CHAPTER 4

PYROLYSED RICE HUSK REINFORCED HIGH ALUMINA CASTABLES

4.1 INTRODUCTION

The type of bond in the refractories indicates the bond phase in refractories. The refractory bricks are termed "carbon bonded," "silicate bonded," "phosphate bonded," "cement bonded," etc. based on bond phase. For centuries, the fired integrity of refractories relied on natural material bonding or the silicate or alumino-silicate bonds derived from vitrification reactions. During the 20th century, bonds initially were synthesized using mineralisers, later followed by the introduction of separate cementitious and glassy bond systems. Skoog and Moore (1988) reviewed the evolution of mullite bonding, identifying the many uses of "mullite-bonded" refractories. Unshaped refractories, in general, use similar aggregate materials as shaped bricks. However, the binders used to form the bonding phase are very different.

One of the most significant developments in bond systems over the past 100 years has been the bond system used for monolithic or unshaped refractories that can be formed and shaped in situ. Monolithic refractory materials are mixtures that contain aggregates and binders prepared ready for use either directly in the condition in which they are supplied or after the addition of suitable liquids. Monolithic refractories have been known for many
years, but it is only since the 1960s that their use has gained general acceptance in the refractories community. Initially, monolithics were used for repair or in less severe positions, but they now account for 60% of refractories production and are used in almost all areas of furnace linings (Lee and Moore et al 1998).

The bond formed in monolithics during processing or service may be of several types:

1. A ceramic (physical) bond is formed by one of the constituents in the body, bridging the refractory grains together on firing. It may be a glass and/or a ceramic bond. These typically are formed from clays on firing.

2. A hydraulic (chemical) cement like silicate or aluminate may be used as the bond. This involves setting and hardening at room temperature when water is added to the system. When it is heated, the hydraulic bond is destroyed and the bond strength may decrease. The bond strength may increase again due to the formation of ceramic bond on firing. These are the most common bonds in modern castables and they are usually based on calcium aluminate (CA) cements.

3. A mineral (chemical) bond, which involves hardening at room temperature or above but below the sintering temperature. The most common bonding materials are phosphoric acid and sodium silicate. This bonding produces high strengths when heated to temperatures of 150°C.
The development of low cement castables since the early 80’s has proven to be a giant leap in refractory application. The techniques and areas of applications have been perfected to have maximum benefits from these materials. The special advantages of prefired cast shapes have shown excellent results compared with brick and other monolithics. The application of slurry gunning and plastic gunning has also shown some improvement in application. Materials for ramming mixes have also improved eliminating the prevalent problems in workplace regarding gas, fumes and toxic vapours along with superior performance.

A reduction of the cement content to 5% - 8% without loss in strength has been achieved by the addition of fine particulate refractory bond material and deflocculant (Parker and Sharp 1982). This promotes a homogeneous distribution of cement and thus the hydraulic bond is fully utilised. The advent of reactive aluminas has permitted better particle-packing efficiency. The advantages of such LCCs include lower cement content and therefore lower water content and easier drying. The lower water content also means reduced porosity (from 25%-30% to 8%-15%), because pores are not created by escaping vapour, conferring higher strength and reduced permeability to aggressive liquids and gases (MacZura et al 1995).

Cement contents are nowadays reduced to less than 1.0 % by

1. The addition of deflocculant
2. Using powders with particle size range of 1-100 μm and 0.01-0.1μm and maintaining a proper particle size distribution so that the finer particles can fill the space between coarser particles
and reduce water consumption and porosity of the castable giving greater strength.

Fumed silica (micro-silica or volatilised silica) and reactive alumina are often used as the fine powder. These phases have low water adsorption and hence the water is used only in the cement bonds. Some low-cement monolithics cannot be cast because of the low water content and therefore are vibration compacted; others flow without vibration (Self Flow Castables, SFCs). These are self-leveling with high flowability and have comparable properties to conventional vibration castables (Brachet et al. 1991). Typically, they are CA cement based with 4.5%-8% water addition. The SFC composition and interparticle surface chemistry are carefully controlled to give self-flowing ability. The higher is the liquid contents in an SFC, the better its flowability. Although conventional castables require 3 days to cure and dry, SFCs need only 8-24 hours for installation. The grading (granulometry) is critical to achieve self-flowing behaviour. When the critical particles are larger in the basic formula, the flowability is poor and the segregation is high. The difference of the ratio of each particle size in the superfine (colloidal) particles has a strong influence on the flowability.

