P(z) = \Delta \rho g \phi_0 (H_{eq} - z) \left( 1 - \frac{H_{eq} + z}{2R} \right),
\]

(2.17)

from Equation (2.11). Using Equation (2.17) in the constant concentration zone, the \( \varepsilon \) and \( \Delta \) correction terms become

\[
\varepsilon = \varepsilon^*(H_{eq}) = \varepsilon^*(z_c) + \frac{H_{eq} - z_c}{H_0 R (1 - z_c/R)} \left( \frac{H_{eq} - z_c}{2} + g \frac{dH_{eq}}{dg} \right),
\]

(2.18)

\[
\Delta = \Delta^*(H_{eq}) = \Delta^*(z_c) + \frac{g(H_{eq} - z_c)^2}{2H_0 R (1 - z_c/R)},
\]

(2.19)
so that Equations (2.11), (2.14) and (2.15) need only be integrated from \(0 < z < z_c\) to calculate \(\varepsilon^*(z_c)\) and \(\Delta^*(z_c)\). With \(\varepsilon\) and \(\Delta\) found, these functions are now used in Equations (2.12) and (2.13) to find \(\phi(0)\) and \(P(0)\) for each value of \(g\).

The above algorithm differs from an earlier algorithm described by Buscall and White (1987). The previously reported algorithm required two derivatives to be determined, essentially both \(dH_{eq}/dg\) and \(d^2H_{eq}/dg^2\). This earlier algorithm was used for some time [de Guingand (1986); Green and Boger (1992)], but has less rigour and is unstable compared with the new method described above. The new algorithm described here involves only one curve fit of the raw data and only one numerical differentiation, thus minimising computational errors and enhancing stability. Another variation on the solution method has also been developed by Miller, et al. (1996).

The computational methods for the iterative solution are detailed in Chapter 4.

### 2.3.2.2 Approximate solution

An approximate solution can be obtained using the mean value theorem of Buscall and White (1987). From Equation (2.11) evaluated at \(z = 0\)

\[
\frac{1}{\phi(z)} \int_0^{H_{eq}} \rho \, dP = \Delta \rho \, g \, H_{eq} \left(1 - \frac{H_{eq}}{2R}\right),
\]

where \(z = \xi\) such that \(0 < \xi < z_c\) but is otherwise unknown. Hence,

\[
P(0) = \Delta \rho \, g \, H_{eq} \phi(\xi) \left(1 - \frac{H_{eq}}{2R}\right).
\]

Applying the mean value theorem to a conservation of mass equation gives

\[
\phi(\xi') \, H_{eq} = \phi_0 \, H_0,
\]

again for a value of \(\xi'\) between \(0 < \xi' < z_c\).
If we assume that $\phi(\xi) = \phi(\xi')$, then Equations (2.21) and (2.22) yield

$$P(0) \approx \Delta \rho \phi_0 H_0 g \left(1 - \frac{H_{eq}}{2R}\right).$$  \hspace{1cm} (2.23)

From Equation (A14) in Appendix A this yields

$$\phi(0) \approx \frac{\phi_0 H_0 \left[1 - \frac{1}{2R} \left(H_{eq} + g \frac{dH_{eq}}{dg}\right)\right]}{\left[H_{eq} + g \frac{dH_{eq}}{dg}\right] \left(1 - \frac{H_{eq}}{R}\right) + \frac{H_{eq}^2}{2R}}. \hspace{1cm} (2.24)$$

$P(0)$ and $\phi(0)$ may thus be directly calculated for each $(g, H_{eq})$ raw data point using the above two equations. Determination of the derivative, $dH_{eq}/dg$, at each point is all that is required.

The mean value ‘approximate’ solution for $P(\phi(0))$ is a very good solution to the compression equations. This is demonstrated graphically in Figure 2.4 for a particular $g$ value and for a particular synthetic function (discussed later). In Figure 2.4a) the scaled concentration profile generated by the algorithm is shown. The equivalent ‘average’ concentration, $\phi(\xi')$, for that particular $H_{eq}$ is indicated. In Figure 2.4b) this value is used in the integral in Equation (2.20) and this $P(0)/\phi(0)$ area is compared with the right side of the integral as calculated by the algorithm, which is the area under the curve. For the synthetic data tested, the relative error between the two calculations remained under 3% for a range of $g$ values and synthetic functions which is excellent given the relative simplicity of the solution. This verifies numerically that the approximate solution is sound.

Note that it does not appear possible to show analytically that this simple solution is an accurate approximation for all functions $P_y(\phi)$ [White (1995)].
Figure 2.4 Numerical validation of the mean value theorem for the approximate solution: a) sample concentration profile from a synthetic function, $P_y = 100 \left(\frac{\phi}{0.18}\right)^8 - 1$, for $g = 5550 \text{ m/s}^2$, showing the equivalent 'average' concentration $\phi(\xi')$; b) comparison of the $P(0)/\phi(0)$ areas as calculated by the algorithm and as by the mean value theorem (scaled units).
2.3.3 CONCENTRATION PROFILE TECHNIQUE

2.3.3.1 Theory

The compressive yield stress curve, $P_y(\phi)$, can be determined from the measurement of the concentration profile of a sample centrifuged to an equilibrium height at a given gravitational acceleration.

Previous work by Tory and Shannon (1965) determined the weight of solids per unit area as a function of the average final solids concentration for CaCO$_3$ slurries settling under normal gravity. Their final concentration was an average concentration of the entire sediment and was directly dependent on the initial concentration of the suspension. Their method for determination of the weight of solids per unit area, however, was the precursor to the determination of the compressive yield stress from the concentration profile of a consolidated suspension.

The theory for determination of $P_y(\phi)$ from an equilibrium concentration profile is defined by Buscall and McGowan (1983), Auzerais, et al. (1990), Bergström (1992) and Bergström, et al. (1992) and is repeated here. In batch settling in a centrifuge, the suspension is subjected to a gravitational acceleration, $g$, which varies with the distance from the centre, $z$, as

$$g = \omega^2 z,$$  \hspace{1cm} (2.25)

where $\omega$ is the angular speed. At equilibrium, the hydrodynamic resistance is zero, thus the force balance on a volume element of suspension, Equation (2.3), reduces to

$$\frac{dP_s}{dz} = \Delta \rho \omega^2 z \phi(z).$$  \hspace{1cm} (2.26)

Using the standard constitutive equation, Equation (2.10), the particle stress, $P_s$, is replaced by the compressive yield stress, $P_y$. 
Integrating Equation (2.26) gives the stress at position z;

\[ P_y(z) = \Delta \rho \omega^2 \int_0^x \phi(x) \, dx, \quad (2.27) \]

where the origin of the x coordinate system is at the centre of the centrifuge. The compressive yield stress, \( P_y(z) \), is equivalent to the cumulative weight of suspension above that point z. Thus to find the full compressive yield stress curve the concentration profile must be progressively integrated from the top of the bed to the bottom for increasing values of z. Details of methods for the integration are given in Chapter 4. This technique is a more direct technique for the determination of \( P_y(\phi) \) than the multiple speed equilibrium sediment height technique, but \( \phi(x) \) must be measured for the centrifuged sample. Methods for the measurement of \( \phi(x) \) are now described.

2.3.3.2 Concentration profile measurement

The measurement of the concentration profile of a consolidated suspension has been done many times and in many ways. The calculation of \( P_y(\phi) \) curves from such profiles, however, has only recently been attempted. Gaudin and Fuerstenau (1959) developed an X-ray absorption device to measure the concentration profiles of settling CaO suspensions in a 1 m column. Chang, et al. (1994) used a similar device for centrifuged Al\(_2\)O\(_3\) suspensions. Kearsey and Gill (1963) used the calibrated transmission of \( \gamma \)-rays through a suspension to determine the concentration profile of settling thoria slurries. Tory and Shannon (1965), Bergström (1992), Bergström, et al. (1992) and Shih, et al. (1994) also used similar \( \gamma \)-ray devices. Auzerais et al. (1990) used a medical computer tomography (CT) scanner to obtain extremely accurate concentration profiles. X-ray photography was used by Ondeyka, et al. (1978) to monitor the settling and compression interfaces of a consolidating coal-fuel oil system. Finally, La Heij, et al. (1996a) used nuclear magnetic resonance (NMR) imaging and Haerle and Haber (1996) used an ultrasound technique on various filter cakes. An advantage of these non-intrusive methods of concentration profile determination, is that profiles may be
obtained relatively quickly, thus dynamic consolidation measurements may be taken. However, adequate resolution of ray absorption measurements can be a problem due to the necessity for a relatively wide beam.

A destructive testing method used here and by Smiles (1976) and Miller, et al. (1995, 1996) involves taking multiple sections from the sediment. The solids concentration of each section is measured by mass loss on drying. The value determined by drying is taken as the concentration at the midpoint height of the cut. The experimental technique used here is detailed in Chapter 4. A similar technique has been used on filter cakes by Smiles (1974), Sherwood, et al. (1991) and Meeten (1993).

### 2.3.4 INITIAL SETTLING RATE TECHNIQUE

The compressive yield stress may be determined from measurements of the initial settling rate from a series of batch settling curves in a centrifuge. Theory for this technique was developed by Buscall and White (1987). Here, the initial settling rate for a sample in a centrifuge is described by:

$$\frac{\mathrm{d}H}{\mathrm{d}t}\bigg|_0 = -\frac{u_0(1-\phi_0)}{r(\phi_0)} \left(1 - \frac{H_0}{2R} - \frac{P_y(\phi_0)}{\Delta \rho g \phi_0 H_0}\right), \quad (2.28)$$

where \(u_0\) is the Stokes settling velocity. A plot of \(\frac{\mathrm{d}H}{\mathrm{d}t}\bigg|_0\) versus \(\frac{1}{g}\) should be linear, with

$$\frac{1}{g} \rightarrow \frac{\Delta \rho \phi_0 H_0}{P_y(\phi_0)} \left(1 - \frac{H_0}{2R}\right) \quad \text{as} \quad \frac{\mathrm{d}H}{\mathrm{d}t}\bigg|_0 \rightarrow 0,$$

as illustrated in Figure 2.5. This intercept is the critical condition for settling to occur. Thus, \(P_y(\phi_0)\) may be calculated. Repeating this procedure for a range of suspensions of varying \(\phi_0\) would result in a complete \(P_y(\phi)\) curve. An equivalent analysis was also developed for batch sedimentation under uniform gravitational acceleration where the condition for settling is \(\Delta \rho g \phi_0 H_0 / P_y(\phi_0) > 1\).
Figure 2.5 Schematic of initial settling rate technique for determination of consolidation parameters, $P_y(\phi)$ and $r(\phi)$; a) determination of initial slope for a single g value, b) determination of intercepts from initial slope versus $1/g$ plot.
There are several problems associated with this initial settling rate technique for $P_y(\phi)$ determination. First, many suspension samples of different concentration must be prepared - a minimum of 5 or 6 concentrations are required for a reasonable $P_y(\phi)$ curve. For each suspension concentration the settling curve must then be measured for a range of gravitational accelerations - again, 5 or 6 points are required for a reasonable line. Thus at least 25-36 settling tests must be prepared and measured. Each settling test should use a fresh sample to avoid any possible history effects. Thus, the volume of suspension required is significant and the experimental workload to obtain a single $P_y(\phi)$ curve is large. De Guingand (1986) also encountered difficulties in fitting a straight line through the initial settling rate data to find the intercept.

An additional problem with this technique is the measurement of the interface to determine the settling rate at $t = 0$. Certain suspensions are known to exhibit a 'lag time'; an initial period in which no settling is observed [Glasrud, et al. (1993)]. Determination of the initial settling rate for such systems is difficult. Ideally, the interface also should be measured whilst spinning to eliminate disturbances caused by starting and stopping. Any possible elastic rebound of the interface on removal of the applied force should also be eliminated. A centrifuge fitted with transparent buckets and a strobe to freeze the motion could be used.

These problems with the initial settling rate technique to determine $P_y(\phi)$ are significant although not insurmountable. The experimental workload required to obtain a single $P_y(\phi)$ curve, however, is arduous compared with other available techniques. Routine work using this technique is thus not feasible, although it could be used to check the validity of other measurement techniques (not done here as several other viable techniques are available).

### 2.3.5 PRESSURE FILTRATION TECHNIQUE

The compressive yield stress function, $P_y(\phi)$, is easily determined using a constant pressure filtration device. A schematic of such a device is shown in Figure 2.6. A
sample of initial concentration $\phi_0$ is placed in a cylindrical cell, initial suspension height $H_0$. A piston is applied to the suspension at a constant pressure $\Delta P$, expelling liquid from the suspension through a permeable membrane. After sufficient time, the suspension consolidates to an equilibrium state. The transient behaviour of the pressure filtration is discussed later in the determination of the hindered settling function. At equilibrium, the pressure exerted by the piston is entirely supported by the suspension network structure. The applied pressure is thus equivalent to the compressive yield stress at that final concentration, such that

$$\Delta P = P_y(\phi_r).$$

(2.29)

where $\phi_r$ is the final concentration of the suspension which at equilibrium is theoretically constant.

**Figure 2.6** Schematic of pressure filtration technique for determination of $P_y(\phi)$; a) initial state, b) equilibrium state.
The final concentration is calculated either by

\[
\phi_f = \frac{\phi_0 H_0}{H_f},
\]

(2.30)

where \(H_f\) is the final equilibrium suspension height, or by mass loss on drying of the entire filter cake.

Repeating the experiment over a range of applied pressures will thus generate the complete \(P_y(\phi)\) curve. The same analysis holds if the suspension is initially structured \((\phi_0 > \phi_g)\); a pressure, \(\Delta P > P_y(\phi_0)\), is all that is required.

The pressure filtration technique has been used for some time in geomechanics to determine the solids stress of soils. Barclay and Ottewill (1970), Callaghan and Ottewill (1974), Shirato, et al. (1970), Meeten (1994) and Sherwood and Meeten (1997) have used a compression cell to examine the compressibility of clays. Bömkès and Wagener (1987) and Holdich (1990) have similarly measured the solids pressure for various suspension systems. Recently, Miller, et al. (1996) used pressure filtration to explicitly determine \(P_y(\phi)\) for \(Al_2O_3\) and \(ZrO_2\) suspensions.

### 2.3.6 HIGH FREQUENCY SHEAR MODULUS TECHNIQUE

The \(P_y(\phi)\) function for a material may be derived from the measurement of the high frequency limit of the shear modulus, \(G_\infty\) [Zwanzig and Mountain (1965); Harrison (1976); Goodwin, et al. (1986)]. The shear modulus, \(G_\infty\), is determined from the velocity of propagation of a shear wave through the material which acts as a Hookean solid [Buscall, et al. (1984)]. Commercial instruments called pulse shearometers are available to make this measurement. Buscall (1982) demonstrated a correspondence between the high frequency shear modulus, \(G_\infty\), and the compressional modulus, \(K\), defined as

\[
K(\phi) = \frac{dP}{d\ln \phi},
\]

(2.31)
for a wide range of materials. Buscall (1982) and Buscall, et al. (1984) determined $K$ from independent centrifuge experiments for a number of systems. By integration of Equation (2.31), the compressive yield stress function, $P_y(\phi)$, is determined.

Preliminary experiments on $\text{Al}_2\text{O}_3$ suspensions by Steven Johnson in the Department of Chemistry at the University of Melbourne using a latest model pulse shearometer, however, failed to produce any meaningful results. The concentration range of the instrument for flocculated suspensions appeared to be too low to be useful. This technique was thus abandoned as a means of determining the $P_y(\phi)$ function for concentrated suspensions.

### 2.3.7 CONSOLIDATION CYLINDER TECHNIQUES

The $P_y(\phi)$ function can be determined using series of consolidation cylinders in two ways. In the first technique, a series of different suspension concentrations are prepared with $\phi_0 > \phi_{\mu}$. For each suspension concentration, a series of cylinders are filled to a range of initial heights. The highest initial height, $H_0$, for which no consolidation occurs at each initial concentration $\phi_0$, is recorded, as illustrated in Figure 2.7a). The compressive yield stress at the bottom of this settling cylinder is thus

$$P_y(\phi_0) = \Delta \rho \, g_0 \, \phi_0 \, H_0,$$

(2.32)

corresponding to the weight of solids in the cylinder, where $g_0$ is normal gravitational acceleration. The $P_y(\phi)$ function is thus determined for the range of initial suspension concentrations prepared.

In the second technique, a single suspension of concentration $\phi_0$ is used. A series of cylinders are filled to a range of initial heights (each above the minimum height in the previous technique) and allowed to consolidate, as illustrated in Figure 2.7b). A concentration profile in each sediment is thus developed. The equilibrium sediment height, $H_{eq}$, attained for each initial height, $H$, is measured.
Figure 2.7 Schematic of two sedimentation cylinder techniques to find $P_y(\phi)$; a) find highest initial height $H_0$, for which no consolidation occurs for a range of $\phi_0 > \phi_y$, b) measure $H_{eq}$ for a range of initial heights $H$.

As derived in Appendix B, the stress at the bottom is

$$P(0) = \Delta \rho \ g \ \phi_0 \ H,$$

and the concentration at the bottom is

$$\phi(0) = \phi_0 \ \frac{dH_{eq}}{dH}.$$  

for each cylinder of initial height $H$. The $P_y(\phi)$ function is thus determined.

In each technique, values for $P_y$ at concentrations very close to $\phi_y$ can be measured. The first technique involves more experimental work since many suspensions of different concentrations must be prepared, and a series of consolidation cylinders must be used for each concentration. The precision of $P_y$ for each concentration, however, is absolute.

In the second technique, experimental work is less, but a differentiation of the raw data is required to extract $P_y(\phi)$ which always introduces error.
Neither consolidation cylinder technique was used in this work. In hindsight, however, these techniques would be very useful for determination of $P_y(\phi)$ data for the design of continuous thickeners where data at very low concentrations are required. See later in chapter for details.

2.3.8 SUMMARY

The strength of a suspension in compression is characterised by the compressive yield stress as a function of concentration, $P_y(\phi)$. Six techniques for the determination of $P_y(\phi)$ have been described. Three of these techniques are used and evaluated in this thesis; the multiple speed equilibrium sediment height technique, the concentration profile technique, and the pressure filtration technique. If $P_y(\phi)$ is a true material property then each technique should produce the same results for any given suspension. This hypothesis is tested in this thesis.

2.4 CONSOLIDATION RATE

In the previous section, the compressive yield stress function was defined to quantify the strength of a suspension under compression. To fully characterise the consolidation process, a second parameter is required to quantify the rate at which consolidation occurs.

The consolidation rate is of vital importance in many industrial operations. The throughput of continuous thickeners and continuous centrifuges is defined by the consolidation rate of the suspension. In filtration equipment, the equilibrium state is rarely attained. The filtration time to reach some required average filter cake concentration is defined by the consolidation rate. The consolidation rate thus defines the physical size of the consolidation equipment necessary to process the given volume of feed suspension. An existing process may be improved by manipulating the
consolidation rate properties of the suspension. Measurement of these properties enables the trial of different additives and operating conditions in the laboratory rather than interrupting the operating plant.

A fundamental parameter quantifying the rate of consolidation of a suspension is required. This parameter should be easily measured and able to be used directly in models for the design of consolidation equipment. In this section, approaches used in the past to quantify the consolidation rate of suspensions are briefly reviewed. The hindered settling function, \( r(\phi) \), in the current consolidation model is then explained in detail. Finally, techniques for measurement of the \( r(\phi) \) function are described.

2.4.1 PREVIOUS WORK

The design of thickeners traditionally used batch settling tests to measure the initial settling rate of the suspension interface [Coe and Clevenger (1916); Kynch (1952); Talmage and Fitch (1955); and others]. Adorján (1976) and de Guingand (1986) have reviewed these early thickening models. These models gave no consideration to the compression region.

The conventional engineering model for filtration is described by Shirato, et al. (1986) and Wakeman, et al. (1991). In this model, the total pressure drop in the fluid phase (equal to the applied piston pressure \( \Delta P \)) is the sum of the pressure drop over the growing compact bed and the pressure drop across the membrane

\[
\Delta P = \eta \alpha c V \frac{dV}{dt} + \eta R_m \frac{dV}{dt},
\]

(2.35)

where \( V(t) \) is the volume of fluid expressed per unit area of membrane, \( \eta \) is the fluid viscosity, \( c \) is the effective solids mass concentration in the filter feed, and \( R_m \) is the membrane hydraulic resistance. The quantity \( \alpha \) is the compact bed hydraulic resistance per unit mass of bed (sometimes called the specific filtration resistance or the specific bed resistance).
For constant $\Delta P$, integrating Equation (2.35) gives

$$\frac{t}{V} = \left(\frac{a c \eta}{2 \Delta P}\right) V + \left(\frac{\eta R_m}{\Delta P}\right) = m_1 V + b. \quad (2.36)$$

In the compact bed formation stage, a plot of $t/V$ versus $V$ should yield a straight line. From the slope, $m_1$, the compact bed resistance, $\alpha$, may be calculated and from the intercept, $b$, the membrane resistance, $R_m$, may be determined.

The compact bed resistance, $\alpha$, determined in the above model is widely used to characterise the filtration rate of suspensions [examples of recent work include: Adorján (1975); Shirato, et al. (1987); Massuda, et al. (1988); Tiller and Yeh (1990); Wakeman (1993); Fathi-Najafi and Theliander (1995); Herwijn, et al. (1995); La Heij, et al. (1996b); Sørensen, et al. (1996)]. There are fundamental problems with the parameter, $\alpha$, which is assumed to be constant as the bed becomes thicker and more concentrated [Tosun, et al. (1993)]. This assumption is contrary to the general consolidation model (Section 2.2.2), which states that the hydrodynamic drag of particles on the fluid is a strong function of concentration. However, remarkably good filtration data have been obtained that fit this semi-empirical model [Wakeman, et al. (1991); Sørensen and Hansen (1993)]. This agreement is not surprising as the full theory [Landman, et al. (1995)] predicts the same behaviour but from a different basis and with different assumptions. The modelling or design of an industrial process is also difficult using the compact bed resistance [Willis, et al. (1974); Bender and Redeker (1981)]. Clearly, a better parameter is required.

### 2.4.2 HINDERED SETTLING FUNCTION, $r(\phi)$

The hindered settling function, $r(\phi)$, accounts for the hydrodynamic interactions between particles in a consolidating suspension and is defined by the following equation for the settling velocity, $u$ [Landman and White (1994)]:

---
where \( u_0 \) is the settling velocity of a single particle in an infinite media (Stokes law for spherical particles).\(^1\) At the infinite dilution limit, \( \phi \to 0 \), particles are unaffected by neighbouring particles, thus \( r(\phi) \to 1 \). As the concentration increases, hydrodynamic interactions between particles hinder the settling velocity and \( r(\phi) \) increases exponentially. The upper limit is \( r(\phi) \to \infty \) as \( \phi \to 1 \). This limit is never reached in practice due to the existence of a maximum close packed concentration \( \phi_{cp} \approx 0.64 \) for random monodisperse hard spheres. The hindered settling function is thus always finite and characterises the consolidation rate of the suspension at all concentrations. The name of this function is thus somewhat misleading since it not only characterises consolidation in the hindered settling region but also in the compression region. In the compression region, the hindered settling function may alternatively be thought of as an inverse function of the permeability; instead of liquid permeating through a solid matrix, solids move through a stationary liquid phase.

Direct measurements of the hindered settling function for suspension systems are scarce. Auzerais, et al. (1990) measured the settling velocity function, \( u(\phi) \), for strongly and weakly floculated stabilised silica suspensions. Davis and Gecol (1994) have proposed a hindered settling function for polydisperse suspensions of spherical particles. The relatively recent emergence of the general consolidation theory described in Section 2.2.2, the relatively few researchers in this field and the unawareness of the importance of this parameter, are reasons for this lack of experimental data. The hindered settling function, \( r(\phi) \), is the definitive parameter to measure since it has a sound fundamental basis and can be used together with the compressive yield stress, \( P_y(\phi) \), in the design of all types of consolidation equipment.

Techniques for the determination of \( r(\phi) \) are now discussed.

---

\(^1\) Buscall and White (1987) define \( u(\phi) \) without the square on the \((1 - \phi)\) due to a slightly different set up of the original force balance.
2.4.3 INITIAL SETTLING RATE TECHNIQUE

The hindered settling function, \( r(\phi) \), may be determined from the same initial settling rate experiments used to find \( P_y(\phi) \) in Section 2.3.4. From Equation (2.28), a plot of \( \frac{dH}{dt} \bigg|_0 \) versus \( \frac{1}{g} \) is again made, noting that

\[
\frac{dH}{dt} \bigg|_0 \rightarrow - \frac{u_0 (1 - \phi_0)}{r(\phi_0)} \left(1 - \frac{H_0}{2R}\right) \text{ as } \frac{1}{g} \rightarrow 0.
\]

Thus \( r(\phi_0) \) may be calculated. Repeating this procedure for a range of suspensions of varying \( \phi_0 \) would result in a complete \( r(\phi) \) curve.

The initial settling rate technique for determination of \( r(\phi) \) suffers exactly the same problems as when used to determine \( P_y(\phi) \). These problems are detailed in Section 2.3.4. However, this technique to measure \( r(\phi) \) is more feasible due to problems encountered with other available \( r(\phi) \) measurement techniques. Measurements of \( r(\phi) \) at low concentrations may also be obtained with this technique.

2.4.4 CONTINUOUS VACUUM FILTRATION TECHNIQUE

The hindered settling function, \( r(\phi) \), may be measured using a steady state filtration device where the filtrate is continuously recycled through the suspension. The suspension begins at an initial height, \( H_0 \), and at equilibrium a sediment of height, \( H_{eq} \), is formed. The equilibrium height is dependent on the applied pressure, \( \Delta P \), and hence on the flowrate through the system, \( q \). The \( r(\phi) \) curve is derived from the measurement of these parameters over a range in applied pressures. Details of the technique are given in Landman and White (1992) and are summarised in Landman and White (1994).

In this work, a preliminary experimental program was initiated using this technique to determine the hindered settling function for some flocculated ZrO\(_2\) suspensions. The apparatus was simply a perspex cylinder (44.2 mm inside diameter, 174 mm high)
mounted on a Buchner funnel with a membrane of Whatman GF/A glass microfibre filter paper, illustrated in Figure 2.8. The cylinder was filled with suspension, then a vacuum was applied. Using a titration column, liquid of similar pH and salt content to the filtrate was added to the top of the cylinder at the same rate of liquid expression into the Buchner flask. The sediment height, the vacuum pressure and the efflux rate were monitored until steady state was attained.

Results from this limited experimental program were poor. Efflux rates through the system were extremely slow with maximum initial flow rates measured in drops per
minute and equilibrium flow rates measured even slower. The flow rate is limited by vacuum filtration which has a 1 atm maximum applied pressure difference. Design of a device using compressed air to provide the driving force might overcome this problem; this was not attempted here. Equilibrium times were of the order of days. Equilibrium sediment heights measured did not correlate at all with the applied vacuum pressure or the equilibrium efflux rate. Problems with channelling in the sediment might explain these anomalous results, although examination of the sediment did not give any evidence for this hypothesis. The sediment / fluid interface was also uneven and made measurement of the true sediment height difficult. Measurements of changes in the equilibrium sediment height for different applied pressures were also small. Large errors would thus propagate in the calculation of \( r(\phi) \).

In consideration of these poor results, this technique was abandoned as a feasible method for \( r(\phi) \) determination.

### 2.4.5 PACKED BED FORMATION TECHNIQUE

Determination of the \( r(\phi) \) function by the packed bed formation technique was developed by Landman, et al. (1995) and is summarised in Landman and White (1994). The technique was used by Eberl, et al. (1995) who successfully modelled the high pressure industrial filtration of flocculated kaolin. In the technique, a pressure filtration cell is used where a piston compresses the suspension and liquid is filtered out through a permeable membrane. The apparatus and experimental method are identical to that in Section 2.3.5 where \( P_r(\phi) \) is determined, but here the filtration rate is also measured.

The initial concentration of the suspension, \( \phi_0 \), must be less than the gel concentration, \( \phi_g \), in this experiment. There are thus two stages in the filtration process as shown in Figure 2.9. In the first stage, a compact bed is developed that grows away from the membrane with time. The compact bed has a concentration gradient \( \phi(z, t) \), where \( \phi > \phi_g \), and a particle stress gradient, where \( P_r(\phi(z, t)) > 0 \). At the top of the bed, height \( z = l(t) \), the concentration is the gel concentration, \( \phi[l(t), t] = \phi_g \) and the compressive
$0 < t < t_{cf}$

$\Delta P$

$h(t)$

$\phi_c$

$l(t)$

$\phi(z, t) > \phi_c$

Developing Compact Bed

Membrane

Water Flux, $V(t)$

$t \geq t_{cf}$

$\Delta P$

$h(t)$

$\phi(z, t) > \phi_c$

Water Flux, $V(t)$

Figure 2.9 The two stages of filtration of an initially un-networked ($\phi_0 < \phi_c$) suspension; a) compact bed formation, b) compact bed consolidation [from Landman, et al. (1995)].

yield stress is zero. At time $t = t_{cf}$ the compact bed reaches the piston and the second stage of filtration begins. Consolidation of the bed proceeds until the bed is uniform in concentration, $\phi_c$, satisfying $\Delta P = P_y(\phi_c)$. Transient concentration profiles in pressure filtration have been measured by Shen, et al. (1994), Tiller, et al. (1995) and Sherwood and Meeten (1997), and modelled by Tiller and Yeh (1987), Davis and Russel (1989), Stamatakis and Tien (1991), Landman, et al. (1991), Landman and Russel (1993), Sherwood (1993), Tiller, et al. (1995) and Tien, et al. (1997).

Analysis of the compact bed formation stage ($t < t_{cf}$) using the exact solution of the Landman and White model predicts a $t/V$ versus $V$ curve that is linear with slope $m_1$. Surprisingly, this linear behaviour agrees well with the approximate solution of Wakeman and Shirato. Comparing the slope for each solution, and using a mean concentration for the developing compact bed, $\phi_m$. 
\[ \phi_m = \frac{3}{4} \phi_r + \frac{1}{4} \phi_g , \]  

(2.38)

the following expression is obtained for the hindered settling function including the characteristic size terms, \( \lambda / V_p \),

\[ \frac{\lambda}{V_p} r(\phi_m) = \frac{2 \Delta P m_1 (\phi_m / \phi_0 - 1)(1 - \phi_m)^2}{\phi_m} . \]  

(2.39)

The complete \( r(\phi) \) curve is obtained by repeating the experiment over a range of applied pressure, \( \Delta P \), measuring the slope of the \( t/V \) versus \( V \) plots, \( m_1 \), and measuring the final equilibrium concentrations of the packed beds, \( \phi_f \), to find the mean concentrations, \( \phi_m \).

A new analysis method for determination of the hindered settling function from packed bed formation measurements has recently been developed by Landman and White (1997). This method does not use the mean concentration, \( \phi_m \), and is theoretically more sound. The new method was not used here (due to its late development) but preliminary analyses of several data sets indicate reasonable agreement with the previous method.

### 2.4.6 PACKED BED FILTRATION TECHNIQUE

The hindered settling function may be determined by constant pressure filtration through a packed bed of known height and concentration. This technique has previously been used to determine the permeability of suspensions by numerous workers [for example Ruth (1935, 1946); Terzaghi and Peck (1948); Kamphuis, et al. (1984); Smiles and Kirby (1987); Holdich (1990); La Heij, et al. (1996b)]. In the context of the general consolidation theory, the hindered settling function \( r(\phi) \), here equivalent to an inverse permeability, can be derived from the same experiment. For a pressure drop \( \Delta P \) across a packed bed of height \( H_r \), concentration \( \phi_r \), the force balance for the fluid phase, Equation (2.2), becomes in one dimension:

\[ -\frac{\lambda}{V_p} \frac{\phi_r r(\phi_r)}{1 - \phi_f} \nu + \frac{\Delta P}{H_r} = 0 , \]  

(2.40)
if the gravitational term is ignored (it being much smaller than pressure term).

