CLAY CERAMIC MATERIALS FOR WATER FILTRATION: PROPERTIES, PROCESSING AND PERFORMANCE

By

Ebenezer Annan
(70050)

Submitted to

Department of Materials Science and Engineering in partial fulfilment of the award of

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at the

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March, 2016

Principal Advisor: Professor Winston O. Soboyejo
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PhD Committee Members:

Recommended by:

Professor Wole Soboyejo (Principal Advisor)

____________________________________
Dr. Olushola S. Odusanya, (Co-supervisor)

____________________________________
Prof. Daniele S. Lantagne, Tufts-University, U.S.A. (Member)

____________________________________
Dr. Karen Malatesta, Princeton University, U.S.A (Member)

Accepted and Approved by:

Professor Charles Chidume, Vice President, Research and Academics – African University
of Science and Technology, Abuja-Nigeria

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DEDICATION

This document is dedicated to my wife: Adwoa Osaebea Annan for her emotional support
and sacrifice during the research and write-up.

Indeed I am indebted to her and our children: Kelvin and Keziah.
ABSTRACT

Ceramic water filters are promising household water treatment technology, as they are capable of removing waterborne pathogens and thereby reducing diarrheal disease. Flow rates are the main quality control criterion for manufacturing, and multiple theoretical flow rate models have been published. This dissertation presents the results of combined experimental and theoretical studies of flow rate variation in ceramic water filters in frustum- and disk-shaped ceramic water filters. Also investigated is how clay mixtures/plasticity affects the strength of the ceramic water filters. Furthermore, residual strengths of filter specimens that had undergone cold-shocking at temperatures 750, 850 and 950 are presented and trends explained via bridging models.

Firstly, in this dissertation six frustum-shaped ceramic water filters of the same clay:sawdust composition were tested. Each ceramic water filter was filled with water and allowed to filter 20 times. Each time, the flow rate and water level are measured for consecutive 12 hours. Permeability values are estimated for each run of the ceramic water filters. Statistical analysis was performed on flow rates (in the first hour), mean flow rates and estimated permeability values. The flow rate values (in the first hour) for the six ceramic water filters were found to be between 1.4 – 3.0 L/hr. An effective permeability was obtained for ceramic water filters with a range of micro- and nano-scale pore sizes. The statistical variations in the flow rates and effective permeabilities were elucidated along with the potency of a multiple ceramic water filter system for scale-up studies in serving communities that need portable water.

Secondly, a systematic literature review of the selected theoretical flow models was done. Three sets of full-size filters and disks were manufactured in triplicate by Potters without Borders (Enderby,
Canada) according to Best Practice recommendations. Manufacturing specifications were selected to achieve desired flow rates of 1 to 3 Liters per hour. Flow rate was controlled by altering: 1) firing temperature (880ºC or 950ºC); and, 2) burn-out material sieve size (top/bottom) (16/30 mesh or 30/60 mesh. The experimental flow data was then compared with three main models in literature describing flow through frustum-shaped ceramic water filters. Yakub et al., model was found to best describe the flow than Schweitzer et al., and Van Halem. Also, equation has been modeled to predict the frustum-shaped size ceramic water filter using the flow rate of the disk ceramic water filter as surrogates.

Thirdly, this dissertation presents the results of an experimental study of the effects of clay mixtures on the plasticity and strengths of fired clays that are used in the processing of porous ceramic water filters for water filtration. Two clays with well characterized initial compositions (Iro and Ewuya clays) are mixed with varying proportions to control their plasticity. The clay mixtures are then fired at temperatures of 750ºC, 850ºC and 950ºC and their mechanical properties of mixtures determined. The results show clay mixtures with 45% - 60% of the Iro clay content and 40% - 55% Ewuya clay content can be used in the production of ceramic water filters with robust mechanical properties. The mechanical properties of the clay mixtures sintered at 850ºC were found to be generally better than those of clay mixtures sintered at 750ºC and 950ºC. Also presented are thermal shock study results on 50% Iro clay - 50% Ewuya clay mixture via the residual strengths measurements. The thermal shock results show that for 50% (Iro clay) - 50% (Ewuya clay) mixture renders good combination for appreciable residual strength and fracture toughness values. The implications of the results are discussed for the mixing of locally available clays for applications in producing ceramic water filters.
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LIST OF PUBLICATIONS


4. Kyle Monahan, Ebenezer Annan, Justine Rayners, Wole Soboyejo and Daniele Lantagne, “Comparative study of modeled and experimental flow in disk and full-size ceramic water filters for water treatment in developing countries” UNC-Water and Health Conference, accepted


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CHAPTER ONE

1.0 BACKGROUND AND INTRODUCTION

1.1 INTRODUCTION

It is estimated that 1.8 million deaths per year and 61.9 million disability adjusted life-years are attributed to the drinking of unsafe water and poor sanitation [1]. The World Health Organization (WHO) also suggests that over 99.8% of the deaths are caused by unsafe water, sanitation and hygiene in developing countries [1]. Furthermore, in developing countries most of the childhood mortality occurs in children that are less than five years old [2]. Many of those who have access to such improved drinking water sources have contamination issues and usually require further treatment at the point of use. This information is confirmed in recent global joint monitoring 2014 report of WHO/UNICEF on progress made on sanitation and drinking water [3].

The global Millennium Development Goals (MDG) target for number of people to improved water sources has been achieved [3]. The target for sanitation, however, was not attained [3] and this may be a predominant force in contaminating the improved water sources. Governments, non-governmental organizations, and researchers have been instrumental in achieving the MDG for improved water sources. It is undisputable fact that inculcating household water treatment systems (HWTS); such as ceramic water filters (CWF) which has high performance [3-11] were paramount.
The important criteria often used in selecting high performance HWTS include: ability to remove pathogens, removal chemical contaminants (such as fluoride and arsenic), flow rate, etc. Other factors to be considered are maintenance cost; purchasing cost; user-friendliness with little or no training; reasonable amount of water to be discharged within reasonable amount of time (flow rate); socially accepted and culturally accepted in the user environment [4]. The main HWTS known as adopted from [5, 6] cover microbiological, chemical and physical aspects of water treatment are:

(i) disinfection (safe water system, chlorination, solar disinfection (SODIS), solar pasteurization, UV irradiation with lamps, and boiling),

(ii) particle filtration (cloth fiber filter; ceramic water filters, bio-sand and other slow sand filter technologies),

(iii) adsorption media (granular activated carbon, and activated alumina, clay),

(iv) (combined system (combined flocculation/disinfection, filtration plus disinfection),

(v) Other approaches (plain sedimentation settling, safe storage, coagulation/flocculation with iron or alum salts, membrane processes).

Boiling method is seen to very effective method in bacterial de-activation. However, according to [7], SODIS and other heating methods are seen to be less efficient of median
record of 35%. This may be due to the lack of appropriate equipment to know the exact temperature at which disinfection can occur.

1.2 **WATER, SANITATION AND HEALTH**

The relationship between water, sanitation and health are undisputable. It is therefore not surprising that joint monitoring programme (JMP) between WHO and UNICEF consistently evaluate issues in these areas and how they relate. In WHO/UNICEF 2014 JMP edition report on ‘progress made on drinking water and sanitation’, MGD target for improved water sources has been surpassed. However, according to same report, the world is unlikely to achieve its MGD sanitation target of 75%; this target aims to reduce the proportion of the global population without access to improved sanitation from 51% in 1990 to 25% in 2015. The concern has been raised about the possibility of even the improved water sources to be contaminated. Improved water sources achieved are frequently contaminated with faecal indicator bacteria [3]. And this will result in increasing infection rate of water-bourne diseases.

Other key findings of the report [3] are enumerated below:

I. By the end of 2012, 89% of the global population used improved drinking water sources, a rise of 13 percentage points in 22 years or 2.3 billion people.

II. By the end of 2012, 64% of the global population used improved sanitation facilities, a rise of 15 percentage points since 1990. Some 2.5 billion people – two-thirds of whom live in Asia, and a quarter in sub-Saharan Africa – still use unimproved sanitation facilities. There are 46 countries where at least half the population is not using an improved sanitation facility.
III. Although declining across all regions, open defecation is practised by 1 billion people, 82% of whom live in 10 countries. Nine out of 10 people defecating in the open live in rural areas.

IV. Wealthy people universally have higher access to sanitation than the poor. In some countries this gap is narrowing. The gap is increasing, however, in rural areas of countries with low coverage and for marginalized and excluded groups.

V. 748 million people – 90% living in sub-Saharan Africa and Asia (43% in Sub-Saharan Africa, and 47% in Asia) – still use unimproved drinking water sources; 82% live in rural areas.

These key findings require team effort from governments, researchers, Non-governmental organizations (NGO’s), etc to improve populations’ access to improved water resources and reduce bacterial contamination of these sources by achieving MDG sanitation target.

1.3 Availability of Water

Over 70% of earth surface is known to be covered with water. The important issue is the percentage of fresh water available for safe drinking. Underground waters are often contaminated and required specialized filters to make them safe for drinking. In the case of fresh water, figure 1.0 below gives a clear picture of the era the world is facing. Surface water continues to dry up mainly due to the adverse climatic conditions. The available ones are also often contaminated with either chemicals or microbial agents that are detrimental to the health of an individual and therefore not safe to drink.
1.4 **WATER TREATMENT METHODS**

Countries have central multi-barrier treatment technologies for water purification before they are pumped to various communities within a certain radius. Many communities depend on the central Government for maintenance of the pipelines to various destinations. However, Governments (especially in developing countries usually) have issues maintaining the pipelines. The main targets of Governments are roads and other infrastructural development. Another issue has to do with technical personnel at the water works stations in the zeal of disinfecting effectively for people far from the treatment centre, often apply more chemicals than required, and therefore those close to the pump source may end up having more chemicals in their water, whereas those far may have less. Also to be mentioned is the corrosive nature of most of the metallic pipelines that are often used; resulting in possible leaching of chemical contaminants into the water. Cracks on the pipelines have also had some infiltration from faecal pollutant sources, industrial water wastes and chemicals from soils. So water from any source; municipal, river, borehole etc, may have some dissolved minerals, microbiological contaminants, and suspended particles. The amount present in the final analysis and whether it is suitable for its intended purpose is essential. Microbial activity such as bacteria, viruses, chemical contaminants such as fluoride, arsenic, iron, magnesium, nitrates, sulphates, PH of water, etc, are number of issues found in drinking waters that provide health risks. Table 1.0 gives main HWTS used at the point of use.
1.5 **POTENTIAL ROLE OF CERAMIC WATER FILTER AND UNRESOLVED ISSUES**

Clay is known to be ancient material, mostly ubiquitous and used for various purposes especially in the developing countries. It is also found in most communities. Those who reside in the rural areas in developing countries are able to identify, tell different locations where these can be mined, and the historical importance of clays in their communities. One important criteria for selecting a HWTS for a community is it social acceptance. Ceramic water filters that are mainly made from clays are already used by most communities in the developing countries.

Ceramic water filter is basically mixture of clays, sawdust, and water moulded, and fired. Sawdust material burns out at temperatures around (400-500) °C, creating pores. The performance of ceramic water filters are judged in dimensions mentioned in figure 1.3.

The effectiveness of the ceramic water filter in production of safe drinking water has been proven by many research articles [4-14]. This proven performance coupled with social and cultural acceptability may heighten its marketability thereby reducing the 748 million people who are still not having access to safe drinking water.

1.6 **RESEARCH OBJECTIVES**

The following are the main research objectives of this research:

I. Much work has been done on flow rate of ceramic water filters and its characteristics however; no work has been reported on the statistical variation in the flow rate for 20 loadings/runs for full size ceramic water filters. This work therefore seeks to
understand the variation in flow for a single filter system and ascertain its efficacy over duration of usage.

II. After characterizing various key components of the ceramic water filter elements, the study seek to ascertain multiple ceramic water filter system that could be used in assessing their potency in serving larger communities.

III. Full size ceramic water filters are compared with disk ceramic water filters in terms of flow and permeability. These include to evaluate effect of particle size on flow of ceramic water filters, explore the effect of firing temperature on the flow rate of ceramic water filters and compare flow rate of disk to frustum-shaped ceramic water filters of same recipe.

IV. Most ceramic water filters are produced from one type of clay. Mateng Ltd, Nigeria uses two types of clays from Nigeria. We seek to understand the physico-mechanical properties of mixture of clays, relation, if any, between strength and plasticity of clay batches. Strength measurements include bending (flexural) strength, modulus, and fracture toughness.

1.7 Scope and Organization of Thesis

Chapter one is on background and introduction of safe drinking water, highlighting scarcity of portable drinking water, importance of household water treatment technologies and the necessity to employ ceramic water filters in the quest of reducing the millions of people not having access to safe drinking water. Brief citations have been made on the efficacy of the
ceramic water filter in anti-microbial activity and influent water turbidity that may clog micro-pores of the filter.

Prior work on ceramic water filters from flow characteristics to anti-microbial activity, removal of chemical contaminants, synthesis of copper and silver nano-particles, and mechanical properties are briefly reviewed in chapter two. Definitions and fundamentals of most concepts as applied to this research work are also briefly presented.

In chapter 3 the research demonstrates flow rate through ceramic water filters proven to be well characterized by Darcy’s equation. Proven analytical equations are reviewed and compared with experimental data. Statistical studies of flow in ceramic water filters in relation to its multiple loadings are investigated and results presented. Also presented is the potential scale-up of the ceramic water filters by considering scale-up ceramic water filter system for a community.

Chapter 4 of this research work looks at the comparing the flow through disk size to full size ceramic water filters. Analytical modelled equation was developed for the prediction of full size filter flow using disk filter as a surrogate. Also, multiple flow through the disk ceramic water filters are also considered and the statistical type of distribution of the flow rate variation is analysed and discussed.

In chapter 5 considers the effects of clay mixtures on toughening and mechanical properties of porous clay ceramics for water filtration. The mechanical properties include modulus, fracture toughness, flexural strength and compressive strength, and these were determined at
three different firing temperatures for the aforementioned plasticity or clay mixtures. Furthermore, presented are thermal shock study results on 50% Iro clay - 50% Ewuya clay mixture via the residual strengths measurements. The thermal shock results show that for 50% (Iro clay) - 50% (Ewuya clay) mixture renders good combination for appreciable residual strength and fracture toughness values. Toughening models are used in explaining the trends observed in the thermal shock results obtained.

Conclusions and Recommendations for future work is given in chapter 6 of this study.
REFERENCES


**FIGURES AND TABLES**

Table 1.0: General properties of household water treatment system

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Availability &amp; Practicality</th>
<th>Technical Difficulty</th>
<th>Cost a</th>
<th>Microbial Efficacy b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling at 100 °C</td>
<td>Varies c</td>
<td>Low-moderate</td>
<td>Varies c</td>
<td>High</td>
</tr>
<tr>
<td>Chemical treatment</td>
<td>High to moderate</td>
<td>Low-moderate</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>Solar disinfection</td>
<td>high</td>
<td>Low-moderate</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>UV lamp treatment</td>
<td>Varies d</td>
<td>Low-moderate</td>
<td>Moderate-High d</td>
<td>High</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Varies e</td>
<td>Low-moderate</td>
<td>Varies e</td>
<td>Varies f</td>
</tr>
<tr>
<td>Sedimentation/filtration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Source:** Sobsey, 2002 [5]

a Categories for annual household cost estimates in US dollars are less than US$10 for low, >US$10-100 for moderate and >US$100 for high.  
b Categories for microbial efficacy are based on estimated order-of-magnitude or \( \log_{10} \) reductions of waterborne microbes by the treatment technology. The categories are \(<1 \log_{10} (\text{<90%})\) is low, 1to 2 \( \log_{10} (90-99\%)\) is moderate and >2 \( \log_{10} (>99\%)\) is high.  
c Depends on heating method at a certain location as well as availability and cost of fuels, which range from high to low.  
d Depends on availability and types of lamps at a certain location, housings, availability and cost of electricity, as well as operation and maintenance needs (pumps and system cleaning methods).  
e Different types of coagulation, flocculation and filtration are available. For filtration process, practicability, availability, and cost depend on the filter medium and its availability: granular, ceramic, fabric, etc. For FC processes, practicability, availability, and cost depend on the FC prices and availability (alum vs. natural plant extracts).  
f For filtration: depends on pore size and...
other properties of the filter medium, which may vary widely. For FC: depends on types of FC effectiveness (alum vs. natural materials).

Table 1.1: Scarcity of portable water in 2002

<table>
<thead>
<tr>
<th>Region</th>
<th>Populations in millions without access to potable water as of 2002 [WHO/UNICEF 04]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latin America &amp; Caribbean</td>
<td>60</td>
</tr>
<tr>
<td>Sub-Saharan Africa</td>
<td>288</td>
</tr>
<tr>
<td>Northern Africa</td>
<td>15</td>
</tr>
<tr>
<td>Developed Regions</td>
<td>15</td>
</tr>
<tr>
<td>Eurasia</td>
<td>20</td>
</tr>
<tr>
<td>Oceania</td>
<td>3</td>
</tr>
<tr>
<td>Western Asia</td>
<td>23</td>
</tr>
<tr>
<td>South-Eastern Asia</td>
<td>115</td>
</tr>
<tr>
<td>South Asia</td>
<td>234</td>
</tr>
<tr>
<td>Eastern Asia</td>
<td>303</td>
</tr>
</tbody>
</table>

Figure 1.0: (a) Trends in global drinking water coverage (%) from 1990-2012; (b) Trends in global sanitation coverage (%) from 1990-2012.

Figure 1.1 - Faecal contamination of drinking water (CFU] of E.Coli/100ml), by source type and MDG region
Figure 1.2: Disappearing Lake Chad: A high profile case of diminishing surface water sources, 1972 (Left) and 2007 (Right). Source: UNEP, 2008

Figure 1.3: Main parameters influencing performance of ceramic water filter [8, 9]
CHAPTER TWO

2.0 LITERATURE REVIEW AND FUNDAMENTALS

2.1 CERAMIC WATER FILTERS

Ceramic water filters (CWF’s) have become very instrumental in water purification especially in countries where access to safe drinking water is limited. There is also growing need and interest within in urban-rural communities of such category of countries. The world health organization (WHO), UNESCO and other NGO’s have committed themselves to making sure as many that live in these areas gain access to safe drinking water. POTTERsforPEACE, a NON-governmental organization has been instrumental in this initiative and continues to help many in establishing factories that produce ceramic water filters (WHO/UNICEF 2000; WHO/UNICEF 2004).

The performance of CWF’s has been investigated and reported by many groups of researchers. The authors have proven that ceramic water filters is among the top five best treatment options for reducing turbidity and bacteria by more than 99% (Sobsey 2002; Sobsey et al., 2007). It is known that CWF’S together with bio-sand filters, are the most sustainable technologies in the field of purification of drinking water in developing countries (Sobsey et al., 2008). In this section, factors and parameters that affect the flow of water through ceramic water filters are briefly explained. Also, the flow mechanisms of the filter element by which the effluent water is purified are described.
2.1.1 Flow Characteristics

The materials that are used for producing CWF’s are in abundance and more importantly eco-friendly. These are clay, bio-diversity (examples sawdust, rice husks, starch); pore generators. Recent improvements have seen noble materials such as silver used as lining in the CWF’s for further purification envisaged (Sobsey et al., 2008). The traditional manufacturing process starts with a combination of clay and fine wood chips (sawdust) taken in the ratio 1:1. This mixture is then moistened with water and pressed into moulds (green-wares) in a hydraulic press. It is then pressed into the required shape. They are kept at room temperature to help green-wares lose water by drying them at room temperature. Once dried these green-wares are fired in a kiln to about 850°C (temperature dependent on clay composition). The sawdust is burnt off during the high temperature of firing, leaving behind the red coloured clay ceramic filter with micro/nano pores in them. If the proportion of sawdust is changed in the mixture, the flow rate will also be affected because of the changes in geometry of the pores formed (Dies 2003; Davies et al., 2010).

The increase in the number of people having access to safe drinking water is undoubtedly, partly due to increase number of people using ceramic water filters. Factors such as ease of use, accessibility locally, low cost, and sustainability of available component have the primary aim of targeting people in the rural/urban areas access to safe drinking water. The base material, clay which is ubiquitous is known and accepted by many. Three main geometrical shapes are often reported and adopted in literature: disk, candle and pot/frustum geometrical shapes (Dies 2003). Figure 1 shows the well-known schemes shapes of ceramic water filters.
2.1.1.1 Porosity and Flow
Total porosity of a solid is defined as the volume of voids divided by total volume of the solid. Since porosity is a measure of the volume of empty space in a solid, filters showing a greater porosity will allow more water to pass through the ceramic body. However, increasing the pore size may compromise the mechanical screening phenomenon during filtration. And therefore important to restrict the sawdust particle size to at least 1mm. The pore diameter from literature for most ceramic water filters has been found to be within the range 0.2-2.5 microns. Filters manufactured using a larger screen size to sieve the sawdust has been shown to reveal no significant difference in flow rates (Klarman 2009). At certain factories, however, filter mix ratios are adjusted to achieve acceptable flow rate ranges according to the particle size of the rice husks received, adding more rice husk to the mixture if it is observed to be smaller (Hagan et al., 2009). This step may indicate probable relationship between burn-out particle size and flow rate. In addition, the use of different burn-out materials, even when sifted to the same screen size, can increase the flow rate but
may also reduce total coliform removal efficiency. This emphasizes the need to develop a new ratio when changing the burn-out material (Klarman 2009).

The two main methods used in the determination of the porosity is by the mercury intrusion porosimetry (MIP) (Yakub 2012) and direct method (van Halem, 2006).

Table 1: Porosity (%) of ceramic water filters from different geographical locations via direct method and Mercury intrusion porosimetry (Van Halem, 2006)

<table>
<thead>
<tr>
<th>Country of origin</th>
<th>Direct method</th>
<th>Mercury intrusion porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porosity [%]</td>
<td>Density [g/mL]</td>
</tr>
<tr>
<td>Cambodia</td>
<td>36</td>
<td>1.26</td>
</tr>
<tr>
<td>Ghana</td>
<td>38</td>
<td>1.22</td>
</tr>
<tr>
<td>Nicaragua</td>
<td>30</td>
<td>1.34</td>
</tr>
<tr>
<td>Nicaragua (no silver)</td>
<td>35</td>
<td>1.30</td>
</tr>
</tbody>
</table>

2.1.1.2 Permeability and Tortuosity

Permeability of a porous ceramics gives a measure of the relative ease at which water molecules goes through it. The tortuosity, however, gives an indication of the chances of capture of contaminants, such as E.coli bacteria, that are carried along with the water by processes such as adsorption, geometrical occlusion and sedimentation. The permeability has a strong direct relation with the total porosity, as to whether the pores are inter-connected, closed or isolated ones. The tortuosity, however, has to do with the path through which the water molecules travel. The material tortuosity ranged from ~10 to ~60. A tortuosity value of, say 10, means for a particle traveling through water molecules to get through the CWF it must travel an effective length 10 times the actual length (or thickness) of the CWF.
Permeability value can be determined by the fitting of flow rate data to the Darcy equation at high R-square value.

2.1.1.3 Flow and Turbidity
Turbidity describes the level of suspended particles in water. The more turbid a water is, the lower the flow rate, thus slowing permeability. This is due to the clogging of the pores by particles during filtration. It is therefore advisable to use clean white cotton cloth (or recommended pre-filtration cloth) before the usage of ceramic water filters. Water turbidity will also affect the ceramic water filter sustainability. Heavy turbid water used will require more regular cleaning of the filter. In a whole the volume of filtered water discharged will be less as compared to less turbid water. Although scrubbing temporarily increased flow rates, ceramic water filters did not achieve their original flow rate and even with scrubbing, flow rates continually diminished (van Halem 2006). Fahlin (2003) found that clogging impeded his research into the hydraulic conductivity of filters. However, some field investigations users have reported that filters provided enough water for additional uses and only 5% of filter disuse was attributed to unsatisfactory flow rates (Brown and Sobsey 2006).

It is usually expedient to measure the flow rate of a ceramic water filter after soaking in water to attain saturation; thus the CWF acclimatize to its daily use and also air within pores are cleared, ensuring flow continuity. Another reason is to make sure suspended aqueous particles will also be flush out. The soaking in water step gives the ideal flow rate. At the factories, filters with flow rates outside 1-3L/hr are discarded and not made available for market in accordance with WHO guidelines (van Halem, 2006). Current manufacturing practice suggests that average minimum flow rate ranged from 1.0 – 3.0 L/hr in the first hour
while the average maximum flow rate ranged from 2.0 – 5.0 L/hr in the first hour (Rayners, 2009; CMG, 2009).

There are a number of factors that affect the flow rate of a ceramic filter. The primary factor is the pore generators; biodiversity used. As the ratio and thus density of the combustible material is increased, there is increased probability that pores may become connected, and larger than desired (Klarman, 2009; Lantagne 2010). The size of the combustible material is equally relevant as type used; clay type will also affect the filter’s hydraulic conductivity and removal (Oyandel-Craver 2008). Others include cracks, nature of water being filtered, and volume of water in filter. The flow rate of filter using turbid water decreases with time. van Halem 2006, demonstrated that the main particles clogging pores biomass and particles. They arrived at this by conducting trials on Nicaraguan filters using chlorine, citric acid, and high pressure backwashing. Interestingly, a number of households associate slow flow rates to high purified water and did not want flow rates increased (Bloem 2008).

