MEMS PRESSURE, TEMPERATURE AND CONDUCTIVITY SENSORS
FOR HIGH TEMPERATURE AND HARSH ENVIRONMENTS

by

Abdolreza Rashidi Mohammadi

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B.Sc, Sharif University of Technology, 1993

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Abstract

Kraft pulp digesters have been used to convert wood chips into pulp for manufacturing a wide variety of paper products. Inside a kraft digester, chemical reactions remove lignin from their wood matrix in a caustic environment (pH~13.5, 170°C, 2 MPa). Data on actual internal operating conditions in a kraft digester is needed to optimize kraft digester operation and obtain maximum production quality. Currently, this information is limited to selected static locations on the periphery of the digester. The objective of this thesis is to develop miniature temperature, pressure, and liquid conductivity sensors for use in autonomous flow-following SmartChips to measure kraft process variables within the digester during their passage through the process.

Combined capacitive pressure and temperature sensors were fabricated by bonding silicon and Pyrex chips using a new polymeric gap-controlling layer and a high temperature adhesive. A simple chip bonding technique involving insertion of the adhesive into the gap between two chips was developed. A silicon dioxide layer and a thin layer of Parylene were deposited to passivate the pressure sensor diaphragm against the caustic environment in kraft digesters. The sensors were characterized at both high temperatures and pressures and no signs of corrosion could be identified on the sensors.

Integrated piezoresistive pressure and temperature sensors consisting of a square silicon diaphragm and high resistance piezoresistors were developed. A new Parylene and silicone conformal coating process were developed to passivate the pressure sensors against the caustic environment. The sensors were characterized up to 2 MPa and 180°C in an environmental chamber. The sensors’ resistances were measured before and after testing in a kraft pulping cycle and showed no change in their values. SEM pictures and topographical surface analyses were also performed before and after pulp liquor exposure and showed no observable changes.

Combined liquid conductivity and temperature sensor packages consisting of a platinum resistance temperature detector (RTD) and a four-electrode conductivity sensor formed by stainless steel electrodes and installed on a polyetheretherketone (PEEK) enclosure were developed. The sensors were characterized up to 180°C at NaOH concentrations of 10-100 g/l in the presence of wood chips and survived with no signs of corrosion.
Preface

The work presented in this dissertation was accomplished at the University of British Columbia under the supervision of Professor Mu Chiao from the Department of Mechanical Engineering, Professor John D.W. Madden from the Department of Electrical and Computer Engineering, and the late Professor Chad P.J. Bennington from the Department of Chemical and Biological Engineering. The idea of the SmartChip was originated by Professor Bennington.

The work presented in Chapter 2 is a version of the following articles:


All aspects of this work comprising the literature review, sensor design, microfabrication, laboratory experiments, analyses, and paper writing were conducted and written by Abdolreza R. Mohammadi under the direction of Professor Mu Chiao. Professor Mu Chiao, Professor Chad Bennington and Dr. Tim Graham provided me with expert advice and editorial suggestions in the first paper. The second article was editorially advised by Professor Mu Chiao and Professor Chad Bennington, and the third one was advised only by Professor Mu Chiao in terms of editorial suggestions.

The work reported in Chapter 3 is a version of the following paper:

All work presented including literature review, sensor design, mask drawing, laboratory experiments, analyses, and paper writing were conducted and written by Abdolreza R. Mohammadi under the direction of Professor Mu Chiao, who provided expert advice and editorial suggestions. The microfabrication of the piezoresistive sensor was carried out by Infineon Technologies SensoNor AS, Oslo, Norway, financially supported by Canadian Microsystem Corporation (CMC).

The work presented in Chapter 4 is a version of the following paper:


All aspects of this work including literature review, sensor design, fabrication, laboratory experiments, analyses, and paper writing were conducted and written by Abdolreza R. Mohammadi under the direction of Professor John Madden, who supplied expert advice and editorial suggestions. Also, Dr. Graham provided me with technical advice on the experiments, and editorial suggestions. The PEEK package, as a casing for the conductivity sensor, was designed and fabricated by Dr. Graham.

The work reported in Chapters 3 and 4 was also presented as a poster at the following conference:


My major contributions with the work presented in this thesis are the following:

- Applied a simple method to bond capacitive pressure sensors using an adhesive
- Used SU-8 polymer as a gap-controlling spacer in capacitive pressure sensors
- Used a new high temperature adhesive material to bond capacitive pressure sensors
- Used Parylene as a chemical protective coating
- Characterized the liquid conductivity sensors for multi-phase digester environments
- Developed sensors for the harsh environment of chemical reactors
- Developed new fabrication/packaging methods for sensors for harsh environment chemical process monitoring
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<tbody>
<tr>
<td>$</td>
<td>Dollar</td>
</tr>
<tr>
<td>°C</td>
<td>Degree celcius</td>
</tr>
<tr>
<td>A</td>
<td>Diaphragm area</td>
</tr>
<tr>
<td>α</td>
<td>One-half the diaphragm length</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>ADC</td>
<td>Analogue-to-digital converter</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>B₁</td>
<td>Resolution using a laboratory instrument</td>
</tr>
<tr>
<td>B₂</td>
<td>Resolution using the IC chip in a digester</td>
</tr>
<tr>
<td>BL</td>
<td>Black liquor</td>
</tr>
<tr>
<td>BOE</td>
<td>Buffered oxide etch</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>C₀</td>
<td>Zero-pressure capacitance</td>
</tr>
<tr>
<td>C₁</td>
<td>Smallest detectable variable increment using a laboratory instrument</td>
</tr>
<tr>
<td>C₂</td>
<td>Smallest detectable variable increment using the IC chip in a digester</td>
</tr>
<tr>
<td>CBF</td>
<td>Cold black liquor filtrate</td>
</tr>
<tr>
<td>Cₐl</td>
<td>Double-layer capacitance</td>
</tr>
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<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>Cₘ</td>
<td>Main capacitance</td>
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<tr>
<td>cm³</td>
<td>Cubic centimeter</td>
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<tr>
<td>cP</td>
<td>Centipoise</td>
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<tr>
<td>Cᵣ</td>
<td>Reference capacitance</td>
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<tr>
<td>d</td>
<td>Gap between two electrodes at zero-pressure</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
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<td>E</td>
<td>Electric field</td>
</tr>
<tr>
<td>ε</td>
<td>Dielectric constant of air</td>
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<td>E’</td>
<td>Young modulus</td>
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<tr>
<td>E₁</td>
<td>Minimum detectable variable in the laboratory</td>
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<tr>
<td>E₂</td>
<td>Minimum detectable variable in a digester</td>
</tr>
<tr>
<td>Ea</td>
<td>Activation energy</td>
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<tr>
<td>EA</td>
<td>Effective alkali</td>
</tr>
<tr>
<td>F</td>
<td>Force due to electric field in liquid</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
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<tr>
<td>F</td>
<td>Smallest detectable temperature increment using the IC chip in a digester</td>
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<tr>
<td>fF</td>
<td>Femtofarad</td>
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<tr>
<td>F_t</td>
<td>Viscous friction force</td>
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<tr>
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<td>Full scale concentration</td>
</tr>
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<td>Full scale height</td>
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<td>Full scale conductivity</td>
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<td>FSO</td>
<td>Full-scale output</td>
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<td>Full scale pressure</td>
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<tr>
<td>g</td>
<td>Gram</td>
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<tr>
<td>GPa</td>
<td>Gigapascal</td>
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<tr>
<td>g/l</td>
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<tr>
<td>hr</td>
<td>Hour</td>
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<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>i</td>
<td>Current in a Wheatstone bridge</td>
</tr>
<tr>
<td>I_1</td>
<td>Driven current</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated circuit</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
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<tr>
<td>K</td>
<td>Conductivity</td>
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<tr>
<td>K'</td>
<td>A constant dependent on electrolyte stoichiometry</td>
</tr>
<tr>
<td>K''</td>
<td>A constant relating to the ion concentration</td>
</tr>
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<td>kHz</td>
<td>Kilohertz</td>
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<td>l</td>
<td>Distance between two electrodes in liquid</td>
</tr>
<tr>
<td>L'</td>
<td>Lignin content</td>
</tr>
<tr>
<td>L_0</td>
<td>Initial lignin content</td>
</tr>
<tr>
<td>LTCC</td>
<td>Low-temperature co-fireable ceramics</td>
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<td>mA</td>
<td>Milliamper</td>
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<td>Microelectromechanical systems</td>
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<td>Megapascal</td>
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<td>mW</td>
<td>Milliwatt</td>
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<tr>
<td>N</td>
<td>Number of bits in an analog-to-digital converter</td>
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nA  Nanoampere
Na+ Sodium ion
Na2CO3 Sodium carbonate
Na2O Sodium oxide
Na2S Sodium sulfide
NaOH Sodium hydroxide
nm Nanometer
nV Nanovolt
O2 Oxygen
OH- Hydroxide ion
p Pressure
PECVD Plasma-enhanced chemical vapor deposition
PEEK Polyetheretherketone
pF Picofarad
pH Measure of acidity or basicity
ppm Part per million
r Ion radius
R Ideal gas constant
Ra Average roughness
RB Resistance of a Wheatstone bridge
RFID Radio-frequency identification
Ro Solution resistance between two outer electrodes
Rs Solution resistance between two inner electrodes
Rs1, Rs2 Solution resistance between outer and adjacent inner electrodes
RTD Resistance temperature detector
S Conductance
s Ion speed
S' Sensitivity
S25 Conductance at temperature 25°C
sccm Standard cubic centimeters per minute
sec Second
Si Silicon
SiC Silicon carbide
SiO2 Silicon dioxide
SOI Silicon on insulator
ST Conductance at temperature T (°C)
<table>
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<td>t</td>
<td>Time</td>
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<tr>
<td>T</td>
<td>Temperature</td>
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<td>t'</td>
<td>Diaphragm thickness</td>
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<tr>
<td>TCO</td>
<td>Temperature coefficient of offset</td>
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<td>TCS</td>
<td>Temperature coefficient of pressure sensitivity</td>
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<td>TMAH</td>
<td>Tetramethylammonium hydroxide</td>
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<td>u</td>
<td>Ionic mobility</td>
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<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>V_i</td>
<td>Input voltage</td>
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<tr>
<td>V_{in}</td>
<td>Voltage difference between two inner electrodes</td>
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<td>V_o</td>
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<td>Deflection</td>
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<td>White liquor</td>
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<td>Year</td>
</tr>
<tr>
<td>ze</td>
<td>Ion of charge</td>
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<tr>
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<td>Faradaic reaction impedance</td>
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<td>α</td>
<td>Temperature coefficient of conductivity</td>
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<tr>
<td>γ</td>
<td>A parameter dependent on the orientation and location of resistors on diaphragm</td>
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<tr>
<td>ΔΦ</td>
<td>Potential difference</td>
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<td>Ω</td>
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<tr>
<td>π</td>
<td>Pi (3.1415926)</td>
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<td>π'</td>
<td>Piezoresistive coefficient (Pa(^{-1}))</td>
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<tr>
<td>λ_m</td>
<td>Limiting molar conductivity</td>
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<td>Molar conductivity</td>
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<td>Micrometer</td>
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<td>Viscosity</td>
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<tr>
<td>ν</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>ω</td>
<td>Frequency</td>
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First of all, I would like to thank my Almighty God who has guided, supported and helped me throughout my life.

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I would like to acknowledge funding support from the Natural Sciences and Engineering Research Council of Canada (NSERC). Moreover, I would like to acknowledge the Canadian Microsystem Corporation (CMC), particularly Mr. Peng Yang, for their financial support to develop piezoresistive pressure sensors. Last but not least, I would like to thank my dear wife, Maryam Nasri, and my beloved son, Parsa R. Mohammadi, for their patience, encouragement, and support. I am very proud of them. I would also like to thank my parents and parents-in-law for always supporting and encouraging me.
1.1 Overview of Pulp and Paper Processes

Pulp and paper production is one of the major world industries and covers a diverse range of products from packing to hygiene products. In 2008, over 360 million tonnes of paper and paperboard and 175 million tonnes of pulp were produced in the world, and the demand for them is growing. The majority of the production is in North America, with 27% for paper and paperboard and 42% for pulp [1]. Canada, with its forests and forestry operations, is one of the leading producers of lumber, pulp, and paper in the world. Canada has over 997 million hectares of land; approximately 45% of its area is covered by forest, which represents 10% of the world’s vegetation.

Figure 1.1 Howe Sound Pulp and Paper’s continuous digester (Port Mellon, BC, Canada).
Papermaking processes roughly include six steps: (1) forestry: wood logs are harvested in the forest and carried to a mill; (2) chip preparation: logs are debarked and cut into approximately 1” long chips; (3) pulp production: the chips are cooked with white liquor, a basic solution for chemically attacking the chips, in a digester to produce pulp; (4) pulp post-processing: the pulp is washed, bleached, and dyed; (5) paper formation: water is drained from the pulp traveling down a moving screen. The resulting paper webs are compressed between rollers to remove the rest of the water. The paper sheets are further compressed and dried using heated rollers; (6) use: the final paper is then rolled for use.

The wide spectrum of paper products available necessitates various mechanical and chemical processes for pulp production. The kraft pulp process, the most common chemical process, chemically treats wood chips to extract lignin (delignification), the wood component in a kraft process. Figure 1.1 shows a photo of the Howe Sound Pulp and Paper’s continuous digester (Port Mellon, BC, Canada).

Figure 1.2 A schematic diagram of a two-vessel kraft continuous digester; (1) chip bin, (2) low pressure feeder, (3) steaming vessel, (4) high pressure feeder, (5) impregnation vessel, (6) cooking zone, (7) washing zone, (8) outlet, (9) final pulp washing [2].
Figure 1.3 A typical temperature profile of a kraft continuous digester.

The goal in a continuous digester is to make a uniform and continuous movement of wood chips through the digester and treat wood chips under optimal cooking conditions to obtain the maximum volume of pulp. As shown in Figure 1.2, a kraft continuous digester operation has briefly the following steps: (1) wood chips are added to the digester through a chip bin which is shaken and aids in the continuous and uniform feed and pre-steaming of the chips at atmospheric pressure. A chip meter, a rotating feeder, is placed at the bottom of the chip bin to control the production rate of the pulp; (2) a low pressure feeder is an intermediate step between the chip bin and the following steaming vessel. A low pressure feeder also acts as a sealer between a chip bin and a steaming vessel; (3) in the steaming cylinder, the air is pumped out from pores inside the wood chips; (4) the chips fall into a high pressure feeder and are pumped away to the top of the following vessel for impregnation; (5) a specified volume of white liquor (concentrated liquor) is added to the impregnation vessel and the liquor can easily penetrate into the voids inside the
chips at high pressure (1.3 MPa), since the air has already been eliminated. The chips are then transferred to the main digester for cooking; (6) the chips move uniformly downwards in the digester and are exposed to the various zones of liquor concentration and temperature, formed by pumping heated liquors inwards and outwards in different axial positions in the digester. These zones produce a uniform and controlled delignification. Black liquor, white liquor mixed with organic constituents due to fragmentation of lignin, is extracted from the digester for chemical addition or heat recovery; (7) liquor comprising fewer solid particles is moved upwards at a slow rate against the chips moving to the bottom of the digester (washing zone), washing the cooked chips. Black liquor inside the chip voids is replaced with the new liquor through a diffusion process; (8) the cooked chips are cooled and discharged at the bottom of the digester and converted to pulp, where a small pressure is applied in the blow unit and (9) the pulp is then washed to remove the remaining chemicals and dissolved lignin. More detailed information on the kraft pulping processes can be found in various textbooks [3, 4, 5]. Figure 1.3 shows a typical temperature profile of a kraft continuous digester.

1.2 Overview of Existing Problems and Research Objectives

The design and optimization of industrial multi-phase chemical reactors, particularly kraft pulp digesters, requires detailed information on the operating conditions within them to obtain the maximum production of the highest quality and most uniform pulp possible. Optimizing the digester would also enhance the operation of the entire fiber line. Continuous digesters, which require uniform and continuous movement of chips through the pulping process, attempt to create uniform and controlled reaction zones so that all wood chips are treated identically. Nevertheless, little information is available about the uniformity in these zones. Furthermore, the increased size of modern digesters is believed to reduce flow uniformity at various locations within them, which has led to operational problems and issues of non-uniform pulp production [6, 7, 8]. To understand and optimize the kraft digester operation, data on the actual operating conditions internal to the digesters is required.

Operational data from kraft digesters is typically taken at the vessel wall, however due to the large diameter of industrial digesters, conditions at the walls may vary from the conditions at the center of the digester. Unfortunately, measuring conditions at the center or anywhere away from
the digester wall without disturbing pulping operations is extremely challenging. The vast amount of sensor data from industrial digesters is obtained from a few static sensor locations used primarily for process control, which is insufficient to evaluate uniformity or validate existing computer models. The installation of additional sensors is limited to the periphery of the digester and enhancing the sensor grid sufficiently to validate or improve modern computer simulations is prohibitively expensive.