Then if \( V(t) \) is the volume of fluid expressed per unit area of membrane, Darcy's law is obtained [Darcy (1856); Ward (1987)]:

\[
v = \frac{dV}{dt} = \frac{k(\phi_f) \Delta P}{\eta H_f},
\]

(2.41)

where

\[
k(\phi_f) = \frac{V_p \eta}{\lambda} \frac{1 - \phi_f}{\phi_f r(\phi_f)}.
\]

(2.42)

The permeability of a packed bed, \( k(\phi_f) \), is thus related to an inverse function of the hindered settling function, \( r(\phi) \). The hindered settling function, including the characteristic size terms, \( \lambda/V_p \), can therefore be determined from the measurement of the efflux rate through a packed bed of known concentration and height by the following equation:

\[
\frac{\lambda}{V_p} r(\phi_f) = \frac{\Delta P}{H_f} \frac{1 - \phi_f}{\phi_f} \frac{1}{dV/dt}.
\]

(2.43)

This form for \( r(\phi) \) is directly comparable with that determined from the previous technique, Equation (2.39).

**2.4.7 SUMMARY**

The hindered settling function, \( r(\phi) \), has been identified as the definitive parameter to characterise the consolidation rate of suspensions. Four techniques for the determination of \( r(\phi) \) have been described. Two of these techniques are used and evaluated in this thesis; the packed bed formation technique, and the packed bed filtration technique. The measurement of \( r(\phi) \) by these techniques has never been systematically investigated before. The implementation of a reproducible technique for the measurement of \( r(\phi) \) for suspensions is a major objective of this thesis.
2.5 COLLOIDAL SURFACE CHEMISTRY

In the previous sections, a comprehensive theory quantifying the consolidation of suspensions in terms of two fundamental parameters, $P_y(\phi)$ and $r(\phi)$ was described. To validate the theory, extensive testing with a range of suspensions having different consolidation characteristics is required. Using a colloidal suspension system (particle diameter less than about 1 μm), inter-particle forces are easily manipulated to produce suspensions with very different bulk properties using the same material [Russel (1980); Tadros (1985, 1986); Leong and Boger (1990); Leong, et al. (1991a); Liddell and Boger (1994)]. For flocculated suspensions, the inter-relationship between surface chemistry and yielding in shear is well established [Buscall, et al. (1990); Leong, et al. (1991b); Leong (1994)]. A similar inter-relationship is expected for the behaviour of suspensions in settling and compression. A well-characterised colloidal particle system with active surface chemistry is thus required. The optimum conditions for consolidation may also be determined by the systematic characterisation of the colloidal surface chemistry of the suspension.

In this section, a brief synopsis of basic colloidal surface chemistry relevant to this thesis is given. Modern detailed coverage and further references are contained in the books of Hunter (1989, 1991) and Shaw (1992). Four major colloidal forces are important: van der Waals attraction, electric double layer repulsion, steric repulsion and bridging flocculation. Each force and its effect on the structure of the suspension are briefly described in turn.

2.5.1 INTER-PARTICLE INTERACTIONS

2.5.1.1 Van der Waals attraction

Aggregation of particles is primarily due to attractive van der Waals forces. The van der Waals forces are caused by fluctuating dipoles on the surfaces of the particles. The
magnitude of the forces is determined by the dielectric and refractive properties of the particle (represented by the Hamaker constant) and is approximately proportional to the particle size. The van der Waals forces are approximately inversely proportional to the inter-particle distance (dependent on the geometry of the system).

For any given system, the van der Waals forces are essentially constant. To prevent aggregation, the van der Waals forces must be screened out by an equally long-range repulsive force.

2.5.1.2 Electric double layer repulsion

Particles naturally acquire a surface charge in a polar (e.g. aqueous) medium. Surface charge results from ionisation or dissolution of surface active groups, or by adsorption of ions from solution onto the surface. Close to the charged surface, ions of opposite charge in solution (counter-ions) are attracted to the surface and ions of like charge (co-ions) are repelled. An electric double layer consisting of the charged surface and a diffuse layer of counter-ions is thus formed. The electric double layer is illustrated for a negatively charged surface in Figure 2.10a). Electrostatic repulsion will result when the diffuse electric double layers on two interacting particles overlap.

The magnitude of the electrostatic repulsion is dependent on the charge density on the particle. The charge density determines the electrostatic surface potential which quantifies the repulsive interaction energy. In Figure 2.10b), the electrostatic potential of the electric double layer as a function of distance from the surface is illustrated. In aqueous solutions, the surface charge density of most oxide surfaces, due to ionisation of metal to acid sites, is determined by the concentration of hydrogen and hydroxyl ions; the latter controlled by the solution pH.

The ‘thickness’ of the diffuse electric double layer is defined by the inverse Debye or decay length, \( l_\alpha \), the distance over which the potential decreases by one exponential factor at low potentials. The double layer thickness is inversely proportional to the
**Figure 2.10** a) Schematic of electric double layer repulsion for a negatively charged surface; b) corresponding schematic of electrostatic repulsion force versus distance from surface.

square root of the ionic strength of the solution. The potential energy for electrostatic repulsion decays exponentially as a function of inter-particle separation.
2.5.1.3 Steric stabilisation

In addition to the van der Waals and electric double layer interactions between colloidal particles, other interactions are possible [Napper (1983); Israelachvili (1991)].

Steric stabilisation is due to the adsorption of polymer on the particle surface. When polymer layers on adjacent particles begin to overlap, an osmotic repulsion and/or an elastic repulsion are felt. This repulsion can screen out the attractive van der Waals forces. The polymeric steric barrier produces an overall repulsion that acts to keep the particles separated, thus forming a stable suspension.

2.5.1.4 Bridging floculation

Bridging flocculation is another inter-particle interaction that occurs when a high molecular weight polymer forms a physical ‘bridge’ between neighbouring particles in suspension. Strong adsorption of the polymer on each particle binds them together. This mechanism is commonly used in clarifiers and thickeners, where small quantities of high molecular weight polymer produce large, voluminous flocs that settle quickly and produce clear supernatants. These loosely structured flocs, however, are difficult to consolidate to high concentrations.

2.5.1.5 Overall interaction (D.L.V.O. theory)

The total interaction energy between particles is the sum of the attractive and repulsive energies. Deryaguin and Landau (1941) and Verwey and Overbeek (1948) independently developed this overall theory for colloidal particle interaction, known as the D.L.V.O. theory.

In Figure 2.11 are attractive ($V_A$) and repulsive ($V_R$) potential energies and the total interaction energy ($V_A + V_R$) for a typical colloidal system. An energy barrier ($V_{max}$) is
Figure 2.11 Typical interaction energy versus particle separation curve. Present due to strong electrostatic repulsion. The magnitude of this potential energy maximum relative to the thermal energy of the particles, kT, determines the stability of the system. If $V_{\text{max}} / kT >> 1$, then particles will remain at high inter-particle separation and the system is stable, or dispersed. If $V_{\text{max}} / kT \geq 1$, slow coagulation$^2$ will occur as particles overcome the energy barrier, and if $V_{\text{max}} / kT < 1$, coagulation will be rapid. Another feature of the total interaction energy curve in Figure 2.11 is the presence of a secondary minimum at relatively large inter-particle distances. If this minimum is moderately deep relative to $kT$, then weak, reversible flocculation at this separation may occur.

$^2$'Coagulation' is strictly defined as aggregation by manipulation of the surface charge of particles. In this thesis, 'flocculation' is used interchangeably to cover all forms of aggregation. Coagulation is also generally irreversible, whereas flocculation is reversible [Hughes (1990)].
2.5.2 MANIPULATION OF SURFACE CHEMISTRY

Knowledge of the surface chemistry of colloidal particles enables the preparation of suspensions having specific bulk properties. Healy (1977) and Leong (1994) provide excellent reviews of the application of colloidal surface chemistry to the processing of mineral suspensions. Pugh and Bergström (1994) detail the application to ceramic processing.

Given that the attractive van der Waals forces are essentially constant for a given particle system, the state of flocculation must be controlled by repulsive forces, namely electric double layer repulsion and steric stabilisation. For most oxide suspensions, electrostatic repulsion is proportional to the solution pH and inversely proportional to the ionic strength. Repulsion due to steric stabilisation is dependent on the thickness and surface coverage of the adsorbed polymer layer.

The effect of pH and ionic strength on the electrostatic repulsion in an aqueous colloidal suspension is illustrated in Figure 2.12 for ZrO₂ [from Leong, et al. (1993a)]. Quantifying the overall interactions between particles is the shear yield stress, \( \tau_y \). At the maximum in the shear yield stress curves (pH 7.0), the net particle surface charge is zero, hence the electrostatic repulsion is zero and the suspension is strongly flocculated due to van der Waals attractions. This point is called the iso-electric point (i.e.p.) or point of zero charge (p.z.c.). Increasing or decreasing the pH away from the i.e.p., the particles become charged and electric double layer repulsion is present, resulting in lower overall particle interaction and a lower \( \tau_y \). Particles are fully dispersed (\( \tau_y = 0 \)) at pH's far from the i.e.p.

The effect of ionic strength on the electrostatic repulsion is also clearly demonstrated in Figure 2.12. Increased ionic strength means the ion density around the particles is high, hence the surface charge is easily screened and thin electric double layers result. No effect on the overall interaction energy is seen at the i.e.p. where there is no electric double layer. Away from the i.e.p., the net force is more attractive at a given pH due to reduced electrostatic repulsion, therefore resulting in the increased \( \tau_y \).
Figure 2.12 Effect of ionic strength on the shear yield stress-pH behaviour of a ZrO$_2$ suspension [from Leong, et al. (1993a)].

The effect of steric stabilisation is demonstrated in Figure 2.13 [from Leong (1994)]. Increasing amounts of a low 2,000 molecular weight (Mw) polyacrylic acid (PAA) were added to ZrO$_2$. The ZrO$_2$ surface was coated with a steric barrier of polymer that reduced the attractive interactions. Increased surface coverage with polymer resulted in lower observed shear yield stresses. The pH of maximum $\tau_y$ or i.e.p. was also shifted to a lower pH with increasing PAA concentration; an effect explained in Leong, et al. (1993b).

The effect of both steric stabilisation and bridging flocculation on $P_y(\phi)$ is dramatically illustrated in Figure 2.14 [from Leong (1994)]. Each curve shown is at the i.e.p. for the system. For ZrO$_2$ stabilised with 2,000 Mw PAA, the $P_y(\phi)$ curve is shifted downwards or to the right, that is, the suspension is more compressible. The addition of
Figure 2.13 Effect of polyacrylic acid (2000 Mw) on the shear yield stress-pH behaviour of a ZrO₂ suspension [from Leong (1994)].

750,000 Mw PAA to ZrO₂, however, shifts the compressive yield stress curve significantly upwards or to the left. The bridging flocculation of the long chained polymer thus inhibits the consolidation of concentrated suspensions, but can be used to produce dilute suspensions with high structural strength (e.g. ceramic membranes).

2.5.3 SUMMARY

The bulk properties of colloidal suspensions may be manipulated by simple control of the surface chemistry. Modification of the suspension pH, the ionic strength or by addition of surface active polymers can have a dramatic effect on the rheology.
Suspensions of the same material can thus be prepared with very different properties. Using a particle system well characterised in terms of its surface chemistry, the consolidation behaviour of suspensions can be fully investigated.

In particular, it may be determined whether the general consolidation model is widely applicable to a range of strongly and weakly flocculated suspensions. The next problem is to manipulate the surface chemistry to optimise the extent of consolidation whilst maintaining a high consolidation rate. These issues are investigated in this thesis.
2.6 CONTINUOUS THICKENER MODEL

The modelling of a continuous thickener is a direct application of the general consolidation theory that uses two parameters to characterise a consolidating suspension; the compressive yield stress, \( P_y(\phi) \), and the hindered settling function, \( r(\phi) \).

In this section, a model for the steady state operation of a continuous thickener is outlined. Design information obtained from the model are the steady state concentration profile in the thickener and the bed height required to produce a given underflow concentration. An opportunity was presented to obtain data on a large scale continuous gravity thickener concentrating bauxite residue or red mud, the waste from alumina production. Verification of the model by comparison of the predicted concentration profile and bed height with that measured on the plant was thus possible. The application and verification of this model have never been done before and are attempted in this thesis.

2.6.1 PREVIOUS WORK

The height, \( H_0 \), required to produce a certain bottom concentration, \( \phi_b \), in a batch thickener is estimated from the total weight of the suspension which is equal to the pressure at the bottom:

\[
P_y(\phi_b) = \Delta p \ g_0 \ \phi_0 \ H_0, \tag{2.44}
\]

where \( g_0 \) is normal gravitational acceleration and \( \phi_0 \) is the initial concentration [de Guingand (1986)]. This equation underestimates the height required for a continuous thickener since the compressive forces never reach equilibrium in continuous flow. Clearly, the consolidation rate must be considered to adequately model a continuous thickener [Shin and Dick (1975); Hogg and Bunnaul (1992)]. Font (1990) proposed a thickener model based on a single batch test where the supernatant interface and the sediment interface are monitored. Adorján (1976) developed a thickener design method
based on compression and permeability measurements. Cooling (1985) and Leonhard (1993) used a finite difference technique based on compressibility and permeability measurements to predict the steady state concentration profile in a continuous thickener. Landman, White and Buscall (1988) similarly applied the general consolidation model, based on the suspension properties $P_y(\theta)$ and $r(\theta)$. The governing equations and the application of these equations are presented here.

### 2.6.2 THEORY

The general consolidation model described in Section 2.2.2 is used to begin the analysis. Several assumptions are made. Plug flow is assumed, and shear at the thickener walls is assumed negligible. The effect of rakes or mixing is also not considered. The cross-sectional area of the thickener as a function of height is a variable in the model, thus diverging, converging and cylindrical thickener shapes can be examined. Here, a thickener with vertical walls, radius $R_0$, and with a converging, conical base of vertical height $z_w$, is studied, as illustrated in Figure 2.15. The coordinate origin is set at the apex of the conical base. The positive z axis is vertically upwards³ and is rescaled as

$$ Y = z \left( \frac{\Delta \rho g \phi_u}{P_y(\phi_u)} \right), $$

(2.45)

where $\phi_u$ is the underflow concentration. The scaled cross-sectional area of the thickener can be written

$$ \alpha(Y) = \begin{cases} \left[ \frac{Y}{Y_w} \right]^2, & 0 < Y < Y_w \\ 0, & Y \geq Y_w \end{cases} $$

(2.46)

where $Y_w$ is the scaled vertical height of the conical base, $z_w$. The feed concentration, $\phi_0$, is assumed to be less than the gel concentration, $\phi_g$ (typical engineering practice). This assumption greatly simplifies the model.

³ Opposite in direction and position to that in Landman, et al. (1988).
Figure 2.15 Definition of variables for the modelling of a continuous gravity thickener for \( \phi_0 < \phi_g \).

The compressive yield stress, \( P_y(\phi) \), and hindered settling function, \( r(\phi) \), are assumed known and able to be fitted to forms such as

\[
P_y(\phi) = \begin{cases} 
0 & , \; \phi \leq \phi_g \\
A \left[ \left( \frac{\phi}{\phi_g} \right)^m - 1 \right] & , \; \phi > \phi_g
\end{cases}
\] (2.47)

and

\[
r(\phi) = (1 - \phi)^n.
\] (2.48)

where A, m and n are fitting constants.
P_y(\phi) is made dimensionless by

\[ f(\phi) = \frac{P_y(\phi)}{P_y(\phi_0)}, \quad (2.49) \]

thus eliminating the constant, A. The r(\phi) function is also made dimensionless by

\[ R(\phi) = \frac{r(\phi)}{r(\phi_0)}. \quad (2.50) \]

The characteristic size terms, \( \lambda/V_p \), in the r(\phi) functions found experimentally in Equations (2.39) and (2.43) are thus eliminated and are not required in the analysis.

From cross-sectionally averaged equations, the total particle volumetric flow rate is

\[ Q_n = \frac{\Delta \rho \ g \ \phi \ A_o \ (1 - \phi_o)^2 \lambda}{V_p \ r(\phi_0) \ (1 - \phi_o/\phi_u)}. \quad (2.51) \]

For \( \phi_0 < \phi_u \), the scaled particle flux, \( \beta \), can then be derived as

\[ \beta = \frac{1}{1 - \phi_o/\phi_u}. \quad (2.52) \]

A consequence of this simple equation is that at steady state the flow rate is not a free parameter and is dictated only by the feed and underflow concentrations of the thickener, and the hindered settling rate of the feed suspension.

The steady state behaviour in a continuous thickener is described by a first-order non-linear differential equation

\[ \frac{dY}{d\phi} = -\frac{f^*(\phi)}{\left( \frac{\phi}{\phi_u} \right) \left( 1 - \frac{\beta}{\alpha(Y) B(\phi, \phi_o, \phi_u)} \right)}, \quad (2.53) \]

where

\[ B(\phi, \phi_o, \phi_u) = \frac{\phi_o (1 - \phi_o)^2}{\phi (1 - \phi)^2} R(\phi) \left( 1 - \frac{\phi}{\phi_u} \right). \quad (2.54) \]
To obtain the concentration profile in the thickener, Equation (2.53) is integrated from the bottom of the bed, \( Y = 0 \), where \( \phi = \phi_u \), to the top, \( Y = L \), where \( \phi = \phi_g \). Concentration profiles generated from synthetic \( P_y(\phi) \) and \( r(\phi) \) data are shown in Figure 2.16 [corrected plots from Landman, et al. (1988)]. In this example, a cylindrical thickener (\( \alpha(Y) = 1 \)) was operated at different \( \phi_0 \) to produce an underflow concentration of \( \phi_u = 0.30 \). The gel concentration for the suspension was set at \( \phi_g = 0.10 \). For a given underflow concentration, \( \phi_u \), the bed height, \( L \), is thus determined.

By solving Equation (2.53) for varying \( \phi_u \), the scaled bed height \( L \) required for a given underflow concentration, \( \phi_u \), is determined. This is plotted in Figure 2.17a) for the system and conditions in Figure 2.16 [corrected plots from Landman, et al. (1988)].

Figure 2.16 Concentration profiles in a steady state cylindrical thickener produced from synthetic data (\( m = 5 \) and \( n = 4.5 \) in Equations (2.47) and (2.48)) [corrected plots from Landman, et al. (1988)].
Figure 2.17 Bed height versus underflow concentration in a steady state cylindrical thickener, from synthetic data ($m = 5$ and $n = 4.5$ in Equations (2.47) and (2.48)); a) scaled plots [corrected plots from Landman, et al. (1988)], b) unscaled plots for a typical mineral suspension.
To obtain the actual thickener bed height, $H$, Equation (2.45) is used:

$$H = \frac{L P_y(\phi_u)}{\Delta \rho g \phi_u} \quad (2.55)$$

The unscaled curves in Figure 2.17a) are plotted in Figure 2.17b) for a typical suspension system. The form of the curves are similar to that of the power law behaviour of $P_y(\phi_u)$, and the effect of $\phi_0$ is reduced.

### 2.6.3 SUMMARY

To design a continuous thickener with $\phi_0 < \phi_b$ based on the model developed by Landman, et al. (1988), the following information is required:

- the thickener shape and dimensions (vertical height of conical section $z_w$, and thickener radius $R_0$),
- the initial feed concentration, $\phi_0$,
- the desired underflow concentration, $\phi_u$,
- the compressive yield stress function, $P_y(\phi)$, and hindered settling function, $r(\phi)$, for the suspension, and
- the gel concentration of the suspension, $\phi_g$.

Using the model, the steady state concentration profile in a thickener may be calculated for given input conditions. Determination of the thickener height required to produce a certain underflow concentration is then possible. This information can be directly used in the design and optimisation of continuous thickeners.

The design of a continuous thickener is a direct application of the general consolidation theory which uses two parameters to characterise a consolidating suspension, the compressive yield stress and the hindered settling function. Verification of the theory is possible using a suspension from an operating thickener. By measurement of the
consolidation parameters of the suspension, the thickener concentration profile and bed height can be calculated and compared with that measured on the plant. Good agreement would mean that the model is valid. The sensitivity of the model to variation in the consolidation parameters can also be evaluated. The effect on thickening performance by changing suspension properties can thus be determined.

2.7 SUMMARY AND DETAILED OBJECTIVES

The theoretical background for the consolidation of suspensions has been reviewed in this chapter. Fundamental parameters, the compressive yield stress, $P_y(\phi)$, and the hindered settling function, $r(\phi)$, are required for the quantitative understanding of the consolidation process. Several techniques are available for the measurement of each of these parameters and the most appropriate techniques have been identified for this research.

Several key areas for investigation were identified:

- to verify that the compressive yield stress, $P_y(\phi)$, is correctly measured using the currently available techniques and is a suspension material parameter,

- to implement a reproducible technique for determination of the hindered settling function, $r(\phi)$,

- to investigate the applicability of the general consolidation model using suspensions with different bulk properties produced by manipulation of the surface chemistry, and

- to apply these techniques and theory to the design of continuous suspension consolidation operations, then verify the model predictions with measurements on an operating thickener.

These four points constitute the four main chapters of the thesis. First though, the experimental materials used in the investigation are detailed in the next chapter.
Chapter 3

EXPERIMENTAL MATERIALS, SAMPLE PREPARATION AND SHEAR YIELD STRESS MEASUREMENT

3.1 INTRODUCTION

In this chapter, the preliminary work performed before the commencement of consolidation experiments is outlined. The basic properties of the materials used in the thesis are described. The methods used to prepare the suspensions for consolidation experiments are detailed. The vane technique for measurement of the shear yield stress of the prepared suspensions is then described.

3.2 EXPERIMENTAL MATERIALS

The choice of particle suspension system for this research was extremely important. Initially it was hoped to use a well-characterised system of monodisperse, spherical particles. Such an ideal system would enable a fundamental investigation of consolidation effects in suspensions. Unfortunately, obtaining such particles in the quantities required for a complete study was not practical (or cost effective!). Instead,
alternative systems were used that were less than ideal but still satisfied a number of criteria.

In the following list are the desired properties of particle suspension systems for consolidation experiments:

- pure, homogenous particles,
- uniform particle shape,
- narrow particle size distribution,
- high solids density material (enhanced consolidation rates),
- rigid particles (no deformation under shear or compression),
- stable over time scale of experiments (4-6 weeks for compression measurements),
- easily controlled flocculation state, microstructure and surface chemistry.

To satisfy these criteria, three aqueous metal oxide systems were chosen; zirconia, titania and alumina. The shear rheology and colloidal surface properties of each system have been studied extensively at the University of Melbourne [Leong and coworkers (1990-1995); Liddell (1996); Scales, et al. (1997a, 1997b); Zhou, et al. (1997)]. These systems model fine particle industrial suspensions and are used as case studies to determine general characteristics of suspensions in settling and compression. Both zirconia and alumina have ceramic applications, and titania is used in the pigment industry. The properties of each particle system are now discussed.

3.2.1 ZIRCONIA, ZrO$_2$

The zirconia, or zirconium oxide (ZrO$_2$), used throughout this thesis was obtained from ICI Australia Operations Pty. Ltd. (now Hanwha Advanced Ceramics Australia Pty. Ltd.), Rockingham, Western Australia. The same grade zirconia from the same company was used in the work of Leong and coworkers (1990-1995) and thus has been well characterised over the last seven years.
A 40 kg sample of ELECTRO-FINE ULTRA 0.5 zirconia was purchased. This grade of zirconia is in the monoclinic form [the most common stable phase, Kirk Othmer (1978a)]. The final stages of the production process of this zirconia involve milling and spray drying. These operations have a significant impact on the observed surface properties of the powder. This particular sample has a slightly higher yttria content ($Y_2O_3$) than the commercial product, but the purity of the product is still over 99.9 wt% ZrO$_2$. A chemical analysis of the zirconia is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_2O_3$</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>556</td>
</tr>
<tr>
<td>CaO</td>
<td>9</td>
</tr>
<tr>
<td>$Fe_2O_3$</td>
<td>28</td>
</tr>
<tr>
<td>S</td>
<td>45</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>36</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>101</td>
</tr>
<tr>
<td>$Y_2O_3$</td>
<td>764</td>
</tr>
</tbody>
</table>

Table 3.1 Chemical analysis of the zirconia as determined by the manufacturer.

This grade of zirconia is used primarily in ceramic manufacturing, where the yttria acts to partially stabilise the zirconia and improve the strength and thermal shock resistance of the final product [Kirk Othmer (1978a)].

The particle size distribution of this zirconia, measured using a Coulter LS130 laser diffraction particle sizer, is shown in Figure 3.1. In this instrument, several drops of the sample suspension are added to 1.5 L of water which is circulated through the measurement chamber. The pH of the water was adjusted to that of the sample to prevent changes in the flocculation state of the suspension. Two methods of sample preparation are compared in Figure 3.1; sonication and high shear mixing. Each method is detailed further in Section 3.3, but little difference is observed in the resulting particle size distribution of the ZrO$_2$ suspensions prepared by either method. Taken from Figure 3.1, the pertinent particle size measurements for the ZrO$_2$ are summarised in Table 3.2.
Figure 3.1 Particle size distribution for ZrO₂ as determined using a Coulter LS130 particle sizer; comparison of suspension preparation methods - sonication and high shear mixing.

<table>
<thead>
<tr>
<th>Size range</th>
<th>Coulter LS130 Size (µm)</th>
<th>Leeds and Northrup Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁₀</td>
<td>0.12</td>
<td>0.17</td>
</tr>
<tr>
<td>d₅₀</td>
<td>0.76</td>
<td>0.47</td>
</tr>
<tr>
<td>d₉₀</td>
<td>1.55</td>
<td>1.57</td>
</tr>
</tbody>
</table>

Table 3.2 Particle size analysis of the ZrO₂ as determined using a Coulter LS130 and as supplied by the manufacturer using a Leeds and Northrup Microtrac (the d₁₀ size range means 10% of the particles by volume lie below this size, etc).
Also tabulated are the corresponding measurements supplied by the manufacturer using a Leeds and Northrup Microtrac.

Agreement between the two instruments is reasonable, although a higher mean particle size was measured by the Coulter LS130. The mean, however, is unrepresentative of the actual particle size distribution which is strongly trimodal. When presented on a number basis, the distribution is shifted almost entirely to the first mode with a mean size of 0.15 μm. Images of the ZrO₂ using a transmission electron microscope (TEM) supported this observation with numbers of very small particles less than 0.2 μm together with larger particles of order 1 μm. The TEM images showed the particles to be amorphous.

Other properties of the zirconia are summarised in Table 3.3.

<table>
<thead>
<tr>
<th>Particle surface area (by BET)</th>
<th>22.6 m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss on ignition</td>
<td>0.6 wt% at 1,100°C</td>
</tr>
</tbody>
</table>

Table 3.3 Other properties of the zirconia used in this thesis, as determined by the manufacturer.

The background electrolyte concentration of the ZrO₂ was 0.05 M KNO₃ equivalent [Leong, et al. (1995b)].

The solids density of this zirconia was measured using a Micromeritics AccuPyc 1330 helium pycnometer at the University of Illinois, Urbana-Champaign. The average density taken from 40 successive measurements was 5.72 ± 0.01 g/cm³.

The density was also measured using 25 mL density bottles. Using 2 drops of concentrated 15.8 M HNO₃ and 2-3 hours in a sonication bath to disperse the powder, a density of 5.78 ± 0.02 g/cm³ was determined from the average of three measurements. These density bottle measurements were considered to be less precise than those obtained by helium pycnometry due to difficult, reproducible dispersion of the powder.

These values compare favourably with the typical theoretical density of 5.7 g/cm³ quoted by the manufacturer for this grade of zirconia.

The value for the solids density of the zirconia used in this thesis was that determined by helium pycnometry.
3.2.2 TITANIA, TiO₂

The titania, or titanium dioxide (TiO₂), used in this thesis was an industrial grade pigment obtained from Tioxide Australia Pty. Ltd., manufactured via the Sulphate Process in Burnie, Tasmania, Australia. A single 20 kg batch was used to ensure consistency between measurements.

This titania was fully characterised in the thesis of Liddell (1996), where it was identified as the organically treated pigment P1. The particles consist of a TiO₂ core and an Al₂O₃ inorganic coating. The organic treatment of the titania with trimethylolpropane (TMP) acts to sterically stabilise the particles, thus reducing the viscosity and shear yield stress compared with untreated TiO₂.

Pertinent properties of the titania are summarised in Table 3.4.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ content</td>
<td>94.5 wt%</td>
</tr>
<tr>
<td>Particle surface area (by BET)</td>
<td>13 m²/g</td>
</tr>
<tr>
<td>Solids density</td>
<td>4.05 g/cm³</td>
</tr>
</tbody>
</table>

Table 3.4 Properties of the titania used in this thesis [from Liddell (1996)].

The particle size distribution by volume of the TiO₂ powder, measured using a Coulter LS130 laser diffraction particle sizer, is shown in Figure 3.2. The pertinent size fractions in the distribution are given in Table 3.5.

3.2.3 ALUMINA, Al₂O₃

The alumina, or aluminium oxide (Al₂O₃), used in this thesis was an AKP-30 grade alumina obtained from Sumitomo Chemical Co. Ltd., Japan. A single 20 kg batch was used to ensure consistency between measurements.

The solids density, measured with 25 mL density bottles and the procedure used for ZrO₂, was 3.94 ± 0.02 g/cm³. The density quoted by Kirk-Othmer (1978b) for this form
Figure 3.2 Particle size distribution for TiO₂ as determined using a Coulter LS130 particle sizer; suspension prepared by sonication, pH 3.5 (dispersed).

<table>
<thead>
<tr>
<th>Size range</th>
<th>Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁₀</td>
<td>0.17</td>
</tr>
<tr>
<td>d₅₀</td>
<td>0.44</td>
</tr>
<tr>
<td>d₉₀</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 3.5 Particle size distribution by volume for TiO₂ as determined using a Coulter LS130.
of $\text{Al}_2\text{O}_3$, is 3.98 g/cm$^3$, and Perry and Green (1994) quote a value of 3.99 g/cm$^3$. The value used for the solids density in this thesis was 3.98 g/cm$^3$.

The particle size distribution by volume of the $\text{Al}_2\text{O}_3$ powder, measured using a Coulter LS130 laser diffraction particle sizer, is shown in Figure 3.3. The pertinent size fractions in the distribution are given in Table 3.6.

The particle size distribution for $\text{Al}_2\text{O}_3$ is thus much narrower than either the $\text{ZrO}_2$ or $\text{TiO}_2$.

3.3 SAMPLE PREPARATION

The preparation of all three metal oxide particle systems was carefully controlled to obtain good, reproducible suspensions. The following procedure, based on that of Leong, et al. (1993a) for the preparation of zirconia suspensions, was used. Differences in this procedure for the preparation of zirconia, titania and alumina are noted.

1. A stock solution was prepared from milli-Q filtered distilled water to which 0.01 M of salt was dissolved. This salt level was chosen to broaden the pH range at which the particles are strongly flocculated, but still allow the particles to be fully dispersed at a reasonable pH. The effect of salt on the flocculation of $\text{ZrO}_2$ suspensions has been fully examined by Leong, et al. (1993a); see Figure 2.12 for details. The effect of salt on $\text{TiO}_2$ and $\text{Al}_2\text{O}_3$ has similarly been studied by Liddell (1996) and Scales, et al. (1997a) respectively. For $\text{ZrO}_2$, the salt used here was $\text{KNO}_3$, for $\text{Al}_2\text{O}_3$, $\text{NaCl}$ was used and for $\text{TiO}_2$ no salt was used since the pH - flocculation state curve for this system was suitable without any salt modification.

2. Polymeric additives, if required, were then added from a concentrated polymer solution to the appropriate amount of stock solution prepared in Step 1. The amount added was based on the dry weight of powder used (dwb%).

3. Samples were prepared at a pH at which the suspension would be fully dispersed. The suspensions were dispersed at either a pH well above or a pH well below the iso-
Figure 3.3 Particle size distribution for Al₂O₃ as determined using a Coulter LS130 particle sizer; suspension prepared by sonication, pH 4.0 (dispersed).

<table>
<thead>
<tr>
<th>Size range</th>
<th>Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁₀</td>
<td>0.13</td>
</tr>
<tr>
<td>d₅₀</td>
<td>0.38</td>
</tr>
<tr>
<td>d₉₀</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 3.6 Particle size distribution by volume for Al₂O₃ as determined using a Coulter LS130.
electric point (i.e.p.) depending on the value of the i.e.p. The pH of the stock solution was adjusted to that of the dispersed state using either concentrated HNO₃ or HCl for low pH or concentrated KOH for high pH. The pH was measured using an Orion Research, model 701A, digital pH meter with an Activon pH probe.

