Factors Affecting the Resistivity of Recovery Boiler Precipitator Ash

by

Ivan Sretenovic

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

© Copyright by Ivan Sretenovic 2012
Factors Affecting Resistivity of Recovery Boiler Ash in the Kraft Pulping Process

Ivan Sretenovic
Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto
2012

Abstract

Electrostatic precipitators (ESPs) are commonly used to control particulate emissions from recovery boilers in the kraft pulping process. The electrical resistivity of entrained particulates is known to affect the performance of ESPs. There are many factors which influence resistivity of particulate matter, such as field strength, time of exposure, particle size, particle composition, temperature, and flue gas composition. The objective of this study was to identify the ideal operating conditions and dust particle characteristics which lead to an optimum dust resistivity and maximized ESP efficiency. The effect of these factors was examined through a variety of experimental and analytical techniques on kraft recovery boiler ash samples and synthetically prepared samples. It was concluded that particle composition, gas composition, and ambient temperature had the most pronounced effects, while the other factors, such as field strength and exposure time, had a smaller impact on particle resistivity.
Acknowledgments

I would like to thank my supervisors, Professor Honghi Tran and Professor Mark Kortschot, for their guidance throughout the course of this project. Special thanks to Sue Mao for her availability to always provide assistance and my lab mates for lending a helping hand when needed. Finally, I would like to thank my family for their unconditional love and support.
# Table of Contents

## Table of Contents

Acknowledgments ...................................................................................................................................... iii

Table of Contents ..................................................................................................................................... iv

List of Figures ........................................................................................................................................ vii

List of Appendices .................................................................................................................................. x

Chapter 1 ................................................................................................................................................... 1

  1 Introduction ......................................................................................................................................... 1
    1.1 Controlling Particulate Matter Emissions ............................................................................... 1
    1.2 Kraft Pulping Process ............................................................................................................ 1

Chapter 2 ................................................................................................................................................... 6

  2 Electrostatic Precipitation Theory and Dust Resistivity ................................................................. 6
    2.1 ESP Operating Principles .................................................................................................. 6
      2.1.1 Dust Charging ............................................................................................................. 6
      2.1.2 Dust Collection and Removal .................................................................................... 9
      2.1.3 Volume and Surface Conduction .............................................................................. 10
      2.1.4 Drift Velocity and Theoretical Efficiency .................................................................... 11
      2.1.5 Industrial Applications of ESPs .............................................................................. 13
    2.2 Role of Dust Resistivity ........................................................................................................... 14
      2.2.1 Definition of Resistivity ........................................................................................... 14
      2.2.2 Effect of Resistivity on ESP Performance ................................................................. 15
      2.2.3 Resistivity and Electrical Breakdown ......................................................................... 17
      2.2.4 Factors Affecting Resistivity ..................................................................................... 19
Chapter 3: Experiment Description.............................. 26
  3.1 Experimental Objective .................................... 26
  3.2 Experimental Setup ......................................... 26
  3.3 Experimental Procedures .................................... 28
Chapter 4: Results and Discussion........................... 32
  4.1 Breakdown Strengths and Resistivities..................... 32
  4.2 Effect of Field Strength ..................................... 34
  4.3 Effect of Particle Size, Bulk Density, and Packing ........ 35
  4.4 Effect of Composition ....................................... 40
     4.4.1 Effect of Chloride Content .............................. 40
     4.4.2 Effect of Carbon Content ............................... 41
     4.4.3 Effect of Melting ....................................... 42
  4.5 Effect of Time of Exposure .................................. 47
     4.5.1 Short-Term Exposure with Varying Field Strength .... 47
     4.5.2 Long-Term Exposure at Constant Field Strength ....... 48
  4.6 Effect of Temperature ........................................ 50
  4.7 Effect of Moisture Content ................................... 53
  4.8 Effect of SO\textsubscript{2} Concentration ....................... 55
Chapter 5: Conclusions ............................................. 58
Chapter 6: Recommendations for Future Work ................. 60
References .......................................................... 61
Appendices .......................................................... 64
List of Tables

Table 1 - Typical Recovery Boiler Ash Composition .............................................. 3

Table 2 – Typical Flue Gas Composition from a Recovery Boiler .......................... 4

Table 3 - Resistivity Categorization ...................................................................... 15
List of Figures

Figure 1 - Summary of the Kraft Recovery Process .............................................................. 2

Figure 2 - Schematic of Single Stage Parallel Plate Electrostatic Precipitator ....................... 7

Figure 3 - Field Charging of Dust Particles ........................................................................ 8

Figure 4 - Diffusion Charging of Dust Particles ................................................................ 8

Figure 5 - Particle Charge as a Function of Particle Radius ............................................. 9

Figure 6 - Volume and Surface Conduction ...................................................................... 10

Figure 7 - ESP Efficiency as a Function of Particle Size .................................................. 12

Figure 8 - Attractive Force Between Dust Layer and Collecting Electrode ....................... 16

Figure 9 - Efficiency as a Function of Dust Resistivity ..................................................... 18

Figure 10 - Resistivity of Various Recovery Boiler Ash Components .............................. 20

Figure 11 - Resistivity as a Function of Pure Carbon Content ....................................... 21

Figure 12 - Change in Resistivity with Temperature ......................................................... 23

Figure 13 - Change in Resistivity of Cement Dust with Moisture Content ....................... 24

Figure 14 - Change in Moisture Content in Flue Gas as a Function of BLS ....................... 25

Figure 15 - Experimental Apparatus for Measuring Resistivity ..................................... 27

Figure 16 - Schematic for Testing Effect of SO₂ and Humidity on Resistivity ................... 28

Figure 17 - Typical VI Curve for Kraft Recovery Boiler Ash Sample ............................... 29

Figure 18 - Breakdown Strengths of 11 Mill Samples ..................................................... 32

Figure 19 - Resistivities of 11 Mill Samples .................................................................... 33
Figure 20 - Effect of Field Strength on Resistivity of Sample 4 ........................................ 34
Figure 21 - Effect of Field Strength on Resistivity of Sample 7b ........................................ 35
Figure 22 - Average Resistivities of Different Particle Size Ranges ......................................... 36
Figure 23 - Micrographs of 10 Mill Ash Samples ...................................................................... 38
Figure 24 - Effect of Bulk Density of Mill Samples on Resistivity ............................................ 39
Figure 25 - Effect of Particle Packing on Resistivity ................................................................. 40
Figure 26 - Effect of Chloride Content on Resistivity ............................................................... 41
Figure 27 - Effect of Carbon Content on Resistivity ................................................................. 42
Figure 28 - Resistivity of Sample 7b Before and After Sample was Melted ................................. 43
Figure 29 - Resistivity of Sample 4 Before and After Sample was Melted ................................. 43
Figure 30 - XRD Spectra for Unmelted Sample 7b ................................................................... 45
Figure 31 - XRD Spectra for Melted Sample 7b ....................................................................... 45
Figure 32 - XRD Spectra for Unmelted Sample 4 ..................................................................... 46
Figure 33 - XRD Spectra for Melted Sample 4 ........................................................................ 46
Figure 34 - Effect of Time and Field Strength on Resistivity for Sample 1c ......................... 47
Figure 35 - Effect of Time and Field Strength on Resistivity for Sample 7b ......................... 48
Figure 36 - Effect of Long Term Exposure on Resistivity ......................................................... 49
Figure 37 - Effect of Temperature on Resistivity of Sample 1a ............................................. 50
Figure 38 - Effect of Temperature on Resistivity of Sample 4 ................................................ 51
Figure 39 - Effect of Temperature on Resistivity of Sample 7b (linear scale) ....................... 52
Figure 40 - Effect of Moisture Content on Resistivity of Sample 4 ............................................. 53
Figure 41 - Effect of Moisture Content on Resistivity of Sample 6a ............................................. 54
Figure 42 - Effect of SO$_2$ Concentration on Resistivity of Sample 5 ............................................. 55
Figure 43 - Effect of SO$_2$ on Resistivity in Dry and Moist Atmosphere for Sample 2 ............... 56
List of Appendices

Appendix 1  EPA Boiler MACT Standards
Appendix 2  Resistivities of Common Materials
Appendix 3  Effect of Field Strength on Resistivity
Appendix 4  Effect of Melting on Resistivity
Appendix 5  Effect of Time of Exposure on Resistivity
Appendix 6  Effect of Temperature on Resistivity
Appendix 7  Effect of Moisture Content on Resistivity
Appendix 8  Effect of SO₂ Concentration on Resistivity
Chapter 1

1 Introduction

1.1 Controlling Particulate Matter Emissions

Particulate matter emissions are strictly monitored and controlled in all industrial plants due to increasingly stringent government regulations. In March of 2011, The United States Environmental Protection Agency created a new set of regulations under the Clean Air Act setting standards based on maximum achievable control technology (MACT). These MACT standards state that existing solid fuel boilers must not exceed the emission limit of 0.039 pounds of particulate matter per million BTU of heat, down from the previous limit of 0.07 pounds of particulate matter per million BTU of heat [1]. A summary of the boiler MACT standards can be found in Appendix 1.

Electrostatic precipitators (ESPs) are common devices used to remove particulates from combustion gases. They are used in coal fired power plants, cement plants, steel mills, and waste incineration plants. In the kraft recovery process, ESPs are used to control emissions of dust formed from the combustion of black liquor in the recovery boiler. The burning of black liquor forms large amounts of particulate matter in the exhaust gas stream. The removal efficiency of ESPs is required to be greater than 99% in order to satisfy the strict government regulations for particulate emissions. The goal of all kraft mills is to stay within these regulations while maintaining their desired rate of production.

