CHAPTER - 6
RHEOLOGICAL CHARACTERIZATION OF HYDROTHERMALLY TREATED LIGNITES

6.0 Studies on Slurriability

The product slurry of the hydrothermal treatment was filtered using vacuum filtration. The solids were air dried before preparing the slurries. The method of preparation of the slurries is given in chapter 2 under 2.15. The solid loadings for the slurries were determined by the ASTM moisture analysis (ASTM D - 3173) procedure. The method for the determination of slurriability is given in chapter 2 under 2.16.1. The viscosities of the LWSs were measured using RV20 Haake viscometer system and the data were reported as apparent viscosities/shear stress values to simplify comparisons. The rheological results could be compared directly to the results reported in the literature by other investigators who have used Haake viscometer for determining flow characteristics. Other investigators reporting apparent viscosity vs shear rate using the Haake viscometer include Funk et al.\textsuperscript{120-124}, Farthing et al.\textsuperscript{125} as well as EPRI sponsored coal-water slurry studies conducted by Babcox and Wilcox.\textsuperscript{126} In all the determinations of slurriability, a viscosity level of 600 mPa.s was used during interpolation between the solids concentration and apparent viscosity.
Researchers\textsuperscript{127-130} have reported different viscosity levels viz., 1000, 800 and 300 mPa.s at a shear rate of 100 s\(^{-1}\) for the determination of slurriability. During the present investigations with the lignite chosen, slurries become pourable only below the viscosity level of 600 mPa.s and hence a level of 600 mPa.s is selected as basis point.

A summary of the maximum solid loadings achievable with the hydrothermally treated lignites is given in Table 6.1 along with the corresponding equilibrium moisture levels and -COOH group contents.

The apparent viscosity values observed during the slurriability tests were plotted against the weight percentages of the solid loadings of the feed and hydrothermally treated lignites. The plots are shown in Figs.6.1 - 6.5. It is generally observed that the values of slurriability of the hydrothermally treated lignites are higher than those of the feed lignites. Also the slurriability values of the treated lignites increase linearly as the temperature of the hydrothermal treatment increases, as can be seen in Fig.6.6. The increase in slurriability of the treated lignites is due to the net result and cumulative effect of the following:

1. Decarboxylation during the hydrothermal treatment,
   reduction in the micropore volume due to plugging by
Fig. 6.1 Variation of apparent viscosity with solids loading (% by Weight)-Hydrothermally treated Neyveli I LWSs.
Fig. 6.2  Variation of apparent viscosity with solids loading (% by weight)-Treated Neyveli I LWS- Finer grind feed stock and feed stock having 42% by wt solids loading.
Fig. 6.3 Variation of apparent viscosity with solids loading (% by weight) for hydrothermally treated Neyveli II LWSs.
Fig. 6.4 Variation of apparent viscosity with solids loading (% by weight) for hydrothermally treated Kutch LWSs.
Fig. 6.5 Variation of apparent viscosity with solids loading (% by weight) for hydrothermally treated South Gujarat LWSs.
Fig. 6.6 Slurriability of treated lignites. Variation with hydrothermal treatment temperature.
### TABLE 6.1