The goal of the overall project is to develop a class of autonomous flow-following sensors that can be released into industrial reactors, measure and record required data, withstand the harsh conditions of the process, and be retrieved from the reactor with the recorded data downloaded and processed. A flow-following sensor package, SmartChip, could be deployed at minimal cost and would provide sufficient data from throughout the vessels to gain a much clearer picture of the internal conditions of the reactors. The SmartChip contains conductivity, pressure and temperature sensors, memory chips, controlling electronics, and batteries for use in high temperature and harsh environment industries to determine the operating conditions inside multi-phase chemical reactors [9]. Specifically for kraft digesters, the SmartChip is designed to follow the path of a wood chip throughout the chemical pulping process and record four variables including temperature, time, solution conductivity and pressure within the digester. The purpose of a kraft cooking process is to extract as much lignin as possible from wood chips. This is performed by chemically attacking the chips and applying the heat for a period of time. The lignin content can then be measured using an aggregate measure (Kappa number) which is used to control the extent of delignification throughout the cooking and depends on the degree of cooking ($H$-factor, a cumulative factor quantifying the time and temperature profile of the cook) and the concentrations of $OH$ and $HS$ ions present in chemical reactions. Combination of temperature and time measured by the SmartChip during the kraft process can be used to determine the $H$-factor. The conductivity data measured by the SmartChip determines the concentration information. Both concentration and $H$-factor are used to compute lignin content in different locations of the digester which is determined using pressure data. For pulp digesters alone, the benefit to Canada is estimated to be over $80$ million/yr/($\%$ improvement) in digester operation. Many such flow-through sensors traveling through the digester would provide information on the distribution of physical and chemical conditions as a function of time and vertical position (based on pressure).
The chemical reactions inside the kraft digester take place at relatively high temperatures in a caustic chemical environment: temperatures up to 175°C, pressures up to 2MPa and \(pH\sim13.5\) due primarily to high concentrations of sodium hydroxide (NaOH). In order to successfully travel along with wood chips through the digester and record data, the SmartChip must be: (1) Small enough to navigate the pumps and channels present in the process; (2) Low cost, as the use of multiple sensors would make the data collection faster; (3) Low power, since the SmartChip is untethered and must carry all necessary power to remain in operation for the eight-hour transit; (4) Temperature compensated up to 180°C; and (5) Resistant to a harsh environment. Figure 1.4 shows an impeller installed at the base of Howe Sound Pulp and Paper’s continuous digester used in the filtration stage. To successfully pass through the opening between the impeller’s blades (10.5 cm x 6.5 cm), the SmartChip needs to be similar to the white mock-up foam (shown in Figure 1.4).

![Figure 1.4 An impeller used in the filtration stage at Howe Sound Pulp and Paper’s continuous digester. A white foam mock-up shown in the Figure is placed in the roughly rectangular gap (10.5 cm x 6.5 cm) between the impeller blades to show the maximum allowable size of a SmartChip.](image)
Chapter 1. Introduction

The overall project proceeds on two tracks: (1) Development of a prototype SmartChip (7.5cm diameter by 4.5cm height) from off-the-shelf electronic components encased in a resealable PEEK package; and (2) Development of a further miniaturized IC-SmartChip, matching the size of a wood chip (3×1.5×0.6 cm³). Recovery of the SmartChip package within a pulp product will be achieved using radio-frequency identification (RFID) technology after the digester operation is finished. The results of the project can be used to troubleshoot and improve a wide-range of industrial reactor systems.

Addressing the above requirements, my Ph.D. thesis investigates solutions that employ MEMS (Microelectromechanical Systems) technology for the fabrication of miniature sensors as a component of the SmartChip. The objective is to develop a planar, liquid conductivity sensor on the SmartChip package to measure the strength of alkali within the digester, a pressure sensor to measure the vertical location of the SmartChip within the digester, and an integrated temperature sensor to permit calculations of the chemical reaction that would be experienced by a wood chip following the SmartChip trajectory. The conductivities, pressures, and temperatures within the digester were expected to range from 100-1800 mS/cm, 1-1.7 MPa, and 120-175°C, respectively.

1.3 Organization of the Thesis

This thesis is presented in an introduction, three main chapters, and a conclusion. Each main chapter corresponds to one of the particular sensors developed for the SmartChip and includes a version of one or a few published, revised, or submitted articles to peer-reviewed journals and conferences.

Chapter 1 briefly reviews pulp and paper processes related to this thesis. It proceeds with existing problems in kraft digesters, followed by engineering solutions proposed in this thesis. Research objectives are described in this chapter.

Chapter 2 reports the development of integrated MEMS capacitive pressure and temperature sensors. In this chapter, a background of capacitive pressure sensors, their advantages and disadvantages, theoretical aspects, existing bonding methods, and temperature effects are reviewed. It is followed by design requirements, design, and fabrication processes. Finally,
experimentation, sensor characterization, and results in industrial pulping liquor are presented and discussed.

Chapter 3 presents the development of combined MEMS piezoresistive pressure and temperature sensors. A brief overview of piezoresistive pressure sensors, design requirements, and design are provided. It is followed by reports on the experiments, sensor characterization, and chemical resistance results.

Chapter 4 provides the development of a new liquid conductivity and temperature sensor package. The electrochemical background and existing conductivity methods are presented and the operation requirements of a conductivity sensor in kraft pulp digesters are reviewed. A sensor design and its specifications are described. Finally, the fabrication process and experimental characterization of the proposed conductivity sensor in industrial liquor and wood chips is discussed.

Chapter 5 summarizes the work presented in this thesis along with selection of the most suitable sensors for the implementation in a SmartChip. This is followed by a discussion of possible accuracies and resolutions in the measurements, the usefulness of the sensors in a digester and potential future work.
CHAPTER 2: Development of a Compensated Capacitive Pressure and Temperature Sensor Using Adhesive Bonding and Chemical-Resistant Coating for Multiphase Chemical Reactors

2.1 Background

Micromachined silicon-based pressure sensors are commercially available for many applications such as automotive, biomedical, and aerospace [10] and are typically offered as piezoresistive devices. Piezoresistive pressure sensors have piezoresistors forming a wheatstone bridge on a silicon diaphragm. Since they are very sensitive to temperature changes, they can be problematic for high temperature applications. Capacitive pressure sensors have advantages in their high pressure sensitivity [11, 12], low temperature sensitivity [13, 14], and low power consumption [15] compared with the more established piezoresistive sensors. Nevertheless, the change in capacitance is normally non-linear with pressure [16] unless a bossed diaphragm [17, 18, 19, 20] or a contact mode (touching electrodes) [21] is used for linearization. Furthermore, stray capacitance [22] and complex signal processing circuitry are two major disadvantages of the capacitive sensors [23]. The sensor must also be protected against the harsh environment of the digester. The operating principle of the capacitive pressure sensor is based on the change in capacitance that results from the external pressure deflecting a thin diaphragm, which reduces the gap between two electrodes [24, 25, 26]. The deflection of a square diaphragm can be calculated using [27]:

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1 A version of this chapter has been published or submitted for publication.

Chapter 2. Development of a Compensated Capacitive Pressure and Temperature Sensor

\[ w(x, y) = \frac{1}{47} p \frac{a^4}{D} \left( 1 - \frac{x^2}{a^2} \right)^2 \left( 1 - \frac{y^2}{a^2} \right)^2 \quad \text{and} \quad D = \frac{Et^3}{12(1 - \nu^2)}, \]  

(2.1)

where \( p \) is the pressure, \( a \) is one-half the diaphragm length, \( w \) is the deflection at different positions \((x\) and \(y\) coordinates) of the diaphragm, \( E' \) is the Young modulus, \( t' \) is the diaphragm thickness, and \( \nu \) is the Poisson’s ratio. Knowing the deflections in different positions of the diaphragm, the capacitance change can then be estimated [17]:

\[ C - C_0 = \int_A \frac{\varepsilon \, dA}{d - w(x, y)} - \frac{\varepsilon \, A}{d}, \]  

(2.2)

where \( C \) is the capacitance at a certain pressure, \( C_0 \) is zero-pressure capacitance, \( \varepsilon \) is the dielectric constant of air, \( d \) is the gap between two electrodes in zero-pressure, and \( A \) is the area of the diaphragm.

To bond a capacitance pressure sensor, wafer bonding techniques, such as anodic bonding [15, 28, 29, 30], fusion bonding [19, 31], solder bonding [32, 33], and glass frit bonding [34, 35] have been used. In the anodic bonding process, metallic interconnections create non-bonded areas and a complex process is required to prevent leakage [29]. Using glass frits or glue to bond the wafer makes it difficult to control the gap distance between electrodes [36]. Hermetic wafer bonding techniques have been used for MEMS packaging [37, 38]. In addition, adhesive wafer bonding technologies for integrated circuits and MEMS packaging have been reviewed [39]. For example, benzocyclobutene (BCB), an inorganic adhesive, was used as the structured adhesive bonding material [40]. Nevertheless, these techniques provide insufficient sealing to ensure the gas-tightness for hermetic bonding [41]. Also, adhesive reflow, which happens during heat curing processes, would cause difficulties in controlling their thickness and makes them unsuitable for forming a precise intermediate gap thickness. Furthermore, wafer-level bonding by different materials, such as polyimide and nafion, has been reported for circuit transfer and MEMS packaging [42, 43]. Nevertheless, polyimide shows a low bonding strength (1.5 MPa at room temperature) and nafion is attacked by alkali at normal temperature and pressure. Parylene has been used as an intermediate layer for wafer-level bonding [44, 45], though it is a
thermoplastic polymer that becomes soft at high temperatures. Recently, SU-8TM, a photosensitive polymer, has been used as a structural adhesive material for wafer bonding [46, 47].

Table 2.1 Comparison of capacitive pressure sensors developed for high pressure/temperature applications.

<table>
<thead>
<tr>
<th>Model</th>
<th>Pressure Range</th>
<th>Temperature Range</th>
<th>Sensitivity</th>
<th>Temperature Coefficient of Offset (TCO)</th>
<th>Chemical Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research [48]</td>
<td>0.1-2 MPa</td>
<td>25-250°C</td>
<td>2 mV/kPa</td>
<td>0.090% FSO/°C</td>
<td>No</td>
</tr>
<tr>
<td>Research [19]</td>
<td>0-0.1 MPa</td>
<td>25-180°C</td>
<td>0.2 pF/kPa</td>
<td>0.014% FSO/°C</td>
<td>Yes</td>
</tr>
<tr>
<td>Research [49]</td>
<td>0.1-0.5 MPa</td>
<td>25°C</td>
<td>6.8 fF/kPa</td>
<td>Not measurable, less than resolution used for measurements (&lt;100fF)</td>
<td>Yes, Using silicon carbide</td>
</tr>
<tr>
<td>Research [50]</td>
<td>0.1-3.8 MPa</td>
<td>25-250°C</td>
<td>1 fF/kPa</td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>Production Motorola MPXY8040A [51]</td>
<td>0.5-0.9 MPa</td>
<td>25-125°C</td>
<td>N/A</td>
<td>0.089% FSO/°C</td>
<td>No</td>
</tr>
</tbody>
</table>

Temperature affects capacitive pressure sensors in two ways: gas expansion in the cavity and packaging stresses [11]. A reference cavity [19, 52] and integrated active CMOS readout circuits [48] have been used to compensate the capacitive pressure sensors against thermal fluctuations. Special high temperature materials, such as silicon carbide (SiC) [53, 54, 55] and low-temperature co-fireable ceramics (LTCC) [56], have replaced silicon for use at extreme temperatures. Devices exposed to harsh environmental conditions must also be protected against the ambient media having a protective coating deposited onto the exposed area to prevent sensor malfunction or degradation due to chemical attack [57]. A variety of materials have been used for packaging in harsh environments [19, 36, 49, 58, 59]. Different types of Parylene (C, D, N, HT) have been shown to be chemical resistant. Parylene HT® (Specialty Coating Systems, Inc.) is chemically resistant to sodium hydroxide (NaOH) and has a maximum operating temperature of 450°C [60, 61]. Parylene C begins to oxidize at 180°C after an hour, but exhibits very high thermal stability in vacuum [60]. Polyetheretherketone (PEEK), which has been used for casings
for devices in harsh environments, withstands temperatures up to 315°C [60, 62]. Nevertheless, its coating technique (TECHTREX™ 71000 Series) needs a 400°C treatment process [63] that can damage other parts of the device. This paper explores the possibility of using Parylene as a coating material in high temperature and alkali environments.

Most capacitive pressure sensors developed in research or in production work operate within low pressure ranges, and chemically resistant capacitive pressure sensors with polymer coatings have not been demonstrated. Table 2.1 compares some of the sensors used in high pressure/temperature applications.

2.2 Sensor Design and Fabrication Process

2.2.1 Requirements

The sensors developed in this work must fulfill five primary requirements: (1) resistance to harsh chemical environment (pH~13.5); (2) temperature compensation up to 180°C; (3) small footprint; (4) pressure range from 0.1-2 MPa (the static pressure changes at a rate of 10 kPa per meter vertically in the digester); and (5) the ability to work at low voltage (2.5 V compared with those used in commercial sensors) to minimize power consumption.

In addition to caustic effects of digester environment, the pressure sensor may be squeezed or affected by possible mechanical impacts from wood chips in the digester. To solve this problem, the sensor will be recessed in the SmartChip package body and a metal or polymer guard with a hole (for pressure exertion) will protect the sensor from direct impact. The SmartChip package is designed to have a density close to liquor soaked wood chips’ (~1.1 g/cm³) and moves along with wood chips. Therefore, the effect of mechanical collisions between them is low. Moreover, within the cook zones, where liquor flow rates are higher, the sensor diaphragm may experience some additional deflection raising the capacitance readings, however, there are few points in digester where this might occur. In these locations, they might also be accompanied by a corresponding rise in temperature. This kind of error can be recognized as peaks in data during data analysis and should not adversely affect the quality of the results. Furthermore, the SmartChip is expected to travel slowly within digester so that
measuring dynamic pressures (rather than static pressures which shows the real vertical location) due to movement can be neglected.

Most commercial pressure sensors have a thin diaphragm (10-20 μm) that is more suitable for low pressure applications (0.1-0.7 MPa). In this paper, we consider a thicker diaphragm to accommodate the required pressure range. The diaphragm has dimensions of 71 μm × 1.6 mm × 1.6 mm.

Figure 2.1 Decreasing full-scale capacitance of a pressure sensor with increasing electrode gap distance.

2.2.2 Design

We decided to use a capacitive pressure sensor for the SmartChip device. An adhesive bonding technique is relatively inexpensive compared with other bonding methods [41], and vertical and lateral feed-through processes can be eliminated [29, 64]. The capacitive pressure
Chapter 2. Development of a Compensated Capacitive Pressure and Temperature Sensor

A sensor has two components: (1) a main capacitor with a silicon diaphragm that deflects under pressure and changes capacitance; and (2) a reference capacitor with fixed capacitance that does not change with pressure. To cancel the temperature effect, both capacitors must have the same gap thickness. A heat-curing adhesive was used to bond silicon wafers with Pyrex glass wafers. The adhesive thickness is the most significant parameter affecting the gap thickness in the capacitor, and to control for this, a photosensitive SU-8 (Microchem, Inc., Newton, MA) polymer layer was used to define the gap thickness around the two capacitors. Figure 2.1 shows simulated capacitance as a function of gap separation thickness between two electrodes. It can be seen that the gap thickness has a significant effect on the slope of the capacitance when the gap is less than 20 μm.

2.2.3 Fabrication Process

Double-side polished silicon wafers (300 μm in thickness) with 300 nm-thick thermally grown silicon dioxide and Pyrex wafers (700 μm in thickness) were used. The fabrication process is shown in Figure 2.2. Two wafers were individually fabricated and then bonded by the SU-8 polymer and adhesive. The sensor diaphragm was formed on the silicon wafer using bulk micromachining method. First, one side of the silicon wafer was patterned by a photoresist SPR 220-7.0 to define the diaphragm position. The silicon dioxide layer was etched with 10:1 BOE (buffered oxide etch) with an etching rate of 0.4 μm/min. After removing the photoresist by acetone, the silicon was etched to a depth of 229 μm, using a time-etch technique with tetramethylammonium hydroxide 25% (TMAH) to realize the silicon diaphragm. The depth of the cavity, and thus the diaphragm thickness, was measured to be 229 μm and 71 μm, respectively, by using a Wyco optical profiling system. A 2μm-thick PECVD (plasma enhanced chemical vapor deposition) silicon dioxide layer was deposited onto the diaphragm for first step of chemical protection against the digester liquor, which is a highly basic solution. We deposited a 100 nm gold layer onto the backside of the silicon wafer to form electrodes and interconnection lines. This process was done by photolithography, using infrared (IR) to align the main electrode on the back side with the diaphragm, and then lifting off the deposited metal with acetone. We finally used photolithography and the lift-off process to make a 100 nm platinum film as a
resistance temperature detector (RTD), with 1500 Ω resistance on the top of the silicon wafer beside the cavity.

Figure 2.2 Sensor fabrication process flow: a) Top electrodes, RTD and silicon diaphragm formation; b) Pyrex wafer with bottom electrodes; c) aligning and holding the silicon and Pyrex wafers; d) applying the heat curing adhesive and cure at 150°C for 10 min; e) Parylene coating for silicon diaphragm protection.
Figure 2.3 Top view of the capacitive pressure sensor: a) silicon diaphragm and platinum RTD and b) Pyrex wafer bonded to silicon substrate by heat curing adhesive between wafers (as seen through glass wafer).
The final cross-section view of the silicon wafer is shown in Figure 2.2(a). The second wafer (Pyrex) was used to pattern the bottom electrodes of the capacitors and their interconnections, as shown in Figure 2.2(b). The process included patterning the photoresist on the Pyrex, and evaporating 100 nm chromium with subsequent lift-off using acetone. To prevent short circuits between the two electrodes in the event they touched at high pressure, we deposited a 300 nm SiO₂ layer on the chromium electrodes by PECVD. As shown in Figure 2.2(c) and Figure 2.2(d), the two fabricated wafers were then aligned and bonded. We spun an 8.5 µm-thick SU-8 layer onto the silicon wafer and patterned it as a square ring around each electrode. The silicon chip and Pyrex chip were then aligned, and brought into contact. A mechanical clamp was used to provide the contact force. A heat curing adhesive RT154 (Resintech, Inc., Gloucestershire, UK) with a viscosity of 500-1000 cP, Young’s modulus of 2 GPa, and resistance to temperature up to 250°C was applied to the edges of the wafers to penetrate between them and create a strong adhesion at high temperature.