1.2 Kraft Pulping Process

The kraft pulping process is the most widely used chemical pulping process. It accounts for two thirds of the world’s pulp production, or about 130 million metric tons per year. The kraft pulping process yields higher pulp strength than other pulping methods, can be used with a
variety of wood species, and is economically favourable in that pulping chemicals can be recovered and reused at an efficiency of up to 97%.

Figure 1 - Summary of the Kraft Recovery Process [2]

The kraft pulping process, summarized in Figure 1, begins by mixing pulping chemicals (NaOH and Na₂S) with wood chips in the digester, a pressurized vessel. This unit operates at about 8 atm and 170°C to chemically separate the wood fibres from the lignin. The wood fibres are then washed, yielding pulp and a by product called black liquor, which consists of water, lignin, and inorganic chemicals. This liquor is concentrated in multiple effect evaporators to raise the solids content to 60-80% and is then fed into the most important unit in the kraft process: the recovery boiler.

The function of the recovery boiler is to burn black liquor in order to generate heat to produce electricity and steam for use elsewhere in the pulping process, while also recovering desired pulping chemicals in the form of smelt. Water for steam formation enters the recovery boiler through the economizer, where it is preheated by the exhaust gases from black liquor combustion. Concentrated black liquor is sprayed into the bottom of the recovery boiler and burned to obtain heat which generates steam from the feedwater in the generating bank. This steam then continues to the superheater to create superheated steam and further continues to a
turbine generator to create electricity. The steam is also used for sootblowing, which is used to remove soot that has been deposited on the tubes in the recovery boiler. The resulting chemicals at the bottom of the recovery boiler are in the form of smelt, consisting of Na$_2$CO$_3$ and Na$_2$S. Smelt is fed to a dissolving tank to form green liquor. This green liquor is further sent to a recaustisizing process in order to be reformed to white liquor, consisting of Na$_2$S and NaOH, the desired pulping chemicals [2].

Under normal recovery boiler operation, about 4kg of particulate matter is formed per 100kg black liquor solids burned. This leads to a flue gas particulate matter loading of 30-60 g per normal cubic meter in the stack gas exiting the recovery boiler. [3]. Dust particles between 0.1-1μm in diameter are formed due to the condensation of vapours in the upper furnace at a temperature of about 800°C. The main component of recovery boiler fly ash is Na$_2$SO$_4$ (up to 80 %), with Na$_2$CO$_3$, K$_2$SO$_4$, NaCl, K$_2$CO$_3$ all being the minor components [4,5]. The ash produced from burning black liquor in the kraft recovery boiler can also contain some carbon particles in the form of entrained char from unburned black liquor. Carbon particles are easy to detect, as they form large flaky black dots in the white salt cake [6]. A typical recovery boiler ash composition is shown in Table 1 [5].

<table>
<thead>
<tr>
<th>Item</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>78.5%</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>8.2%</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>6.8%</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.5%</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

The flue gas also contains varying amounts of O$_2$, N$_2$, CO$_2$, and H$_2$O. A typical flue gas composition is shown in Table 2 [5]. CO, H$_2$, H$_2$S, SO$_2$ are also present in the exhaust gas, but in much smaller concentrations.
Table 2 – Typical Flue Gas Composition from a Recovery Boiler

<table>
<thead>
<tr>
<th>Item</th>
<th>Composition in Wet Flue Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>53.0%</td>
</tr>
<tr>
<td>H₂O</td>
<td>26.5%</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.7%</td>
</tr>
<tr>
<td>O₂</td>
<td>2.0%</td>
</tr>
</tbody>
</table>

The exhaust gas is passed through an ESP in order to remove more than 99% of the particulate matter. In order for the ESP to achieve this efficiency, the dust resistivity (the tendency to oppose the flow of current – this will be discussed in more detail later in this thesis) must be in a desirable range so that the particles can be sufficiently charged and collected.

In order to maximize recovery boiler energy recovery, the trend with newer mills has been to burn more concentrated black liquor (>75% BLS) in the recovery boiler. This leads to a lower water vapour concentration in the exhaust gas due to the high solids content of the black liquor. The amount of water vapour in the exhaust gas is an important parameter with respect to performance of the electrostatic precipitator at the recovery boiler outlet. This is because increased amounts of moisture in the exhaust gas lead to a more favourable resistivity and make it easier for the particulate matter to be electrostatically precipitated out from the gas stream. The largest source of water vapour in the exhaust gas is the water in the black liquor, while other sources of water vapour in the exhaust come from the hydrogen in the black liquor and humidity in the combustion air.

Burning more concentrated black liquor leads to a higher furnace temperature due to the smaller amount of latent heat consumed by the vaporization of water. A higher furnace temperature releases less SO₂ from the char bed and most of this SO₂ is consumed by the reaction with NaOH which produces Na₂SO₄. A lower SO₂ concentration in the exhaust is suspected to affect dust resistivity, making its removal more difficult. In addition, a higher furnace temperature favours the production of sodium carbonate from sodium and CO₂, leading to a higher carbonate.
concentration in the dust formed. A higher carbonate concentration tends to lead to the formation of smaller ash particles. A smaller particle size is also suspected to have an effect on resistivity and may pose ESP performance issues.

The electrostatic precipitator is located downstream of the economizer, where the temperature of the gas is about 160°C-210°C [5,7]. Particle sizes of the ash are generally uniform, with most of the particles not exceeding 1 micron in size [8]. Some precipitators experience opacity problems, which may be attributed to the resistivity of the ash, but the reason for this has not been extensively researched in the field of kraft recovery. Tests have been performed to investigate the behaviour of resistivity of major recovery boiler components (sodium carbonate, sodium sulphate, and sodium chloride); however, effects of operating conditions and particle characteristics on resistivity of recovery boiler ash samples have not been studied.
Chapter 2

2 Electrostatic Precipitation Theory and Dust Resistivity

2.1 ESP Operating Principles

2.1.1 Dust Charging

An ESP works by generating an electric field between two electrodes through which the dirty exhaust gas passes. There are two types of electrodes in all precipitator designs: discharge electrodes, which are negatively charged and have a small radius of curvature, and collecting electrodes which are positively charged and have a large surface in order to maximize the area on which the particulate matter can collect.

There exist several types of ESPs which are used for various applications. Discharge electrodes consist of either long thin wires with a weight at the base which hangs between collecting electrodes, or a rigid frame holds the discharge electrodes are held in place between collecting electrodes. Collecting electrodes can either be tube electrodes, where the discharge wire hangs axially in the center of a cylindrical collecting electrode and the gas flows axially, or plate electrodes where discharge wires hang between parallel plates and gas flows perpendicular to the wires. Precipitators can be dry-type, where the deposited ash layer is removed from the collecting electrode mechanically by rapping, or wet-type, where the deposited ash layer is removed by a stream of water. Finally, precipitators can be single-stage, where the charging and collection of dust particles occurs simultaneously, or multi-stage, where particles are charged then subsequently collected in the following stage of the precipitator [9]. A schematic diagram of a typical single-stage dry type parallel plate precipitator, which is most commonly used in the kraft pulping process, is shown in Figure 2 below.
The particle charging process begins adjacent to the discharge electrodes where free electrons are generated. A voltage of 30 - 120kV is applied between the two electrodes which causes neutral gas molecules adjacent to the discharge electrodes to collide and ionize, releasing free electrons and creating positive gas ions [11]. Under the influence of the strong electric field, these electrons migrate away from the discharge electrode, colliding with other neutral gas molecules to release more free electrons and generate more positive ions. This constant ionization gives off a visible glow in the vicinity of the discharge electrode, which is why this phenomenon is known as the corona current. At a certain distance from the discharge electrode, the electric field strength is not strong enough to sustain the corona current; instead, free electrons adhere to neutral gas molecules, giving them a negative charge.

There are two different mechanisms through which anions and free electrons give dust particles a negative charge. For larger dust particles (>1μm in diameter) field charging occurs, whereby free electrons and anions adhere to the surface of neutral dust particles, giving them a negative charge. When no more ions can adhere to the surface of a dust particle, it is said that the dust
particle has reached its saturation charge. Generally, the bigger the particle size, the bigger the magnitude of its saturation charge. The mechanism of field charging is shown in Figure 3 below.

![Diagram of Field Charging of Dust Particles](image)

**Figure 3 - Field Charging of Dust Particles**

For smaller dust particles (<0.5μm in diameter) diffusion charging occurs, whereby anions and electrons in the vicinity of neutral dust particles induce a dipole, giving the dust particles a partial negative charge on one side and partial positive on the other. This is shown in Figure 4 below.

![Diagram of Diffusion Charging of Dust Particles](image)

**Figure 4 - Diffusion Charging of Dust Particles**

A combination of field charging and diffusion charging occurs with particles between 0.5μm and 1μm in diameter [12]. The theoretical charge as a function of particle size based on Cochet’s charging model, which takes into account both field and diffusion charging, is shown in Figure 5 below [13]. The resistivity of dust particles plays an important role in particle charging and will be discussed further in this thesis.
2.1.2 Dust Collection and Removal

Once the particles have been negatively charged, they migrate towards the positively charged collecting electrodes under the influence of the electric field. The precipitator is run at the maximum allowable operating voltage in order to maximize the speed at which the particles migrate; however, if the voltage is too high, a momentary discharge of current between the discharge and collecting electrodes occurs in the form of a spark. The maximum operating voltage is limited by the amount of sparking that occurs in the precipitator, with the desired amount being 50-100 sparks per minute [11]. Once the particles hit the collecting electrode their charge is only partially discharged; some charge remains on the particle in order to keep it adhered to the collecting plate. The dust particles remain adhered to the collecting plate as a result of a combination of the adhesive force (due to dissimilar charge between the particle and the electrode) and physical adhesive forces between particles due to their morphology and surface texture.