**DATA ON SLURRIABILITY OF HYDROTHERMALLY TREATED LIGNITES**

<table>
<thead>
<tr>
<th></th>
<th>SLURRIABILITY WT%* (Bone Dry Solids)</th>
<th>EQUILIBRIUM MOISTURE % by weight</th>
<th>-COOH CONTENT meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NEYVELI I LWS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEED</td>
<td>42.52</td>
<td>23.20</td>
<td>2.28</td>
</tr>
<tr>
<td>HTT 200</td>
<td>44.35</td>
<td>17.40</td>
<td>2.27</td>
</tr>
<tr>
<td>HTT 230</td>
<td>45.51</td>
<td>15.09</td>
<td>2.25</td>
</tr>
<tr>
<td>HTT 260</td>
<td>47.93</td>
<td>11.69</td>
<td>2.07</td>
</tr>
<tr>
<td>HTT 290</td>
<td>51.28</td>
<td>8.01</td>
<td>1.81</td>
</tr>
<tr>
<td>HTT 320</td>
<td>52.79</td>
<td>4.44</td>
<td>1.73</td>
</tr>
<tr>
<td><strong>NEYVELI I LWS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FINER GRIND</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEED</td>
<td>35.24</td>
<td>9.73</td>
<td>—</td>
</tr>
<tr>
<td><strong>NEYVELI I LWS (FINE)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HTT 290</td>
<td>44.25</td>
<td>7.21</td>
<td>1.79</td>
</tr>
<tr>
<td><strong>NEYVELI I (42% FEED)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HTT 290</td>
<td>53.04</td>
<td>8.36</td>
<td>1.80</td>
</tr>
<tr>
<td><strong>NEYVELI II LWS</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>FEED</td>
<td>40.01</td>
<td>22.99</td>
<td>2.21</td>
</tr>
<tr>
<td>HTT 260</td>
<td>43.85</td>
<td>12.66</td>
<td>2.16</td>
</tr>
<tr>
<td>HTT 290</td>
<td>48.52</td>
<td>7.69</td>
<td>1.93</td>
</tr>
<tr>
<td>HTT 320</td>
<td>49.54</td>
<td>5.76</td>
<td>1.78</td>
</tr>
<tr>
<td><strong>KUTCH LWS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEED</td>
<td>46.87</td>
<td>41.50</td>
<td>1.49</td>
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<tr>
<td>HTT 260</td>
<td>50.55</td>
<td>9.67</td>
<td>1.21</td>
</tr>
<tr>
<td>HTT 290</td>
<td>53.40</td>
<td>6.89</td>
<td>1.03</td>
</tr>
<tr>
<td>HTT 320</td>
<td>55.50</td>
<td>4.30</td>
<td>0.87</td>
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<tr>
<td><strong>SOUTH GUJARAT LWS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEED</td>
<td>48.89</td>
<td>20.42</td>
<td>1.82</td>
</tr>
<tr>
<td>HTT 260</td>
<td>51.13</td>
<td>12.89</td>
<td>1.37</td>
</tr>
<tr>
<td>HTT 290</td>
<td>54.30</td>
<td>8.85</td>
<td>0.99</td>
</tr>
<tr>
<td>HTT 320</td>
<td>55.45</td>
<td>5.04</td>
<td>0.79</td>
</tr>
</tbody>
</table>

* Slurriability is defined as the maximum percentage by weight of bone dry solids present in the LWS having an apparent viscosity of 600 mPa s at 100 s⁻¹ shear rate.
waxy matter and subsequent reduction in equilibrium moisture levels.

2. Changes in particle size distribution as explained under 5.4

3. Removal of hydrophilic inorganic constituents.

It is to be noted that the trend of the increase in slurriability values of the untreated lignites viz., South Gujarat > Kutch > Neyveli I > Neyveli II is retained even after hydrothermal treatment at a particular temperature. The slurriability percentages for the treated lignites could not be compared with some of the treated foreign lignites or subbituminous coals since the comparable viscosity levels are different.

Some available data for foreign lignites from the literature, are shown below:

**Indian Head (North Dakota) Lignite**

<table>
<thead>
<tr>
<th>Solids Loading wt %</th>
<th>Apparent Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.5</td>
<td>345 mPa.s at 410 s⁻¹</td>
</tr>
<tr>
<td>Hot water dried using autoclave at</td>
<td></td>
</tr>
<tr>
<td>270°</td>
<td>50.8</td>
</tr>
<tr>
<td>1106 mPa.s at 410 s⁻¹</td>
<td></td>
</tr>
<tr>
<td>300°</td>
<td>52.4</td>
</tr>
<tr>
<td>1007 mPa.s 410 s⁻¹</td>
<td></td>
</tr>
<tr>
<td>330°</td>
<td>53.8</td>
</tr>
<tr>
<td>735 mPa.s at 410 s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>
Indian Head (North Dakota)
Untreated 40.8  800 mPa.s at 100 s\(^{-1}\)
Hot water dried at
330° in
Process development unit 55.5  800 mPa.s at 100 s\(^{-1}\)

South Hallsville (Texas)
Untreated 42.7  800 mPa.s at 100 s\(^{-1}\)
Hot water dried at
330° in PDU 55.5  800 mPa.s at 100 s\(^{-1}\)