Ultra low cement castables (ULCCs) with 0.2%<CaO<1% have improved hot strengths over low cement castables (LCCs). If the CaO: Al₂O₃: SiO₂ ratio is optimised, mullite needles are formed with little glass resulting in the strengthening of the structure at high temperature. ULCCs are used increasingly in such refractory concretes. Since hydratable aluminas are free of CaO, they can be when used with Al₂O₃ aggregates and they can provide bonding up to 1800°C.
There has been research in the past decade or so into in situ self-forming bonds (e.g., the formation of spinel from MgO- and Al₂O₃- matrix components). Fuhrer et al (1998) have examined the reaction of spinel with the CA₆ phase in CA bond. Alumina-spinel castables find wide use in steel ladles, concast tundishes, snorkels and lances. Magnesia-spinel mixed-grain systems find application as fired brick in cement kilns. However, other aggregates can be bonded with aluminate cements. For example, SiC castables are used as lining material in incinerators.

4.1.1 Dispersion and Flow Characteristics

Dispersion technology using superfine powder has helped to improve the flow properties and quality of low cement castable refractories. Alumina cement acts as a hardening agent. Alumina cement (AC) produces multi-valent ions that help the fine powder flocculate to give sufficient curing strength in low cement castables. In addition, both hydration of AC and reaction between AC and superfine powder help the low cement castable refractories gain higher curing strength.

Workability of a castable refractory depends mostly on the flow characteristics of the super fine particles in it. In a powder-water dispersion system, electrostatic double layers form on the solid liquid boundary. Their interaction force varies depending on the concentration of those ions determining the surface potential. For metal oxides, the ion species are H⁺ and OH⁻ and so the surface electric charges of a particle and hence its flow properties vary with the pH of the aqueous solution. If we know the pH value for an apparent surface charge (or zeta potential), we can explain how the pH influences the entire flow behaviour. Among the many kinds of superfine oxide...
powder, superfine powders of alumina and silica have been the basic materials in developing low cement castables.

The amount of water for mixing is greatly reduced by applying the deflocculation-flocculation or dispersion-flocculation technique, to clay or superfine powders in order to produce these castables. This significantly improves the bulk density in comparison to that of traditional castables, containing more alumina cement (called CAC) as a binder. The CaO in AC lowers the refractoriness of castables, while the low cement castables have high refractoriness, making their corrosion resistance and volume stability at high temperatures much better. (Eguchi et al 1989)

Castable refractories need a pot life long enough to maintain the flow properties from mixing until the completion of furnace construction. To keep superfine particles well dispersed and to secure good flow properties (or pot life) with low water content, it is necessary to deactivate multi-valent cations dissolved from AC during the casting work. The deactivation is complete with a large quantity of dispersant. Once it is complete, the flow properties in a dispersed state of the particle-water system will control the performance of the castable refractory.

The series of steps involved in castable refractory are as follows:

1. Proper choice of ingredients to achieve the desired pot life, strength and volume stability at operating conditions.
2. Dry mixing of constituent materials.
3. Proportioning with requisite amount of water.
4. Applying vibration to make the mass to move and occupy the desired shape.

5. Curing for 24 hours to fully hydrate the cement phases to form hydrates.

6. Heating schedule to achieve crack free cast body.

7. Continuous heating to develop ceramic bonding.

4.1.2 Design of Experiment

Recently there has been an increased demand for monolithic refractories. As the furnace construction is simplified, resulting in labour reduction and energy. Castable refractories in particular are widely used. The use of castables for ladles and blast furnace troughs has tremendously increased.

The refractory materials used in troughs are subjected to vigorous conditions due to the periodical action of hot metal and molten slag. At present, Al₂O₃-SiC-C based castables are being used for this purpose. Nowadays Si₃N₄ is added in the range of 15 to 20 wt.% with SiC to improve the properties (Banerjee 1998). The addition of any non-oxides such as silicon nitride powder to any castable increases the cost. This study analyses the effect of addition of pyrolysed rice husk in high alumina castable and its property evaluation.