A layer of dust particles builds up on the surface of the collecting plate until the thickness of the dust layer is thick enough to interfere with the electric field in the precipitator. At this point,
rapping occurs (for dry-type precipitators), a process through which the collecting plates vibrate or are mechanically struck in order to shake off the deposited layer of dust. This dust is collected at the bottom of the precipitator in dust collection hoppers, which are occasionally emptied. Alternatively, wet-type ESPs exist where a stream of water is used to remove the deposited dust layer from the collecting electrodes, although these are much less common [14].

2.1.3 Volume and Surface Conduction

There are two independent conduction paths through which electrons can travel: through the body of the particulate material, termed volume conduction, and through a thin film of an adsorbed conducting material on the surface of the particulate material, termed surface conduction. Volume conduction is a function of the particle matrix constituents and is the dominant mechanism at elevated temperatures. Surface conduction is dominant at lower temperatures and is mainly a function of the composition of the gas stream. This is the principle behind flue gas conditioning, whereby a conditioning agent such as steam or SO₃ is injected into an exhaust gas stream before it enters the ESP in order to increase surface conductivity (decrease dust resistivity) [15]. At intermediate temperatures, both conduction mechanisms are significant. The differences in conduction paths are depicted in Figure 6 below.

![Figure 6 - Volume and Surface Conduction](image-url)
2.1.4 Drift Velocity and Theoretical Efficiency

All negatively charged particles in the inter-electrode space move toward the collecting electrode perpendicular to the direction of gas flow at a speed called the migration or drift velocity. This velocity can be calculated as follows:

\[ w_p = \frac{q \cdot E_p \cdot C}{6 \cdot \pi \cdot a \cdot \mu} \]  

(1)

where \( w_p \) is the migration velocity, \( q \) is the charge on the particle, \( E_p \) is the field strength, \( C \) is the Cunningham slip correction factor, \( a \) is the particle diameter and \( \mu \) is the viscosity of the gas stream. The higher a particle drift velocity, the more likely the particle is to be removed from the exhaust gas stream. From this velocity, one can calculate the theoretical collection efficiency of an ESP for a given set of conditions from the Deutsch-Anderson equation as follows [16]:

\[ \eta = 1 - e^{\frac{-A_p \cdot w_p}{Q}} \]  

(2)

where \( \eta \) is the theoretical collection efficiency, \( A_p \) is the total collection area, and \( Q \) is the volumetric flow rate of the gas stream. This model is based on several simplifying assumptions:

- Particles are assumed to be at their saturation charge immediately upon entering the ESP
- There is no particle re-entrainment into the gas stream
- There is no excessive sparking within the deposited dust layer (back corona)

These assumptions hold for dusts with moderate resistivities, but do not hold for dust types with excessively high or low resistivities. [17]. In the case of high or low resistivity dust, the actual collection efficiency of a precipitator may be significantly lower than the calculated theoretical collection efficiency.

Many other factors also influence the efficiency of ESPs. An important factor is power input to the precipitator, which may be hindered by mechanical deficiencies of the precipitator, such as misaligned electrodes causing uneven current distribution. Reduced power input also occurs when very fine dust is present as the voltage required to achieve the desired current increases.
This is because particles between 0.1 and 1 μm are most difficult to charge. ESP efficiency as a function of particle size based on the Deutsch-Anderson model is shown in Figure 7 below.

![Figure 7 - ESP Efficiency as a Function of Particle Size. Typical Recovery Boiler Ash Range is Shown with the Dotted Line [8]](image)

In addition to poor charging capacity and deteriorated collection efficiency, fine particles are also undesirable because they can accumulate around the discharge electrode, causing a shielding effect and decreasing the rate of ion formation [6]. These problems can be overcome by using improved transformer-rectifier controllers that allow the precipitator to run at the highest possible voltage without excessive sparking, increasing current input and decreasing emissions [8].

Another problem that reduces ESP efficiency is dust build up on discharge electrodes due to the sticky nature of some dusts. This can eventually cause the formation of crusty deposits on the surface of discharge electrodes, limiting the power input. Dust resistivity also plays a role in dust deposits on the discharge electrodes. This can be corrected with optimized rapping controls in order to remove the deposits.
Problems with gas flow may also cause increases in emissions from ESPs. If the gas flow distribution is uneven, the particulate loading is not uniform throughout the precipitator. This causes the current to be lower where dust loading is higher, leading to less particle removal. Gas sneakage, which is when fractions of the gas pass through the inter-electrode space without being exposed to the electric field, also leads to deteriorated ESP performance, and can be corrected by installing appropriate baffles to ensure proper gas flow [8].

2.1.5 Industrial Applications of ESPs

Dry electrostatic precipitators are most commonly used to control emissions of carbonaceous fuels in the power generation industry. The most common application is for power generating plants using coal fired boilers. Different coal types result in different particulate and flue gas properties, which ultimately have to be considered when designing an appropriate ESP for the boiler. It is known that the quantity of SO$_3$ in the flue gas, which is a conditioning agent, affects the resistivity of the resulting fly ash particles. Moderate sulphur lignite coals exhibit best removal efficiencies, as the resistivity of the fly ash is in the ideal range for removal while lower sulphur coals result in a smaller amount of sulphur trioxide in the flue gas to the point where precipitation becomes difficult. Other coal types such as sub bituminous, lignites, and brown coals don’t pose resistivity problems and are readily removed [18].

In an effort to reduce reliance on fossil fuels, there has been an increasing interest in biomass fired plants to generate steam. Wood chip combustion is a common fuel source for generating energy and does not pose a problem for electrostatic precipitation. However, if combustion conditions in the boiler are upset, this can lead to a release of various organic compounds which promote high resistivity by coating the dust with an insulating layer. This problem can be overcome by changing the combustion conditions in the boiler. Chicken litter and municipal wastes can also be incinerated for energy recovery instead of being land filled. Ash from chicken litter does not require any ash conditioning because of the high moisture content in the exhaust gas, but may form large flaky deposits which can short circuit the system. Municipal waste, on the other hand, poses some problems arising from carryover of char flakes from incomplete combustion of paper, as well as general corrosion issues from the possible formation of acidic gases. Exhaust streams from municipal incinerators potentially contain acidic gas and high heavy
metal content, so they are faced with the most severe emission regulations. Because of these strict regulations, ESPs for municipal incinerators are coupled with some form of scrubbing system, either before or after the precipitator [19].

There are several uses of ESPs in the pulp and paper industry such as at the recovery boiler exit in the kraft recovery process as described throughout this thesis; however, ESPs are also common in timber debarking and lime sludge burning in the kraft recovery process. When timber is debarked, the bark is combusted and used as fuel. There is a risk of some carryover of coarse carbon particles which, if not removed, can pose problems because of the low carbon resistivity. Sludge produced from pulp and paper mills can also be incinerated to generate energy. ESPs are generally used for these applications, as high moisture content in the flue gas allows for efficient removal [19].

2.2 Role of Dust Resistivity

2.2.1 Definition of Resistivity

Electrical resistivity is a geometry independent property describing the tendency of a material to oppose the flow of electric current. Resistivity, which has units of Ω·m, differs from resistance as it is a material property, independent of sample size and geometry. Resistivity is defined as the ratio of field strength to current density and represents the normalized resistance of a specimen of material per unit length and area:

$$\rho = \frac{R A}{l}$$  \hspace{1cm} (3)

where $\rho$ is the resistivity, $R$ is the resistance of the specimen, $A$ is the cross sectional area, and $l$ is the specimen length or thickness. Generally, dust is categorized as low, medium, or high resistivity as follows:
<table>
<thead>
<tr>
<th>Resistivity</th>
<th>Measurement Range (kΩ·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>$10^{-1}$ to $10^{2}$</td>
</tr>
<tr>
<td>Normal</td>
<td>$10^{2}$ to $10^{5}$</td>
</tr>
<tr>
<td>High</td>
<td>$&gt;10^{5}$</td>
</tr>
</tbody>
</table>

Resistivities of common materials can be found in Appendix 2. Although very little work has been done in the field of measuring recovery boiler precipitator ash resistivity, it has been reported from two sources that kraft recovery boiler ash has resistivities between $10^{2}$ and $10^{6}$ kΩ·m. It is uncommon for dusts to have resistivities which exceed $10^{6}$ kΩ·m [3,6].

### 2.2.2 Effect of Resistivity on ESP Performance

Dust resistivity affects the performance of electrostatic precipitators in three main ways:
- It determines the rate of particle charging and the magnitude of particle charge
- It determines how strongly particles adhere to the collecting electrode
- It determines when electrical breakdown in the dust layer will occur

High resistivity particles are charged more slowly than low resistivity particles. Studies by Yu and Adamiak have shown that an order of magnitude increase in particle resistivity leads to a 10-fold decrease in particle charging rate [20, 21]. Furthermore, the saturation charge for highly resistive particles is about one-third of that for conductive dusts [14]. This is confirmed by Adamiak who claims that for particles of very high resistivity, commonly used charging models may not apply as particles may never reach their saturation charge, regardless of charging time [20]. Because of this, the residence time in an ESP may not be long enough for a particle of very high resistivity to achieve its saturation charge, leading to a lower attraction to the collecting electrode and lower ESP removal efficiency.
Resistivity also determines the fate of particles when they eventually reach the collecting electrode. If the particle resistivity is high, the dust has a tendency to retain its electrical charge. This means that once they are deposited, particles have a strong attraction to the collecting electrode and are difficult to remove once the dust layer builds up. The electrostatic attractive force between the dust layer and collecting electrode is shown as a function of current density for a variety of dust resistivities in Figure 8 below. It can be seen that dusts with higher resistivities show a much higher attractive force to the collecting electrode [17].