Eagle Butte (Wyoming)
Untreated 44.6  800 mPa.s at 100 s\(^{-1}\)
Hot water dried at
330° in PDU 62.4  800 mPa.s at 100 s\(^{-1}\)

Spring Creek (Montana)
Untreated 48.4  800 mPa.s at 100 s\(^{-1}\)
Hot water dried at
330° in PDU 63.0  800 mPa.s at 100 s\(^{-1}\)

Usibelli Subbituminous\(^2\) Coal (Alaska)
Untreated 44.0  800 mPa.s at 100 s\(^{-1}\)
Hot water dried at 339° 62.0  800 mPa.s at 100 s\(^{-1}\)

Australian Brown Coal
Untreated 28.5  300 mPa.s at 100 s\(^{-1}\)
Hot water dried at 330° 48.0  300 mPa.s 100 s\(^{-1}\)

With respect to slurriability, the treated Neyveli lignite is found to approximately match with either treated North Dakota lignite or South Hallsville (Texas) lignite. In general it can be concluded that the slurriability percentage is lignite specific and varies with conditions of hydrothermal treatment.
The causes for poorer slurriability of the hydrothermally treated Neyveli I and II lignites and the better slurriability of Kutch and South Gujarat lignites were already explained in Chapter 3 under 3.7 based on petrological reasons, and the impact of the presence of certain petrological constituents on the chemical and physical characteristics of the hydrothermally treated lignites.

The particle size distribution of the feed lignite and the variation in the particle size distribution after hydrothermal treatment are other reasons for the higher slurriabilities of Kutch and South Gujarat lignites, compared to those of Neyveli I and II lignites.

6.0.1 Energy Density of Hydrothermally Treated Lignite - Water Slurries.

The increase in energy density of the hydrothermally treated lignite is evident. A comparison between the calorific values of as mined lignite and the treated LWS at its slurriability level is given below:
<table>
<thead>
<tr>
<th>Lignites</th>
<th>Calorific value of the as mined lignites, (kcal/kg)</th>
<th>Slurriability of the treated lignites (% by wt)</th>
<th>Calorific value of treated LWS at its slurriability level (kcal/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neyveli I</td>
<td>3593</td>
<td>52.79*</td>
<td>3516</td>
</tr>
<tr>
<td>Neyveli II</td>
<td>3081</td>
<td>49.54*</td>
<td>3243</td>
</tr>
<tr>
<td>Kutch</td>
<td>2474</td>
<td>53.40*</td>
<td>3255</td>
</tr>
<tr>
<td>South Gujarat</td>
<td>3505</td>
<td>55.45*</td>
<td>3543</td>
</tr>
</tbody>
</table>

### 6.1 Effect of Particle - Particle Interaction on Hydrothermally Treated Lignite-Water Slurries

The significance and the application of the parameter 'volume fraction of solids at maximum packing $\phi_m$' were discussed in chapter-4 under 4.2 with respect to raw lignites. As the magnitude of $\phi_m$ reflects mainly inter-particle interaction on slurries, it is necessary to determine the values of $\phi_m$ for hydrothermally treated lignites also. This will enable better understanding of the modifications in inter-particle interactions after hydrothermal treatment under different process conditions. The procedure for determination of $\phi_m$ was already given in chapter-4 under 4.2. The data used for the determination of volume fraction at maximum packing are furnished in
Tables 6.2.1 - 6.2.5 for Neyveli I, Neyveli II, Kutch and South Gujarat lignites. The plots for $\phi_m$ values determined are shown in Figs.6.7 - 6.20. The following inferences could be made after analysing the data of $\phi_m$ for different treated lignites.

1. Comparing the feed lignite with the treated lignite, there is considerable improvement in the values of solids volume fraction at maximum packing. The change in the values of $\phi_m$ for the hydrothermally treated lignites are due to the following reasons.

A. This change may probably be due to a change in the particle size distribution spectrum between a top size and a bottom size during the treatment as explained in Chapter 5 under 5.4

B. The inter-particle repulsive forces could have got increased consequent to the increase in hydrophobicity of the hydrothermally treated lignites. Due to this the particles could have slipped past one another and the net result is a denser packing than the dense random packing of dry solid spheres.