The low viscosity of the heat curing adhesive allowed it to penetrate into the gaps due to capillary effects. It covered the entire bonding area, but could not pass through the SU-8 rings. The package was then heated at 150°C for 10 min to cure the adhesive. The heating process is to give maximum bonding performance, according to the manufacturer’s data sheet (Resintech, Inc.).

Figure 2.3 shows the top view of the sensor and bonding area covered by SU-8 and the adhesive. We used a two-part high temperature conductive epoxy (MGchemicals, Inc., Surrey, BC, Canada) to connect thin wires to the pads, under a microscope. The sensor was then put into an epoxy (J-B Weld, Inc., Sulphur Springs, TX), which also had a high resistance to the chemicals in kraft digesters (commonly known as “liquor”).

To test for chemical resistance, three samples of silicon chips that had been deposited with silicon dioxide were prepared. To increase the adhesion of Parylene to silicon dioxide, the first two samples were cleaned and treated with oxygen plasma (pressure 500 mT, O₂ flow rate 100 sccm, power 300 watts, temperature 20°C, time 60 sec). The samples were then exposed to silane adhesion promoter (A-174, Gamma-Methacryloxypropyltrimethoxysilane) overnight and baked in an oven at 115°C for 30 min. The third sample was not treated with the silane adhesion promoter. The three samples were then conformally coated with 4-µm thick Parylene films. The first sample was coated with Parylene HT® and the other two samples were coated with Parylene
C. J-B weld epoxy was used to mount the outer edges of the silicon chips leaving a window (~ 1 cm x 1 cm) for liquor exposure. In addition, fabricated pressure sensors were coated with Parylene C.

2.3 Results and Discussion

2.3.1 Experimental Setup

A steel pressure/temperature chamber with a 10 pin electrical feed-through was used to characterize the sensors. The pressure was controlled, from atmospheric pressure to 2 MPa, using a nitrogen gas cylinder, a regulator, and a pressure gauge. A calibrated PX61C1-200AV commercial pressure transducer, with an accuracy of 1.0% (Omegadyne, Inc., Sunbury, OH), was used as a measurement reference. The reference sensor was positioned away from the chamber on the high pressure line to limit thermal error being introduced as the chamber was heated.

The chamber temperature was controlled by an Omega CN7800 controller with an STH102-060 tape heater wound around the chamber and a type-T thermocouple positioned close to the sample. The complete apparatus allowed for the characterization of the test sensor from 0.1 to 2 MPa, over a temperature range of 25 to 170°C. We used a Boonton 72BD capacitance meter with a resolution of 1 fF to measure the sensor capacitance. A common ground was used for the pressure chamber and the capacitance meter to minimize the effect of parasitic capacitance and external noise. Furthermore, the measurement cable was a 10 wire high temperature ribbon cable which added some offset capacitance to the measurement but allowed the separation and position of the measurement lines to be kept constant throughout all the measurements thereby minimizing disturbances in the measurement lines. An NI USB-9162 analogue to digital converter (ADC) was used to capture and store the output of the capacitance meter, the thermocouple, and the reference pressure sensor outputs simultaneously using the Labview software suite from National Instruments. All readings were continuously recorded vs. time with a sampling rate of 0.55 Hz. Figure 2.4 shows the testing setup used for the measurements.
Figure 2.4 Testing setup used for sensor measurement including pressure chamber, thermocouple, temperature controller, reference commercial pressure sensor, ADC, capacitance meter, data line to computer, and pressure line connected to nitrogen gas cylinder.

The capacitive pressure sensor was placed inside the chamber pressurized by nitrogen and connected to the capacitance meters via a high temperature cable. Since the ADC sampling rate was low (0.55 Hz), the chamber was pressurized and vented very slowly and the temperature ramp rate was carefully controlled; a rate of \(~1.7^\circ C/min\) was used for all experiments. The characterization of the sensors was carried out over the full pressure range, from atmospheric pressure to 2 MPa at various temperatures, from room temperature to 170\(^\circ\)C, though the temperature accidentally rose to 180\(^\circ\)C at atmospheric pressure in some experiments. Future work is required to validate the working condition of the sensor up to 180\(^\circ\)C, which may be reached locally in older digesters.
2.3.2 Results of Non-Coated Sensor in Nitrogen Medium

To test for leakage of the pressure sensor cavity, the sensor was left at 2 MPa pressure and 170°C for 4 hrs while the capacitance was monitored; no capacitance drop was observed at 2 MPa, and no signs of leakage could be seen. The change in capacitance vs. pressure at room temperature is shown in Figure 2.5, which correlates well with the theoretical expectations based on equations (2.1) and (2.2).

![Figure 2.5 A comparison of the main capacitor with theory, based on equations (2.1) and (2.2) at room temperature.](image)

The capacitance vs. pressure (Figure 2.6) is shown for three different temperatures, for both the main and the reference capacitors in the pressure sensor. At atmosphere pressure, the capacitance of the main and reference capacitors were 2.715 pF and 2.560 pF, respectively. The sensor showed an offset of 0.155 pF. The full-scale change in capacitance was 0.450 pF at 25°C.
and 0.505 pF at 170°C for the main capacitor. The reference capacitor showed an increase of only 23 fF and 49 fF at 25°C and 170°C, respectively, over the full pressure range. The average sensitivities of the main capacitor, in the pressure range of 1 MPa to 1.7 MPa, which is the operational range inside a kraft digester, were 0.244 fF/kPa and 0.276 fF/kPa, for 25°C and 170°C, respectively. While the main capacitor is sensitive to both pressure and temperature, the reference capacitor is only sensitive to temperature, so that a comparison of the main and reference capacitor outputs can be used to eliminate the temperature effects.

![Figure 2.6](image)

Figure 2.6 Response of the capacitors to pressure at different temperatures. The capacitance of the main capacitor increases with both temperature and pressure. The reference capacitor, however, is only sensitive to temperature and will not increase with pressure.

The increase in the sensor capacitance with temperature may be due primarily to shrinkage of the heat curing adhesive, since it is a thermoset material that shrinks with heating. The material has an elastic behavior so that the original interface thickness is restored after cooling.
Chapter 2. Development of a Compensated Capacitive Pressure and Temperature Sensor

Figure 2.7 Response of the capacitive pressure sensor as a function of temperature at atmospheric pressure.

The thermal and mechanical properties of SU-8 and the heat curing adhesive are similar. Coefficients of thermal expansion of SU-8 and the heat curing adhesive are 52 ppm/°C and 55 ppm/°C, respectively. Also, the Young modulus of both materials is reported to be 2 GPa, according to the manufacturers’ data sheets (Microchem and Resintech). Figure 2.7 shows the change in capacitance due to temperature at atmospheric pressure for both the main and reference capacitors. As the adhesive covers most of the bonding area, the compression force due to the adhesive shrinkage reduces the adhesive thickness at elevated temperatures. In both capacitors, the capacitances begin to increase with a low slope as a parabolic curve which becomes saturated before leveling off as the temperature reaches 160°C. The total thickness change due to the shrinkage from 25°C to 170°C was determined to be 1 µm by comparing the result with the theory [equations (2.1) and (2.2)]. As both main and reference capacitors have the
same construction, they behave similarly in variable temperatures, and thus, the reference capacitor can be used to compensate for changes due to temperature.

Figure 2.8 shows the subtracted outputs of the main and reference capacitors as functions of pressure at different temperatures that give rise to the temperature compensated data. The sensor readings at high temperatures (127-170°C) are closer to each other compared with those at room temperature and show a non-linear response.

![Figure 2.8 Subtracted outputs of main (Cm) and reference (Cr) capacitors as a function of pressure at different temperatures. Equation (2.3) is the final compensated sensor output, as shown in the dashed line.](image)

To use the sensor at different pressures and temperatures, a calibration formula is needed to convert capacitance to pressure. Ideally, all of the curves in Figure 2.8 should overlap, but due to thermal errors and geometric property mismatches, they are not identical. A final calibration curve, optimized for the operational range of the digester (120-170°C and 1-1.7 MPa), was used.
to determine the performance of the sensor. It was obtained by averaging the curves for 127°C and 170°C (Figure 2.8) as shown in equation (2.3):

\[
C = 0.0194p^3 - 0.0057p^2 + 0.1614p + 0.1585 ,
\]

where C is compensated capacitance (pF) and p is pressure (MPa). The average sensitivity of the sensor can be calculated to be 0.257 fF/kPa, from 1 to 1.7 MPa. As we envision deploying a number of SmartChips to obtain enough information during testing of an industrial digester, each pressure sensor must be calibrated independently.

![Figure 2.9 A comparison of uncompensated and compensated outputs of the capacitive pressure sensor at different temperatures with a commercial pressure sensor.](image)

A comparison between the temperature compensated and uncompensated sensor readings is shown in Figure 2.9. The room temperature calibration curve, based on the main capacitor
readings (Figure 2.5), was used to derive the uncompensated capacitance data in the form of measured pressure units. In other words, the main capacitor data measured at different temperatures was substituted in the same formula for the main capacitor calibration curve (Figure 2.5), showing possible main capacitor readings measurable at high temperatures. For example, at 170°C, the main capacitor reading at atmospheric pressure would be 1.393 MPa and will rise to 3.153 MPa at an applied pressure of 2 MPa.

Figure 2.10 Resistance of the platinum RTD as a function of temperature.

The compensated pressure is calculated from the calibration curve in Figure 2.8, where the main and reference capacitances are subtracted to compensate for thermal errors, which dramatically improves the accuracy of the pressure reading at elevated temperatures. Since the sensor is not ideal, the compensated outputs still have some thermal errors. Nevertheless, the compensation has been optimized for the operational range of the digester, 120-170°C and 1-1.7 MPa. The maximum thermal error due to temperature in these ranges is measured as ±1.74%
FSO. The thermal error may be improved in the future by using alternative structures and adhesives, and by changing the geometry to reduce the effect of adhesive shrinkage.

By combining the pressure and temperature sensor, the packaging requirements are simplified, ultimately reducing the final cost of the SmartChip. The characteristics of the onboard platinum RTD are shown in Figure 2.10, calibrated to a commercial RTD from Omegadyne Inc. The RTD wire has dimensions of 43 mm × 50 µm × 60 nm and a sensitivity of 2.68 Ω/°C.

Figure 2.11 SEM pictures of silicon chip sample surfaces. a) coated with Parylene C, after liquor exposure. The silicon surface is corroded; b) coated with Parylene HT®, after liquor exposure. The dark pinholes on the surface already existed before liquor exposure.
2.3.3 Results of Parylene-Coated Sensors and Silicon Chip Samples in a Kraft Digester Liquor Medium

Three silicon chip samples were exposed to kraft cooking liquor in a pressure chamber at 2MPa for a complete digester temperature cycle and time (see Figure 1.3). Figure 2.11 compares SEM pictures of samples coated with Parylene C (Figure 2.11(a) with no silane adhesion promoter) and Parylene HT® (Figure 2.11(b) with silane adhesion promoter A-174). From Figure 2.11(a), the surface of the silicon chip protected with Parylene C was corroded as a result of the Parylene degradation. The liquor has penetrated underneath the Parylene film probably because of inadequate adhesion to silicon, since no adhesive promoter was used. Figure 2.11(b) shows the surface of the silicon chip coated with adhesion promoter and Parylene HT® after exposure to liquor, and no corrosion can be identified. Energy dispersive X-ray spectroscopy (EDX) was used to analyze Parylene HT-coated chips, that showed approximately 33% silicon and 67% oxygen on the surfaces before and after exposure to liquor. This confirmed that the silicon dioxide layer on the chip surface was completely protected by Parylene HT®. Figure 2.12 compares the results of a roughness test done by the Wyco optical profiling system on silicon chip samples coated with Parylene HT®, before and after their exposure to liquor. Average roughness, $R_a$, remained the same, about 0.01 µm. The same roughness in the two graphs means that no corrosion on the silicon surface was made after liquor exposure and thus Parylene has been able to protect the silicon surface in the liquor.

To assess sensor performance in kraft liquor, sensors that were coated with Parylene C were tested in liquor medium in a pressure chamber. Figure 2.13 compares the results of pressure sensor readouts in nitrogen and in liquor at room temperature, indicating a good correlation between them. The effect of Parylene film deposited on the silicon diaphragm is negligible, since it has a thickness of 4 µm and a Young’s modulus of 2.7 GPa, compared to the values for the silicon diaphragm, which are 71 µm and 130 GPa, respectively. A comparison of the sensor responses to temperature in both nitrogen and liquor media is shown in Figure 2.14. This particular sensor failed at around 140°C in liquor due to packaging issues, in that liquor leaked through the edges of the sensor chip, probably due to poor adhesion between Parylene C and silicon dioxide.
Figure 2.12 The results of roughness measurements using a Wyco optical profiling system on silicon chip surfaces coated with Parylene HT® that showed the same average roughness ($R_a=0.01 \ \mu m$): a) before liquor exposure; b) after liquor exposure. The same roughness in the two graphs means Parylene has been able to protect the silicon surface in the liquor.
Figure 2.13 A comparison between sensors tested in nitrogen and in a liquor environment, at room temperature.

In an ideal fabrication process, Si and Pyrex wafers should be individually treated by adhesion promoter after being fabricated, to ensure even coverage, and then coated with Parylene HT® after bonding to minimize untreated areas that could allow liquor leakage.
Figure 2.14 A comparison of the sensor response to temperature in nitrogen and in a liquor environment.

3.1 Background

Micromachined silicon-based pressure sensors are commercially available for many applications such as automotive, biomedical, and aerospace [10] and are typically offered as piezoresistive devices. Piezoresistive pressure sensors have advantages in their robustness, linearity, simple measurement circuitry, and immunity to electromagnetic noise. However, difficulties in temperature compensation and fabrication control (that would affect sensor offset) are the two major drawbacks of piezoresistive sensors compared with capacitive sensors. Piezoresistive pressure sensors typically have two longitudinal piezoresistors ($R_1$ and $R_3$) and two transverse piezoresistors ($R_2$ and $R_4$) forming a Wheatstone bridge on a silicon diaphragm. The piezoresistors measure strain at the diaphragm edges and generate an electrical output proportional to the diaphragm deflection. The output voltage is calculated based on the equation (3.1):

$$V_o = \frac{R_1 R_3 - R_2 R_4}{(R_1 + R_2)(R_3 + R_4)} V_i$$

(3.1)

If the bridge is initially balanced, $V_o = 0$. When applying a pressure to the sensor bending the diaphragm downward, the first two piezoresistors extend, increasing their resistances, and the other two shorten, decreasing their resistances.

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2 A version of this chapter has been accepted for publication or presented as a poster.


Piezoresistive sensors are often produced by a bulk micromachining technique. The sensor’s diaphragm is formed by etching the back of the Si wafer. Junction-isolated resistors are then formed on the diaphragm by selectively doping to make the Wheatstone bridge on the diaphragm edges. A surface micromachining technique as an alternative method has been used to produce piezoresistive pressure sensors. The advantage of this method is the possibility of making small devices with a high packing density, but the maximum deflection of the diaphragm is limited by the thickness of the sacrificial layer and thus it can limit the measuring pressure range [65].

Commercial micromachined silicon-based pressure sensors are available in many applications, but chemically resistant piezoresistive pressure sensors with polymer coatings have not been demonstrated. Table 3.1 compares the present pressure sensor with a best match of commercial pressure sensors (Merit Sensor Systems, 7000 series).

Table 3.1 Comparison of present and commercial pressure sensors

<table>
<thead>
<tr>
<th></th>
<th>Sensors in this paper</th>
<th>Commercial Sensors [66]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die Size (mm)</td>
<td>3×3</td>
<td>1.6×2.2</td>
</tr>
<tr>
<td>Pressure Range (MPa)</td>
<td>0.1-2.1</td>
<td>0.1-3.5</td>
</tr>
<tr>
<td>Max Compensated Temperature (ºC)</td>
<td>180</td>
<td>150</td>
</tr>
<tr>
<td>Compensation Method</td>
<td>Linear calibration function</td>
<td>Active or passive</td>
</tr>
<tr>
<td>Sensitivity (mV/V.kPa)</td>
<td>0.116</td>
<td>0.005</td>
</tr>
<tr>
<td>Input Voltage (V)</td>
<td>2.5</td>
<td>5-15</td>
</tr>
<tr>
<td>Power Consumption (mW)</td>
<td>0.3</td>
<td>5-37</td>
</tr>
<tr>
<td>Non-Linearity @ 25 ºC</td>
<td>±7.9%FSO</td>
<td>±0.2%FSO</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

3.2 Sensor Design

The sensors developed in this work fulfill five primary requirements: (1) high sensitivity in the pressure range from 0.1-2 MPa (the static pressure changes at a rate of 10 kPa per meter vertically in the digester); (2) the ability to work at low voltage (2.5 V) to minimize power consumption without decreasing sensitivity; (3) temperature compensation up to 180ºC; (4) resistance to a harsh chemical environment (pH~13.5); and (5) small footprint. Previously, we developed harsh environment capacitive pressure sensors using adhesive bonding techniques
[67, 68], however, the fabrication process was unique and was not available in commercial foundry services. In this work, we developed piezoresistive pressure sensors that are fabricated by a commercial process. The combined pressure and temperature sensors consist of a silicon diaphragm having a Wheatstone bridge and a 4,500 Ω buried piezoresistive wire on the silicon chip as a temperature sensor which was used for pressure sensor compensation and temperature measurement.