Figure 8 - Attractive Force Between Dust Layer and Collecting Electrode

Because of this adhesive force, highly resistive dusts frequently present rapping problems as the mechanical striking or vibration of the collecting electrodes is insufficient to remove persistent dust layers. Recent advances in rapping strategies and energizing systems have improved ESP efficiencies, but high resistivity dust still poses efficiency problems in many ESPs [22]. Conversely, dusts with low resistivity are easier to charge, but tend to give up their charge readily. The electrostatic force which attracts the dust layer to the collecting electrode is lost
quickly and some dust particles become re-entrained in the gas stream. Because of this, particles with very low resistivity are also undesirable as they are not removed by the precipitator and lead to lower removal efficiencies.

There exists an optimum dust resistivity whereby the particles can be charged readily, have enough electrostatic attraction to the collecting electrode so they do not become re-entrained in the gas stream, but can also be readily removed from the collecting electrode during the rapping process. [23]

2.2.3 Resistivity and Electrical Breakdown

In order to maximize the efficiency, electrostatic precipitators are operated at the highest allowable field strength to maximize particle charging rates and migration velocity; however, the maximum field strength is limited by electrical breakdown (in the form of sparks) in the dust layer and inter-electrode space. A sparking rate of 50-100 sparks per minute is desirable for a precipitator to operate at its maximum efficiency. Beyond this rate, sparking becomes excessive and can also lead to the back corona phenomenon. This occurs when there is so much sparking that the negative charge on the deposited ash layer is completely neutralized. The sparking also causes a net migration of positive ions from the collecting electrode into the inter-electrode space, neutralizing the desirable negatively charged particles. The deposited dust layer has a unique field strength depending on the properties of the ash at which electrical breakdown occurs constantly. This is called the breakdown strength or dielectric strength. The actual field strength in the dust layer, represented by the equation below, must not exceed the dielectric strength of the deposited dust layer:

\[ E_{\text{ash}} = j \cdot \rho < E_b \]  \hspace{1cm} (4)

where \( E_{\text{ash}} \) is the actual field strength in the dust layer, \( j \) is the current density, \( \rho \) is the resistivity, and \( E_b \) is the breakdown or dielectric strength of the material. It can be seen from this equation that for a given current density in the dust layer, dusts with higher resistivities will cause larger field strength and have a higher tendency to break down [24]. In-situ and pilot scale experiments have shown that there exists a critical resistivity value at which significant disturbance in the precipitator occurs [25]. This critical resistivity is usually on the order of \( 10^5-10^6 \) k\( \Omega \cdot \)m. In this...
resistivity range, the field strength in the ash layer can exceed the breakdown strength, which is usually on the order of 10 kV/cm, at a normal operating current density of $10^{-3}$-$10^{-4}$ A/m$^2$ [26,27]. For instance, if a precipitator was operating at a current density of $10^{-3}$ A/m$^2$ to remove a dust with a high resistivity of $10^6$ kΩ·m, the resulting field strength in the dust layer would be 10kV/cm. This is close to (or may even exceed) the breakdown strength, leading to excessive sparking and disruption of the desired electrical conditions in the precipitator. Figure 9 below shows a typical graph of efficiency as a function of electrical resistivity of dust [27].

![Figure 9 - Efficiency as a Function of Dust Resistivity](image)

As mentioned earlier, for a given operating voltage, beyond the critical resistivity, excessive sparking begins to occur, causing an electrical discharge that leads to a sudden drop in voltage and deterioration of collection efficiency.
2.2.4 Factors Affecting Resistivity

2.2.4.1 Particle Size and Morphology

It is known from studies on various coal fired boiler ash samples that particle size, particle size distribution, and particle morphology may have an effect on the resistivity of a deposited dust layer. This is because all of these factors affect the way that the dust packs when it forms a deposit on the collecting electrode [19]. The broader the particle size distribution, the more interstitial spaces between larger particles are filled with smaller particles, leading to more contact between particles and a larger contact surface area for conduction of current [28]. In addition, particles may have different charging and conducting characteristics depending on whether they are surrounded by other particles or whether they are isolated stand-alone particles [29]. This implies that particles which are in flight in the inter-electrode space and particles which have been deposited on the collecting electrode may exhibit different apparent resistivities. Particle morphology and surface texture can affect particle packing and contact area, and hence the cohesiveness of the dust when it forms a deposit on the collecting electrode.

2.2.4.2 Particle Composition

Different components in recovery boiler ash conduct electric current differently. Samuelsson [ref] investigated the resistivity of three major recovery boiler ash components: Na$_2$SO$_4$, Na$_2$CO$_3$, and NaCl. The resistivity of these components as a function of temperature is shown in Figure 10 [6].
It is evident that NaCl, despite the fact that it is present in lower quantities in recovery boiler ash, could play a significant role in increasing ash resistivity even at low concentrations. Na₂SO₄ and Na₂CO₃ exhibit similar resistivities up to a temperature of about 150°C, beyond which their resistivities differ with a change in temperature. This implies that their volume conduction is similar but surface conduction differs. Samuelsson’s study shows the resistivity of three individual recovery boiler components, but does not consider other recovery boiler ash components present in significant quantities such as K₂SO₄ and K₂CO₃. In addition, it does not report resistivities of actual mill recovery boiler ash samples.

A separate study of coal fired boiler ash investigated the effect of pure carbon content on resistivity, shown in Figure 11 below [7]. The trend implies that there is a critical carbon content beyond which there is a sudden drop in resistivity.
This effect could play a role in kraft recovery boiler ash, as some ash samples contain large flakes of unburned black liquor particles which contain high levels of carbon and sodium; however, the trend presented here is for coal fired boiler ash, which may behave differently from recovery boiler ash. The effect of presence of black liquor char in recovery boiler ash will be discussed later in this thesis.

2.2.4.3 Time of Exposure

It is important to consider the effect of time of exposure on resistivity of deposited ash. If a deposited ash layer on the surface of a collecting electrode is not removed by the rapping process, an increase in resistivity would only increase the attractive force of the dust to the collecting electrode and make subsequent rapping processes less efficient. Nichols [30] reports that a long term exposure of a coal fired boiler ash sample to an electric field can lead to an increase in resistivity at high temperatures. This may due to a migration of electrical carrier ions, primarily sodium. Nichols claims that in laboratory resistivity cell experiments, sodium ions migrated from the negative electrode to the positive electrode under the influence of the electric
field, causing an increase in resistivity of the dust layer because of the uneven distribution of the sodium electrical carrying ion [30]. Experiments by Sullivan confirmed that there is an increase in resistivity of coal fired boiler ash with time, although the mechanism by which this occurs is not addressed [31].

2.2.4.4 Field Strength

Some high resistivity dusts are known to exhibit a different resistivity with varying field strength, known as non-ohmic behaviour. This is due to the increase in effective contact area between dust particles because of increased cohesive interparticle compressive forces caused by elevated field strengths [32]. Potter and Goard reported that ash samples taken from a coal combustion plant exhibited a decrease in resistivity of up to two orders of magnitude with a 50-fold increase in field strength. This can make a significant difference in precipitators which remove dusts with resistivities higher than the critical resistivity value. An increase in the applied voltage can reduce the dust resistivity to below the critical value, significantly increasing removal efficiency [24].

2.2.4.5 Temperature

Temperature has a significant effect on resistivity of ash particles. At temperatures below 150°C, conduction is governed by the gas stream composition as surface resistivity is low and volume resistivity is maximized. This is because at lower temperatures moisture and other gases present have a higher tendency to adsorb onto the surface of dust to provide a path for electrical conduction, minimizing surface resistivity. At relatively higher temperatures, conduction is mostly governed by the composition of the dust; surface resistivity is maximized while volume resistivity is minimized [33]. Volume resistivity of insulating materials decreases with increasing temperature due to more molecular movement and increased lattice vibrations which gives rise to more conduction and decreased resistivity [34]. At about 150°C surface resistivity is high due to the reduced tendency of conductive film formation on the surface of dust particles, and volume resistivity is still relatively high. Because of this, a peak resistivity occurs around this temperature [7]. In Figure 12 below, volume resistivity is represented by the solid line with triangular data points, surface resistivity is represented by the dashed line with circular data...
points, and the composite resistivity curve is shown with the square points. The reciprocal of the composite (effective) resistivity is the sum of the reciprocals of the volume and surface resistivity[7].

![Figure 12 - Change in Resistivity of Coal Fly Ash with Temperature][1]

2.2.4.6 Gas Stream Composition

The gas within which the particulate matter is entrained also plays a large role in the resistivity of the dust. This is because physical adsorption and condensation of components in the gas stream onto the dust particles can create a lower resistance conduction path on the particle surface. For many industrial boilers, conditioning agents such as SO₃ and NH₃ are used in order

[1]: #Figure-12-Change-in-Resistivity-of-Coal-Fly-Ash-with-Temperature-7
to increase surface conductivity and decrease resistivity. It is also known that moisture plays a large role in decreasing resistivity of coal fired boiler ash, even at temperatures above the dew point [17]. The effect of increasing moisture content on the resistivity of cement dust is shown in Figure 13 below [10].

![Figure 13 - Change in Resistivity of Cement Dust with Moisture Content](image)

In the kraft pulping process, this is an important parameter as moisture content in the exhaust stream is greatly dependent on the black liquor solids fraction. The recent trend is that mills have been burning black liquor with a greater solid fraction in order to maximize energy recovery; however, this leads to a decreased moisture content in the flue gas and a higher dust resistivity. Figure 14 below shows the change in water vapour content in the exhaust gas as a function of the solid fraction in the black liquor.
Figure 14 - Change in Moisture Content in Flue Gas as a Function of BLS

We can see from this figure that a change in solids content from a low range (around 65% BLS) to a high value (around 80% BLS) would lead to a drop in moisture content from about 30% to about 20% in the flue gas. The effect of this change could be significant in ash resistivity, and will be discussed in the results section of this thesis.