In practice filters will not continuously be filled with water; thus the water head will not be constant. And as water goes through the filter element the water head is lowered. van Halem, 2006, has demonstrated the relation between the volume of water and flow rate (Figure 2).
2.1.2 Filtration Mechanisms

It has been established how the ratio, type and particle size of the combustible materials affect pore structure of ceramic water filter. And thus most filters performance are rated to a large extent in relation to the dimensions of these pores. Ceramic water filters are no exception, they predominant mechanism is mechanical screening: where interconnected pores that contribute to flow rates are of dimensions smaller than the particles of the contaminants. Disadvantage of this mechanism has to do with the possible clogging of pores, thereby reducing flow rate. Figure 3 shows types of pore structures (van Halem, 2005, originally from Xiaolon, 2005).

![Figure 3: Types of pores (Xialong, 2005)](image)
Another CWF filtration mechanism is Sedimentation. It is sometimes referred to as precipitation. In this case particulates due to larger densities than water slowly moves through the water-head and rest on the surface of the filter element. These particles are usually removed by a cleaning the filter.

Other impurities in water may also be removed by adsorption. Adsorption is due to the attractive forces or van der forces between two particles and as a result the impurities are stacked on the surface of the filter element. It usually works in combination with a chemical activity, were there is exchange of ions. Note that the effluent water is of a higher PH value than influent. This is because of the cations (Na+, Ca+, Al+) that may dissolve in the water during the filtration process via ceramic water filters. Further details are given in section 2.5.

2.1.3 Microbial Removal

Aside chemical contaminants are pathogens such as bacteria (example E. Coli, vibrio cholerae, Campylobacter jejuni, C. coli, etc ), viruses (examples Adenovirus, Norwalk, Rotavirus etc), protozoa (E.g Entamoeba histolica, Giardia intestinalis, Cryptosporidium parvum, etc), and parasites or helminths (examples Trematodes, Cestodes, Nematodes species) (Clasen et al., 2006), are major causes of spread of diseases (WHO 2004).

Earlier publications on removal of microbes are tabulated in Table 2. The effectiveness of the ceramic water filter in microbe removal is mainly due to two mechanisms; mechanical screening and colloidal silver impregnation. The removal efficiency is done using indicator organisms. And this is often in literature done by using Escherichia coli (Lantagne 2001; Fahlin 2003; Campbell 2005; van Halem 2006; Yakub 2012). Logarithm (10) Return Values
(LRV) ranging from 2-5 has been recorded for various researchers, with some mimicking the waters in the field. Some also could not find the corresponding log return value since the *E. coli* count in most filtered were zero (Lantagne 2001, Campbell 2005). Using *Cryptosporidium parvum* oocysts and *Giardia Lamblia* cysts, Lantagna, 2001 found LRV of 4.3 and 5, respectively. Similar results were obtained for the removal of sulphite reducing *Clostridium* oocysts for a ceramic water filter produced in Nicaragua (van Halem 2006). This continued research using *MS2* bacteriphages as virus indicators found unsatisfactory logarithm return values (< 1) and therefore not suitable for sustainable treatment system. However, it was observed to decrease diarrhoeal cases in 80 Cambodian households (UNICEF/WSP, 2007). Other testing done on low cost ceramic water filter (CWF) effectiveness in bacterial and viral removal for period 2000-2010 are given in Table 2.
<table>
<thead>
<tr>
<th>References</th>
<th>Bacterial type</th>
<th>Reduction</th>
<th>%</th>
<th>LRV(log10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sagara(2000)</td>
<td>Escherichia coli</td>
<td></td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>Lantagne(2001)</td>
<td>Cryptosporidium parvum</td>
<td></td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>Dies 2003</td>
<td>Escherichia coli</td>
<td>&gt;98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coulbert(2005)</td>
<td>Escherichia coli</td>
<td></td>
<td></td>
<td>99.8</td>
</tr>
<tr>
<td>Franz(2005)</td>
<td>Escherichia coli</td>
<td></td>
<td></td>
<td>92-100</td>
</tr>
<tr>
<td>McAllister(2005)</td>
<td>Bacteria, Viruses</td>
<td>99</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Clasen et al(2006)</td>
<td>Escherichia coli, Clostridium spores</td>
<td></td>
<td></td>
<td>3.6.8</td>
</tr>
<tr>
<td>Halem (2006)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oyanedel-Craver &amp; Smith (2008)</td>
<td>Escherichia coli, Viruses</td>
<td>&gt;97.8</td>
<td>&lt;90</td>
<td>3.3-4.9</td>
</tr>
<tr>
<td>Brazil ABNT NBR 14908</td>
<td>Escherichia coli, Viruses</td>
<td></td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2 - Some literature on bacterial and viral testing adopted from Simons et al. (2011)
2.1.4 Virus Removal

Virus removal remains a challenge with ceramic water filters due to the small sizes of viruses. Silver which is used against bacterial has not been effective against virus deactivation. It has also been found that the LRV of MS2 bacteriophages is slightly reduced in filters with colloidal silver and therefore it has been suggested that colloidal silver application does not have a positive effect on virus removal. However, ceramic water filters have not been found to be effective at removing MS2 bacteriophages in filters with or without colloidal silver (van Halem 2006).

RDI-C adds laterite, an iron-oxide rich compound, to their filter mix as it is thought to provide additional viral binding sites (Hagan et al. 2009). However, although a 1-2 logarithm 10 reduction (90-99%) in MS2 was documented, no significant difference was found between filters with or without laterite (Brown 2007). Likewise, Bloem et al., 2009 produced ceramic water filters with increased laterite did not show improved removal efficiencies but increased flow rate. The mean LRV was less than 0.5 for all of the filters tested, with or without laterite. Ceramic water filters with laterite were also heavier and more porous (Bloem et al., 2009).

2.2 Fundamentals of Clays

Clays are ubiquitous materials. However, each clay belongs to type that has unique characteristics in terms of atomic arrangement or structure, chemical compositions and application.
2.2.1 Structure of Clays Minerals

Clay minerals are phyllosilicates that belong to three principle groups. These are Montmorillonite, Illite and Kaolinite. Montmorillonite layered silicates (MLS) has 2:1 layered structure (Figure 4). Illite also has 2:1 layered structure and kaolinite 1:1 layered structure. Phyllosilicates are two-dimensional arrays of silicon-oxygen tetrahedral and two-dimensional arrays of aluminum or magnesium-oxygen-hydroxyl octahedral. For silicon-oxygen sheets, silicon atoms are co-ordinated with four oxygen atoms. With silicon atom at the center, oxygen atoms are located on the four corners of a regular tetrahedron (Figure 5). In the sheet, three neighbouring tetrahedral share three of the four oxygen atoms of each tetrahedron and the fourth oxygen atom of each tetrahedron is pointing downward.

In the case of Al-Mg-O-HOH sheets (Figure 6), the Al or Mg atoms are coordinated with six oxygen atoms or OH groups. A regular octahedron has its corners occupied by oxygen or OH groups and Al or Mg at the center. Sharing of oxygen (or OH groups) with neighbouring octahedron results in a sheet structure. The sheet is called an octahedral sheet or the alumina or magnesia sheet. The tetrahedral and octahedral sheets have similar symmetry and identical dimensions, which helps in sharing of oxygen atoms between these sheets. If the sharing occurs between one silica and one alumina sheet, it is called 1:1 layer minerals. When one alumina sheet shares two oxygen atoms from silica sheets, it is called 2:1 layered mineral. Within each layer there is a repetition of structure and therefore it is referred as a unit cell. The distance between a certain plane in the layer and the corresponding plane in the next layer is referred to us the basal or d-spacing.
Figure 4: Structure 2:1 Phyllosilicates

Figure 5: A single Si–O tetrahedron and the structure of the tetrahedral sheet (Reproduced by permission of the McGraw-Hill companies from R.E. Grim, Applied Clay Mineralogy, McGraw-Hill, New York, 1962) [14]
Figure 6: A single Al–O octahedron and the structure of the octahedral sheet (Reproduced by permission of the McGraw-Hill companies from R.E. Grim, Applied Clay Mineralogy, McGraw-Hill, New York, 1962) [14]

Figure 7 - Perspective drawing of the kaolinite structure taken from Brindley (Reproduced by permission of MIT Press from G.W. Brindley, “Ion Exchange in Clay Minerals,” in Ceramic Fabrication Processes, Ed. by W.D. Kingery, John Wiley, New York, 1958, pp. 7–23).
Figure 8 - Schematic representation of the structure of kaolinite, pyrophyllite, and mica (muscovite).

<table>
<thead>
<tr>
<th></th>
<th>Kaolinite</th>
<th>Pyrophyllite</th>
<th>Mica (Muscovite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$</td>
<td>$\text{Al}_2\text{Si}<em>4\text{O}</em>{10}(\text{OH})_2$</td>
<td>$\text{KAl}_2\text{Si}_3\text{O}_8(\text{OH})_2$</td>
</tr>
<tr>
<td>Mineral formula</td>
<td>$\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$</td>
<td>$\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 2\text{H}_2\text{O}$</td>
<td>$\text{K}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2\cdot 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Crystal class</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{1}$</td>
<td>$C2/c$</td>
<td>$C2/c$</td>
</tr>
<tr>
<td>Density</td>
<td>2.6 g cm$^{-3}$</td>
<td>2.8 g cm$^{-3}$</td>
<td>2.8 g cm$^{-3}$</td>
</tr>
<tr>
<td>c-Lattice parameter</td>
<td>7.2 Å</td>
<td>18.6 Å</td>
<td>20.1 Å</td>
</tr>
</tbody>
</table>

Table 3 – Chemical composition and crystallography of some clay minerals

2.2.2 Processing of Clays

Generally, ceramics are brittle and fracture with little or no deformation. And therefore ceramics cannot be formed into shape by normal deformation processes used for metals. In the case of Clay products, classified as traditional ceramics, the art of forming or molding and burning has been an ancient practice. Burnt clay has been found dating back about 6500 B.C and commercialized by 4000 B.C. These two processes have been possible due to change in rheological properties (plasticity of clay–water mixture) of the clay introduced when mixed with a water or liquid or binder.

In addition, after drying the heat treatment of the fine particles of the clay causes the particles to agglomerate into cohesive, much stronger, finished product. The essentials for processing of clays are preparation of fine particles, mixed with water or liquid, shape them (mold) and made them harder via firing or heating (Figure 9). It is important to note that ability of clays
to maintain their strength during forming (with appropriate clay-water) and drying is a valuable unique property. A stronger, denser green body is achieved after firing or heating in the required temperature range depending on application.

![Typical flow diagram for fired clay processing](image)

Figure 9: Typical flow diagram for fired clay processing

The critical factors to consider in forming and firing of clays are nature of the raw materials and their preparation. The nature of the clays relates to the particles size and particle-size distribution (and also of pore-formers), whiles the preparation has to do with clay: water ratio, temperature firing range, mode or nature of drying, rate of heating or firing. Typical clay materials have a particle-size distribution which ranges from 0.1 to 50 microns for individual particles. In the case of ceramic water filters, the pore – former, sawdust has at least 1mm particle size. For plastic forming, the coherence of the mass and its yield point are determined by the capillarity of the liquid between particles; this force is inversely
proportional to the particle size. However, if all the materials were of a uniform fine particle size, it would not be feasible to form a high concentration of solids. In addition, during the drying of a molded ceramic body, shrinkage occurs from the removal of water molecules/films between particle sheets. Since the number of films increases as particle size decreases, bodies prepared with a liquid binder and fine-particle materials have a high shrinkage. This may result in warping and distortion if not even or uniform drying is ensured.

After drying of ceramic body, further densification is ensured. Ceramic materials are often fired to the temperature range 700 °C to 1800 °C. This depends on the compositions and the desired properties. During firing further sintering of the particle mass occurs; sufficient atomic mobility, and grain growth pre-occurs sintering. The surface tension forces are allowed to consolidate the ware and reduce porosity. The volume shrinkage which occurs is just equal to the porosity decrease and varies from 30 or 40 %, depending on the forming process and ultimate density of the fired ware. The most pressing problem with firing clay product is ensuring uniform heating as well as maintaining even heating rate. These two parameters can introduce micro cracks that may undermine the efficiency of the ceramic product depending on the application.

Some clay products are often glazed after or during firing. The most common is to fire the ceramic ware without a glaze to the required temperature, and then a glaze is applied to the body and fired at a low temperature. Alternatively, the ware is fired to a low temperature; then apply glaze, the glaze and the body is then fired at a higher temperature. The last option is to apply the glaze to the dried but unfired ware, and then heat them together in a one-fire process with careful caution to modifications on the surface of the ceramic piece.
There are other processing and forming methods for other category of ceramics. For instance Silicon Carbide for abrasives is manufactured by electrically heating mixtures of sand and coke to a temperature of 2200 °C, producing SiC and carbon Monoxide. In the case of Barium titanate capacitors, chemically purified titania and barium carbonate are used as raw materials.

![Diagram of Nano-composite Structures]

Figure 10: Schematic Nano-composite Structures

### 2.3 MODELING FLOW THROUGH CERAMIC WATER FILTERS

The flow through a porous media is often described a Darcy equation (Bear, 1972). Since then it has be employed in various areas of studies including membrane filtration processes (ref-refxx). The Darcy equation is of the form

\[
Q = \frac{KA\Delta P}{\mu L}
\]

where \(Q\) is the discharge from the porous media, \(A\) is the surface area which holds the water, \(\Delta h\) is the change in head of water due to gravity flow, \(K\) is the hydraulic conductivity of the
porous structure and $L$ is the thickness of the porous media through which the water needs to percolate. The hydraulic conductivity $K$, term is defined as

$$K = \gamma k / \mu$$  \hspace{1cm} (2)

where $\mu$ is the viscosity of water at a given temperature, $\gamma$ is the specific gravity of water at that particular temperature and $k$ is the intrinsic permeability defining the porosity and interconnectivity of the porous media.

Another important equation for flow through pipe channels is the Poiseuille law (or sometimes called the Hagen-Poiseuille law). This law is applicable to laminar, viscous and incompressible flow and is given by:

$$Q = \frac{\pi r^4}{8 \mu L} \Delta P$$  \hspace{1cm} (3)

Where, $Q$ is the volumetric flow rate, $r$ is the radius of the pipe, $\mu$ is the dynamic viscosity of the fluid (water) and $\Delta P$ is the pressure drop across the pipe of length, $L$.

The main approach by which ceramic water filters are manufactured is by introducing carbonaceous materials, which burns out during sintering processing of the ceramic green body. Lee et al., (2001) had a linear polynomial fit describing the relation between the volume fraction of biodiversity material in a ceramic based composite and the porosity. Yakub, 2012 research study confirms a linear fit with R-square value greater than 95%.
Two main methods exist for the determination of porosity of ceramic bodies. They are the mercury intrusion porosimetry/gas adsorption techniques and the direct method. The latter adopts Archimedes principle, where the volume of the ceramic piece is measured when saturated in water and when dry. By simple difference and knowledge of the density of water, the percentage porosity of the ceramic body is estimated. It is important to note that mercury intrusion porosimetry (MIP) is often used due to its high accuracy. Using MIP, porosities of ceramic water filters from three different locations; Ghana (39%), Nicaragua (37%), and Cambodia (43%) were determined (Van Halem, 2006). Percentage porosities determined via direct method had comparative results within the (30-39) %. With above mentioned porosity values mean flow rate values for ceramic water filters (in the order above) were 2.4L/hr, 0.85L/hr and 0.76L/hr.

2.3.1 Modelling Flow through Frustum-shaped Ceramic Water Filters
Schweitzer et al. 2013 have modelled the flow through ceramic water filters. In their analysis, they assumed uniform thickness for the walls and bottom of the frustum-shaped ceramic water filter. Schweitzer and co-workers initiated their modelling by Darcy equation (Bear 1972). We present modified Schweitzer et al., 2013 modelled equation for flow rate of frustum-shaped ceramic water filters. We make the equation general by allowing for differences in thicknesses of the walls and bottom of the ceramic water filter. The flow through the ceramic water filter has parameters shown in Figure 1.

The flow rate for the bottom and side of the ceramic water filter following similar procedure of Schweitzer et al. 2013 are given in equations (1) and equation (3).
\[
Q_b = \frac{K \pi r_e^2 \rho gh(t)}{\mu t_b} 
\]

where \( \rho \) is density of fluid (in this case water), \( \text{Area (}\pi r_o^2\text{)} \), \( g \) is the acceleration due to gravity, and \( h(t) \) is the height of the water-head. Also, \( t_b \) and \( t_s \) are the respective thicknesses of bottom and sides of the ceramic water filter, whiles \( Q_s \) and \( Q_b \) are the respective flow rates through side and bottom of the ceramic water filter, and \( \theta \) as angle of inclination at the corners. The flow through an annular element along the sides of the filter is given by:

\[
Q_s = \frac{2\pi K \rho g}{\mu t_s} \int_0^{h(t)} (h-y)(r_o + y \tan \theta) dy 
\]

Integrating of equation 2 gives

\[
Q_s = \frac{\pi K \rho g}{t_s \mu} [r_o h^3(t) + \frac{\tan \theta h^3(t)}{3}]
\]

The total flow, \( Q \), through the side and bottom of filter is, therefore, given by the sum of equations (1) and (3).

\[
Q = \frac{K \pi \rho gh(t)}{\mu} \left[ \frac{r_e^2}{t_b} + \frac{r_o h(t)}{t_s} + \frac{h^2(t)}{3t_s} \tan \theta \right]
\]

Thus, a more general expression for the flow rate through the frustum-shaped ceramic water filter following Schweitzer et al., 2013 derivation procedure (Yakub 2012; Yakub et al., 2013) is given in equation 4. Note that this is expressed as a function of the height of water-head in the ceramic water filter. The height of the water level in the ceramic water filter is a function of time, which depends on the volumetric flow rate and the filter geometry. The volume of water, \( V(t) \), contained in the frustum-shaped ceramic water filter at any given time is given as:
\[
V(t) = \pi \left[ R^2 h(t) + Rh^2(t) \tan \theta + \frac{h^3(t) \tan^2 \theta}{3} \right]
\]  

(8)

2.2.2 Flow through Disk- and Frustum-shaped ceramic Water Filters: Modeling

(a). Van Halem 2006

\[
Q_f = \frac{\pi k h}{t_s} \left\{ \left( r_1 - r_o \right) h^2 + r_o h \right\} + \frac{k \pi r_o^2 h}{t_b}
\]

(9)

Where \( r_1 \) and \( r_o \) are top and bottom radii of frustum-shaped filter, \( t_b \) is the thickness of the bottom of the frustum-shaped ceramic filter; \( t_d \) is the thickness of the disk filter.

Disk ceramic water filter flow rate expression

\[
Q_d = \frac{k_d \pi r_d^2 h}{t_d}
\]

(10)

Where \( t_s = t_d \) ie thickness of disk = thickness of side, \( r \) is the radius of the disk,

Re-arranging equation (7)

\[
\frac{Q_d}{r_d^2} = \frac{\pi k_d h}{t_d}
\]

(11)

Re-arranging (6) and putting in equation (8)

\[
Q_f = \frac{Q_d}{r_d^2} \left\{ \left( r_1 - r_o \right) h^2 + r_o h \right\} + \frac{Q_d r_o^2 t_d}{r_d^2 t_b}
\]

(12)
\[ \frac{Q_f}{Q_d} = \frac{1}{r_o^2} \left[ \frac{(r_i - r_o)h^2}{3L} + r_o h + \frac{r_o^2 t_d}{t_b} \right] \]  

(13)

The expression equation (10) is modelled to predict the flow rate of disk CWF via flow rate of the frustum-shaped CWF and vice versa. This is unique for Van Halem, 2006 flow modelled equation.

(b). Schweitzer et al., 2013

Expression of flow rate

\[ Q_f = \frac{\pi kh}{t} \left[ r_o^2 + r_o h + \frac{1}{3} h^2 \tan \phi \right] \]  

(14)

Where \( t \) is the thickness of side (which is assumed to be same as thickness of bottom), hydraulic conductivity, \( k_s = k_b = k \); \( r_o \) is the radius of the bottom of the frustum-shaped filter.

Putting equation (8) into equation (11) gives

\[ \frac{Q_f}{Q_d} = \frac{1}{r_d^2} \left[ \frac{r_i^2}{3L} + r_o h + \frac{1}{3} h^2 \tan \phi \right] \]  

(15)

(c). Yakub et al 2013 (or Annan et al. 2014)

\[ Q_f = \frac{\pi kh}{t} \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3t_s} \right] \]  

(16)

Re-arranging equation (8) and noting that \( t_d = ts \); \( kd = kf = k \)

\[ \frac{Q_f t_d}{r_d^2} = \pi kh \]  

(17)
Put equation (14) into (13)

$$\frac{Q_f}{Q_d} = \left( \frac{t_d}{r_o^2} \right) \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3t_s} \right]$$  \hspace{1cm} (18)

The equations (10), (12) and (15) can be used to predict the flow rate of the disk ceramic water filter depending on the model.

In the case where the hydraulic conductivity of the disk ceramic water filter is different from the frustum-shaped ceramic water filter (of which they are both from the same production materials), it is significant to re-deduce the disk–frustum shaped filter relationship.

### 2.4 Fundamentals of Porosimetry

Ceramic water filters contain pores in their structure which allows water molecules to flow through but often small enough to prevent microbes. The size and other characteristics such as skeletal density, tortuosity, of the pores are instrumental to microbial activity as well as the strength of the structure.

Porosimetry is a technique used in characterizing the pore structure of ceramics. The main technique used is called Mercury Intrusion Porosimetry (MIP). MIP is not only applicable over a wide range of pore sizes, but also the fundamental data it produces (such as the volume of mercury intruded into the sample as a function of applied pressure) is indicative of various characteristics of the pore space. This is used to reveal a variety of physical properties of the solid material itself.
Figure 11: Various liquids resting on a solid surface. The different angles of contact are illustrated for wetting and non-wetting liquids.

The angle of contact of the liquid-vapour surface to the solid-vapour surface at a point on the liquid-solid vapour interface characterizes the interfacial tension present between the solid, liquid, and vapour (Webb 2001). Figure 11 shows five liquids of different surface tensions resting on the same surface material. The different surface energies compel liquids to assume varying contact angles relative to the solid surface. When a liquid has low surface tension (low surface energy) on a solid surface of higher surface tension, it will spread out on the surface forming a contact angle less than $90^\circ$. This is referred to as wetting. When the surface energy of the liquid exceeds that of the solid, the liquid will form a bead and the angle of contact will be between $90^\circ$ and $180^\circ$; this is a non-wetting liquid relative to the surface.

Water has a contact angle $< 90^\circ$, while the mercury has a contact angle $> 90^\circ$. This is because of the differences in surface energy (or surface tension) of the two liquids and their substrate. In general, when a liquid has a lower surface energy than its substrate it tends to spread out (or “wets” the surface) and forms an acute angle with the substrate. However, if the liquid has a higher surface energy than its substrate, it tends to form a bead and
make an obtuse angle with the substrate. An important implication of this is the acute contact angle that is observed in capillary tubes that contain water (Figure 12a) and obtuse angle of contact in capillary tubes that contain non-wetting fluids such as mercury (Figure 12b).


Washburn 1921, derived an equation describing the equilibrium of the internal and external forces on the liquid-solid-vapour system in terms of these three parameters. It states concisely that the pressure required to force a non-wetting liquid to enter a capillary of circular cross-section is inversely proportional to the diameter of the capillary and directly proportional to the surface tension of the liquid and the angle of contact with the solid surface. This physical
principal was incorporated into an intrusion-based, pore-measuring instrument by Ritter & Drake, 1945.

Washburn’s equation, upon which data reduction is based, assumes that the pore or capillary is cylindrical and the opening is circular in cross-section. As has been stated, the net force tends to resist entry of the mercury into the pore and this force is applied along the line of contact of the mercury, solid, and (mercury) vapour.

The magnitude of force tending to expel the mercury is given as below:

\[ F_E = 2\pi \gamma \cos \theta \] \hspace{1cm} (19)

; Where \( \gamma \) is the surface tension. An external pressure to force the mercury into the pore is also given by

\[ F_I = \pi r^2 P \] \hspace{1cm} (20)

; \( \pi r^2 \) is the cross-sectional area of the pore opening. Balancing the intrusion and the extrusion forces, the Washburn equation is derived.

That is,

\[-2\pi \gamma \cos \theta = \pi r^2 P \] \hspace{1cm} (21)

\[-\pi D \gamma \cos \theta = (\pi D^2 P)/4 \] \hspace{1cm} (22)

This equation (22) is Washburn’s equation in terms of diameter, D). The relationship between applied pressure and minimum pore size into which mercury will be forced to enter is given below as:

\[ D = -4\gamma \cos \theta / P \] \hspace{1cm} (23)
The above equation (23) gives insight into a simple relation existing between pore size and applied pressure on mercury. Thus, for a given liquid-solid system, the numerator is constant, showing the size of pore into which mercury will intrude is inversely proportional to the applied pressure. In other words, mercury under external pressure \( P \) can resist entry into pores smaller than \( D \), but cannot resist entry into pores of sizes larger than \( D \). Hence, during mercury intrusion at any pressure, it can be determined which pore sizes have been invaded with mercury and which sizes have not.

Basic operation of MIP can be expounded by using Washburn’s equation. Washburn’s equation was not applied until about 20 years later by Henderson et al., 1967. After Washburn using it to determine the pore size distribution of a number of clays and bauxite, Ritter and Drake constructed the first mercury porosimeter (Ramachandran et al., 2001; Vanbrakel et al., 1981).