### 3.2.1 Sensitivity

Sensitivity is one of the most significant performance criteria of a pressure sensor and is defined as the normalized output signal change due to the applied pressure per pressure change over a reference signal and can be expressed as [65].

\[
S' = \pi' \gamma \left( \frac{L}{D} \right)^2, \tag{3.2}
\]

where \( S' \) is sensitivity, \( L \) is diaphragm length, \( D \) is diaphragm thickness, \( \gamma \) is a parameter dependent on the orientation and location of the resistors on the diaphragm and \( \pi' \) (Pa\(^{-1}\)) is the piezoresistive coefficient. Sensitivity increases with the diaphragm length but reduces with the diaphragm thickness. However, controlling diaphragm thickness is often more difficult in a batch fabrication process of silicon pressure sensors [69].

Manufacturers of commercial piezoresistive pressure sensors intend to produce sensors with a linear behavior so that their output is predictable by a simple first-order equation. In order to linearize sensors, manufacturers often prefer thicker diaphragms with shorter lengths, especially for sensors working at higher pressure ranges. This would limit the sensor sensitivity as shown by the equation (3.2). Because the present sensor will integrate with an autonomous device which records the measured data in a flash memory, the linearity of the sensor is not critical as the data would be processed after recovery. This helps us design more sensitive sensors.

In order to increase the sensitivity, the piezoresistors should be placed on the diaphragm edges, which have the maximum stress [70]. The actual dimensions of the diaphragm and thus the position of its edges may change as much as ±17.5 μm due to fabrication errors. Therefore, to handle the highest strain on the edges, the longitudinal lengths of the piezoresistors should
minimally be the same as the tolerance amount (35 µm). Also, the distance between two transverse piezoresistors on the same edge should be the same as the tolerance amount.

### 3.2.2 Supply Voltage and Power Consumption

Most commercial pressure sensors are designed to use high voltage (5-30 V), which consumes high power. Because the autonomous SmartChip uses limited battery power with a continuous voltage of 2.5 V, the maximum power consumption for the sensory system, excluding electronics, is designed for 10 mW. The design of the present pressure sensor is based on 0.3 mW power consumption. The temperature sensor will consume 1.1 mW of power. In order to reduce power consumption, the ratio of the piezoresistors’ length to width (which is related to piezoresistor resistance) should be high enough to increase resistance and decrease current with a fixed supply voltage. Piezoresistors with a length of 45 µm and a width of 5 µm were chosen to provide a 10,000 Ω resistance. For each diaphragm edge, two parallel resistors were placed in the middle of the edge to double the resistance.

### 3.2.3 Temperature Compensation

Historically, piezoresistive pressure sensors have suffered from temperature sensitivity [69]. Uncompensated, they can work up to 55°C with accuracies on the order of 1% FSO. However, at temperatures greater than 55°C, due to their inherent cross sensitivity, the sensor must be compensated to retain accuracy. Since the pulp digester operates at temperatures from 120 to 180°C, the sensor outputs should be temperature compensated. The environmental temperature changes affect the piezoresistive silicon pressure sensor’s temperature coefficient of offset (TCO) and temperature coefficient of pressure sensitivity (TCS). The typical TCO and TCS of a silicon piezoresistive pressure sensor are 2-8% and 16-22% respectively, in a range of 100°C [71]. Six possible sources of temperature drift are responsible for changes in TCO and TCS, including temperature dependence of the piezoresistive coefficient, resistor mismatch among four resistors [69, 72], trapped gas expansion, junction leakage current, oxide stress, and packaging effects [69].

There are two basic approaches for temperature compensation:
• Passive: The temperature compensation is performed by connecting additional resistors to
the bridge.
• Active: The temperature compensation is done by connecting supplementary electronics
elements (amplifier, microprocessor) to one of the bridge arms. These arms are controlled by
temperature sensors which change the voltage of the arm as a function of temperature.

Moreover, temperature compensation can be done using double Wheatstone bridge [73]. A
pressure sensor based on silicon on insulator (SOI) technology has good linearity and sensitivity
at elevated temperatures above 200ºC. A buried SiO₂ layer is developed to isolate leakage
currents between the top silicon layer for the detecting circuit and body silicon at high
temperatures [74].

There are three parameters that can be changed during sensor design and which may affect
the behavior of the sensor at different temperatures: diaphragm length, thickness and material.
However the commercial foundry service we are using has restrictions on the film thickness and
materials. Their technology includes only two options of diaphragm thicknesses; 3.1 µm and
23.1 µm. Because the present sensor must work in a high pressure application, the thicker
diaphragm was used in the sensor design. Therefore, we were able to only change the diaphragm
length. Four diaphragm lengths (400 µm, 600 µm, 1000 µm and 1300 µm) were chosen for
different designs. The effect of diaphragm length on temperature compensation of the sensor
output is characterized. In order to compensate the sensor outputs, a linear behavior of output
voltages versus temperature was sought in sensors with different diaphragm lengths using
experimental data. This linear calibration function, which appears at certain diaphragm lengths,
was used to convert the sensor readings at different temperatures to room temperature outputs.

3.2.4 Small Footprints

The overall SmartChip dimensions must be similar to that of a typical wood chip added to
the digester (3×1.5×0.6 cm³). This would allow the SmartChip to follow the flow of the wood
chip bed as the SmartChip moves through the digester; these dimensions must include all the
components needed for autonomous operation. Therefore, the entire piezoresistive pressure
sensor package must be small enough so that it can be installed on the SmartChip. This
requirement is met by using the commercial MEMS fabrication technique. The software MEMS Pro V7.0 L-Edit was used to create mask drawings.

### 3.2.5 Chemical Resistance to Harsh Environment

The pulp digester has a high corrosive environment consisting of sodium hydroxide (NaOH, pH~13.5), sodium sulfide (Na$_2$S), and other organic constituents from the fragmentation of lignin. The sensors developed in this work must be passivated against this corrosive environment. Chemically resistant materials, such as silicon carbide (SiC) [53, 54, 55], have replaced silicon for use in extreme environments. Devices exposed to chemical environmental conditions must also be protected against the ambient media requiring a protective coating deposited onto the exposed area to prevent sensor malfunction or degradation due to chemical attack [57]. A variety of materials have been used for packaging in harsh environments [19, 58, 49, 59]. Polyetheretherketone (PEEK), which has been used for casings for devices in harsh environments, withstands temperatures up to 315°C [60, 62]. Nevertheless, its coating technique (TECHTREX™ 71000 Series) needs a 400°C treatment process [63] that can damage other parts of the device. Silicone has a thermal stability up to 300°C. A special silicone conformal coating (Fine-L-Kote™ SR, Techspray Inc.) has been used as a chemical resistant material for harsh environment applications. Low-temperature Hot-wire chemical vapor deposition (HWCVD) has been used to coat substrates with fluorocarbons (e.g. Teflon) films which are resistant to temperatures up to 260°C [75]. Parylene has been used in electronic components. The benefits of Parylene coating include room temperature conformal deposition, pinhole-free, excellent adhesion to most substrates, high moisture impermeability, high temperature and chemical resistance. Several types of Parylene materials with slightly different chemical structures are available for different applications. Parylene HT® has fluorine atoms instead of hydrogen atoms, making it highly thermal resistant. It is also chemically resistant to sodium hydroxide (NaOH) and has a maximum operating temperature of 450°C. Parylene C begins to oxidize at 135°C after 24 hours, but exhibits high thermal stability in a vacuum. Parylene is the only polymer that can practically use a vapor deposition process at room temperature. The three-step deposition process includes vaporization of solid dimmers to gaseous ones, pyrolysis of gaseous dimmers to
monomers, and finally Parylene deposition Figure 3.1 [60]. This paper explores the possibility of using Parylene as a coating material in high temperature and alkali environments.

![Chemical structure of Parylene](image)

**Figure 3.1** Three steps of vapor deposition process of Parylene including vaporization of solid dimmers to gaseous ones (H₂), pyrolysis of gaseous dimmers to monomers, and Parylene deposition, showing also the chemical chains.

### 3.3 Fabrication Process

#### 3.3.1 Die Fabrication

A fabrication process based on MultiMEMS technology from SensoNor [76] was used to make piezoresistive pressure/temperature sensors. The MultiMEMS process is useful for prototyping as well as large volume manufacturing of piezoresistive and thermal detection devices. The process combines the long-term, stable buried piezoresistors (used for temperature sensor) and sensitive surface piezoresistors (used for Wheatstone bridge) in diaphragm-based devices. Boron implantation and thermal diffusion processes were used to make buried or surface resistors and conductors in the silicon wafer. The silicon wafer was also micromachined using a wet etching technique to realize the diaphragms. The top glass wafer with a cavity and a through-hole was separately made for diaphragm protection against mechanical impacts. The bottom glass wafer was used to hermetically seal the silicon cavity.
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Figure 3.2 a) schematic diagram of the Infineon SensoNor MPW process [76], b) top view layout of the sensor, c) fabricated die including top glass for mechanical protection; silicon chip consisting of a diaphragm, wires and pads; and bottom glass for cavity sealing.

The fabrication process was completed with triple-stack anodic bonding of silicon with top and bottom glass wafers in a vacuum environment, forming absolute pressure sensors. Moreover, the fabrication process can be achieved by making a through-hole in the bottom glass and hermetically sealing the top glass. In this case, pressure is applied from the bottom glass and the diaphragm deflects upward. Figure 3.2 shows the schematic diagram of the Infineon SensoNor MPW process, the top view layout of the sensors and the fabricated dies, which include top and bottom glasses, a silicon diaphragm and piezoresistive resistors.

3.3.2 Packaging

For testing purposes, we used standard package CQZ08005 (ceramic base, 80 pins, cavity size 7.62 × 7.62 mm²) to package dies. The dies were placed in the middle of the package cavity with a high temperature epoxy (J-B Weld, Inc., Sulphur Springs, TX), which had a high operating temperature (up to 260°C) and high chemical resistance. The die pads were wire bonded to the package pins. To increase the adhesion of Parylene to silicon and the package body, the packages were treated with oxygen plasma (pressure 500 mT, O₂ flow rate 100 sccm,
power 300 watts, temperature 20°C, time 60 sec). Some of the packages were prepared for coating with Parylene C at UBC and the remaining were coated with Parylene HT® at a commercial facility (Specialty Coating Systems, Inc.). For Parylene C coatings, the packages were exposed to a silane adhesion promoter (A-174, Gamma-Methacryloxypropyltrimethoxysilane, isopropanol: DI water: A-174 with a ratio 100:100:1) using a stirrer for five hours and dried in air for 30 minutes. They were then soaked in isopropanol for five minutes and dried with air gun. The dried samples were baked in an oven at 115°C for 30 minutes (adapted from the Berkeley Microlab Laboratory Manual). A Parylene coater, model PDS 2010 Labcoter® 2 (Specialty Coating Systems, IN) was used to coat packages with 4-µm thick Parylene C films. The coater has a maximum capacity of 80 µm film thickness in each run. For coating a 1µm-thick film, 1.55 g Parylene material was used. The material was heated at 150°C under a vacuum (1 Torr) and the Parylene started to vaporize. The gaseous material was then pyrolyzed at 680°C under a vacuum (0.5 Torr) in a furnace to form Parylene monomers. The monomers were then polymerized at room temperature under 50 mTorr as a conformal coating on the sensor in a stainless steel deposition chamber [60]. The die surroundings, except the top glass and the pad areas, were potted into J-B weld epoxy for further protection against liquor. A special silicone conformal coating (Fine-L-Kote™ SR, Techspray Inc.) was sprayed on the Parylene-coated wires for a second chemical protection and electrical insulation. Based on the manufacturer’s datasheet, it has an operating temperature up to 200°C, tensile strength of 4.1 MPa, and high chemical and thermal shock resistances. The high flexibility of the coating prevents the wires from detaching from the pads due to thermal expansion.

We also considered an alternative packaging in order to protect the sensor against liquor. A similar die (gauge pressure sensor) which was opened from the bottom glass for pressure exertion was stuck on a bare package which already had a 1 mm hole in the middle of its cavity and then wire bonded. All other steps of coating and packaging were similar to the above. The Parylene film was conformally deposited on the back of the die cavity where the pressure is applied. In this case, the liquor is exposed only to the back of the silicon diaphragm, which results in the protection of the wires and piezoresistors on the topside of the diaphragm.
3.4 Results and Discussion

3.4.1 Experimental Setup

A steel pressure/temperature chamber with a 10 pin electrical feed-through was used to characterize the sensors. The pressure was applied from 0.1 to 2 MPa using a nitrogen gas cylinder, a regulator, and a pressure gauge. A calibrated PX61C1-200AV commercial pressure transducer with an accuracy of 1.0% (Omegadyne, Inc., Sunbury, OH) was used as a measurement reference. To limit thermal error being introduced as the chamber was heated, the reference sensor was positioned away from the chamber on the high pressure line. The chamber temperature was controlled by an Omega CN7800 controller with an STH102-060 tape heater wound around the chamber and a type-T thermocouple positioned close to the sample. The complete apparatus allowed characterization of the test sensor from 0.1 to 2 MPa over a temperature range of 25 to 180°C. An NI USB-9162 analogue-to-digital converter (ADC) captured and stored outputs from the sensor, the thermocouple, and the reference pressure sensor using the Labview software suite from National Instruments. This setup tests the sensor with the electronics being external to the chamber, considering only the effect of temperature on the sensor. A parallel work is being done to characterize the real electronics of the SmartChip system at high temperatures [77].

The piezoresistive pressure sensors were individually placed inside the steel pressure/temperature chamber, pressurized by nitrogen and connected to the ADC via a high temperature cable. A DC input voltage of 2.5 V was applied to the sensor Wheatstone bridge. To test for leakage within the pressure sensor cavity, the sensor was left at 2 MPa pressure and 180°C for four hours while the output voltage was monitored; no voltage drop was observed at 2 MPa and there were no signs of visible leakage from the rear cavity of the sensors with diaphragm lengths of 400 µm and 1000 µm. The ADC sampling rate is low (0.55 Hz), therefore, it is necessary to pressurize and vent the chamber very slowly and to carefully control the temperature ramp rate; a rate of ~1.7°C/min was used for all experiments. The characterization of the sensors was carried out over the full pressure range from atmospheric pressure to 2 MPa at various temperatures from room temperature to 180°C. To measure transient response of the sensor, a pressure step from atmosphere pressure to 2 MPa at room temperature was applied to
the sensor. An NI USB-6009 ADC with a sampling rate of 1 KHz was used to measure and record the transient response in the sensor output.

![Sensor output voltage versus pressure at different temperatures](image)

Figure 3.3 Sensor output voltage versus pressure at different temperatures (the sensor with a diaphragm length of 1000 µm).

### 3.4.2 Sensor Characterization

For sensors with a diaphragm length of 1000 µm, Figure 3.3 shows the sensor output voltage versus pressure at different temperatures. At atmospheric pressure the output voltage of the sensor measured 39.5 mV. The full-scale change in the Wheatstone bridge output was 603.5 mV at 25°C and 496 mV at 180 °C. Figure 3.4 shows the Wheatstone bridge output of the sensor with the smallest diaphragm length, 400 µm, as a function of pressure at different temperatures. There is an interlaced result with temperature. This result may be due to little change in output voltage with pressure as a result of little change in stress in the piezoresistors’ locations. The
sensors with diaphragm lengths of 600 µm and 1300 µm were tested and showed leakage within their sealed cavity due to anodic bonding problems, therefore it was impossible to characterize them in the chamber.

Figure 3.4 Sensor output voltage versus pressure at different temperatures (the sensor with a diaphragm length of 400 µm).

Figure 3.5 shows the change in sensor (with a diaphragm length of 1000 µm) output voltage with various temperatures for sensors under different pressures. A calibration formula is required to accurately measure pressure at different temperatures. Because of the linear behavior of the output with temperature, this calibration was performed using only two calibration points. There was an identical slope in the curves of the output voltage versus the temperature at different pressures between 0.9 MPa and 2.07 MPa at temperature range of 90-180°C. The pressure slope was 0.6 mV/°C and used for temperature compensation in this temperature range. The
temperature was compensated by the compensation curve $Y = aX + b$ using the driven slope shown in Figure 3.5.

![Graph](image)

Figure 3.5 Sensor output voltage versus temperature at various pressures (the sensor with a diaphragm length of 1000 µm).

Figure 3.6 shows the temperature compensated sensor output as a function of pressure at different temperatures. The sensor readings at high temperatures (110-180°C) are closer to each other compared with those at room temperature. In order to use the sensor at different pressures and temperatures, the same calibration formula is required to convert voltages to pressures. A final calibration curve, optimized for the operational range of the digester (120-180°C and 1-1.7 MPa), was used to determine the performance of the sensor. This calibration curve was obtained by averaging the curves of 110°C and 180°C (Figure 3.6) as shown in the following equation (3.3).
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\[ V = -0.0487p^2 + 0.3588p + 0.0651, \]  \hspace{1cm} (3.3)

where \( V \) is the compensated output voltage and \( p \) is the pressure. The average sensitivity of the sensor is calculated as 0.116 mV/V.kPa from 1 to 1.7 MPa.

Figure 3.6 Temperature compensated sensor output versus pressure at various temperatures (the sensor with a diaphragm length of 1000 µm). Equation (3.3) is the final compensated sensor output and is shown in the dashed line.

A comparison between the temperature compensated and the uncompensated sensor readings is shown in Figure 3.7. The room temperature calibration curve based on the sensor readings (Figure 3.3) was used to derive the uncompensated voltage data as a measured pressure unit. To derive this curve, the sensor data measured at different temperatures was substituted into the same formula of the room temperature calibration curve (Figure 3.3) to show the possible sensor readings measurable at high temperatures. For example, at 180°C, the sensor reading at
atmospheric pressure would be 0.072 MPa and will rise to 1.505 MPa at an applied pressure of 2.07 MPa. The compensated pressure is calculated using the calibration curve equation (3.3); this compensates for thermal errors and dramatically improves the accuracy of the pressure reading at elevated temperatures.