Four batches of ULCC castables were made and their properties such as Density, microstructure, Cold Modulus of Rupture (Cold MOR), Hot Modulus of Rupture (Hot MOR), Modulus of Elasticity (MOE) and Thermal Shock Resistance (TSR) were studied.
Our aim in the second experiment was to show addition of pyrolysed rice husk gives better strength compared to the addition of silicon nitride and silicon carbide powders to high alumina castable.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Experiment 1

The raw materials used in this work include tabular alumina from Alcoa, micro-silica 971U from Elkem and Secar 70 cement from Lafarge. The castable was designed as ultra low cement $\text{Al}_2\text{O}_3$ castable with maximum particle size 2.8mm. The castable composition was designated as A1, A2, A3 and A4 with 0%, 5%, 10% and 15% pyrolysed rice husk respectively. Pyrolysed rice husk was synthesised by firing rice husk at $720^\circ \text{C}/3$ hours in a sealed container. The flowchart for the formation of ultra low cement castables is shown in Figure 4.1. The compositional details are as tabulated in Table 4.1.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>90</td>
<td>86</td>
<td>81</td>
<td>78</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pyrolysed Rice husk</td>
<td>0</td>
<td>3</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Grain size Maximum (mm)</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>$&gt;0.045$ mm (%)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>$&lt;0.045$ mm (%)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

The mixtures were dry mixed for three minutes and wet mixed for further three minutes after adding water, using Hobart D340 mixer. All the
Figure 4.1 Flow chart for the formation of ultra low cement castables
samples were cast using a vibration table working at 0.4 mm of amplitude and 60 Hz of frequency. After casting, the samples were cured for 24 hours in mould at room temperature and for another 24 hours after removing from the mould at room temperature, then dried at 110°C for 24 hours. Samples were fired at 1100°C and 1400°C in both nitrogen (N₂) atmosphere and coke bed (CB) atmosphere. Samples of size 150 x 25 x 25 mm were prepared for determination of bulk density, apparent porosity, cold modulus of rupture (Cold MOR), Hot Modulus of Rupture (Hot MOR) and thermal shock resistance (TSR). Each data was the average of three samples.

Bulk Density and apparent porosity was measured by Archimedes principle. The modulus of elasticity was determined using elastosonic Method (Pundit Portable Ultrasonic Non Destructive Digital Indicating Tester London).

The strength of refractories can be sensitive to temperature and a brittle to ductile transition often is observed once any glass phase starts to soften. Hence, both cold and hot modulus of rupture was measured. Modulus of rupture was measured by three-point bending test configuration using Nietzsche (422/D/3, GmbH, Germany) machine. The span length was 12.5 cms. The Modulus of rupture was calculated from the formula

\[ \text{MOR} = \frac{3ML}{2bd^2} \]  

where \( \text{MOR} \) = modulus of rupture (kg/cm²)
\( M \) = load (kgs)
\( L \) = span length (cms)
\( b \) = width of the sample (cms)
\( d \) = thickness of the sample (cms)
Thermal shock resistance was measured for fired samples at 1400°C. These samples were subjected to 1000°C for 30 minutes and quenching the samples in air for another 30 minutes. The thermal shock resistance is measured from Resistance (R) parameter. The R parameter was calculated from the formula

\[
R = \frac{\sigma (1-\mu)}{E \alpha}
\]  

(4.2)

where \( \sigma \) is the MOR of the sample in MPa  
\( \mu \) is the poisson’s ratio  
\( E \) is the Modulus of elasticity GPa  
\( \alpha \) is the coefficient of thermal expansion \( \times 10^{-6} / ^\circ C \)

Strength-after-thermal shock and E-after-thermal shock were measured after 4 cycles. The thermal expansion was measured at 1000°C (Netzsch-GmbH electronic dilatometer 402 E).