The ultimate effect on the value of $\phi_m$ is the resultant of A and B.
### Table 6.2.1

**Data for Determination of Volume Fraction at Maximum Packing and Correlation Plots - Treated Lignites**

<table>
<thead>
<tr>
<th>Solids Weight %</th>
<th>Solids Volume Fraction $\phi$</th>
<th>Relative Viscosity $(\mu_r)$</th>
<th>$(\mu_r - 1)^{-1}$</th>
<th>$(\sqrt{\mu_r} - 1)^{-1}$</th>
<th>$\phi_m$</th>
<th>$\phi_m / \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NEYVELI I (FEED)</td>
<td>$\phi_m = 0.415$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water holding Capacity : 23.20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NEYVELI I HTT 200</td>
<td>Density : 1.3469 g/ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>0.3925</td>
<td>350.6</td>
<td>0.0029</td>
<td>0.0564</td>
<td>1.149</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>0.4044</td>
<td>455.1</td>
<td>0.0022</td>
<td>0.0492</td>
<td>1.1597</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>0.4164</td>
<td>560.3</td>
<td>0.0018</td>
<td>0.0441</td>
<td>0.469</td>
<td>1.1263</td>
</tr>
<tr>
<td>45</td>
<td>0.4285</td>
<td>672.6</td>
<td>0.0015</td>
<td>0.401</td>
<td></td>
<td>1.0945</td>
</tr>
<tr>
<td>46</td>
<td>0.4408</td>
<td>908.2</td>
<td>0.0011</td>
<td>0.0343</td>
<td></td>
<td>1.0640</td>
</tr>
<tr>
<td>NEYVELI I HTT 230</td>
<td>Density : 1.3850 g/ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>0.3699</td>
<td>380.5</td>
<td>0.0026</td>
<td>0.0540</td>
<td>1.2436</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>0.3807</td>
<td>425.3</td>
<td>0.0024</td>
<td>0.0510</td>
<td>1.2083</td>
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</tr>
<tr>
<td>44</td>
<td>0.3916</td>
<td>488.6</td>
<td>0.0021</td>
<td>0.0474</td>
<td>0.460</td>
<td>1.1747</td>
</tr>
<tr>
<td>45</td>
<td>0.4026</td>
<td>549.9</td>
<td>0.0018</td>
<td>0.0445</td>
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<td>1.1426</td>
</tr>
<tr>
<td>46</td>
<td>0.4138</td>
<td>654.9</td>
<td>0.0015</td>
<td>0.0407</td>
<td></td>
<td>1.1116</td>
</tr>
<tr>
<td>NEYVELI I HTT 260</td>
<td>Density : 1.4133 g/ml</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>0.3589</td>
<td>243.0</td>
<td>0.0041</td>
<td>0.0685</td>
<td>1.2761</td>
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<tr>
<td>43</td>
<td>0.3903</td>
<td>346.0</td>
<td>0.0029</td>
<td>0.0568</td>
<td>1.1735</td>
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</tr>
<tr>
<td>44</td>
<td>0.4010</td>
<td>449.9</td>
<td>0.0022</td>
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<td>0.458</td>
<td>1.1421</td>
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<tr>
<td>45</td>
<td>0.4118</td>
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<td>0.0020</td>
<td>0.0470</td>
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<td>1.1122</td>
</tr>
<tr>
<td>46</td>
<td>0.4227</td>
<td>607.3</td>
<td>0.0016</td>
<td>0.0423</td>
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<td>1.0835</td>
</tr>
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</table>
### TABLE 6.2.2