4. The quantity of powder for the required solids concentration was added to the solution from Step 3.

5. Two methods for dispersal of the powder were used;

   a) small samples (< 100 mL) were sonicated for 2 min using an ultrasonic horn (Branson Sonifier 450, 20 kHz, 0.75" (19.05 mm) diameter horn, operated at 30-40% of the maximum power output of 450 W),

   b) large samples (up to 400 mL) were mixed using a high shear mixer for 5 min (Janke and Kunkel, Ultra-Turrax operated at 10,000 rpm).

   Both these methods of dispersion were found to produce reproducible suspensions.

6. After allowing to cool, the samples were adjusted to their correct pH using 1-5 M KOH or HNO₃ for ZrO₂ and TiO₂, and NaOH or HCl for Al₂O₃.

7. The samples were then rested for at least 24 hours.

The solids concentration for each sample was measured by mass loss on drying of a small sub-sample (1-5 g). The sub-samples were dried in an oven at 120-140°C for at least 24 h and then cooled in a desiccator before weighing.

3.4 SHEAR YIELD STRESS MEASUREMENT

3.4.1 DEFINITION AND VANE TECHNIQUE

The shear yield stress, \( \tau_y \), of particulate suspensions is an extremely important rheological parameter. \( \tau_y \) is the minimum applied shear stress required for a material to flow. Its magnitude is related to the strength of inter-particle interactions and the
suspension microstructure. It determines, for example, the pumping energy required to start-up a suspension pipeline [Darby (1988)], and the angle of repose of a slumping suspension [Robinsky (1975)]. It also hinders particle settling, which can be a problem in pipelines. The shear yield stress is of great engineering importance [Nguyen and Boger (1992)], although there is some controversy over the existence of the shear yield stress at very low shear rates [Barnes and Walters (1985)].

In compression thickening, the $\tau_y$ of the underflow must be low enough to pump the suspension to the disposal area and to flow away from the discharge point. This fixes the maximum allowable compression in the thickener. In ceramic casting, the suspension $\tau_y$ must be low enough for it to flow into all corners of the mould. When the mould is removed before firing the $\tau_y$ must be sufficiently high for it to retain its shape.

The shear yield stress, $\tau_y$, was measured for all samples prior to any consolidation measurements. Shear yield stress as a function of solids concentration and pH was also measured for various samples. A relationship between the shear and compressive yield stresses was sought from these measurements.

The shear yield stress was measured using the vane technique as developed by Nguyen and Boger (1983, 1985a). In the vane technique, a four bladed vane connected to a spring is inserted into the sample, the spring is slowly tightened and the maximum torque is measured, $T_{\text{max}}$. The shear yield stress is then calculated based on the assumption of a cylindrical yielding surface defined by the geometry of the vane. For a vane of height $H_v$, diameter $D_v$, as illustrated in Figure 3.4a), the shear yield stress is related to $T_{\text{max}}$ by

$$\tau_y = \frac{T_{\text{max}}}{\frac{\pi D_v^3}{2} \left(\frac{H_v + 1}{D_v} + \frac{1}{3}\right)}$$  \hspace{1cm} (3.1)

from Nguyen and Boger (1983).

---

1 Alternatively, if the suspension is highly thixotropic, the high $\tau_y$ underflow can be broken down by a high shear pump. Higher underflow concentrations can thus be attained.
Figure 3.4 Schematic of vane technique for measurement of the shear yield stress of suspensions; a) dimensions of vane, b) experimental configuration using a Haake RV3 Rheometer.

3.4.2 EXPERIMENTAL APPARATUS AND METHOD

A Haake RV3 viscometer was used to measure the shear yield stress using the vane technique. This instrument, illustrated in Figure 3.4b), consists of a variable speed motor connected to a torsion head, which is connected to a vane immersed in the sample. On a console, the motor speed is controlled and the torque exerted on the vane is displayed. The torque data can be logged by a computer if required. Several torsion heads of varying spring constants and a range of vanes of differing dimensions were available to measure suspensions over a wide range in shear yield stress ($1 - 10^4$ Pa).

There is an optimum rotational speed for the application of torque to the vane [Nguyen and Boger (1983)]. Too fast and the true $\tau_y$ will be overshot. Too slow and creeping of the suspension structure will occur and the true $\tau_y$ will never be reached. Liddell (1996) also investigated this effect in a comprehensive study of the yielding process. From this study, a rotational speed of 0.2 rpm was used throughout this work. With this speed, the maximum torque was usually attained within one or two minutes.

Before all shear yield stress measurements, the sample was stirred vigorously to homogenise the suspension, then tapped on the bench to remove any air bubbles entrained in sample. The torque scale zero was checked for each measurement.

Typical errors for $\tau_y$ measurements using the vane technique were of the order of $\pm 5$-10\%, in agreement with other researchers.
Chapter 4

COMPRESSIVE YIELD STRESS MEASUREMENT

4.1 INTRODUCTION

The objective of this chapter is to examine various techniques for the determination of the compressive yield stress for suspensions. Three experimental techniques are fully evaluated. Two are based on centrifugal settling to an equilibrium state and one is based on pressure filtration to equilibrium. The conversion of the raw data to generate $P_y(\phi)$ for each of these techniques is analysed. The techniques are then compared in terms of experimental difficulty and in terms of the accuracy of the resulting $P_y(\phi)$ data.

4.2 MULTIPLE SPEED EQUILIBRIUM SEDIMENT HEIGHT TECHNIQUE

The theory for the multiple speed equilibrium sediment height technique is outlined in Chapter 2, Section 2.3.2. The implementation of this theory is now discussed.
4.2.1 EXPERIMENTAL EQUIPMENT

Two centrifuges were used for the bulk of the work; a Sigma 3K-10 (12 tube capacity, radius \( R = 149.6 \) mm, speed range 200-4,800 rpm) and a Jouan CT 4.22 (28 tube capacity, radius \( R = 167.6 \) mm, speed range 300-3,600 rpm). Both centrifuges were temperature controlled; the operation temperature was set at 20°C in all tests. To extend the range of the \( P_f(\phi) \) data, a custom built low speed centrifuge based on a rotating vertical bicycle wheel (3 tube capacity, radius \( R = 397.6 \) mm, speed range 70-400 rpm) and a high speed Beckman J2-2M/E centrifuge (6 tube capacity, radius \( R = 126.5 \) mm, speed range 550-13,000 rpm) were used, both at the Chemical Engineering Department of the University of Illinois, Urbana-Champaign, Illinois, USA.

Flat bottomed, cylindrical centrifuge tubes are necessary for this technique to ensure a constant radial stress distribution in the sample. To measure the sediment height, the tubes must also be transparent. For low speed work (less than 1,800 rpm), standard glass sample vials (100.0 mm high, 22.5 mm inside diameter) were used. For higher operational speeds, round bottomed, polycarbonate centrifuge tubes (Nalgene, 103.0 mm high, 26.5 mm inside diameter) were used. To form a flat bottom in these tubes, a small quantity of epoxy resin was put in the tubes with a syringe and allowed to set in an upright position. Similarly treated tubes of various diameters were used for the centrifuge tube diameter study.

4.2.2 EXPERIMENTAL PROCEDURE

The following is the experimental procedure used to obtain the raw \((g, H_{eq})\) data for the multiple speed equilibrium sediment height technique:

1. Weigh mass of empty centrifuge tube + lid, \( M_c \).
2. Measure tube height, \( H_t \), and height of tube base, \( H_b \).
3. Determine initial solids concentration of the suspension, $\phi_0$, by measuring the mass loss on drying of a small sub-sample.

4. Fill centrifuge tube with suspension to 90-95% of the tube capacity.

5. Measure initial suspension height, $H_0$.

6. Weigh filled centrifuge tube + sample + lid, $M_s$.

7. Centrifuge sample at a constant speed, $S$, centrifugal acceleration, $g$.

8. Measure height of the interface between the sediment and the supernatant by taking an average of the highest and lowest parts of the interface.

9. Repeat step 8 until the interface height has reached an equilibrium value, $H_{eq}$, over a 24 hour period.

10. Increase speed of centrifuge to a new value and repeat steps 8 and 9.

11. Repeat until 5-7 equilibrium heights are obtained for different speeds. The spacing between the speeds should be exponentially distributed.

The maximum centrifuge speed should produce a final equilibrium height roughly a third to a half of the initial height. A moderate degree of compression is thus achieved and errors in measurement of $H_{eq}$ are minimised.

The time required to reach equilibrium depended on the suspension and on the centrifuge speed. At low speeds, over a week was usually necessary; at higher speeds, equilibrium could usually be attained in several days. A complete centrifuge experiment thus typically required 3 to 5 weeks to complete.

An example of $(g, H_{eq})$ raw data obtained from a centrifuge run is shown in Figure 4.1. Also shown are curve fits to the data and the corresponding slopes, $dH_{eq}/dg$, used in the determination of $P_y(\phi)$. The $H_{eq}$ versus $g$ curve is exponentially decreasing with $g$ and is approximately linear on logarithmic coordinates.
Figure 4.1 Typical $(g, H_{eq})$ raw data and slope, $dH_{eq}/dg$, from the multiple speed equilibrium sediment height technique ($ZrO_2$, pH 5.7, $\phi_0 = 0.151$); a) normal coordinates, b) logarithmic coordinates.
To convert these \((g, H_{eq})\) raw data to a \(P_y(\phi)\) curve, two alternatives are available; an approximate solution, and a full iterative numerical solution. Each solution method is now discussed and evaluated in turn.

### 4.2.3 APPROXIMATE SOLUTION FOR \(P_y(\phi)\)

The approximate solution is based on Equations (2.23) and (2.24), as derived in Chapter 2, Section 2.3.2.2. \(P(0)\) is thus calculated directly for each measured \((g, H_{eq})\) point. To calculate \(\phi(0)\), the derivative, \(dH_{eq}/dg\), is required at each point. This derivative is determined from a curve fit of the \((g, H_{eq})\) data. The accuracy of the resulting \(P_y(\phi)\) curve is thus directly dependent on the goodness of fit of the raw data. In Figure 4.2, the corresponding \(P_y(\phi)\) function for the data in Figure 4.1 is shown.

The effects of random measurement errors on the approximate solution for \(P_y(\phi)\) are calculated in Appendix C. Typical errors are shown as error bars in Figure 4.2. Here, the error in \(\phi\) varied from 2.0-2.9% while the error in \(P_y\) varied from 1.8-1.7%. Note that the error bars in \(P_y\) are smaller than the size of the data symbols. The \(\phi\) error is significant for large \(\phi\) and acts to shift the \(P_y(\phi)\) curve either to the left or to the right. The effect on the approximate solution of curve fitting the \((g, H_{eq})\) data is discussed with the iterative solution in the next section.

### 4.2.4 ITERATIVE SOLUTION FOR \(P_y(\phi)\)

The algorithm for the numerical iterative solution for \(P_y(\phi)\) is outlined below. Implementation of this algorithm was done in Microsoft FORTRAN.
Figure 4.2 Typical $P_y(\phi)$ data determined using the approximate solution for the multiple speed equilibrium sediment height technique; $(g, H_{eq})$ data from Figure 4.1 (ZrO$_2$, pH 5.7, $\phi_0 = 0.151$).

**INPUT**

$\Delta \rho$, $R$, $\phi_0$, $H_0$, $(g, H_{eq})$, $N$

where $N$ = number of fitted data points for the $(g, H_{eq})$ data.

**OUTPUT**

$P_y(\phi)$

*Step 1.* Curve fit $(g, H_{eq})$ raw data.

*Step 2.* Create a new smoothed data set of $N$ points based on the curve fit and evaluate $dH_{eq}/dg$ at each point.

*Step 3.* Using the approximate solution, make an initial guess for $P_y(\phi)$.
Step 4. For i = 1, N do Steps 5-8 for each g_i.

Step 5. Set ε* = 0.

Set Δ* = 0.

Step 6. Starting at z = 0 where φ(z) = φ(0) and P(z) = P(0) from the previous iteration, solve

$$\frac{dP}{dz}, \frac{dε^*}{dz}, \frac{dΔ^*}{dz} \text{ (and } \frac{dM}{dz})$$

from z = 0 to z = z_c, numerically using a Runge-Kutta technique on Equations (2.11), (2.14), (2.15) and (4.1).

Step 7. For the interval, z_c < z < H_{eq}, sum the additional terms to determine ε and Δ using Equations (2.18) and (2.19).

Step 8. Calculate φ(0) and P(0) from Equations (2.12) and (2.13).

Step 9. Check convergence of P_y(φ) solution with previous iteration. Iterate Steps 4-8 until the convergence criterion is met.

Step 10. Output P_y(φ) results.

Several points can be made regarding this algorithm. First, to start the iterative solution, the initial guess for the P(0) versus φ(0) curve does not have to be the approximate solution. Alternatively, upper or lower bounds for P(0) and φ(0) could be used - it was found that the convergence rate was not affected.

During the numerical solution of the set of differential equations, a mass conservation check was also performed by simultaneously integrating the differential equation,

$$\frac{dM}{dz} = φ,$$

(4.1)

where M is the cumulative concentration of solids in the centrifuge tube.
Convergence of the solution was achieved by checking that the difference between the sum of all Δ's in successive iterations was smaller than a specified tolerance. Other convergence criterion may also be used. Excellent convergence was usually attained within three iterations.

A critical part of the algorithm is the accurate determination of the unknown $z_c$ at which point the solution of the differential equations is halted. There are a number of techniques by which $z_c$ is estimated. The first involves the examination of the pressure function in the constant concentration region, $z_c < z < H_{eq}$, given by Equation (2.17). This is a quadratic function in $z$ and is a more slowly decreasing function of $z$ than the $P(z)$ function obtained from the numerical integration in the region $0 < z < z_c$.

Illustrated in Figure 4.3, $z_c$ is determined by finding the point of intersection between

![Figure 4.3](image_url)  

**Figure 4.3** Schematic of stopping criteria used in the iterative solution for the multiple speed equilibrium sediment height technique (scaled units).
these two curves. In theory, at the point of intersection, the two intersecting curves should possess the same slope thus giving a smooth, continuous pressure distribution. In practice, however, this is difficult to achieve numerically and a certain tolerance is allowed.

The second stopping criterion that is used to determine \( z_c \) is to look for the point where \( \phi \leq \phi_0 \) since at this point, \( \phi(z_c) = \phi_0 \). For typical functions of \( P(z) \), \( \phi \) drops off steeply near \( z = z_c \), especially for high \( g \) values. This is demonstrated in later figures when concentration profiles for synthetic data are examined. The error in the calculated value of \( z_c \) is thus not significant if this criterion is not exactly met.

Other less accurate stopping criteria may also be used, especially in early iterations when the initial guess may be some way from the final solution. In order of decreasing accuracy, these check when \( z \geq H_{eq} \) or \( P(z) \leq 0 \), as illustrated in Figure 4.3.

In the algorithm, the concentration profile, \( \phi(z) \), at each \( g \) is determined for the solution of \( dP/dz \) in Equation (2.11). Extrapolation of the \( P_y(\phi) \) curve to \( P_y(\phi_g) = 0 \) is thus necessary to determine the concentrations at the top of the sediment that are less than the first value of the calculated \( P_y(\phi) \). Three extrapolation techniques were used, as illustrated in Figure 4.4:

i) a polynomial was fitted to the known \( P_y(\phi) \) data and extrapolated back to \( P_y = 0 \), or

ii) the tangent at the first \( P_y(\phi) \) point was used to linearly extrapolate back to \( P_y = 0 \), or

iii) a value for \( \phi_g \) was input and used to linearly interpolate to the first \( P_y(\phi) \) point.

Each technique was evaluated on several data sets using various curve fitting methods. The resulting \( P_y(\phi) \) curves were relatively insensitive to the extrapolation technique although the polynomial extrapolation proved to be the most stable. The use of either logarithmically distributed data or very small increments between the smoothed \((g, H_{eq})\) data generated more realistic \( P_y(\phi) \) curves at the low end.

Where ever possible, however, the \((g, H_{eq})\) raw data was extrapolated back to \((g_0, H_0)\), where \( g_c \) is the minimum critical gravitational acceleration required for consolidation to begin [Buscall (1990)]. The extra \((g, H_{eq})\) data generated \( P_y(\phi) \) data right down to
Figure 4.4 Schematic of techniques for extrapolation of $P_y(\phi)$ data to $P_y(\phi_g) = 0$.

$P_y(\phi_g) = 0$ and proved to be more stable and more realistic than extrapolating the $P_y(\phi)$ data.

4.2.5 EVALUATION OF APPROXIMATE AND ITERATIVE SOLUTIONS

To test the algorithms, synthetic $(g, H_{eq})$ data were generated from known $P_y(\phi)$ functions. The synthetic data were entered in the algorithms, then the generated $P_y(\phi)$ data were compared with the original exact solution. Two types of $P_y(\phi)$ function were used:

a) a power law of the form

$$P_y(\phi) = A \left[ (\phi / \phi_g)^n - 1 \right],$$

(4.2)
b) an exponential of the form

\[ P_y(\phi) = A [e^{m\phi} - e^{m\phi_0}], \]  \hspace{1cm} (4.3)

where A and m are constants. The precise forms of the functions used for various values of m are shown in Figure 4.5. These curves represent a wide range in the compression behaviour of suspensions, although the power law curve of order 8 is the most realistic, being based on experimental data. The suspension characteristics used for all the curves were based on experimental results. The values used were \(\phi_0 = 0.194\), \(H_0 = 88.5 \text{ mm}\), \(\Delta\rho = 1,210 \text{ kg/m}^3\) and \(R = 155.8 \text{ mm}\). From these \(P_y(\phi)\) functions, synthetic (\(g, H_{\text{eq}}\)) data sets were generated by solving the main differential equation.

Figure 4.5 Synthetic compressive yield stress functions used for validation of the multiple speed equilibrium sediment height technique. Shown are the exponents for power law and exponential functions.
Equation (2.11), using $P = P_y(\phi)$ in the compression region, and with appropriate boundary conditions. See Appendix D for details on the generation of these synthetic data sets. An example of the form of the synthetic data generated from an 8\textsuperscript{th} order power law function is given in Figure 4.6. The synthetic $(g, H_{eq})$ were now entered in the algorithm and the generated $P_y(\phi)$ data were compared with the original exact solution to determine the algorithm’s performance.

To model real experimental data, only a limited number (7) of these generated $(g, H_{eq})$ points were used. The number and spacing of the points chosen were typical of those obtained experimentally. The spacing of the points was roughly logarithmic with $g$ since the change in $H_{eq}$ at low $g$ is greater. The points used from the 8\textsuperscript{th} order power law function are shown in Figure 4.6.

**Figure 4.6** Typical synthetic raw data generated from an 8\textsuperscript{th} order power law function for $P_y(\phi)$.
One of the dominant factors determining the accuracy of the solution is the type of curve fitting used on the raw $H_{eq}$ versus $g$ data. Curve fitting is necessary because, as noted, typically only a small number of data points are measured. The curve fit is critical since it is used to determine the derivative $dH_{eq}/dg$ at each point and the accuracy of the derivative is strongly dependent on the goodness of the curve fit. The derivative is used in the equations for calculating $\varepsilon$ and $\phi(0)$. The curve fit used therefore affects both the approximate solution and the iterative solution to a similar degree by shifting the $P_y(\phi)$ curve either to the left or to the right. The type of curve fit, however, has no effect on the calculated $P(0)$.

Several different curve fitting techniques were evaluated. These included polynomial fits of order 1 through 5 and a generalised cross validation technique [Craven and Wahba (1979)] that optimises the fit between a spline and a polynomial of any order. Both these techniques were tried using normal and logarithmic coordinates. The results for several of the better curve fits are compared against the exact solution in Figure 4.7 and Figure 4.8. In general, the best solutions were found to be for second or third order polynomials, fitted on logarithmic coordinates. The equations for these curve fits are of the general form

$$\log_{10} H_{eq} = a_1 + a_2 \log_{10} g + a_3 (\log_{10} g)^2 + a_4 (\log_{10} g)^3 + \ldots$$

(4.4)

where $a_1$, $a_2$, $a_3$ etc. are constants. The use of higher order fits or of substantial splining were found to make the $P_y(\phi)$ curve oscillate about the true solution and thus should not be used, although they are useful in some circumstances when other curve fitting fails. The fitted curve must be as smooth as possible and must be a monotonically decreasing function with increasing $g$. In all cases, it is essential that the curve fitting results are viewed visually to determine whether they are satisfactory.

The accuracy of the iterative solution for all the data tested was generally very good. In Figure 4.7 are the percentage differences between the iterative solution and the exact solution for the parameters, $P_y$ and $\phi$, for second and third order logarithmic curve fits of an 8th order power law function. The solution tended to deviate from the exact solution at both high and low $g$ (or $\phi$) in each case, but the average of the different curve fits used
Figure 4.7 Comparison of the exact solution (8th order power law) with that generated from the iterative solution; a) 2nd and 3rd order fits, b) and c) the % difference from the exact curve for $P_y$ and $\phi$ respectively (also shown are the mean differences and the 99% confidence intervals).
Figure 4.8 Comparison of the exact solution (8th order power law) with that generated from the approximate solution; a) 2nd and 3rd order fits, b) and c) the % difference from the exact curve for $P_y$ and $\phi$ respectively (also shown are the mean differences and the 99% confidence intervals).
was very close to the predicted curve. The error at the low end is due to extrapolation. The average error for $\phi$ was less than 0.5%, while the average error for $P_y$ was about 5%; this error being amplified by the error in $\phi$ due the power law nature of the curve. The error for the other curves tested was similar to that shown for this example. For a fuller analysis of the raw data, several of the best curve fits should thus be used and the results averaged to determine the best $P_y(\phi)$ curve.

The approximate solution was then compared with that determined by iteration. For all types of curve fitting, the approximate solution always underestimated the concentration, $\phi(0)$, shifting the curve from the true solution to lower $\phi$. The largest shift always occurred for higher values of $g$ (that is, large $\phi$), with the approximate curve lying closer to the iterative curve at lower $\phi$. In Figure 4.8, the corresponding approximate solution for the same $(g, H_{eq})$ data used in Figure 4.7 is shown. Here, the difference between the approximate solution and the exact solution for various curve fits in terms of $\phi$ was less than 1.0%, about twice the error associated with the iterative solution. The error in $P_y$ as a result ranged from 5-10%. In general, the iterative solution is thus more accurate than the approximate solution, as expected.

To simulate the effect of experimental error, random noise was added to the $H_{eq}$ versus $g$ test data. Noise levels from 1 to 10% were applied to the $H_{eq}$ data. The $g$ data was assumed to contain no error. Typical values for the percentage error of $H_{eq}$ for mineral suspensions studied in this thesis were less than 2%. In Figure 4.9 are results for the iterative solution on data containing 2% noise (data generated from the 8th order power law). Even though the variation from the exact values is now larger, again especially for high $g$ values, the average of the iterative solutions for various sets of ‘noisy’ input data is close to the exact value. To minimise this sort of random error, several centrifuge tubes of the same sample should be run simultaneously and the resulting $P_y(\phi)$ curves averaged.

The error due to experimental error or noise is now compared with the error associated with using the iterative and the approximate solution. This is crucial since it determines whether or not it is worthwhile to use the full iterative solution. Comparing Figure 4.7, Figure 4.8 and Figure 4.9, the variation in the $P_y(\phi)$ curves due to the noise is greater
Figure 4.9 Examples of the effect of 2% noise in $H_{eq}$ data on the iterative solution compared with the exact solution ($8^{th}$ order power law).

than that associated with both methods of solution. Therefore, if multiple runs cannot be made to minimise this random noise, the approximate solution may as well be used. The iterative solution, however, is still more accurate and if available will always give a more reliable result. The approximate solution, though, is perfectly suited to establish general trends in any particular system if absolutely correct values are not essential.

Besides errors in the measurement of $H_{eq}$, other errors also affect the accuracy of the compressive yield stress curve. Errors in the measurement of the initial concentration $\phi_0$ and the initial height $H_0$ are directly translated to the error in both $\phi(0)$ and $P(0)$. The error in the density difference $\Delta \rho$ is also directly translated to the error in $P(0)$. The effect of the error in the centrifuge radius $R$ is more complicated and affects both $\phi(0)$
and \( P(0) \) but should be relatively small in most cases since this can be measured accurately. However, at low speeds, when the carriers holding the centrifuge tubes are not horizontal, an angled sediment interface is formed. This is accounted for by taking an average sediment height across the tube. Sometimes it is not possible to use flat bottomed tubes if high speeds and/or high concentrations are required; instead round bottomed tubes are used for strength considerations. The consolidation in the lower region of the tube is therefore non-linear. An average centrifuge radius must then be used to account for this curvature which will have a larger associated error. All of these errors mentioned here must be considered when the results generated using the iterative technique are evaluated. These error sources will also affect the results generated from the approximate solution in exactly the same way.

The equilibrium concentration and pressure profiles in the suspension, \( \phi(z) \) and \( P(z) \), for each \( g \) point, are calculated as part of the iterative algorithm. These profiles may be compared with those predicted by the exact solution. The theoretical profiles are generated in the production of the synthetic \( H_{eq} \) versus \( g \) data. Figure 4.10 shows a selected set of these concentration profiles for the 8\(^{th}\) order power law synthetic data set overlaid on those produced by the algorithm. Agreement is generally very good which further validates the results. It can be seen from this plot that the concentration drops off steeply as \( z \to z_c \) at medium to high \( g \).

The calculated critical height, \( z_c \), the interface between the constant concentration region and the collapsing region, may also be compared with the theoretical \( z_c \) at each \( g \). In Figure 4.11, \( z_c \) is shown for the 8\(^{th}\) order power law function. Also shown is the corresponding \( H_{eq} \) curve. The difference between the theoretical and the calculated \( z_c \) curves is not shown since agreement is again excellent.

### 4.2.6 SUMMARY

An accepted engineering technique for the determination of the \( P_y(\phi) \) function is to use the multiple speed equilibrium sediment height technique in a centrifuge. Conversion of
Figure 4.10 Comparison of theoretical and calculated concentration profiles (8th order power law) for a selected number of $g_2$ values: 1) 76 m/s², 2) 520 m/s², 3) 1,076 m/s², 4) 2,187 m/s², 5) 3,298 m/s², 6) 4,964 m/s², 7) 5,520 m/s².

The raw data from this experiment to generate the $P_y(\phi)$ data, however, is not a trivial exercise. The new iterative solution and the approximate solution (each detailed in Chapter 2, Section 2.3.2) were evaluated using synthetically generated data. From this study, a number of main conclusions are made:

- It can now be said with confidence that the multiple speed equilibrium sediment height technique is valid for the determination of the compressive yield stress.

- In general, the iterative solution is more accurate than the approximate solution which tends to underestimate $\phi$ (up to approximately 2%).
Data generated from: \( P_y = 100[(\phi/0.18)^8 - 1] \)

\[ z / H_0 \]

\[ g \ (m/s^2) \]

**Figure 4.11** Typical behaviour of \( H_{eq} \) and \( z_c \) with \( g \) (generated from a synthetic \( P_y(\phi) \) function - 8th order power law).

- In most cases, satisfactory results can be obtained using the approximate solution, especially if only one set of raw data are available.

- Although the approximate solution has been used before, it is the first time that there has been justification for it and that its shortfalls have been quantified.

- The success of both the iterative and the approximate solutions relies heavily on the curve fitting method used on the raw data. For a fuller analysis, a number of curve fits to the \((g, H_{eq})\) raw data should be utilised and the resulting \( P_y(\phi) \) functions averaged.
4.3 CONCENTRATION PROFILE TECHNIQUE

The compressive yield stress function can be determined from the concentration profile of a suspension consolidated in a centrifuge that has reached equilibrium. This technique is an alternative to the multiple speed equilibrium sediment height technique for finding $P_y(\phi)$. The determination of $P_y(\phi)$ from the concentration profile is relatively straightforward; the theory was outlined in Chapter 2, Section 2.3.3. The implementation of this theory is now discussed.

4.3.1 SECTIONING MEASUREMENT OF CONCENTRATION PROFILE

The experimental technique described below was used to determine the concentration profiles of consolidated suspensions in this thesis. Other non-destructive measurement techniques used by other workers have been reviewed in Chapter 2.

*PART 1 - CONSOLIDATION OF SAMPLE*

1. Consolidate a suspension sample at a single centrifuge speed following Steps 1 to 9 in Section 4.2.2 for the multiple speed equilibrium sediment height technique.

2. Pour off supernatant (check pH of supernatant first if desired) and weigh tube + sample - supernatant + lid, $M_{ns}$. [Mass measurements, $M_c$, $M_s$ and $M_{ns}$ are used to check mass conservation].

*PART 2 - SECTIONING OF SAMPLE*

3. For section i, set sectioning depth of spatula, $(H_d)_i$, using small metal ruler and tighten locking nut on clamp to fix depth (see Figure 4.12).
Figure 4.12 Sectioning measurement technique to determine the concentration profile of a sediment in a centrifuge tube; a) set sectioning depth of spatula, b) scrape off layer of sediment, c) transfer sediment layer to weighing tin.
4. Weigh mass of weighing tin, \( (M_d)_i \).

5. Insert spatula inside centrifuge tube and rotate to scrape off the prescribed layer of sediment and transfer sample to weighing tin.

6. Weigh initial mass of weighing tin + sample, \( (M_i)_i \).

7. Repeat steps 3 to 6, increasing the sectioning depth each time. Sections are initially 0.5 mm thick at the top of the sediment; the region of greatest concentration change. Larger sections of up to 4.0 mm are taken towards the bottom of the centrifuge tube where further concentration change is small. From 15 to 30 sections for each sediment can be taken.

8. Dry weighing tins in an oven set at 120-130°C for at least 24 hours.

9. Remove tins from oven and allow to cool in a desiccator.

10. Weigh final mass of each weighing tin + sample, \( (M_f)_i \).

**PART 3 - CALCULATION OF CONCENTRATION PROFILE**

First, determine the rotational speed, \( \omega \),

\[
\omega = S \frac{2 \pi}{60}, \quad (4.5)
\]

where \( S \) is the centrifuge speed in revolutions per minute (rpm).

For each section, \( i \); calculate the actual height of the bottom of the section from the base of the bed, \( H_i \),

\[
H_i = H - H_b - \left( (H_d) \right)_i, \quad (4.6)
\]

the average height, \( \left( (H_{avg})_i \right) \),

\[
\left( (H_{avg})_i \right) = \frac{H_i + H_{i-1}}{2}, \quad (4.7)
\]
the average mass concentration, \( (\phi_m)_i \),

\[
(\phi_m)_i = \frac{(M_i)_i - (M_i)_f}{(M_i)_i - (M_i)_f},
\]

and hence the average volume concentration, \( \phi_i \),

\[
\phi_i = \frac{(\phi_m)_i \rho_f}{\rho_s - (\phi_m)_i (\rho_s - \rho_f)}.
\]

Thus, plot the concentration profile of the suspension; \( \phi_i \) versus \( (H_{avg})_i \).

A typical concentration profile measured from a consolidated ZrO\(_2\) suspension is shown in Figure 4.13a). Errors in \( \phi \) and \( z \) are determined by standard error analysis (see Appendix E for details). Here, the calculated error bars are \( \pm 0.3 \) mm for \( z \) and \( \pm 0.0005-0.002 \) for \( \phi \), which are smaller than the symbols on the plot. The precision and accuracy of the measured concentration profile are thus excellent.

### 4.3.2 DETERMINATION OF \( P_y(\phi) \) FROM CONCENTRATION PROFILE

The compressive yield stress curve, \( P_y(\phi) \), can be calculated from the raw concentration profile data by two methods, each described in detail in Appendix E. In the first method, \( P_y(\phi) \) is calculated directly from the raw concentration profile data by integrating Equation (2.27) discretely at each \((z, \phi)\) point using a trapezoidal rule;

\[
P_y(z) = \Delta \rho \omega \int_0^z x \phi(x) \, dx.
\]

In the second method, the concentration profile is fitted to a standard equation such as

\[
\phi(s) = a + b \log_{10}(s + d) + c (\log_{10}(s + d))^2,
\]

(4.10)
Figure 4.13 a) Example of the concentration profile of a consolidated suspension measured by sectioning - error bars are smaller than the symbols (ZrO₂, pH 5.4, φ₀ = 0.178); b) corresponding Pᵧ(φ) determined from data in a) using two solution methods.
where a, b, c and d are constants and s is the distance from the top of the bed. The curve fit for \( \phi(s) \) is substituted in a transformed Equation (2.27) that is then solved numerically. Care must be taken when integrating since the origin of the x-coordinate is the centre of the centrifuge.