A typical mercury intrusion porosimetry test involves a sample into a container such that contaminant gases and vapours (usually water) can be removed and, when contaminants are evacuated, allow mercury to fill the container. The external pressure on mercury is increased toward ambient while the volume of mercury entering larger openings in the sample bulk is continuously monitored. When pressure has returned to ambient, pores of diameters down to about 12 mm have been filled. The sample container is then placed in a pressure vessel for the remainder of the test. At 414 MPa, a typical for commercial porosimeter equipment will force mercury into pores down to about 0.003 micro-meters in diameter. The volume of mercury that intrudes into the sample due to an increase in pressure from \( P_i \) to \( P_{i+1} \) is equal to the volume of the pores in the associated size range \( r_i \) to \( r_{i+1} \), sizes being determined by
substituting pressure values into Washburn’s equation. Most often than not, the MIP is complemented by Gas adsorption techniques such as nitrogen adsorption and helium pycnometry.

There is an electronic means of detecting the rise and fall of mercury within the capillary are much more sensitive, providing even greater volume sensitivity down to less than a microliter. The measurement of a series of applied pressures and the cumulative volumes of mercury intruded at each pressure comprises the raw data set. A plot of these data is called the intrusion curve; whiles when pressure is reduced, mercury leaves the pores resulting into the extrusion curve.

MIP can give a number of vital data about the material under consideration. This data include: material volume and density, skeletal density, true density, percentage porosity, pore volume distribution, etc. An important parameter is the permeability and the pore size of the material, especially in this study.

Permeability is the inherent ability of a porous medium to transmit a fluid. It is a property of the material that tells how quickly a fluid moves within the materials pores. Katz and Thompson 1987, deduced two important relations for determining the absolute permeability of materials from single data of mercury intrusion porosimetry. The first equation is given as

\[
K = \frac{1}{226} \left( \frac{L_e}{\sigma_o} \right)^2 \frac{\sigma}{\sigma_o} \tag{24}
\]

The second equation is given as:
\begin{equation}
K = \frac{1}{\phi^2} \left( \frac{L_{\text{c}}}{L_{\text{c}}^{\max}} \right)^2 \phi S(L_{\text{max}})
\end{equation}

where \( K \) is the intrinsic permeability; \( L_{\text{max}} \) is the pore size at which conductance is maximum; \( L_{\text{c}} \) is the pore breakthrough size, \( \phi \) is the porosity of the ceramic water filter and \( S(L_{\text{max}}) \) is the fractional volume of connected pore space composed of pore widths of size \( L_{\text{max}} \) and larger.

Section 2.2 of this thesis briefly explains how permeability can be obtained via Darcy equation and Hagen-Poiseuille law. By combining Darcy’s law (equation 6) with the Poiseuille’s law (equation 7) and applying what is known as the capillary bundle model (in which pores are treated as bundle of capillary tubes of varying sizes), Hager (Hager, 1998) derived an expression for the tortuosity.

### 2.5 Adsorption and Filtration

Adsorption is defined as a process used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. It is a fundamental property having origin in attractive forces between molecules. The force field creates a region of low potential energy near solid surface and, as a result, the molecular density close to the surface is generally greater than in the bulk gas. In the case of multi-component system, composition of the surface layer generally differs from that of the bulk gas and as such the surface adsorbs the various components with different affinities. Adsorption is known to mainly involve various chemical species that may migrate via inter-facial surface into another (possibly) solid phase. The material on which adsorption occurs is termed adsorbent, whereas adsorbed
species is termed adsorbate. Adsorption can be termed chemisorption or physical adsorption, depending on nature of surface forces. In physical adsorption, relatively weak inter-molecular forces are in play whereas chemisorptions there is significant electron transfer (resulting in a chemical bond between the adsobate and the solid surface). The term biosorption is also often used to describe the adsorption process that has microbes and viruses as adsorbate. Generally if adsorption occurs in the liquid phase, there exists a little difference in molecular density between the adsorbed and fluid phases. It is relevant to also know that there are hydro-philic and hydro-phobic adsorbents.

The factors affecting adsorption process include:

(i) surface area

(ii) nature and initial concentration of adsorbate

(iii) PH of solution

(iv) temperature

(v) interfering substances

(vi) nature (and dose of adsorbent)

And since adsorption is a surface phenomenon, the extent of adsorption is directly proportional to the specific surface area, so for a more powdered and porous solid the greater the percentage of adsorbate per unit weight. The fundamental equation governing adsorption solid-liquid process is given by equation (2.3)

\[
q_t = \frac{(c_0 - c_t)V}{m} \tag{26}
\]
Where $q(t)$ (mg/g) is the amount of adsorbate per mass unit of adsorbent at a time, $t$, $C_0$ (mg/L) and $C_t$ (mg/L) are the initial and at a time $t$ concentration of adsorbate, respectively, $V$ (L) is the volume of the solution, and $m$ (g), is the mass of the adsorbent. In a solid–liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm and found to be in conformity with equation (2.3) above. Isotherms, which expresses the relation between concentration of adsorbate and extent of accumulation on the adsorbent surface at constant temperature, are used mostly in modelling of most adsorption processes (Sundaram et al., 2008).

The most widely used models to describe the adsorption process in water and wastewater applications were developed by (i) Langmuir, (ii) Brunauer, Emmet, and Teller (BET), and (iii) Freundlich. The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms reflecting apparent multilayer adsorption. This means that when the limit of adsorption is a monolayer, BET isotherms reduce to Langmuir expression. It is important to know that the two equations are limited by assumption of the uniform energies of adsorption on the surface. The two; Langmuir and Freundlich, equations are given respectively below as

$$\frac{q_e}{q_m} = \frac{b C_e}{1 + b C_e}$$  \hspace{1cm} (27)

Where $q_e$ (mg/g) is the amount of adsorbate per mass unit of adsorbent at equilibrium, $C_e$ is the liquid-phase concentration of the adsorbate at equilibrium (mg/L), $q_m$ is the maximum
adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg).

\[ q_e = K_F C_e^{1/n} \]  

(28)

Where \( K_F \) (mg/g) (L/mg) \(^{1/n} \) is the Freundlich capacity factor and \( 1/n \) is the Freundlich intensity parameter. The constants in the Freundlich isotherm are determined by plotting log\( (q_e) \) versus log\( (C_e) \).

According to Meenakshi et al., 2008, there are three main stages, theoretically, for mass transport of adsorbates. These are

I. Mass transfer from the bulk of the absorbent to the surface of it (often called bulk diffusion or external mass transfer)

II. Intra-particle diffusion of species through liquid filled pores

III. Systematic accumulation of absorbate at the adsorbent sites

Adsorption diffusion models are used for modelling rate determining step which is either intra-particle diffusion or liquid film diffusion. In physical adsorption process the mass action or transfer process is very rapid and can be neglected for kinetic studies. Adsorption diffusion models are used to describe the process of film deposition and intra-particle diffusion. Two main models used in the liquid film deposition model are (i) linear driving force rate law and (ii) film diffusion mass transfer rate equation whereas intra-particle diffusion has (i) Homogeneous solid diffusion model (HSDM) (Cooney, 1999; from

In linear driving force rate law for a liquid/solid adsorption system, the rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law. The rate of accumulation is given by

\[ V_p \left( \frac{\partial \bar{q}}{\partial t} \right) \]  

(29)

Where \( \bar{q} \) represents average solute concentration in the solid, and \( V_p \), the volume of the particle. It is known that the rate of solute transfer across the liquid film is proportional to the surface area of the particle \( A_s \) and the concentration driving force \( (C - C_i) \). And therefore, it equals to \( k_f A_s (C - C_i) \), where \( k_f \) represents the film mass transfer coefficient (Cooney, 1999). From the above discussion it is obvious that

\[ V_p \left( \frac{\partial \bar{q}}{\partial t} \right) = k_f A_s (C - C_i) \]  

(30)

Where \( C_i \) and \( C \) denote the concentration of solute at the particle/liquid interface and in the bulk of the liquid far from the surface, and \( A_s/V_p \) defined as the particle-surface area per unit volume, \( S_o \). The equation resulting from the \( S_o \) substitution is termed the ‘linear driving force’ rate law.

The film diffusion mass transfer rate equation presented by Boyd et al., 1947) is

\[ \ln \left\{ 1 - \frac{q_t}{q} \right\} = -R' t \]  

(31)

\[ R' = \frac{3D}{r_0^2 \Delta r' R'} \]  

(32)
Where $R_l^1$ (min$^{-1}$) is liquid film diffusion constant, $D_{el}^1$ (cm$^2$/min) is effective liquid film diffusion coefficient, $r_o$ (cm) is radius of adsorbent beads, $\Delta r_o$ (cm) is the thickness of liquid film, and $k'$ is equilibrium constant of adsorption.

Under intra-particle diffusion model, HSDM can describe mass transfer in an amorphous and homogeneous sphere (Cooney, 1999) and the mathematical expression given as

$$
\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)
$$

(33)

where $D_s$ is intra-particle diffusion coefficient, $r$ radial position, and $q$ the adsorption quantity of solute in the solid varying with radial position at time $t$.

Weber and Morris 1964 and Alkan et al., 2007 found out that for many adsorption processes the uptake of solute varies almost proportional to $t^{1/2}$ rather to the contact time, $t$.

$$
q_t = K_{int} t^{1/2}
$$

(34)

Where, $K_{int}$ is the intra-particle diffusion rate constant. If intra-particle diffusion is the sole rate limiting step, then the plot of $q_t$ against $t^{1/2}$ must pass through the origin. However, the adsorption kinetics may be controlled by both film diffusion and intra-particle diffusion simultaneously.

Another intra-particle diffusion model proposed by Dumwald-Wagner (Wang et al., 2004) is given as
A plot of $\log(1-F^2)$ vs $t$ should be linear and the rate constant $K$ can be obtained from the slope. Dumwald-Wagner model proved to be reasonable to model different kinds of adsorption systems such as p-toluidine adsorption from aqueous solutions onto hyper-cross-linked polymeric adsorbents.

2.5.1 Fluoride Removal

Fluoride is a naturally occurring element in minerals, geochemical deposits, and natural water systems and enters food chains through either drinking water or eating plants and cereals (Sushree et al. 2006). And found to occur naturally as sellaite (MgF2), fluorspar (CaF2), cryolite (Na3AlF6) and fluorapatite $[3\text{Ca}_5\text{(PO}_4)_2\text{Ca(F,Cl}_2)]$. According to the World Health Organization (WHO), the tolerance limit of fluoride content of drinking water is 1.5 mg/L (WHO, 1993). Fluoride concentrations in the range (1.5-4) mg/L results in dental fluorosis whereas with prolonged exposure within 4-10mg/L progresses to skeletal fluorosis. Fluoride which is nearly insoluble in water has been found in many groundwater bodies at levels around 30mg/L, notably in Africa, USA, and Asia (Wang et al., 2002; Agarwal et al., 2003; Moges et al., 1996; Gaciri and Davies, 1992; Chernet et al., 2002; Mjengera and Mkongo, 2002; Moturi et al., 2002). The main methods used in defluoridation from aqueous solutions are membrane techniques and adsorption techniques (alumina based adsorbents, Clays and Soils, Carbon, Zeolites and layered double hydroxides (M. Mohapatra et al. 2009). The adsorption techniques have been found to be most effective and widely used because of its low maintenance cost and even appreciable fluoride removal at low concentrations. Using hydroxyappatite (HA)-Clay filters, Yakub et al., 2013 were able to demonstrate high fluoride removal rate.
2.5.2 Removal of Other Chemical Contaminants

When water contains chemical contaminants that are above permissible limits, their effects when used as drinking water are of great health concerns. Aluminum, Barium, Arsenic, mercury, etc. are contaminants that may cause ill-effects when the quantity exceeds the WHO guidelines.

Arsenic may occur naturally, and excess exposure to arsenic in drinking-water may result in a significant risk of cancer and skin lesions. The presence of nitrate and nitrite in water has been associated with methaemoglobinaemia, especially in bottle-fed infants, of which an obvious symptom is a bluish skin. Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater or other organic wastes into surface water and groundwater. Particularly in areas with aggressive or acidic waters, the use of lead pipes and fittings or solder can result in elevated lead levels in drinking-water, which cause adverse neurological effects.

Arsenic leaching into water bodies has been recorded in several places including Cambodia, Nepal, Vietnam, Bangladesh etc. PoUTS mentioned in literature to remove arsenic from drinking water include iron coated sand, activated seawater-neutralized red mud (Genchi-Fuhrman et al., 2004), mixture of powdered iron, sulphur and hydrogen peroxide, sunlight or ultraviolet rays, zero-valent iron appended with limestone (Kanel et al., 2006, Lackovic et al., 2000), coagulation (E.P.A. 2000), iron oxide coated sand and manganese oxide coated sand tested by Thirunavukkarasu et al. in 2002, ENPHO and MIT made Kanchan MIT Filter
Arsenic can also be removed using ceramics made of clay (Kolshi Filter, Nepal) with high Fe content.

Metallic compounds found to leach from filters, aluminum and silver were below WHO guidelines. Barium, copper, manganese and silicone also have been found to be less than WHO guidelines. Filters were found to retain zinc (van Halem 2006). Arsenic was found in the effluent water above the provisional WHO guideline of 10 μg/L. The amount is worrying, but decreased from 200 μg/L to a mean of 17 μg/L after 12 weeks. The graphs below also show that most concentrations rapidly decrease in the course of time, so only new filters will produce effluents with these elements, with the exception of silicon in Cambodian filters. Naturally, the clay of which the filter element is composed determines which elements are present in the material (Van Halem 2006). Other naturally occurring chemicals, such as uranium and selenium, are known to also give rise to health concern when they are present in excess.
2.6 Fracture Mechanics and Toughening Mechanisms

Clay ceramics are known for their intrinsic brittle behaviour (Kingery 1965). This behaviour often results in breakages of products that are sintered from clay ceramics. Ceramic water filters are no exception from these class of products, although accredited with high performance efficiency in several dimensions of water purification. The breakages associated with clay ceramic water filters occur during drying, firing and transportation.

Figure 13 - Effluent and influent concentrations of barium, copper, manganese and silicon (Van Halem, 2006)
This section reviews basic fracture mechanics rules to understand porous clay ceramics fracture behaviour, toughening mechanisms fundamentals are given along with brief review on thermal shock response.

Fracture is the separation or fragmentation of a solid body into two or more parts in response to imposed stress and at temperatures that are low relative to melting point of the material. The mechanism of fracture is simply separation of bonds, and this is often preceded by stretching of the bonds.

2.6.1 Brief Historical Perspective

Inglis (1931) and Griffith (1921) are accorded serious initial research work in fracture mechanics. Griffith (1921) extended the work of Inglis by deriving an expression for predicting brittle stress in glass. Adopting thermodynamic arguments and concept of notch stress concentration factors, he obtained a condition of unstable crack growth in brittle materials such as glass.

George Irwin (1975) developed a crack driving force parameter called stress intensity factor and concepts of linear elasticity in solving fracture problems. Other interesting research works include William (1975), Wells (1961) and Rice (1968) work on J-integral. McClintock et al (1995) have proposed three parameter fracture mechanics approaches for characterizing the crack driving force under full plastic condition.

2.6.2 Fracture Types and Crack Growth Modes

The main types of fracture are ductile and brittle fractures. Ductile fracture is characterized by appreciable plastic deformation prior to crack propagation. Materials that exhibit this type of fracture has high absorption energy before fracture. On the other hand there is little or no
plastic deformation with low energy absorption accompanying a brittle fracture. Comparatively, brittle fracture has a high crack propagation velocity than ductile fracture. The direction of crack is nearly perpendicular to the direction of applied stress, yielding a relatively flat surface. Figure 14 (a) –(c) below shows the types of fracture.

Figure 14 - a) Highly ductile fracture in which the specimen necks down to a point. (b) Moderately ductile fracture after some necking. (c) Brittle fracture without any plastic deformation.

Three modes of crack growth have been identified. They are crack opening mode (MODE I), in-plane shear mode (MODE II), and out-of-plane shear mode (MODE III). Mode II and Mode III are sometimes referred to us sliding and tearing mode respectively. Schematic of the fracture modes are as shown in figure below.
2.6.3 Stress Concentration and Griffith’s Criterion

The measured strength of brittle materials are lower than their theoretical values computed based on atomic bonding energies. This is mainly due to defects. The defects are microscopic flaws or cracks that may exist on the surface or interior of the material. The flaws are detrimental to fracture strength because an applied stress may be amplified or concentrated at the tip, the magnitude of this amplification depends crack orientation and geometry.
Figure 16 - (a) The geometry of surface and internal cracks. (b) Schematic stress profile along the line in (a), demonstrating stress amplification at crack tip positions.

Inglis (1913), using figure 16 above modeled stress concentrations around notches with radii of curvature, notch length $a$, and stress concentration factor, $K_t$. For elastic deformation, $K_t = \frac{\text{maximum stress around notch tip}}{\text{remote stress away from notch}} = 1 + \frac{2(a/\rho)^{1/2}}{}$

Failure is, therefore, likely to initiate from the notch tip, when the applied or remote stresses are significantly below the fracture strength of the un-notched material. Subsequent work by Neuber (1945) extended the work of Inglis (1913) to include the effects of notch plasticity on stress concentration factors.

Griffith was the first person to propose a thermodynamic criterion for growth of unstable crack extension in a brittle solid (Griffith, 1921). He proposed that a brittle material has fine
cracks capable of producing stress concentration of sufficient magnitude so that theoretical cohesive strength reached in local regions at nominal stress is below the theoretical value. Simply put, Griffith criterion states that:

“A crack will advance if the release of strain energy is greater than the energy invested to create the new surface (i.e., exposed surface of the crack).”

Micro-cracks that spread in brittle fracture produces increase in the surface area of the sides of the crack. This requires energy to overcome the cohesive force of the atoms, or an increase in surface energy. Elastic strain energy is released as the crack spreads.

Adopting thermodynamic principle and stress concentration concepts, he developed the energy balanced equation for an elliptical flaw in a plate subjected to uniaxial loading

\[ U_T = -\frac{\pi \sigma^2 a^2 B}{E} + 4a \gamma B \]  \hspace{1cm} (36)

\[ \frac{dU_T}{da} = 0 \]  \hspace{1cm} (37)

\[ \frac{dU_T}{da} = -\frac{2\pi \sigma^2 a B}{E} + 4 \gamma B = 0 \]  \hspace{1cm} (38)

\[ \Rightarrow \sigma_e = \sqrt{\frac{2\gamma E}{\pi a}} \]  \hspace{1cm} (39)
Where $\sigma_c$ is the Griffith’s fracture stress for brittle materials, and thus does not account for plastic work. $B$ is the thickness of specimen, $a$ is crack length, $\gamma_s$, surface energy. Also, 

$E'=E/(1-\nu^2)$, for plane strain and $E'=E$, for plane stress.

Orowan (1950) modified the critical stress expression to account for plastic work in materials that undergo plastic deformation prior to failure. Orowan proposed the expression

$$\sigma_c = \sqrt{\frac{2(\gamma_s + \gamma_p)E'}{\pi a}} \quad (40)$$

where $\gamma_p$ is the plastic energy term.

The strain energy release rate, $G$, which was first proposed by Irwin (Soboyejo, 2003) is given by the expression below

$$G = -\frac{1}{B} \frac{d(U_L + U_E)}{da} \quad (41)$$

Where $U_L$ is the potential energy of the loading system, $U_E$ is the strain energy of the body and $B$ is the thickness of the body. Fracture should initiate when $G=G_c$, critical value given by

$$G_c = 2\left[\gamma_s + \gamma_p\right] \quad (42)$$
G is a measure of the crack driving force and $G_c$ is the measure of initial resistance of a brittle material to resist cracking which is a key materials reliability. Note that for brittle materials as clay ceramics, plastic energy portion is neglected, that is $G_c = 2\gamma_s$.

2.6.4 Relation between Strain Energy Rate and Stress Intensity Factor

The stress concentration/intensity factor, $K$, earlier basically defined in equation 43, using fracture mechanics (via Linear elastic fracture mechanics) can be also be defined as

\[ K = f\left(\frac{a}{w}\right)\sigma, \sqrt{\pi a} \]  \hspace{1cm} (43)

$K$ is a measure of a materials resistance to brittle fracture when crack is present. It has unit MPa$\sqrt{\text{m}}$. $f(a/w)$ is a dimensionless quantity that depends on crack length, $a$ and specimen geometry (width, $w$). The $f(a/w)$ has a value nearly unity for a plate of infinite width with a through thickness.

Depending on the type of mode of fracture, stress intensity factor can be written as in the above equation 43. The relationship between the strain energy release rate, $G$, and the stress intensity factor, $K$, for mode I loading is given by

\[ G_I = \frac{K_I^2}{E} \]  \hspace{1cm} (For plane stress) \hspace{1cm} (44)
\[ G_I = \frac{(1-\nu^2)}{E} K_I^2 \]  
(For plane strain) \hspace{1cm} (45)

Also for Mode II

\[ G_{II} = \frac{(1-\nu^2)}{E} K_{II}^2 \]  \hspace{1cm} (46)

Mode III fracture has the relation

\[ G_{III} = \frac{(1+\nu)}{E} K_{III}^2 \]  \hspace{1cm} (47)

Since the energy release rate is a scalar quantity, \( G \) total per unit of crack edge can be computed by simple addition of the various equations depending on the type of fracture mode being considered. In three dimensional solid subjected to all three fracture modes I, II and III, total energy release rate, \( G_{\text{tot}} \) is given as below:

\[ G_{\text{tot}} = \frac{(1-\nu^2)}{E} \left[K_I^2 + K_{II}^2 \right] + (1-\nu)K_{III}^2 \]  
(For plane strain) \hspace{1cm} (48)

\[ G_{\text{tot}} = \frac{1}{E} \left[K_I^2 + K_{II}^2 \right] \]  
(For plane stress) \hspace{1cm} (49)
Plappally 20011 and Yakub et al., 2014 have used R-curve behaviour of fracture specimen as a tool in understanding fracture behaviour under load control. R-curve is done by plotting the stress intensity factor against crack displacement.

2.6.5 Thermal Shock Response

When there is sudden or rapid change in temperature for materials, it has the potency of inducing drastic changes in local stress/strains stages. Downward quench (cold shock) and upward quench (hot shock) conditions are often used in assessing materials resistance to rapid thermal changes. The rapid changes in temperature can cause crack initiation, and crack nucleation/growth.

Kingery (1995) and Hassleman (1963) are associated with important research investigations into thermal resistance of materials. According to Kingery (1995) when heat temperature coefficient is so large such that the materials change immediately to surrounding temperature, then the temperature difference to initiate fracture is given as:

\[ \Delta T_c = S \sigma \frac{(1-\nu)}{E\alpha} \]

(50)

Where \( S \) is shape factor, \( \sigma \) – fracture stress, \( E \) – Elastic modulus, \( \alpha \) – Co-efficient of thermal expansion, \( \nu \) - Poisson’s ratio and \( R \), fracture resistance parameter = \((1-\nu)/E\alpha\). Increasing \( R \), increases resistance to fracture initiation due to thermal shock. For smaller, \( h \),

\[ \Delta T_c = SK \sigma \frac{(1-\nu)}{E\alpha h} = \frac{S}{hR} \]

(51)
\( R' = K \sigma' \frac{(1-\nu)}{E \alpha} \) \hspace{1cm} (52)

The above equations were developed for a homogeneous, isotropic body with physical properties that are independent of temperature. From equations (51) and (52), high values of thermal conductivity and strength, along with low values of the elastic modulus, Poisson’s ratio, and thermal expansion, will lead to the best thermal shock resistance. Kingery (1955) also demonstrated that placing compressive surface stresses in spherical samples of zirconia leads to improved thermal stress resistance.

Hasselman (1963a) gave a theoretical framework for the temperature difference required to cause the fracture of a body of low initial temperature subjected to radiation heating is given as below:

\[
\Delta T_e = \left[ \frac{A}{\rho b} \right]^{1/4} \left[ \frac{k \sigma' (1-\nu)}{E \alpha} \right]^{1/4}
\] \hspace{1cm} (53)

A is geometry constant, b is size constant, \( \rho \) – density, k is the emissivity.

This means that low emissivity will improve thermal shock resistance parameter. In his second paper on thermal shock investigations, Hassleman (1963) proposed factors that affect the cracks in materials. Adopting the Griffith’s theory that crack will propagate as long as elastic energy released is equal to or greater than effective surface energy, he determined the following two damage resistance parameters, \( R^* \) and \( R^{**} \).
\[ R^* = \frac{E}{(\sigma^*)^2 (1-\nu)} \]  

(54)

\[ R^{**} = \frac{E_{\text{eff}}}{(\sigma^*)^2 (1-\nu)} \]  

(55)

\( \gamma_{\text{eff}} \) is the effective surface energy. Therefore materials designed to have a high fracture resistance would have low damage resistance. The equations are applicable to only the first thermal shock cycle. Increasing the porosity has a negative effect on the fracture resistance parameter R*, because increasing the porosity decreases the thermal conductivity. However, it increases the damage resistance because it decreases the elastic energy stored in the material. Increasing the surface energy increases R** and can be accomplished by including a second phase.