Figure 3.7 A Comparison between uncompensated and compensated outputs of the present sensor and a commercial pressure sensor at various temperatures (the sensor with a diaphragm length of 1000 µm).

Because the sensor is not ideal, the compensated outputs still have some thermal errors. Figure 3.8 shows the maximum thermal error over the full range of temperature as a function of pressure. The maximum thermal error of the compensated readings at a pressure range of 1-1.7 MPa is ±0.72% full-scale output (FSO).

By combining the pressure and temperature sensor, the packaging requirements are simplified, ultimately reducing the final cost of the SmartChip. The characteristics of the
onboard piezoresistive temperature sensor are shown in Figure 3.9, calibrated to a commercial RTD from Omegadyne Inc. It showed a sensitivity of 12.67 Ω/°C.

![Graph showing maximum sensor thermal error over temperature range from 25-180°C versus pressure (sensor diaphragm length of 1000 µm). The maximum thermal error in the operating pressure range of the digester, 1-1.7 Mpa, is less than ±0.72% FSO.]

Figure 3.8 Maximum sensor thermal error between 25-180°C versus pressure (sensor diaphragm length of 1000 µm). The maximum thermal error in the operating pressure range of the digester, 1-1.7 Mpa, is less than ±0.72% FSO.

Figure 3.10 shows the transient response of the sensor to a pressure step from the atmospheric pressure to 2 MPa at room temperature. The output voltages were normalized to the maximum pressure. The rise time was measured to be 1.1 s based on the time required for the response to rise from 10% to 90% of the difference between maximum and minimum outputs. However, the actual measured time may be less than this amount due to possible error in the speed of opening the pressure valve.
Figure 3.9 Resistance of the onboard piezoresistive temperature sensor as a function of temperature.

### 3.4.3 Chemical Protection Result

The Parylene C-coated packages were initially tested in pulp liquor at 2 MPa pressure and moderate temperatures up to 120°C to check for adhesion performance and integrity of the coatings. Visual inspection of the samples under a microscope showed no sign of etching and corrosion on the samples. To test the chemical resistance of the Parylene HT®-coated packages, the resistances of all the piezoresistors including the Wheatstone bridge (20,000 Ω) and temperature sensor (4,500 Ω) were carefully measured first, before being exposed to pulp liquor. The packages were then exposed to kraft cooking liquor in a pressure chamber at 2MPa for a complete digester temperature cycle and time (see Figure 1.3). The resistances of all the piezoresistors were measured again after liquor exposure. No changes in resistances could be identified that demonstrated a complete protection of the sensors against the liquor and there was no detaching of wires from pads due to thermal expansion.
Figure 3.10 Transient response of the sensor to the pressure step from atmospheric pressure to 2 MPa at room temperature, showing the rise time based on the time required for the response to rise from 10% to 90% of the difference between maximum and minimum outputs. The shown rise time may be lower due to errors arisen from manually opening the cylinder valve.

Visual inspection of the packages after liquor exposure (Figure 3.11) under a microscope showed no corrosion on the dies or packages. Furthermore, the silicon surfaces of the sensor diaphragms were examined by a scanning electron microscope (SEM) before and after liquor exposure. As shown in Figure 3.12, no differences can be observed on the sensor surface before and after liquor exposure. Moreover, the surfaces were topographically analyzed before and after liquor exposure using a Wyco optical profiling system (model Wyko NT1100). The surface analyses showed the same average roughness for the surfaces (Ra=0.01 µm).
The packages having the backside through-holes were exposed to the liquor with the same condition as above. Because the exposed areas of the silicon diaphragms had been hidden inside the ceramic package and were not available for SEM and topographical analysis, we examined them only using visual inspection and electrical tests. Visual inspection under a microscope showed no apparent signs of corrosion on the back of the packages. Furthermore, the resistance test indicated the same resistances of the Wheatstone bridge (20,000 Ω) and temperature sensor (4,500 Ω) before and after liquor exposure. Figure 3.13 shows the back of the package with a through-hole, which was exposed to the liquor. It should be noted that the presence of a small defect in the Parylene film or Parylene-silicon adhesion would cause a serious degradation in the device when exposing it to the liquor, and therefore the electrical measurement would give an open-circuit signal. Other failure modes, such as detaching wirebonds due to thermal expansion would also cause an open circuit in the Wheatstone bridge. Thus, resistance measurement alone can be the first step to testing the chemical protection performance of the SmartChip device.
Figure 3.12 SEM pictures of Parylene-coated silicon diaphragms, a) before liquor exposure, b) after liquor exposure.
Figure 3.13 Back view of the package including a through-hole for pressure exertion (sealed cavity by top glass).
CHAPTER 4: Development of a Liquid Conductivity and Temperature Sensor Package for Use in High Temperature and Harsh Environment of Multiphase Chemical Reactors

4.1 Background

Electrical conductivity of a solution is an intrinsic measure of how well it conducts ions, and is a function of temperature, the ionic species present and ionic concentration. Conductivity measurements have been extensively used in many industries to evaluate the purity of a non-specific liquid media or the concentration of a solution. Some of the most common applications of conductivity measurement are: controlling of water purity in cooling towers, heat exchangers and boilers [78], brewing processes [79], monitoring and control of demineralization [80], batch neutralization [81], water treatment [82], and leak detection [83], ion chromatography [84], oceanography [85], pharmaceutical processes [86], water purity [87], chemical processes [88], and treatment of liquids such as milk [89], juice [90], wine [91] and beer [92].

The objective of this chapter is to demonstrate a method for simultaneously measuring ionic conductivity and temperature that is compact enough and sufficiently low power to be effective in the SmartChip. The conductivity has been traditionally measured in kraft pulp digesters to determine the concentration of alkali. The current section describes electrochemical phenomena, a comparison between existing conductivity methods, and provides background on the pulping operation. The sensor requirements, the selection of the most suitable methods for the SmartChip, and the experimental characterization of the proposed conductivity sensor are discussed in the sections that follow.

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3 A version of this chapter has been submitted for publication or presented as a poster.

4.1.1 Electrochemical Phenomena

Electrical current in all media occurs via the flow of charge propelled by a potential difference. However, the mechanism of charge flow in liquids is different than metals: In metals, free electrons migrate within the atomic structure, while the flow of charge in electrolytic liquids is via ion migration. The dissolved ions are larger, less concentrated and have much lower mobility compared with electrons in metals. Hence the conductivity of electrolytes is generally lower than that of metals. The concentration vs. conductivity relationship is not a simple one as ionic interactions can greatly affect the conductivity of a solution [93].

4.1.1.1 Conductivity vs. Ion Mobility

When a potential difference (ΔΦ) is applied between two electrodes a distance, \( l \), apart in a solution, positive ions tend to migrate toward negative electrode and negative ions move toward positive electrode. The potential difference forms an average electric field (\( E = \frac{ΔΦ}{l} \)) that exerts a force, \( F \), on each ion of charge, \( ze \), and pulls it toward the opposite electrode:

\[
F = ze \Delta Φ . \tag{4.1}
\]

A viscous friction force which is proportional to the ion speed, \( s \), is exerted on the ion,

\[
F_r = s \cdot 6 \pi \eta r , \tag{4.2}
\]

where, \( r \), is hydrodynamic radius of ion and, \( η \), is viscosity. The balance of electrostatic and viscous forces leads to ions travelling at a speed which is proportional to local electric field, \( s = uE \), where \( u \) is ionic mobility [93, 94]. Conductivity, \( K \), of a solution depends on the number of ions as well as the mobility. Strong electrolytes are completely ionized even at high concentrations. According to Kohlrausch’s law [93, 95], strong electrolytes at low concentrations have conductivities which change with the square root of concentration,

\[
Λ_m = Λ_m^o - K \sqrt{C} , \tag{4.3}
\]
where $\Lambda_m$ is molar conductivity, $\Lambda_m^\circ$ is limiting molar conductivity when ions have no interaction with each other (infinite dilution), and $K'$ is a constant which depends on electrolyte stoichiometry. The concentration dependence becomes more complicated at the high concentrations typically encountered in the pulping process.

![Diagram](image)

Figure 4.1 Effect of relaxation on ionic movement, a) the ionic atmosphere is spherically symmetric in absence of an electric field, b) the atmosphere is distorted in presence of an applied electric field indicated by the arrow [93].

To describe the effect of ionic movement on the conductivity, it is assumed that an ion attracts other ions with opposite charges, forming an ionic spherical atmosphere around it and lowering the energy and chemical potential of the central ions due to electrostatic interaction with their ionic atmosphere. Because other ions forming the atmosphere can’t adjust themselves with the moving ion, the atmosphere consists of a lot of other ions behind it and no ions in front of it, lagging the center of the atmosphere charge (Figure 4.1). This relaxation effect causes decrease in ion mobility. The second effect of the ionic atmosphere is that viscous drag in the presence of the ionic atmosphere is enhanced due to movement of the atmosphere in opposite direction as it responds to the applied field [93]. This electrophoretic effect reduces ion mobility and conductivity. Conductivity increases at very high frequencies because ion motions are smaller than the size of the solvation sphere, and do not deform the solvation sphere, thereby
Chapter 4. Development of a Liquid Conductivity and Temperature Sensor

Reducing the effective ion size and drag. According to the Debye-Falkenhagen law, high frequencies are required to overcome these relaxation effects in solutions [96].

Figure 4.2 Conductivity of NaOH solution as a function of effective alkali concentration. The data is extracted from handbooks [97, 98].

4.1.1.2 Conductivity vs. Concentration

Strong electrolytes are completely dissociated in water at low concentrations and their conductivity is directly proportional to their concentration. As concentration increases, ion density increases which results in a corresponding decrease in ion mobility, due to the electrophoresis effect. The electrolytic conductivity reaches a maximum and increasing the concentration further will in fact reduce the conductivity of the solution. In concentration ranges where conductivity is a function of concentration, a conductivity measurement can be used to
determine the concentration of a known solution. Figure 4.2 shows conductivity of NaOH solution vs. concentration [97, 98]. Peak effective alkali concentrations of NaOH in the kraft process can typically reach 85 g/l as Na₂O in fresh (white) liquor, and drop down to 11 g/l as Na₂O in spent (black) liquor, where conductivity is clearly increasing with concentration, thus enabling conductivity measurements to be used to estimate concentration.

4.1.1.3 Polarization and Electrical Double Layer

When a voltage is applied to the electrodes, positive and negative ions migrate toward negative and positive electrodes, respectively. This leads to the accumulation of ions at positive and negative electrodes known as the double layer. Also, when electrodes are placed into a solution, chemical interactions cause ions to be adsorbed on the electrodes and therefore charge accumulations happen on electrodes, again contributing to the double layer. This layer creates a capacitive impedance that reduces the apparent conductance [99]. Ions and molecules can also deliver charges to or accept charges from electrodes. The impedance of this electron transfer and of an insulating gas phase layer that can develop on each electrode is a barrier for conductance, leading to a decrease in apparent conductivity. These effects lead to false conductivity readings [100, 101]. The effects of both the polarization and double layer can be minimized using low-amplitude, kiloHertz frequency alternating currents [102], limiting the accumulation of charge at electrode surfaces and reducing electron transfer. At high frequencies the surface impedance is minimal.

4.1.2 Existing Conductivity Methods

There are two basic approaches for liquid conductivity measurement, contacting and inductive. In the inductive, non-contacting, method toroidal sensors are often employed. These sensors are used in solutions which are corrosive and where fouling of the electrode surface is a significant issue. Electrodeless conductivity sensors don’t have sensing electrodes in direct contact with the solution. They consist of two aligned toroidal coils with the analyte solution to passing through the centers of coils, forming a secondary loop for the first coil and primary loop for the second coil. They typically operate like a transformer by inducing an alternating current
in the solution loop and using the second coil to measure this current [103]. Similar eddy current transducers for conducting electrolytes have also been described [104]. They are an effective method for monitoring interface level of liquids which have different conductivities. A special inductive sensor has been developed using a coil wound with a two-layer wire around a tube to measure concentration of electrolytic solutions [105]. The sensor works based on the change of inductance of the coil at different concentrations of the solution. Although these sensors are non-contact and thus attractive for use in corrosive and fouling environments, the need for coils results in a relatively large footprint and a more involved fabrication procedure, both of which are ideally avoided in making compact, low cost sensors.

Most conductivity sensors measure conductance using a two-electrode contacting method. This method is performed by applying an alternating voltage between two electrodes in a solution and measuring current flow between them. However, this method has polarization and fouling problems which result in an apparent change in conductivity due to in fact to changes at the electrodes. Fouling is a particular issue in pulping operations [106].

One approach to overcoming this problem with the two electrode measurement is using porous electrodes where the electrode’s surface area is generally increased by 100 times or more. This effect can be further enhanced by coating the surface with a catalyst, normally platinum-black, in order to decrease the impedance between the electrodes and electrolyte thus increasing the speed of charge transfer. The porous electrode approach is suitable where kinetics limitations are an issue, but in situations such as pulping where plugging of pores is possible, it is not ideal. An alternative is to use of the four-electrode method [107]. An alternating current is applied between two outer electrodes while the voltage difference between the two inner sense electrodes enables the resistance to be determined, as shown in Figure 4.3. As the impedance of the measuring instrument connected to inner electrodes is much higher than the resistance between two outer electrodes, the current flowing through inner circuit is almost zero. Minimal charge transfer between two inner electrodes means that potential drop due to fouling and reactions at the sense electrode surfaces will be negligible.

Much work has been done on both methods of contacting measurement. For example, two-electrode and four-electrode MEMS-based silicon liquid conductivity and temperature sensors have been developed [107]. A micro four-electrode electrolytic conductivity sensor was fabricated to measure conductivity of blood [108]. A conductance cell with a low
electrode/solution impedance was also developed [109]. However, these sensors can’t be used in harsh environments. The background and methods used in our approach are now described.

![Figure 4.3 Equivalent model of four-electrode electrolytic conductivity measurement.](image)

Figure 4.3 Equivalent model of four-electrode electrolytic conductivity measurement. $I_1$ is driven current flow to outer electrodes, $V_0$ is measured voltage across inner electrodes, $C_{dl}$ is double-layer capacitance of each electrode, $Z_F$ is Faradaic impedance of each electrode, $R_{s1}$ and $R_{s2}$ are solution resistance between outer and adjacent inner electrodes and $R_s$ is solution resistance between two inner electrodes [107].

An equivalent circuit of four-electrode configuration is shown in Figure 4.3. Each electrode generates a double-layer capacitance ($C_{dl}$) and a Faradaic reaction impedance ($Z_F$) which is associated with equilibrium or nonequilibrium electrochemical reactions in the interface of electrode and solution. These two parameters depend on surface potential, ionic species, and concentration and their overall effect is defined as electrode impedance ($Z_e$). This electrode impedance may change over time due to fouling. Use of high frequencies enables the electrode resistance to be minimized, even in the case of light fouling, since the surface capacitance has an impedance that drops with increasing frequency. $R_{s1}$ and $R_{s2}$ are solution resistance between outer and adjacent inner electrodes and $R_s$ is solution resistance between two inner electrodes. Only double layer exists in an ideally polarized electrode [107]. The voltage drop between the two inner electrodes is the sum of the drop across the electrode impedances ($Z_e^3$ and $Z_e^4$) and the voltage drop across $R_s$. Providing that the inner electrodes are connected to a very high impedance device (e.g. a voltmeter) so that the current through these electrodes is very small, the
measured voltage drop from these sense electrodes is well described as the product of the current $I_1$ and the resistance, $R_s$.

Table 4.1 A comparison between three types of conductivity sensors (two-electrode, four-electrode, and inductive)

<table>
<thead>
<tr>
<th></th>
<th>Two-electrode</th>
<th>Four-Electrode</th>
<th>Inductive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>Very low to high conductivities</td>
<td>Very low to high conductivities</td>
<td>Low to high conductivities</td>
</tr>
<tr>
<td>Maintenance</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Complexity</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Polarization</td>
<td>Moderate</td>
<td>Low</td>
<td>Zero</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Size</td>
<td>Smallest</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>RTD Response</td>
<td>Fast</td>
<td>Fast</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Table 4.1 compares the contact methods (two and four-electrode) and the inductive approach for electrolytic conductivity measurement. As discussed the main advantage of the inductive method is that it is more resistant to fouling and Faradaic interactions, while its main drawbacks are size and sensitivity. Contacting conductivity sensors have electrodes which are susceptible to fouling, corrosion and polarization, especially in highly concentrated solutions, and are subject to high maintenance. But electrodeless sensors having toroidal coils are embedded in chemically resistant polymers and are immune to these kinds of problems; they need cleaning only when their cell constants may change due to fouling or coating inside their polymeric casings. However, RTDs embedded inside inductive sensors may respond slowly to temperature changes since the thermal conductivity of the polymers are low. Both kinds of conductivity sensors can measure a wide range of conductivity, from low conductivities (e.g. water, though contacting is best for extremely pure water) to very high conductivities (e.g. concentrated salt solutions). Since the solution makes a loop around the inductive sensors, the system is large and has a geometry that is harder to miniaturize than the simple electrode structure of a contacting conductivity probe. Contacting conductivity sensors used for highly concentrated solutions also need large cell constants to be able to accurately measure conductivity. Scaling down the contacting conductivity sensor makes them more susceptible to fouling and polarization, invalidating the
readings. Also, scaling down the inductive conductivity sensors makes them useless as their sensitivity rapidly falls down.