The concentration of sulfur dioxide (SO$_2$) in the gas stream is also suspected to play a role in dust resistivity. Dalmon and Tidy reported that SO$_2$ somewhat lowers dust resistivity in ash from coal fired boilers, but much less effectively than SO$_3$, a commonly used conditioning agent which is known to lower dust resistivity by forming a thin conductive layer on the surface of dust particles [35]. Recovery boiler exhaust can have SO$_2$ concentrations up to 200ppm, which may affect dust particle resistivity, but its effects on recovery boiler ash have not been examined in previous studies. The effects of SO$_2$ on resistivity of recovery boiler ash will be discussed in the results section of this thesis.
Chapter 3

3 Experiment Description

3.1 Experimental Objective

Electrical resistivity of the particulate matter which is to be removed plays an important role in ESP operation and removal efficiency. As discussed in the previous section, many studies have been done to interpret the significance of dust resistivity and its relation to precipitator performance; however, factors which affect the resistivity of ash have not been studied extensively, particularly for kraft recovery boiler ash. In this study, a variety of experimental techniques were used to systematically examine the way that field strength, exposure time, composition, particle size, temperature, moisture content, and SO$_2$ concentration affect resistivity of kraft recovery boiler ash. Tests were performed on 11 different mill samples as well as samples which were synthetically created from the main recovery boiler ash components. The objective of this study is to identify the ESP operating parameters and ash properties which have a large impact on resistivity in order to optimize it and achieve maximum ESP efficiency.

3.2 Experimental Setup

Methods of testing bulk resistivity of powders are described in the ASTM Standard Test Methods for DC Resistance or Conductance of Insulating Materials and the ASME Power Test Code 28: Determining the Properties of Fine Particulate Matter [36, 37]. A dust sample 0.5 cm in thickness, representative of a dust layer deposited on an ESP collecting electrode, is placed in between two parallel circular stainless steel (SS) electrodes. A direct current high voltage (HV) supply is hooked up to each electrode in order to create a uniform field strength in the dust layer of up to 16 kV/cm, simulating actual precipitator conditions. An electrically insulating ring made of glass filled (GF) Teflon is placed as a concentric circle just inside the circumference of the bottom electrode to ensure that the two electrodes do not make direct contact and to ensure that the flow of current through the dust layer is linear. A standard mass to provide 10 g/cm$^2$ of
pressure is attached to the top electrode, which is surrounded by a glass filled Teflon support piece to ensure that the electrode is lowered directly on top of the dust sample and makes good contact across the entire surface. A schematic of the experimental apparatus is shown in Figure 15 below.

![Schematic of Experimental Apparatus](image)

**Figure 15 - Experimental Apparatus for Measuring Resistivity**

The samples were dried in an oven and then placed in the resistivity apparatus at room temperature and atmospheric conditions to test for effects of particle size and packing, sample composition, and field strength. Experiments for time of exposure to the electric field were performed inside an oven at 100°C. The apparatus was placed inside an oven and an electrical feedthrough was installed on the oven wall to connect the apparatus to the high voltage power supply. To test for effects of temperature on resistivity, the temperature of the sample was varied from 20°C to about 280°C.

To test the effects of moisture content on resistivity, the setup was slightly more complicated. The resistivity apparatus was placed in a polymethylpentene isolating chamber inside the oven in order to maintain the desired humidity. Air was bubbled through a humidification unit and the temperature of the water in this unit was controlled in order to get the desired moisture content in the gas stream. This humidified gas stream was then fed to the oven and through a copper coil in order to preheat it before it was sent to the isolating chamber. A schematic is shown in Figure 16. To test the effects of SO₂ concentration, a mixture of 1000ppm SO₂ in air mixture was fed directly into the oven from a gas cylinder. Depending
on the experiment, a separate stream of dry or humidified air was also fed directly into the oven. When the system reached steady state and the SO₂ concentration in the oven was stabilized, the experiment was performed.

3.3 Experimental Procedures

Eleven samples from seven different mills were analyzed in order to determine their electrical resistivity and identify effects of particle characteristics and operating conditions on resistivity. The resistivity was measured by placing a fixed volume of the sample into the cup of the conductivity apparatus, and the top was levelled by drawing a straight edge across the surface of the cup. The disk electrode was gently lowered onto the surface of the sample, making sure not to press down and pack the dust sample. All samples were dried to eliminate effects of moisture content. The desired voltage was then applied, starting from zero and rising in small steps until the breakdown voltage was reached. The current was observed for each step increase in voltage and the breakdown voltage was identified by a sudden observable increase in the current as shown in Figure 17 below.
The breakdown field strength was determined by dividing the breakdown voltage by the dust layer thickness. Resistivity measurements were computed from the current and voltage readings and the geometry of the dust sample using equation (1).

Particle size was analyzed qualitatively by inspecting scanning electron microscope (SEM) photographs of each sample. Particle size experiments were also performed with synthetic ash samples consisting of Na₂SO₄, Na₂CO₃, and NaCl by taking resistivity measurements of the mixture with the same chemical composition but varying grain sizes.

Dusts which have different resistivities at different field strengths are called non-ohmic. Dust samples were tested for non-ohmic behaviour by varying the field strength and monitoring the corresponding resistivity.

Figure 17 - Typical VI Curve for Kraft Recovery Boiler Ash Sample with the Red Line Indicating Electrical Breakdown
The bulk density of the samples was measured by placing a fixed volume of the sample in a graduated cylinder and tapping it gently to allow the dust to settle, then taking the mass reading. The effect of packing was investigated by varying the mass of the weight on the top electrode.

In order to investigate the effect of composition, synthetic ash samples were prepared consisting of a mixture of pure Na₂SO₄, Na₂CO₃, and NaCl. The molar ratio of Na₂SO₄ to Na₂CO₃ was kept constant at 4:1, while the NaCl content was varied from 0 to 30 mole % (Cl/Na). These components were mixed together, melted, ground and sieved with a 90 μm sieve tray.

The effect of melting was investigated with several mill samples by melting them at 800°C and sieving them to eliminate large particles, then taking resistivity measurements. It was presumed that when the samples were solidified, the sulphate and carbonate components would form a solid solution and solidify as one phase. In addition, x-ray diffraction analysis was performed on the dust samples prior to and after melting. The purpose of this experiment was to evaluate whether individual recovery boiler ash particles were all of uniform composition consisting of a solid solution of more than one phase or whether each particle had one phase consisting of only one component.

The effects of time of exposure to the applied electric field were investigated in two ways. Tests for short term time of exposure were performed by continuously applying an electric field from 2-8 kV/cm for approximately a 30 minute period and monitoring the change in resistivity over time. Long term time of exposure was investigated by exposing a dust sample to a 2 kV/cm field for a period of about 16 hours and monitoring the dust resistivity over time.

It is known that temperature plays an important role in dust resistivity. To test for the effect of temperature, the resistivity apparatus was placed inside an oven. Sample temperatures were varied from 20 – 280°C and resistivities were measured.

To test the effects of moisture content on dust resistivity, a dry air stream was fed through the humidification flask and fed into the isolating chamber inside the oven, which was kept at a constant temperature of 150°C. The temperature of the water in the humidification flask was varied from 20-100°C in order to get the desired moisture content in the outlet saturated gas
stream. The dust sample was exposed to the conditions in the isolating chamber by raising the
top disk electrode and allowing the moisture to adsorb onto the dust particles for 15 minutes,
after which it was lowered and the voltage was applied. To test the effects of SO₂ concentration
on resistivity, a similar setup was used. SO₂ gas was fed from a pressurized cylinder directly into
the oven along with a stream of dry or moist air. The flow rates were adjusted accordingly in
order to achieve the desired SO₂ concentrations in the oven. When the system reached steady
state, the top disk electrode was lowered onto the dust later and the voltage was applied.
Chapter 4

4  Results and Discussion

4.1  Breakdown Strengths and Resistivities

Each of the 11 samples were tested as outlined in the previous section in order to find their breakdown strength at 100°C. Samples 1a, 1b, and 1c were all from the same mill, collected at different times from different precipitators. Samples 6 and 7 were from the same mill, with samples 6a and 6b being from one recovery boiler in the mill and samples 7a and 7b being from a different recovery boiler in the same mill. The breakdown strengths are summarized in Figure 18 below.

![Breakdown Strengths of 11 Mill Samples](image)

**Figure 18 - Breakdown Strengths of 11 Mill Samples**

It can be observed that the breakdown strengths of all samples are fairly close, ranging between 10-12 kV/cm as expected. This is because breakdown in a dust layer occurs due to breakdown of the air pockets in the interstitial spaces between dust particles, and is not strongly dependent on the properties of the dust itself [38].
The samples were tested at a field strength 90% of the breakdown strength and at 100°C in order to minimize moisture in the dust sample which could affect the readings. The critical resistivity is indicated by the dotted red line. The results summarized in Figure 19 below are single measurements taken under the previously stated conditions.