4.2.2 Experiment 2

This experiment deals with the property evaluation of high alumina castables with non-oxide additions. The raw materials used in this work include tabular alumina from Alcoa, micro-silica 971U from Elkem, Secar 70 cement from Lafarge, silicon nitride powders (Mitsubishi) and the silicon carbide (Grindwell Norton). In this experiment, the addition of pyrolysed rice husk to ULCC is compared with additions of silicon nitride and silicon carbide. The compositional details are as tabulated in Table 4.2.
Table 4.2 Composition of experiment 2

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>81</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Pyrolysed Rice husk</td>
<td>9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Si}_3\text{N}_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiC</td>
<td>-</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td><strong>Grain size Maximum (mm)</strong></td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>$&gt;0.045\text{ mm (%)   }$</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>$&lt;0.045\text{ mm (%)   }$</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

The castable compositions C1 and C2 required 8% water whereas composition C3 required 7% water. Based on these compositions, three kgs of mix were made in a high intensity mixer and cast into bars. After removal from the moulds, they were dried at 110°C for 24 hours. Then these bars were fired at 1400°C/6 hours in a coke bed atmosphere. Samples of size 150 x 25 x 25 mm were prepared for determination of bulk density, apparent porosity, cold modulus of rupture (CMOR) and hot modulus of rupture (HMOR). Each data was an average of three samples. XRD, Mercury porosimetry (micromeritics corp. 9320, Poresizer) and SEM were taken to study phase formation, pore size distribution and microstructure.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Experiment 1

4.3.1.1 Physical Properties

The Bulk density and apparent porosity of the samples A1, A2, A3, and A4 after drying, firing at 1100°C and 1400°C in both static nitrogen atmosphere and in coke bed atmosphere are given in Table 4.3 and Table 4.4. Bulk density increase and apparent porosity increase with pyrolysed rice husk
because of lower density and higher porosity of rice husk. Castables have lower porosity after drying due to hydration and coagulation of the ultra fines and cement with water.

<table>
<thead>
<tr>
<th>Bulk Density (g/cm³)</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C x 3hrs</td>
<td>2.89</td>
<td>2.79</td>
<td>2.58</td>
<td>2.38</td>
</tr>
<tr>
<td>1100°C x 3hrs/N₂</td>
<td>2.90</td>
<td>2.82</td>
<td>2.59</td>
<td>2.35</td>
</tr>
<tr>
<td>1100°C x 3hrs/CB</td>
<td>2.90</td>
<td>2.82</td>
<td>2.59</td>
<td>2.35</td>
</tr>
<tr>
<td>1400°C x 6hrs/N₂</td>
<td>2.90</td>
<td>2.83</td>
<td>2.60</td>
<td>2.36</td>
</tr>
<tr>
<td>1400°C x 6hrs/CB</td>
<td>2.91</td>
<td>2.83</td>
<td>2.60</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Table 4.4 Apparent porosity of castables

<table>
<thead>
<tr>
<th>Apparent Porosity (%)</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C x 3hrs</td>
<td>14.7</td>
<td>17.7</td>
<td>20.6</td>
<td>23.6</td>
</tr>
<tr>
<td>1100°C x 3hrs/N₂</td>
<td>16.3</td>
<td>19.4</td>
<td>23.4</td>
<td>28.1</td>
</tr>
<tr>
<td>1100°C x 3hrs/CB</td>
<td>16.3</td>
<td>19.4</td>
<td>23.4</td>
<td>28.1</td>
</tr>
<tr>
<td>1400°C x 6hrs/N₂</td>
<td>16.4</td>
<td>19.5</td>
<td>23.5</td>
<td>28.2</td>
</tr>
<tr>
<td>1400°C x 6 hrs/CB</td>
<td>16.4</td>
<td>19.5</td>
<td>23.4</td>
<td>28.0</td>
</tr>
</tbody>
</table>

N₂ - Nitrogen atmosphere
CB - Coke bed atmosphere

4.3.1.2 Modulus of rupture

Cold modulus of rupture is measured after 24 hours drying at 110°C, after firing at 1100°C and 1400°C in both static nitrogen atmosphere and coke bed atmosphere and the results are shown in Figure 4.2. Hot modulus of rupture is measured for fired samples and the results are shown in Figure 4.3. The
Figure 4.2 Cold modulus of rupture Vs pyrolysed rice husk content (Wt. %)
Figure 4.3  Hot modulus of rupture Vs pyrolysed rice husk