In both methods, it is assumed that the measured concentration, \( \phi \), the average volume fraction of the interval, is equal to the concentration at the midpoint of the interval. This assumption is also implicitly made when the concentration profile is measured using non-destructive radiation absorption techniques.

In Figure 4.13b) is a typical example of the \( P_y(\phi) \) curve determined by the two methods from the concentration profile in Figure 4.13a). Agreement between the methods is excellent. The error bars for the discrete solution are determined by standard error analysis (see Appendix E for details). Here, the error in \( \phi \) varied from 0.3-0.5% while the error in \( P_y \) varied from 50-5%. The large error in \( P_y \) for low \( \phi \) is due to the rapid change in concentration at the top of the bed. The numerical curve fitting technique is more accurate than the discrete technique due to smoothing of any random variation in the concentration profile. The discrete technique, however, is simpler to implement and is reasonably accurate.

### 4.3.3 VALIDATION

The concentration profile technique is validated by a similar method to that used for the multiple speed equilibrium sediment height technique. Beginning with a synthetic \( P_y(\phi) \) function, the required concentration profile for a particular g value is determined by solution of the main differential equation, Equation (2.11). This concentration profile is then curve fitted and used in the numerical solution for \( P_y(\phi) \). Good agreement between the original \( P_y(\phi) \) function and the numerical solution of the concentration profile derived from that function, would validate the concentration profile technique.

The above validation procedure is illustrated in Figure 4.14. The concentration profiles for two particular g values were determined from a synthetic function of the form,
Figure 4.14 Validation of the concentration profile technique for determination of $P_y(\phi)$; a) $\phi(z)$ profiles determined from a synthetic $P_y(\phi)$ function for two particular $g$ values, b) comparison of numerical integration of data in a) with the original $P_y(\phi)$ function.
$P_y = 100[(\phi/0.18)^8 - 1]$, in Figure 4.14a). These profiles were curve fitted and integrated numerically, then compared with the original function in Figure 4.14b). Agreement with the original $P_y(\phi)$ function is excellent for both concentration profiles tested. The numerical method for determination of $P_y(\phi)$ from a measured concentration profile is therefore validated.

### 4.3.4 OPTIMUM CENTRIFUGE SPEED

In theory, any centrifuge speed can be used to determine the $P_y(\phi)$ function for a suspension from the concentration profile of the equilibrated sediment. In practice, there is an optimum speed to obtain reliable data in the $P_y(\phi)$ range required. In Figure 4.15 and Figure 4.16, the concentration profiles and corresponding $P_y(\phi)$ curves for samples centrifuged at a range of speeds for weakly flocculated ZrO$_2$ and TiO$_2$ suspensions are shown. Although the concentration profiles for each speed are very different in shape, overlap of the calculated $P_y(\phi)$ curves are generally good. The $P_y(\phi)$ curves, however, tend to diverge from the true $P_y(\phi)$ function at the higher concentrations. The upper part of each curve is determined from the concentration profile near the bottom of the centrifuge tube where the rate of increase in concentration is small; illustrated by the flattening of the concentration profile. The calculated $P_y$ for these concentrations is thus relatively high. The most accurate $P_y(\phi)$ data is therefore obtained from that part of the concentration profile where there is rapid change in concentration.

To further verify this observation, plotted in Figure 4.17 are the scaled concentration profiles from Figure 4.15 and Figure 4.16 as $\phi/\phi(0)$ versus $H/H_{eq}$ where $\phi(0)$ is the bottom concentration. Here, the concentration profiles clearly become flatter with increasing centrifuge speed and thus the amount of meaningful information for calculation of $P_y(\phi)$ is reduced.

To obtain a complete $P_y(\phi)$ curve, several samples centrifuged at a range of speeds should be measured. Where overlap of the $P_y(\phi)$ data occurs, the data determined from
Figure 4.15 Effect of centrifuge speed on: a) concentration profile, and b) compressive yield stress ($\text{ZrO}_2$, pH 4.9, $\phi_0 = 0.150$).
Figure 4.16 Effect of centrifuge speed on: a) concentration profile, and b) compressive yield stress ($\text{TiO}_2$, pH 5.7, $\phi_0 = 0.291$).
Figure 4.17  Scaled concentration profiles from Figure 4.15 and Figure 4.16; a) ZrO$_2$, pH 4.9, $\phi_0 = 0.150$, b) TiO$_2$, pH 5.7, $\phi_0 = 0.291$. 
the sample centrifuged at the higher speed is preferred. If only a single sample is used, then the speed chosen should yield a concentration profile where the greatest concentration change occurs across the concentration range of interest. The bottom concentration should thus be above the maximum concentration of interest, but not too high such that only a small region of the measured concentration profile is useful.

4.3.5 SUMMARY

The concentration profile technique is an accurate technique for the determination of $P_y(\phi)$ for a suspension. A suspension sample centrifuged to equilibrium can be sectioned in 0.5 mm pieces; the concentration of each piece is determined by mass loss on drying. To determine $P_y(\phi)$, the measured concentration profile is integrated down the bed in one of two methods. In the first, the raw $\phi(z)$ profile is integrated discretely using a trapezoidal rule. In the second, the raw $\phi(z)$ data is fitted to a curve and then integrated numerically. Good agreement between the methods was shown and the concentration profile technique was validated using data generated from a synthetic $P_y(\phi)$ function. Finally, an optimum centrifuge speed should be used to extract the best $P_y(\phi)$ data from the measured concentration profile.

4.4 PRESSURE FILTRATION TECHNIQUE

The theory for determination of $P_y(\phi)$ by pressure filtration was outlined in Chapter 2, Section 2.3.5. The implementation of the pressure filtration technique is now discussed.
4.4.1 EXPERIMENTAL EQUIPMENT

Two filtration devices were used to measure $P_y(\phi)$. The first device was built in the Chemical Engineering workshop at the University of Melbourne. The successful design and commissioning of this filtration device was a major component of this thesis. The second device was designed and built in the Department of Chemical Engineering, University of Illinois, Urbana-Champaign, Illinois, USA. Each device is now described.

4.4.1.1 Filtration device - University of Melbourne

The primary purpose of the filtration device designed and built at the University of Melbourne was to measure $r(\phi)$. Of secondary importance was the ability to measure $P_y(\phi)$. The requirements of the design were therefore:

i) an accurate and direct measurement of the suspension solids pressure,

ii) an accurate measurement of piston displacement and filtration volume with time for $r(\phi)$ determination,

iii) a bleed line in the piston. The piston may then be removed after forming the packed bed without damaging the bed or membrane. The filtrate could then be replaced on top of the bed and filtered through the bed as a second means of $r(\phi)$ determination.

The design of the filtration device was based on that of Wakeman, et al. (1991) and is illustrated in Figure 4.18. Essentially, the device consisted of a cylinder holding the suspension on a membrane (0.8 µm Millipore) supported by a sintered stainless steel disc, on a perforated stainless steel plate, in turn supported by a solid steel assembly bolted to the cylinder. A piston, with a bleed line, was used to compress the suspension in the cylinder. Two cylinders were used; an aluminium cylinder (280.1 mm high, 40.20 mm inside diameter) and a stainless steel cylinder (306.8 mm high, 28.40 mm inside diameter). To apply pressure to the piston, a pneumatic cylinder was used with a
Figure 4.18 Schematic of filtration device at the University of Melbourne for measurement of $P_y(\phi)$ and $r(\phi)$.

The line pressure range of 0-600 kPa. (Other alternatives are to use a mechanical testing machine (not available) or to apply weights to the piston). The lower limiting pressure of the system was about 50 kPa, below which the frictional resistance of the o-ring in the piston became significant. A pressure transducer (Philips, P13) mounted on the face of the piston directly measured the solids pressure in the cylinder. A pressure gauge in the bleed line measured the hydrostatic pressure in the cylinder. A rotary encoder on the shaft of the piston measured the piston displacement (0.16 mm/pulse). An electronic balance (A&D Mercury, FA-2000) measured the efflux rate from the filter. The filtration data was logged on a PC using a custom written program in Visual Basic.
4.4.1.2 Filtration device - University of Illinois

The filtration device at the University of Illinois is described by Miller, et al. (1996) and was based on a previous device by Lange and Miller (1987). The device was similar to that at the University of Melbourne. The compression cylinder was stainless steel and smaller (94.05 mm high, 25.37 mm inside diameter). Load to a piston was applied and controlled by a screw driven mechanical testing machine (Instron, Model 4502) and displacement of the crosshead was recorded. Pressure and displacement measurement and control were thus excellent. The pressure range of this device was 50 kPa to 12 MPa, much higher than the device at the University of Melbourne.

4.4.2 EXPERIMENTAL PROCEDURE

The following is the experimental procedure used to measure $P_y(\phi)$ for the pressure filtration technique using the apparatus at the University of Melbourne. The procedure used at the University of Illinois is described by Miller, et al. (1996).

1. Grease filtration cylinder and o-ring in piston with silicone grease until resistance is minimised. Assemble filtration device with a new filter membrane and ensure piston is aligned with cylinder.

2. Determine initial solids concentration of suspension, $\phi_0$, by measuring the mass loss on drying of a small sub-sample.

3. Fill filtration cylinder with suspension ($\approx$200 mL for 28.40 mm diameter cylinder, $\approx$350 mL for 40.20 mm diameter cylinder). Measure mass used by mass loss in suspension sample container.

4. Insert piston and fill bleed line with suspension.

5. Close bleed valve.
6. Determine initial suspension height, $H_{0}$, from measurement of distance of piston from top of cylinder and length of cylinder and piston.


8. Quickly increase pressure to desired value and maintain until equilibrium is attained (no piston movement over several hours).

9. Release pressure, open bleed valve, dismantle, then press out packed bed using piston.

10. Measure final packed bed height, $H_{f}$.

11. Weigh mass of packed bed, $M_{b}$.

12. Record final mass of filtrate, $M_{f}$.

13. Determine final concentration of packed bed, $\phi_{f}$, by one of three methods:

   i) mass loss on drying of entire bed, or

   ii) section bed, measure the concentration of each section then determine the average concentration from the resulting concentration profile, or

   iii) from the overall height change during filtration.

14. Repeat entire procedure at next pressure using either a fresh sample from a bulk quantity of suspension, or using the reslurried packed bed and filtrate.

The filtration time is inversely proportional to the applied pressure [Landman, et al. (1991)] and varied from 6 h for high pressures to over 40 h for low pressures. The filtration time depended on the initial suspension concentration - the higher the initial concentration, the longer the filtration time. The filtration time is also proportional to the bed height squared. For the device at the University of Illinois, times were significantly faster; 20 min at high pressures to just over an hour for low pressures. The shorter times were due to the smaller sample volume used.
4.4.3 VALIDATION

After constant pressure filtration, a uniform concentration profile is predicted by the general consolidation theory. In Figure 4.19, the concentration profiles of final packed beds for several experiments are shown for the device at the University of Melbourne. The concentration profile was determined by taking small samples along the packed bed, then measuring the mass loss on drying of each sample. At low pressures, full consolidation was not achieved, possibly due to the relatively large sample volumes and long filtration times and the comparatively large piston resistances. At higher pressures, reasonably uniform profiles are achieved. Concentration profiles of consolidated Al$_2$O$_3$

![Graph](image)

**Figure 4.19** Typical concentration profiles of packed beds formed by constant pressure filtration; device at University of Melbourne, cylinder diameter = 40.20 mm (ZrO$_2$, pH 5.2, $\phi_0 = 0.052-0.055$).
suspensions measured by the device at the University of Illinois were relatively uniform [Miller, et al. (1996)].

Comparison of $P_y(\phi)$ results from the devices at the University of Melbourne and at the University of Illinois was possible but difficult. In Figure 4.20, strongly flocculated ZrO$_2$ was used in each device and the compressive yield stress was measured over a range in concentration. The initial concentration for ZrO$_2$ ($\phi_g \approx 0.08$) used at the University of Illinois was $\phi_0 = 0.16$, compared with $\phi_0 = 0.05$ and 0.08 at the University of Melbourne. Agreement between the two devices is reasonable, even with the variation in initial concentration and slight variation in the suspension pH around the i.e.p.

![Figure 4.20](image)

**Figure 4.20** Comparison of pressure filtration devices at the University of Illinois and at the University of Melbourne for determination of $P_y(\phi)$ for similar ZrO$_2$ suspensions.
Errors in the pressure filtration technique primarily arise from measurement errors in the final concentration of the packed bed, $\phi_f$. Miller, et al. (1996) fully evaluated the errors involved in the determination of $\phi_f$ from the mass loss on drying of the entire bed, and from the height change in filtration from the initial suspension height. They found that the mass loss method was more robust and less prone to experimental error. This finding was confirmed and the mass loss method was used in all experiments.

### 4.4.4 SUMMARY

The pressure filtration technique is a direct measurement of $P_y(\phi)$ for a suspension. Two devices were used and results from each device compared well.

### 4.5 WALL EFFECTS

The centrifuge tube wall or filtration cylinder wall can potentially affect the $P_y(\phi)$ measured using the above techniques. In this section, this wall effect is investigated and a minimum tube or cylinder diameter required to attenuate the effect for compression measurements is recommended.

### 4.5.1 RESULTS

The effect of centrifuge tube diameter on the measured $P_y(\phi)$ curve was investigated using two suspension systems. In Figure 4.21 and Figure 4.22, the $P_y(\phi)$ curve determined using the multiple speed technique is shifted right or downwards with increasing tube diameter for strongly flocculated $\text{ZrO}_2$ and $\text{TiO}_2$ respectively. De Guingand (1986) also observed a similar effect for bauxite residue. Buscall (1982) examined the tube diameter effect for low concentration attapulgite suspensions and
Figure 4.21 Effect of centrifuge diameter on $P_y(\phi)$ determined by the multiple speed technique; symbols - approximate solution, lines - iterative solution ($ZrO_2$, pH 7.1, $\phi_0 = 0.150$).

found an effect at very low $g$ that vanished at higher $g$. No effect was found for polystyrene latex.

Narrow tubes thus apparently restrict the compression of the suspension and generate unrealistically high $P_y(\phi)$ results. From these limited data it is difficult to identify a minimum tube diameter at which the effect on $P_y(\phi)$ was negligible. A tube diameter of 26.5 mm was used in all experiments, this being the widest practical centrifuge tube whilst minimising systematic errors due to wall effects. In comparison, the cylinder diameters used in the pressure filtration technique were 28.40 mm and 40.20 mm.
Figure 4.22 Effect of centrifuge diameter on $P_y(\phi)$ determined by the multiple speed technique; symbols - approximate solution, lines - iterative solution ($\text{TiO}_2$, pH 6.9, $\phi_0 = 0.246$).

4.5.2 DISCUSSION

Wall effects are caused by the radial transmission of upward acting shear stresses from the wall into the suspension that resist the downward acting compressive forces. Near the wall, the governing stress balance is thus

$$P_s(\phi) - \tau_y(\phi) = P_y(\phi).$$  \hspace{1cm} (4.11)

The distance the wall shear stress extends into the suspension is dependent on the shear yield stress of the suspension, $\tau_y(\phi)$; a function of concentration. In a centrifuged sample the shear yield stress is greatest at the bottom (highest concentration), thus the
wall shear stress extends the furthest into the suspension. In Figure 4.15a), Figure 4.16a) and Figure 4.17a), the flattened concentration profiles measured near the centrifuge tube bottoms are evidence of the existence of wall effects due to large $\tau_y(\phi)$.

The shear zone and lines of constant concentration for a suspension centrifuged to equilibrium in a narrow tube are postulated in Figure 4.23. On a radial cross-section through the tube, the concentration near the walls is lower than in the bulk unsheared zone in the centre. In the determination of the concentration profile by sectioning, the measured average concentration for each section is slightly lower than the bulk concentration in the unsheared zone. The $P_y(\phi)$ function determined by the concentration profile technique where wall effects are significant is therefore offset to the left. The offset is largest for the upper part of the $P_y(\phi)$ function, corresponding to data determined near the bottom of the centrifuge tube where the radial concentration

![Diagram](image_url)

**Figure 4.23** Schematic of postulated concentration profile of a suspension centrifuged to equilibrium showing the effect of the centrifuge tube walls; solid lines - constant concentration, dashed lines - zero shear stress.
difference between the wall and the centre is the greatest. The deviation of the upper part of the $P_y(\phi)$ curves from the true $P_y(\phi)$ functions in Figure 4.15b) and Figure 4.16b) is thus explained.

The wall effect similarly affects the multiple speed equilibrium sediment height technique. Here, the measured equilibrium heights are higher than the true equilibrium heights with no wall effect. The offsets are larger at higher speeds, leading to a similar leftward shift of the $P_y(\phi)$ curve for narrow centrifuge tubes. The results in Figure 4.21 and Figure 4.22, where the $P_y(\phi)$ functions measured from samples in narrow centrifuge tubes are to the left of those measured in wider tubes, are thus explained.

To minimise wall effects in the centrifuge methods of $P_y(\phi)$ determination, a centrifuge tube must be used with a diameter wide enough such that the shear zone is small in comparison with the unsheared bulk suspension. A sufficiently wide diameter tube is possibly impractical if $P_y(\phi)$ data for highly concentrated suspensions (with correspondingly high $\tau_y(\phi)$ values) are required. A means of reducing the error in $P_y(\phi)$ due to wall effects is to measure $P_y(\phi)$ from a sample centrifuged at a higher speed than necessary, then ignore the upper part of the $P_y(\phi)$ curve. Overlap with $P_y(\phi)$ data determined at a lower speed is also possible.

Michaels and Bolger (1962) have theoretically computed for dilute suspensions the minimum diameter at which compression will occur for a suspension with a given $\tau_y(\phi)$ and $P_y(\phi)$. Application of their formulation to the concentrated ZrO$_2$ and TiO$_2$ suspensions used here, however, gave unrealistically high minimum centrifuge tube diameters.

Auzerais, et al. (1990) used a medical computer tomography (CT) scanner to measure the radial and axial concentration profiles in centrifuge tubes. A concave interface was observed suggesting an effect where, at a given sediment height, the centrifugal forces are greater at the walls than the centre. This effect, illustrated in Figure 4.24, might partly nullify any wall effect caused by the shear yield stress of the suspension. However, low in the compression region, furthest from the centrifuge centre, this effect is probably minor.
Figure 4.24 Schematic showing greater gravitational acceleration at walls of centrifuge tube due to greater distance from centre.

A two dimensional model is required to completely understand the effect of walls on the compression rheology of suspensions in a finite container.

4.5.3 SUMMARY

Wall effects are a real phenomenon in compression rheology and must be treated seriously. The $P_y(\phi)$ function was found to shift to the right with increasing tube diameter for ZrO$_2$ and TiO$_2$ suspensions. This trend agreed with results from several independent workers using a variety of suspension systems. To obtain absolutely quantitative $P_y(\phi)$ results, the tube diameter must be wide enough such that wall shear effects are minor. A tube diameter of 26.5 mm was used in all experiments in this thesis, this being the widest practical centrifuge tube whilst minimising systematic errors due to wall effects.
4.6 COMPARISON OF MEASUREMENT TECHNIQUES

In this section, the two centrifuge techniques and the pressure filtration technique are compared and evaluated.

4.6.1 TYPICAL RESULTS FOR COMPARISON

Combined results from all three measurement techniques are compared in Figure 4.25 and Figure 4.26. The results are for strongly flocculated ZrO$_2$ and TiO$_2$ (pH 7.6 and 6.9)

![Comparison of techniques for measurement of $P_y(\phi)$; LSC, MSC and HSC correspond to low, medium and high speed centrifuges respectively (ZrO$_2$, pH 7.6, $\phi_0 = 0.15$).](image)

**Figure 4.25** Comparison of techniques for measurement of $P_y(\phi)$; LSC, MSC and HSC correspond to low, medium and high speed centrifuges respectively (ZrO$_2$, pH 7.6, $\phi_0 = 0.15$).
respectively). The results span a substantial range of solids concentration ($\phi = 0.10$ to 0.45) and compressive yield stress (4 orders of magnitude). Three centrifuges were used to obtain results over this large range using the multiple speed equilibrium sediment height technique. These are referenced in Figure 4.25 and Figure 4.26 as the low, medium and high speed centrifuges (LSC, MSC and HSC). Concentration profiles were determined from the high and low speed centrifuged samples and the resulting $P_y(\phi)$ curves agree with those from the multiple speed equilibrium sediment height technique. The pressure filtration results are also consistent with the two centrifuge techniques; however only the upper range of pressures was accessed due to experimental constraints. Good agreement between filtration and batch sedimentation experiments using flocculated clay has also been observed by Dell and Sinha (1966).
The moderate agreement between the three measurement techniques is good evidence that the compressive yield stress is a material property of a suspension. The two centrifuge techniques and the filtration technique compress by different consolidation mechanisms. In centrifugation, the expelled water from the suspension network is forced upwards through the structure and hinders consolidation. However, in pressure filtration, the expelled water flows downwards and contributes to the compression. In both cases, at equilibrium, it is the sediment structure that supports the applied stress. The agreement between the results thus suggests that the compressive yield stress is independent of the path taken to reach the final condition (that is, $P_y(\phi)$ is a material property). This finding agrees with that of Miller, et al. (1996).

### 4.6.2 ADVANTAGES AND DISADVANTAGES OF EACH TECHNIQUE

Which technique should be used? Given that all three techniques agree reasonably well, the accuracy of each technique, the ease of use, and the time to obtain results must be considered. A comparison of each technique is given in Table 4.1.

<table>
<thead>
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<th>Technique:</th>
<th>Multiple Speed</th>
<th>Concentration Profile</th>
<th>Pressure Filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples per run:</td>
<td>2-28$^1$</td>
<td>2-8$^1$</td>
<td>1</td>
</tr>
<tr>
<td>Conc. accuracy:</td>
<td>± 4%</td>
<td>± 0.5%</td>
<td>± 1%</td>
</tr>
<tr>
<td>Pressure accuracy:</td>
<td>± 2%</td>
<td>± 5%</td>
<td>± 2%</td>
</tr>
<tr>
<td>Measurement time:$^2$</td>
<td>30 min</td>
<td>60 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Equipment time:</td>
<td>4-5 weeks</td>
<td>1 week</td>
<td>1 day</td>
</tr>
<tr>
<td>Analysis time:$^2$</td>
<td>10 min</td>
<td>15 min</td>
<td>5 min</td>
</tr>
<tr>
<td>No. data points:$^3$</td>
<td>5-6</td>
<td>15-30</td>
<td>5-6</td>
</tr>
</tbody>
</table>

*Table 4.1* Comparison of $P_y(\phi)$ measurement techniques; 1. Dependent on centrifuge size. 2. Per sample. 3. Minimum number of data points required - greater accuracy is achieved with more points, but times increase proportionally.

The multiple speed technique is time consuming - attainment of the equilibrium state for 5 or 6 speeds can require over a month for the mineral suspensions studied here.
Measurement time per sample is low, but data analysis is moderately complex and accuracy is moderate. The concentration profile technique requires a suspension to reach an equilibrium height at a single centrifuge speed - about a week. Sectioning of the sediment is laborious - requiring about an hour per sample - but the accuracy of the concentration profile and the resulting $P_y(\phi)$ curve is good since many sections can be taken. Pressure filtration requires a custom built apparatus, but results of moderate accuracy can be obtained in a day for a single sample of low volume. As an industrial engineer, the concentration profile technique is clearly the method of preference to use. Centrifuges are widely available, multiple samples can be tested simultaneously, data analysis is simple and straightforward and results can be obtained in just over a week. The disadvantage is the laborious sectioning of each sample; this could be automated if necessary. If the sample number is large, and results are not urgent then the multiple speed technique is more attractive. Therefore, the technique to be applied is dictated by the particular circumstance.

4.7 CONCLUSIONS

Three experimental techniques for determination of the compressive yield stress function for suspensions were evaluated. Two were based on centrifugal settling to an equilibrium state and one was based on pressure filtration to equilibrium. Each technique was independently validated with good results.

Wall effects on compression were found to be significant. A minimum centrifuge tube or filtration cylinder diameter is required to minimise errors due to wall effects.

Similar suspensions were tested using each technique and the agreement between each technique was good. The parameter, $P_y(\phi)$, was thus verified as being a material property of consolidating suspensions.

Finally, the techniques were compared in terms of accuracy, ease of use, and experimental, equipment and measurement time per sample. The most appropriate technique was found to be dictated by the particular circumstance.
Chapter 5

HINDERED SETTLING FUNCTION MEASUREMENT

5.1 INTRODUCTION

Experimental and computational procedures for the determination of the compressive yield stress function have been fully examined and evaluated. It is now the objective in this chapter to similarly develop reproducible techniques for the determination of the hindered settling function.

Two techniques are examined; the packed bed formation technique and the packed bed filtration technique. Each technique is evaluated separately and then compared. The reproducibility of the $r(\phi)$ measurements is investigated by examination of the effects of suspension preparation and filtration cylinder diameter.

5.2 MEASUREMENT OF $r(\phi)$ BY THE PACKED BED FORMATION TECHNIQUE

The first technique examined for the determination of $r(\phi)$ is the packed bed formation technique. The theory for this technique is discussed in Chapter 2, Section 2.4.5.
5.2.1 EXPERIMENTAL PROCEDURE

The filtration apparatus and experimental procedure are described in Chapter 4, Sections 4.4.1 and 4.4.2. The device used was that at the University of Melbourne.

The initial rate of descent of the piston was always ensured to be greater than the initial sedimentation rate (measured by batch sedimentation - see Appendix F). The effect of sedimentation on filtration behaviour was recently examined by Tiller, et al. (1995) who found a significant effect on the calculated specific filtration resistance for kaolin suspensions. Here, the sedimentation effect on the measured $r(\phi)$ is assumed negligible.

The filtration or efflux rate was determined by two methods. In the first method, the filtrate mass was measured by the electronic balance as a function of time. The filtrate volume was then determined using the fluid density. In the second method, the displacement of the piston was measured by the rotary encoder. The filtrate volume was then determined by multiplying by the cylinder cross-sectional area. Typical filtration rate curves measured using each technique are shown in Figure 5.1a) for ZrO$_2$.

Good agreement between the two methods was always observed, thus validating the measurement and logging equipment. The data determined from the filtrate mass always appeared slightly below that determined from the piston displacement. The difference was most likely due to the loss of filtrate trapped in the sintered disk and perforated plate that support the membrane, and due to evaporation in the collection beaker. A wide funnel was placed and sealed over the collection beaker to minimise this evaporation loss. The piston displacement method for determination of the filtration rate was preferred over the filtrate mass method.

The raw filtration rate data was plotted as $t/V$ versus $V$. The corresponding curves for the data in Figure 5.1a) are shown in Figure 5.1b). The initial slope, $m_1$, was measured by linear regression for the calculation of $r(\phi)$. The data determined by the filtrate mass method was again always offset from the data determined by the piston displacement method. However, the initial slope was independent of the measurement method. In Figure 5.2, a typical series of $t/V$ versus $V$ plots over a range of applied pressures are shown for a strongly flocculated ZrO$_2$, using the device at the University of Illinois.
Figure 5.1 Typical filtration rate plot illustrating two different measurement methods on the device at the University of Melbourne (ZrO$_2$, pH 6.9, $\phi_0 = 0.050$, cylinder diameter = 40.20 mm); a) $V$ versus $t$, b) $t/V$ versus $V$. 
Figure 5.2 Filtration rate data determined using the device at the University of Illinois (ZrO₂, pH 7.6, φ₀ = 0.156).

The gel concentration of the suspension is required for calculation of r(φ). Tiller and Khatib (1984) determined φ₉ by two methods from sedimentation experiments. An estimate for φ₉ is made from a simple batch sedimentation test where a sample of concentration φ₀ < φ₉ is allowed to settle to equilibrium in a measuring cylinder. The gel concentration is determined from the average sediment concentration, φₐvg, by

\[ φ₉ \approx φₐvg = \frac{φ₀ H₀}{Hₐ} \]  \hspace{1cm} (5.1)

The gel concentration determined by this technique is over-estimated since a small amount of compression will always occur. A better estimate is obtained by repeating the batch settling experiment using a range of initial heights. A plot of φₐvg versus the initial sediment height, H₀, is extrapolated to H₀ → 0, where φₐvg → φ₉. Batch settling experiments to find φ₉ for the suspensions in this thesis are detailed in Appendix F.
5.2.2 CALCULATION OF $r(\phi)$

To calculate $r(\phi)$, Equation (2.39) is used. The filtration rate is defined per unit area of membrane, thus the slope $m_1$ determined from the $t/V$ versus $V$ plot must be multiplied by the membrane area squared. The $r(\phi)$ calculations were done on a spreadsheet; sample calculations are included in Appendix G.

In Figure 5.3 are typical $r(\phi)$ data determined by the packed bed formation technique. Reasonable agreement between the devices at the University of Melbourne and the University of Illinois is observed for similar samples. The initial concentration used for samples at the University of Illinois was greater than the gel concentration (for ZrO$_2$,

![Graph](image)

**Figure 5.3** Typical $r(\phi)$ data for ZrO$_2$ determined by the packed bed formation technique using filtration devices at the University of Melbourne (pH 6.5-6.9, $\phi_0 = 0.046-0.050$), and at the University of Illinois (pH 7.6, $\phi_0 = 0.156$).
$\phi_g \approx 0.08$), thus the two stage filtration theory used to determine $r(\phi)$ is not strictly valid. However, excellent linear behaviour of $t/V$ versus $V$ plots is observed for this device, as illustrated in Figure 5.2 for the data in Figure 5.3. It appears then that for $\phi_0 > \phi_g$ the compression region grows away from the membrane in a manner comparable to the movement of the packed bed surface in the case for $\phi_0 < \phi_g$. The filtration data can thus be analysed in the same way. For the University of Illinois device, two methods for determination of $\phi_r$ are also compared in Figure 5.3; that from the mass loss on drying of the entire packed bed, and that from the height difference after filtration. These methods agree well.

The effects of random measurement errors on the calculated $r(\phi)$ are determined by standard propagation of error methods in Appendix G. The error bars in Figure 5.3 are calculated concurrently with the $r(\phi)$ data on the same spreadsheet. Errors in $\phi_m$ are greater at low $\phi$ where the equilibrium concentration profile is not entirely constant (see Chapter 4, Section 4.4.3). Errors in the function $r$ are also greater at low pressure because the calculation of $r$ also includes $\phi_m$ and it is also where the relative pressure error is high.

5.2.3 VALIDATION

5.2.3.1 Fresh samples versus re-slurried sample

The effect of using fresh samples from the one original bulk suspension for each pressure is compared with re-slurrying the packed bed after each pressure and reusing the sample for the next pressure. This effect is important if only small quantities of suspension are available.

To evaluate this effect, 2 L of a weakly flocculated ZrO$_2$ suspension was prepared by combining five 400 mL separately prepared batches. One 400 mL sample from the bulk suspension was repeatedly filtered to form the packed bed, then re-slurried with the filtrate to return it to its original state. The sample was mixed for 24 hr with a paddle
impeller at 100 rpm, sonicated for 5 min, then rested for 24 hr before filtered at the next higher pressure. Fresh samples from the remaining bulk suspension were separately filtered, each at a different pressure. The results from this experiment are shown in Figure 5.4. Note that the pH and initial suspension concentration varied slightly through the filtration runs due to evaporation and other incidental material losses. The $r(\phi)$ data from the re-slurried sample agrees with that from the fresh samples.

Thus, if the suspension sample volume is limited, reuse of the sample for each filtration is a feasible option. More time must be allowed for the reproducible re-slurrying of the sample to return it to the original state. However, if the suspension structure is

![Graph](image_url)

**Figure 5.4** Effect on $r(\phi)$ determined by the packed bed formation technique using the same sample for each successive pressure by re-slurrying the packed bed, compared with using a fresh sample at each applied pressure (filtration device at University of Melbourne, cylinder diameter = 40.20 mm).
compression history dependent, the original state might never be re-attained and separate, fresh samples must be used.