![Figure 19 - Resistivities of 11 Mill Samples](image)

The resistivity of each mill sample was measured several times, replacing the test specimen with a fresh one after each measurement was taken. The variation of readings between different specimens of a given mill sample varied by less than 25%, which is insignificant when presenting the data on a logarithmic scale. It can be seen that most of the mill samples have a resistivity of about $10^4$-$10^5$ kΩ·m, with the exception of sample 4 which exhibits significantly higher resistivity of about $10^7$ kΩ·m. This mill reported opacity problems, meaning that the precipitator was not operating efficiently enough to meet regulations. This was most likely due to the fact that the resistivity of this dust is above the critical value, causing difficulties in charging, rapping problems, and excessive sparking, leading to abnormal electrical conditions in the precipitator.
4.2 Effect of Field Strength

It was expected that the dust would exhibit non-ohmic behaviour (a change in resistivity with field strength) due to the increase in effective particle contact area under higher field strengths, giving rise to more conduction. The most pronounced effect of field strength on resistivity was for Sample 4, as depicted in Figure 20 below. The final data point on the right side of the figure at a field strength of 10 kV/cm indicates that after a subsequent 1kV/cm increase in field strength, breakdown occurred.

For this sample, a decrease of about half an order of magnitude was seen with an increase in field strength from 6 kV/cm to 10 kV/cm. The least pronounced effect on field strength was observed with sample 7b, which showed almost perfectly ohmic behaviour as the resistivity remained fairly constant throughout the entire range of field strengths. This can be seen in Figure 21 - Effect of Field Strength on Resistivity of Sample 7b below.
This sample exhibits a similar resistivity at low and high field strengths, and the change with field strength is not appreciable; nonetheless, an increase in field strength still causes a slight decrease in resistivity. All the other mill samples exhibited non-ohmic behaviour as an increase in field strength led to a decrease in resistivity. The results for all mill samples can be found in Appendix 5. These results imply that an increased field strength can be advantageous when operating a recovery boiler ESP, not only because of an increased charging rate and migration velocity, but also because the resistivity of a highly resistive ash sample could be decreased to below the critical value and could improve ESP operation.

4.3 Effect of Particle Size, Bulk Density, and Packing

The effect of particle size was investigated by synthesizing recovery boiler ash samples of various particle sizes and equal compositions of Na$_2$SO$_4$, Na$_2$CO$_3$, and NaCl. Pure Na$_2$SO$_4$, Na$_2$CO$_3$, and NaCl were mixed together and ground to the desired particle size in an electric grinder. The particles were then sieved and split into four categories of particle sizes as described earlier. Resistivity measurements were taken and are depicted in Figure 22 below.
This figure implies that the electrical resistivity of a given dust sample is not greatly dependent on particle size for particles in this size range, as the total contact area for conduction is independent of particle size in a monodisperse system [28]. However, this particle size is not representative of actual recovery boiler ash samples, as recovery boiler ash samples are usually in the sub-micron range. In addition, it is likely that particle size distribution also plays a role in resistivity, as it affects the way that particles pack when they form a dust layer. Because of this, it was necessary to analyze actual mill samples and to investigate the effects of particle packing on resistivity.

Particle size of various dust samples from mill recovery boiler ESPs was examined qualitatively by analyzing photographs from a scanning electron microscope. Most of the dust samples had particles in the 0.1 – 1 μm range as expected. Some samples had a majority of particles around 1 μm in diameter, while other samples had a majority of particles in the sub-micron range. The micrographs are shown in Figure 23 below.
The sample which had the smallest particle size was clearly sample 4, which had the highest resistivity of about $10^7$ kΩ·m. The sample with largest particle size (but similar bulk density) was sample 5, which had a resistivity of about $2 \times 10^4$ kΩ·m. Most of the other samples had similar particle sizes of about 1 μm and resistivities between $10^4$ – $10^5$ kΩ·m. One sample that had relatively small particle size with a fairly low resistivity was sample 2. Although the composition of the samples differed and despite the exception of sample 2, these images imply that smaller particle size leads to a higher resistivity of ash when considering actual mill ESP dust samples.

As newer mills operate with higher black liquor solids content, there is a higher concentration of carbonate in the dust, favouring formation of smaller particles. This may pose precipitator problems not only due to potentially high resistivity, but also because smaller particles (~0.3μm) are most difficult to charge and remove, as shown in Figure 7.

**Figure 23 - Micrographs of 10 Mill Ash Samples**
The effect of bulk density of the 11 samples on resistivity was also investigated in this study. The results of resistivity experiments at 100°C and 90% of the breakdown voltage are summarized in Figure 24.

![Graph showing the effect of bulk density on resistivity.](image)

**Figure 24 - Effect of Bulk Density of Mill Samples on Resistivity**

An expected trend was that samples with higher bulk density would have lower resistivity because of more interparticular contact [35]. However, from the results presented in the figure above, there is no evident trend when comparing the bulk density of the 11 mill samples. This is most likely because factors such as the composition and particle size of the samples differed, making it impossible to draw any definite conclusion regarding the effect of bulk density. However, the effect of packing fraction on resistivity was investigated and showed results which agreed well with the ones reported by Dalmon and Tidy [35].

Effect of packing fraction was examined by increasing the pressure of the top electrode on the dust layer being tested. Loosely packed monodisperse spherical particles with random packing pack at a density of about 0.5, while maximum random packing for spherical particles is about 0.64 [28]. The effects of increasing the weight on the top electrode for three different samples are shown in Figure 25 below.
It is evident that a higher pressure on the dust layer will cause the particles to pack more closely together, increasing the contact area between particles. This decreases the resistivity until maximum particle packing is achieved (at approximately 50g/cm²), after which an increased pressure on the dust layer can no longer increase the packing and no longer has an effect on the resistivity.

4.4 Effect of Composition

4.4.1 Effect of Chloride Content

From previous studies, it is known that sodium chloride has a significantly higher resistivity than all other recovery boiler ash components, but effects of varying chloride content in kraft recovery boiler ash samples have not been studied before. The results of varying chloride content on resistivity at 100°C and 90% of the breakdown voltage are shown in Figure 26 below.
There is a clear trend that chloride content increases dust resistivity. It can be seen that an increase from 1% to 10% sodium chloride can cause an increase in resistivity of more than half an order of magnitude, while an increase from 1% to 20% can cause an increase of almost an entire order of magnitude. The results of the resistivity test of pure sodium chloride also agree closely with literature values of sodium chloride resistivity at about $10^7$ kΩ·m when approaching the breakdown strength [6]. This implies that dust samples with a higher chloride content have higher resistivity, making them more difficult to capture by an ESP.

### 4.4.2 Effect of Carbon Content

The fraction of carbon content in the ash from coal combustion has been reported to have an effect on resistivity [7]. Recovery boiler ash can contain some carbon in the form of char from unburned black liquor. This char is entrained in the gas stream with the ash leaving the recovery boiler and may have an effect on the dust resistivity. The effect of carbon content was studied by adding varying amounts of charred black liquor to a mill dust sample. The effects on resistivity are shown in Figure 27 - Effect of Carbon Content on Resistivity.
It can be seen that an increase in carbon content in the ash sample tends to decrease the resistivity of the sample. This may be attributed to the fact that the carbon-rich charred black liquor particles which are entrained in the ash may also have a high sodium content. Sodium decreases dust resistivity because it is the primary charge carrier in recovery boiler ash. This result implies that slight entrainment of unburned black liquor in the gas stream may be beneficial to dusts with high resistivity as it can lead to a slight reduction in dust resistivity, facilitating particle removal.

4.4.3 Effect of Melting

Several mill samples were melted at a temperature of 800°C then solidified and ground in order to find the resistivity of the resulting powder after melting. This was done in order to investigate whether recovery boiler ash components condense and solidify each as one phase or whether they co-condense and form a solid solution. A change in resistivity prior to melting and after melting under the same test conditions indicates that there is some physical change in the particle’s molecular structure. Figure 28 shows the effect of melting Sample 7b on its resistivity.
It is evident that the resistivity of the sample after it has been melted and ground is considerably lower than prior to melting. Figure 28 also shows that the breakdown strength of the melted sample was lower, indicated by the dashed lines. This was also investigated for Sample 4 below.
It can be seen that the same trend is evident with Sample 4 as with the previous sample. The melted sample shows a resistivity more than one order of magnitude lower, and also leads to a lower breakdown strength. Effects of melting on other mill samples can be found in Appendix 3. In order to further investigate the effects of melting on physical properties of the dust sample, an x-ray diffraction analysis was performed.

The original mill samples 7b and 4 were both analyzed for composition prior to melting using the x-ray diffraction technique. Figure 30 shows that sodium sulphate was identified as the main component in sample 7b, with some carbonate present, as expected. Some peaks were unidentified, implying that there were some other components in the sample unidentifiable by this technique. A similar result was obtained for sample 4. In sample 4, shown in Figure 32, sodium sulphate was readily identified as the major component. Some of the peaks suggested that sodium carbonate was also present, but could not be identified with complete certainty due to its much lower content. There were some peaks that were unaccounted for, suggesting some impurities or other components that could not be readily identified.

Both sample 7b and sample 4 were melted and ground to a fine particle size in order to perform the x-ray diffraction analysis, shown in Figures 31 and 33 below. It can be seen that the XRD spectra for the two samples after melting are very similar. These analyses allowed Burkeite \((2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3)\) to be easily identified. This implies that when the samples were melted, the sodium sulphate and sodium carbonate components co-solidified as a solid solution.

These analyses imply that when recovery boiler ash is formed, the ash particles condense and solidify in individual phases, as shown in the XRD spectra of the unmelted samples. They do not form a solid solution in the way that the melted samples do. This plays a large role in resistivity, as the original recovery boiler ash samples are much more resistive than the melted samples.
Figure 30 - XRD Spectra for Unmelted Sample 7b

Figure 31 - XRD Spectra for Melted Sample 7b
Figure 32 - XRD Spectra for Unmelted Sample 4

Figure 33 - XRD Spectra for Melted Sample 4
4.5 Effect of Time of Exposure

4.5.1 Short-Term Exposure with Varying Field Strength

Samples were subject to varying field strengths between 2-8 kV/cm for a period of 30 minutes at a temperature of 150°C while the resistivity was monitored throughout in order to identify changes in resistivity over time. The results for three different samples are shown in the figures below.