Hot modulus of rupture (Kg/cm²) at 1400°C

Pyrolysed rice husk (Wt.%)

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14
- 15

H00Cx3hrs/N₂  1100Cx3hrs/CB  1400Cx6hrs/N₂  1400Cx6hrs/CB

Figure 4.3  Hot modulus of rupture Vs pyrolysed rice husk
strength at 110°C comes from hydraulic bonding and coagulation at low temperatures. Ceramic bonding along with reinforcement of pyrolysed rice husk at high temperature is responsible for high temperature strength.

In Figure 4.2, the sample (A1) with 0% pyrolysed rice husk shows better strength when fired at 1400°C than at 1100°C. However, there is no much difference between nitrogen atmosphere and coke bed atmosphere. The strength of samples (A2, A3 & A4) at 110°C/24 hours is lower than sample A. This is due to increase in porosity of samples A2, A3 & A4 as the content of pyrolysed rice husk is increased. Hence at 110°C/24 hours, the strength decreases as the porosity of the sample increases. The strength of samples fired at 1400°C/6 hours is higher than samples fired at 1100°C/3 hours. This trend is observed for sample A1 & A2. However, for the sample A3, the strength at 1100°C is slightly higher than samples fired at 1400°C. In addition, there is no much difference between samples fired at 1400°C in static nitrogen atmosphere and coke bed atmosphere.

The hot MOR of castables fired at 1400°C is better in both A1 and A2 samples. However, the reverse trend is observed for castable A3. In sample A3, HMOR of samples fired at 1100°C in static nitrogen is higher than that of the samples fired at 1400°C. The reason for this behaviour is that as the sample becomes more porous, it loses its strength due to the oxidation of the whiskers.

4.3.1.3 Modulus of Elasticity

Modulus of elasticity of fired samples without thermal cycles and that of the samples after 4 cycles of thermal shock is shown in Figures 4.4 & 4.5. In
Figure 4.4 Modulus of elasticity Vs pyrolysed rice husk content (Wt.%)
Figure 4.5 Modulus of elasticity after four cycles of thermal shock

Pyrolysed rice husk content (Wt. %)

Modulus of elasticity (GPa)
Figure 4.4 MOE decreases with increase in porosity and MOE at 1400°C is greater than MOE at 1100°C. In Figure 4.5, after 4 cycles of thermal shock, MOE increases with increase in porosity and MOE of samples fired at 1400°C is slightly lower than samples fired at 1100°C.

4.3.1.4 Thermal Shock Resistance

Strength after thermal shock and E after thermal shock have become popular characterisation methods of thermal shock damage (Whittemore and Pavlica 1997). Figure 4.6 shows the MOR after four cycles of thermal shock. Table 4.5 shows values for thermal resistance after 4 cycles. Sample C shows higher value of R parameter.

Table 4.5 R parameter after four cycles of thermal shock

<table>
<thead>
<tr>
<th>T°C and atmosphere</th>
<th>R – Parameter (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A1</td>
</tr>
<tr>
<td>1400°C /N₂</td>
<td>520</td>
</tr>
<tr>
<td>1400°C /CB</td>
<td>475</td>
</tr>
</tbody>
</table>

4.3.2 Experiment 2

4.3.2.1 Physical Properties

Table 4.6 shows the bulk density and apparent porosity of castables C1, C2 and C3 measured by Archimedes Principle.
Figure 4.6  Modulus of rupture after four cycles of thermal shock
Table 4.6 Apparent porosity and bulk density of castables C1, C2 and C3

<table>
<thead>
<tr>
<th>Properties</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Porosity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110°C x 24 hours</td>
<td>20.0</td>
<td>15.7</td>
<td>12.5</td>
</tr>
<tr>
<td>1400°C x 6 hours (CB)</td>
<td>22.8</td>
<td>18.9</td>
<td>16.7</td>
</tr>
<tr>
<td>Bulk Density (g/cm³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110°C x 24 hours</td>
<td>2.59</td>
<td>2.86</td>
<td>2.93</td>
</tr>
<tr>
<td>1400°C x 6 hours (CB)</td>
<td>2.60</td>
<td>2.84</td>
<td>2.92</td>
</tr>
</tbody>
</table>

4.3.2.2 Phase Analysis

The XRD of samples C1, C2 and C3 are shown figure 4.7. The major peaks in XRD of all the samples belong to alumina. The minor phases of corresponding compounds are also shown in Figure 4.7.