2.6.6 Toughening Mechanisms

Toughening of clay ceramics is very relevant knowing their brittle nature. Ceramic water filters that are also fabricated from such class of materials are no different though stronger. In this sub-section, fundamental understanding and concepts to guide the design of tougher materials are elucidated with special emphasis on crack-bridging and visco-elastic toughening schemes. This is because the research attempts to toughen porous clay ceramics which adopts these mechanisms. The main key concept in this area is the shielding of crack-tip(s) from applied stresses. When this is done, higher levels of remote stresses can be applied to a material before fracture critical conditions.
The main crack-tip shielding concepts identified over the last four decades include:

(i) Transformation toughening
(ii) Crack bridging
(iii) Crack tip blunting
(iv) Visco-elastic toughening
(v) Crack tip trapping
(vi) Crack deflection
(vii) Micro-crack shielding and anti-shielding
(viii) Twin toughening

Many of the crack-tip toughening mechanisms are known to occur in composites, it is therefore significant to briefly give two main schemes in reinforcement. The first is brittle matrices with strong, stiff brittle reinforcements. The second is brittle reinforcement with ductile reinforcements. Such reinforced materials are known to have low modulus, intermediate strength and good or appreciable ductility. There are also ductile matrices such as metals and polymers. In this research emphasis is on brittle matrices and possibility of reinforcing them with ductile phases.
Figure 17- Crack-tip shielding mechanisms. Frontal zone: (a) dislocation cloud; (b) micro-crack cloud; (c) phase transformation; (d) ductile second phase. Crack-wake bridging zone: (e) grain bridging; (f) continuous-fiber bridging; (g) short-whisker bridging; (h) ductile second phase bridging. From B. Lawn, reprinted with permission from Cambridge University Press). [Soboyejo 2003]

2.6.6.1 Transformational Toughening
The tetragonal (t) phase of Zirconia was found to transform to monoclinic (m) phase on application of a critical stress (Garvie et al., 1975). Evans and Heur (1980) also studied
toughening of ceramics via martensitic transformation occurring in the immediate vicinity of the crack tip. They deduced from the transformational equations the Helmholtz free energy.

Both experimental analysis and models deduced were done via studying stress field at the crack tip, as well as behind wake fields. As the crack-tip stresses are raised, particles ahead of the crack tip undergo stress induced martensitic phase transformations at speeds close to that of sound (Green et al., 1989). The unconstrained transformation yields a dilatational strain of approximately 4% and a shear strain of approximately 16%, which are consistent with the lattice parameters of the tetragonal and monoclinic phases, Fig. 18 (a).
Evans and Heuer (1980) first of all derived the stresses and strain energies that are believed to develop after the transformation has taken place in the material, and then deduced from their derivation the transformation condition using the change in Helmholtz free energy (change in thermodynamic state). In addition, they derived relations for the transformation stress and the transformation zone (in the matrix) at the immediate vicinity of the crack tip where the second phase – particles will undergo transformation.

Mcmeeking and Evans (1982) studied the size of the transformed zone that is associated with Mode I crack under small-scale transformation conditions. Budiansky et al (1983) developed an expression for estimating the height of the transformed zone. Their derivation was based on the assumption that transformation occurs when the mean stress level at the crack tip exceeds a critical stress value ($\sigma_c^T$) (Mcmeeking and Evans (1982).

\[
h = \frac{\sqrt{3}}{12\pi} \left( \frac{K}{\sigma_c^T} \right) (1 + \nu)^2
\]

Where $h$ is half height of the transformed wake, $K$ is the far field stress intensity factor and $\nu$ is the Poisson’s ratio.
For purely dilational transformation, the toughening is expressed also by Budiansky et al (1983);

$$
\Delta K = \frac{0.22E_c f \varepsilon_c^T \sqrt{h}}{1-\nu}
$$

(57)

Where $\varepsilon_c$ is the elastic modulus of the composite, $f$, is the volume fraction of the transformed particles, and $\varepsilon_c^T$ is the transformation volume strain. The above continuum model assumes volume fraction of the transformed material to be constant with increasing distance, $x$, from the crack face (Soboyejo, 2003). However, to account for ‘$f$’ varying with increasing distance from the crack face, an integral is introduced, as below;

$$
\Delta K = \frac{0.22E_c f \varepsilon_c^T}{1-\nu} \int_0^h \frac{f(x) dx}{2\sqrt{x}}
$$

(Marshall et al., 1990)

(58)

where $f(x)$ is a mathematical function representing the fraction of transformed Zirconai as a function of distance, $x$, from the crack. Also in literature is an expression involving Gibbs free energy during the transformation form one phase to another,

$$
\sigma_c^T = \frac{\Delta G}{\varepsilon_c^T}
$$

(Becher, 1986)

(59)
2.6.6.2 Crack Bridging
This section will concentrate on bridging with ductile reinforcement. It is important to note that there are crack bridging by stiff elastic whiskers/fibers, as well as on de-bonding or fiber pull-out as illustrated in figure 19.

![Diagram of crack bridging](image)

Figure 19 - Schematic illustration of crack bridging by (a) ductile particles and (b) stiff elastic whiskers.

The fundamental approach used in understanding the bridging via ductile phase reinforcement is via energy approach. In here, the ductile phase toughening by crack bridging may be attributed to the plastic work required for the plastic stretching of the
constrained ductile spherical particles. For small-scale bridging in which the size of the bridging zone is much smaller than the crack length, the increase in strain energy, $G_{ss}$, due to the plastic work required for the stretching of the ductile phase is given by (Soboyejo et al., 1996, Kajuch et. al., 1995; Bloyer et al., 1996, 1998; Lou and Soboyejo, 2001):

$$\Delta G_{ss} = V_f C \sigma_y \xi$$

(60)

Where $V_f$ is the volume fraction of ductile phase that fails in a ductile manner, $C$ is a constraint parameter (which is usually between 1 to 6), $\sigma_y$ is uniaxial yield stress and $\xi$ is a plastic stretch parameter. In terms of stress intensity factor, $K$:

$$K_{ss} = \left( K_o + E f \sigma_o \chi \right)^{1/2}$$

(61)

$K_{ss}$ is the steady state toughness, $K_o$ is the crack initiation toughness (which equal to brittle matrix toughness, $E$ is young’s modulus, $\nu$ is Poisson ratio, $f$ is the volume fraction, $\sigma_o$ is the flow stress of ductile reinforcement, $t$ is equivalent to half of the layer thickness and $\chi$, is work rupture.

Budiansky et al., (1988) theoretically investigated the fracture toughness of a composite material reinforced with ductile metal particles. Budiansky and Co-workers developed an expression for the toughening ration by employing elastic springs, elastic-plastic springs and rigid-plastic springs for the bridges (Figures 20). These are formed in the wake of crack and subsequent propagation through a ceramic material.

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For small-scale bridging, the extent of ductile phase toughening can be expressed as

$$K_c = K_m + \Delta K_b = K_m + \sqrt{\frac{2}{\pi \alpha \nu}} \int_0^b \frac{\sigma_\nu}{\sqrt{x}} \, dx$$  \hspace{1cm} (62)
Where $K_m$ is the matrix fracture toughness, $x$ is the distance behind the crack tip and $L$ is the bridge length. Toughening ratio due to small-scale bridging (under monotonic loading) is expressed as:

$$
\lambda_0 = \frac{K_c}{K_m} = 1 + \frac{1}{K_m} \sqrt{\frac{2}{\pi}} \alpha \left( \frac{\sigma_y}{\mu} \right) \frac{dx}{\sqrt{x}}
$$

(Li and Soboyejo, 2000; Lou and Soboyejo, 2001)

Also, toughening due to small-scale bridging by ductile phase reinforcements may be idealized using elastic-plastic spring model (Budiansky et al., 1983; Evans 1988; Rose, 1987).

$$
\lambda = \frac{K}{K_m} = \left[ 1 + \frac{\sigma_y^2}{KK_m} (1 + \frac{2\mu_p}{\mu_y}) \right]^{1/2}
$$

($K_m$ is the matrix toughness, $\sigma_y$ is the uniaxial yield stress, $\mu_y$ is the crack face displacement, $K$ is a dimensionless spring-stiffness co-efficient, $\mu_p$ is the total plastic displacement to failure.

$$
\Delta K_h = (\lambda - 1)K_m
$$

For the case of a rigid-plastic spring, when the critical plastic value of the difference between the crack face displacement at yield, the toughening ratio is given as
\[ \lambda = \left[ 1 + \frac{2E\sigma_{y}\mu_{p}}{K_{m}^{2}(1-v^{2})} \right]^{1/2} \]  

(66)

Fett and Munz (1994) through investigation revealed that on large-scale bridging, the 
shielding \( \Delta K_{\text{lab}} \) may thus be expressed as

\[ \Delta K_{\text{lab}} = \int_{L} \alpha\sigma(x)h(a,x)dx \]  

(67)

Where \( L, \) is the length of the bridge zone, \( \alpha \) is a constraint or triaxiality factor, \( \sigma(x) \) is a 
traction function along the bridge zone and \( h(a,x) \) is a weight function given by Fett and 
Munz (1994):

\[ h(a,x) = \frac{2}{\sqrt{\pi a a W}} \sqrt{\frac{1}{(1-x/a)^{v+1}}} \left[ 1 + \sum_{\nu,\mu} A_{\nu,\mu}(a/w) (1-x/a)^{v+1} \right] \]  

(68)

Where \( a, \) is the crack length and \( W, \) is the specimen width. Fett and Munz co-efficients, \( A_{\nu,\mu}, \) 
are given in Table 4 below for a single-edge notched bend specimen.
Figure 22 - Schematic of weighted/distributed bridging tractions.

Table 4 - Summary of Fett and Munz (1994) Parameters for Single-Edge Notched Bend Specimen Subjected to Weighted Crack Bridging Fractions

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu )</td>
<td>0</td>
<td>0.4980</td>
<td>2.4463</td>
<td>0.0700</td>
<td>1.3187</td>
</tr>
<tr>
<td>1</td>
<td>0.5416</td>
<td>-5.0806</td>
<td>24.3447</td>
<td>-32.7208</td>
<td>18.1214</td>
</tr>
<tr>
<td>2</td>
<td>-0.19277</td>
<td>2.55863</td>
<td>-12.6415</td>
<td>19.7630</td>
<td>-10.986</td>
</tr>
</tbody>
</table>

Total stress intensity factor, \( K_c \), may be estimated from linear superposition (\( K_c = K_m + \Delta K_b \)) and the toughening ratio for large-scale bridging can be determined from \( K_c / K_m \).

2.6.6.3 Crack-tip blunting
As crack tips move from brittle to ductile phase, they can be blunted, Figure 23(a). Crack tip blunting may also occur via de-bonding along the interface of a composite, Figure 23(b). Critical strain is usually used in understanding crack growth in ductile phase. This assumes that fracture occurs when the strain at a characteristic distance from the crack-tip exceeds a
critical value. When the crack-tip is blunted by a ductile phase, the critical strain value is increased by the presence of a ductile phase, Figure 23(b).

Figure 23 - Schematic illustration of (a) crack-tip blunting by ductile phase and associated change in crack-tip stress fields, and (b) crack-tip blunting by de-bonding along two-phase boundary. (Courtesy of Dr. Fan Ye.)

Chan (1992) in their micromechanical developed model for the near-field effective strain distribution for composite in a ductile-phase reinforced brittle matrix composite could be described by the Hutchinson-Rice–Rosengren (HRR) field.

2.6.6.4 Visco-elastic Toughening
McNaney et al. (1999) investigated the effect of viscous grain bridging on cyclic fatigue-crack growth in monolithic ceramics subjected to elevated temperature conditions. They
developed a micro-mechanical model for modelling crack-tip shielding under cyclic mechanical loading. The model accounts for microstructural parameters, viscosity, and thickness of the grain-boundary film, load frequency, cyclic load amplitude, and load ratio. The shielding was due to crack bridging via the viscous response of a grain boundary phase. The bridging forces are transmitted across the crack via the shear resistance, \( \tau \), of the grain boundary phase.

At the crack surface field, \( \sigma(z,t) \), two components are usually considered; far-field stress \( \sigma_T(z,t) \) and thermal shock bridging stress \( \sigma_B(z,t) \) opposing thermal stresses.

Implies

\[
\sigma(z,t) = \sigma_T(z,t) - \sigma_B(z,t)
\]

(69)

Figure 24 – McNaney (1999) bridging model

McNaney (1999) assumes that bridging effect arises from viscous stresses resisting the relative movement of the grains extending across crack opening. The grains across COP are
with dimension, $P$, $h$, in the z-direction and $w$, normal to the plane of the COP. The viscous bridging stress is modelled as

$$
\sigma_B(z,t) = \frac{2L_f}{\delta h} \eta \left( 1 + \frac{h}{w} \right) p u \left( 1 - \frac{2u}{p} \right)
$$

(70)

$\delta f$ is the separation between adjacent grains and $\eta$ is viscosity of the glassy inter-granular phase. $L_f$ is a covering pre-factor to allow for partial covering of the COP by the granular lath bundles.

Adopting the above normalization,

$$
\tilde{\sigma}_B(z,t) = 2L_f \left( 1 + \frac{h}{w} \right) \left( \frac{p}{h} \right) \left( \frac{H}{E} \right) \left( \frac{\eta}{E \Gamma} \right) \frac{d u}{dt} \left( 1 - \frac{2H \alpha \Delta T \tilde{u}}{p} \right)
$$

(71)

Where $\tilde{\sigma}_B(z,t) = \frac{\sigma_B(z,t)}{E \alpha \Delta T}$, $\tilde{u}(z,t) = \frac{u(z,t)}{H \alpha \Delta T}$, and $t$ is time normalized by $\Gamma$.

It is important to note that when $U(z,t) > p/2$; Laths are no more in contact with solid. This means the bridging length, $L_B$, has an upper bound over which the viscous bridging can occur. Also, when

$$
\frac{2H \alpha \Delta T \tilde{u}}{p} \approx 1
$$

(72)
Crack opening is comparable to grain length, p. Normalized COP at maximum opening under parabolic assumption is given by

$$u(z,t) = 2\sqrt{2} \frac{K_m(a)}{K_p} \sqrt{\frac{z}{H} - 1 + \frac{a}{H}}$$

(73)

Note:

$$H - a \leq z \leq L_b + H - a$$; when $$z = L_b + H - a$$; is put into equation (73) to obtain the upper bound for bridging length. The integro-differential equation for crack opening profile in the presence of thermal shock and viscous bridging is obtained using Fett and Munz (1994) expressions.

$$u(z,t) = \frac{1}{H} \int_{H-a}^{z} w(z,H-\xi) w(\zeta,H-\xi) \left[ \bar{\sigma}_T - \bar{\sigma}_B \right] \, d\zeta \, d\xi$$

(74)

Where

$$\bar{\sigma}_B = \begin{cases} 
2\gamma \frac{du}{dt} (1 - 2\mu u), & H - a \leq z \leq H - a + L_b \\
0, & H - a + L_b < z \leq H 
\end{cases}$$

And $$\gamma$$ and $$\mu$$ are two dimensionless constants that relates the macrostructure variables brick half height and thermal relaxation time, $$\Gamma$$, is the grain dimensions, $$P$$, $$h$$, and $$w$$, are viscous relaxation time of the inter-granular glassy phase $$\eta / E^*$$. 

$$\gamma = L_f \left(1 + \frac{h}{w}\right) \left(\frac{P}{h}\right) \left(\frac{H}{\delta}\right) \left(\frac{\eta}{E^* \Gamma}\right)$$

(75)
\[ \mu = \frac{H \alpha \Delta T}{p} \]  

(76)

The Integro-differential equation is most often than not solved numerically to obtain a self-consistent solution for the COP.

Soboyejo et al., (2001) reported on the role viscous crack bridging plays (in the reduction of the crack growth driving force) on the high temperature refractory during thermal shock. Thermal cycling at peak temperatures of 1150°C and 1500°C and down quench temperature of 400°C was done. They conducted fracture toughness tests to determine the changes in the fracture toughness with temperature by subjecting a single edge notch (SEN) specimens to a three-point bend loading at various temperature (25°C, 400°C, 650°C, 900°C, 1150°C, and 1500°C). They observed viscous glassy phases in the fracture surfaces (Figure 2.18). Furthermore, Soboyejo et al., 2001, then suggested cracking/damage due to thermal shock may be alleviated by incorporating an additional amount of glassy phases into the starting powder of the samples they used for testing. They also suggested that bridges are visco-elastic in nature, and idealized bridges using a spring-dashpot model (Maxwell model). The model suggest that the relaxation time of the bridges can be controlled via the Young’s modulus, E and the viscosity, \( \eta \) \((\tau = \eta/E)\), where the relaxation time is a measure of the time the initial stress, \( \sigma_0 \), in the material reduces to zero if a linear decay having a slope comparable to the initial slope, \( d\sigma_0/dE \), were retain from time, \( t = 0 \) to time \( t = \tau \).
Figure 25 - Photomicrograph showing crack bridging by viscous glassy phase (Soboyejo, 2001).

Other toughening mechanisms such as crack deflection, crack trapping and Micro-Crack Shielding and anti-shielding are well considered (Soboyejo 2003).


Evans and Charles (1977) studied the behaviour of pre-crack ceramics in high temperature condition. They analysed a number of factors but with emphasis on crack length, specimen
geometry and thermal properties. Using AlO$_3$ and ZrO$_2$ cylindrical test pieces, they investigated un-crack ‘green’ bodies critical fracture temperatures before proceeding to pre-crack temperatures. The quenching was done in a salt solution. The crack extensions were also recorded along other physico-mechanical properties.

The Figures 26 and 27 are important results relating the minimum crack length to prevent the propagation of crack of pre-cracked ceramic cylinders.

![Figure 26](image)

**Figure 26** – Crack length as a function of approximate analytical method with equivalent finite result showing the effects of crack density.
Figure 27 – Plot of relative minimum crack length, $a_{\text{min}}/r_0$, needed to prevent crack propagation in pre-cracked cylinders showing size effects.
Swain (1990) also studied the degradation of thermal shocked of ceramic composite, alumina-zirconia, by using the R-curve approach. He utilized a simplified fracture mechanics approach from which elastic modulus decreases with strain and resulted in a significant reduction of the peak stress intensity factor during thermal shock. The R-curve behaviour of micro-cracks represents the crack growth resistant of a dominant crack resulting from coalescing of multiple parallel cracks subjected to severe thermal environment (Gogosti, et al., 1976; Bahr, et al., 1986; Bahr, et al., 1987; Soboyejo, 2003).

The effect of the crack length on stress intensity factor, K, of a thermally shocked cylindrical ceramic specimen is shown in figure 2.9. Also showed is the flexural strength reduction trend that results from the thermal shock and the influence of specimens size dependencies are as shown in Figure 29-31.
Figure 29 - Calculated values of the thermal-shock generated stress intensity factor for 2-mm-radius bars of the alumina-zirconia material subjected to a $\Delta T = 500^\circ$C. The two curves are calculated on the basis of the dynamic modulus $E_0$ and tangent modulus with the Biot modulus ($\beta$) = 15.
Figure 30 - The influence of specimen size ($r_0$) on the thermal-shock generated stress intensity factor for constant $\Delta T = 600{^\circ}C$. 
Figure 31 - Comparison of the applied stress intensity factor for a through-thickness crack in flexure of beams of various thicknesses. Also shown is the superimposed R-curve and crack arrest positions.

For the larger specimens, more significant strength degradation is predicted. Among the main outcomes of Swain (1990) study was that as the strain increased, there was a sharp decrease in the elastic modulus. This leads to a remarkable reduction in the peak stress intensity factor for specimens subjected to thermal shock.
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CHAPTER THREE

3.0 STATISTICS OF FLOW AND THE SCALE-UP OF CLAY CERAMIC WATER FILTERS

3.1 INTRODUCTION

It is estimated that 1.8 million deaths per year and 61.9 million disability adjusted life-years are attributed to the drinking of unsafe water and poor sanitation (WHO/UNICEF 2000). The World Health Organization (WHO) also suggests that over 99.8% of the deaths are caused by unsafe water, sanitation and hygiene in developing countries (WHO/UNICEF 2000). Furthermore, in developing countries most of the childhood mortality occurs in children that are less than five years old (WHO/UNICEF 2004).

Those who have access to improved water may also experience contamination between the source and the point-of-use. Hence the key is to ensure that people have access to improved water at the point-of-use. This is crucial for the achievement of the Millennium Development Goals (MDG) of halving the number of people without access to improved water supply and sanitation by the year 2015 (WHO/UNICEF 2004). To achieve this target, it is important to explore point-of-use water purification methods (Murcott 2006; Sobsey 2002) that can improve the health and well-being of people in rural/urban areas in the developing world.

Several point-of-use treatment systems (Murcott 2006; Sobsey 2002) can be used to provide microbiological, chemical or physical water treatment. They include: (i) disinfection (chlorination, solar disinfection (SODIS) (Liu and Fitzpatrick 2010); solar pasteurization; UV irradiation with lamps, and boiling), (ii) particle filtration (cloth fiber; ceramic filter, bio-sand and other slow sand filter technologies) (Heather et al. 2010; Yakub et al. 2013); (iii)
adsorption media (granular activated carbon, and activated alumina, clay) (Liu and Fitzpatrick 2010; Yakub and Soboyejo 2013); (iv) combined system (combined flocculation and disinfection, filtration) (Liu and Fitzpatrick 2010; Preston et al. 2010) and (v) other approaches (plain sedimentation settling, safe storage, flocculation with iron or alum salts, membrane processes) (Preston et al. 2010; Davies et al. 2010). Within the range of possible water treatment methods, water filters are one of the highly rated systems for the removal of turbidity (Van Halem et al. 2009; Brown et al. 2009; Brown et al. 2010), fluoride removal (Yakub and Soboyejo 2013) and bacteria inactivation (Van Halem et al. 2009; Brown et al. 2009; Brown et al. 2010; Oyanedel-Craver and Smith 2008, Yakub et al. 2013). Filters are advantageous because they are relatively inexpensive (Van Halem et al. 2009; Brown et al. 2009).

Ceramic water filters are produced from a mixture of clays and sawdust. The mixtures are then moulded into pot shapes using steel moulds that are subjected to hydraulic pressure. After drying, the green bodies are treated at ~ 850°C (Yakub and Soboyejo 2013; Yakub et al. 2013; Van Halem 2006). During the heating process, the carbonaceous materials are burnt at temperatures between 400 and 500°C and sintered between 800°C and 900°C (Yakub and Soboyejo 2013; Yakub et al. 2013; Van Halem et al. 2009; Brown et al. 2009; Brown et al. 2010; Oyanedel-Craver and Smith 2008; Van Halem 2006). They are then furnace-cooled (to minimize thermal shock) and dipped in water for 24 hours. After dipping to saturation, the filters are soaked in colloidal silver or silver nitrate (Yakub and Soboyejo 2013; Yakub et al. 2013; Van Halem et al. 2009; Brown et al. 2009; Brown et al. 2010; Oyanedel-Craver and Smith 2008; Van Halem 2006) to introduce a coating layer that disinfects microbial pathogens (Dies 2003). Although the use of ceramic water filters has been promoted by Non-
Governmental Organizations such as Potters for Peace (Liu and Fitzpatrick 2010), our current understanding of the flow and permeability in ceramic water filters is limited (Liu and Fitzpatrick 2010; Dies 2003; Lantagne 2003; Swanton 2008).

Prior work on flow through porous ceramic water filters has been carried out by Van Halem 2006, Yakub 2012, Yakub et al. 2013, Schweitzer et al. 2013, and Bear 1972. The Darcy equation (Bear 1972) is very instrumental in flow studies. Van Halem et al. 2009, Yakub 2012 and Yakub et al. 2013 used Darcy flow concepts to model the flow through porous ceramic water filters. Yakub 2012 also considered the flow through the sides and base of the frustum-shaped ceramic water filters. Flow characteristics of frustum-shaped ceramic water filters with varying sawdust content to clay were also studied by Yakub et al. 2013. However, the earlier models did not fully explore the statistical variations in the Darcy flow parameters and the applicability of the Darcy flow model under scenarios in which the filters are used multiple times.

The most recent publication on flow modelling, Schweitzer et al. 2013, deduced equations that can be used to compute the flow rate of frustum- and parabolic-shaped ceramic water filters (with uniform thickness of side and bottom). They performed tests on ceramic water filters for three runs (every 8 hours per day). This indeed suggested that, barring clogging, increasing the frequency of loading of the filter or runs may increase the volume of water produced. The hydraulic conductivities obtained in their work (k =1.2 x10^{-7} m/s for parabolic-shaped ceramic water filters and k = 0.78 x 10^{-7} m/s for frustum-shaped ceramic water filters) were found to be comparable to previous estimates in literature (Oyane-Craver and Smith, 2008; Van Halem, 2006).
However, the dependence of flow rate on permeability or the hydraulic pressure head has not been statistically fully explored under enough multiple loadings or runs. Therefore, the objectives of the paper are to: (a) explore and expand variations in flow rate (in the first hour) values and permeability (in the first hour) values for 20 runs of six frustum-shaped ceramic water filters; (b) give an insight into the spread of flow rate (in the first hour) values and permeability (in the first hour) values using statistical distribution tools; (c) understand the behaviour or spread of the mean flow rate values and effective permeability values using statistical tools within the context of Darcy’s equation and (d) assess the scale-up potential of the ceramic water filters in serving a community. The implications of the results are then discussed.

3.2 CERAMIC WATER FILTER MATERIALS AND PRODUCTION
Two types of clays were used in the fabrication of the filters. They are ‘Ewuya’ and ‘Iro’ which were mined from Abeokuta in southern Nigeria. The ‘Ewuya’ is a high plastic clay compared with the ‘Iro’. The sawdust was obtained from nearby carpentry workshops wood chippings in Abeokuta. Similarly clays were also sieved mixed with sieved sawdust. It was sieved through 1mm pores. The Clay types are treated to powdered form and mixed in required percentages. Biodiversity (in this case sawdust) and water are added and moulded into frustrum shape [11]. The molded shapes then dried for two weeks before firing. At around 500°C all the sawdust was burnt out leaving behind micro-pores in the filter. Figure 4 gives images of the fabrication process. The filter element is usually impregnated with colloidal silver for disinfection purposes, before distribution to customers.
3.3 Porous Material Characterization

X-ray diffraction (XRD) analysis was carried out on as received clays and also on the sintered product. Using XPERT-PRO diffractometer (PANalytical BV, Netherlands) with theta/theta geometry, the system was operated in a cobalt tube at 35 kV and 50 mA. The goniometer was equipped with automatic divergence Slit and a PW3064 spinner stage. The XRD patterns of all specimens were recorded in the 10.0°-50° 2θ range, with a step size of 0.017° and a counting time of 14.1565s per step. Qualitative phase analysis was conducted using the X’pert HighscorePlus search match software (PANalytical B.V, ALMELO, The Netherlands).