5.2.3.2 Filtration cylinder diameter effect

The effect of the filtration cylinder diameter on the hindered settling function potentially has a similar effect to that found for the compressive yield stress in Section 4.2.5.

The effect of the cylinder diameter on $r(\phi)$ for a strongly flocculated ZrO$_2$ suspension is shown in Figure 5.5. Two filtration cylinders of diameters 28.40 mm and 40.20 mm

![Graph showing the effect of filtration cylinder diameter on the hindered settling function.](image)

**Figure 5.5** Effect of the filtration cylinder diameter on $r(\phi)$ determined by the packed bed formation technique for ZrO$_2$ suspensions (device at University of Melbourne).
were used. The cross-sectional area of the larger diameter cylinder was 2.00 times that of the smaller cylinder. The \( r(\phi) \) data obtained using each filtration cylinder superimpose on each other well. The effect of doubling the cross-sectional area for filtration and any wall effects on the \( r(\phi) \) results thus appear to be negligible for the cylinder diameters used here.

### 5.2.4 UNUSUAL FILTRATION RATE BEHAVIOUR

In Figure 5.6 are typical filtration rate curves determined from the device at the University of Melbourne. In the later stages of filtration a period of increased filtration rate is evident, characterised by a flattening in the \( t/V \) versus \( V \) curves. The flattening in the curves is more pronounced with increasing pressure. This unusual filtration behaviour was observed for both the 28.40 mm and 40.20 mm filtration cylinders, but was not observed for the device at the University of Illinois (see Figure 5.2).

A possible explanation for this effect is channelling. Conceivably, at a certain solids concentration, channels may form that would enhance the consolidation rate since water may easily escape in open channels rather than through a packed bed. The channels would then close when another certain solids concentration is attained, allowing consolidation of the packed bed to continue as normal. This phenomenon of transient channelling is consistently observed in batch settling experiments [e.g. Coe and Clevenger (1916); Dell (1970); Scott (1968, 1970); Glasrud, et al. (1993); Vesilind and Jones (1993); Chen, et al. (1996)].

The effect was probably not seen for the device at the University of Illinois because \( \phi_0 \) was always greater than \( \phi_{c} \). There, the concentration range for the formation of channels was probably already exceeded before filtration began.

The effect on the calculated \( r(\phi) \) values due to this unusual filtration rate behaviour is small if not negligible. In the calculation of \( r(\phi) \), only the initial filtration rate, characterised by the slope, \( m_1 \), and the final concentration of the packed bed, \( \phi_f \), are required. The actual consolidation mechanism that occurs between the initial filtration
Figure 5.6 Filtration rate data showing unusual behaviour midway through the filtration (ZrO₂, pH 6.5-6.9, φ₀ = 0.047-0.050, device at University of Melbourne, cylinder diameter = 40.20 mm).

stage and the final consolidation of the packed bed is irrelevant. The agreement between the two filtration devices in Figure 5.3 corroborates this hypothesis.

5.3 MEASUREMENT OF r(φ) BY THE PACKED BED FILTRATION TECHNIQUE

The second technique examined for the determination of r(φ) is the packed bed filtration technique. The theory for this technique is discussed in Chapter 2, Section 2.4.6.
5.3.1 EXPERIMENTAL PROCEDURE

The following procedure was used to determine \( r(\phi) \) by packed bed filtration. The device at the University of Melbourne was used.

1. Form a packed bed of height, \( H_p \), constant concentration, \( \phi_p \), by the packed bed formation technique (see Section 5.2.1).

2. Release pressure, open bleed valve and remove piston using compressed air in the bleed line (damage to the membrane and packed bed surface is thus minimised).

3. Carefully replace filtrate on top of bed.

4. Insert piston and fill bleed line with filtrate.

5. Close bleed valve.


7. Increase pressure to a value equal or less than that used to form the packed bed and maintain until an equilibrium efflux rate, \( dV/dt \), is attained.

8. Release pressure, open bleed valve, dismantle, remove remaining filtrate and measure final bed height and concentration as for previous technique.

The efflux rate, \( dV/dt \), increased linearly with applied pressure for pressures less than the packed bed formation pressure, as illustrated in Figure 5.7 for a typical \( \text{ZrO}_2 \) suspension. In the calculation of \( r(\phi) \), the ratio of \( \Delta P \) to \( dV/dt \) is required, thus any value of \( \Delta P \) less than or equal to that used to form the packed bed may be used.

Several hours were usually required to attain an equilibrium efflux rate.
5.3.2 CALCULATION OF $r(\phi)$

To calculate $r(\phi)$, Equation (2.43) is used. The calculation was done on a spreadsheet; a sample calculation is included with the packed bed formation technique calculation in Appendix G. Again, the efflux rate, $dV/dt$, is defined per unit area of membrane.

In Figure 5.8 are typical $r(\phi)$ data determined by the packed bed filtration technique. This technique was only used at the University of Melbourne, there being no facility to withdraw the piston on the device at the University of Illinois. The data in Figure 5.8...
Figure 5.8 Comparison of typical $r(\phi)$ data determined by the packed bed formation technique and the packed bed filtration technique ($\text{ZrO}_2$, pH 6.7-7.1, $\phi_0 = 0.082-0.085$, device at University of Melbourne, cylinder diameter = 40.20 mm).

are compared with data determined by the constant pressure filtration and compaction technique. Agreement is excellent in this case. Further comparisons of the two techniques are made in the next section.

Errors in the packed bed filtration technique are again determined in Appendix G. The magnitude of errors in $r(\phi)$ are similar to those calculated for the packed bed formation technique.
5.4 COMPARISON OF MEASUREMENT TECHNIQUES

In this section the packed bed formation technique and the packed bed filtration technique are compared and evaluated.

5.4.1 TYPICAL RESULTS FOR COMPARISON

Typical results from both \( r(\phi) \) measurement techniques are compared in Figure 5.8 and Figure 5.9. In these and other results, the data determined by packed bed filtration always appear to the right or below that determined by packed bed formation.

The concentration range for the packed bed filtration technique is inherently higher, being based on the final bed concentration, \( \phi_f \), rather than on a mean concentration, \( \phi_{mv} \), for the packed bed formation technique. The overall \( r(\phi) \) function, however, should be the same for each technique. The different concentration basis for each technique is thus not an explanation for the observed differences in the results.

Differences between the results could be due to non-uniform concentration profiles in the formed packed beds. A concentration gradient in the final packed bed would lead to errors in the packed bed filtration technique since the bed permeability is not constant. The packed bed filtration technique is dependent on both the concentration and height of the packed bed. The applied pressure in the packed bed filtration technique may change the concentration profile within the bed leading to further errors [Sherwood and Meeten (1997)].

Channelling in the packed bed or damage to the surface of the packed bed, causing short circuiting of regions in the packed bed and a higher filtration rate, would result in a lower \( r(\phi) \) value.

Another explanation for differences in the observed results is possible theoretical problems in the derivation of \( r(\phi) \) for either technique. In the packed bed formation technique, the choice of the mean concentration, \( \phi_{mv} \), is somewhat empirical. The
Figure 5.9 Comparison of typical \( r(\phi) \) data determined by the packed bed formation technique and the packed bed filtration technique (ZrO\(_2\), pH 6.6-6.8, \( \phi_0 = 0.050-0.052 \), device at University of Melbourne, cylinder diameter = 40.20 mm).

average chosen in Equation (2.38) appears to be sound when tested with synthetic data [Landman, et al. (1995)]. Problems incurred using real data, particularly with the measurement of \( \phi_b \) and \( \phi_f \), may explain the observed differences between the techniques.

5.4.2 ADVANTAGES AND DISADVANTAGES OF EACH TECHNIQUE

The long experimental time is a major disadvantage of both techniques. Obviously, the packed bed formation technique is faster than the packed bed filtration technique since a
packed bed must be formed by the first technique before the second technique may be used. The experimental time to form a packed bed of constant concentration was very long (from 6 h at high pressure, to 40 h at low pressure). The filtration time to attain steady state through the packed bed was then several hours. The total time required to obtain four or five points for an \( r(\phi) \) curve was thus up to two weeks, including turnaround time between pressures. The experimental time could be shortened by reducing the sample volume, as for the device at the University of Illinois where filtration times were significantly shorter.

The packed bed formation technique appears to be more robust than the packed bed filtration technique. As was discussed in the previous section, experimental problems are greatly reduced for the packed bed formation technique. Random experimental errors in each technique are similar. The packed bed formation technique was therefore used for the results in this thesis.

Another inherent advantage of the packed bed formation technique for determination of \( r(\phi) \) is that \( P_y(\phi) \) is also determined at the same time (see Chapter 4, Section 4.4).

5.5 CURVE FITTING AND PARTICLE SIZE ESTIMATION

5.5.1 CURVE FITTING

Curve fitting of the \( r(\phi) \) data is desirable for several reasons. First, a functional form is easily incorporated into models for the design of consolidation equipment. Second, extrapolation of the curve to low concentrations that are otherwise difficult to obtain data at using this technique is possible. Finally, an estimation of the suspension particle size is obtained from the extrapolated intercept.
Several functional forms have been used to fit $r(\phi)$ data [references in Landman and White (1992, 1995); Eberl, et al. (1995)]. Two forms are used here that satisfy the criteria $r(\phi) \rightarrow 1$ at $\phi = 0$;

\[
\frac{\lambda}{V_p} r(\phi) = C (1 - \phi)^n,
\]

(5.2)

\[
\frac{\lambda}{V_p} r(\phi) = C 10^{n\phi}.
\]

(5.3)

Typical fits for the above functions are shown in Figure 5.10 for a ZrO$_2$ suspension. A simple power law fit may also be used, but the criteria at $\phi = 0$ is not satisfied.

---

**Figure 5.10** Typical hindered settling function and curve fits determined by the packed bed formation technique ($\text{ZrO}_2$, pH 6.5-6.9, $\phi_0 = 0.046$-0.050, device at University of Melbourne, cylinder diameter = 40.20 mm).
5.5.2 PARTICLE SIZE ESTIMATION

An estimation of the suspension particle size is obtained by examination of the intercept of the \( r(\phi) \) curve fits. For each curve fit in Equations (5.2) and (5.3), the extrapolated intercept \( r(\phi) \to 1 \) at \( \phi = 0 \) gives

\[
\frac{\lambda}{V_p} = C. \tag{5.4}
\]

Assuming spherical particles of radius, \( a_p \), the Stokes drag coefficient is \( \lambda = 6 \pi \eta a_p \), and the particle volume is \( V_p = \frac{4}{3} \pi a_p^3 \). The equivalent particle diameter, \( d_p \), is thus

\[
d_p = 2a_p = 2 \sqrt{\frac{9 \eta}{2C}}. \tag{5.5}
\]

The accuracy of the calculated particle size is completely dependent on the extrapolated curve fit. For the ZrO\(_2\) suspension in Figure 5.10, the particle size calculated from the average intercept of the two curve fits is \( d_p = 0.12 \text{ \mu m} \). An indication of the effect of error in the extrapolated intercept is shown in Table 5.1.

<table>
<thead>
<tr>
<th>( C ) (Pa.s/m(^2))</th>
<th>( d_p ) (\text{\mu m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^9 )</td>
<td>4.24</td>
</tr>
<tr>
<td>( 10^{10} )</td>
<td>1.34</td>
</tr>
<tr>
<td>( 10^{11} )</td>
<td>0.42</td>
</tr>
<tr>
<td>( 10^{12} )</td>
<td>0.13</td>
</tr>
<tr>
<td>( 10^{13} )</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 5.1 Particle diameter calculation from intercept of hindered settling function, \( C \).

These particle sizes are consistent with the measured fundamental particle size of ZrO\(_2\) in Chapter 3. The order of magnitude of the measured \( r(\phi) \) function is thus confirmed.
5.6 CONCLUSIONS

The development of a reproducible technique for measurement of the hindered settling function was a major objective of this thesis. A pressure filtration device was successfully built and operated to determine \( r(\phi) \). Results from two techniques compared reasonably well and particle size estimations from the results were good. The effect of the suspension preparation method and the filtration cylinder diameter were evaluated and no effect major effect was observed. The reproducibility of the results was thus confirmed.

Each technique was evaluated in terms of accuracy, ease of use and experimental measurement time. The packed bed formation technique is the best technique for determination of the hindered settling function.

With the measurement of \( r(\phi) \) now possible, the full general consolidation model can be used to model transient and time dependent consolidation processes such as filtration and continuous thickening.
Chapter 6

COMPRESSION RHEOLOGY: RESULTS AND DISCUSSION

6.1 INTRODUCTION

Experimental and computational techniques for the characterisation of suspensions by the parameters $P_y(\phi)$ and $r(\phi)$ were fully evaluated in the previous two chapters. Here, extrinsic parameters affecting the compression rheology of suspensions are investigated. The general consolidation model described in Chapter 2 is thus fully evaluated. The conditions for maximum consolidation are also determined.

Investigated are variations in the structural state of the suspension before compression begins. The initial suspension structure is dependent on the flocculation state, the initial concentration, the method of preparation, and any prior shear or compression history of the suspension. The effect of steric stabilisation on compression is also investigated. Finally, the compressive yield stress is correlated with the shear yield stress for several suspension systems.

6.2 RESULTS - EFFECT OF STRUCTURAL STATE

Shear and compression rheology are controlled by the structural state of the suspension [references in Van den Temple (1979)]. This structure is determined by the strength of
inter-particle interactions and by the arrangement and number of bonds between particles in the suspension. Of interest is the relation between suspension structure and the extent and rate that a suspension will consolidate under a given applied pressure. The structure continually changes during consolidation thus further complicating the matter. The effect on the compression rheology of parameters that change the suspension structure is now investigated.

6.2.1 FLOCCULATION STATE

The compression rheology of metal oxide suspension systems can be controlled by the flocculation state of the sample. As discussed in Chapter 2, the pH of the suspension fixes the surface charge on the particles, which then determines the magnitude of electrostatic repulsion between them. At the iso-electric point (i.e.p.), repulsion is minimised and the suspension is strongly flocculated. At pH's not far removed from the i.e.p. the suspension is weakly flocculated due to the repulsive interactions from particle surface charges. Far from the i.e.p., electrostatic repulsion is so high that the particles are dispersed. In Figure 6.1, the effect of particle aggregation with changing pH is illustrated by the changing particle size distributions of increasingly flocculated ZrO₂ suspensions. The trimodal distribution of the dispersed suspension disappears to become monomodal as the suspension becomes weakly flocculated. Particles less than 0.5 μm form aggregates of mean size 1.3 μm. As the suspension is strongly flocculated, the mean aggregate size shifts upwards, skewing the distribution. Note that measurement of the aggregate size for strongly flocculated suspensions is unrealistic since a suspension in this state is really a continuous network. However, the observed trend of increasing aggregate size with increasing degree of flocculation is a good indicator of the changing structure of the suspension.

In Figure 6.2, the effect on compression for ZrO₂ suspensions with varying pH is shown. When the ZrO₂ is strongly flocculated at the i.e.p. of pH 7.0-7.2, the suspension is the least compressible, that is, for the same compressive stress the suspension is compressed only to a moderate concentration. Weakly flocculated ZrO₂ is easier to compress and
concentrations 0.03-0.04 by volume higher are attained for the same applied stress. At pH's far from the i.e.p., suspensions are fully dispersed, which on settling (much slower than flocculated suspensions) form a hard, highly concentrated layer on the bottom [Lange and Miller (1987)]. A sharp interface between the supernatant and the sediment is also not seen. The measurement of the compressibility of dispersed systems is thus not possible using both centrifuge techniques, and although not tried, pressure filtration would be difficult due to the formation of the hard, compact layer. These trends with pH were also seen for Al₂O₃ and TiO₂, although these results are not reported here. The trends agree with those observed by Chang, et al. (1994), Leong (1994), Velamakanni,
Figure 6.2 Effect of pH on $P_y(\phi)$; ZrO$_2$, $\phi_0 = 0.15$ (determined using the multiple speed technique).

et al. (1994), Channell and Zukoski (1997) and Franks and Lange (1997) for similar particle systems.

The effect of flocculation is better shown in Figure 6.3 by replotting the data in Figure 6.2 as $P_y$ versus pH for a series of constant concentration lines. The maximum in $P_y$ is at the i.e.p. (pH $\approx 7.2$) for all concentrations. This figure clearly shows that a greater compressive stress is required to produce the same concentration for strongly flocculated systems than for weakly flocculated systems. Figure 6.3 can be compared with the corresponding plot of shear yield stress, $\tau_y$, versus pH shown in Figure 6.4. In each plot, the pH of maximum $P_y$ and $\tau_y$ is identical. A relationship between $P_y$ and $\tau_y$ is developed later in the chapter.
Figure 6.3 Plot of $P_y$ versus pH for lines of constant concentration taken from Figure 6.2 plus additional data.
Figure 6.4 Shear yield stress versus pH for ZrO$_2$ of various concentrations.

The effect of flocculation on the hindered settling function was briefly investigated. The r(\(\phi\)) curves for weakly and strongly flocculated ZrO$_2$ suspensions are shown in Figure 6.5a). The corresponding P$_y$(\(\phi\)) data are shown in Figure 6.5b), where, as expected, the weakly flocculated data is to the right. An obvious difference in the r(\(\phi\)) results is not apparent. The weakly flocculated suspension has a slightly higher r(\(\phi\)) curve, especially at higher concentrations. This result is inconclusive and more experimental work is required. The r(\(\phi\)) function, however, has been suggested to be only weakly dependent on structural changes to the suspension [Eberl, et al. (1995)].
Figure 6.5 Effect of flocculation state on a) $r(\phi)$, and b) $P_y(\phi)$, for ZrO$_2$ suspensions; measured using the packed bed formation technique (device at University of Melbourne, cylinder diameter = 40.20 mm, fresh samples for each pressure).
6.2.2 INITIAL CONCENTRATION

The initial concentration, $\phi_0$, of the suspension used for the determination of the consolidation parameters $P_y(\phi)$ and $r(\phi)$ has an important influence on the values determined. A significant dependence of $P_y(\phi)$ on $\phi_0$ is shown in Figure 6.6 for strongly flocculated $\text{Al}_2\text{O}_3$ at its i.e.p.; that is, when $\phi_0$ increases, the $P_y(\phi)$ curve generally moves upwards or to the left and the suspension is less compressible. The same effect of $\phi_0$ on $P_y(\phi)$ is apparent for both strongly and weakly flocculated ZrO$_2$ as shown in Figure 6.7 and Figure 6.8. In each of the above cases, $P_y(\phi)$ was determined by the multiple speed technique. The $\phi_0$ effect thus appears to be a property of these metal oxide suspensions.

![Graph showing the effect of initial concentration on $P_y$](image)

**Figure 6.6** Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for strongly flocculated $\text{Al}_2\text{O}_3$ (pH 9.3-9.4) determined by the multiple speed technique.
Figure 6.7 Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for strongly flocculated ZrO$_2$ (pH 6.8-7.2) determined by the multiple speed technique.

In Figure 6.9, the $\phi_0$ effect is shown for weakly flocculated ZrO$_2$ determined by the concentration profile technique. The effect of $\phi_0$ on $P_y(\phi)$ is of similar extent to that in Figures 6.6, 6.7 and 6.8, but the trend is reversed in this case - that is, as $\phi_0$ increases, the $P_y(\phi)$ curve moves to the right and the suspension is more compressible. The initial concentration range in this experiment, however, is higher than that used in the experiments using the multiple speed technique. The initial concentrations used in each set of experiments only overlap at the lowest concentration. In Figure 6.9, no difference is observed between the $P_y(\phi)$ curves for $\phi_0 = 0.112$ and $\phi_0 = 0.178$. Conceivably, the trend with increasing initial concentration might reverse at a certain intermediate initial concentration for this system. A small reverse in the trend is also observed for strongly flocculated Al$_2$O$_3$ with $\phi_0 = 0.353$ in Figure 6.6. It is not expected that the effect of $\phi_0$
Figure 6.8 Effect of initial concentration, $\phi_0$, on $P_y(\phi)$ for weakly flocculated ZrO$_2$ (pH 5.6-5.7) determined by the multiple speed technique.

The trend in the data suggests that $P_y(\phi)$ is dependent on the technique used to determine $P_y(\phi)$. The agreement between the $P_y(\phi)$ results determined by the multiple speed technique and the concentration profile technique for the same sample was verified more than 20 times [see Chapter 4 and also Miller, et al. (1996)]. Further work is required to confirm the observed reversal in the trend with increasing $\phi_0$. Explanations for these initial concentration effects are postulated later in the chapter.
Figure 6.9 Effect of initial concentration on $P_y(\phi)$ for weakly flocculated ZrO$_2$ (pH 5.2-5.4) determined by the concentration profile technique.

The initial suspension concentration also appears to be an important factor in the determination of the hindered settling function. In Figure 6.10a, the effect of the initial concentration on $r(\phi)$ for strongly flocculated ZrO$_2$ suspensions is shown. The $r(\phi)$ curve is observed to shift significantly downwards as $\phi_0$ increases and approaches $\phi_b$. In Figure 6.10b, the corresponding $P_y(\phi)$ curve for the data determined in Figure 6.10a) is shown. A $\phi_0$ effect is not observed in the $P_y(\phi)$ data although errors in the technique could mask a minor effect.
Figure 6.10  a) Effect of initial concentration, $\phi_0$, on $r(\phi)$ for strongly flocculated ZrO$_2$ suspensions (packed bed formation technique using fresh samples at each pressure, device at University of Melbourne, cylinder diameter 40.20 mm). b) Corresponding $P_y(\phi)$ data determined with the $r(\phi)$ data in a).
6.2.3 STERIC STABILISATION

Polymeric additives change the surface chemistry of suspended particles and consequently affect the compression rheology. The addition of low molecular weight (Mw) polyacrylic acid (PAA) coats the particles with a thin layer of polymer that reduces the attractive forces between the particles by a steric separation (as discussed in Chapter 2, Section 2.5.2). In Figure 6.11, 1.0 dwb% of 2000 Mw PAA is added to a ZrO₂ suspension and Pₚ versus pH is plotted for a range of constant φ and compared with that of no additive. The effect on the compression behaviour is to shift the pH of maximum flocculation to a lower pH, and to increase the concentration for a given

![Figure 6.11](image)

**Figure 6.11** Effect of pH on Pₚ(φ) for ZrO₂ with and without 2000 Mw polyacrylic acid, φ₀ = 0.176 (multiple speed technique, curves taken at constant concentration).
compressive pressure. The suspensions are thus more compressible with the addition of low molecular weight PAA. The shear yield stress is similarly reduced by such an addition of PAA - see Figure 2.13 in Chapter 2.

6.2.4 SUSPENSION PREPARATION

The structural state of a suspension is strongly affected by the method used to prepare and flocculate the suspension [Leong (1994)]. The colloidal suspensions here are prepared from dry powder which typically consist of large agglomerates of particles formed from the process of spray drying and storage. To utilise the full colloidal surface area of the particles, these agglomerates must be dispersed to the primary particles before flocculation [Healy (1977)]. If primary particles are not formed, a very different structure is produced from the agglomerates which behave as large particles with a low overall surface area.¹

In this section, the compression rheology from two different suspension preparation methods is compared; sonication and high shear mixing. The effect of dilution on the structure of a suspension prepared by each of these methods is then investigated. An objective of these experiments was to explain the initial concentration effects observed previously.

6.2.4.1 Sonication and high shear mixing

The method of suspension preparation for rheological and compressional study is very important. In Figure 6.12, suspensions of weakly flocculated ZrO₂ were prepared by two methods and the Pₚ(φ) function was measured for each suspension. Refer to Chapter 3 for details of the suspension preparation methods used. The Pₚ(φ) curve for the suspension prepared by sonication is shifted slightly to the right compared with the

¹ Particulate suspensions produced from a wet process do not suffer these problems.
Figure 6.12 Effect of preparation method on $P_y(\phi)$ for weakly flocculated ZrO$_2$ (pH 5.5-5.7, $\phi_0 = 0.100-0.104$) determined by the concentration profile technique.

suspension prepared by high shear mixing using the Ultra-Turrax mixer. Agreement between the curves, however, is generally good and little effect due to the suspension preparation method is observed for these weakly flocculated ZrO$_2$. This agreement correlates with the unchanged particle size distribution of the suspensions prepared using each method as was shown in Figure 3.1. For strongly flocculated ZrO$_2$ (not shown here), little effect due to the suspension preparation method is also observed.

In Figure 6.13, a concentrated stock suspension of ZrO$_2$ ($\phi_0 = 0.262$) sterically stabilised with 1.0 dwb% 2000 Mw PAA was prepared in the weakly flocculated state (pH 6.0) using the high shear Ultra-Turrax mixer (solid line). 50 mL sub-samples were then sonicated for 1 min (dotted line). The $P_y(\phi)$ curve is shifted to the right for the
Figure 6.13 Effect of preparation method on $P_y(\phi)$ for weakly flocculated ZrO$_2$ sterically stabilised with 1.0 dwb% 2000 Mw PAA (pH 6.0, $\phi_0 = 0.262$) determined by the multiple speed technique.

additionally sonicated sample and is a stronger effect than that seen for the purely weakly flocculated sample with no steric stabilisation.

6.2.4.2 Dilution effects

To investigate the stability of the suspension structure, various suspensions were prepared, and each diluted in several ways. Samples of ZrO$_2$ suspension were prepared at $\phi = 0.15$ in the dispersed state (pH 3-4) using both sonication and the high shear Ultra-Turrax mixer. Suspensions were then adjusted to both the weakly and strongly
flocculated states, then diluted with distilled water to $\phi = 0.10$. To re-homogenise the suspensions after dilution, the suspensions were either re-sonicated or re-stirred using a low shear mixer. The grid of experiments performed is illustrated in Table 6.1.

<table>
<thead>
<tr>
<th>Initial $\phi_0$</th>
<th>Initial pH</th>
<th>Preparation</th>
<th>Final pH (Run 1)</th>
<th>Final pH (Run 2)</th>
<th>Preparation</th>
<th>Final $\phi_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>3-4</td>
<td>Sonication</td>
<td>5.4-5.6</td>
<td>7.0-7.2</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>0.10</td>
<td>3-4</td>
<td>High shear</td>
<td>5.4-5.6</td>
<td>7.0-7.2</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>0.15</td>
<td>3-4</td>
<td>Sonication</td>
<td>5.4-5.6</td>
<td>7.0-7.2</td>
<td>Dilute + low shear</td>
<td>0.10</td>
</tr>
<tr>
<td>0.15</td>
<td>3-4</td>
<td>High shear</td>
<td>5.4-5.6</td>
<td>7.0-7.2</td>
<td>Dilute + low shear</td>
<td>0.10</td>
</tr>
<tr>
<td>0.15</td>
<td>3-4</td>
<td>Sonication</td>
<td>5.4-5.6</td>
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<tr>
<td>0.15</td>
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<td>5.4-5.6</td>
<td>7.0-7.2</td>
<td>Dilute + sonication</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Table 6.1 Grid of experiments performed to determine the effect of preparation and dilution on $P_\gamma(\phi)$ for both weakly and strongly flocculated ZrO$_2$ suspensions (Runs 1 and 2 respectively).

The $P_\gamma(\phi)$ results from these 12 samples are not shown since very little difference in the compression rheology was observed between the differently prepared samples. The samples diluted from $\phi = 0.15$ to $\phi = 0.10$ showed very similar $P_\gamma(\phi)$ behaviour to those samples prepared initially at $\phi = 0.10$. Both the initial preparation method (sonication or high shear mixing) and the final preparation method after dilution (sonication or low shear mixing) had little effect on the $P_\gamma(\phi)$ behaviour. Finally, both the weakly and strongly flocculated suspensions behaved in the same way (although shifted as in Figure 6.2). The effects of dilution on the compression rheology of these ZrO$_2$ suspensions flocculated only by electrostatic forces (pH and ionic strength) are thus negligible.

In contrast, dilution had a significant effect on the sterically stabilised ZrO$_2$ suspensions. In Figure 6.14, 100 mL samples of the weakly flocculated stock suspension prepared in Section 6.2.4.1 ($\phi_0 = 0.262$) were diluted to $\phi_0 = 0.10$ in two ways: first by just stirring in water (dotted line); second by stirring in water and then sonicking for 2 min (dashed line). The resulting $P_\gamma(\phi)$ curves each lie significantly to the left of that for the original concentrated suspension (solid line). The trend observed by variation of the initial suspension concentration from the multiple speed technique in Section 6.2.2 is again reversed.
Figure 6.14 Effect of dilution on $P_y(\phi)$ for weakly flocculated ZrO$_2$ sterically stabilised with 1.0dwb% 2000 Mw PAA as determined by the multiple speed technique; • base suspension, high shear 5 min, ○ diluted just by stirring in water, □ diluted then sonicated for 2 min.

It is important to note that the PAA concentration on a dry weight basis is the same after dilution, however, on a volumetric basis, the PAA concentration is decreased by the dilution. If the PAA is not strongly bound to the particle surface, then on dilution the polymer would solubilise and become less effective in sterically stabilising the particles. The decrease in steric stabilisation would explain the shift to the left of the $P_y(\phi)$ curves. Sonication of the diluted suspension only partially recovers the original state.

In Figure 6.15, 50 mL samples of the stock suspension were diluted by stirring in water as before. The pH was adjusted to the strongly flocculated state (pH 4.5-4.6 for this PAA sterically stabilised sample), then one sample was sonicated for 20 s (dotted line),
while the other sample was just stirred (dashed line). The strongly flocculated suspensions are less compressible than the weakly flocculated suspension (solid line) in agreement with the results in Section 6.2.3. The strongly flocculated structure also appears stable since the $P_y(\phi)$ function is unchanged by further sonication. The compression results of these strongly flocculated, sterically stabilised suspensions thus appear to be independent of their method of preparation.

In summary, for suspensions both strongly and weakly flocculated by only electrostatic forces (pH and ionic strength), the measured $P_y(\phi)$ is unaffected by dilution. For sterically stabilised suspensions (using 2000 Mw PAA) that are strongly flocculated,
$P_x(\phi)$ is again unaffected by dilution, but if weakly flocculated, the measured $P_x(\phi)$ function is shifted to the left.

### 6.2.5 COMPRESSION HISTORY

The effect of compression history before measurement of the $P_x(\phi)$ function is an important consideration in the reproducibility of $P_x(\phi)$ measurements. In this section, a series of weakly and strongly flocculated ZrO$_2$ suspensions were prepared in bulk at two initial concentrations, $\phi_0 = 0.10$ and $\phi_0 = 0.19$, as illustrated in Table 6.2.

<table>
<thead>
<tr>
<th>$\phi_0$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>5.4-5.6</td>
</tr>
<tr>
<td>0.19</td>
<td>5.4-5.6</td>
</tr>
<tr>
<td>0.10</td>
<td>7.0-7.2</td>
</tr>
<tr>
<td>0.19</td>
<td>7.0-7.2</td>
</tr>
</tbody>
</table>

Table 6.2 Grid of ZrO$_2$ suspensions prepared for compression history experiments listed in Table 6.3 (400 mL samples prepared using high shear Ultra-Turrax mixer).

Samples from each of these bulk prepared suspensions were subjected to four different compression cycles, as illustrated in Table 6.3.

<table>
<thead>
<tr>
<th>Compression History</th>
</tr>
</thead>
<tbody>
<tr>
<td>One compression cycle</td>
</tr>
<tr>
<td>Two compression cycles (reslurried by low shear mixing)</td>
</tr>
<tr>
<td>Two compression cycles (reslurried by sonication)</td>
</tr>
<tr>
<td>Three compression cycles (reslurried by low shear mixing)</td>
</tr>
</tbody>
</table>

Table 6.3 Compression history cycles imposed on samples of each suspension in Table 6.2.

The number of individual samples in this experiment was thus 16. For each compression cycle, the suspension was centrifuged to an equilibrium state at 3000 rpm. Samples were reslurried with the supernatant to reproduce the initial solids
concentration by either low shear mixing or by sonication. After the final compression cycle, the $P_y(\phi)$ function for each sample was then determined using the concentration profile technique.

In Figure 6.16, the $P_y(\phi)$ results for the strongly flocculated ZrO$_2$ at $\phi_0 = 0.19$ are presented. After two compression cycles, the $P_y(\phi)$ function is shifted slightly to the right, meaning the suspension is able to be compressed to a higher concentration for the same applied pressure. The $P_y(\phi)$ function is shifted by an equal amount irrespective of the method used to reslurry the suspension between compression cycles. After a third compression cycle, a further shift of the $P_y(\phi)$ function to the right was observed, although this shift was not consistent across the entire concentration range.