**DATA FOR DETERMINATION OF VOLUME FRACTION AT MAXIMUM PACKING AND CORRELATION PLOTS - TREATED LIGNITES**

<table>
<thead>
<tr>
<th>Solids Weight %</th>
<th>Solids Volume Fraction φ</th>
<th>Relative Viscosity (μr)</th>
<th>(μr - 1)^-1</th>
<th>(VR - 1)^-1</th>
<th>φm</th>
<th>φm / φ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NEYVELI I HTT 290</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density : 1.4168 g/ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>0.3819</td>
<td>190.1</td>
<td>0.0053</td>
<td>0.0782</td>
<td>0.483</td>
<td>1.264</td>
</tr>
<tr>
<td>48</td>
<td>0.4130</td>
<td>350.3</td>
<td>0.0029</td>
<td>0.0564</td>
<td>0.483</td>
<td>1.1695</td>
</tr>
<tr>
<td>50</td>
<td>0.4342</td>
<td>477.4</td>
<td>0.0021</td>
<td>0.0480</td>
<td>0.483</td>
<td>1.1124</td>
</tr>
<tr>
<td>51</td>
<td>0.4449</td>
<td>525.7</td>
<td>0.0019</td>
<td>0.0456</td>
<td>0.483</td>
<td>1.0856</td>
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<tr>
<td>52</td>
<td>0.4557</td>
<td>793.0</td>
<td>0.0013</td>
<td>0.0368</td>
<td>0.483</td>
<td>1.0599</td>
</tr>
</tbody>
</table>

Water holding Capacity : 8.01%

| **NEYVELI I HTT 320** |
| Density : 1.3910 g/ml | | | | | | |
| 45 | 0.3790 | 135.7 | 0.0074 | 0.0939 | 0.515 | 1.3588 |
| 48 | 0.4090 | 298.4 | 0.0034 | 0.0614 | 0.515 | 1.2592 |
| 50 | 0.4293 | 445.5 | 0.0022 | 0.0497 | 0.515 | 1.1996 |
| 52 | 0.4500 | 529.9 | 0.0019 | 0.0454 | 0.515 | 1.1444 |
| 53 | 0.4605 | 654.1 | 0.0015 | 0.0407 | 0.515 | 1.1183 |

Water holding Capacity : 4.44%
### TABLE 6.2.3

**DATA FOR DETERMINATION OF VOLUME FRACTION AT MAXIMUM PACKING AND CORRELATION PLOTS - TREATED LIGNITES**

<table>
<thead>
<tr>
<th>Solids Weight %</th>
<th>Solids Volume Fraction $\phi$</th>
<th>Relative Viscosity $\mu_r$</th>
<th>$(\phi_r - 1)^{-1}$</th>
<th>$(\phi_{m} - 1)^{-1}$</th>
<th>$\phi_m$</th>
<th>$\phi_m / \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NEYVELI II (FEED)</strong></td>
<td>$\phi_m = 0.409$</td>
<td>Water holding Capacity: 22.99%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NEYVELI II HTT 260 Density: 1.3153 g/ml</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.3563</td>
<td>175.7</td>
<td>0.0057</td>
<td>0.0816</td>
<td>0.450</td>
<td>1.2630</td>
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<td>41</td>
<td>0.3668</td>
<td>232.5</td>
<td>0.0043</td>
<td>0.0702</td>
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<td>1.2268</td>
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<td>42</td>
<td>0.3774</td>
<td>315.6</td>
<td>0.0032</td>
<td>0.0596</td>
<td></td>
<td>1.1924</td>
</tr>
<tr>
<td>43</td>
<td>0.3880</td>
<td>500.8</td>
<td>0.0020</td>
<td>0.0468</td>
<td></td>
<td>1.1598</td>
</tr>
<tr>
<td>45</td>
<td>0.4097</td>
<td>735.3</td>
<td>0.0014</td>
<td>0.0383</td>
<td></td>
<td>1.0984</td>
</tr>
<tr>
<td><strong>NEYVELI II HTT 290 Density: 1.3536 g/ml</strong></td>
<td></td>
<td>Water holding Capacity: 7.69%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>0.3516</td>
<td>170.9</td>
<td>0.0059</td>
<td>0.0828</td>
<td>0.504</td>
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<td>0.0026</td>
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<td>1.2854</td>
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<td>1.2209</td>
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<tr>
<td>48</td>
<td>0.4233</td>
<td>574.1</td>
<td>0.0017</td>
<td>0.0436</td>
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<td>1.1906</td>
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<tr>
<td><strong>NEYVELI II HTT 320 Density: 1.4012 g/ml</strong></td>
<td></td>
<td>Water holding Capacity: 5.76%</td>
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<td>47</td>
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<td>0.0451</td>
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<td>1.1983</td>
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<td>0.0402</td>
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<td>1.1696</td>
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<td>889.2</td>
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<td>0.0347</td>
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<td>1.1153</td>
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</table>
## Table 6.2.4
### Data for Determination of Volume Fraction at Maximum Packing and Correlation Plots - Treated Lignites