X-ray fluorescence (XRF) spectroscopy of the clay samples was also conducted to determine the chemical compositions. The XRF data was collected using Thermo Fisher ARL9400 XP+ Sequential XRF spectrometer equipped with a WinXRF software. The samples were powdered in a tungsten-carbide milling pot to achieve particle sizes less than 75micron. The samples were dried at 100°C and roasted at 1000°C to determine Loss On Ignition (LOI) values. 1g Sample was mixed with 6g Lithium tera-borate flux and fused at 1050°C to make a stable fused glass bead. For trace element analyses the sample was mixed with a PVA binder and pressed into a pellet using a 10ton press.
3.4 **Flow Experiments**
The ceramic water filters were soaked in water for 12 hours prior to the flow experiments. This was done to avoid transient flow phenomena during the early stages of the flow experiments. Each saturated ceramic water filters were then mounted in the receptacles and filled with 9 Liters of water at the start of the experiments. The flow through the filters was then measured by recording the volume of water discharged from the ceramic water filter after each hour. In this section, six frustum-shaped ceramic water filters of the same clay:sawdust composition were tested. Each time, the flow rate and water level are measured for consecutive 12 hours. Statistical analysis was performed on flow rates (in the first hour), mean flow rates and estimated permeability values.

3.4.1 Statistical Experimental study
The flow experiments were performed 20 times to determine the variability in the flow parameters which were fitted using the modified Darcy equation for frustum-shaped ceramic water filters. In this way, the permeability values and their standard deviations were obtained along with the tested statistical distributions that may characterize the measured flow rates.

3.4.2 Scale-up of Ceramic Water Filters
The scale-up filtration system experiments were conducted to explore the feasibility of filtering water on a larger scale to potentially serve a community. Five ceramic water filters were connected in series with a pipe, thus having common discharged outlet. The system had a main supply that was filled with water and is connected to the filtration system. Each ceramic water filter is initially ensured to be full with 9 Liters of water before start of timing. The volume of water that flowed out of the common outlet at every hour time interval is
recorded and this was continued for 12 continuous hours. The results obtained in this experiment are recorded in Figure 9.

3.5 RESULTS AND DISCUSSIONS
3.5.1 X-ray Diffraction and X-ray Fluorescence Analysis

The XRD diffraction patterns obtained for the clays are presented in Figure 2.0. These show the minerals in Ewuya and Iro. The Ewuya clay contained mostly kaolinite, and silica while the Iro clay has silica, mica and montmorillonite prior to firing. However, after firing, the fired clays were found to contain allophone (Aluminum silicate hydrate and potassium silicate hydroxide), Figure 3.0.

The chemical compositions of Ewuya and Iro clays are presented in Table 1. These shows that the Ewuya clay contained ~74.43 wt % SiO₂, 11.46 wt % Al₂O₃, 4.51 wt % Fe₂O₃, 1 wt % TiO₂, 1.13 wt % K₂O and trace amounts of MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, Cr₂O₃ and NiO. The Iro clay contained 61.88 wt % SiO₂, 15.14 wt % Al₂O₃, 8.84 wt % Fe₂O₃, 0.8 wt % TiO₂, 0.84 wt % K₂O, and trace amounts of MnO, MgO, CaO, Na₂O, P₂O₅, Cr₂O₃, and NiO. Hence the major difference between the Ewuya and Iro was in the Al₂O₃ and SiO₂ contents. The more plastic Iro clay had a higher Al₂O₃ content of ~15.14 wt % compared to the Ewuya clay that contained ~11.46 wt % Al₂O₃. Conversely, the Iro clay contained ~61.88 wt % SiO₂ compared to the Ewuya clay that contained ~74.43 wt % SiO₂. Hence, the mixing of the Ewuya and Iro clays produced a composite clay with intermediate silica and alumina contents that optimized the plasticity and the thermal shock resistance of the clay mixtures during hydraulic pressing and sintering, respectively.
3.5.2 Flow Through Ceramic Water Filters

The mean flow rates obtained for the 20 runs for each ceramic water filter of the six ceramic water filters that were tested are presented in Figures 3 (a-f). The individual flow rates were found to be between ~ 1.4 and ~ 3.0 L/hr during the first hour of the flow. However, the flow rates decreased with increasing time. This was due to the decrease in the hydraulic pressure and possibly clogging or unclogging for increasing flow durations (Van Halem 2006, Schweitzer et al. 2013, Yakub 2012). The measured flow rate variations are presented in Figure 3 for different durations with their analytical modelled plot. These show clearly that the flow rates vary significantly as a function of time and variations in the individual filters. Also, for a single ceramic water filter, no clear trend was observed for measured flow rate from one run to the next run, over the entire 20 runs. Furthermore, the variations in the flow rates would be expected to result in variations in the permeabilities extracted from the overall flow data (Yakub and Soboyejo 2013; Yakub et al. 2013; Davies et al. 2010; Brown et al. 2009; Brown and Sobsey 2010; Oyanedel-Craver and Smith 2008; Van Halem 2006).

The mean flow rate of water discharge for the six filters was 2.3 L/hr during the first hour of discharge. The effective permeability of each ceramic filter was also obtained by fitting the measured flow rate data to equation 4. The permeability values for the six filters were found to be between ~ 0.44 x 10^{-14} m^2 and ~ 2.54 x 10^{-14} m^2, with an average value of 1.19 x 10^{-14} m^2 (hydraulic conductivity, \( k \) is 1.46 x 10^{-7} m/s). The average effective permeability value is found to be very comparable to permeability values found for ceramic water filters from Cambodia (1.37 x 10^{-7} m/s) and Ghana (1.3 x 10^{-7} m/s) in Van Halem’s 2006 work. Also the average effective permeability computed is well within the hydraulic conductivity range (1.15 x 10^{-7} m/s to 5.01 x 10^{-7} m/s) obtained by Oyanedel-Craver and Smith 2008 for three ceramic
water filters. Furthermore, Yakub et al. 2013 found permeability values between $\sim 0.1 \times 10^{-14}$ m$^2$ to $5.0 \times 10^{-14}$ m$^2$. There exists a linear dependence of the flow on the permeability which therefore suggests that the effective permeability approach captures the trends in the flow rate data.

Variability in the permeabilities and flow rates are presented in histograms in Figure 4 (a-f) and Figure 5 (a-f), respectively, for the six filters that were each tested over 20 runs. In each case, the filters exhibited statistical variations attributable to pore clogging and unclogging, and changes in crack sizes within the porous structures (Schweitzer et al. 2013, Van Halem 2006; Dies 2003; Yakub 2012; Plappally et al. 2011). The variations in the flow rates were found to be reasonably characterized by normal distributions that fitted the measured experimental data. The distribution of the flow rate (in the first hour and mean), and permeabilities (in the first hour and mean) obtained for 20 runs are fairly normally distributed and this is confirmed using Kolmogorov-Smirnov Normality test, ORIGIN PRO software statistical tool (OriginLab Co-operation, Northampton, Massachusetts-U.S.A.).

Furthermore, the average flow rates obtained for the six filters were found to increase with increasing permeability values. At the 0.05 level, all data drawn for flow rate (in the first four) and the permeabilities were significantly normally distributed. Ceramic water Filters F4 and F6 were found to have effective permeability P-values fairly close to the chosen 0.05 alpha value. This, therefore, depicts a weak dependence in terms of the distribution being normally distributed. The mean flow rate P-values of ceramic water filter F6 was found to be 0.03 and thus, failed normality test. Table 2 and 3 give the P-values computed using
Kolmogorov-Smirnov Normality test, ORIGIN PRO software statistical tool (OriginLab Co-operation, Northampton, Massachusetts-U.S.A).

3.5.3 Scale-up Potential of Ceramic water Filters

The scale-up filtration system experiments conducted suggest that it is possible to scale up the number of water filtration systems to serve communities. For five ceramic water filters connected in series, average flow rate of 7 Liters per hour in the first hour. The system was able to produce a total volume of 23 Liters of water, with decreasing water-head, within the first 5 hours (check Figure 9.0). Fig. 8 shows the arrangement of ceramic water filters for the multiple filter studies. The cumulative water discharge over time obtained are plotted in Fig. 9. Average flow rate of 7 L/hr (in the first hour) was found for five ceramic water filters connected in parallel. Therefore, with an average flow rate of 7 Liters per hour (L/hr) and considering the World Health Organization (WHO) guidance for daily safe drinking water 2 Liters per day, the volume of water that flowed out of the common outlet (at maximum water-head for 10 continuous hours, 7 L/hr x 10 hrs =70 L) can serve a community of 35 people. Such a system will prove capable of producing safe drinking water for eight different (four members) households for a day. Even with decreasing water-head for continuous 12 hours, the average flow rate was 4.5 L/hr, producing 37 L volume of water (extrapolation from Figure 9). Based on the parameters obtained from this study, at maximum water-head for 10 hours, a community of five hundred and twenty five (525) people could be served by 15 multiple-filter systems. These 15 systems should be located at accessible positions in the community. It is important to well characterize the individual ceramic water filters of the multiple-filter system in terms of flow. Moreover, the number of filters used in the multiple-filter system can be increased to serve even larger communities. The results obtained from
the current work, therefore, suggest the possibility of having a combined multi-filter system that is connected to water obtained from a bore-hole or a polluted source. However, one problem with such multi-filter systems is that, if one ceramic water filter unit is cracked or not functioning well, the entire water discharged is contaminated. Furthermore, as a way of reducing the total number of ceramic water filters in multiple-filter systems, larger ceramic water filters can be produced. These can be designed by considering the fracture toughness, pressure induced strength and Darcy’s flow equation. The key condition for operation without fracture would be to ensure that the stress intensity factor, $K$, applied to the cracks in the ceramic water filters are less than the fracture toughness ($K_{IC}$).

3.6 IMPLICATIONS
The implications of the above results are quite significant. First, they show that the variations in the flow rates across the water filters are well characterized by normal distributions during the first hour of flow. Furthermore, the effective permeability values associated with the 20 consecutive flows through filters under investigation were well characterized by normal distributions. This suggests that 20 consecutive filter tests can be used to establish the variabilities in the initial flow rates and permeabilities of the filters. The initial flow rates are easier to estimate, especially within rural village settings in which ceramic water filters are used. However, they do not capture the overall trends in the flow over the period of discharge. Hence, the effective permeabilities are needed to determine a material parameter that captures the effective flow through the porous structures of the filters. However, these require more detailed analyses of flow data that are probably well beyond the capabilities of most ceramic water filter factory engineers. Hence, simple softwares are needed to enable
engineers to establish the variabilities in the effective permeabilities and effective applications in quality control.

In any case, the correlations established between the effective permeabilities and the flow rate after the first hour suggest that either the permeability or flow rate approach may be used to characterize and test the filters. Further work is clearly needed to characterize the statistical variations in the flow rate parameters at different stages of the filter life. There is also a need to establish the acceptable variances in filter flow rates and permeabilities over 2-3 year periods in which most ceramic water filters are expected to provide filtered water at rates between ~ 1 and ~3 Liters per hour. These are clearly the challenges for future work.

3.7 CONCLUSION
This paper presents the results of combined analytical and experimental study of flow through frustum-shaped ceramic water filters (CWFs). The statistical variations in flow rates were found to be well described by normal distributions. The average flow rate were 2.12 Liters per hour for first hour use, while the permeabilities (in the first hour) were between ~ 3.0 x 10^{-14} \text{ m}^2 and ~ 10.3) x 10^{-14} \text{ m}^2. The flow through frustum-shaped ceramic water filters was well described by Darcy’s equation. The results suggest portable water can be obtained by adopting filter testing methods that involve the use of 20 tests in the establishment of the statistical variations in flow rates and effective permeabilities for effective filter quality control. The average flow rate and effective permeabilities were found to be well characterized by the normal distribution. The linear dependence between of flow rates (in the first hour) on the measured permeabilities suggests that filter quality may be assessed using either flow rate or permeability measurements.
The multiple ceramic water filter study also shows that a combination of filters may be used to provide drinking water for communities of different sizes. Since the overall flow rates from multiple filter systems scale with the number of filters, the filters sizes and the number of filters can be scaled to provide adequate drinking water for communities. Furthermore, the multiple filters can be placed in strategic locations within the rural communities to provide easy access to safe drinking water in rural/urban communities in the developing world.
REFERENCES


FIGURES

Figure 1: Schematic diagram of Ceramic water Filter

Figure 2: X-Ray diffraction (XRD) patterns of clays showing peak minerals identified: (a) Ewuya Clay, (b) IRO Clay, and (c) Fired Clay

Note: P – Kaolinite, Q – Silica, R – Silica, S – Mica, T – Montmorillonite, U - Aluminum silicate hydrate, V - Potassium aluminum silicate hydroxide

Figure 2: X-Ray diffraction (XRD) patterns of clays showing peak minerals identified: (a) Ewuya Clay, (b) IRO Clay, and (c) Fired Clay
Figure 3 ((a)-(f)): Experimental and analytical flow rate plots of ceramic water filters (a) filter, F1, (b) filter, F2, (c) filter, F3, (d) filter, F4, (e) filter, F5, (f) filter, F6.
Figure 4 (4a-4f): Permeability (in the first hour of 20 runs) distribution of ceramic water filters
(a) filter, F1, (b) filter, F2, (c) filter, F3, (d) filter, F4, (e) filter, F5, (f) filter, F6.
Figure 4 ((a)-(f)): Permeability (in the first hour) distribution of ceramic water filters (a) filter, F1, (b) filter, F2, (c) filter, F3, (d) filter, F4, (e) filter, F5, (f) filter, F6.
Figure 5 ((a)-(f)): Flow rate (in the first hour) distribution of ceramic water filters (a) filter, F1, (b) filter, F2, (c) filter, F3, (d) filter, F4, (e) filter, F5, (f) filter, F6.
Figure 6 ((a)-(f)): Relation between flow rate and permeability of ceramic water filters in the first hour ((a) filter F1, (b) filter F2, (c) filter F3, (d) filter F4, (e) filter F5, (f) filter F6).
Figure 7((a – (b)): Histogram with normal distribution fit curve of flow rates for ceramic water filters F1 to F6
Figure 8 ((a)-(f)): Histogram with normal distribution fit curve of effective permeabilities for ceramic water filters F1 to F6.
Figure 9: Volume of water produced via scale-up system

TABLES

Table 1: X-ray fluorescence (XRF) of Clays

<table>
<thead>
<tr>
<th>% COMPOSITION</th>
<th>EWUYA CLAY</th>
<th>IRO CLAY</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>74.43</td>
<td>61.88</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.00</td>
<td>0.80</td>
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<tr>
<td>Al₂O₃</td>
<td>11.46</td>
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</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.51</td>
<td>8.84</td>
</tr>
<tr>
<td>MnO</td>
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</tr>
<tr>
<td>MgO</td>
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<td>1.19</td>
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<td>CaO</td>
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</tr>
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<td>Na₂O</td>
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<td>K₂O</td>
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<td>P₂O₅</td>
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<td>0.01</td>
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<tr>
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<td>NiO</td>
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<td>&lt;0.01</td>
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<td>ZrO₂</td>
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</tr>
<tr>
<td>CuO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
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<tr>
<td>Loss on Ignition (L.O.I)</td>
<td>6.12</td>
<td>10.20</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.47</td>
<td>99.93</td>
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Table 2 (a) – Statistical test analysis of ceramic water filters (F1- F6) in the first hour

<table>
<thead>
<tr>
<th>Filter Parameter</th>
<th>Filter 1, F1</th>
<th>Filter 2, F2</th>
<th>Filter 3, F3</th>
<th>Filter 4, F4</th>
<th>Filter 5, F5</th>
<th>Filter 6, F6</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>K1</td>
<td>Q1</td>
<td>K2</td>
<td>Q2</td>
<td>K3</td>
<td>Q3</td>
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<tr>
<td>P-Value</td>
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<td>0.40</td>
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<td>Normality Test</td>
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<td>PNT</td>
<td>PNT</td>
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<tr>
<td>$R$-squared Value</td>
<td>0.76</td>
<td>0.98</td>
<td>0.94</td>
<td>0.93</td>
<td>0.84</td>
<td>0.97</td>
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</table>

Table 2 (b) – Statistical test analysis of ceramic water filters (F1-F6) for average flow rate and effective permeability

<table>
<thead>
<tr>
<th>Filter Parameter</th>
<th>Filter 1, F1</th>
<th>Filter 2, F2</th>
<th>Filter 3, F3</th>
<th>Filter 4, F4</th>
<th>Filter 5, F5</th>
<th>Filter 6, F6</th>
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<tbody>
<tr>
<td></td>
<td>K1</td>
<td>Q1</td>
<td>K2</td>
<td>Q2</td>
<td>K3</td>
<td>Q3</td>
</tr>
<tr>
<td>P-Value</td>
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<td>0.18</td>
<td>0.56</td>
<td>0.35</td>
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<tr>
<td>Normality Test</td>
<td>PNT</td>
<td>PNT</td>
<td>PNT</td>
<td>PNT</td>
<td>PNT</td>
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<tr>
<td>Pearson’s $r$</td>
<td>0.26</td>
<td>0.61</td>
<td>-0.41</td>
<td>-0.31</td>
<td>0.36</td>
<td>0.07</td>
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</table>

Note for tables 2 (a) and 2 (b):

- Pearson’s $r$ – Pearson’s correlation co-efficient between average flow rate and effective Permeabilities.
- Normality test verified at an alpha, $\alpha$-value of 0.05.

(a) Filters; F1-F6 are porous clay ceramic water filters.
(b) Kn, (where n is an integer 1-6) are permeability histogram data in the first hour of flow experiment.
(c) Qn, (where n is an integer 1-6) are flow rate histogram data in the first hour of flow experiment.
(d) PNT – Passed Kolmogorov- Smirnov Normality test.
(e) FNT – Failed Kolmogorov- Smirnov Normality test.
(f) $R$-squared – Linear fit correlation numeric measure between Kn and Qn.
CHAPTER FOUR

4.0 COMPARATIVE FLOW STUDY OF FRUSTUM- AND DISK- SHAPED CERAMIC WATER FILTERS

4.1 INTRODUCTION
Household water treatment and safe storage (HWTS) technologies can be cost-effective interventions to improve household drinking water quality for the 783 million people that do not have access to an improved water source (Clasen et al. 2007; WHO/UNICEF 2012). An estimated 1.2 billion more people drink water that is at risk of contamination at the source or during collection, transportation or storage (Clasen et al. 2007; WHO/UNICEF 2012). This could be mitigated by HWTS. Locally manufactured ceramic "pot" water filters (CWFs) are as considered one of the most promising HWTS technologies (CDC 2008a). CWFs mostly have approximately 8 to 10L capacity, silver-treated ceramic filtering elements that suspend in a safe storage container that is fitted with a tap for dispensing treated water.

In laboratory investigations, CWFs have been reported to effectively remove >99% of protozoan (Lantagne 2001; van Halem 2006) and 90-99.99999% of bacterial organisms from drinking water (Lantagne 2001; van Halem 2006; Brown and Sobsey 2010, Yakub et al. 2013). Filter use has also been associated with a 49% reduction in diarrheal disease among users (Brown et al. 2008; Plapally et al. 2009) as well.

Filters are manufactured by pressing a mixture of locally-sourced clay and a burn-out material, such as sawdust or rice husk, into the filter shape. After pressing, filters are allowed to dry before being fired into a ceramic state (~800-900°C). The specific ratio of clay to burn-out material is determined during factory establishment by testing prototype filters for
flow rate and microbiological efficacy. Throughout production, each filter’s flow rate is measured and filters that meet the factory-established acceptable flow rate are packaged for sale or distribution. Silver is added as a bacteriocide, either by application to fired filters or included in the filter mixture. This is currently done in 52 factories worldwide (CMWG 2011).

Manufacturing practices vary widely both among and within factories (CMWG 2011). Hence, there are variations in 1) filter shape, 2) flow rate testing and 3) bacterial de-activation testing. To address quality control concerns, the Ceramics Manufacturing Working Group (CMWG) - comprising of individuals from governmental and non-governmental organizations, filter factories, filter consultants and academia have developed “Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment” to guide factories in manufacturing efficacious filters (CMWG 2011; Rayners et al., 2013). The CMWG recommends research to understand the effects of different burn-out materials with regards to quantity and particle size on filter pore size and structure, total pore area, porosity, hydraulic conductivity and bacterial de-activation.

Some research articles that use Darcy’s equation as a fundamental equation for the modeling of flow through CWF include: Fahlin 2003; Miller 2009; Peabody 2009; Elmore et al., 2011; Eriksen 2011; Yakub et al., 2013; Schweitzer et al., 2013. These models are also shape dependent. Hence, the models by Van Halem 2006; Yakub et al., 2013 and Schweitzer et al., 2013, are for frustum-shaped filters, while the remaining are either for parabolically-shaped or cylindrically-shaped ceramic water filters. However, in the case of disk ceramic water filters, there are relatively low publications (Lee 2001; Dianjun et al., 2013) is sparse.
The objectives of this research are to: (a) understand the effects of sawdust particle size on flow through disk ceramic water filters; (b) explore the effects of firing temperature on the flow rate of water through ceramic water filters and (c) compare the flow rate of disk and frustum-shaped ceramic water filters of the same recipe. The chapter also includes: an analytical model for prediction of flow rate in frustum-shaped ceramic water filters using disk-shaped ceramic water filters as surrogates. Finally, the chapter has statistical analysis of the variations in flow rate values and permeability (in the first hour) values obtained for 20 runs on disk-shaped ceramic water filters. The implications of the results are discussed for applications of ceramic water filter.

4.2 MATERIALS AND METHODS
4.2.1 Processing of Ceramic Water Filters

Three sets each of frustum-shaped and three sets of disk shaped filters were processed by Potters Without Borders (Enderby, Canada). Clay, kyanite and sawdust were measured by weight (Kg) in the ratio of 74.75:10:15.25. Spruce pine and fir sawdust was twice screened with either US sieves 16/30 or 30/60. Frustum-shaped filters and disk-shaped filters were then produced with 16/30 sawdust that was fired to 880°C. One set of filters and disks was also manufactured with 30/60 sawdust. These were fired to 880°C and the other to 950°C. The mixture clay ad sawdust were dry mixed for 10 minutes, then approximately 35% water by weight was added gradually, before further mixing for ~15 minutes. A 20-ton hydraulic press was then used to press filters and disks with 44.82MPa (6500psi) and 53.78MPa (7800psi) (piston diameter, 0.06m; piston area, 0.0025 m²) filters with burn-out material sieved with 30/60 and 16/30 mesh, respectively. Filters of the same batch were fired together
in a 30 cubic foot insulating firebrick, natural gas fuelled, downdraft kiln for 10 hours to peak temperature, followed by a one-hour soak.

4.2.2 Flow Experiments

Frustum-shaped and disk-shaped ceramic water filters were saturated in deionized (DI) water for 24 hours before starting the flow experiments. Each saturated frustum-shaped ceramic water filter was filled with approximately 10L prior to the start of flow experiment. The disk-shaped ceramic water filters were filled to same hydraulic level (1000 ml of de-ionised water). Flow was inferred from effluent measurement that were carried out with a scale (AD50 & AD100, TORBAL Clifton, New Jersey, U.S.A.) connected to a computer with ProCell software. The mass of water was transferred to Excel (Microsoft Corporation, Redmond, WA, U.S.A.) every minute until the filters emptied as determined by the reduction in water mass. Flow through the filters was measured initially in triplicate. Subsequently, flow through selected disk ceramic filters were then repeated for 20 loadings. In all, three conditions but six disk-shaped filters were selected; two of each 30/60 at 950°C, 30/60 at 880°C and 16/30 at 950°C (Table 1). The flow rate and permeability in the first hour was computed and recorded, and the normality of the data was investigated.

4.3 **Modeling of Flow through Disk- and Frustum-Shaped Ceramic Filters**

In 2006, Van Halem compared the flow characteristics of frustum shape ceramic water filters from Ghana, Cambodia and Nicaragua. She deduced flow rate equations for the bottom (equation 1) and sides (equation 2) of frustum shaped ceramic water filter.
\[ Q_b = k \frac{\pi r_b^2 h_w}{t_b} \] (1)

\[ Q_s = 2\pi \frac{k}{t_s} \left[ \frac{(r_1 - r_2)}{6L} h_w^3 + \frac{1}{2} r_2 h_w^2 \right] \] (2)

The flow rate equation (3) for the frustum-shaped ceramic water filter was then obtained by summing equation (1) and equation (2).

\[ Q(m^3/\text{s}) = \frac{\pi k}{t_s} \left[ \frac{(r_1 - r_2)}{3L} + r_2 h_w^2 \right] + \frac{\pi k}{t_b} \left[ r_2^2 h_w \right] \] (3)

where \( Q \) is the flow rate of the frustum shaped ceramic water filter, \( Q_s \) flow rate of the side, \( Q_b \) is the flow rate of the bottom section of the frustum-shaped ceramic water filter, \( t_s \) is the thickness of the filter wall, \( t_b \) is the thickness of filter bottom, \( r_1 \) is the radius at the top of the filter, \( r_2 \) is the radius at the bottom of the filter, and \( k \) is the hydraulic conductivity.