![Figure 6.16](image)

**Figure 6.16** Effect of compression history on $P_y(\phi)$ for strongly flocculated ZrO$_2$ (pH 7.0-7.1, $\phi_0 = 0.190-0.197$) as determined by the concentration profile technique.
The same general trends in Figure 6.16 were observed for the other suspensions in Table 6.2 that were prepared at different initial concentrations and in different flocculation states. In all cases, the pre-compressed samples were able to be compressed to slightly higher concentrations on subsequent compression cycles. Note that the clear and uniform trends observed in Figure 6.16 for the strongly flocculated ZrO₂ at \( \phi_0 = 0.19 \) were not always observed for these other suspension conditions.

### 6.3 DISCUSSION

Manipulation of the flocculation state of a suspension is an extremely useful mechanism to attain a highly concentrated product in an industrial consolidation process. Changing the surface chemistry in the suspension is often cheaper than the high capital cost of installing additional consolidation equipment [Wakeman, et al. (1989)]. For the metal oxide suspension systems examined here, adjustment of the pH is an easy way to control the flocculation state of the system. The optimum state for maximum consolidation under a given applied pressure is to make the suspension only very weakly flocculated. Here, the \( P_y(\phi) \) function is shifted far to the right whilst still maintaining a clear supernatant and moderate consolidation rates. The salt level should be controlled to attain a weakly flocculated state at a reasonable pH, and so that the suspension in that state it is not highly sensitive to small changes in pH. In addition to weak flocculation of the suspension, steric stabilisation of the particles in suspension using a low molecular weight polymer, further reduces the compressive yield stress for a given concentration. The combined effect of weak flocculation and steric stabilisation on the ZrO₂ suspensions increased the concentration at a given applied pressure approximately 0.06-0.09 volume fraction - a significant result.

It is useful to normalise the \( P_y \) and \( \tau_y \) versus pH plots in Figure 6.3 and Figure 6.4 with respect to the maximum yield stress for each concentration. The normalised plots are shown in Figure 6.17. The data in both the \( P_y \) and \( \tau_y \) plots collapse on to single curves, independent of the concentration. The collapse of the \( \tau_y \) curves has also been seen by Leong, et al. (1993a), Liddell (1996), Ramakrishnan and Malghan (1996) and Scales, et
Figure 6.17 a) Plot of normalised $P_y$ versus pH for data from Figure 6.3. b) Plot of normalised $\tau_y$ versus pH for data from Figure 6.4.
In the $\tau_y$ plot there is a pH at which the particles become fully dispersed and the shear yield stress is zero (pH 5.5 and pH 10.3 for the acidic and basic regimes respectively). In the $P_y$ plot, however, a zero compressive yield stress is not observed for the range in pH of the suspensions studied. The overall agreement in the shape of the $P_y$ and $\tau_y$ curves suggest that the mechanism of breaking bonds between particles in shear is related to that of the mechanism of breaking bonds in compression. The difference between the $P_y$ and $\tau_y$ curves for the weakly flocculated suspensions ($\tau_y = 0$, $P_y > 0$) suggest a different mechanism for compression in the weakly flocculated state.

A significant effect of the initial suspension concentration on $P_y(\phi)$ was found in Section 6.2.2. The magnitude of the effect is illustrated in Figure 6.18 by replotting the data in

**Figure 6.18** Plot of $P_y$ versus $\phi_0$ for lines of constant concentration taken from Figure 6.7 and Figure 6.8 for strongly and weakly flocculated ZrO$_2$; filled symbols - strongly flocculated (pH 6.8-7.2), unfilled symbols - weakly flocculated (pH 5.6-5.7).
Figure 6.7 and Figure 6.8 as $P_y$ versus $\phi_0$ for a series of constant concentration lines. Over the range in initial concentrations used, the measured compressive yield stress increased 40-60% for the strongly flocculated ZrO$_2$ and 80-140% for the weakly flocculated ZrO$_2$. A similar order of effect is also observed for Al$_2$O$_3$ from Figure 6.6. Two explanations are postulated here for these initial concentration effects [also observed by Miller, et al. (1995) for Al$_2$O$_3$ and cement paste]. The first explanation is based on kinetic considerations; the second is based on structural considerations.

In the kinetic model, if the initial state is a weakly structured, open network of particles with few connecting bonds, then under compression, particles have space to move to a semi-ordered state at a high concentration [Chang, et al. (1991); Zhou and Uhlig (1993)]. However, if the initial suspension is already highly concentrated, then a rigid suspension structure may constrain the movement of particles under compression. The concentration achieved will thus be lower since the particles cannot pack as well compared with if they had started in the diluted state. The initial concentration effects seen in Figures 6.6, 6.7 and 6.8 follow the trend suggested by this argument.

Another qualitative mechanism that describes these initial concentration effects is based on an examination of the suspension microstructure. Two suspensions of the same initial concentration may have very different microstructures. Various models for the structure of flocculated suspensions have been postulated [Van den Tempel (1979); Stewart and Sutton (1984); Bhatty, et al. (1989); Shih, et al. (1990); Stenfge (1993); Potanin, et al. (1995); Potanin and Russel (1996)]. A model proposed by Michaels and Bolger (1962) considers the basic structural units to be clusters of particles - flocs. These flocs group to form aggregates. These aggregates then join to form extended networks that give the suspension its structural properties. A two-dimensional schematic of such a structure is shown in Figure 6.19a). A suspension thus may consist of dense aggregates of particles joined by relatively few bonds and contain large void spaces between the aggregates. Evidence for this type of structure has been obtained by Farrow and Warren (1989) using floc size and density measurements. The other extreme in configuration for a flocculated suspension is a dense structure of interlinked chains of flocs such as illustrated in Figure 6.19b). The formation of such a flocculated network has been simulated by ballistic aggregation [Healy (1992); Healy et al. (1993)].
Figure 6.19 Schematic of two possible microstructures of a flocculated suspension; a) aggregated structure, b) interlinked chain-like structure (the number of flocs in each drawing is the same).

Here, each new particle allowed to fall on a growing network is stuck irreversibly in the position where it hits a previously placed particle. Large voids and long chains of particles are evident from this simulation\(^2\). Now, the compressive yield stress is

\(^2\) If repulsive forces on the particles are increased (particles are less sticky), a denser network is observed since incoming particles seek low energy regions. The higher concentrations attained by weakly flocculated and sterically stabilised suspensions are thus correctly simulated.
proportional to the number of bonds between particles - characterised by the coordination number, the average number of nearest neighbours to each particle [Van den Tempel (1979); Kapur, et al. (1997)]. The initial compression of an aggregated structure involves the yielding of relatively few bonds and inter-aggregate fluid is expelled rapidly. The second, slower stage of compression involves the squeezing out of the intra-aggregate fluid as flocs within the aggregates move closer together. In comparison, the compression of a chain-like structure involves the continuous yielding of many bonds - similar to the second stage compression of an aggregated structure. It is conceivable that the microstructure at any particular concentration might progressively change from an aggregated structure to a homogenous chain-like structure as the initial concentration of the suspension increases. The compressive yield stress would thus directly increase for a given concentration. Although this argument has no experimental basis, it again explains the \( P_y(\phi) \) trends observed in Figures 6.6, 6.7 and 6.8 when the initial concentration of the suspension is changed.

The initial concentration effects may be caused by a combination of both the kinetic and the structural models. To further understand the initial concentration effects, the effect on compression of different methods of suspension preparation was examined. For both weakly and strongly flocculated ZrO\(_2\) suspensions with no polymeric additives, negligible difference was observed between sonicated and high shear mixed samples and for samples prepared at a higher concentration then diluted to the test concentration. The reproducibility of the suspension preparation methods and the \( P_y(\phi) \) measurement techniques are thus further validated. The observed initial concentration effects are thus not caused by differences in the preparation of the suspensions at each concentration.

Of concern is the observed change in direction of the \( P_y(\phi) \) trend with initial concentration at high initial concentrations (Figure 6.9). The mechanism for this change in trend is not understood and it is difficult to postulate a mechanism to explain it. Further work is required to investigate this initial concentration phenomena.

The effect of the initial suspension concentration in consolidation tests has important ramifications when industrial processes are examined. For example, in the optimisation or design of thickeners, samples for consolidation tests should either be taken from the thickener feed-well directly after flocculation, or prepared at the concentration and
conditions in the feed stream. The suspension sample to be tested will thus have a representative structure to that in the actual process. It should be noted however that if the initial concentration is below the gel concentration $\phi_c$, the final equilibrium height in the centrifuge or pressure filter will be low and hence measurement accuracy will suffer.

In Section 6.2.4, the compression rheology of PAA sterically stabilised ZrO$_2$ suspensions was sensitive to the preparation method. For weakly flocculated, sterically stabilised samples, sonication shifted the $P_r(\phi)$ curve to the right. For strongly flocculated, sterically stabilised samples, no difference was observed between sonicated or sheared suspensions (contrary to that observed by Mills, et al. (1991) for flocculated polystyrene latex suspensions under shear). Weak bonding between the polymer and the particle surface may explain this behaviour. When weakly flocculated, the sonication may evenly distribute the polymer around the particles in suspension, indicating that the suspension structure is weakened by the sonication and is more compressible. When diluted, the polymer may detach from the particle and solubilise. The suspension would then become unstable, as observed by the shift of the $P_r(\phi)$ curves to the left, and approach the case where no polymer is added. Dilution of strongly flocculated suspension has no effect perhaps because the network bonding is strong enough to prevent movement of the polymer. Samples of sterically stabilised, weakly flocculated suspensions thus should be sonicated separately before compression to separate the particles as much as possible. Sterically stabilised, strongly flocculated suspensions are stable and are less of a problem. The effect of initial concentration was not examined for the sterically stabilised suspensions.

The compression history effects observed in Section 6.2.5 can be used advantageously in an industrial consolidation process. A two or more stage compression process with intermediate shearing between stages may increase the final product concentration. Although the effect of multiple compression stages was only small for the ZrO$_2$ suspensions examined here, a larger effect might be evident for other suspension systems and is certainly worth investigation. Liddell and Boger (1994) also observed significant rheological differences for TiO$_2$ suspension systems consolidated by two different pressure filtration operations. A high pressure operation produced a stronger material in shear (higher viscosity and shear yield stress) than that produced under low
pressure at the same concentration. This knowledge of the effect of compression history on the rheology was useful in the optimisation of the production process.

### 6.4 CORRELATION BETWEEN SHEAR AND COMPRESSIVE YIELD STRESSES

It is useful to compare the shape and order of magnitude of $P_y(\phi)$ and $\tau_y(\phi)$ curves. In Figure 6.20a) are plots of $\tau_y(\phi)$ and $P_y(\phi)$ on log-log coordinates for strongly and weakly flocculated ZrO$_2$ with no additives. The data are fitted to power laws of the forms

$$P_y(\phi) = A \phi^m,$$

$$\tau_y(\phi) = D \phi^p,$$

where $A$, $m$, $D$ and $p$ are constants. For the data in Figure 6.20a), the values for these constants are listed in Table 6.4.

<table>
<thead>
<tr>
<th>pH</th>
<th>A</th>
<th>m</th>
<th>D</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>6.3×10^8</td>
<td>6.7</td>
<td>7.4×10^6</td>
<td>5.6</td>
</tr>
<tr>
<td>5.7</td>
<td>4.7×10^8</td>
<td>6.9</td>
<td>1.1×10^7</td>
<td>6.3</td>
</tr>
</tbody>
</table>

**Table 6.4** Power law constants for fit of ZrO$_2$ data in Figure 6.20a).

The exponents, $m$ and $p$ are approximately equal (within fitting error) for both the $\tau_y(\phi)$ and $P_y(\phi)$ curves as evidenced by their parallel nature in Figure 6.20a). The pre-exponential factors for $P_y(\phi)$, A, are between 40 and 90 times greater than that for $\tau_y(\phi)$, D, as evidenced by the axis scales in Figure 6.20a). A relation between $\tau_y(\phi)$ and $P_y(\phi)$ may be written by the substitution of Equation (6.2) in Equation (6.1) to yield

$$P_y(\phi) = A \left( \frac{\tau_y(\phi)}{D} \right)^{m/p}.$$  

(6.3)

If $m$ and $p$ are equal then a linear relation between $P_y$ and $\tau_y$ is obtained. For the strongly and weakly flocculated ZrO$_2$ in Figure 6.20a), the $P_y$ versus $\tau_y$ plots are shown in Figure 6.20b).
Figure 6.20  a) Compressive and shear yield stresses as a function of concentration for both weakly and strongly flocculated ZrO₂.  b) Compressive yield stress prediction from shear yield stress using data in a).
The corresponding curves for strongly and weakly flocculated TiO$_2$ are shown in Figure 6.21. The values for the power law fitting constants for these $P_y(\phi)$ and $\tau_y(\phi)$ curves are shown in Table 6.5.

<table>
<thead>
<tr>
<th>pH</th>
<th>A</th>
<th>m</th>
<th>D</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>3.0×10$^{16}$</td>
<td>32</td>
<td>2.7×10$^{4}$</td>
<td>4.4</td>
</tr>
<tr>
<td>5.8</td>
<td>1.3×10$^{15}$</td>
<td>32</td>
<td>7.0×10$^{4}$</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 6.5 Power law constants for fit of TiO$_2$ data in Figure 6.21a).

The $P_y(\phi)$ curves for TiO$_2$ are extremely steep for $\phi > 0.40$. The $\tau_y(\phi)$ curves are also expected to diverge at a similar concentration. The magnitudes of the exponents, $m$ and $p$, are very different for the $\tau_y(\phi)$ and $P_y(\phi)$ curves for TiO$_2$. The relationship found for ZrO$_2$, where the exponents were similar for both $\tau_y(\phi)$ and $P_y(\phi)$, is thus not a generic property of suspensions and is material dependent. More experimental work using a range of materials is required to further investigate the relation between the rheology of suspensions in shear and compression.

The combined $P_y$ versus $\tau_y$ plots for TiO$_2$ in Figure 6.21b) are in different positions when compared with those for ZrO$_2$ in Figure 6.20b). Again, this difference is a consequence of the very different shear and compression rheology for ZrO$_2$ and TiO$_2$.

The prediction of $P_y(\phi)$ from $\tau_y(\phi)$ measurements is extremely useful since the determination of $P_y(\phi)$ can take many weeks using the commonly available centrifuge methods, whereas $\tau_y(\phi)$ measurements can be completed in days. From the limited data in Figure 6.20a), which show similar power law exponents for both strongly and weakly flocculated ZrO$_2$, a relation dependent on the state of floculation of the material could also be developed.

A problem with the relation between $P_y$ and $\tau_y$ is the limited overlap of $P_y(\phi)$ and $\tau_y(\phi)$ data. Measurement of $\tau_y(\phi)$ is only possible up to a certain concentration using the vane technique, beyond which the preparation of a homogenous sample is impossible. The insertion of the vane in a highly concentrated suspension can also destroy the structural integrity of the suspension leading to incorrect readings. Measurement of low $P_y(\phi)$ data close to the gel concentration is possible using a low speed centrifuge as was illustrated in Figures 4.25 and 4.26 in Chapter 4. The limiting factor in the successful
Figure 6.21  a) Compressive and shear yield stresses as a function of concentration for both weakly and strongly flocculated TiO$_2$. b) Compressive yield stress prediction from shear yield stress using data in a).
prediction of $P_y$ from $\tau_y$ is thus the measurement of $\tau_y$ at the required concentration attained in the compression process. In a continuous thickening application where the compressive forces are not large, the $\tau_y$ of the underflow is low enough to be measured since it must be pumpable. The $P_y$ at the thickener bottom could thus be estimated.

It is perhaps obvious, but extrapolation of either the $P_y(\phi)$ or $\tau_y(\phi)$ curves to predict the compression rheology of the suspension is inherently dangerous.

Other workers have also compared the compression rheology with the shear rheology for various systems. Shin and Dick (1975) first compared $P_y(\phi)$ and $\tau_y(\phi)$ for water treatment plant sludges and found a linear relation. Buscall, et al. (1986, 1987, 1988) compared $P_y(\phi)$ with $\tau_y(\phi)$ for polystyrene latex. Alderman, et al. (1991) and Meeten and Sherwood (1994) found that $P_y(\phi)/\tau_y(\phi) \approx 8.3$ for bentonite clay suspensions. Meeten (1994) also examined bentonite clay suspensions and related $P_y$ to $\tau_y$ via Poisson’s ratio, $\nu$, assuming linear elastic theory. Channell and Zukoski (1997) also used a similar approach to model flocculated $\text{Al}_2\text{O}_3$ suspensions. Using Poisson’s ratio to predict $P_y(\phi)$ from $\tau_y(\phi)$ data, however, is difficult since small changes in $\nu$ produce large changes in $P_y$. The empirical approach to relate $P_y(\phi)$ to $\tau_y(\phi)$ is the best technique currently available.

### 6.5 CONCLUSIONS

In this chapter, the general consolidation model was tested using suspensions with a range of bulk properties. It was found that compression rheology is dependent on the structural state of the suspension as controlled by the surface chemistry. Factors investigated were the flocculation state, the initial concentration, steric stabilisation by polymeric additives, preparation methods, and prior shear and compression history.

As found in Chapters 4 and 5, the consolidation properties of a given suspension can be measured consistently using several different techniques. To measure $P_y(\phi)$ and $\tau(\phi)$ reproducibly, regardless of the technique used, the suspension preparation method and prior shear and compression history on the system must be carefully controlled.
From this investigation, the conditions to attain maximum consolidation can be stated. The techniques listed below shift the $P_y(\phi)$ curve to the right; thus for the same applied stress, a higher concentration is attained. In order of effectiveness, these are:

- weak flocculation - as controlled by pH and ionic strength,
- steric stabilisation of the suspension particles with a low molecular weight polymer,
- a low initial suspension concentration, and
- the use of multiple compression stages.

The effect of each technique listed above for a particular suspension system in a particular consolidation process would vary. The techniques may be combined to further enhance the consolidation.

The effect of the initial suspension concentration on the measurement of both $P_y(\phi)$ and $r(\phi)$ was significant. To obtain reliable data, the actual initial concentration of the process suspension should be used in the measurements. Explanations based on kinetic and structural considerations were postulated for these initial concentration effects.

A simple empirical relation between $P_y(\phi)$ to $\tau_y(\phi)$ was developed. Prediction of $P_y$ based on an experimentally fast and simple measurement of $\tau_y$ is then possible. A generic relationship between $P_y(\phi)$ and $\tau_y(\phi)$ for suspensions was not found.
Chapter 7

CONTINUOUS THICKENER MODELLING AND DESIGN

7.1 INTRODUCTION

With the systematic investigation of the suspension consolidation parameters, $P_y(\phi)$ and $r(\phi)$, now complete, a demonstration of the application of these parameters to a real consolidation problem is desired. Eberl, et al. (1995) have already successfully predicted the behaviour of kaolin suspensions in high pressure filtration from measured $P_y(\phi)$ and $r(\phi)$ data. A model for steady state continuous gravity thickening has been similarly developed (see Chapter 2, Section 2.6), but has never been applied to an industrial problem. In this chapter, an industrial continuous gravity thickener is modelled based on $P_y(\phi)$ and $r(\phi)$ measurements of the process suspension. Both the steady state concentration profile and the bed height in the thickener required to produce a certain underflow concentration are predicted from the model. Optimisation of the thickener by manipulation of the suspension properties is then possible.

As a case study, samples were obtained from a large scale continuous gravity thickener concentrating bauxite residue or red mud, the waste from alumina production. The $P_y(\phi)$ and $r(\phi)$ functions of thickener underflow samples were measured and entered in the model. Here, the concentration profile and bed height predicted from the model are compared with those measured at the actual plant. A sensitivity analysis on the model is then performed to determine the effect of variations in the measured parameters.
7.2 CONTINUOUS THICKENER CASE STUDY

The red mud continuous thickener in this case study is at the Alcoa alumina refinery at Wagerup, Western Australia [Marunczyn and Laros (1992); Cooling (1995)]. The dimensions of the thickener are illustrated in Figure 7.1. The thickener radius is \( R_0 = 37.5 \text{ m} \). The liquid level is 10.95 m above the apex of the conical base. The vertical height of the conical base is \( z_w = 6.65 \text{ m} \). The conical base is truncated at a height \( z_b = 0.71 \text{ m} \) above the apex.

The red mud enters the central thickener feed-well where flocculant is added under strong agitation. The flocculated red mud then enters the quiescent thickener just below the liquid surface at an initial concentration of \( \phi_0 = 0.0194 \). Supernatant overflows the outer rim of the thickener and is returned to the process. A series of rakes of different radial length rotate in the thickener and move sediment towards the centre where the underflow is removed. The effect of rakes is not considered in the thickener model and is a complex problem [Chandler (1983)]. Underflow from the thickener, at a concentration of \( \phi_u = 0.2522 \), is pumped by centrifugal and positive displacement pumps to the disposal area.

The concentration profile in the thickener was measured by sampling the bed at various heights using a long probe [Cooling (1995)]. The sample location was a distance 18.9 m from the thickener centre. The measured thickener concentration profile is shown in Figure 7.2.

![Figure 7.1 Approximate scale drawing of the red mud continuous thickener at Wagerup, Western Australia.](image-url)
Figure 7.2 Measured continuous thickener concentration profile at Wagerup, 18.9 m from the thickener centre.

The total thickener underflow throughput when the concentration profile was measured was 260 tonne/h. The equivalent solids volumetric throughput using the measured underflow concentration is $Q_p = 42.5 \, m^3/h$.

### 7.3 SUSPENSION PROPERTIES

A sample of red mud from the Wagerup thickener was taken from the underflow stream both before and after the centrifugal pump. Ideally, the actual feed to the thickener should be used, but as flocculation of the feed occurred in the feed-well, representative samples of the flocculated feed entering the thickener were unobtainable. The
underflow sample thus has a shear and compression history that could affect the measured consolidation properties. Red mud is also highly thixotropic - shear reduces the viscosity and shear yield stress and these properties only slowly recover over time [Nguyen (1983); Nguyen and Boger (1985b); Green, et al. (1994); Pashias, et al. (1996); Pashias (1997)]. These facts must be considered when the results are analysed.

The red mud sample was a typical underflow sample from the Wagerup thickener. The sample was fully characterised by Pashias (1997) and some of that data is used here.

The solids density for the red mud was \( \rho_s = 3,150 \text{ kg/m}^3 \) [Pashias (1997)].

The particle size distribution for the red mud is detailed in Table 7.1.

<table>
<thead>
<tr>
<th>Size range</th>
<th>Size (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{10} )</td>
<td>1.242</td>
</tr>
<tr>
<td>( d_{50} )</td>
<td>13.52</td>
</tr>
<tr>
<td>( d_{90} )</td>
<td>132.6</td>
</tr>
</tbody>
</table>

**Table 7.1** Particle size distribution by volume for red mud at Wagerup as determined using a Coulter LS130 [from Pashias (1997)].

The gel concentration for the red mud, measured by batch settling, was \( \phi_g = 0.24 \) (see Appendix F). However, examination of the measured thickener concentration profile in Figure 7.2, where the concentration near the top of the bed suddenly increases from 0.0038 to 0.10-0.15, indicates that the true gel concentration is likely to be in this range. The \( \phi_g \) determined from a single batch settling experiment is thus significantly overestimated. The value chosen for modelling the profile was \( \phi_g = 0.0871 \) (from curve fitting). A sensitivity study is conducted in Section 7.6 to determine the effect of variation in \( \phi_g \).

The \( P_y(\phi) \) function for the red mud sample, measured by the multiple speed centrifuge technique by Pashias (1997), and also measured by the packed bed formation technique, is shown in Figure 7.3. Good agreement between each technique is observed, although pressure filtration data was only obtainable at relatively high pressures. A significant difference between the samples taken before and after the centrifugal pump is evident, thus highlighting the thixotropic nature of the red mud. None of this data, however, lie in the concentration range of the operating thickener. This is a major problem as
Figure 7.3 Compressive yield stress of red mud thickener underflow.

extrapolation of the data to lower concentrations must be done. For the thickener model, the $P_y(\phi)$ data from before the centrifugal pump is fit to Equation (2.47), where $A = 3.83 \times 10^{-3}$ Pa, $m = 11.8$ and $\phi_g = 0.0871$.

The $r(\phi)$ function for red mud is shown in Figure 7.4, as measured by the packed bed formation technique. The data obtained is at high concentrations and only over a very small concentration range. The $r(\phi)$ data must thus again be extrapolated. For the thickener model, the $r(\phi)$ data is fit to Equation (5.2) (solid line in Figure 7.4), where $C = 2.156 \times 10^{11}$ Pa.s/m² and $n = -4.329$. The error associated with each $r(\phi)$ fitting parameter is large.
Figure 7.4 Hindered settling function for red mud thickener underflow measured by the packed bed formation technique (device at University of Melbourne, cylinder diameter = 28.40 mm, $\phi_0 = 0.176-0.182$).

7.4 THICKENER MODEL

The algorithm for the determination of the concentration profile, $\phi(z)$, and the bed height, $H$, for a continuous gravity thickener is outlined below. Implementation of this algorithm was done in Microsoft FORTRAN.

INPUT $\Delta \rho, \phi_g, \phi_0, \phi_u, z_0, z_w, R_0, P_y(\phi), r(\phi), N$

where $N =$ number of steps in concentration profile required.

OUTPUT $\phi(z), H$. 
Chapter 7

Step 1. Scale thickener heights using Equation (2.45); $z_b \rightarrow Y_b$, $z_w \rightarrow Y_w$.

Step 2. Calculate $P_y(\phi_u)$ from Equation (2.47).

Calculate $r(\phi_0)$ from Equation (2.48).

Calculate scaled flux, $\beta$, from Equation (2.52).

Step 3. Start at bottom of bed, where $\phi = \phi_u$ and $Y = Y_b$.

Step 4. Determine scaled cross-sectional area, $\alpha(Y)$, from Equation (2.46).

Step 5. Determine scaled $r(\phi)$ function, $R(\phi)$, from Equation (2.50).

Step 6. Determine scaled $P_y(\phi)$ derivative, $f'(\phi)$, from Equations (2.47) and (2.49):

$$f'(\phi) = \frac{m}{\phi_g} \left( \frac{\phi}{\phi_g} \right)^{m-1} \left[ \left( \frac{\phi_u}{\phi_g} \right)^m - 1 \right].$$  \hspace{1cm} (7.1)

Step 7. Determine $B(\phi, \phi_0, \phi_u)$ from Equation (2.54).

Step 8. Integrate $dY/d\phi$ in Equation (2.53) using a Runge-Kutta technique.

Step 9. Decrease $\phi$ by $(\phi_g - \phi_u)/N$.

Step 10. Repeat Steps 4-9 until $\phi = \phi_g$. The scaled bed height, $Y = L$, is thus determined.

Step 11. Re-dimension concentration profile and bed height using Equations (2.45) and (2.55); $\phi(Y) \rightarrow \phi(z)$, $L \rightarrow H$.

Step 12. Output $\phi(z)$ and $H$.

To determine the bed height versus underflow concentration curve, the entire algorithm is repeated for a range of $\phi_u$ starting from $\phi_0$. The final bed height, $H$, is recorded for each $\phi_u$ value.

It should be noted that the solution of the differential equation, Equation (2.53), can diverge and become intractable [discussed in Landman, et al. (1988)]. In the denominator of Equation (2.53), the criteria, $[\beta / \alpha(Y)] B(\phi, \phi_0, \phi_u) < 1$, must always be
satisfied. For certain values of $\phi_0$, $\phi_u$ and/or the $\alpha(Y)$ function, this criteria is not met for certain $\phi$. The numerical solution of the differential equation then halts. The thickener therefore cannot operate with these parameters.

7.5 CONTINUOUS THICKENER MODEL

The thickener dimensions and measured suspension properties detailed in Sections 7.2 and 7.3 were entered in the model. In Figure 7.5a), the concentration profile predicted from the model is compared with that measured at the plant. Agreement is poor. For an underflow concentration of $\phi_u = 0.2522$, a bed height of 2.88 m is predicted, whereas the actual bed height is about 8.70 m.\(^1\) In Figure 7.5b), the bed height required to produce a certain underflow concentration is plotted. For a bed height of 8.70 m, an underflow concentration of $\phi_u = 0.35$ is predicted from this plot, whereas the actual underflow concentration is $\phi_u = 0.2522$. The solution diverged for $\phi_u < 0.31$ (dashed line indicates the height at which the solution halted). At low $\phi_u$ the solution is close to the singularity at the apex of the conical section ($\alpha(0) = 0$). The criteria, $[\beta / \alpha(Y)] B(\phi, \phi_0, \phi_u) < 1$, was not met at a certain $\phi$ in the solution and the solution failed. The predicted concentration profile in Figure 7.5a) is thus not completely correct since the solution failed at $\phi \approx 0.12$. The failure of the solution so close to $\phi_u$ at the top of the bed does not explain the poor agreement between the measured and predicted concentration profiles.

There are many possible causes for the large discrepancies between the measured and predicted concentration profiles and bed heights. The effects of variations in the measured suspension parameters are evaluated in the next section. Other possible effects, including raking and channelling are then discussed.

The thickener throughput is checked using Equation (2.51). The solids throughput calculated with this equation is completely dependent on the value used for $(\lambda/V_p) r(\phi_0)$. From extrapolation of the $r(\phi)$ curve fit in Figure 7.4 to $\phi = \phi_0$, the solids throughput is $Q_p = 0.029 \text{ m}^3/\text{h}$. Using different, but equally valid, $r(\phi)$ curve fitting parameters to the

\(^1\) Bed heights quoted are measured from the apex of the conical base, that is, including $z_0$. \hfill
Figure 7.5  a) Comparison of the measured red mud continuous thickener concentration profile at Wagerup, with that predicted from the model using measured suspension parameters.  b) Corresponding bed height versus underflow concentration plot (the dashed curve indicates where the solution diverged for that range in $\phi_u$).
raw data in Figure 7.4 (C = 3.0 \times 10^{10} \text{ Pa.s/m}^2, n = -8.258), Q_p = 0.19 \text{ m}^3/\text{h}. The actual solids throughput is \( Q_p = 42.5 \text{ m}^3/\text{h} \). To obtain this \( Q_p \) value using Equation (2.51), \((\lambda/V_p) \, r(\phi_0) = 1.58 \times 10^8 \text{ Pa.s/m}^2\), two orders of magnitude smaller than that predicted from the extrapolated \( r(\phi) \) data. The particle size predicted using \( C = 1.58 \times 10^8 \text{ Pa.s/m}^2 \) in Equation (5.5) is \( d_p = 10.7 \mu\text{m} \), comparable with the measured average particle size, \( d_{50} = 13.52 \mu\text{m} \) in Table 7.1. Extrapolation of the \( r(\phi) \) data measured by the packed formation technique to find \((\lambda/V_p) \, r(\phi_0) \) is thus completely inappropriate for the prediction of the thickener throughput when \( \phi_0 \ll \phi_e \). The existence of channels in the sediment could explain the problem. Chandler (1983) found that the permeability (inversely proportional to \( r(\phi) \)) measured by filtration techniques can be \( 10^5 \) higher if channels exist. An alternative measurement technique for \( r(\phi) \) at low concentrations is required. Direct measurement of the settling velocity of the flocculated particles at the required concentration may be a superior technique.

In the design of a new thickener, the thickener solids throughput is normally fixed. The design problem is to determine the thickener area required for a particular throughput - again dependent on \((\lambda/V_p) \, r(\phi_0) \) in Equation (2.51). The accurate measurement of \((\lambda/V_p) \, r(\phi_0) \) is thus a major area for further investigation.

### 7.6 SENSITIVITY ANALYSIS

The effects of variations in the measured suspension parameters on the predicted thickener concentration profile and bed height are evaluated here in a systematic sensitivity analysis.