<table>
<thead>
<tr>
<th>Solids Weight %</th>
<th>Solids Volume Fraction $\phi$</th>
<th>Relative Viscosity $\mu_r$</th>
<th>$(\mu_r - 1)^{-1}$</th>
<th>$\gamma(\mu_r - 1)^{-1}$</th>
<th>$\phi_m$</th>
<th>$\phi_m / \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KUTCH (FEED)</td>
<td>$\phi_m$ = 0.435</td>
<td>Water holding Capacity : 20.42%</td>
<td></td>
<td></td>
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<tr>
<td>KUTCH HTT 260</td>
<td></td>
<td>Water holding Capacity : 9.67%</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Density : 1.3562 g/ml</td>
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<tr>
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<td>0.488</td>
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<td>48</td>
<td>0.4277</td>
<td>235.3</td>
<td>0.0043</td>
<td>0.0697</td>
<td>0.488</td>
<td>1.1410</td>
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<tr>
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<td>0.0028</td>
<td>0.0556</td>
<td>0.488</td>
<td>1.1129</td>
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<td>50</td>
<td>0.4494</td>
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<td>0.0020</td>
<td>0.0466</td>
<td>0.488</td>
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<td>51</td>
<td>0.4604</td>
<td>677.9</td>
<td>0.0015</td>
<td>0.0399</td>
<td>0.488</td>
<td>1.0599</td>
</tr>
<tr>
<td>KUTCH HTT 290</td>
<td></td>
<td>Water holding Capacity : 6.89%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density : 1.4073 g/ml</td>
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<tr>
<td>50</td>
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<tr>
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<td>0.585</td>
<td>1.3194</td>
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<td>1.2883</td>
</tr>
<tr>
<td>53</td>
<td>0.4649</td>
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<td>0.0018</td>
<td>0.0443</td>
<td>0.585</td>
<td>1.2583</td>
</tr>
<tr>
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<td>0.4758</td>
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<td>0.0403</td>
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<td>1.2295</td>
</tr>
<tr>
<td>KUTCH HTT 320</td>
<td></td>
<td>Water holding Capacity : 4.30%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density : 1.4133 g/ml</td>
<td></td>
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<td></td>
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<tr>
<td>52</td>
<td>0.4483</td>
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<td>0.0760</td>
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<td>1.3049</td>
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<td>0.0457</td>
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<td>0.0426</td>
<td>0.585</td>
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### TABLE 6.2.5

**DATA FOR DETERMINATION OF VOLUME FRACTION AT MAXIMUM PACKING AND CORRELATION PLOTS - TREATED LIGNITES**

<table>
<thead>
<tr>
<th>Solids Weight %</th>
<th>Solids Volume Fraction $\phi$</th>
<th>Relative Viscosity $\mu_r$</th>
<th>$(\mu_r - 1)^{-1}$</th>
<th>Water holding Capacity</th>
<th>$\phi_m$</th>
<th>$\phi_m / \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOUTH (FEED)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\phi_m = 0.474$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOUTH GUJARAT</td>
<td></td>
<td></td>
<td></td>
<td>Water holding Capacity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HTT 290 Density</td>
<td>1.3020 g/ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density :</td>
<td>1.3005 g/ml</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water holding Capacity : 8.85%</td>
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<td>1.1729</td>
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<td>50</td>
<td>0.4686</td>
<td>466.4</td>
<td>0.0021</td>
<td>0.0486</td>
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<td>1.1161</td>
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<tr>
<td>51</td>
<td>0.4801</td>
<td>572.3</td>
<td>0.0018</td>
<td>0.0436</td>
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<td>1.0894</td>
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<td>52</td>
<td>0.4916</td>
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<td>0.0013</td>
<td>0.0372</td>
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<td>1.0639</td>
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<td></td>
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</tr>
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<td>HTT 260 Density</td>
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<td>Density :</td>
<td>1.3005 g/ml</td>
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<tr>
<td></td>
<td>Water holding Capacity : 12.89%</td>
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<td>275.4</td>
<td>0.0036</td>
<td>0.0641</td>
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<td>1.1729</td>
</tr>
<tr>
<td>50</td>
<td>0.4686</td>
<td>466.4</td>
<td>0.0021</td>
<td>0.0486</td>
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<td>1.1161</td>
</tr>
<tr>
<td>51</td>
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<td>572.3</td>
<td>0.0018</td>
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<td>779.1</td>
<td>0.0013</td>
<td>0.0372</td>
<td></td>
<td>1.0639</td>
</tr>
<tr>
<td>SOUTH GUJARAT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HTT 320 Density</td>
<td>1.3020 g/ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density :</td>
<td>1.3020 g/ml</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Water holding Capacity : 5.04%</td>
<td></td>
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<td></td>
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<td></td>
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<td>0.0033</td>
<td>0.0612</td>
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<td>1.1122</td>
</tr>
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<td>0.0399</td>
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<td>0.0012</td>
<td>0.0363</td>
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<td>1.0772</td>
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</table>
Fig. 6.7 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli 1 HTT 200
Fig. 6.8 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli I HTT 230