Schweitzer et al. 2013 and Yakub et al. 2013 also considered frustum shaped ceramic water filters. They obtained equations 4 and 5, respectively as the flow rate expressions. These are given by:

\[ Q = \frac{\pi h(t)}{t} \left[ r_o^2 + h(t) + \frac{1}{3} \tan \phi(h(t))^2 \right] \] (4)

where \( h(t) \), the water-head is a function of time, \( t \); \( r_o \) is the bottom radius of frustum-shaped filter, \( \phi \) is the angle of inclination at the corners for Frustum-shaped filters and the other constants have their usual meaning.

\[ Q = \pi h \left[ \frac{r_o^2}{t_o} + \frac{r_o^2}{t_s} + \frac{h^2 \tan \phi}{3t_s} \right] \] (5)
The rate at which the water height decreases with time, \( \frac{dh}{dt} \) can be determined analytically. The expression for flow rate, \( \frac{dh}{dt} \), was obtained for frustum-shaped ceramic water filters was deduced by Schweitzer et al. 2013. Following similar approach, \( \frac{dh}{dt} \) expressions for Van Halem 2006 and Yakub et al. 2013 were obtained. The \( \frac{dh}{dt} \) expressions for Schweitzer et al. 2013, Van Halem 2006, and Yakub et al. 2013 models are given by equations (6), (7) and (8) respectively.

\[
\frac{dh(t)}{dt} = -\frac{kh}{d} \frac{1/3 \tan \phi h^2 + r_o h + r_o^2}{\tan^2 \phi h^2 + 2r_o \tan \phi h + r_o^2}
\]  

(6)

\[
\frac{dh}{dt} = kh \left[ \frac{(r_i - r_o)^2 h^2}{L^2 + 2r_o (r_i - r_o) h + r_o^2} \right]
\]  

(7)

\[
\frac{dh}{dt} = kh \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3 t_s} \right]
\]  

(8)

Note that all the \( \frac{dh}{dt} \) equations were deduced by combining the equations for the flow rate, radius of filter at any height, and the geometry of the frustum-shaped filter (given by equation 9).

\[
\frac{dV}{dt} = \pi (r_n(t))^2 \frac{dh}{dt}
\]  

(9)

where the \( r_n \) is the radius of the frustum-shaped filter at any height. Equations (6), (7) and (8) were solved numerically via Euler’s method or Excel iteration. The height at any time, \( t \) was
then substituted into the respective flow rate expression to obtain the analytical flow rate values. The final is estimated via reducing the sum of the squares of the differences.

The disk-shaped ceramic water filter has a flow rate expression that is the same expression given in equation (1). Equation (1) is re-arranged in equation (10), assuming the following:

(i) hydraulic conductivity of disk is same as that of the frustum-shaped ceramic water filter,
(ii) thickness of the disk, t_d, is equal to thickness of side walls of frustum-shaped filter, t_s, and
(iii) the hydraulic conductivity of the bottom section of the frustum-shaped filter is equal to hydraulic conductivity of the side walls of the frustum-shaped ceramic water filter.

\[
\frac{Q_d}{r_d^2 t_d} = \pi k h
\]  

(10)

Note that t_d = t_s; k_d = k_f = k; and r_d is the radius of the disk. Substituting equation (10) into flow rate expressions of the three models: Schweitzer et al. 2013, Van Halem 2006 and Yakub et al. 2013 gives the equations (11) - (13) respectively.

\[
\frac{Q_f}{Q_d} = \left( \frac{1}{r_d^2} \right) \left[ r_o^2 + r_o h + \frac{h^2 \tan \phi}{3} \right]
\]  

(11)

\[
\frac{Q_f}{Q_d} = \left( \frac{1}{r_d^2} \right) \left[ \left( r_f - r_o \right) h^2 + \frac{r_o h}{3L} \right] + \left[ \frac{r_s^2 t_d}{t_b} \right]
\]  

(12)

\[
\frac{Q_f}{Q_d} = \left( \frac{t_d}{r_d^2} \right) \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3 t_s} \right]
\]  

(13)

Equations (11) – (13) were used for predicting the flow rates for the disk ceramic water filter and the frustum-shaped. Detailed proof is given in section 2.3 (and Appendix) of this thesis.
The experimental flow data for the manufactured ceramic water filters and discs was compared to each selected model by plotting in Excel and generation of $R^2$ values. Student’s t-tests were performed against the experimental flow data to determine statistical difference. Flow data for discs was compared to the bottom flow rate ($Q_b$). An equation relating flow between disc and filter flow was derived and assessed against the flow rate data by plotting in Excel and generation of $R^2$ values.

### 4.4 RESULTS AND DISCUSSIONS

#### 4.4.1 Models and Frustum-Shaped Ceramic Water Filters

The modeled flow in the first hour ranged from $1.77 \pm 0.73$, $1.97 \pm 0.92$, and $1.78 \pm 0.78$ Liters/hour for van Halem, Schweitzer et al., and Yakub et al., respectively, across all tests (Figure 1). The 16-30:880°C filters account for the majority of the standard error.

The experimental flow ranged from $1.92 \pm 0.11$, $1.28 \pm 0.04$ and $2.80 \pm 0.17$ Liters/hour in the first hour for 30-60:950°C, 30-60:880°C and 16-30:880°C full-sized filter sets, respectively. The low standard deviation between triplicate filter tests suggests manufacturing variability within each filter set was limited, although highest in the larger sieve size filters. The first-hour experimental flow data were significantly different between the three sets ($p<0.001$). Experimental first hour flow rates were higher in filters made with larger burn-out material and higher firing temperatures. The modeled one hour filter model fit was 48% - 52%, 72-77% and 51-66% for 30-60:950°C, 30-60:880°C and 16-30:880°C full-sized filter sets, respectively. Ten hour full-size filter model fit was 5%, 7-8% and 5-
17% for 30-60:950 °C, 30-60:880 °C and 16-30:880 °C full-sized filter sets, respectively (Table 2).

Comparing modeled equations to experimental results, first hour experimental flow rates were consistently significantly different than all modeled (van Halem, Schweitzer et al., and Yakub et al., ) flow rates (p<0.05). The fit between the first hour models and experimental data varied by filter set, with the 30-60:800°C visually appearing to be a relatively good fit with the models, but deviating lower after one hour, and the other two sets deviating from the model within the first hour. Only 5-17% of full-size filter models data match experimental data using ten hour flows (Table 2).

4.4.2 Effects of Sieve Size and Firing Temperature on Flow Rate for Frustum-shaped Ceramic Water Filter

Larger sieve sizes lead to larger pore spaces in the filter, thereby leading to higher flow rates. The temperature regime of sintering and the rate of firing could affect the average pore size in the ceramic water filter. These inherent parameters which directly affect flow through ceramic water filters were not accounted for in the models. The effect of the sawdust size or sieve size was observed to be pronounce than the effect of the sintering temperature. Also, it was seen that all flow models fit better with 30-60:880°C (average 36% of flow within 20% error from experimental), followed by 16-30:880°C (average 29% of flows within error) and finally 30-60:950°C (average 21% of flows within error). This suggests that understanding the influence of the type and size of clay, burnout material used, and firing temperature on the resulting hydraulic conductivity, and the homogeneity of that value across a single filter, would provide a more reliable model.
4.4.3 Modelled Relationship for Disk and Frustum-shaped Ceramic Water Filters

The experimental disk flow ranged from 0.18 ± 0.005, 0.11 ± 0.005, and 0.24 ± 0.008 Liters/hour in the first hour for 30-60:950 °C, 30-60:880 °C and 16-30:880 °C filter sets, respectively (Figure 2). The low standard deviation between triplicate disk tests suggests manufacturing variability within each filter set was limited. Experimental disk first-hour flow values for 30-60:950 °C, 30-60:880 °C and 16-30:880 °C disk filter sets were all significantly different (p<0.001). Experimental flow rates for disks were highest in the disks made with larger burn-out material and higher firing temperature. The modeled one hour disk filter model fit was 0%, 0-87% and 0-89% for 30-60:950 °C, 30-60:880 °C and 16-30:880 °C full-sized filter sets, respectively. Ten hour disk filter model fit was 0-35%, 32-66% and 0-99% for 30-60:950 °C, 30-60:880 °C and 16-30:880 °C full-sized filter sets, respectively (Table 2).

The ratio of flow rate for frustum-shaped ceramic water filter to the flow rate of disk-shaped ceramic water filter for the set of filters are given in Table 2. The expressions deduced are promising because of its ability to nearly predict the flow rate during the first hour of the flow through the ceramic water filters. Table 4 presents data obtained for the flow rate through disk and frustum-shaped filters during the first five hours.

4.4.4 Multiple Flow and Disk ceramic water filters

The time dependence of flow rate obtained from the six filters (three recipes) that were studied are presented in Figures 1(a). The flow rates were observed to vary between 0.1L/h
to 0.15 L/h. The flow rates (in the first hour) were also observed to vary between 0.16 L/h to 0.28 L/h. The filters DF3 and DF4 (Table 1) had the slowest flow rate (in the first hour) value, 0.098 L/h, as compared to 0.14L/h for filters DF1 and DF2; 0.15 L/h for filters DF5 and DF6. The hydraulic conductivities (for the first hour) obtained for the disk-shaped ceramic water filters investigated ranged from 0.09 cm/h to 0.17 cm/h. Disk-shaped ceramic water filters of the same recipe were observed to have hydraulic conductivity values very close to each other.

For each specific disk-shaped filter, a very small increase in flow rate was observed from one loading to the next. This was observed over the entire 20 runs. This may be due to macro-erosion of particles of the fired clay mixtures within the pore structure. It may also lead to a gradual increase in the pore size over a long time. This is consistent with observation by Schweitzer et al. 2013, who have suggested that, barring clogging, increasing the frequency of loading may increase the volume of water produced.

Figures 2 and 3 show the variability of flow (in the first hour) and hydraulic conductivity (in the first hour) respectively. They were obtained for flow through six disk ceramic filters (three recipes/sets) tested over 20 loadings. The histogram obtained for each ceramic water filter exhibited statistical variations due to possible changes in pore sizes and or minor cracks within the pore structure (Schweitzer et al., 2013; Van Halem 2006; Yakub et al., 2013; Annan et al., 2014) are presented in Figure 2 and Figure 3. With the exception of the hydraulic conductivity (in the first hour for the 20 runs) of disk ceramic filter DF6, the remaining disk ceramic filters had both flow rate and hydraulic conductivity (in the first hour) that were reasonably characterized by normal distribution (Table 3). Table 5 shows that DF1 to DF6 mean flow rates (over the entire 20 loadings) passed the normality distribution test at
a chosen 0.05 alpha level. The P-values computed using Kolmogorov-Smirnov normality test (via OriginPRO software statistical tool) results of the flow rates and k are presented in Tables 4 and 5. The P-value obtained for the flow rate through DF6 (in the first hour) was 0.06; nearly failed the normality test.

4.5 IMPLICATIONS
The implications of this research are significant. First, it provides flow rate data for disk-shaped and frustum-shaped ceramic water filters that were produced from same recipe for three sets. This brings to the fore the effect of dust particles (especially insoluble) on flow rate. The cleanliness of the room and filters are also important in the filtration process. Hence, the need for users of ceramic water filters to adhere to hygienic conditions, possibly clean cloth over the section where the filter is positioned.

Secondly, the ratio obtained for comparing flow rate of disk-shaped filter to frustum-shaped filter using experimental data is reasonably comparable to the analytical ratio flow rate for the same recipe/set. This implies the equations deduced can be used to estimate the flow rate of either disk filter or frustum-shaped filter and/or vice-versa. Water and environmental engineers may be able to come up with a flow rate data sheet for various combinations of clay ceramic materials of disk-shaped and Frustum-shaped ceramic water filters. This would be great assistance to manufactures of ceramic water filters who would like to produce other shaped filters and has no idea about flow rate adherence to WHO standard. It does give potential for scaling with bands/banks of disks. Engineers can provide series or parallel connection of disk-shaped filters that may be produce same quantity of portable water.
Finally, the use of disk-shaped ceramic water filters will more appealing to urban residents. Packaging for disk-shaped ceramic water filters would be easier and nicer, considering the shape than the frustum-shaped ceramic water filter. This will encourage the wider user of ceramic water filters and thus potential lower cost of disk-shaped filters.

Furthermore, with regard to comparing models for flow through frustum-shaped size ceramic water filter, Yakub et al., model was observed to contain some improvements from the Schweitzer et al., model and therefore higher level of accuracy. These improvements include: (1) generalization of the equation to add differential side and bottom wall thickness, and (2) adding calculation of a range of hydraulic conductivity values from $h(t)$, which allowed results to better approximate experimental flow. As manufacturing variables can influence the hydraulic conductivity of resultant filters, and that models such as the Yakub et al., model which calculate a variable hydraulic conductivity have greater accuracy. The earliest model, van Halem did not contain these improvements, and also lacked an assessment of the filter slope. Thus, the relatively poorer performance is not surprising. Newer filter models have shown increasing accuracy, suggesting that further development of ceramic filter models might provides more representative results for flow rate in full-size and disk filters.

### 4.6 Conclusion and Future Work

This chapter presents the results of a combined experimental and theoretical study of flow rates through disk-shaped and frustum-shaped ceramic water filters. Analytical expressions were obtained for the flow rates by assuming Darcy’s flow. The resulting expression was shown to appreciably predict the flow rates of the full size filter using the disk ceramic water filter as a surrogate.
The flow through disk ceramic water filters for (multiple loadings) increases with increasing number of runs during the first 20 runs. The statistical variations in the flow rate and the permeability are also well described by the normal distributions for the disk-shaped ceramic water filters examined in this study. The flow rates (in the first hour) were also found to range between 0.16 L/h and 0.28 L/h for the disk-shaped ceramic water filters, while, the hydraulic conductivities (for the first hour) of the disk ceramic water filters investigated ranges from 0.09 cm/h and 0.17 cm/h. The average flow rate was found to range from 0.09 L/h to 0.16 L/h for the disk-shaped ceramic water filters.

Future research on theoretical flow models should work to improve the quality of the models with further refinement, including manufacturing variable terms. Future experimental testing of filter and disk flow should be conducted on a larger number of samples to verify the results herein, with a larger number of manufacturing variables, normal use and be conducted over a longer time from to capture the changing flow patterns over time.
REFERENCES


FIGURES AND TABLES

Table 1(a): Ceramic water filters description

<table>
<thead>
<tr>
<th>Filter Manufacturing Details</th>
<th>Disk-shaped Filter code</th>
<th>Frustum-shaped Filter code</th>
</tr>
</thead>
<tbody>
<tr>
<td>30/60 @ 950 °C</td>
<td>DF1</td>
<td>FF1</td>
</tr>
<tr>
<td>30/60 @ 950 °C</td>
<td>DF2</td>
<td>FF2</td>
</tr>
<tr>
<td>30/60 @ 880 °C</td>
<td>DF3</td>
<td>FF3</td>
</tr>
<tr>
<td>30/60 @ 880 °C</td>
<td>DF4</td>
<td>FF4</td>
</tr>
<tr>
<td>16/30 @ 880 °C</td>
<td>DF5</td>
<td>FF5</td>
</tr>
<tr>
<td>16/30 @ 880 °C</td>
<td>DF6</td>
<td>FF6</td>
</tr>
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</table>

Table 1(b): Manufacturing variables in study disks and full-size filters.

<table>
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<th>Set Number:</th>
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<th>3</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
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<td>16/30</td>
<td>30/60</td>
<td>30/60</td>
<td></td>
</tr>
<tr>
<td><strong>Manufacturing Variables</strong></td>
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<td><strong>Firing Temperature (°C)</strong></td>
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<td>950</td>
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<td><strong>Disks</strong></td>
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Table 2.

(a) Percent of 1 hr and 10 hr model flows falling within 20% of the experimental flow for full-size filters, disks, and the disk-to-filter equations, respectively.

<table>
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<tr>
<th>Filter Code</th>
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<th>DF3&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF4&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF5&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF6&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>Disk ±20% Q&lt;sub&gt;exp&lt;/sub&gt;</td>
<td>Disk-to-Filter ±20% Q&lt;sub&gt;exp&lt;/sub&gt;</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>%, 1 hr</td>
<td>%, 10 hr</td>
<td>%, 1 hr</td>
<td>%, 10 hr</td>
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<td>%, 10 hr</td>
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<td>5</td>
<td>89</td>
<td>99</td>
<td>89</td>
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</tbody>
</table>

(b) Normality test analysis of disk ceramic water filters (DF1-DF6) for flow rate (in the first hour, Q<sub>n</sub>) and permeability, K<sub>n</sub> (in the first hour)

<table>
<thead>
<tr>
<th>Filter Code</th>
<th>DF1&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF2&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF3&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF4&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF5&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DF6&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Q&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Q&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>K&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Q&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>P-Value</td>
<td>0.97</td>
<td>0.87</td>
<td>1.00</td>
<td>0.82</td>
<td>0.24</td>
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</table>

<table>
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<tr>
<th>Normality Test</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
<th>PNT&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
</table>

Note: The normality test was verified at an alpha, α-value of 0.05.

Footnotes:
(a) Filters; DF1-DF6 are disk ceramic water filters.
(b) K<sub>n</sub>, (where n is an integer 1-6) are permeability histogram data in the first hour of flow.
(c) Q<sub>n</sub>, (where n is an integer 1-6) are flow rate histogram data in the first hour of flow experiment.
(d) PNT – Passed Kolmogorov-Smirnov Normality test.
(e) FNT – Failed Kolmogorov-Smirnov Normality test.
Table 3: Normality test analysis of disk ceramic water filters (DF1-DF6) mean flow rate values

<table>
<thead>
<tr>
<th>Filter Code</th>
<th>DF1(^a)</th>
<th>DF2(^a)</th>
<th>DF3(^a)</th>
<th>DF4(^a)</th>
<th>DF5(^a)</th>
<th>DF6(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Value</td>
<td>0.87</td>
<td>0.82</td>
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<td>0.50</td>
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<td>PNT(^b)</td>
<td>PNT(^b)</td>
<td>PNT(^b)</td>
<td>PNT(^b)</td>
<td>PNT(^b)</td>
<td>PNT(^b)</td>
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</tbody>
</table>

Note: The normality test was verified at an alpha, \(\alpha\)-value of 0.05.

Footnotes:

(f) Filters; DF1-DF6 are disk ceramic water filters.

(g) PNT – Passed Kolmogorov-Smirnov Normality test.

(h) FNT – Failed Kolmogorov-Smirnov Normality test.

Table 4: Comparative data for flow rate (in the first hour) of disk- and frustum-shaped Filters

(a) FF1 and DF1

<table>
<thead>
<tr>
<th>Time/hrs</th>
<th>Disk Flow Rate, Q</th>
<th>Frustum-Shaped , Q</th>
<th>Experimental Q Ratio</th>
<th>Modeled Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Van Halem</td>
</tr>
<tr>
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<td>1.85</td>
<td>9.7</td>
<td>11.3</td>
</tr>
<tr>
<td>2</td>
<td>0.18</td>
<td>1.64</td>
<td>9.1</td>
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</tr>
<tr>
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</tr>
<tr>
<td>5</td>
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(b) FF2 and DF2
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<tr>
<th>Time/hrs</th>
<th>Disk Flow Rate, Q</th>
<th>Frustum-Shaped, Q</th>
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<th>Modeled Ratio Van Halem</th>
<th>Schweitzer</th>
<th>Yakub</th>
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<tbody>
<tr>
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(c) FF3 and DF3

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<th>Modeled Ratio Van Halem</th>
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<th>Yakub</th>
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<tr>
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<tr>
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(d) FF4 and DF4
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<th>Van Halem</th>
<th>Schweitzer</th>
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(e) FF5 & DF5

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<th>Schweitzer</th>
<th>Yakub</th>
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(f) FF6 & DF6
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<th>Experimental Q Ratio</th>
<th>Modeled Ratio</th>
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<tr>
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<td>Van Halem</td>
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<td>0.28</td>
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<td>1.71</td>
<td>10.7</td>
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Figures
Figure 1 (a): Behaviour of mean flow rate of disk ceramic water filters for all sets/recipes

Figure 1 (b): Experimental flow rate ($Q_{exp}$) and models for recipes.
(a) DF1

(b) DF2
(c) DF3

(d) DF4
Figure 2: Histogram of flow rate (in the first hour) with normality fit curve for disk ceramic water filters
DF1

DF2
DF3

DF4
Figure 3: Histogram of hydraulic conductivity (in the first hour) with normality fit curve for disk ceramic water filters
(a) DF1

(b) DF2
(c) DF3

(d) DF4
(e) DF5

(f) DF6

Figure 4: Histogram of mean flow rate with normality fit curve for disk ceramic water filters
APPENDIX

Appendix 1: Deducing the dh/dt for models

(a). Van Halem 2006

\[ Q(t) = \frac{\pi kh}{t_s} \left\{ \frac{(r_i - r_o)h^2}{3L} + r_o h \right\} + \frac{k\pi_o^2 h}{t_b} \]  

(1)

The change in volume with time is equivalent to flow rate, that is

\[ \frac{dV(t)}{dt} = Q(t) \]  

(2)

\[ \frac{dV(t)}{dt} = \pi [r_c(t)]^2 \frac{dh}{dt} \]  

(3)

In Van Halem’s model, the variation in radius as the water level drops is given by

\[ r_c(t) = \frac{(r_i - r_o)z}{L} + r_o \]  

(4)

Equation (4) into (3) gives

\[ \frac{dV(t)}{dt} = \pi \left[ \frac{(r_i - r_o)z}{L} + r_o \right]^2 \frac{dh}{dt} \]  

(5)

Simplifying the above equation (5) and making dh/dt the subject gives

\[ \frac{dh}{dt} = \frac{Q(t)}{\pi \left[ \frac{(r_i - r_o)z^2}{L^2} + \frac{2r_o(r_i - r_o)z}{L} + r_o^2 \right]} \]  

(6)

Putting equation (1) into (6), we have the rate of change of the height

\[ \frac{dh}{dt} = k \left[ \frac{(r_i - r_o)h^2}{3t_i L} + \frac{r_o h}{t_s} + \frac{r_o^2}{t_b} \right] \]  

(7)
This differential equation can be solved numerically or by Euler’s method.

(b). Schweitzer et al 2013

\[
\frac{dh(t)}{dt} = -k h \left( \frac{1}{3} \tan \phi h^2 + r_o h + r_o^2 \right)
\]
\[
\frac{dh}{d \tan^2 \phi h^2 + 2r_o \tan \phi h + r_o^2}
\]

For full prove of \( \frac{dh}{dt} \) for equation (8) refer to Schweitzer et al 2013. However, the approach is same as in SI (c).

(c). Yakub et al 2013 (or Annan et al. 2014)

\[
Q(t) = \pi k h \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3t_s} \right]
\]
\[
r_z = r_o + z \tan \phi
\]

Equations (2), (3), (9) and (10) are combined to obtain

\[
\frac{dh}{dt} = \frac{Q(t)}{\pi [r_z(t)]^2} = \frac{\pi k h \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3t_s} \right]}{\pi [r_o + h \tan \phi]^2}
\]
\[
\frac{dh}{dt} = k h \left[ \frac{r_o^2}{r_o^2 + 2r_o h \tan \phi + \tan^2 \phi h^2} \right]
\]

**Appendix 2**: Modelling of relation between frustum-shaped and disk ceramic water filters

(a). Van Halem 2006
Where $r_1$ and $r_o$ are top and bottom radii of frustum-shaped filter, $t_b$ is the thickness of the bottom of the frustum-shaped ceramic filter; $t_d$ is the thickness of the disk filter.

Disk ceramic water filter flow rate expression

$$Q_d = \frac{k_d \pi r_d^2 h}{t_d}$$ (13)

Where $t_c = t_d$ ie thickness of disk = thickness of side, $r$ is the radius of the disk.

Re-arranging equation (13)

$$\frac{Q_d}{r_d^2} = \frac{\pi k_d h}{t_d}$$ (14)

Re-arranging (12) and putting in equation (14)

$$Q_f = \frac{Q_d}{r_d^2} \left\{ \frac{(r_1 - r_o)h^2}{3L} + r_o h \right\} + \frac{Q_d r_o^2 t_d}{r_d^2 t_b}$$ (15)

$$\frac{Q_f}{Q_d} = \frac{1}{r_o^2} \left[ \frac{(r_1 - r_o)h^2}{3L} + r_o h + \frac{r_o^2 t_d}{t_b} \right]$$ (16)

(b). Schweitzer et al. 2013

Expression of flow rate

$$Q_f = \frac{\pi k h}{t} \left[ r_o^2 + r_o^2 h + \frac{1}{3} h^2 \tan \phi \right]$$ (17)

Where $t$ is the thickness of side (which is assumed to be same as thickness of bottom), hydraulic conductivity, $k_s = k_b = k$; $r_o$ is the radius of the bottom of the frustum-shaped filter.

Putting equation (14) into equation (17) gives
\[
Q_f = \frac{1}{r_d^2} \left[ r_o^2 + r_o h + \frac{1}{3} h^2 \tan \phi \right]
\] (18)

(c). Yakub et al 2013 (or Annan et al. 2014)

\[
Q_f = \pi k h \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3 t_s} \right]
\] (19)

Re-arranging equation (13) and noting that \( t_d = t_s; k_d = k_f = k \)

\[
\frac{Q_f t_d}{r_d^2} = \pi k h
\] (20)

Put equation (20) into (19)

\[
\frac{Q_f}{Q_d} = \left( \frac{t_d}{r_d^2} \right) \left[ \frac{r_o^2}{t_b} + \frac{r_o h}{t_s} + \frac{h^2 \tan \phi}{3 t_s} \right]
\] (21)

The equations (16), (18) and (21) can be used to predict the flow rate of the disk filter depending on the model.