Both contacting and inductive methods have been used in kraft pulp digesters to measure conductivity of the pulp liquor [110]. However, because they have been mounted through the very thick walls of the digester they are expensive (installation cost for each sensor is $30,000-$50,000) and measure the conductivity of only a very limited portion of the digester. Furthermore, they typically use voltages that are significantly higher than those available on conventional chips to operate, which is a challenge to replicate in a battery operated device. Also, all are too large to be used in SmartChip. In the next section we demonstrate that the four-electrode method is a reasonable choice for use in the SmartChip due to its simpler geometry.

4.1.3 Concentration, Conductivity and Temperature Ranges in Kraft Pulping

The kraft pulping process is used as the first stage to produce pulp from wood chips. An aqueous alkaline solution, white liquor, and wood chips are fed and heated in the kraft digester in order to extract lignin from wood. Temperature profile is a key variable in the kraft pulping process, as the reaction rate is exponentially related to temperature, as is cooking time. Variations in the temperature-time curves between chips lead to significant variation in the resulting pulp. Conventionally, temperatures of locations in the digester such as the liquor circulators, the heated steam, and several vertical locations of the digester near the wall are measured during the process. Also, it is essential to carefully monitor the alkali concentration within the kraft process. Alkali concentration determines the amount of wood which can be processed for a volume of liquor.

The term “effective alkali” \( (EA) \) is typically used to describe the strength of alkali. It is sum of the \( \text{OH}^- \) producing salt contributions. \( \text{NaOH} \) is completely ionized and one \( \text{OH}^- \) is produced for two atoms of \( \text{Na}_2\text{S} \), meaning that contribution of \( \text{Na}_2\text{S} \) is half of that for \( \text{NaOH} \) in effective alkali. When wood chips are cooked with white liquor in a kraft digester, the hydroxide and sulfide are consumed and lignin is extracted from wood chips. The purpose of a kraft cooking process is to extract as much lignin as possible from wood chips. This is performed by chemically attacking the chips and applying the heat for a period of time. The lignin content can then be measured using an aggregate measure (Kappa number) which is based on the volume of
potassium permanganate solution consumed by one gram of the pulp and used to control the extent of delignification throughout the cooking. The lignin content can be calculated using:

\[
\ln \left( \frac{L'_0}{L'} \right) = K^* \cdot H,
\]

where \( L' \) is the lignin content achieved by a certain amount of cooking (\( H \)-factor), \( L'_0 \) is initial lignin content in the wood chips, \( K^* \) is a constant relating to the concentrations of \( OH^- \) and \( HS^- \) ions present in chemical reactions, and \( H \) is an accumulative factor qualifying the time and temperature profile of the cook that can be calculated based on:

\[
H = \int_0^t \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{373} \right) \right] dt,
\]

where \( t \) is time (hr), \( T \) is temperature (°K), \( E_a \) is the activation energy, and \( R \) is the ideal gas constant [5].

The resulting black liquor has more suspended non-conductive organic materials and less residual alkali. Since electrolyte conductivity is largely determined by the \( OH^- \) content, conductivity is correlated with the extent to which a volume of electrolyte is active. Typical white and black liquors have ranges of effective alkali 80-100 g/l as Na\(_2\)O and 11-17 g/l as Na\(_2\)O, respectively [2], depending on the type of digester. A conductivity range of 100-1800 mS/cm was chosen as the typical operating range of conductivity in a kraft pulp digester [111]. Figure 4.4 shows a schematic digester indicating time, temperature and concentration in different zones. Temperature and two main inorganic compounds in liquor including sodium hydroxide (NaOH) and sodium sulfide (Na\(_2\)S) affect local liquor conductivity. Previous work showed that at the concentrations present in pulping, sodium carbonate does not contribute significantly to conductivity [112].
Chapter 4. Development of a Liquid Conductivity and Temperature Sensor

Figure 4.4 A schematic diagram of a kraft continuous digester showing temperature, time intervals, and effective alkali concentrations in different zones. A=upper impregnation vessel, B=lower impregnation vessel, C=upper dig, D=extraction zone, E=cooking zone, F=washing zone, WL=white liquor, BL=black liquor, and CBF=cold black liquor filtrate.

4.2 Sensor Design

The combined conductivity and temperature sensor developed in this work consists of a four-electrode contacting conductivity sensor, a 1000 Ω platinum RTD enclosed in a stainless steel container and positioned close to sensor electrodes, and a polymer package. When a potential is applied between two outer electrodes, a current is passed in solution by ions. When no electrolysis occurs in the solution, the current is proportional to the voltage based on Ohm’s law [113].

\[ \Delta \Phi = I \cdot R_O \]

where \( \Delta \Phi \) is the applied voltage, \( I \) is the current, and \( R_O \) is the resistance between the two outer electrodes in the solution. As the inner electrodes are placed in the path of the current, part of the
current induced voltage difference is between the inner electrodes \( V_{in} \). As the impedance of the instrument measuring voltage difference is very high compared with the resistance between the two inner electrodes in the solution, almost no current passes through the external circuit connected to the inner electrodes, thereby minimally affecting the current. In addition, providing that the input impedance of the voltmeter is large compared to the sensing electrode impedance, the voltage drop will be almost entirely across the voltmeter. The conductance \( S \) between electrodes is given by equation (4.7):

\[
S = \frac{1}{R_s} = \frac{I}{V_{in}}. 
\] (4.7)

The resistance of the solution between the sensing electrodes \( R_s \) is related to the distance between inner electrodes and the concentration [114]. The objective is to measure conductance of a volume of solution between the two inner electrodes. The cell constant \( \theta \) [100] which is the ratio of the solution conductivity to the conductance,

\[
K = \theta . S, 
\] (4.8)

can be determined using solutions such as potassium chloride having well known conductivities at particular temperatures and concentrations [115]. The conductivity \( K \) then can be computed using equation (4.8) [84].

The sensors developed in this work were designed to fulfill five primary requirements: (1) planar structure to match the wood chip shape; (2) temperature compensation up to 180°C to enable operation in the digester; (3) the ability to work at low voltage (less than 2.5 V) to minimize power consumption and avoid the need for voltage conversion; (4) resistance to harsh chemical environment (pH~13.5) as found in the pulping process, and (5) the ability to determine conductivity in order to relate it to effective alkali.

The simpler geometry of the planar, contacting method makes it a reasonable starting point. We demonstrate that it can effectively measure conductivity with the sensitivity required.
4.2.1 Structure

The conductivity sensor needs to be small enough to be fit to the SmartChip package. Inductive conductivity sensors typically employ 3-D toroids, a large secured cell constant, and need a circulation loop of liquid through the middle of coils. Therefore, the inductive method is not employed. The two-electrode method is simple to construct but is very sensitive to fouling and polarization issues. Given these consideration a planar four-electrode method which consisted of two driven outer electrodes (4 mm diameter) and 2 sensing inner electrodes (0.5 mm diameter) is selected for the SmartChip conductivity sensor, as shown in Figure 4.5(a) in the initial prototype device. The distances between two outer electrodes and two inner electrodes are 20 mm and 16 mm, respectively. An epoxy (J-B Weld, Inc., Sulphur Springs, TX), which is highly resistance to the liquor, is used to seal electrodes in the package.

4.2.2 Temperature Compensation

The mobility of ions in a solution depends on concentration of ions, temperature and applied electrical field. The temperature coefficient of conductivity for liquids is typically positive (compared with metals which have negative coefficient) and is almost constant for a specific solution; the temperature effect is instantaneous, repeatable and large - in the range of 1-3% per ºC depending on type of electrolyte [116]. The coefficient for sodium hydroxide is around 2% per ºC. This increase in conductivity due to temperature can be compensated for using a linear equation with reference to 25°C [88, 116, 117].

\[
S_T = S_{25} \left(1 + \alpha (T - 25)\right),
\]

where \(S_T\) is conductance at operating temperature \(T\) (°C), \(S_{25}\) is conductance at 25°C and \(\alpha\) is temperature coefficient. However, in the real case, the temperature effect is a bit nonlinear and the temperature coefficient can vary as a function of both temperature and chemical concentration. In industry, when an unknown electrolyte is investigated, the temperature coefficient of conductivity is assumed to be 0.02°C\(^{-1}\) [118]. The behavior of conductivity with temperature in pulping liquors has been determined to be linear [119]. Once the conductivity is related back to 25°C, Figure 4.2 is used to estimate concentration. The combination of
temperature, time and \( \text{OH} \) concentration, as measured by the SmartChip, can then be used to estimate the degree of delignification of a wood chip [5].

### 4.2.3 Power Consumption

Most commercial conductivity sensors are designed to use voltages (16-35 V) well beyond those of a single battery cell which is not practical in our case because of the extra circuitry needed to boost voltage and the associated losses that would be incurred in this conversion. Because the autonomous SmartChip uses limited battery power with a continuous voltage of 2.5 V, the maximum power consumption for the sensor system, excluding electronics is designed to be 10 mW. The design of the present conductivity sensor is based on drawing 1 mA current in outer electrodes and on average consuming 5 mW power over the expected range of conductivity and temperature.

### 4.2.4 Chemical Resistance to Harsh Environment

The kraft digester environment consists of highly caustic chemicals and some organic constituents from lignin fragmentation, making it a harsh environment. Thus, the conductivity sensor which is in contact with liquor should be chemical resistant. In the presence of aggressive chemicals, noble metals such as platinum and gold are the best choice as they are resistant to corrosion. Also, titanium has been used as the contacting electrodes. However, they are very expensive and not ideal for developing a low cost SmartChip. Today, most electrodes of contacting conductivity sensors are made with graphite or stainless steel [115]. As graphite is brittle, stainless steel 316 is chosen as the electrode material. It is not only resistant to corrosive chemicals, but also hot NaOH is often used to clean the surface of this steel. Moreover, the sensor has a sealed package and acts as a protective enclosure for the electronics processing and recording data. The package body is made from PEEK material which withstands chemicals and temperatures up to 315°C [60, 62].
4.3 Results and Discussion

4.3.1 Experimental Setup

A steel pressure/temperature chamber with an electrical feed-through was used to characterize the sensors. The chamber temperature was controlled by an Omega CN7800 controller with an STH102-060 tape heater wound around the chamber and an RTD placed in a stainless steel container, embedded in the package, and positioned close to the sensor electrodes. As the micro-bubbles are generated in the solution at temperatures close to 90°C affecting the readings, the chamber was pressurized to 2 MPa using a nitrogen gas cylinder, a regulator and a pressure gauge to keep the liquor from boiling (It has been shown that pressures under 100 MPa don’t affect the result of conductivity measurement [120]).

An Agilent 33220A function generator was used to generate an AC sinusoidal constant current of 1 mA at 20 KHz across the outer electrodes over the full range of concentrations and temperatures. An HP 34401A digital multi meter with a resolution of 10 nA was used in series with function generator to measure current flow through outer electrodes. An identical digital multi meter with a resolution of 100 nV was also used to measure voltage drop across inner electrodes. The outputs of two multi meters were captured using a GPIB parallel cable and an 82357B high speed USB/GPIB interface. An NI USB-9162 analogue to digital converter (ADC) was used to capture the RTD output. Both GPIB and ADC readings were recorded using the Labview software suite from National Instruments. All readings were continuously recorded vs. time with a sampling rate of 0.55 Hz. The conductivity sensor package was placed in a beaker including liquor inside the chamber pressurized by nitrogen and connected to the multimeters and ADC via a high temperature cable. Since the ADC sampling rate was low (0.55 Hz) and in order to maintain good temperature uniformity, the chamber was heated very slowly (at a rate of ~1.7°C/min). The characterization of the sensors was carried out in NaOH solution with and without the presence of wood chips over the full EA range of 10-100 g/l as Na₂O, from room temperature to 140°C, though the maximum 170°C temperature of digester operation.

Figure 4.5 shows the conductivity sensor embedded in the initial prototype package and the test setup for the measurement including the chamber, the instruments and the sensor package. The maximum temperature measured was 140°C. The liquor started to splash at temperatures more than this point, even at high pressures, making the measurement unstable. To monitor the
effect of liquor type, some of the temperature tests were done at atmospheric pressure from room temperature up to 80°C in a Pyrex beaker on a hotplate. Since the sensor itself does not have a restricted solution volume over which the measurements are made, conductivity was measured at various depths in the beaker to determine any geometrical restrictions on current distribution. Based on these measurements the sensor was spaced 23 mm from the beaker bottom to avoid edge effects.

4.3.2 Characterization of the Sensor in White Pulping Liquor

The next step is the measurement of resistance and the establishment of the cell constant. To select the appropriate value of the applied current for all measurements, magnitudes of up to 1.8 mA were applied to the outer electrodes inside the liquor at room temperature at 20 kHz. This particular frequency was the minimum frequency at which no significant fluctuations were observed in the readings. The aim is to use as low a current as possible, thereby minimizing power expenditure, but nevertheless to be accurate.
Figure 4.5 a) the SmartChip package comprising four-electrode conductivity sensor and RTD, b) testing setup including measurement instruments, temperature chamber, current regulator, hotplate, sensor package, and nitrogen cylinder.

Figure 4.6 shows the effect of increasing applied current on the measured conductance. The conductance started to rise with an increase in the applied current and after a point it leveled off at all concentrations. The reason for the change in conductance with applied current may be that the field distribution is a function of current at lower currents. The relatively close spacing between the electrodes where currents are applied and the nearest sense electrode may make the setup sensitive to such changes, particularly as most of the resistance will be near the electrodes that generate current. An applied current of 1 mA is chosen for subsequent experiments as in this range the conductance is no longer a function of current, and power expenditure is still reasonable (milliwatts range).
Figure 4.7 demonstrates that the cell constant is independent of concentration. The Conductivity data was extracted from Figure 4.2 while conductance information was measured using different concentrations at 25°C. The cell constant, which is the slope of conductivity vs. conductance, is found to be $\theta = 0.76 \text{ cm}^{-1}$.

The measured conductance vs. EA concentration of NaOH at 25°C is shown in Figure 4.8 which is in agreement with theory. At low concentrations, NaOH is completely dissolved in water and conductivity is proportional to concentration, while with increasing the concentration numerous ions participating in charge transfer have more difficulty to move and pass each other due to the electrophoresis effects. This causes a decrease in the curve slope at higher concentrations. The white liquor concentration in typical kraft process doesn’t go beyond 100 g/l.
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The conductance as a function of temperature was measured for different NaOH concentrations (Figure 4.9). As there was a linear behavior of conductance vs. temperature, the data in Figure 4.9 was linearly extrapolated up to 180°C which is the maximum local temperature in some older digesters. The dashed lines are representatives of extrapolated data, and the lines are fits. The relative change in conductance with temperature, as shown in Figure 4.10, was found to be 2 % per degree Celsius.

Figure 4.7 Conductivity of NaOH solutions as a function of measured conductance. The cell constant was calculated as 0.76 cm⁻¹.
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Figure 4.8 Measured conductance vs. EA concentration of NaOH at 25°C, showing a range of concentrations typical in a digester.

According to equation (4.9), the slope of each curve of a specific concentration in Figure 4.9 equals the measured conductance at 25°C multiplied by temperature coefficient ($\alpha$). The coefficients of $\alpha$ at different concentrations can be calculated from the information in Figure 4.9, and are shown in Figure 4.10. Equation (4.9) assumes the coefficient to be independent of concentration, but in practice there is a slight variation. A reason for the change with concentration is that mobility of ions is a function of concentration, dropping as ions are more closely spaced [118, 111]. Raising temperature is known to increase the mobility of ions at high concentrations more than those at low concentrations and this is seen in the concentration dependence of $\alpha$ plotted in Figure 4.10.
In practical implementation in a kraft digester, once conductivity has been measured and temperature is known, the equivalent conductivity at 25°C is estimated using a temperature coefficient of $\alpha = 0.02{^\circ}C^{-1}$. The conductivity at 25°C is then used to estimate concentration using the curve in Figure 4.8 (or Figure 4.2 for larger concentration ranges). Figure 4.11 shows that temperature compensation of the measurements made at 80°C leads to a good match with measured conductivities at 25°C. As a unique temperature coefficient was assumed for temperature compensation, the compensated outputs still have some errors.
The final step is to relate the conductivity at 25°C back to the concentration, which is done using Figure 4.2. The uncertainty in this conversion is on the order of 11% in the absolute value of the conductivity measurements. It is a function of slope in Figure 4.9, measured temperature, measured conductance at 25°C and the cell constant and is determined using the square root of the sum of the partial uncertainty squares. The next challenge is to extend this approach to solution containing wood chips, and then determine if these measurements are appropriate for determining H-factor.
4.3.3 Test Result in Presence of White Liquor and Wood Chips

Since the sensor package is going to travel through a two-phase continuous digester containing liquor and wood chips, the conductivity readings will change due to presence of chips and dissolved molecules. Therefore, the sensor was also characterized in presence of both wood chips and liquor under two conditions. In the first sample preparation, 2 cm × 1.5 cm × 1.5 mm wood chips were dried in a microwave oven for 2 minutes and then NaOH solutions with EA concentration of 50, 100 and 140 g/l as Na₂O were immediately poured on the dried chips and the mixture was left over night at room temperature in order for penetration to occur without significant delignification. The purpose of this preparation was to observe the effect of uncooked chips on conductance. The mixture was then transferred to a beaker such that they completely surround the surface of the prototype SmartChip with the conductivity sensor. The conductance...
measurements at 25°C showed an approximately 50% decrease compared with the value of conductance in the presence of only white liquor (Figure 4.12). The conductance of the liquor extracted from the mixture was also measured alone (without wood chips) to check for any change in its conductivity and concentration. The results are compared with conductivity value of the mixture in Table 4.2. The conductance test showed an approximately 20% decrease in the conductance compared with that in new white liquor. Although used at low temperature, the soaking liquor was brown in color indicating the dissolution of substances from the wood chips. The viscosities measured in both white and extracted liquors didn’t change significantly, meaning that it is not the reason for the drop in the conductance of the solution. \( pH \) measurements were performed using \( pH \) Alkacid Tester (\( pH \) range 12.0-14.0, Fisher Scientific, Canada) and showed a change in \( pH \) from 13.75 to 14.0 corresponding to \( EA \) concentrations of 10 g/l to 100 g/l, respectively. Although these measurements were qualitative and the results are approximate, changes in \( pH \) can clearly be determined using changes in brightness of colors. In addition, soaked wood chips didn’t affect \( pH \) values, suggesting that there is no chemical reaction at room temperature and the \( OH^- \) concentration remained the same in both liquors. The reason for the change in conductivity may be that some of the salt is absorbed in the wood (does not react by diffuses in), and this leads to a drop in concentration, and hence conductivity.