4.3.2.3 Modulus of Rupture

Both cold MOR and hot MOR are given in figure 4.8. Hot MOR is conducted after soaking the sample at 1400°C for 30 minutes. The decrease in cold MOR of C1 is due to the increase in apparent porosity after pyrolyzed husk impregnation. However, at the same time, due to reinforcement of pyrolysed rice husk, better strength is obtained at 1400°C. This may be due to the formation of whiskers, which gives resistance to crack propagations at high temperatures.
Figure 4.7  XRD pattern of castables C1, C2 & C3
Figure 4.8 Cold and hot modulus of rupture of compositions C1, C2 & C3

<table>
<thead>
<tr>
<th>Composition</th>
<th>CMOR</th>
<th>HMOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>250</td>
<td>150</td>
</tr>
<tr>
<td>C2</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>C3</td>
<td>150</td>
<td>50</td>
</tr>
</tbody>
</table>
4.3.2.4 Pore Size Distribution Studies

The pore size distribution of C1, C2, C3 are given in Figures 4.9. and 4.10. All the samples show a small peak at around 60 μm and at around 10 μm. This peak may due to the non-homogeneous packing and adsorbed water present in the system. The castable C1 shows a unimodal pore size distribution with a median pore diameter of 0.445 μm and C2 and C3 shows a bimodal pore size distribution with a median pore size of 0.851 μm and 1.476 μm. The castable has a high pore volume compared to C2 and C3 as shown in the Figures 4.8 and 4.9.

The sample with pyrolysed husk (C1) shows a single prominent peak. The Figure 4.1 reflects the interconnected voids extending to the surface of the compact. Mercury intrusion starts from surface pores and then proceeds along interconnected particle packing channels before entering interior voids. As compared with small pores, large voids need less pressure for mercury intrusion to take place based on the Washburn equation. However, if large voids exist inside the matrix, the particle packing channels will act as throats or necks regulating mercury intrusion. For all the samples, at the end of extrusion, most of the intruded mercury remains in the matrix (Zheng and Reed 1992). The incorporation of rice husk has created lot of small open pores in the matrix.

The double peak of sample C2 and C3 shows that during firing of the sample some of silicon nitride and silicon carbide particles have been oxidised creating bimodal distribution of pores.
Figure 4.9 Pore size distribution of Cl.
Figure 4.10 Pore size distribution of C2 & C3.
4.3.2.5 Microstructure

Figure 4.11 (a) to (d) shows the microstructure of castable C1. The microstructure confirms the presence of whiskers in castable C1. Figure 4.10 (a) shows whiskers across the matrix. Figure 4.10 (b) shows whiskers of thickness 1 to 2 \( \mu \text{m} \) that bridges across the voids. Figure 4.10 (c) shows a lengthy whisker across the matrix. Figure 4.10(d) shows a cluster of whiskers.

4.4 CONCLUSIONS

The following conclusions are drawn from the above experiments:

1. There is not much difference between samples fired at 1400°C in static nitrogen atmosphere and coke bed atmosphere.
2. Pyrolysis of rice husk fired at different atmosphere does not show significant difference.
3. Thermal shock resistance increases with pyrolysed rice husk content.
4. The result shows that incorporation of pyrolysed rice husk in the system increases the hot modulus of rupture to a significant level.
5. The whiskers offer high strength to the castable of composition C1.

The present study confirms the effectiveness of pyrolysed rice husk as reinforcement in castables. Therefore, composition B with 9% pyrolysed rice husk is the optimum composition and can be tried for industrial usage.
Figure 4.11 SEM micrographs of C1
(a) Thick whiskers across the matrix
(b) Whiskers across the void
(c) A long whisker across the matrix
(d) Cluster of whiskers