The greatest error in the model is most likely due to extrapolation of the \( P_y(\phi) \) and \( r(\phi) \) data to low concentrations. The effect on the predicted concentration profile of changing the gradient and position of the \( P_y(\phi) \) function is examined in Figure 7.6 and Figure 7.7. To determine the effect of changing the gradient, the \( P_y(\phi) \) function required to best fit the measured concentration profile was found by trial and error (using the measured \( r(\phi) \) function). A range of \( P_y(\phi) \) functions were entered in the model; a range
Figure 7.6  a) Compressive yield stress functions for determination of the concentration profiles in a red mud continuous thickener; including curve fits of the raw data, and curve fits using a range of the exponent m to form bed heights of 8.70 m.  b) Corresponding concentration profiles predicted for the continuous thickener at Wagerup using the $P_y(\phi)$ functions in a).
in the curve fit exponent, \( m \), were used and the pre-exponential factors, \( A \), were varied to form bed heights of 8.70 m. The \( P_y(\phi) \) functions used are shown in Figure 7.6a. As the exponent increases, the gradient of the \( P_y(\phi) \) function increases as expected (by design, the curves intersect at \( \phi_0 \)). Also in Figure 7.6a are the measured \( P_y(\phi) \) functions from Figure 7.3, including the extrapolated curve fit used to determine the concentration profile in Figure 7.5a).

The effect of these \( P_y(\phi) \) functions on the predicted thickener concentration profile is illustrated in Figure 7.6b). As the curve fit exponent \( m \) increases, the concentration profiles become steeper near the bottom and shift to the right. The measured concentration profile data is best fit using an exponent \( m = 10 \). This value is comparable with that of the measured \( P_y(\phi) \) where \( m = 11.8 \), as indicated by the similar gradients of the curves in Figure 7.6a). The \( P_y(\phi) \) function required to generate the measured concentration profile, however, is positioned well to the left of the measured \( P_y(\phi) \) data and extrapolated curve.

To determine the effect of moving the \( P_y(\phi) \) function horizontally, a range of \( P_y(\phi) \) functions were entered in the model using a constant exponent, \( m = 10 \), and a range of the pre-exponential factor, \( A \). The \( P_y(\phi) \) functions used are shown in Figure 7.7a), including the best fit to the measured concentration profile where \( A = 0.853 \). As the pre-exponential factor increases, the \( P_y(\phi) \) curve is moved to the left. The effect of these \( P_y(\phi) \) functions on the predicted thickener concentration profile is shown in Figure 7.7b). As the pre-exponential factor increases, the bed height increases but the shapes of the concentration profiles remain the same. The bed height is very sensitive to the value of the pre-exponential factor. The change in \( A \) from 0.2 to 1.0 shifted the \( P_y(\phi) \) function only 0.02-0.05 volume fraction units to the left, but the predicted bed height changed from 3.40 m to 9.98 m, a significant difference. The effects of errors in extrapolation of the measured \( P_y(\phi) \) data on the predicted concentration profile are thus large.

The effect of variation in \( r(\phi) \) on the predicted thickener concentration profile is similarly examined. In Figure 7.8, the concentration profiles predicted for a range of the \( r(\phi) \) curve fit exponent, \( n \), are shown (using the \( P_y(\phi) \) function where \( m = 10 \)). As the curve fit exponent \( n \) increases, the predicted bed height increases but the shapes of the concentration profiles remain the same. The overall effect of variation in the \( r(\phi) \)
Figure 7.7  a) Compressive yield stress functions for determination of the concentration profiles in a red mud continuous thickener; including curve fits of the raw data, and curve fits using a constant exponent m and a range of pre-exponential factor A.  b) Corresponding concentration profiles predicted for the continuous thickener at Wagerup using the $P_y(\phi)$ functions in a).
Figure 7.8 Effect of variation in the hindered settling function on the predicted concentration profile of the red mud continuous thickener at Wagerup.

The function is small. The value for the exponent has been experimentally measured for several systems and all fall in the range 4.0-6.5 [Richardson and Zaki (1954); Buscall, et al. (1982); Kops-Werkhoven and Fijnaut (1982); Auzerais, et al. (1990); Al-Naafa and Sami Selim (1992)]. The variation in the predicted concentration profile for this range in exponent n is small, particularly since the concentration range of interest is low. The effects of errors in extrapolation of the measured r(\phi) data on the predicted concentration profile are thus minor.

Examined next is the effect of variation in the gel concentration, \( \phi_g \), on the predicted bed height. The \( P_y(\phi) \) data in Figure 7.3 (for the red mud taken before the centrifugal pump) is curve fitted using different values for \( \phi_g \). The effect on the bed height is shown in Table 7.2. As \( \phi_g \) increases, the bed height required decreases since the solution halts
<table>
<thead>
<tr>
<th>Gel concentration, $\phi_g$</th>
<th>Bed height, H (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0871</td>
<td>2.88</td>
</tr>
<tr>
<td>0.15</td>
<td>2.49</td>
</tr>
<tr>
<td>0.20</td>
<td>1.94</td>
</tr>
</tbody>
</table>

**Table 7.2** Effect of variation in gel concentration on the predicted bed height of the continuous thickener at Wagerup.

when the concentration reaches $\phi_g$. The predicted bed height, however, is a relatively minor function of the gel concentration, $\phi_g$, and does not explain the large difference observed between the measured and predicted bed heights.

Finally, the effect of variation in the feed concentration, $\phi_0$, on the predicted bed height is examined. Using the $P_y(\phi)$ function that gives the best fit to the measured concentration profile, a range in $\phi_0$ less than the gel concentration are entered in the model. In Figure 7.9, the predicted bed height slowly increases as $\phi_0$ increases. The feed concentration is thus another parameter that has a minor effect on the predicted bed height. The difficulty encountered with accurate measurement of the suspension feed concentration in the thickener feed-well is therefore not a major problem in the model.

In this sensitivity analysis, the measured $P_y(\phi)$ function clearly has the strongest effect on the predicted concentration profile and bed height in a continuous thickener. Accurate measurement of $P_y(\phi)$ in the concentration range of interest thus is essential and should be the first priority in thickener design or optimisation. To obtain $P_y(\phi)$ data at low concentrations, the consolidation cylinder techniques discussed in Chapter 2, Section 2.3.7, or very low speed centrifuge techniques should be employed. In this case, accurate measurement of the $r(\phi)$ function was not essential. Measurement of $r(\phi)$ in the concentration range of interest, however, is desirable to prevent errors in extrapolation.
Figure 7.9 Effect of variation in the feed concentration on the predicted bed height of the red mud continuous thickener at Wagerup.

7.7 DISCUSSION

The differences observed between the measured and predicted concentration profile and bed height of the Wagerup thickener can now be rationalised. Suggestions for improvements to obtain better agreement are made.

The effect of rakes was ignored in the model and could be a major reason for the observed differences in the results. Rakes not only move the sediment towards the central discharge point and prevent ‘funnelling’ in the thickener [Dixon (1980)], but the action of rakes also increases the underflow concentration [Comings, et al. (1954); Dell and Keleghan (1973); Lockyear (1977); Siddique and O’Donnell (1993)]. The effect
that rakes have on the suspension structure is complex and is not well understood. The low shearing action of rakes can break the structure of the suspension and enable the achievement of higher underflow concentrations [Shin and Dick (1975); Weizhong and Uhlherr (1992); Holdich and Butt (1995, 1996)]. Rakes can also retard the formation of channels in the sediment through which liquid may easily rise [Dell (1970); Scott (1968, 1970); Sarmiento and Uhlherr (1977); Osborne (1990)]. Raking can thus decrease the consolidation rate. Ideally, channelling should be encouraged in the hindered settling region of the thickener to attain a high throughput, then rakes should be used in the compression region to attain a high underflow concentration. The influence of shear on compression rheology has not been resolved and is a major area for further investigation.

The nature of the samples used to characterise the consolidation properties of the suspension in the thickener are another major source of error. Suspension samples for $P_y(\phi)$ and $r(\phi)$ measurement were taken from the underflow stream. The suspension underflow has been subjected to a shear and compression history that will definitely affect the measured consolidation parameters, especially since red mud is highly thixotropic. This prior shear and compression history is the most likely cause for the large differences observed between the measured and predicted results. Ideally, samples for consolidation rate and compression measurements should be taken immediately after the flocculated suspension leaves the feed-well and enters the thickener. Consolidation cylinder experiments are the best technique to determine $P_y(\phi)$ at low concentrations. To determine $r(\phi)$ at low concentrations, settling velocity measurements of individual flocs are possibly the best technique to use.

Better methods for measurement of the concentration profile in the operating thickener should be used. In the model, a uniform concentration across any horizontal cross-section is assumed. This assumption should be checked since a certain degree of segregation and funnelling will always occur near the central feed-well and discharge point. Direct sampling of the thickener at various heights using a probe is time consuming and difficult to penetrate lower regions of the sediment. Faster, indirect methods are available. A $\gamma$-ray sensor developed by Simic and Johnston (1992) enables the determination of the concentration profile in real time. Conductivity methods can
also be feasible for particular systems [Holdich (1990)]. Indirect concentration profile measurements have several advantages. Profiles across the thickener radius can easily be measured to construct a complete picture of the concentration gradients in the thickener. The assumption of uniform concentration across any horizontal cross-section can then be checked. The effects of changing flocculation conditions, feed composition and feed input rate can also be monitored in real time.

Finally, short-circuiting or funnelling in the thickener is an effect that may contribute to the observed differences in the results. Funnelling occurs when material from the central feed-well flows at a high rate directly to the central underflow discharge point. The effective volume of the thickener is thus reduced and a low underflow concentration is attained. The funnelling effect is evaluated by changing the thickener radius and dimensions of the conical base in the thickener model. Funnelling is detected by measurement of the thickener concentration profile across the thickener radius. Further work is required to determine whether funnelling is a real effect.

7.8 CONCLUSIONS

In this chapter, the Landman, et al. (1988) model for a continuous gravity thickener was tested for the first time. Data from a red mud thickener at the alumina refinery in Wagerup, Western Australia was used. In the model, the consolidation parameters of the suspension, the compressive yield stress and hindered settling functions, are entered. The concentration profile and bed height in the thickener are then predicted for any given feed or underflow concentration or thickener shape.

Agreement between the measured thickener concentration profile and that predicted from the measured consolidation parameters was poor. A sensitivity analysis indicated that the bed height is extremely sensitive to the position of the $P_y(\phi)$ function and the gradient of the $P_y(\phi)$ function affects the shape of the concentration profile. The model, however, is only weakly dependent on the $r(\phi)$ function, the feed concentration and the gel concentration. The poor agreement of the model with the measured data was most likely due to poor determination of the consolidation parameters - $P_y(\phi)$ in particular.
The $P_y(\phi)$ and $r(\phi)$ data were both determined at concentration ranges above that in the thickener; thus extrapolation of the data was required for the model. Alternative techniques to determine $P_y(\phi)$ and $r(\phi)$ at the required concentrations are essential. For $P_y(\phi)$, the sedimentation cylinder technique is recommended; for $r(\phi)$, a settling velocity measurement technique is recommended.

The position that samples are taken for determination of the consolidation parameters is critical and could also explain the poor agreement observed. Ideally, samples should be taken immediately after the flocculated suspension leaves the feed-well and enters the thickener. Any shear and compression history effects are therefore eliminated.

The effect of rakes in the thickener is not considered in the model and could have a major influence on the concentration profile and underflow concentration.

Measurement of the consolidation parameters should be repeated using samples taken from the feed-well discharge and using techniques that measure the parameters over the appropriate concentration range. The thickener concentration profile should then be measured across the thickener radius and compared with that predicted from the model.

The application of the consolidation parameters, $P_y(\phi)$ and $r(\phi)$, has thus been demonstrated. With some refinement, the model and techniques described here are a viable means for design and optimisation of continuous thickeners for the concentration of suspensions.
Chapter 8

CONCLUSIONS

In this thesis, the general consolidation model developed by Buscall and White was used to characterise suspensions in settling and compression. The model has two main parameters - the compressive yield stress function and the hindered settling function. Techniques for the reproducible measurement of these consolidation parameters were fully investigated. Several aqueous metal oxide suspension systems prepared under different conditions were used to evaluate the model. Finally, the application of the parameters to the design and optimisation of a continuous thickener was achieved.

The following are the major conclusions and achievements of this research:

- Three experimental techniques for the determination of the compressive yield stress function, \( P_y(\phi) \), were validated both independently and with each other. It was thus verified that \( P_y(\phi) \) is a material property characterising the strength of a suspension in compression.

- A pressure filtration device was successfully built and operated to determine the hindered settling function, \( r(\phi) \), using two techniques. With the direct measurement of \( r(\phi) \) now possible, the full general consolidation model can be used to model transient and time dependent consolidation processes such as filtration and continuous thickening.

- Compression rheology depends on the structural state of the suspension. The state of flocculation, the initial suspension concentration, the presence of any polymeric additives, and the method used to prepare the suspension all change the structural
state and hence the compression rheology to varying degrees. The optimisation of
the consolidation process by manipulation of the structural state of the suspension
using these effects is now possible.

- The Landman, et al. (1988) model for a continuous gravity thickener using the
  consolidation parameters $P_y(\phi)$ and $r(\phi)$ was tested for the first time using data
  measured from an operating thickener. With some refinement, the model and
  techniques are a viable means for design and optimisation of continuous thickeners
  for the concentration of suspensions

Other findings:

- Three techniques for measurement of $P_y(\phi)$ were evaluated in terms of accuracy,
  ease of use, and experimental equipment and measurement time per sample. The
  most appropriate technique is dictated by the particular circumstance

- Two techniques for measurement of $r(\phi)$ were evaluated in terms of accuracy, ease
  of use and experimental measurement time. The best technique is the packed bed
  formation technique.

- Wall effects on compression are significant. A minimum centrifuge tube or
  filtration cylinder diameter is required to minimise errors due to wall effects.

- Initial concentration effects are significant in the measurement of both $P_y(\phi)$ and
  $r(\phi)$. The actual initial concentration of the process suspension should be used in
  consolidation measurement techniques.

- In modelling a continuous thickener, the predicted concentration profile and bed
  height is highly sensitive to the measured $P_y(\phi)$ function for the suspension. The
  model is only weakly sensitive to the $r(\phi)$ function, the feed concentration and the
  gel concentration. To reduce errors, the $P_y(\phi)$ and $r(\phi)$ functions should be measured
  over the concentration range in the thickener. At low concentration, $P_y(\phi)$ is best
  measured by a sedimentation cylinder technique, while for $r(\phi)$ a settling velocity
  measurement technique is recommended.
The following suggestions for further work are evident from this research:

- Further quantify the relationship between the shear yield stress and the compressive yield stress using a range of suspension systems.

- Develop an semi-automated device for routine measurement of the hindered settling function by the packed bed formation technique.

- Further investigate the effect of the initial suspension concentration on the measured $P_y(\phi)$ and $r(\phi)$ functions.

- Investigate the error involved in the determination of the gel concentration by a single sedimentation cylinder experiment versus multiple sedimentation cylinder experiments extrapolated to zero sediment height.

- Repeat the continuous thickener modelling and design study in Chapter 7 using the recommendations from that study for consolidation parameter determination and thickener concentration profile measurement.

- Quantify the effects of shear and shear history on consolidation. In continuous thickeners, the benefits of rakes and multiple thickener stages where the underflow is sheared after each stage, could then be evaluated.
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References


References


References


References


References


References


References


References


Appendix A

MULTIPLE SPEED TECHNIQUE: THEORY

A.1 INTRODUCTION

In this appendix, theory for the full iterative solution of the multiple speed equilibrium sediment height technique is given. This theory is a modification of the original theory presented by Buscall and White (1987).

A.2 THEORY

Beginning with Equation (2.11)

$$\frac{dP}{dz} = -\Delta \rho g \phi \left(1 - \frac{z}{R}\right), \quad (2.11)$$

can be rewritten as

$$\Delta \rho g \int_0^{h_p} \phi \, dz = \int_0^{P(0)} \frac{dP}{1 - z/R}. \quad (A.1)$$
Using conservation of mass

\[ \int_0^{H_g} \phi \, dz = \phi_0 H_0, \quad (A.2) \]

with Equation (A.1) gives

\[ \Delta \rho g \phi_0 H_0 = \int_0^{P(0)} \frac{dP}{1 - z/R}. \quad (A.3) \]

Differentiating this equation with respect to \( g \), noting that both \( z \) and \( P(0) \) are functions of \( g \), and rearranging gives

\[ \frac{dP(0)}{dg} = \Delta \rho \phi_0 H_0 - \frac{1}{R} \int_0^{P(0)} \frac{dP}{(1 - z/R)^2} \frac{dz}{dg}. \quad (A.4) \]

An alternate integration of Equation (2.11) gives

\[ \int_0^{P(z)} \frac{dP}{\phi(P)} = \Delta \rho g Z(z), \quad (A.5) \]

where \( Z(z) \) is defined as

\[ Z(z) = \int_z^{H_g} \left( 1 - \frac{z}{R} \right) dz = (H_{eq} - z) \left( 1 - \frac{H_{eq} + z}{2R} \right). \quad (A.6) \]

For fixed \( P(z) \), the left hand side of Equation (A.5) is fixed so that differentiating that equation with respect to \( g \) gives

\[ 0 = Z(z) + g \frac{dZ}{dg}, \quad (A.7) \]

and using the definition of \( Z(z) \), this produces

\[ \frac{dZ}{dg} = \left( 1 - \frac{H_{eq}}{R} \right) \frac{dH_{eq}}{dg} - \left( 1 - \frac{z}{R} \right) \frac{dz}{dg}. \quad (A.8) \]
for fixed $P(z)$. This can be rewritten as

$$g \frac{dz}{dg} = \frac{Z(z) + \left(1 - \frac{H_{eq}}{R}\right) g \frac{dH_{eq}}{dg}}{1 - z/R}. \quad (A.9)$$

Hence, from Equation (A.4)

$$\frac{dP(0)}{dg} = \Delta \rho \phi \_H \_g \_0 \left[ 1 \frac{1}{g R} \int \frac{dP}{(1 - z/R)^2} \right] \left( Z(z) + \left(1 - \frac{H_{eq}}{R}\right) g \frac{dH_{eq}}{dg} \right), \quad (A.10)$$

which can be written as

$$\frac{dP(0)}{dg} = \Delta \rho \phi \_H \_g \_0 (1 - \varepsilon), \quad (A.11)$$

where $\varepsilon$ is a function of $g$ and is given by

$$\varepsilon = \frac{1}{\Delta \rho \phi \_H \_g \_R} \int_{0}^{P(0)} \frac{dP}{(1 - z/R)^2} \left( Z(z) + \left(1 - \frac{H_{eq}}{R}\right) g \frac{dH_{eq}}{dg} \right), \quad (A.12)$$

or by using Equation (2.11)

$$\varepsilon = \frac{1}{\phi \_H \_R} \int_{0}^{P(0)} \frac{dz}{(1 - z/R)^2} \left( Z(z) + \left(1 - \frac{H_{eq}}{R}\right) g \frac{dH_{eq}}{dg} \right), \quad (A.13)$$

since $P = P(0)$ at $z = 0$ and $P = 0$ at $z = H_{eq}$.

Now, differentiating Equation (A.5) with respect to $g$ and rearranging gives

$$\phi(0) = \frac{dP(0)}{dg} \frac{d(gZ(0))}{dg}. \quad (A.14)$$

Thus, substituting in Equation (A.11)

$$\phi(0) = \frac{\phi \_H \_g \_0 (1 - \varepsilon)}{d(gZ(0))}. \quad (A.15)$$
\[
\phi(0) = \frac{\phi_0 H_0(1 - \varepsilon)}{\left( H_{eq} + g \frac{dH_{eq}}{dg} \right) \left( 1 - \frac{H_{eq}}{R} \right) + \frac{H_{eq}^2}{2R}}.
\]  
(2.12)

In order to get an expression for \( P(0) \), Equation (2.11) is written as

\[
\phi(z) = \frac{1}{\Delta \rho g} \frac{dP}{dz},
\]  
(2.16)

using the definition for \( Z(z) \) in Equation (A.6). Integration, using Equation (A.2) gives

\[
\int_0^h \frac{dP}{dz} dz = \Delta \rho g \phi_0 H_0.
\]  
(A.17)

Integrating this by parts and using the definition of \( Z(z) \) gives

\[
P(0) = \Delta \rho g \phi_0 H_0 (1 - \Delta),
\]  
(2.13)

where \( \Delta \) is a function of \( g \) given by

\[
\Delta = \frac{1}{R} \int_0^h \frac{dz P(z)}{\Delta \rho g \phi_0 H_0 (1 - z / R)}.
\]  
(A.18)

Differentiation of Equations (A.13) and (A.18) with respect to \( z \) then gives the Equations (2.14) and (2.15) respectively.
Appendix B

SEDIMENTATION CYLINDER TECHNIQUE: THEORY

B.1 INTRODUCTION

In this appendix, theory for the second sedimentation cylinder technique described in Chapter 2, Section 2.3.7 is detailed.

B.2 THEORY

The general force balance, Equation (2.3), for constant gravitational acceleration, \( g_0 \),

\[
\frac{dP}{dz} = -\Delta \rho g_0 \phi, \tag{B.1}
\]

can be rewritten as

\[
\int_0^{H_p} dP = \Delta \rho g_0 \int_0^\phi dz. \tag{B.2}
\]

Using conservation of mass

\[
\int_0^{H_p} \phi \, dz = \phi_s H, \tag{B.3}
\]
with Equation (B.2) gives

$$P(0) = \Delta \rho \, g_0 \, \phi_0 \, H.$$  \hspace{1cm} (B.4)

where H is the initial height parameter.

An alternate integration of Equation (B.1) gives

$$\int_0^{P(z)} \frac{dP}{\phi(P)} = \Delta \rho \, g_0 \int_z^{H_{\text{eq}}} \frac{dz}{z} = \Delta \rho \, g_0 \, (H_{\text{eq}} - z).$$  \hspace{1cm} (B.5)

At \( z = 0 \), Equation (B.4) applies, thus Equation (B.5) becomes

$$\int_0^{\Delta \rho \, g_0 \, \phi_0 \, H} \frac{dP}{\phi(P)} = \Delta \rho \, g_0 \, H_{\text{eq}}.$$  \hspace{1cm} (B.6)

Now, differentiating Equation (B.6) with respect to H and rearranging gives

$$\phi(0) = \phi_0 \left/ \frac{dH_{\text{eq}}}{dH} \right.$$  \hspace{1cm} (B.7)

The Equations (B.4) and (B.7) are used to determine the \( P_y(\phi) \) function.
Appendix C

MULTIPLE SPEED TECHNIQUE: APPROXIMATE SOLUTION ERROR ANALYSIS

C.1 INTRODUCTION

In this appendix, random measurement errors associated with the approximate solution of \( P_s(\phi) \) for the multiple speed equilibrium sediment height technique are evaluated. Miller, et al. (1996) have done a similar error analysis of this technique.

C.2 ERROR THEORY

The two main equations for the determination of \( P_s(\phi) \) from \((g, H_{eq})\) raw data are:

\[
P(0) \approx \Delta \rho \phi_0 H_0 g \left( 1 - \frac{H_{eq}}{2R} \right), \tag{2.23}
\]

and

\[
\phi(0) \approx \frac{\phi_0 H_0 \left[ 1 - \frac{1}{2R} \left( H_{eq} + g \frac{dH_{eq}}{dg} \right) \right]}{\left( H_{eq} + g \frac{dH_{eq}}{dg} \right) \left( 1 - \frac{H_{eq}}{R} \right) + \frac{H^2_{eq}}{2R}}. \tag{2.24}
\]
Multiple Speed Technique: Approximate Solution Error Analysis

Assuming that random errors in all parameters are independent, the error in $P(0)$, denoted $E[P(0)]$, is written using standard error propagation methods [Taylor (1982)]:

$$
\frac{E[P(0)]}{P(0)} = \sqrt{\left(\frac{E[\Delta P]}{\Delta P}\right)^2 + \left(\frac{E[\phi_0]}{\phi_0}\right)^2 + \left(\frac{E[H_0]}{H_0}\right)^2 + \left(\frac{E[g]}{g}\right)^2 + \left(\frac{E[1-H_{eq}/2R]}{1-H_{eq}/2R}\right)^2}
$$

(C.1)

where

$$
E[1-H_{eq}/2R] = E[H_{eq}/2R] = \frac{H_{eq}}{2R} \sqrt{\left(\frac{E[H_{eq}]}{H_{eq}}\right)^2 + \left(\frac{E[R]}{R}\right)^2}
$$

(C.2)

Similarly, the error in $\phi(0)$, is written as:

$$
\frac{E[\phi(0)]}{\phi(0)} = \sqrt{\left(\frac{E[\phi_0]}{\phi_0}\right)^2 + \left(\frac{E[H_0]}{H_0}\right)^2 + \left(\frac{E[1/2R(H_{eq} + g \frac{dH_{eq}}{dg})]}{1/2R(H_{eq} + g \frac{dH_{eq}}{dg})}\right)^2}

\left(\frac{E[H_{eq} + g \frac{dH_{eq}}{dg}] \left(1 - \frac{H_{eq}}{R}\right) + \left(\frac{H_{eq}^2}{2R}\right)}{H_{eq} + g \frac{dH_{eq}}{dg} \left(1 - \frac{H_{eq}}{R}\right) + \left(\frac{H_{eq}^2}{2R}\right)}\right)^2
$$

(C.3)

where

$$
E\left[\frac{1}{2R}(H_{eq} + g \frac{dH_{eq}}{dg})\right] = E\left[H_{eq}/2R\right] + E\left[g \frac{dH_{eq}}{dg}\right]

= \frac{H_{eq}}{2R} \sqrt{\left(\frac{E[H_{eq}]}{H_{eq}}\right)^2 + \left(\frac{E[R]}{R}\right)^2}

+ \frac{g}{2R} \frac{dH_{eq}}{dg} \sqrt{\left(\frac{E[g]}{g}\right)^2 + \left(\frac{E[R]}{R}\right)^2 + \left(\frac{E[dH_{eq}/dg]}{dH_{eq}/dg}\right)^2}
$$

(C.4)
and

\[
E \left[ \left( H_{eq} + g \frac{dH_{eq}}{dg} \right) \left( 1 - \frac{H_{eq}}{R} \right) + \left( \frac{H_{eq}^2}{2R} \right) \right] = E \left[ \frac{H_{eq}^2}{2R} \right] + \left( \frac{H_{eq} + g \frac{dH_{eq}}{dg} \left( 1 - \frac{H_{eq}}{R} \right)}{H_{eq} + g \frac{dH_{eq}}{dg}} \right)^2 \times \left( \frac{E_{H_{eq}} + g \frac{dE_{H_{eq}}}{dg}}{H_{eq} + g \frac{dH_{eq}}{dg}} \right)^2 + \left( \frac{1 - \frac{H_{eq}}{R}}{1 - \frac{H_{eq}}{R}} \right)^2
\]

\[
= \frac{H_{eq}^2}{2R} \left[ 2 \left( \frac{E_{H_{eq}}}{H_{eq}} \right)^2 + \left( \frac{E_R}{R} \right)^2 + \left( \frac{H_{eq} + g \frac{dH_{eq}}{dg} \left( 1 - \frac{H_{eq}}{R} \right)}{H_{eq} + g \frac{dH_{eq}}{dg}} \right)^2 \right]
\]  \hspace{1cm} (C.5)

The gravitational acceleration, \( g \), is calculated from the centrifuge speed, \( S \), as

\[
g = \omega^2 R = \left( \frac{2 \pi}{60} S \right)^2 R.
\]  \hspace{1cm} (C.6)

The error in \( g \), \( E[g] \), is thus

\[
E[g] = g \sqrt{2 \left( \frac{E[S]}{S} \right)^2 + \left( \frac{E[R]}{R} \right)^2}.
\]  \hspace{1cm} (C.7)

### C.3 ERROR EVALUATION

Random measurement error values used for parameters in the approximate solution are summarised in Table C.1.
Table C.1 Typical measurement errors for parameters in the approximate solution of $P_y(\phi)$ from the multiple speed equilibrium sediment height technique.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Random Error</th>
<th>% Relative Error Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density difference, $\Delta \rho$</td>
<td>$\pm 10 \text{ kg/m}^3$</td>
<td>0.2-0.8%</td>
</tr>
<tr>
<td>Centrifuge radius, $R$</td>
<td>$\pm 0.0002 \text{ m}$</td>
<td>0.1%</td>
</tr>
<tr>
<td>Initial concentration, $\phi_0$</td>
<td>$\pm 0.001$</td>
<td>0.2-1.0%</td>
</tr>
<tr>
<td>Initial height, $H_0$</td>
<td>$\pm 0.0005 \text{ m}$</td>
<td>0.5-0.8%</td>
</tr>
<tr>
<td>Equilibrium heights, $H_{eq}$</td>
<td>$\pm 0.0005 \text{ m}$</td>
<td>0.5-4.0%</td>
</tr>
<tr>
<td>Centrifuge speed, $S$</td>
<td>$\pm 1.0 \text{ rpm}$</td>
<td>0.02-0.5%</td>
</tr>
<tr>
<td>$dH_{eq}/dg$ slopes</td>
<td>$\pm 10^{-7}$-$10^{-6}$ $\text{s}^{-2}$</td>
<td>0.5-5.0%</td>
</tr>
</tbody>
</table>

There are several parameters associated with the initial conditions of the experiment, namely $\Delta \rho$, $R$, $\phi_0$ and $H_0$. Each of these parameters should be measured as accurately as possible for errors to be of the order of 0.2-1.3%. By inspection of Equations (2.23) and (2.24), the effect of these errors on $P(0)$ and $\phi(0)$ are evaluated. Error in $\Delta \rho$ affects only $P(0)$. The relative errors in both $\phi_0$ and $H_0$ are directly translated to equal relative errors in both $P(0)$ and $\phi(0)$. Errors in the initial measurements of $\phi_0$ and $H_0$ thus tend to slide the $P_y(\phi)$ curve along itself rather than shift it up or down.

The effect of errors in $g$, $H_{eq}$, $R$ and $dH_{eq}/dg$ on both $P(0)$ and $\phi(0)$ must be evaluated numerically using the equations derived in the previous section. The largest error arises from the measurement of $H_{eq}$ and $dH_{eq}/dg$.

C.4 REFERENCE

Appendix D

SYNTHETIC DATA GENERATION

D.1 INTRODUCTION

Detailed here are the theory and algorithm used to generate synthetic raw data to evaluate the multiple speed centrifuge technique and the concentration profile technique in Chapter 4. The code for the generation of the synthetic data was written by Maria Eberl of the Department of Mathematics at the University of Melbourne.

D.2 GENERATION OF $H_{eq}(g)$ AND $\phi(z)$ DATA FROM A $P_y(\phi)$ CURVE

In a suspension consolidated in a centrifuge, with $\phi_0 > \phi_g$, two regions must be considered; a constant concentration region, $\phi = \phi_0$, and a compression region, $\phi = \phi(z)$; see Figure D.1. In the compression region, the main governing equation, Equation (2.11), applies;

$$\frac{dP}{dz} = -\Delta \rho g \phi \left(1 - \frac{z}{R}\right).$$  (2.11)
Equation (2.11) can be rewritten as

$$\frac{d\phi}{dz} = \frac{-\Delta \rho g \phi(1 - \frac{z}{R})}{\frac{dP}{d\phi}}. \quad (D.1)$$

For a given $P(\phi)$ function and a certain $g$, the above first order differential equation can be solved to find the concentration profile, $\phi(z)$, in the compression region.

In the constant concentration region, $\phi = \phi_0$, where at the top $P(H_{eq}) = 0$, Equation (2.17) applies:

$$P(z) = \Delta \rho g \phi_0 (H_{eq} - z) \left(1 - \frac{H_{eq} + z}{2R} \right). \quad (2.17)$$

At the critical height, $z_c$, Equation (2.17) can be solved for $H_{eq}$ using the quadratic formula:

$$H_{eq} = R - \sqrt{R^2 - \left(2Rz_c - z_c^2 + \frac{2R P(z_c)}{\Delta \rho g \phi_0} \right)}, \quad (D.2)$$

since $H_{eq} < R$. An iterative solution of the concentration profile to find $H_{eq}$ for a certain $g$ is then possible. Starting at the bottom, $z = 0$, the bottom concentration, $\phi(0)$, is guessed. Equation (D.1) is solved using a Runge-Kutta integration until $\phi \leq \phi_0$ where $z = z_c$. Equation (D.2) is then solved to find $H_{eq}$. 