**Appendix 3**: Cumulative volumetric equations for the various models

Van Halem’s Model

\[
V(t) = \frac{\pi (r_i - r_o)^2 h^3}{3L^2} + \frac{\pi (r_i - r_o) h^2 r_o}{L} + \pi r_o^2 h
\] (22)

Schweitzer et al 2013 Model

\[
V(t) = \pi r_o^2 [h_o - h(t)] + \pi r_o \tan \phi [h_o - h(t)]^2 + \frac{\pi}{3} \tan^2 \phi [h_o - h(t)]^3
\] (23)
Yakub et al 2013 (or Annan et al. 2014) Model

This expression is same as in equation (23)

\[ V(t) = \pi \sigma_o^2 [h_o - h(t)] + \pi \sigma_o \tan \phi [h_o - h(t)]^2 + \frac{\pi}{3} \tan^2 \phi [h_o - h(t)]^3 \]  

(24)
CHAPTER FIVE

5.0 CLAY MIXTURES AND THE MECHANICAL PROPERTIES OF MICRO-AND NANO-POROUS CERAMIC WATER FILTERS

5.1. INTRODUCTION

Clays are ubiquitous materials and that are culturally accepted as building materials in most cultures (James 2009, Liu et al. 2010). In most cases, these include applications of porous clay ceramics as building blocks that also provide thermal comfort, as a result of their low thermal diffusivities (Sultan et al., 2002; Robinet et al. 1996; Soboyejo et al. 2001).

More recently, micro- and nano-porous clay ceramics have been developed for applications in water filtration, termed ceramic water filters (Yakub 2012; van Halem 2006; Lantagne 2001). They have also been shown to remove bacteria (Yakub et al. 2013; van Halem 2006) and chemical contaminants (Yakub and Soboyejo 2013) from contaminated water. There is, therefore, the potential to integrate giant porous ceramic water filters as in the form of buildings in urban/rural communities (Annan et al. 2014). Porous alumina-silicates also exhibit high melting points and can therefore be applied as refractory ceramics in metal melting industry (Bodsworth 1994).

Most of the early buildings in Africa were constructed from clay and silt (James 2009). The clay structural products, classified as traditional ceramics structures, were generally produced by forming/molding, drying and burning/firing (James 2009). These processes were facilitated by the control of clay mixtures with appropriate proportions of plastic and less plastic clays, water and binder materials.
Furthermore, after drying, the heating of the fine particles of the clay causes the particles to agglomerate into cohesive, much stronger, finished/sintered product. However, the shrinkage of clays and the effects of mechanical loads can induce cracking in such structures (Liu et al. 2010). Cracking can also be exacerbated by the effects of thermal cycling and the environment (Sultan et al., 2002; Robinet et al. 1996). These setbacks are often mitigated or solved by the addition of other materials such as cement, laterite, fibers, and also heating rate/regime.

Generally, in an effort to improve strength and fracture toughness of traditional ceramics, materials such as industrial waste materials example blast furnace slag (Savastano et al. 2001), agricultural waste materials (include natural fibres from sisal) Yan et al. 2000; Joseph et al. 1999; Zhong et al. 2007; Tan et al. 2012), banana trunk (Sapuan et al. 2007), eucalyptus trees (Tonoli et al. 2010), sugar cane bagasse (Ghazali et al. 2008; Monteiro et al. 1998; Teixeira et al. 2012) and millet (Adegunwa et al. 2014) are added. These improved strengths and fracture toughness are demonstrated by Maleque et al. 2007; Pavithran et al. 1987; 1988. Composite theories (Ritchie 1988; Evans 1990) and crack-tip shielding concepts have also been used, respectively, to explain the observed improvements in strength and fracture toughness.

The clay composite structure (CCS) has been applied to the design of porous ceramic filters that are used for water filtration (Van Halem 2006; Yakub et al. 2013; Lantagne 2001; V. A. Oyanedel-Craver, and J. A. Smith, 2008). These structures, which are often referred to as ceramic water filters (CWF), are generally produced from mixtures of clay, water and
sawdust. They are typically fired at about 850°C (Yakub 2012; Yakub et al. 2012). The sticky nature of the clay or mixture may also affect the strength and the mechanical robustness of the fired clay.

During the firing process of ceramic water filters, the carbonaceous material, sawdust, is burned out at temperatures of around 450-550°C, leaving behind a nano-/micro porous structure in the clay mixture matrix (Yakub et al. 2012). The nano-/micro-porous structures produced are capable of removing micro-organisms from water by geometrical occlusion/size exclusion process (Yakub 2012; van Halem 2006). Hence, it is important to optimize the clay proportions and thus, the strength of clay mixtures that are used in the production of clay composite structure (CCS) filters, without compromising flow.

Yakub et al. 2012, have studied the strength and fracture toughness of one clay composite condition. Nevertheless, van Halem 2006 expressed concern as to how cracks in CCS filters can be an avenue for micro-organism transport into filtered water. Also, Lantagne 2001, studied the causes of frequent breakages of the lips of clay composite structure (CCS) filters and suggested the following remedial actions: (a) Cautious use of CCS filters, since ceramics fracture and (b) the purchasing of extra CCS filters to allow for the replacement of broken filters.

Furthermore, prior research has shown that the flexural strength decreases with increasing grog content (Watter 2010). Plappally et al. 2011 have also used statistical regression modelling to develop mathematical relationships between the porosity and strength of clay ceramics. Indeed, Plappally and co-workers were able to relate the constituents of the
ceramic water filter to the mechanical properties (Yakub et al. 2012; Larson et al. 1974). Yakub 2012, also considered ceramic water filters with Redart clay with varying sawdust content. Yakub et al., 2012, also suggested that, as the porosity increases, the flexural strength decreases.

Beyond the molding stage, the thermal shock that is usually associated with the firing of clays can also affect the strength and fracture toughness of fired clays (Hasselman 1970; Larson 1974; Soboyejo et al. 2001). This is predominantly due to the formation and growth of cracks under thermal shock conditions. Such cracks can occur under down-quench (cold shock) or up-quench (hot shock) thermal shock conditions.

The thermal shock behaviour of fired clays has been shown to depend on material properties, such as the thermal expansion co-efficient, α, the thermal conductivity, λ, the thermal diffusivity, k, the Young’s modulus, E, the fracture toughness, KIC, the ultimate tensile strength (UTS), the heat transfer coefficient, h, specimen size, H, and the duration of thermal shock, t (Hasselman 1970). The effects of these parameters have been modelled in empirical thermal shock models (Baker et al. 2006; Saadaouï et al. 1991; Lou et al. 2002; Fett and Munz 1994; Budiansky et al. 1988; McNaney et al. 1999; Lu and Fleck 1998) and more recent fracture mechanics models (Saadaouï et al. 1991; Lou et al 2002; Fett and Munz 1994) over the past five decades.

However, although nano- and micro-porous CCS water filters undergo cracking due to thermal shock under firing and cooling conditions, the authors are not aware of prior studies of the thermal shock resistance of clays that are relevant to the processing of CCS water
filters. Furthermore, there have been no integrated efforts to determine the plasticity, strength, fracture toughness and thermal shock resistance of clay mixtures that are relevant to water filtration. This will be explored in this paper using a combination of experiments and models.

This paper will examine the mechanical properties of clay mixtures that are associated with the processing and application of porous clay filters. The clay mixtures will be produced from mixtures of plastic clays and less plastic clays. The plasticity studies will be used to identify the clay mixtures with adequate balance of plasticity and resistance to tearing during molding operations to form clay filters.

The thermal shock resistance of fired clay mixtures will also be studied to provide some insights to the underlying resistance of the clays to crack growth during the firing of porous clay mixtures for applications in clay ceramic water filters. The goal will be to identify the clay mixtures with the required balance of mechanical properties required for robust applications in sustainable buildings.

This paper is divided into five sections. Following the introduction, the materials and experimental methods are described in section 2. The models for the prediction of mechanical properties are then presented in section 3 before discussing the results in Section 4. Salient conclusions arising from this work are presented in section 5.
5.2 MATERIALS AND EXPERIMENTAL METHODS

5.2.1 Material Processing

5.2.1.1 Ceramic Water Filter Manufacturing

_Ewuya and iro_ clay were used in the fabrication of the ceramic water filters (Annan et al. 2014). They were mined in Abeokuta, Ogun State, in Southern Nigeria. The chemical compositions of the clays are given in Table 1. These clays were mixed with sawdust that was obtained from a saw mill in Sapon Market, Abeokuta, Nigeria. The clays and the sawdust were sieved through 1 mm pores. They were then mixed in the volume ratios of 50% clay to 50% sawdust. 2.0 Liters of water was added before molding the clay/sawdust mixtures into a frustum shape (Yakub 2012; Oyanedel-Craver and Smith 2008). The clay mixture proportions that were used in the fabrication of the ceramic water filters are summarized in Table 2).

The molded frustum shapes were air dried for two weeks before firing. The firing involved heating in a locally made clay kiln from room-temperature (~25-30°C) to 850°C. This was done at a rate of 45-100°C/hr. This was then followed by furnace-cooling to room-temperature in air. The temperature variations were measured with a type K thermocouple.

During heating, the sawdust was burnt off at a temperature of ~ 500°C (Yakub et al. 2012; Yakub 2012; Plappally et al. 2011). The initial heating rate of 45°C per hour was increased to 100°C per hour at temperatures above 500°C. After firing and furnace cooling, specimens for microstructural analyses and mechanical property measurements were fabricated from the ceramic water filters. The specimens were prepared by mixing clays according to proportions shown in Table 1.
Plasticity Index (PI)

The PI is a measure of the range of moisture content over which the soil remains plastic (Andrade et al. 2011; Atterberg 1911; Bekker 1981; Baran 2001). It is the numerical difference between the liquid limit (LL) and the plastic limit (PL) for a particular material. The Cassagrande device (Controls Testing Equipment Ltd, Hertfordshire, United Kingdom) was used to determine the PI of the different batches. The PI was determined from the following expression:

\[ PI = LL - PL \] (1)

where LL and PL are liquid limit and plastic limit of the clays, respectively. Standard test for LL, PL and PI of soils were closely followed as possible (ASTM Standard D4318). A detailed description of the method that was used for the determination of the plasticity indices of the clays can be found in reference (Andrade et al. 2011; Husein et al. 1999). Table 1 also gives the results of the PI determine various clay mixture proportions via the LL and PL values.

5.2.2 X-Ray Diffraction and X-Ray Fluorescence Analyses

X-Ray Diffraction (XRD) analysis was carried out on the as-received clays and the sintered clay mixtures. The XRD analysis was performed using a PANalytical X’ Pert Pro MPD diffractometer (PANalytical BV, Almelo, The Netherlands) with theta/theta geometry. The system was operated in a cobalt tube at 35 kV and 50 mA. The goniometer was equipped with an automatic divergence slit and a PW3064 spinner stage.
The XRD patterns of all the two primarily clay powders (Iro and Ewuya) and the fired clay powders/mixtures were recorded in the 10°-50°, 20 range, with a step size of 0.017° and a counting time of 14.1565s per step. Qualitative phase analysis was conducted using the X’pert Highscore Plus search-match software package (PANalytical B.V, ALMELO, The Netherlands).

X-Ray Fluorescence (XRF) spectroscopy was also used to determine the chemical compositions of the clay samples. The XRF data was collected using a Thermo Fisher ARL9400 XP+ Sequential XRF spectrometer that was equipped with the WinXRF software package (Thermo Fisher Scientific Inc., Ecublens, Switzerland).

The samples were milled in a tungsten-carbide milling pot to achieve particle sizes that were less than 75 microns. They were then dried at 100°C and roasted at 1000°C to determine the Loss On Ignition (LOI) values. A gram of the sample was mixed with 6g of Lithium Teraborate flux and fused at 1050°C to make a stable fused glass bead. For trace element analyses, the sample was mixed with a PVA binder and pressed into a pellet using a 10 tonne press.

5.2.3 Flexural Strength

The flexural strengths of the fired clay mixtures were measured in an Instron Model 3366 electromechanical testing machine (Instron, Canton, Massachusetts, United States America) instrumented with a 5 kN load cell. Rectangular specimens of dimensions (length, \( L=17.5\text{cm} \); breadth, \( B=2.5\text{cm} \), and width, \( W=1\text{cm} \)) were used. The edges of the rectangular specimens were polished to have straight edges and ensure uniformity during testing. The
Flexural tests were carried out at a displacement rate of 0.5 mm/min using a loading span, $S$, of 15 cm. The flexural strengths (modulus of rupture), $\sigma$, were determined from the following expression:

$$\sigma = \frac{3PS}{2BW^2}$$

(2)

where, $P$ is applied load at the onset of failure, $B$ is breadth, $W$ is depth or width, and $S$ is the loading span.

5.2.4 Fracture Toughness

Fracture toughness tests were performed on single edge notched bend (SENB) specimens. The experiments were carried out in an Instron 3366 electro-mechanical testing machine (Instron, Canton, Massachusetts-United States of America) at displacement rate of 0.5 mm/min. The peak load at fracture was recorded for the specimens had the same dimensions as the flexural strength specimens. However, fracture toughness specimens had initial notch-to-width ratios ($a/w$) of $\sim 0.45$. The fracture toughness was then computed from equation (3) (Yakub et al. 2012; Saadaoui et al. 1991).

$$K = \frac{PS}{BW^{3/2} \times f(a/w)}$$

(3)

where $P$ is failure load, $S$ is the loading span and $f(a/w)$ is given by:

$$f(\frac{a}{w}) = \frac{3(\frac{a}{w})^{3/2} [1.99 - (\frac{a}{w}) [1 - (\frac{a}{w})^3] \times [2.16 - 3.83 (\frac{a}{w}) + 2.7 (\frac{a}{w})^3]]}{2[1 + 2(\frac{a}{w})[1 - (\frac{a}{w})]^{3/2}}$$

(4)
5.2.5 Thermal Shock Experiments

The cold shock method (Baker et al., 2006; Saadaoui et al., 1991) was used to measure thermal shock resistance in this work. The specimens had dimensions (length, L=17.5cm; breadth, B=2.5cm, and width, W=1cm). They were heated to temperatures of 750°C, 850°C and 950°C at a heating rate of 10°C/min. The heated specimens were then cold shocked to a temperature of ~ 5°C in water.

After cold shock, the specimens were oven dried at 110°C to remove water molecules from closed pores. The residual strengths of the specimens were then measured using flexural strength measurements, which were carried out using procedures described previously in section 2.4. Other specimens were cold shocked for 5 cycles, 10 cycles, 15 cycles and 20 cycles. These were then tested to determine their residual strengths and fracture toughness values after thermal shock cycling.

5.3 MODELING

5.3.1 Modeling of Crack-Tip Shielding

The thermally-induced stresses (due to thermal shock) and the shielding contributions from the bridging ligaments can be modelled using fracture mechanics approaches. For cold quench conditions, the crack opening tractions exerted by the thermally-induced stresses (due to thermal shock) can be modelled using the approach of Lu and Fleck (Lu and Fleck1998). This gives:

\[ \sigma(z, t) = -E_\alpha \alpha(\Delta T) + \frac{E_\alpha}{2H} J^H_\alpha(z, t) \Delta T \]

(5)
where, \( H \) is half height of the specimen, \( E^* \) is the Young’s modulus in the presence of plane stress, \( \alpha \) is the thermal expansion coefficient over the shock temperature range and \( \Delta T \) is the change in specimen temperature.

The crack-tip shielding due to small-scale bridging can be determined from the expression (Soboyejo et al. 2001):

\[
\Delta K_{SSB} = \frac{\sqrt{2}}{\pi} \int_0^L \sigma(x) \sqrt{x} \, dx
\]  
(6)

Similarly, the crack tip shielding due to large-scale crack bridging can also be determined from the expression:

\[
\Delta K_{LSB} = \int_0^L \alpha \sigma(x) h(\alpha, x) \, dx
\]  
(7)

where, \( L \) is the length of the bridging zone, \( \alpha \) is a constraint/triaxiality factor, \( \sigma(x) \) is a traction function along the bridge zone, and \( h(\alpha, x) \) is a weight function, given by Fett and Munz, 1994.  

\[
h(\alpha, x) = \sqrt{\frac{2}{\pi \alpha}} \frac{1}{\sqrt{1 - \frac{x}{\alpha}}} \times \left[ 1 + \sum_{\nu, \mu} \frac{A_{\nu\mu}(\mu)}{(1 - \frac{x}{\alpha})} \left( 1 - \frac{x}{\alpha} \right)^{v+1} \right]
\]  
(8)

where \( a \) is the crack length and \( w \) is the specimen width.

In the case of the viscoelastic bridges at high temperatures, the shielding due to the viscoelastic bridging ligaments can be idealized using the approach of Baker et al. 2006 and
McNaney et al. 1999. The shielding due to viscoelastic crack bridging can be determined by incorporating the viscous bridging stress into the small scale bridging expression equation (6) or large scale bridging expression equation (7), depending on crack parameters. In this case, the traction function along the bridge zone is given by:

\[ \sigma(x) = \frac{L_\gamma \eta v(x)}{h} \left[ d - u(x) \right] \left( 1 + \frac{h}{\lambda_d} \right) \]  

where \( \eta \) is the viscosity of the bridging elements and known to vary exponentially with the inverse of the temperature, \( T \), that is \( \eta \propto \exp(1/T) \); \( d \) is the bridge height, \( h \) is the thickness and \( \lambda_d \) is the width of the bridge, \( v(x)=2du(x)/dt \) is the velocity.

Modeling of Viscoelasticity and Viscoelastic Crack Bridging

The microstructural analysis of the crack profiles for thermally shock clay composite specimens reveal the presence of viscoelastic bridges (Soboyejo et al. 2001; Baker et al. 2006; Rahbar et al. 2011). The viscoelastic bridges are often somewhat necked down as a result of the viscoelastic deformation that occurs under cyclic thermal effect (Soboyejo et al. 2001). It is, therefore, important to model the viscoelastic phenomenon that occurs under thermal cyclic conditions.

The viscoelastic bridging has been modeled by Soboyejo et al. 2001. This was accomplished by the use of spring and dashpot models assumed to be connected in series, referred to us Maxwell modelling of viscoelastic crack bridging. The Maxwell model is illustrated in Figure 1. In most studies of viscoelasticity, the time dependent of the glassy bridges can be modeled using appropriate combinations of springs and dashpots (Courtney et al. 1990 and Findley et al. 1989).
Baker *et al.* 2006 have used fracture mechanics to quantify the viscoelastic toughening of refractory ceramics. This model incorporates the material properties, microstructural variables and parameters of the viscoelastic bridges. Baker *et al.*, 2006 have derived a fully consistent solutions of the viscoelastic toughening levels for aluminosilicate refractory ceramics. This is for viscoelastic bridges with dimensions characteristic of the large scale bridging model (Rahbar *et al.* 2011). For a mode I crack of length, a, the stress intensity factor at the crack tip when assumed the temperature and the stress distributions are not affected by the presence of the crack is given by (Baker *et al.* 2006; Rahbar *et al.* 2011):

\[
\frac{K(z, t)}{K_0} = \frac{1}{\sqrt{\pi a}} \int_{-H}^{H} W(z, a) \sigma(z, t) \, dz
\]  

(10)

where \( K_0 = \sqrt{\pi H E \alpha \Delta T} \) is a normalizing constant for stress intensity, \( E \) is the Young’s modulus, \( 2H \) is the thickness of the plate, and \( W(z, a) \) is the weight function. Also, the normalized stress field, \( \overline{\sigma}(z, t) \), is given by:

\[
\overline{\sigma}(z, t) \equiv \frac{\sigma(z, t)}{E \alpha \Delta T} = 2 \sum_{n=1}^{\infty} \exp \left( -B_n z \alpha \Delta T \right) \frac{\sin \beta_n}{\beta_n} \left[ \cos \left( \beta_n z / H \right) - \frac{\sin \beta_n}{\beta_n} \right]
\]  

(11)

Where \( \Delta T \) is the temperature difference between initial temperature of the plate and the ambient temperature, and \( \beta_n \) arises from the imposition of homogeneous boundary conditions: \( \frac{\partial T}{\partial z} = \frac{\beta_n}{H} (\Delta T) \), at the lateral surfaces, \( z = \pm H \). The constant Bi is the Biot number which for infinite plate is found to satisfy, \( \beta_n \tan \beta_n = Bi \) (Lu and Fleck, 1998). A Biot number, Bi, of 10 was for the current experimental conditions.
The viscous bridging stress is modeled as a function of the crack opening displacement (COD) \( u(z,t) \) and the rate of change of the crack opening displacement (Baker \( et \) \( al. \) 2006). This is given by:

\[
\sigma_g(z,t) = \frac{2L_f}{\delta h} \eta \left(1 + \frac{h}{w}\right) \rho \ddot{u} \left(1 - \frac{2u}{p}\right)
\]

(12)

where \( L_f \) is a covering pre-factor to allow for partial coverage of crack opening profile and other terms have their usual meanings. Baker \( et \) \( al. \) 2006 have also shown that the normalized crack opening displacement can be expressed as:

\[
\ddot{u}(z,t) = \frac{u(z,t)}{H_0} = L(\ddot{\varphi}) - 2\gamma u(z)L\left(1 - 2\mu \ddot{u}\right)
\]

(13)

where \( L \) is the linear operator and the two dimensionless constants, \( \gamma \) and \( \mu \), relate the microstructural variable, plate half height and the thermal relaxation time \( \Gamma \).

## 5.4 RESULTS AND DISCUSSION

### 5.4.1 Chemical Compositions

The chemical compositions of the Ewuya and Iro clays are presented in Table 2. The major differences between the Ewuya and Iro clays are in their \( Al_2O_3 \) and \( SiO_2 \) contents. Ewuya clay contains \( \sim 74.43 \) wt. % \( SiO_2 \), 11.46 wt. % \( Al_2O_3 \) while Iro clay has 61.88 wt. % \( SiO_2 \), and 15.14 wt. % \( Al_2O_3 \). The more plastic Iro clay had a higher \( Al_2O_3 \) content of \( \sim 15.14 \) wt. % compared to the Ewuya clay that contained \( \sim 11.46 \) wt. % \( Al_2O_3 \). Conversely, the Iro clay contained \( \sim 61.88 \) wt. % \( SiO_2 \) compared to the Ewuya clay that contained \( \sim 74.43 \) wt. % \( SiO_2 \).\(^{20}\)
Hence, mixing of the Ewuya and Iro clays produced composite clays with intermediate silica and alumina contents that optimized the plasticity and the thermal shock resistance of the clay mixtures during hydraulic pressing and sintering, respectively. Figure 2((a) – (c)) shows X-ray diffraction patterns of the various samples and the resulting minerals identified by X’Pert High Score Plus software.

5.4.2 Flexural Strength

Table 3 shows the dependence of flexural strength on clay mixtures. The specimen IE5 (50% (Iro clay) batch that was sintered at 850°C had a flexural strength of 2.7 MPa. This is close to 2.88 MPa, which is the flexural strength of the clay batch IE9 (100% Iro clay). The specimen IE3 (30% of Iro clay) had flexural strength value which is greater than the flexural strength values of all the other batches. The maximum flexural strength, 3.21MPa was for IE3 (30% Iro Clay). The flexural strength was observed to increase from 2.22MPa for IE6 (60% Iro clay) to 2.88MPa for IE9 (100% Iro clay).

5.4.3 Youngs Moduli

The Young’s moduli obtained for IE5 (50% Iro Clay) at 850°C was 0.89 GPa (Table 2). The Young’s moduli of the sintered clay mixtures were observed to have increase with increasing Iro clay content up to IE6 (60% of Iro clay). The clay mixture, IE1 (100% Ewuya clay) had the lowest young’s moduli. This suggests that the clays with the high Iro clay content have higher moduli. No clear trend was observed for clay mixtures from IE7 (75% Iro clay) to 100% (Iro clay) clay mixtures.
Yakub et al. 2012, investigated strengths of porous ceramics with controlled porosity measurement. Their work showed that there is no clear relation between Young’s moduli and porosity. However, their Young’s moduli increased with decreasing average pore size. Also, the Young’s moduli and hardness values were not strictly functions of porosity, but depended on pore morphology, pore size distribution (and arrangement) and microstructure (Yakub et al. 2012).

5.4.4 Fracture Toughness

The measured fracture toughness values of sintered clay mixtures are presented in Table 2. This shows that the fracture toughness values of the fired clay mixtures vary with clay mixtures. IE5 (50% Iro Clay proportion) was found to have fracture toughness values of $0.18 \pm 0.01 \text{MPa} \sqrt{m}$ after sintering at 850ºC. The maximum fracture toughness value was found to be $0.24 \pm 0.01 \text{MPa} \sqrt{m}$ for IE3 (30% Iro clay). The fracture toughness values obtained for IE3 (30% Iro Clay proportion) to IE6 (60% Iro Clay proportion) after sintering 850ºC were between $0.15 \pm 0.02 \text{MPa} \sqrt{m}$ and $0.24 \pm 0.01 \text{MPa} \sqrt{m}$. Hence, increasing the Iro clay content has only a modest effect on the fracture toughness.