In a second sample preparation, 67 g of wood chips were cooked in 1 liter white liquor (10.3 g/l as Na\(_2\)O) for one hour at 175°C in a 5 liter (model 409MII, M/K Systems Inc., Peabody, MA) laboratory batch digester. The conductance of remaining liquor (black liquor) was measured to be 48.4 mS at 25°C, corresponding to an \( EA \) concentration of 3.7 g/l as Na\(_2\)O. These semi-cooked chips are similar to chips in the middle of digester where the first step of cooking is done at 175°C. The wood chips were washed and dried in a microwave oven for 2 min and then divided into separate NaOH solutions with \( EA \) concentration of 50, 100 and 140 g/l as Na\(_2\)O. Again the mixture is left over night at room temperature and then inserted into a beaker in order to surround the SmartChip. As shown in Figure 4.12, the average conductance decrease due to cooking compared with white liquor conductance at 25°C is 30%. Again, the viscosities measured in both white and cooked liquors didn’t show significant change and thus this is not the reason for the drop in the conductance of the solution. The \( pH \) measurements on a mixture of white liquor and cooked wood chips showed no change in \( pH \) values compared with corresponding white liquors while \( pH \) measurements on the remaining liquor extracted after
cooking in the digester (3.7 g/l) showed approximately a drop of 0.5 pH unit compared with white liquor (10.3 g/l). Since pH and ion concentration are closely related and a small change in pH produces a significant change in concentration, accurate pH measurements can also be used to determine OH⁻ concentrations in different cooking zones. This 0.5 unit change in pH corresponds to a 0.68 mole/l change in the OH⁻ concentration that correlates with our conductance measurements. Another reason for the change in conductivity may be that the path of current flow is extended in the presence of cooked wood chips and more extended in present of soaked chips, compared with that in pure white liquor.

Figure 4.12 A comparison of measured conductance in white liquor, a mixture of cooked wood chips and white liquor, and a mixture of soaked wood chips and white liquor. An average of 30% and 50% decrease in measured conductance in cooked chips and soaked chips, respectively, were observed compared with conductance of white liquor.
Figure 4.13 Behaviour of a mixture of cooked wood chips and white liquor and a mixture of soaked wood chips and white liquor at high temperatures showing that conductance increases linearly with temperature in all cases.

Table 4.2 A comparison between measured conductance in white liquor, a mixture of soaked wood chips with white liquor, and liquor extracted from mixture of soaked chips and white liquor.

<table>
<thead>
<tr>
<th>NaOH EA concentration (g/l as Na₂O)</th>
<th>Measured conductance (mS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>White liquor</td>
</tr>
<tr>
<td>50</td>
<td>351</td>
</tr>
<tr>
<td>100</td>
<td>538</td>
</tr>
<tr>
<td>140</td>
<td>563</td>
</tr>
</tbody>
</table>

Figure 4.13 compares the measured conductance of six prepared samples including three with soaked chips in white liquor and three with cooked chips in white liquor at temperatures
up to 80°C. The conductance remains a linear function of temperature even in presence of wood chips.

Temperature coefficients of measurements made in the presence of wood chips were computed from Figure 4.13 and the results are shown in Table 4.3. Comparison between white liquor, soaked and cooked temperature coefficients suggests that presence of different multiphase materials doesn’t change the temperature coefficient substantially.

Table 4.3 A comparison between temperature coefficients of white liquor, mixture of soaked wood chips and white liquor, and mixture of cooked wood chips and white liquor.

<table>
<thead>
<tr>
<th>NaOH EA concentration (g/l as Na₂O)</th>
<th>Temperature coefficient α (°C⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>White liquor</td>
</tr>
<tr>
<td>50</td>
<td>0.0189</td>
</tr>
<tr>
<td>100</td>
<td>0.0219</td>
</tr>
</tbody>
</table>

Implementation of the conductivity sensor in a digester will require a series of steps that are now described. The aim is the estimation of lignin content in the pulp using the combination of temperature, time and concentration, as measured by the SmartChip. In order to produce an estimate, the information in Figure 4.12 is used to relate the measured conductances in presence of wood chips back to those in pure liquor (without wood chips). As seen in Figure 4.12, the degree of cooking changes the conductance by approximately 30%. Assuming that this change can be shown to be consistent, and is a repeatable function of the degree of cooking, it should be possible to make a reasonable determination of concentration based on conductivity in the presence of chips. Figure 4.9 or ultimately similar plots that take into account the presence of chips are then used to relate the converted conductances at high temperatures back to 25°C. The concentration estimate is obtained using the plot of concentration and conductance shown in Figure 4.8. The measured temperature as a function of time during the kraft process obtained using the SmartChip enables the estimation of the $H$-factor using equation (4.5). Once both concentration and $H$-factor are computed, the final lignin content is estimated using the equation (4.4). Multiple measurement cycles can be used to estimate the distribution of cook. Perhaps most importantly, the pressure sensor will enable variations in conductivity to be determined as a
Chapter 4. Development of a Liquid Conductivity and Temperature Sensor

function of height in the reactor, thereby helping to establish the causes of variations in the degree of cooking. This information will help optimize digester operation and design.

There may be some issues when estimating the concentration at different locations in a digester. The first challenge is to differentiate the change in conductivity due to the presence of wood chips and their degree of cooking from the effect due to change in concentration. This issue can be resolved using temperature, time and position measured by SmartChip as well as concentration of liquor that are routinely measured at the inlets and outlets near the digester wall. These four parameters can give an idea of cooking in the known locations of the digester. Given that there are conductivity sensors regularly spaced along the digester walls, these data will help validate or calibrate SmartChip readings. The estimation of cooking at different locations of a digester can help recognize if the change in conductivity is due to presence of wood chips or change in concentration.

\[ \text{pH} \] measurements can also be helpful as they consider the effect of only \( OH^- \) concentration. Since the ionic radius of \( OH^- \) (0.14 nm) is lower than that of sulfide (0.18 nm) and hydrosulfide, the mobility of \( OH^- \) in the liquor is expected to be higher than that of \( HS^- \), as confirmed in the data presented in Table 4.4. The number of \( OH^- \) ions in the liquor is much higher than the number of \( HS^- \) ions. As a result \( OH^- \) ions dominate conductance, as suggested in Table 4.4 for a white liquor with a typical sulfidity (which is the ratio of sodium sulfide to the sum of the sodium sulfide and sodium hydroxide weight) of 25%. As shown, the contribution of \( OH^- \) to measured conductivity is estimated to be 71.6% while the contribution of \( HS^- \) is only 5.8% in total conductivity. The contribution of \( OH^- \) in the measured conductivity is 12.28 times more than that of \( HS^- \). Although the effect of \( Na^+ \) is high, it doesn’t have chemically any contribution in delignification. These effects were considered in infinitely dilute solutions and molar conductivities at higher concentrations are lower than these amounts. Thus, a conductivity measurement sensor in the SmartChip can help recognize the effect of hydroxide and estimate \( EA \) concentration assuming that all essential ions are equally consumed in the process. The combination of accurate temperature measurement as a function of time, measurement of height in the digester thanks to pressure and determination of concentration as a function of position, are expected to provide key information that will help optimize pulping inside what has hitherto been a black box.
Table 4.4 Estimated effects of different ions on measured conductivity for a white liquor with 25% sulfidity. Molar conductivities are corresponding to aqueous solutions at infinite dilution and 25°C.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molar conductivity (10^{-4} m^2 S mol^{-1}) [97]</th>
<th>Contribution in conductivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH^-</td>
<td>198</td>
<td>71.6</td>
</tr>
<tr>
<td>HS^-</td>
<td>65</td>
<td>5.8</td>
</tr>
<tr>
<td>Na^+</td>
<td>50.08</td>
<td>22.6</td>
</tr>
</tbody>
</table>
CHAPTER 5: Discussion and Conclusions

The development of pressure, temperature, and ionic conductivity sensors has been discussed so far. The aim of this chapter is to give a summary of previous chapters, review the advantages and drawbacks of the sensors, and choose the most suitable sensors for implementation in a SmartChip. This is followed by a discussion of errors in the measurements and an estimation of sensor accuracies and resolutions. Moreover, the usefulness of the developed sensors in a SmartChip for digester monitoring will be examined, followed by a discussion of the direction of future work.

5.1 Summary

The design and optimization of industrial multi-phase chemical reactors requires data on the actual operating conditions internal to them. Currently, it is very challenging to access the center of the reactors without disturbing the process operation. Process information is primarily limited to selected static locations on the periphery of the reactors, where sensors are installed through walls and are used for online measurements and control.

An autonomous flow-following sensor package, SmartChip, has been proposed to measure and record pressure, temperature, and conductivity in a kraft digester. As part of the SmartChip system, this thesis developed miniaturized sensors to measure pressure, temperature, and liquid conductivity inside kraft pulp digesters that have a caustic chemical environment (pH~13.5, temperatures up to 175°C, and pressures up to 2 MPa). The developed liquid conductivity sensors are used to measure the strength of alkali within the digester. Pressure sensors are used to measure the vertical location of the SmartChip within the digester. The temperature measured by the sensors will allow calculations of chemical reactions that are experienced by a wood chip following the SmartChip trajectory. All this information, recorded as a function of time, is used to monitor chemical process variables throughout the digester.

In Chapter 2, the development of an integrated capacitive pressure and temperature sensor with a new fabrication process and material for use in the high temperature and harsh environment of a kraft pulp digester was described. The gauge capacitive pressure sensor was
fabricated by bonding silicon and Pyrex chips using a polymeric gap-controlling layer (SU-8) and a high temperature, low viscosity bonding adhesive. A simple chip bonding technique involving insertion of the adhesive into the gap between the two chips was developed. The pressure sensor consists of two capacitors, a main one with a silicon diaphragm that is sensitive to both pressure and temperature, and a reference capacitor with fixed capacitance that is sensitive only to temperature. A comparison of the main and reference capacitor outputs is used to eliminate the temperature effects. A platinum thin-film wire was patterned on top of a silicon chip to form an RTD with a nominal resistance of 1,500 Ω. A silicon dioxide layer and a thin layer of Parylene were deposited to passivate the pressure sensor diaphragm, and the sensors were embedded into epoxy for protection against the caustic environment in kraft digesters. The sensors were characterized up to 2 MPa and 170°C in an environment chamber. Parylene-coated silicon chips were tested for a full kraft pulping cycle with no signs of corrosion.

In Chapter 3, the development of an integrated piezoresistive pressure and temperature sensor was reported for use in multi-phase chemical reactors, primarily kraft pulp digesters. Sensor designs with different diaphragm lengths were fabricated and tested. The absolute pressure sensor with a diaphragm length of 1000 µm showed a high sensitivity (0.116 mV/V.kPa) and low power consumption (0.3 mW). In addition, the sensor’s output voltages at different temperatures were compensated using only two calibration points – this was due to the linear behavior of output voltages versus temperature at the operating temperature range of the digester. A 4,500 Ω buried piezoresistive wire was patterned on the silicon chip to measure temperature. The sensors were characterized up to 2 MPa and 180°C in an environment chamber. The sensor was packaged and passivated against the caustic environment in kraft digesters using a 4 µm-thick Parylene HT® coating, a chemical resistant epoxy, and a silicone conformal coating, and showed complete chemical protection at the high temperature in a digester. The sensors’ resistances were measured before and after test in a kraft pulping cycle and showed no change in their values. SEM pictures and topographical surface analyses were also performed before and after pulp liquor exposure and showed no observable changes.

In Chapter 4, a combined liquid conductivity and temperature sensor package was described for use in multi-phase chemical reactors, particularly kraft pulp digesters. It consists of a chemically resistant PEEK package sealing SmartChip’s electronics against corrosive liquor, a four-electrode planar conductivity sensor embedded on the package body, and a 1,000 Ω
platinum RTD enclosed in a stainless steel container for temperature measurement. The sensors were tested up to \(140^\circ\text{C}\) at NaOH concentrations of 10-100 g/l as Na\(_2\)O with and without presence of wood chips in an environment chamber. The temperature compensation was performed using a linear equation. An average power of 5 mW was consumed during the conductivity measurements, which is sufficiently low to ensure relatively minor battery drain. The sensor packages were tested for a full kraft pulping cycle and survived with no signs of corrosion.

### 5.2 Sensor Selection

As mentioned in Chapter 1, two types of pressure sensors have been developed in this work. Generally, piezoresistive pressure sensors have advantages of immunity to electromagnetic coupling, ease of signal processing, and high signal level, but they suffer from instability due to leakage, costly temperature compensation, and need for high power. On the other hand, capacitive pressure sensors benefit from long-term stability, low power, and less temperature dependence, but they are non-linear, non-immune to parasitic effects, and dependent on a complicated circuit for capacitive measurements. It is also difficult to control the cavity gap and make a sealed interconnection. Table 5.1 compares technical issues in the capacitive and piezoresistive pressure sensors and solutions that each sensor offers to resolve some of the issues. The developed piezoresistive pressure sensors meet all requirements; only leakage currents are an issue at high temperatures. As shown, the developed capacitive pressure sensors have more issues compared to piezoresistive pressure sensors including immunity to parasitic effects, need for complicated circuitry, low lifetime, cavity air expansion at high temperatures, and temperature drift due to change in the adhesive thickness. Based on this comparison, piezoresistive pressure sensors are chosen to be used in a SmartChip.

The second important variable that is measured in a kraft digester is temperature. Two types of temperature sensors were developed in this work, piezoresistive sensors and platinum RTDs. Generally, sensitivity of piezoresistive temperature sensors is higher than that of platinum RTDs. This is due to the high thermal dependence of piezoresistive materials. As sensitivity is the most important requirement in the measurements in a kraft digester, the doped piezoresistors were chosen as temperature sensors for the SmartChip. In addition, a four-electrode approach was
selected for the ionic conductivity sensor since it can be fabricated as a planar sensor on the SmartChip package and is not susceptible to fouling.

Table 5.1 A comparison between the developed capacitive and piezoresistive pressure sensors

<table>
<thead>
<tr>
<th>Pressure sensor specifications</th>
<th>Issues and solutions offered in the developed piezoresistive pressure sensors</th>
<th>Issues and solutions offered in the developed capacitive pressure sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linearity</td>
<td>Non-linear, but the data will be easily post-processed</td>
<td>Non-linear, but the data will be easily post-processed</td>
</tr>
<tr>
<td>Immunity to coupling</td>
<td>Immune to electromagnetic coupling as it uses an DC power supply</td>
<td>Difficult to immune it against parasitic effects as it uses an AC power supply</td>
</tr>
<tr>
<td>Ease of signal processing</td>
<td>Easy to use a DC volt meter for measuring sensor outputs</td>
<td>Need for a complicated circuit for measuring capacitance</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Having a high average sensitivity (0.116 mV/V.kPa)</td>
<td>Having a low average sensitivity (0.257 fF/kPa)</td>
</tr>
<tr>
<td>Cavity environment</td>
<td>Vacuum, no gas expansion effect at high temperatures</td>
<td>Air, expansion effect at high temperatures</td>
</tr>
<tr>
<td>Supply voltage, Consumed power</td>
<td>Low voltage (2.5 V), Low power (0.3 mW)</td>
<td>Low voltage, Low power</td>
</tr>
<tr>
<td>Cost of development</td>
<td>More fabrication cost due to using a multi-step technique, but less characterization cost due to using an established and controllable fabrication technique</td>
<td>Less fabrication cost due to using a low-cost adhesive bonding technique, but more characterization cost due to using a less controllable fabrication technique</td>
</tr>
<tr>
<td>Difficulty of temperature compensation</td>
<td>No need for a costly real-time compensation technique as the data will be post-processed for compensation</td>
<td>Using a real-time compensation technique</td>
</tr>
<tr>
<td>Offset drift due to temperature</td>
<td>High drift, but it can be compensated</td>
<td>Low drift</td>
</tr>
<tr>
<td>Stability</td>
<td>Highly sensitive to leakage, Long lifetime</td>
<td>Low leakage, Low lifetime due degradation of adhesive</td>
</tr>
<tr>
<td>Fabrication control</td>
<td>Difficult to balance and align piezoresistors making offset drift; it can be compensated using data post-processing</td>
<td>Difficult to control the cavity gap at high temperatures due to change in adhesive thickness</td>
</tr>
</tbody>
</table>

5.3 Sensor Accuracy and Resolution

Implementation of the developed sensors in a kraft digester requires considering accuracy and resolution terms in a SmartChip sensor package. The aim is to estimate the final accuracy of the sensors and minimum measurable increments of variables using a SmartChip.