Sample 1c exhibits typical behaviour representative of most of the other samples, with a change in resistivity as field strength changes, but no evident change in resistivity over time. This type of behaviour is called non-ohmic behaviour, as was discussed in previous sections of this report.

Figure 34 - Effect of Time and Field Strength on Resistivity for Sample 1c
Sample 7b showed no change in resistivity over time or with field strength, as the resistivity remained constant throughout the experiment. Effects of time and field strength on the resistivity of other mill samples can be found in Appendix 4.

From this set of experiments, it could be concluded that short term exposure to a varying electric field does not cause a significant permanent change in resistivity. However, it was suspected that a longer exposure to an electric field would have an effect on resistivity. Tests for long-term exposure to a constant field strength were performed next.

4.5.2  Long-Term Exposure at Constant Field Strength

Samples were exposed to a low 2 kV/cm field strength in order to ensure no breakdown occurs over a period of 16 hours at 150°C while monitoring the resistivity during the course of the entire experiment. The results are shown in Figure 36.
It is evident that there is an increase in resistivity of about half an order of magnitude after the 16 hour exposure to the electric field. The sample was dried prior to exposure to the electric field, so the increase in resistivity cannot be attributed to the drying of residual moisture. The increase in resistivity may be due to either a chemical or electrical change in dust properties which inhibits its ability to conduct current. This implies that there is a different resistivity of a dust particle which is entrained in the gas stream and a dust particle which has been deposited on the collecting electrode. In addition, this result implies that the longer a dust particle remains on a collecting electrode, the higher its resulting resistivity will be and the harder it will be to remove this dust layer by means of rapping, leading to deteriorated ESP performance.

Figure 36 - Effect of Long Term Exposure on Resistivity
4.6 Effect of Temperature

The effect of temperature on resistivity of the 11 mill samples was studied by varying the temperature from $20^\circ C$ to about $280^\circ C$. It was expected that there would be a peak resistivity at the point where surface conduction becomes insignificant and volume resistivity is still high. This result can be observed in Figure 37 below.

![Figure 37 - Effect of Temperature on Resistivity of Sample 1a](image)

It can be seen that for Sample 1a, after about $50^\circ C$, there is an increase in resistivity until the temperature increases to about $150^\circ C$. Beyond this temperature, the resistivity began to decrease until the end of the experiment. This same test was performed for the other ten samples. The results for Sample 4 are shown in Figure 38 below.
Sample 4 shows a similar trend as the previous sample. The only difference is that the peak resistivity of this sample occurs at about 115°C. All the other samples tested showed a similar trend, with the maximum resistivities all occurring around 150°C. The effects of temperature on resistivity of other mill samples can be found in Appendix 6. The peak in resistivity occurs most likely because all the moisture on the surface of the dust particles is driven off when the sample is heated up to the dew point, and any residual moisture which is in the particle matrix is driven off as the temperature is further increased after the dew point. Beyond around 115-150°C, surface conduction no longer plays a significant role (surface resistivity is minimized) and volume resistivity is the dominant mechanism. Beyond this temperature, volume resistivity begins to diminish and there is an increase in conduction as lattice vibrations of the particle matrix increase, allowing more current to flow. A reason why the peak in resistivity occurs at slightly different temperatures for different samples may be because of their hygroscopicity, as different samples may have a tendency to absorb moisture more readily than others. Because of

Figure 38 - Effect of Temperature on Resistivity of Sample 4
this, the moisture is driven off at lower temperatures for less hygroscopic dusts and at higher temperatures for more hygroscopic dusts.

In order to emphasize the effect of temperature on resistivity, the resistivity of sample 7b as a function of temperature is shown in the figure below on a linear scale. The dashed lines represent the typical recovery boiler precipitator temperature range.

![Graph showing effect of temperature on resistivity of sample 7b (linear scale)](image)

**Figure 39 - Effect of Temperature on Resistivity of Sample 7b (linear scale)**

When plotted on a linear scale, the peak resistivity is much more obvious than when looking at the results on a logarithmic scale. It can be seen that if a precipitator is operated on the colder end of the temperature range, the resistivity (above $3 \times 10^5 \text{k}\Omega\cdot\text{m}$, approaching the critical value) is about one order of magnitude higher than if it was operated at the hotter end of the temperature range (about $3 \times 10^4 \text{k}\Omega\cdot\text{m}$, well below the critical value). This could be very significant with dusts that have a high resistivity, as an increase in temperature of about 50°C could drop the resistivity to well below the critical value.
4.7 Effect of Moisture Content

Moisture is suspected to play a large part in resistivity of kraft recovery boiler ash as it is absorbed by the dust particles and is adsorbed on the surface of the dust particles to create another electrical conduction path. Moisture content in recovery boiler exhaust gas varies greatly depending on black liquor hydrogen content, combustion air humidity, and most importantly the fraction of black liquor solids. Moisture content was varied from 0-70% at 150°C and the resulting effects on resistivity for Sample 4 are shown in Figure 40 below. The dashed lines indicate typical moisture content in recovery boiler exhaust gas.

![Figure 40 - Effect of Moisture Content on Resistivity of Sample 4](image)

From these results, it can be seen that an increase in water vapour content in the exhaust stream can play a huge part in decreasing the resistivity of the dust. The graph shows a somewhat linear correlation, with an increase in moisture content from 0 to 10% causing the most significant decrease in resistivity of about one order of magnitude, with subsequent 10% increments in moisture content causing a smaller decrease in resistivity for this particular sample. Results for Sample 6a are more representative of all the other mill samples tested and are shown in Figure 41. The dashed lines indicate typical moisture content in recovery boiler exhaust gas.
Sample 6a behaved very similarly to all the other mill samples tested, for which the results can be found in Appendix 7. This sample shows a fairly linear relationship between moisture content and resistivity. Compared to Sample 4, this sample shows a much bigger decrease in resistivity with moisture content, as the original increase from 0 to 10% moisture causes a drop in resistivity of more than one order of magnitude, and each subsequent 10% increment causes about half an order of magnitude decrease in resistivity. This result implies that Sample 4 is less hygroscopic and has a lower tendency to adsorb water, hence increasing the moisture content is not as effective in decreasing resistivity as it is with the other samples.

These results have very important industrial implications in controlling emissions from kraft recovery boilers. If a mill typically operates at 65% black liquor solids, its exhaust gas stream would typically contain about 30% moisture, while a mill that operates at 80% black liquor solids would contain only about 20% moisture. This could cause a significant increase in resistivity of the resulting recovery boiler ash. Although it is a priority for mills to operate their boilers with a black liquor solids content that maximizes the boiler’s heat and chemical recovery, it is evident that the recent trend of increasing black liquor solids content may lead to increased precipitator problems due to a lower moisture content in the exhaust gas stream.
4.8 Effect of SO$_2$ Concentration

It was suspected that the concentration of SO$_2$ would play a large role in decreasing dust resistivity. Similarly to water vapour in the exhaust stream, SO$_2$ can also adhere to the surface of dust particles to increase surface conductivity and decrease dust resistivity. The SO$_2$ concentration in the recovery boiler exhaust gas can range from very low concentrations (1-2ppm) for boilers burning liquor with high solids content which operate at hot bed temperatures, or higher concentrations (up to 300ppm) for boilers which burn black liquor with a lower solids content and operate at a lower bed temperature [39]. The SO$_2$ concentration was varied from 0-500 ppm at 150°C and the resulting effects on Sample 5 are shown in Figure 42 below. Effects of varying SO$_2$ concentration on other mill samples can be found in Appendix 8.

![Figure 42 - Effect of SO$_2$ Concentration on Resistivity of Sample 5](image-url)
At concentrations above 100ppm, no effect of SO$_2$ concentration on resistivity was observed, most likely because no more SO$_2$ could adsorb to the dust particle surface above this concentration. It can be seen, however, that varying the SO$_2$ concentration from 0 to 100ppm has a very pronounced effect on the electrical resistivity of the sample. These results show that an increase in SO$_2$ concentration causes a linear decrease in resistivity.

Because recovery boiler exhaust typically has a moisture content of about 25%, the effect of SO$_2$ concentration on resistivity was also investigated in a humid atmosphere for Sample 2. The results are shown in the figure below.

![Figure 43 - Effect of SO$_2$ on Resistivity in Dry and Moist Atmosphere for Sample 2](image)

It can be seen that at a moisture content of 25%, increasing SO$_2$ concentration has a less pronounced effect on resistivity than in a dry atmosphere. This may be attributed to the fact that there is a smaller effective surface area on the ash particles for the SO$_2$ to adsorb onto in the presence of adsorbed water molecules. Nevertheless, it can be seen that an increase in SO$_2$ concentration still leads to a linear decrease in resistivity.

This has a very important industrial implication, as an increase from 0 to 100 ppm in SO$_2$ concentration can lead to a decrease in resistivity of about half an order of magnitude under typical recovery boiler exhaust conditions, and decrease of an order of magnitude in dry air. This
is especially important to consider with high resistivity dusts, as an increase in SO$_2$ concentration could have a significant enough effect to drop a dust’s resistivity below the critical threshold. These observations once again imply that boilers operating at a high solids content would result in the formation of a dust with higher resistivity due to the decreased concentration of SO$_2$ in the resulting flue gas stream.
Chapter 5

5 Conclusions

The purpose of this study was to investigate the effect of various factors on resistivity of recovery boiler ash. From experimental analysis of 11 different mill samples and several synthetically prepared samples, several key conclusions can be drawn:

1. Breakdown strengths of all samples were similar, implying that dust particle characteristics do not play an important role in this parameter. Breakdown occurs in the interstitial spaces of air between dust particles, hence breakdown strength is not strongly dependent on the properties of the particles themselves.