The clay mixture IE2 (15% Iro clay) had fracture toughness value of $1.12 \text{MPa} \sqrt{m}$. This value was observed to double for IE3 (30% Iro clay) fracture. This suggests that thorough clay mixing of the Ewuya and Iro clays were achieved, giving the mixture appreciable factors for effective sintering. As the Iro clay proportion increases, the mixture gradually loses its uniformity, thereby affecting properties of the sintered clay mixture (Plappally et al. 2011;
Yakub et al. 2012). Finally, it is important to note that specimen with 30% Iro clay had the highest fracture toughness, flexural strength and Young’s modulus.

5.4.5 Thermal Shock Behaviour

The dependence of residual flexural strengths on number of shock cycles is presented in Figure 3. Significant changes in residual strength were observed in all samples after the fifth cold shock cycle. Thereafter, smaller changes in the residual strength were observed as the number of shock cycles increased. The flexural strengths of the pristine specimens were found to be (2.78±0.14) MPa, (3.25±0.16) MPa and (2.42±0.12) MPa at firing temperatures of 750°C, 850°C and 950°C, respectively.

The flexural strengths (at a particular firing temperature) were observed to decrease with increasing number of quench cycles. The residual flexural strength values were observed to range (0.46±0.02)MPa to (3.25±0.16)MPa for 850°C firing temperature. Similar decreasing trend was observed in the cold shock specimens for both 750°C and 950°C. However, residual strength for cold shock specimens that were quenched from 950°C were lower than those that were quenched from 750°C or 850°C.

The above results suggest that, for the clays (Ewuya clay and Iro clay) that were used in this study, the optimum strength and fracture toughness of the fired clays can be achieved by sintering at ~ 850°C. The trends in the residual strengths may also be better understood by considering the role of the bridging ligaments that were observed in the wakes of the cracks that were formed after cold shock (Figures 5 – 7). These show clearly that bridging ligaments were formed in the cracks that were induced as a result of cold shock.
Similar bridged cracks have been observed in other aluminosilicate-based ceramics in prior work (Lou et al. 2002; Fett and Munz 1994; McNaney et al. 1999; Lu and Fleck 1998). These have also been shown to give rise to viscoelastic crack bridging at elevated temperatures (above the glass transition temperatures of glassy phases) in the clay ceramics, and elastic crack bridging below the glass transition temperatures (Saadaoui et al. 1991; Lou et al. 2002).

5.4.6 Modeling of Crack-Tip Shielding

The shielding due to viscoelastic crack bridging idealized by Baker et al. 1999 can be estimated by use of equation (6) and equation (7) depending on crack parameters. The estimated value was computed using data summarized in Table 4 and Tables 5 – 7. The results are presented in Figure 8. These show that crack tip shielding due to viscoelastic crack bridging decreases with increasing shock temperature, ΔT.

The trends in the computed crack-tip shielding levels explain the trends in the fracture toughness values of the cold shocked specimens presented in Figure 4. Similar results have also been reported by Rabhar et al. 2001, and Soboyejo et al. 2001. The computed crack tip stress intensity increases to a maximum before decreasing with increasing crack tip distance (Figure 9-11). Multiple cracks are observed in specimens fired at higher temperatures, Figure 7.

The residual room-temperature fracture toughness values may be explained by superposing the shielding due to room-temperature elastic crack bridging on the initiation fracture...
toughness or matrix fracture toughness. Hence, the residual strengths should correspond to the conditions at which the effective stress intensity factor (crack driving force) is equal to the matrix fracture toughness. Under such conditions, the trends in the residual strengths should correspond to the trends in the residual strengths associated with the different ligaments that are produced after cold shock from different temperatures.

Finally in this section, it is important to discuss the effects of viscoelastic deformation on the overall toughening. This can be understood by considering the effects of the stress relaxation on the overall toughening levels associated with the bridging tractions. Such bridging tractions will only be significant when the shock durations are much less than the relaxation time, \( \tau \), which is given by Equation (13) in Section 3.2. The relaxation time represents the time during which the crack-bridging stresses are significant and must be greater than the shock duration (Table 4). This shows that viscoelastic crack bridging are effective and that the bridging stresses do not decay significantly during the duration of the cold shock process. In such situations, the thermally-induced applied stresses may increase to a maximum value.

It is also important to note here that the viscosity of the intergranular glassy phase is dependent on temperature (The viscosity varies from about \( 10^5 \) Pa.s at 1000°C to \( 10^2 \) Pa.s at 1400°C). Hence, the viscous bridges produced at higher temperatures, for instance at 950°C, are too low to provide any significant toughening effect. This implies that, as the ratio of the viscosity to the Young’s modulus becomes lower, the role of viscoelastic crack bridging becomes less significant. The crack-tip stress intensity factors for the bridges are given in Figures 9 – 11.
5.5 IMPLICATIONS
The implications of the above results are quite significant. First, the results show effects of clay mixtures on toughening of sintered porous ceramics for water filtration applications. It also show that the toughening and strength can be controlled by the mixing of clays with differences in alumina content. The blending of such clay results in clays with intermediate plasticity. However, in the current study, the Iro clay does not appear to have a significant effect on the strength and fracture toughness values of the clays fired at 850°C. Hence, the main use of the Iro clay is in plasticizing the clay mixtures to reduce the incidence of cracking during the molding of the clay filters.

The current work also suggests that the optimum strength and fracture toughness of the fired clays can be achieved by mixing of clays in appropriate proportions that were sintered at ~850°C. The clay mixtures sintered at 850°C were found to have appreciable strength and fracture toughness. It is important to investigate clay mixtures fired at lower and higher temperatures. The clay mixtures fired at higher temperatures that are above 850°C may induce cracks (Yakub et al. 2012).

Such nano-/micro-cracks reduce the reduce strengths and fracture toughness of the filters (Yakub et al. 2012). They may also provide pathways for bacterial and viral contamination of the water, as it passes through the porous structure of the filters. The sintering of such clay mixtures at lower temperatures could result in lesser fracture toughness and strengths values (Yakub et al. 2012). This is suggested to be due to incomplete sintering of the clay mixtures (Yakub et al. 2012; Soboyejo et al. 2001)).
The right choice of sintering temperature must be explored for clays that are used in the fabrication of ceramic water filters. This can be achieved by mixing high plastic clays with less plastic clays to form clays with intermediate plasticity. Such clay mixtures facilitate molding of clays into complex filter shapes, without compromising the thermal shock resistance and mechanical properties (strength and fracture toughness). This is true for clay mixtures with plastic clay proportions of up to 60 volume percent in this research.

The above trends suggest that clay mixtures can be optimized for molding without significantly altering the basic mechanical properties of the fired clays that are relevant to water filtration. Similarly, the current work also suggests that the clay microstructures can be optimized to improve the amount of crack-tip shielding that can be achieved at room-temperature and elevated-temperature. In both bases, the formation of uncracked ligaments during thermal shock-induced cracking, results in crack-tip shielding by crack bridging (Figures 5-7) and Figure 8).

However, the shielding is by elastic crack bridging at room-temperature, and viscoelastic crack bridging at elevated-temperature (Budiansky et al. 1988; McNaney et al. 1999). Hence, the trends in the measured residual strengths (after cold shock treatment) are consistent with the trends in the predicted crack-tip shielding due to elastic bridging by the un-cracked ligaments that were formed due to crack growth under thermal shock conditions. This suggests that the overall resistance to crack growth can be optimized by controlling the amount of viscoelastic crack bridging that occurs above the glass transition temperature, and the amount of elastic crack bridging that occurs during crack extension below the glass transition temperature.
In general, the effects of viscoelastic deformation can be controlled by using different mixtures of clays to produce viscoelastic crack bridges with well controlled relaxation times. Essentially, the relaxation times must be long compared to the shock durations. If this is so, then the bridging tractions will remain high during the duration of the shock durations. The bridging tractions will, therefore, shield the crack tips from the applied thermal stresses, when the effects of stress relaxation associated with the clay mixtures are small. The two dimensionless constants $\gamma$ and $\mu$ can also be used to characterize the extent of shielding effect from viscoelastic toughening (Rahbar et al. 2011).

The viscosity-temperature profiles of the bridging ligaments may also be controlled by doping with alkali oxides, such as Na$_2$O and K$_2$O that can change the effective viscosities over the range of temperatures that are relevant to the processing of ceramic water filters.

5.6 SUMMARY AND CONCLUDING REMARKS

This paper presents the results on an experimental study of the clay mechanical properties (plasticity, strength, fracture toughness) and thermal shock behavior that are relevant to ceramic water filters. Salient conclusions arising from this work are summarized below.

(1) The mixture of high silica and lower silica clays can be used to achieve clays with a range of plasticity, strength, fracture toughness and thermal shock resistance. An Iro clay weight percentage of ~ 30wt.% - 60wt.% show promising combination of flexural strengths and fracture toughness at a firing temperature of ~ 850°C.

(2) The residual strengths obtained after cold shock of the fired bricks decreases with increasing number of cold shock cycles. This is associated with the formation of shock-
induced cracks that contain bridging ligaments that shield the crack-tips from the applied stresses due to thermal shock. These bridging ligaments, which are visco-elastic above the glass transition temperatures and elastic below the glass transition temperatures, shield the crack tips from the stresses due to thermal shock.

(3) The trends in the measured residual strengths (after cold shock) are consistent with the predictions in the crack-tip shielding due to elastic ligament bridging (below the glass transition temperature) and viscoelastic crack bridging (above the glass transition temperature). These shielding effects reduce the applied crack driving forces (due to thermal shock) to effective crack driving forces that are sufficient to promote shock-induced crack growth over the range of cold shock temperatures that was explored.

(4) The shielding due to viscoelastic crack bridging can be controlled by the viscoelasticity of the clay mixtures that form the uncracked bridging ligaments that bridge the cracks, following the onset of cracking due to thermal shock. The shielding is effective when the duration of thermal shock is much less than the relaxation times associated with the clay mixtures. The optimal thermal shock resistance and residual strength levels were associated with elastic/viscoelastic crack bridges produced after sintering at 850°C.
ACKNOWLEDGMENTS
This research was supported by Carnegie Corporation project at the University of Ghana, Ghana, the World Bank STEP B Program, the African Centers of Excellence Programs Program and Princeton University. The mechanical properties determination work was undertaken at School of Engineering, Tufts University, United States of America. The authors would like also to acknowledge technical staff of Mateng Nigeria Ltd, Abeokuta, Nigeria, for assistance with the production of the ceramic water filters.
REFERENCES


### FIGURES AND TABLES

Table 1 – Clay mixtures and plasticity indices

<table>
<thead>
<tr>
<th>CWF Specimen Code</th>
<th>Clay Proportion (%)</th>
<th>Plasticity Index (PI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE 1</td>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>IE 2</td>
<td>15.0</td>
<td>85.0</td>
</tr>
<tr>
<td>IE 3</td>
<td>30.0</td>
<td>70.0</td>
</tr>
<tr>
<td>IE 4</td>
<td>45.0</td>
<td>55.0</td>
</tr>
<tr>
<td>IE 5</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>IE 6</td>
<td>60.0</td>
<td>40.0</td>
</tr>
<tr>
<td>IE 7</td>
<td>75.0</td>
<td>25.0</td>
</tr>
<tr>
<td>IE 8</td>
<td>90.0</td>
<td>10.0</td>
</tr>
<tr>
<td>IE 9</td>
<td>100.0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2 - Chemical composition of clays

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>EWUYA Clay (%)</th>
<th>IRO Clay (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>74.43</td>
<td>61.88</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.46</td>
<td>15.14</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.51</td>
<td>8.84</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.00</td>
<td>0.80</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>0.24</td>
<td>1.19</td>
</tr>
<tr>
<td>CaO</td>
<td>0.22</td>
<td>0.53</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.14</td>
<td>0.33</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.13</td>
<td>0.84</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>NiO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Loss on Ignition (L.O.I)</td>
<td>6.12</td>
<td>10.20</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>99.47</strong></td>
<td><strong>99.93</strong></td>
</tr>
</tbody>
</table>
Table 3 – Mechanical properties of specimens sintered at 850°C

<table>
<thead>
<tr>
<th>Iro Clay Proportion/ (Batch Code) (%)</th>
<th>Mechanical Properties of specimen at 850°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s Modulus (GPa)</td>
<td>Flexural Strength (MPa)</td>
</tr>
<tr>
<td>0 (IE1)</td>
<td>0.5721±0.03</td>
<td>1.95±0.10</td>
</tr>
<tr>
<td>15 (IE2)</td>
<td>0.6362±0.03</td>
<td>2.46±0.12</td>
</tr>
<tr>
<td>30 (IE3)</td>
<td>0.5749±0.03</td>
<td>3.21±0.16</td>
</tr>
<tr>
<td>45 (IE4)</td>
<td>0.6097±0.03</td>
<td>2.40±0.12</td>
</tr>
<tr>
<td>50 (IE5)</td>
<td>0.8989±0.04</td>
<td>2.70±0.14</td>
</tr>
<tr>
<td>60 (IE6)</td>
<td>0.5998±0.03</td>
<td>2.22±0.11</td>
</tr>
<tr>
<td>75 (IE7)</td>
<td>0.4174±0.02</td>
<td>2.37±0.12</td>
</tr>
<tr>
<td>90 (IE8)</td>
<td>0.6163±0.03</td>
<td>2.58±0.13</td>
</tr>
<tr>
<td>100 (IE9)</td>
<td>0.5364±0.03</td>
<td>2.88±0.14</td>
</tr>
<tr>
<td>Parameter</td>
<td>Symbol</td>
<td>Numerical Value</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>--------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Half height of specimen</td>
<td>H</td>
<td>$5 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>E</td>
<td>$0.85 \times 10^9$ Pa</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$k$</td>
<td>$3.5 \text{ Wm}^{-1}\text{k}^{-1}$</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>$S$</td>
<td>$969 \text{ JKg}^{-1}\text{K}^{-1}$</td>
</tr>
<tr>
<td>Density</td>
<td>$\rho$</td>
<td>$(1.3\text{-}1.96) \times 10^3 \text{ Kgm}^{-3}$</td>
</tr>
<tr>
<td>Co-efficient of thermal expansion</td>
<td>$\alpha$</td>
<td>$5.5 \times 10^{-6} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>Thermal Diffusivity</td>
<td>$D=k/(sp)$</td>
<td>$2.22 \times 10^{-6} \text{ m}^2\text{s}^{-1}$</td>
</tr>
<tr>
<td>Thermal relaxation time</td>
<td>$\Gamma=H^2/k$</td>
<td>4.06</td>
</tr>
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Table 5(a) – Microstructural details of the bridges for specimens fired at 750°C

<table>
<thead>
<tr>
<th>Cold shock cycles, N</th>
<th>Bridge length, $p(\mu m)$</th>
<th>Bridge width, $w(\mu m)$</th>
<th>Bridge Depth, $h(\mu m)$</th>
<th>Bridge Separation $\delta (\mu m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>51.35</td>
<td>0.75</td>
<td>0.75</td>
<td>400.05</td>
</tr>
<tr>
<td>10</td>
<td>31.55</td>
<td>0.56</td>
<td>0.56</td>
<td>361.08</td>
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<tr>
<td>15</td>
<td>30.63</td>
<td>0.42</td>
<td>0.42</td>
<td>229.14</td>
</tr>
<tr>
<td>20</td>
<td>18.12</td>
<td>0.31</td>
<td>0.31</td>
<td>160.18</td>
</tr>
</tbody>
</table>
Table 5(b) – Microstructural details of the bridges for specimens fired at 850°C

<table>
<thead>
<tr>
<th>Cold shock cycles, N</th>
<th>Bridge length, p(µm)</th>
<th>Bridge width, w(µm)</th>
<th>Bridge Depth, h(µm)</th>
<th>Bridge Separation, δ (µm)</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>52.40</td>
<td>0.78</td>
<td>0.78</td>
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<tr>
<td>10</td>
<td>35.40</td>
<td>0.58</td>
<td>0.58</td>
<td>358.09</td>
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<tr>
<td>15</td>
<td>28.50</td>
<td>0.54</td>
<td>0.54</td>
<td>230.14</td>
</tr>
<tr>
<td>20</td>
<td>20.15</td>
<td>0.30</td>
<td>0.30</td>
<td>160.16</td>
</tr>
</tbody>
</table>

Table 5(c) – Microstructural details of the bridges for specimens fired at 950°C

<table>
<thead>
<tr>
<th>Cold shock cycles, N</th>
<th>Bridge length, p(mm)</th>
<th>Bridge width, w(µm)</th>
<th>Bridge Depth, h(µm)</th>
<th>Bridge Separation, δ(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.67</td>
<td>0.52</td>
<td>0.71</td>
<td>430.06</td>
</tr>
<tr>
<td>10</td>
<td>0.94</td>
<td>0.41</td>
<td>0.42</td>
<td>370.09</td>
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<tr>
<td>15</td>
<td>1.15</td>
<td>0.38</td>
<td>0.25</td>
<td>230.11</td>
</tr>
<tr>
<td>20</td>
<td>1.72</td>
<td>0.25</td>
<td>0.15</td>
<td>110.13</td>
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</table>
Table 6 - Summary of Fett and Munz (1994) parameters for Single-Edge Notched Bend Specimen (SEN'B) subjected to weighted crack bridging fractions. 16

<table>
<thead>
<tr>
<th>ν</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.4980</td>
<td>2.4463</td>
<td>0.0700</td>
<td>1.3187</td>
<td>-3.067</td>
</tr>
<tr>
<td>1</td>
<td>0.5416</td>
<td>-5.0806</td>
<td>24.3447</td>
<td>-32.7208</td>
<td>18.1214</td>
</tr>
<tr>
<td>2</td>
<td>-0.19277</td>
<td>2.55863</td>
<td>-12.6415</td>
<td>19.7630</td>
<td>-10.986</td>
</tr>
</tbody>
</table>

Table 7 – Predicted residual strength of cold shocked specimens

<table>
<thead>
<tr>
<th>Number of Quench Cycle (N)</th>
<th>750°C</th>
<th>850°C</th>
<th>950°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.512881</td>
<td>3.653396</td>
<td>2.435597</td>
</tr>
<tr>
<td>5</td>
<td>2.459016</td>
<td>2.435597</td>
<td>2.035129</td>
</tr>
<tr>
<td>10</td>
<td>2.217799</td>
<td>2.245902</td>
<td>1.449649</td>
</tr>
<tr>
<td>15</td>
<td>1.744731</td>
<td>1.915691</td>
<td>1.058548</td>
</tr>
<tr>
<td>20</td>
<td>1.508197</td>
<td>1.679157</td>
<td>0.721311</td>
</tr>
</tbody>
</table>
Figure 1 – Maxwell spring and dashpot model for crack bridging by viscous glassy phases

Figure 2(a) - XRD patterns showing peak minerals identified of Ewuya Clay

Note: P – Kaolinite, Q – Silica
Figure 2(b) - XRD patterns showing peak minerals identified of Iro Clay

R – Silica, S – Mica, T – Montmorillonite,

Figure 2(c) - XRD patterns showing peak minerals identified of Fired composite (fired clay with sawdust)

Note: U - Aluminum silicate hydrate and V - Potassium aluminum silicate hydroxide
Figure 3 – Dependence of flexural strength on number of quench cycles (N).

Figure 4 – Dependence of fracture toughness on number of quench cycles (N).
Figure 5 – Optical image of specimen after cold shock at 750°C

Figure 6 – Optical image of specimen after cold shock at 850°C
Figure 7 – Optical image of specimen after cold shock at 950°C

Figure 8 – Crack-tip stress intensity factor for viscous bridging
Figure 9 – Tip shielding effect for specimen cold shocked from 750°C

Figure 10 - Tip shielding effect for specimen cold shocked from 850°C
Figure 11 - Tip shielding effect for specimen cold shocked from 950°C
CHAPTER SIX

6.0 OVERALL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUDING REMARKS
This thesis presents the results of an experimental and theoretical modelling of ceramic water filters. The main areas of investigations are a) Statistics of flow and scaling of ceramic water filters, b) Flow study of disk- and full- size ceramic waters filters and c) Strength and plasticity of clays and (d) thermal shock behaviour of ceramic water filters at varying firing temperatures. The salient conclusions arising from this study are summarized below under each theme.

Part A – Statistics of Flow and the Scaling of Ceramic Water Filters
This results of combined analytical and experimental study of flow through frustum-shaped ceramic water filters show that the modeled analytical expression captures the experimental trend in flow rate of the ceramic water filters. The statistical variations in flow rates were found to be well described by normal distributions. The average flow rate was 2.3 L/hr for first hour use at maximum water-head, with the effective permeability values for the six filters ranging between (0.44 - 2.54) x 10^{-14} m^2. Permeability values for the first hour of use can be deduced from the Darcy equation. The flow through frustum-shaped ceramic water filters was well described by Darcy’s equation. The results suggest reasonable filtered water can be obtained by adopting filter testing methods that involve the use of 20 tests in the establishment of the statistical variations in flow rates and effective permeabilities for effective filter quality control. The average flow rate and effective permeability values were found to be well characterized by the normal distribution. The linear dependence between of
flow rates (in the first hour) on the measured permeability values suggests that filter quality may be assessed using either flow rate or permeability measurements.

The multiple ceramic water filter study also shows that a combination of filters may be used to provide drinking water for communities of different sizes. Since the overall flow rates from multiple filter systems scale with the number of filters, the filter sizes and the number of filters can be scaled to provide adequate drinking water for communities. Furthermore, the multiple filters can be placed in strategic locations within the rural communities to provide easy access to safe drinking water in rural/urban communities in developing countries.

Part B - Comparative Flow Study of Frustum- and Disk-Shaped Ceramic Water Filters

Furthermore, with regard to comparing models for flow through frustum-shaped size ceramic water filter, Yakub et al., model was observed to contain some improvements from the Schweitzer et al., model and therefore higher level of accuracy. These improvements include: (1) generalization of the equation to add differential side and bottom wall thickness, and (2) adding calculation of a range of hydraulic conductivity values from h(t), which allowed results to better approximate experimental flow. As manufacturing variables can influence the hydraulic conductivity of resultant filters, and that models such as the Yakub et al., model which calculate a variable hydraulic conductivity have greater accuracy.

Analytical expressions were obtained for the flow rates ratio for disk-shaped and frustum-shaped ceramic water filters via Darcy’s flow of the Van Halem 2006, Schweitzer et al.,2012 and Yakub et al., 2012. The resulting expression was shown to predict the flow rates through the ceramic water filter to an appreciable limit. The flow through disk ceramic water filters
for (multiple loadings) increases with increasing number of runs during the first 20 runs. The statistical variations in the flow rate and the permeability are also well described by the normal distributions for the disk-shaped ceramic water filters examined in this study. The flow rates (in the first hour) were also found to range between 0.16 L/h and 0.28 L/h for the disk-shaped ceramic water filters, while, the hydraulic conductivities (for the first hour) of the disk ceramic water filters investigated ranges from 0.09 cm/h and 0.17 cm/h. The average flow rate was found to range from 0.09 L/h to 0.16 L/h for the disk-shaped ceramic water filters.

Part C – Strength and Plasticity of Porous clay Ceramics

1. The XRD, XRF and FT-IR analysis of the clays and fired clay mixtures indicate the presence of kaolin, silica, montmorillonite and metal-silicate hydrate/hydroxide. The major bonds in the mixtures are also quantitatively similar.

2. The Iro clay has a higher PI number than the Ewuya Clay. The differences are attributed largely to the differences in the alumina and silica contents, which give rise in clay hydration and plasticity.

3. The Iro clay percentages of ~ 30 wt. % were found to result in the best combination of compressive/flexural strengths and fracture toughness. A firing temperature of ~ 850°C was also observed to result in the best balance of compressive/flexural strength and fracture toughness. The initial sawdust volume fraction and clay plasticity did not have any clear effects on the compressive/flexural strengths and the fracture toughness values of the fired clay.

4. The analysis of the thermal shock experimental results shows that specimens sintered at 850°C give appreciable strength and fracture toughness combination for all quench thermal
cycles. Fracture toughness decreasing with increasing thermal quench cycles and affected by uniformity of pore/porosity.

5. Strength measured values are affected by uniformity of pore distribution and porosity of a sintered porous ceramic for water purification application.

6.2 SUGGESTIONS FOR FUTURE WORK

In order to extend the study in this thesis, the following possible suggestions are given:

1. In this study, six ceramic water filters were tested over 12 hours consecutive period. The flow rate and the effective permeability values are computed via Darcy Equation. However, to minimize variation in flow rate values and establish reliance on other flow parameters, there is a need to study ceramic water filters flow rates and permeability values over 2-3 year periods in which most the ceramic water filters are expected to provide filtered water.

2. Future research on theoretical flow models should work to improve the quality of the models with further refinement, including manufacturing variable terms. Also, future experimental testing of filter and disk flow should be conducted on a larger number of samples to verify the results herein, with a larger number of manufacturing variables, and be conducted over a longer time from to capture the changing flow patterns over time.

3. This research study is limited in that the flow rates were ascertained only during first use, not during use over time. This time period was chosen as the most relevant time for manufacturing quality control, but our results provide no information on normal use (including user cleaning
recommendations\textsuperscript{6}) or end-of-life conditions. Future research should consider above mentioned limitations of this study.

4. In this study, it was shown that the viscosity-temperature profiles of the bridging ligaments may also be controlled by doping with alkali oxides, such as Na\textsubscript{2}O and K\textsubscript{2}O that can change the effective viscosities over the range of temperatures that are relevant to the processing of ceramic water filters. Further work is clearly needed to develop such microstructures for applications in nano- and micro-porous caly ceramics for ceramic water filters.

5. The mechanism underlying clay plasticity has not been fully explored. Future work should look at the ‘Considere criterion’ and the Hollomon’s equation as applied to the plastic regime of materials under uniaxial stress.