Accuracy is defined as the uncertainty of a measurement value with respect to an absolute standard. To discuss accuracy of the readings in the measurements performed in the
pressure/temperature chamber, the sources of errors need to be reviewed. Basically, errors may arise from instrument, sensor, or calibration inaccuracies.

Another term in the measurements is the sensor resolution that is the degree to which smaller differences can be detected and is limited by the resolution of external instruments in the chamber measurements or on-board devices in a SmartChip. The resolution of an instrument is expressed as the number of bits (N) it uses that quantizes the whole output of a sensor into $2^N$ steps. The common instruments in the market usually have very high resolutions over 16 bits. Environmental errors such as thermal noise may reduce the effective resolution; however, in all experiments performed on the sensors, no noise was observed.

5.3.1 Integrated Piezoresistive Pressure and Temperature Sensor

Environmental temperature changes have two effects on the sensors including temperature coefficient of offset (TCO) and temperature coefficient of pressure sensitivity (TCS). The following possible sources of temperature drift can be responsible for the two mentioned changes:

1) Resistance of piezoresistors increases with temperature. As the piezoresistors placed on the four edges of the diaphragm have the same values, the equation 3.1 is theoretically balanced at zero pressure and should remain balanced at higher temperatures. But as the bridge becomes unbalanced at pressures other than zero, the temperature effects will be different at high temperatures. This effect can be observed in Figure 3.5. It is compensated using a linear equation as described in Chapter 3. However, the compensated data still has some error due to calibration definition. It was determined to be ±1.5% of readings in the operating range of a typical digester.

2) Some of the current flowing through the Wheatstone bridge deviates to the substrate. The leakage current density rises with the temperature, doping level, and amount of metallic contaminations. Various junctions in the MultiMEMS process have different leakage current densities. However, only the junctions of p-type piezoresistive surface conductors that connect piezoresistors in a Wheatstone bridge and the underneath n-type epitaxial layer have the largest contribution to the total leakage current according to the manufacturer. The leakage currents in the other junctions are neglected. The leakage current density is typically 16 fA/µm$^2$, corresponding to 98% of the total current density and reaches a maximum of 16 pA /µm$^2$ due to
metallic contaminations made by the die-sawing process. In order to avoid maximum leakage currents, the epitaxial layer and the substrate are short-circuited together. The leakage current is proportional to the total area of the junction. The total area of the surface conductor/epitaxial layer was calculated to be 85,000 \( \mu \text{m}^2 \). This area should make a leakage current of 1.352 nA-1.352 \( \mu \text{A} \) at the junction. On the other hand, the total current passed through the Wheatstone bridge equals:

\[
I = \frac{V_l}{R_B} = \frac{2.5V}{20,000\Omega} = 125 \mu \text{A} .
\]

Thus, neglecting the contamination effects, only 0.001\% of the total current in the developed sensor bridge is leaked at room temperature. However, temperature has the most effect on the
leakage current. Figure 5.1 shows the leakage current normalized to its value at room temperature as a function of temperature according to manufacturer. The total leakage current rises from 0.001% at room temperature to 1.3% of the current passed through the Wheatstone bridge at 180°C.

3) Resistor mismatch among four resistors can cause a constant offset voltage in the sensor at room temperature. Since resistance increments with changing temperature are not uniform, the offset generated by the resistor mismatch can have a temperature-dependent contribution on TCO; however, its effect can be determined using a simple calculation. The sensor offset at room temperature was measured to be 38 mV. In addition, the input voltage applied to the sensor was measured as 2.5 V. As the resistance values of piezoresistors on each diaphragm edge are the same and were measured to be 20,000 Ω, the total Wheatstone bridge resistance would be 20,000 Ω. Thus, the offset resistance (ΔR_B) at room temperature can be calculated as below:

\[
V_o = \frac{\Delta R_B}{R_B} V_i \Rightarrow 0.038 = \frac{\Delta R}{20,000} \times 2.5 \Rightarrow \Delta R_B = 304 \Omega \text{ at room temperature.}
\]

Figure 3.5 may be used to determine the behavior of the output voltage with temperature. As the surface piezoresistors were used on the Wheatstone bridge, the offset resistance would increase with the temperature on the order of 0.13% per degree Celsius.

4) The top surface of the diaphragm is usually coated with SiO2 to passivate the junctions. Due to the expansion difference between Si and SiO2 by a high temperature fabrication process, there would be stress between the two elements at room temperature, affecting the pressure offset. In addition, packaging stress has a similar effect on the result. The sensors were calibrated in presence of these effects, thus compensating for them.

On the other hand, the accuracy of instruments used for the measurements in the pressure chamber has the most effect on the reading accuracy. The instruments include the following accuracies.

- Voltage generator (Agilent E3630A) accuracy: ±0.5% of reading
- ADC (NI USB-9219, 24-bit) accuracy: ±0.1% of reading
- Reference pressure sensor (Omegadyne PX61C1-200 AV) accuracy: ±1% of reading
- Thermocouple (T-Type) accuracy: ±0.375% of reading
Chapter 5. Discussion and Conclusions

Another group of uncertainties is from calibration and the uncertainties in the pressure measurements at a constant temperature. Raising pressure using nitrogen gas blows samples. As a result, the temperature inside the chamber initially goes down a few degrees Celsius and then starts to go up when the pressure goes up. Thus, the temperature variation makes another error at high temperatures. In addition, the developed sensor itself has inaccuracies at different temperatures.

Compensation accuracy: ±1.5%

Sensor accuracy at room temperature: ±0.4%

Temperature variation: ±2.5%

\[ UT = \sqrt{U_1^2 + U_2^2 + \cdots} = \sqrt{0.5^2 + 0.1^2 + 1^2 + 0.375^2 + 1.5^2 + 0.4^2 + 2.5^2} = \pm 3.17\% \]

The piezoresistive temperature sensor also showed a maximum of ±1.9% of temperature readings at the operating range of the digester.

The smallest detectable pressure and height increments in a digester depend on the resolution of measurement instruments. The ADC used in the laboratory measurements in the pressure chamber had a 24-bit resolution, while the number of bits in the IC chip being developed for the final SmartChip is designed to be 12. Based on these inputs, the smallest detectable pressure and height increments in the chamber and a real digester can be calculated as follows:

FSO=full sale output

FSP=full scale pressure

FSH=full scale height

\[ S' = \text{average pressure sensitivity} = \frac{FSO}{FSP} = \frac{564 \text{ mV}}{2.07 \text{ MPa} - 0.1 \text{ MPa}} = 0.286 \text{ mV/kPa} \]

\[ B_1 = \text{resolution using the laboratory ADC} = \frac{FSO}{2^N} = \frac{564 \text{ mV}}{2^{24}} = 0.034 \mu\text{V} \]

\[ B_2 = \text{resolution using the IC chip in a digester} = \frac{FSO}{2^N} = \frac{564 \text{ mV}}{2^{12}} = 0.138 \text{ mV} \]

\[ C_1 = \text{smallest detectable pressure increment using the laboratory ADC} = \frac{B_1}{A} = \frac{FSP}{2^N} = \frac{2.07 \text{ MPa} - 0.1 \text{ MPa}}{2^{24}} = 0.117 \text{ Pa} \]
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\[ C_2 = \text{smallest detectable pressure increment using the IC chip in a digester} = \frac{B_2}{A} = \frac{FSP}{2^N} = \frac{2.07\text{MPa} - 0.1\text{MPa}}{2^{12}} = 0.48 \text{ kPa} \]

\[ D = \text{height sensitivity in a digester} = \frac{\text{Digester pressure range}}{FSH} = \frac{(1.7\text{MPa} - 1\text{MPa})}{60m} = 0.117 \text{ kPa/cm} \]

\[ E = \text{smallest detectable height increment in a digester} = \frac{FSH}{2^N} = \frac{60m}{2^{12}} = 1.5 \text{ cm} \]

\[ F = \text{smallest detectable temperature increment using the IC chip in a digester} = \frac{180^{\circ}C - 25^{\circ}C}{2^{12}} = 0.04^{\circ}C \]

5.3.2 Ionic Conductivity and Temperature Sensor

Two types of factors are effective in determining the accuracy of ionic conductivity measurements, instruments, and reading compensation. The instruments used for the laboratory measurements include the following accuracies.

- Function generator (Agilent 33220A) accuracy: ±1% of reading
- Digital multi meter (HP 34401A, 21 bit) accuracy for voltage measurement: ±0.1% of reading
- Digital multi meter (HP 34401A, 21 bit) accuracy for current measurement: ±0.14% of reading
- Platinum RTD (Omega thin film B) accuracy for temperature measurement: ±0.3% of reading
- ADC (NI USB-9162, 24-bit) accuracy for resistance measurement: ±0.1% of reading

The second group of uncertainties in the ionic conductivity measurements is related to conversion of readings measured by the instruments at high temperatures back to concentrations at 25°C. They include the cell constant and temperature coefficient of conductivity as follows.

- Uncertainty in the cell constant: ±3.5%
- Uncertainty in the temperature coefficient of conductivity: ±12%

The final uncertainty in the conductivity measurements is due to presence of wood chips in liquor. Ionic conductivity is usually measured in solutions, however, the aim of this research was to measure the ionic conductivity in a mixture of solid and solutions and then acquire the conductivity of the solution from the measured data. This conversion may make ±10% uncertainty in the result due to the possibility of a different arrangement or compaction of wood chips and liquor on the sensor electrodes.
The total uncertainty in the ionic conductivity measurements at high temperatures and relating them back to the concentration at room temperature is determined using the square root of the sum of the partial uncertainty squares as follows.

\[ U_T = \text{total uncertainty} = \sqrt{U_1^2 + U_2^2 + \cdots} = \sqrt{1^2 + 0.1^2 + 0.14^2 + 0.3^2 + 0.1^2 + 3.5^2 + 12^2 + 10^2} = \pm 16\% \]

The smallest detectable conductivity increment in a digester depends on the resolution of the measurement instruments. The multi meter used in the laboratory measurements had 21 bits, while the number of bits in the IC chip being developed for the final SmartChip is designed to be 12. Based on these inputs, the smallest detectable conductivity increments in the laboratory and a real digester can be calculated as follows:

\[ \text{FSO} = \text{full scale output} \]
\[ \text{FSK} = \text{full scale conductivity} \]
\[ \text{FSC} = \text{full scale concentration} \]

\[ S' = \text{average sensor sensitivity} = \frac{\text{FSO}}{\text{FSC}} = \frac{440.7 \text{ mS}}{100 \text{ g/l} - 10 \text{ g/l}} = 4.9 \text{ mS/(g/l as Na}_2\text{O)} \]

\[ B_1 = \text{resolution using the laboratory multi meter} = \frac{\text{FSO}}{2^N} = \frac{440.7 \text{ mS}}{2^{21}} = 0.21 \mu\text{S} \]

\[ B_2 = \text{resolution using the IC chip in a digester} = \frac{\text{FSO}}{2^N} = \frac{440.7 \text{ mS}}{2^{12}} = 0.11 \text{ mS} \]

\[ C_1 = \text{smallest detectable conductivity increment using the laboratory multi meter} = \frac{\text{FSK}}{2^N} = \frac{335 \text{ mS/cm}}{2^{21}} = 0.16 \mu\text{S/cm} \]

\[ C_2 = \text{smallest detectable conductivity increment using the IC chip in a digester} = \frac{\text{FSK}}{2^N} = \frac{335 \text{ mS/cm}}{2^{12}} = 82 \mu\text{S/cm} \]

\[ E_1 = \text{minimum detectable concentration in the laboratory} = \frac{\text{FSC}}{2^N} = \frac{90 \text{ g/l}}{2^{21}} = 0.043 \text{ mg/l as Na}_2\text{O} \]

\[ E_2 = \text{minimum detectable concentration in a digester} = \frac{\text{FSC}}{2^N} = \frac{90 \text{ g/l}}{2^{12}} = 22 \text{ mg/l as Na}_2\text{O} \]
5.4 Sensor Usefulness in a Kraft Digester

The objective of the overall project was to develop a flow-following sensor package, SmartChip, that can be released into kraft digesters and measure and record sufficient data from throughout the vessels to gain a much clearer picture of the internal conditions of the digesters. Three sensors were developed to measure pressure, temperature, and ionic conductivity within kraft digesters. In this section, usefulness of the selected sensors being implemented in an IC SmartChip in a kraft digester will be discussed using calculations performed in section 5.3. It is assumed that the specifications of the IC SmartChip are the same as the instruments used in the laboratory measurements.

The piezoresistive pressure sensors were developed to measure the vertical location of the SmartChip within the digester. The sensors developed in this work were resistant to the harsh environment of the digester and their readings were compensated for using post-processing. As calculated in section 5.3.1, the piezoresistive sensors showed a total uncertainty of ±3.17% of the readings. That means if a sensor reads a voltage or measures a corresponding pressure in a digester, this measured pressure may be inaccurate in the range of ±3.17%. For example, a sensor may measure 1.3 MPa pressure in a digester, but in reality this point may be in the range of 1.259-1.341 MPa. This gives a total uncertainty of ±41 kPa, which corresponds to a ±3.5m height and is four times more than the accuracy expected (±10 kPa) [121] in a SmartChip. On the other hand, the smallest detectable height increment in a digester using the IC SmartChip was calculated to be 1.5 cm. As a result, accuracy is a limiting factor in the measurements of the SmartChip’s position in a digester. Given a digester height of 60m, a pressure sensor implemented in a SmartChip can on average measure height increments as large as one tenth of the total height of a digester. As the pressure sensor is so small and consumes only 0.3 mW power, using a few pressure sensors in a SmartChip may provide more accurate information on the SmartChip position in a digester.

The second sensor developed as a component of a SmartChip was an integrated piezoresistive temperature one for measuring temperature in a digester and permitting calculations of the chemical reaction that would be experienced by a wood chip. The accuracy of ±1.9% of temperature readings is still far from the expected accuracy (±0.25°C) [121] in a digester. But the resolution (0.04°C) supported by the IC electronics can meet the required resolution of 0.1°C in a digester. One solution to increase the accuracy of the data is to use both
an RTD and piezoresistive temperature sensor in a SmartChip, and compare the results of two sensors. The second solution is to use the data obtained from conventional temperature sensors which are installed in particular locations of a digester wall and compare them with the measured data using the SmartChip.

A third sensor, a planar, liquid conductivity one on the SmartChip package was developed to measure the strength of alkali within the digester. The sensor developed in this work was temperature compensated and resistant to the harsh environment of a digester. As calculated in section 5.3.2, the conductivity sensor showed a total uncertainty of ±16% of the readings. For example, a concentration of 70 g/l as Na₂O may be in the range of 70±11 g/l as Na₂O. This accuracy is much higher than the expected accuracy (±2.7 g/l as Na₂O) [121] in a digester. However, using the IC SmartChip results in a resolution of 22 mg/l as N₂O compared with the expected resolution (270 mg/l as Na₂O) in a digester. As a result, the accuracy of the developed sensor is a limiting factor in the conductivity measurements. There may also be some challenges when estimating the concentrations at different locations in a digester. The first challenge is to differentiate the change in conductivity due to the presence of wood chips and their degree of cooking from the effect due to change in concentration. The second issue is the effect of compaction of the wood chips on the sensor electrodes. This effect may change the path of the current which is assumed to be through liquor and thus reduce the measured conductance. These issues take place due to using the planar electrodes and lack of a cell in the sensor. To resolve this problem, a physically secured cell can be installed on the electrodes so that it is filled only with liquor. A screen embedded in the sensor could avoid entrance of any solid particles to the cell and only conductivity of the liquor is measured. In addition, given that there are temperature and conductivity sensors regularly spaced along the digester walls, these data will help validate or calibrate SmartChip readings. The estimation of cooking at different locations in a digester can help recognize if the change in conductivity is due to the presence of wood chips or a change in concentration. Moreover, a pH sensor implemented in the SmartChip may be used to measure the concentration of OH⁻, which has a contribution in the measured conductivity 12.28 times more than that of HS⁻ and can help estimate the concentration of the liquor at different locations in a digester.
Implementation of the pressure, temperature, and conductivity sensors in a digester will require a series of steps that are shown in Figure 5.2. The aim is the estimation of lignin content in the pulp using the combination of temperature, time, and concentration at different locations of a digester, as measured by the SmartChip. The measured temperature as a function of time during the kraft process obtained using the SmartChip enables the estimation of the $H$-factor using the equation (4.5). The conductivity sensor is used to determine the alkali concentration within the digester. Once both the concentration and $H$-factor are computed, the final lignin content is estimated using the equation (4.4). The pressure sensor will enable variations in lignin content to be determined as a function of height in the reactor, thereby helping to establish the causes of variations in the degree of cooking. The combination of these data is expected to provide key information that will help optimize digester operation and design that has hitherto been a black box.
5.5 Future Work

Liquid conductivity, pressure, and temperature sensors were developed in this thesis. Other new and promising directions may be worth pursuing in the future, such as:

- Using advanced adhesives with higher operating temperatures than 180°C for bonding capacitive pressure sensors
- Lowering the Parylene film thickness to a few hundred nanometers and characterizing them
- Characterizing other potential coatings such as polyimide as a chemically protective layer on the sensors
- Developing other potential sensors to be integrated into the SmartChip for monitoring more variables such as pH and HS⁻ ion concentration in a kraft pulping process
- Developing fully integrated sensors all on one chip
- More scaling down of the sensors for use in a miniature SmartChip
- Integrating the proposed sensors with electronics in a SmartChip, characterizing them in a laboratory, and testing them in a real digester
- Extending the SmartChip to other applications such as chemical processes
- Developing the conductivity sensors with alternative electromagnetic methods
- Developing a wireless powering and communication system for the SmartChip
Bibliography


[88] G.K. McMillan and D.M. Considine, Process/Industrial Instruments and Controls Hand