2. Resistivities of most mill samples were between $10^4$ and $10^5$ kΩ·m, with one sample (Sample 4) having a resistivity of about $10^7$ kΩ·m. The mill from which this sample was taken reported opacity problems with their precipitator, which can most likely be attributed to the abnormally high resistivity of the ash. The ash from this mill also had the smallest particle size. These observations also suggest that mills are more likely to experience precipitator problems due to high resistivity dust rather than low resistivity dust.

3. At higher field strengths, resistivity of recovery boiler ash tends to decrease. This suggests that higher field strengths in electrostatic precipitators are not only beneficial because of increased charging rates and dust migration velocities, but also because of decreased dust resistivity.

4. Sodium chloride, a significant component of recovery boiler ash, tends to increase resistivity of the ash sample as its fraction in the dust sample is increased. Because of this, dusts with a higher chloride content could be higher to capture, and low chloride content in the recovery boiler ash is desirable.
5. Entrained charred black liquor particles slightly decrease the resistivity of the dust sample. This implies that slight entrainment of unburned black liquor particles could be beneficial for high resistivity dusts as its presence could make it easier to achieve desired removal efficiencies.

6. Short term exposure to the electric field plays little role in changing dust sample’s resistivity; however, long term exposure increases electrical resistivity. This implies that the longer a dust sample remains adhered to a collecting electrode, the more its resistivity will increase over time and the stronger the collected dust layer will adhere to the collecting electrode, making it more difficult to remove over time.

7. There is a peak resistivity for recovery boiler ash samples at a temperature of about 150°C. This implies that, depending on the dust, there is a range of favourable temperature (ie. either above or below the peak resistivity temperature) at which the precipitator should be operated in order to avoid problems with high resistivity ash.

8. Increased moisture content as well as increased SO₂ concentrations in the exhaust gas stream cause a decrease in resistivity as both components increase surface conduction for recovery boiler dusts. This implies that a recovery boiler which burns black liquor with a lower solids content would form ash which would be less likely to pose precipitator problems as it would have lower resistivity due to the increased moisture and SO₂ content.
Chapter 6

6 Recommendations for Future Work

This study investigated several key factors that influence resistivity of recovery boiler ash through experimental analysis of recovery boiler ash samples from different mills; however, with increasingly stringent environmental regulations for particulate emissions, research is necessary to keep improving electrostatic precipitator performance. One factor which should be investigated in more detail is the effect of particle size and size distribution. A wider range of particle sizes should be investigated, as well as a wider variety of particle size distributions. This study concluded that packing density plays a large role in dust resistivity, implying that a larger particle size distribution could also play a role. To further look into the extent to which these factors investigated play a role in efficiency of electrostatic precipitators, it is recommended that further experiments be performed with a lab-scale electrostatic precipitator and monitor its efficiency with various dust samples. In addition, more detailed dust composition analyses beyond XRD would be useful in identifying other minor recovery boiler ash components and determining their effect on resistivity.
References


Appendices

Appendix 1    EPA Boiler MACT Standards

Table A1 – EPA Boiler MACT Standards

<table>
<thead>
<tr>
<th>Subcategory</th>
<th>Particulate matter (PM)</th>
<th>Hydrogen chloride (HCl)</th>
<th>Mercury (Hg)</th>
<th>Carbon monoxide (CO) (ppm @3% oxygen)</th>
<th>Dioxin/furan (TEQ) (ng/dcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing—Coal Stoker</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>270</td>
<td>0.003</td>
</tr>
<tr>
<td>Existing—Coal Fluidized Bed</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>82</td>
<td>0.002</td>
</tr>
<tr>
<td>Existing—Pulverized Coal</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>160</td>
<td>0.004</td>
</tr>
<tr>
<td>Existing—Biomass Stoker/other</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>490</td>
<td>0.005</td>
</tr>
<tr>
<td>Existing—Biomass Fluidized Bed</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>430</td>
<td>0.02</td>
</tr>
<tr>
<td>Existing—Biomass Dutch Oven/Suspension Burner ...</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>470</td>
<td>0.2</td>
</tr>
<tr>
<td>Existing—Biomass Fuel Cells</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>690</td>
<td>4</td>
</tr>
<tr>
<td>Existing—Biomass Suspension/Grate</td>
<td>0.039</td>
<td>0.035</td>
<td>0.00000046</td>
<td>3,500</td>
<td>0.2</td>
</tr>
<tr>
<td>Existing—Liquid</td>
<td>0.0075</td>
<td>0.000033</td>
<td>0.00000035</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Existing—Gas 2 (Other Process Gases)</td>
<td>0.043</td>
<td>0.0017</td>
<td>0.000013</td>
<td>9.0</td>
<td>0.08</td>
</tr>
<tr>
<td>Existing—non-continental liquid</td>
<td>0.0075</td>
<td>0.000033</td>
<td>0.00000078</td>
<td>160</td>
<td>4</td>
</tr>
<tr>
<td>New—Coal Stoker</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>6</td>
<td>0.003</td>
</tr>
<tr>
<td>New—Coal Fluidized Bed</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>18</td>
<td>0.002</td>
</tr>
<tr>
<td>New—Pulverized Coal</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>12</td>
<td>0.003</td>
</tr>
<tr>
<td>New—Biomass Stoker</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>160</td>
<td>0.005</td>
</tr>
<tr>
<td>New—Biomass Fluidized Bed</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>260</td>
<td>0.02</td>
</tr>
<tr>
<td>New—Biomass Dutch Oven/Suspension Burner</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>470</td>
<td>0.2</td>
</tr>
<tr>
<td>New—Biomass Fuel Cells</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>470</td>
<td>0.003</td>
</tr>
<tr>
<td>New—Biomass Suspension/Grate</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.00000035</td>
<td>1,500</td>
<td>0.2</td>
</tr>
<tr>
<td>New—Liquid</td>
<td>0.0013</td>
<td>0.000033</td>
<td>0.00000021</td>
<td>3</td>
<td>0.002</td>
</tr>
<tr>
<td>New—Gas 2 (Other Process Gases)</td>
<td>0.0067</td>
<td>0.0017</td>
<td>0.00000079</td>
<td>3</td>
<td>0.08</td>
</tr>
<tr>
<td>New—non-continental liquid</td>
<td>0.0013</td>
<td>0.000033</td>
<td>0.00000078</td>
<td>51</td>
<td>0.002</td>
</tr>
</tbody>
</table>

EMISSION LIMITS FOR BOILERS AND PROCESS HEATERS

[Pounds per million British thermal units]
Appendix 2  Resistivities of Common Materials

Figure A1 – Resistivities of Common Materials

Resistivity $\rho$ (k$\Omega\cdot$m)
Appendix 3  Effect of Field Strength on Resistivity

Figure A2 – Effect of Field Strength on Resistivity of Sample 1a

Figure A3 – Effect of Field Strength on Resistivity of Sample 1b
Figure A4 – Effect of Field Strength on Resistivity of Sample 1c

Figure A5 – Effect of Field Strength on Resistivity of Sample 2
Figure A6 – Effect of Field Strength on Resistivity of Sample 3

Figure A7 – Effect of Field Strength on Resistivity of Sample 5
Figure A8 – Effect of Field Strength on Resistivity of Sample 6a

Figure A9 – Effect of Field Strength on Resistivity of Sample 6b
Figure A10 – Effect of Field Strength on Resistivity of Sample 7a
Appendix 4  Effect of Melting on Resistivity

Figure A11 – Effect of Melting on Resistivity of Sample 1a

Figure A12 – Effect of Melting on Resistivity of Sample 6a
Appendix 5  Effect of Time of Exposure on Resistivity

Figure A13 – Effect of Time of Exposure on Resistivity of Sample 1a

Figure A14 – Effect of Time of Exposure on Resistivity of Sample 2
Figure A15 – Effect of Time of Exposure on Resistivity of Sample 3

Figure A16 – Effect of Time of Exposure on Resistivity of Sample 4
Figure A17 – Effect of Time of Exposure on Resistivity of Sample 5

Figure A18 – Effect of Time of Exposure on Resistivity of Sample 6a
Figure A19 – Effect of Time of Exposure on Resistivity of Sample 6b

Figure A20 – Effect of Time of Exposure on Resistivity of Sample 7a
Appendix 6  Effect of Temperature on Resistivity

Figure A21 – Effect of Temperature on Resistivity of Sample 1b

Figure A22 – Effect of Temperature on Resistivity of Sample 2
Figure A23 – Effect of Temperature on Resistivity of Sample 3

Figure A24 – Effect of Temperature on Resistivity of Sample 5
Figure A25 – Effect of Temperature on Resistivity of Sample 6a

Figure A26 – Effect of Temperature on Resistivity of Sample 6b
Figure A27 – Effect of Temperature on Resistivity of Sample 7a

Figure A28 – Effect of Temperature on Resistivity of Sample 7b
Appendix 7  Effect of Moisture Content on Resistivity

Figure A29 – Effect of Moisture Content on Resistivity of Sample 1a

Figure A30 – Effect of Moisture Content on Resistivity of Sample 1b
Figure A31 – Effect of Moisture Content on Resistivity of Sample 1c

Figure A32 – Effect of Moisture Content on Resistivity of Sample 7a
Appendix 8  Effect of SO$_2$ Concentration on Resistivity

Figure A33 – Effect of SO$_2$ Concentration on Resistivity of Sample 2

Figure A34 – Effect of SO$_2$ Concentration on Resistivity of Sample 4
Figure A35 – Effect of SO$_2$ Concentration on Resistivity of Sample 6a