Figure D.1  Geometry of centrifuge tube for generation of synthetic data.
A mass balance is used to check the initial $\phi(0)$:

$$\int_0^{z_c} \phi \, dz + \phi_0 (H_{eq} - z_c) = \phi_0 \, H_0,$$  \hspace{1cm} (D.3)

and the process is repeated with a new guess for $\phi(0)$ until the mass balance agrees. The next value for $g$ can then be inputted. The algorithm used was coded in FORTRAN and is outlined below.

INPUT $\Delta \rho, R, \phi_0, H_0, P_y(\phi), g, N$

where $N$ = number of steps in concentration profile required.

OUTPUT $\phi(z), z_c, H_{eq}$

**Step 1.** Guess $\phi(0)$.

**Step 2.** Solve $\frac{d\phi}{dz}$ in Equation (D.1) from $z = 0, \phi = \phi(0)$, until $\phi \leq \phi_0$ and $z = z_c$.

**Step 3.** Find $H_{eq}$ from Equation (D.2).

**Step 4.** Check mass balance in Equation (D.3).

**Step 5.** Adjust guess for $\phi(0)$.

**Step 6.** Repeat Steps 2-5 until mass balance agrees.

**Step 7.** Output $\phi(z), z_c, H_{eq}$.

If $H_{eq}$ is known for a certain $g$, an alternate, more direct method for determination of the concentration profile is possible. Starting at the top of the bed, $z = H_{eq}$, Equation (2.17) is solved until $P(z) > P(z_c)$, then Equation (2.11) is solved with $\phi = \phi(P)$ until $z = 0$. Mass conservation is inherently satisfied in this method and no iteration is necessary.
Appendix E

DETERMINATION OF $P_y(\phi)$ FROM CONCENTRATION PROFILE

E.1 INTRODUCTION

In this appendix, two methods are given for the determination of $P_y(\phi)$ from the concentration profile of a suspension consolidated to equilibrium in a centrifuge. The first is a discrete solution based on a trapezoidal rule, the second is a numerical solution based on a curve fit of the concentration profile. The principal equation is repeated here;

$$P_y(z) = \Delta \rho \omega^2 \int_0^x x \phi(x) \, dx. \quad (2.27)$$

E.2 DISCRETE SOLUTION

A simple method to integrate Equation (2.27) is to apply the trapezoidal rule to find the applied pressure in each measured section of the bed, then sum the pressures to find the total compressive pressure at each height.
The trapezoidal rule for integrating a function \( f(x) \) between \( a \) and \( b \) is written as

\[
\int_a^b f(x) \, dx = \frac{h}{2} \left[ f(a) + f(b) \right] - \frac{h^3}{12} f''(\xi), \tag{D.1}
\]

where the integration interval is \( h = b - a \) and \( f''(\xi) \) is the error term [Burden and Faires (1993)].

The concentrations measured by sectioning the bed are the average concentrations of each section. It is assumed that the measured concentration, \( \phi_i \), of section \( i \), is equal to the concentration at the midpoint of the interval, \( (H_{\text{avg}})_i \), defined as

\[
(H_{\text{avg}})_i = \frac{H_i + H_{i-1}}{2}, \tag{E.2}
\]

where the section heights, \( H_i \), are measured from the base of the centrifuge tube. The coordinate system origin in Equation (2.27) is the centre of the centrifuge. A transformation of coordinates is useful;

\[
(z_{\text{avg}}) = R - (H_{\text{avg}}). \tag{E.3}
\]

The integral in Equation (2.27) may then be written discretely starting from the top of the bed to find \( P_y \) at position \( (z_{\text{avg}})_i \)

\[
P_y((z_{\text{avg}})_i) = \Delta \rho \omega^2 \left\{ \int_{z_{\text{eq}}}^{(z_{\text{avg}})_1} x \phi \, dx + \int_{(z_{\text{avg}})_1}^{(z_{\text{avg}})_2} x \phi \, dx + \ldots + \int_{(z_{\text{avg}})_{i-1}}^{(z_{\text{avg}})_i} x \phi \, dx \right\}. \tag{E.4}
\]

The integration is illustrated in Figure E.1. Applying the trapezoidal rule gives

\[
P_y((z_{\text{avg}})_i) = \Delta \rho \omega^2 \left\{ \frac{(z_{\text{avg}})_i - z_{\text{eq}}}{2} \left[ (z_{\text{avg}})_1 \phi_1 + z_{\text{eq}} \phi_2 \right] + \frac{(z_{\text{avg}})_2 - (z_{\text{avg}})_1}{2} \left[ (z_{\text{avg}})_2 \phi_2 + (z_{\text{avg}})_1 \phi_3 \right] + \ldots + \frac{(z_{\text{avg}})_i - (z_{\text{avg}})_{i-1}}{2} \left[ (z_{\text{avg}})_i \phi_i + (z_{\text{avg}})_{i-1} \phi_{i+1} \right] \right\}. \tag{E.5}
\]
Figure E.1 Schematic of trapezoidal rule for calculation of $P_y(\phi)$ from sectioning analysis of concentration profile.
The algorithm to calculate $P_Y(\phi)$ based on Equation (E.5) is set out below. The algorithm was coded in Microsoft FORTRAN but may also be easily set up on a spreadsheet.

**INPUT**
\[ \rho_s, \rho_f, \omega, R, \phi_0, H_{eq}, (H_i, (M_i)_i, (M_r)_i), N \]

where $N = \text{number of sections measured}$.

**OUTPUT**
\[ \left( (H_{avg})_i, \phi_i, (P_y)_i \right) \]

**Step 1.** Set data for first point.
- Set $\phi_1 = \phi_0$;
- Set $(H_{avg})_1 = H_{eq}$;
- Set $(z_{avg})_1 = R - H_{eq}$;
- Set $(P_y)_1 = 0$.

**Step 2.** For $i = 2, N+1$ do Steps 3-7.

**Step 3.** Set $\phi_m_i = \frac{(M_r)_i - (M_i)_i}{(M_i)_i - (M_r)_i}$.

**Step 4.** Set $\phi_i = \frac{(\phi_m)_i \rho_f}{\rho_s - (\phi_m)_i (\rho_s - \rho_f)}$.

**Step 5.** Set $(H_{avg})_i = \frac{H_i + H_{i-1}}{2}$.

**Step 6.** Set $(z_{avg})_i = R - (H_{avg})_i$.

**Step 7.** Set $(P_y)_i = \Delta \rho \omega^2 \left\{ \frac{(z_{avg})_i - (z_{avg})_{i-1}}{2} \right\} \left\{ (z_{avg})_i \phi_i + (z_{avg})_{i-1} \phi_{i-1} \right\} + (P_y)_{i-1}$

**Step 8.** Output $\left( (H_{avg})_i, \phi_i, (P_y)_i \right)$.
E.3 NUMERICAL SOLUTION

The numerical determination of $P_x(\phi)$ from concentration profile data involves curve fitting the profile to a suitable equation, then solving the integral in Equation (2.27) numerically. To best curve fit the concentration profile, $\Phi(x)$, whose coordinate system origin is the centre of the centrifuge, a transformation of the $x$ coordinate is required:

$$x = s + (R - H_{eq}), \quad (E.6)$$

where $s = 0$ at $H = H_{eq}$ and $s = H_{eq}$ at $H = 0$. The coordinate transformation is best explained in Figure E.2. The concentration profile is thus:

$$\Phi(x) = \begin{cases} 
0 & , \quad 0 < x < (R - H_{eq}) \\
\phi(x - (R - H_{eq})) & , \quad (R - H_{eq}) < x < R.
\end{cases} \quad (E.7)$$

Concentration profiles of consolidated suspensions have been found to best fit an equation of the form:

$$\phi(s) = a + b \log_{10}(s + d) + c \left( \log_{10}(s + d) \right)^2, \quad (4.10)$$

where $a$, $b$, $c$ and $d$ are constant coefficients. Other simpler or more complex equations may also be used. The form in Equation (4.10) was also similar to that used by Miller, et al. (1996).

Substituting the transformation in the integral in Equation (2.27) gives

$$\Phi(z) = \int_{x}^{x} \Phi(x) \, dx$$

$$= \int_{x - H_{eq}}^{x - H_{eq}} \Phi(x) \, dx$$

$$= \int_{x - H_{eq}}^{x - H_{eq}} \phi(x - R + H_{eq}) \, dx$$

$$= \int_{s - R + H_{eq}}^{s + R - H_{eq}} (s + R - H_{eq}) \phi(s) \, ds \quad (E.8)$$

This algorithm was coded in Microsoft FORTRAN and used a standard routine from Numerical Recipes [Press, et al. (1994)] to do the integration.
Figure E.2  Schematic of coordinate transformations for numerical determination of $P_y(\phi)$ from concentration profile measurements; a) centrifuge tube layout, b) $\phi(H)$ coordinate system, c) $\phi(s)$ coordinate system, d) $\Phi(x)$ coordinate system.
INPUT $\Delta \rho$, $\omega$, $R$, $\phi_0$, $H_0$, $H_{eq}$, $(H_{avg}, \phi_1)$, $N$

where $N =$ number of intervals the fitted concentration profile is to be integrated.

OUTPUT $P_y(\phi)$ curve.

Step 1. Transform vertical coordinate system by

$$s_i = H_{eq} - (H_{avg}).$$

Step 2. Curve fit $(s, \phi)$ data to the form

$$\phi(s) = a + b \log_{10}(s + d) + c \left(\log_{10}(s + d)\right)^2.$$  \hfill (4.10)

using a curve fitting package to find the parameters $a$, $b$, $c$ and $d$. (Table Curve for Windows was used here).

Step 3. For $i = 1, N$ do Steps 4-6.

Step 4. Set $z_i = \frac{H_{eqi}}{N}$.

Step 5. Find $\phi(z_i)$ from Equation (4.10) in Step 2.

Step 6. Solve

$$P_y(z_i) = \Delta \rho \omega^2 \int_{z_i}^{z_i - R + H_{eq}} (s + R - H_{eq}) \phi(s) \, ds.$$

Step 7. Output $(\phi_1, (P_y))$. 
E.4 ERROR THEORY FOR DISCRETE SOLUTION

Errors are calculated using standard error propagation methods [Taylor (1982)]. Random measurement errors in all parameters are assumed to be independent. Equations for the discrete solution are defined in Chapter 4, Section 4.3.

Solids mass concentration, $\phi_m$:

$$\phi_m = \frac{M_f - M_i}{M_i - M_t}, \quad (4.8)$$

$$E[\phi_m] = \phi_m \sqrt{\left(\frac{\sqrt{\frac{E[M_f]}{M_f}}^2 + E[M_i]}{M_f - M_i}\right)^2 + \left(\frac{\sqrt{\frac{E[M_i]}{M_i}}^2 + E[M_t]}{M_i - M_t}\right)^2} \quad (E.9)$$

Solids volume fraction, $\phi$:

$$\phi = \frac{\phi_m \rho_f}{\rho_s - \phi_m (\rho_s - \rho_f)}, \quad (4.9)$$

$$E[\phi] = \phi \sqrt{\left(\frac{E[\phi_m]}{\phi_m}\right)^2 + \left(\frac{E[\rho_f]}{\rho_f}\right)^2 + \left(\frac{E[\rho_s - \phi_m (\rho_s - \rho_f)]}{\rho_s - \phi_m (\rho_s - \rho_f)}\right)^2} \quad (E.10)$$

where

$$E[\rho_s - \phi_m (\rho_s - \rho_f)] = \sqrt{E[\rho_s]} + \phi_m (\rho_s - \rho_f) \left(\frac{E[\phi_m]}{\phi_m}\right)^2 + \left(\frac{\sqrt{E[\rho_s]} + E[\rho_f]}{\rho_s - \rho_f}\right)^2 \quad (E.11)$$

Section height, $H_i$, and average height of section, $(H_{avg})$:

$$H_i = H_t - H_b - (H_d), \quad (4.6)$$
Appendix E

\[
E[H_i] = \sqrt{E[H_i]^2 + E[H_b]^2 + E[H_d]^2},
\]
\[
= \sqrt{3} E[H]
\]
\[
(H_{avg})_i = \frac{H_i + H_{i-1}}{2},
\]
\[
(E[H_{avg})_i = \frac{1}{2} \sqrt{E[H_i]^2 + E[H_{i-1}]^2}.
\]

Average section height from centre of centrifuge, \((z_{avg})_i\):

\[
(z_{avg})_i = R - (H_{avg})_i.
\]

\[
E[z_{avg}] = \sqrt{E[R]^2 + E[H_{avg}]^2}.
\]

Centrifuge rotational speed, \(\omega\), and centrifugal acceleration, \(g\):

\[
\omega = \frac{2\pi}{60} S,
\]
\[
E[\omega] = \frac{2\pi}{60} E[S],
\]
\[
g = \omega^2 R,
\]
\[
E[g] = g \sqrt{\left(\frac{E[\omega]}{\omega}\right)^2 + \left(\frac{E[R]}{R}\right)^2}.
\]

Compressive yield stress, \((P_y)_i\):

\[
(P_y)_i = \Delta \rho \omega^2 \frac{1}{2} \left[ (z_{avg})_i - (z_{avg})_{i-1} \right] \left[ (z_{avg})_i \phi_i + (z_{avg})_{i-1} \phi_{i-1} \right] + (P_y)_{i-1},
\]

\[
(E.5)
\]
\[ E[P_y] = \frac{\Delta \rho \omega^2}{2} \left( \frac{(z_{\text{avg}})_i - (z_{\text{avg}})_{i-1}}{2} \left( (z_{\text{avg}})_i \phi_i + (z_{\text{avg}})_{i-1} \phi_{i-1} \right) \right)^2 \times \left( \frac{E[\Delta \rho]}{\Delta \rho} + 2 \frac{E[\omega]}{\omega} + \frac{E[(z_{\text{avg}})_i - (z_{\text{avg}})_{i-1}]}{(z_{\text{avg}})_i - (z_{\text{avg}})_{i-1}} \right)^2 \right. \\
\left. + \frac{E[(z_{\text{avg}})_i \phi_i + (z_{\text{avg}})_{i-1} \phi_{i-1}]}{(z_{\text{avg}})_i \phi_i + (z_{\text{avg}})_{i-1} \phi_{i-1}} \right)^2 + \left( \frac{E[P_y]}{P_y} \right)^2 \right), \quad (E.18) \]

where

\[ E[(z_{\text{avg}})_i - (z_{\text{avg}})_{i-1}] = \sqrt{E[(z_{\text{avg}})_i] + E[(z_{\text{avg}})_{i-1}]}, \quad (E.19) \]

\[ E[(z_{\text{avg}})_i \phi_i - (z_{\text{avg}})_{i-1} \phi_{i-1}] = \left( \frac{E[(z_{\text{avg}})_i]}{z_{\text{avg}}_i} \right)^2 + \left( \frac{E[\phi_i]}{\phi_i} \right)^2 \]

\[ + \left( \frac{E[(z_{\text{avg}})_{i-1}]}{z_{\text{avg}}_{i-1}} \right)^2 + \left( \frac{E[\phi_{i-1}]}{\phi_{i-1}} \right)^2 \right), \quad (E.20) \]

**E.5 ERROR EVALUATION FOR DISCRETE SOLUTION**

Random measurement errors used for parameters in the discrete solution of the concentration profile technique are similar to those for the multiple speed technique and are summarised in Table E.1.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Random Error</th>
<th>% Relative Error Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density difference, $\Delta \rho$</td>
<td>$\pm 10 \text{ kg/m}^3$</td>
<td>0.2-0.8%</td>
</tr>
<tr>
<td>Centrifuge radius, $R$</td>
<td>$\pm 0.0002 \text{ m}$</td>
<td>0.1%</td>
</tr>
<tr>
<td>Initial concentration, $\phi_0$</td>
<td>$\pm 0.001$</td>
<td>0.2-1.0%</td>
</tr>
<tr>
<td>Heights, $H_i$</td>
<td>$\pm 0.0002 \text{ m}$</td>
<td>0.2-2%</td>
</tr>
<tr>
<td>Masses, $(M_i, M_{i'}, M_{i''})$</td>
<td>$\pm 0.0002 \text{ g}$</td>
<td>&lt; 0.01%</td>
</tr>
<tr>
<td>Centrifuge speed, $S$</td>
<td>$\pm 1.0 \text{ rpm}$</td>
<td>0.02-0.5%</td>
</tr>
</tbody>
</table>

Table E.1 Typical measurement errors for parameters in the discrete solution of $P_y(\phi)$ from the concentration profile technique.

These measurement errors are used in the calculation of error bars for $P_y$ and $\phi$ using the equations in the previous section.

E.6 REFERENCES


Appendix F

GEL CONCENTRATION DETERMINATION FROM BATCH SETTLING EXPERIMENTS

F.1 INTRODUCTION

Detailed here are batch settling results used to find the suspension gel concentrations, \( \phi_v \), for the calculation of \( r(\phi) \) functions in Chapters 5, 6 and 7. The initial settling rate was also measured in these experiments.

F.2 EXPERIMENTAL RESULTS

The batch settling experiments were performed in 50 mL measuring cylinders. The sediment height as a function of time was measured for each sample in two separate cylinders. The initial height was measured as the meniscus of the supernatant after settling was considerably advanced. At short times, the sediment height was thus sometimes measured to be higher than the initial height.

The settling curves (sediment height versus time) always followed classic hindered settling behaviour; a constant settling rate period, then an exponential decay to an equilibrium sediment height. The settling curves for each suspension tested are not
shown here. Instead, a typical settling curve to illustrate the general form is shown in Figure F.1.

For each suspension, the initial experimental conditions, the gel concentration calculated from the equilibrium sediment height using Equation (5.1), and the measured initial settling rate, are tabulated in Table F.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>pH</th>
<th>$\phi_0$</th>
<th>$\phi_i$</th>
<th>$\frac{dH}{dt} @ t = 0$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>5.2</td>
<td>0.051</td>
<td>0.103</td>
<td>7.29x10$^{-2}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>5.6</td>
<td>0.059</td>
<td>0.080</td>
<td>1.45x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>5.8</td>
<td>0.050</td>
<td>0.081</td>
<td>5.77x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>6.0</td>
<td>0.050</td>
<td>0.075</td>
<td>5.08x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>6.4</td>
<td>0.050</td>
<td>0.073</td>
<td>5.08x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>6.8</td>
<td>0.049</td>
<td>0.079</td>
<td>7.97x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>6.9</td>
<td>0.021</td>
<td>0.081</td>
<td>7.91x10$^{-4}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>7.0</td>
<td>0.050</td>
<td>0.075</td>
<td>4.73x10$^{-6}$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>7.1</td>
<td>0.082</td>
<td>0.091</td>
<td>7.76x10$^{-7}$</td>
</tr>
<tr>
<td>Red Mud</td>
<td>13 - 14</td>
<td>0.178</td>
<td>0.24</td>
<td>2.22x10$^{-6}$</td>
</tr>
</tbody>
</table>

Table F.1  Summary of settling experiments to estimate the gel concentration, $\phi_g$, for the determination of $r(\phi)$.

Plotted in Figure F.2 are the gel concentrations versus pH for the ZrO$_2$ suspensions in Table F.1. Two interpretations of this data are possible. First, consideration of the entire data indicates a minimum in the gel concentration at an intermediate flocculation level (pH 6.2-6.5). In a closer examination of the data, the two outermost points could be ignored. The result for the pH 5.2 suspension could be ignored since this sediment interface was hazy, indicating partial dispersal of the suspension. The pH 7.1 suspension result is also questionable since a strongly flocculated suspension at this semi-dilute concentration is very unstable. The relatively wide spread of the data is thus narrowed considerably. In this second interpretation of the data, the gel concentration for ZrO$_2$ is relatively independent of the flocculation state of the suspension. The average gel concentration of the remaining data is $\phi_g = 0.078$. Further work is required to clarify the effect of flocculation state on gel concentration. The multiple
sedimentation cylinder technique, described in Chapter 5, Section 5.2.1, is suggested as an improved method for determination of the gel concentration for this study.

The initial settling rate in Table F.1 decreased linearly with increasing initial concentration, as expected. However, the data did not correlate well with any other measured parameter. These results were thus disregarded.

Figure F.1 Typical settling curve to determine the gel concentration of a ZrO₂ suspension (pH 6.9, φ₀ = 0.021).
Figure F.2 Gel concentration, $\phi_g$, versus pH for ZrO$_2$ suspensions of various $\phi_0$. 
Appendix G

r(\phi) SAMPLE CALCULATIONS AND ERRORS

G.1 INTRODUCTION

Detailed here are sample calculations for the determination of r(\phi) from both the packed bed formation technique and the packed bed filtration technique. Also included are details of error calculations for each technique.

G.2 SAMPLE CALCULATION

A spreadsheet used to calculate (\lambda/V_p)\beta(\phi) from both the packed bed formation technique and the packed bed filtration technique for a typical ZrO\textsubscript{2} suspension is shown in Table G.1. Also in this table are error calculations which are detailed in the next section.
<table>
<thead>
<tr>
<th>Sample (reslurried):</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material:</td>
<td>ZrO₂</td>
<td>ZrO₂</td>
<td>ZrO₂</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>pH:</td>
<td>6.8</td>
<td>6.7</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Tube Diameter (mm):</td>
<td>28.40</td>
<td>28.40</td>
<td>28.40</td>
<td>28.40</td>
</tr>
<tr>
<td>Filtration Area, A (m²):</td>
<td>6.33×10⁻⁴</td>
<td>6.33×10⁻⁴</td>
<td>6.33×10⁻⁴</td>
<td>6.33×10⁻⁴</td>
</tr>
<tr>
<td>Error, A (m²):</td>
<td>3×10⁻⁶</td>
<td>3×10⁻⁶</td>
<td>3×10⁻⁶</td>
<td>3×10⁻⁶</td>
</tr>
<tr>
<td>Initial Conc., φₐ:</td>
<td>0.051</td>
<td>0.052</td>
<td>0.051</td>
<td>0.050</td>
</tr>
<tr>
<td>Gel Conc., φₑ:</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
<td>0.075</td>
</tr>
<tr>
<td>Final Conc., φᵢ:</td>
<td>0.308</td>
<td>0.333</td>
<td>0.353</td>
<td>0.362</td>
</tr>
<tr>
<td>Error, φᵢ:</td>
<td>0.005</td>
<td>0.005</td>
<td>0.002</td>
<td>0.001</td>
</tr>
</tbody>
</table>

**Packed bed formation:**

| Mean Conc., φₐ:     | 0.250   | 0.269   | 0.284   | 0.290   |
| Error, φₐ:          | 0.004   | 0.004   | 0.002   | 0.001   |
| Slope, m₁ (s/m⁶):   | 9.67×10¹² | 5.84×10¹² | 4.62×10¹² | 4.87×10¹² |
| Error, m₁, 1.0% (s/m⁶): | 1×10¹¹  | 6×10¹⁰  | 5×10¹⁰  | 5×10¹⁰  |
| Slope, m₁ (s/m³):   | 3.88×10⁶ | 2.34×10⁶ | 1.85×10⁶ | 1.95×10⁶ |
| Error, m₁ (s/m³):   | 5×10⁴   | 3×10⁴   | 2×10⁴   | 2×10⁴   |
| Pressure Diff., ΔP (Pa): | 120000  | 304000  | 450000  | 565000  |
| Error, ΔP (Pa):     | 10000   | 5000    | 10000   | 8000    |
| (λ / Vₚ) r(φₐ) (Pa.s/m²): | 8.18×10¹² | 1.18×10¹³ | 1.38×10¹³ | 1.84×10¹³ |
| Error, [(λ / Vₚ) r(φₐ)] | 7.5×10¹¹ | 4.8×10¹¹ | 5.0×10¹¹ | 5.8×10¹¹ |

**Packed bed filtration:**

| Pressure Diff., ΔP (Pa): | 110000  | 283000  | 460000  | 539000  |
| Error, ΔP (Pa):          | 4000    | 3000    | 4000    | 5000    |
| Slope, dV/dt (m³/s):     | 2.59×10⁻¹⁰ | 4.53×10⁻¹⁰ | 4.39×10⁻¹⁰ | 6.14×10⁻¹⁰ |
| Error, dV/dt, 1.0% (m³/s): | 3×10⁻¹²  | 5×10⁻¹²  | 4×10⁻¹²  | 6×10⁻¹²  |
| Bed Height, Hᵢ (m):      | 0.0490  | 0.0443  | 0.0421  | 0.0329  |
| Error, Hᵢ (m):           | 0.0005  | 0.0005  | 0.0005  | 0.0005  |
| (λ / Vₚ) r(φₜ) (Pa.s/m²): | 1.23×10¹³ | 1.79×10¹³ | 2.89×10¹³ | 2.98×10¹³ |
| Error, [(λ / Vₚ) r(φₜ)] | 5.3×10¹¹ | 4.5×10¹¹ | 5.6×10¹¹ | 6.3×10¹¹ |

*Table G.1* Typical calculation of \((λ/Vₚ)r(φ)\) for the packed bed formation technique and the packed bed filtration technique (data in Figure 5.9).
G.3 ERROR THEORY

Errors are calculated using standard error propagation methods [Taylor (1982)], assuming that random errors in all parameters are independent.

G.3.1 PACKED BED FORMATION

The main equation for determination of \( \frac{\lambda}{V_p} r(\phi) \) from the packed bed formation technique is

\[
\frac{\lambda}{V_p} r(\phi_m) = \frac{2 \Delta P m_1 (\phi_m/\phi_0 - 1)(1 - \phi_m)^2}{\phi_m},
\]

(2.39)

where

\[
\phi_m = \frac{3}{4} \phi_f + \frac{1}{4} \phi_g.
\]

(2.38)

The error, denoted \( E\left[\frac{\lambda}{V_p} r(\phi_m)\right] \), is

\[
E\left[\frac{\lambda}{V_p} r(\phi_m)\right] = \left(\frac{\lambda}{V_p} r(\phi_m)\right) \left[ \left(\frac{E[\Delta P]}{\Delta P}\right)^2 + \left(\frac{E[m_1]}{m_1}\right)^2 + \left(\frac{E[\phi_m - 1]}{\phi_m - 1}\right)^2 \right]^{1/2} \left[ \left(\frac{E[1 - \phi_m]}{(1 - \phi_m)^2}\right)^2 + \left(\frac{E[\phi_m]}{\phi_m}\right)^2 \right],
\]

(G.1)

where

\[
E\left[\phi_m - 1\right] = E\left[\frac{\phi_m}{\phi_0} - 1\right] = \frac{\phi_m}{\phi_0} \sqrt{\left(\frac{E[\phi_m]}{\phi_m}\right)^2 + \left(\frac{E[\phi_0]}{\phi_0}\right)^2},
\]

(G.2)
\[ r(\phi) \text{ Sample Calculations and Errors} \]

and

\[ E[(1 - \phi_m)^2] = 2(1 - \phi_m)E[\phi_m], \quad (G.3) \]

and

\[ E[\phi_m] = \sqrt{\left(\frac{1}{3} \overline{E[\phi_f]}\right)^2 + \left(\frac{1}{4} \overline{E[\phi_r]}\right)^2}. \quad (G.4) \]

**G.3.2 PACKED BED FILTRATION**

The main equation for determination of \((\lambda/V_p)r(\phi)\) from the packed bed filtration technique is

\[ \frac{\lambda}{V_p} r(\phi_f) = \frac{\Delta P}{H_f} \left( 1 - \phi_f \right) \frac{1}{\phi_f} \frac{dV}{dt}. \quad (2.43) \]

The error, denoted \(E\left[\frac{\lambda}{V_p} r(\phi_f)\right]\), is

\[ E\left[\frac{\lambda}{V_p} r(\phi_f)\right] = \left( \frac{\lambda}{V_p} r(\phi_f) \right) \frac{\left( \overline{E[\Delta P]} \right)^2 + \left( \overline{E[H_f]} \right)^2 + \left( \overline{E[dV/dt]} \right)^2}{\left( \overline{E[\phi_f]} \right)^2 + \left( \overline{E[\phi_r]} \right)^2}. \quad (G.5) \]

**G.4 ERROR EVALUATION**

Random measurement error values used in the calculation of \(r(\phi)\) from both the constant pressure filtration and compaction technique and the packed bed filtration technique are summarised in Table G.2 and Table G.3 for the devices at the Universities of Melbourne and Illinois respectively.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Range</th>
<th>Random Error Range</th>
<th>% Relative Error Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial conc., $\phi_0$</td>
<td>0.02-0.08</td>
<td>± 0.001</td>
<td>1.0-5.0%</td>
</tr>
<tr>
<td>Gel conc., $\phi_g$</td>
<td>0.10-0.15</td>
<td>± 0.002-0.004</td>
<td>1.3-4.0%</td>
</tr>
<tr>
<td>Final conc., $\phi_f$</td>
<td>0.20-0.40</td>
<td>± 0.001-0.005</td>
<td>0.2-2.5%</td>
</tr>
<tr>
<td>Initial height, $H_0$</td>
<td>0.27 or 0.30 m</td>
<td>± 0.001 m</td>
<td>0.3%</td>
</tr>
<tr>
<td>Final height, $H_f$</td>
<td>0.01-0.08 m</td>
<td>± 0.0005 m</td>
<td>0.6-5.0%</td>
</tr>
<tr>
<td>Pressure, $\Delta P$</td>
<td>5×10^4-6×10^5 kPa</td>
<td>± 2-10 kPa</td>
<td>0.3-20%</td>
</tr>
<tr>
<td>Slope, $m_1$</td>
<td>$10^6-10^7$ s/m²</td>
<td>± $10^4-10^5$ s/m²</td>
<td>1.0%</td>
</tr>
<tr>
<td>Flux, dV/dt</td>
<td>$10^{11}-10^9$ m³/s</td>
<td>± $10^9-10^7$ m³/s</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

**Table G.2** Typical measurement errors for parameters in the determination of $r(\phi)$ by either the packed bed formation technique or the packed bed filtration technique for the device at the University of Melbourne.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Range</th>
<th>Random Error Range</th>
<th>% Relative Error Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial conc., $\phi_0$</td>
<td>0.15-0.30</td>
<td>± 0.001</td>
<td>0.3-0.7%</td>
</tr>
<tr>
<td>Gel conc., $\phi_g$</td>
<td>0.10-0.15</td>
<td>± 0.002-0.004</td>
<td>1.3-4.0%</td>
</tr>
<tr>
<td>Final conc., $\phi_f$</td>
<td>0.24-0.51</td>
<td>± 0.001-0.002</td>
<td>0.2-1.3%</td>
</tr>
<tr>
<td>Initial height, $H_0$</td>
<td>0.0134 or 0.0334 m</td>
<td>± 0.0001-0.0003 m</td>
<td>0.3-2.2%</td>
</tr>
<tr>
<td>Final height, $H_f$</td>
<td>0.004-0.020 m</td>
<td>± 0.0001 m</td>
<td>0.5-2.5%</td>
</tr>
<tr>
<td>Pressure, $\Delta P$</td>
<td>5×10^4-10^7 kPa</td>
<td>± 1 kPa</td>
<td>0.01-2.0%</td>
</tr>
<tr>
<td>Slope, $m_1$</td>
<td>$5\times10^5-10^8$ s/m²</td>
<td>± $5\times10^5-10^6$ s/m²</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

**Table G.3** Typical measurement errors for parameters in the determination of $r(\phi)$ by the packed bed formation technique for the device at the University of Illinois.

Measurement errors are generally greater for the University of Melbourne device.

Using the error values in Table G.2 and Table G.3, the errors for $\phi$ and $(\lambda/V_p)r(\phi)$ are calculated for both the packed bed formation technique and the packed bed filtration technique using the equations in the previous section. The error ranges for each device are summarised in Table G.4.
<table>
<thead>
<tr>
<th>Device</th>
<th>Melbourne</th>
<th>Illinois</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error range $\phi_m$</td>
<td>0.3-1.6%</td>
<td>1.0-1.3%</td>
</tr>
<tr>
<td>Error range $(\lambda/V_p) r(\phi_m)$</td>
<td>3-10%</td>
<td>3-9%</td>
</tr>
<tr>
<td>Error range $\phi_f$</td>
<td>0.3-1.6%</td>
<td>-</td>
</tr>
<tr>
<td>Error range $(\lambda/V_p) r(\phi_f)$</td>
<td>2-5%</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table G.4** Error ranges for $r(\phi)$ determined by the packed bed formation technique and the packed bed filtration technique for devices at the University of Melbourne and at the University of Illinois.

**G.5 REFERENCE**