$\phi_m = 0.460$
Fig. 6.9  Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli I HTT 260
Fig. 6.10 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli I HTT 290
Fig. 6.11 Plot of $\frac{1}{\mu_r - 1}$ vs solids volume fraction for Neyveli I HTT 320
Fig. 6.12 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli II HTT 260
Fig. 6.13  Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli II HTT 290
Fig. 6.14  Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Neyveli II HTT 320
Fig. 6.15 Plot of \([\mu_r - 1]^{-1}\) vs solids volume fraction for Kutch HTT 260
Fig. 6.16 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Kutch HTT 290
Fig. 6.17 Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for Kutch 320
Fig. 6.18 Plot of $[\mu_r - 1]^{-1}$ vs solid volume fraction for South Gujarat HTT 260

\[\varphi_m = 0.523\]
Fig. 6.19  Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for South Gujarat HTT 290
Fig. 6.20  Plot of $[\mu_r - 1]^{-1}$ vs solids volume fraction for South Gujarat HTT 320

Solids volume fraction

$\phi_m = 0.558$
2. The trend in the increase of the values of $\phi_m$ with increase in hydrothermal treatment temperatures is found to depend mainly on the feed lignite characteristics. In the case of Neyveli I, the values of $\phi_m$ decrease from 0.469 to 0.458 from a treatment temperature of 200° to 260°. From 260° the value of $\phi_m$ increases from 0.458 to 0.515 up to 320°. This observation is supported by the determinations of particle size distribution for the treated Neyveli I lignites. There is a shortening of the spectrum of particle size distribution for the lignites treated at 200° to 260° and thereafter there is a steady improvement towards widening of the spectrum of particle size distribution up to 320° (Ref. Table 5.19). Moreover, from 260° the steady increase in hydrophobicity of the surfaces starts and the effect of the repulsive forces due to increase in hydrophobicity dominates the effect due to the changes in the spectrum of particle size distribution. This dominating effect of the repulsive forces resulting in the increase of $\phi_m$ could be observed from a treatment temperature of 260°.

3. In the case of Neyveli II, the values of $\phi_m$ increase from 0.450 at 260° to 0.504 at 290° and thereafter the value remains unaltered even at 320°. This is again supported by the determination of the particle size distribution of the treated Neyveli II lignite. The
spectrum of particle size distribution gets widened when treated at 290° (Ref. Table 5.19). The widened particle size distribution remains same even at a treatment temperature of 320°. Hence the value of $\phi_m$ remains unaltered after treatment at 290°. Probably the effect due to repulsive forces are not reflected in altering $\phi_m$ value after a treatment temperature of 290°. Eventhough the $\phi_m$ values for Neyveli II at treatment temperatures of 290° and 320° remain same as 0.504, it is found that the slurriability increases by 1.0% (from 48.52% to 49.54%) for a temperature rise from 290° to 320°. The cause for such an observation is not clear. A possible view may be that the variation of the slurriability is more sensitive to small changes in hydrophobicity alone of the lignite than to changes in the value of $\phi_m$ which depends both on changes of particle size distribution and the hydrophobicity.

4. The values of $\phi_m$ for Kutch lignite increases from 0.488 at the treatment temperature of 260° to 0.585 at 290°. Thereafter, the value of $\phi_m$ remains constant even at the treatment temperature of 320°. The increase in slurriability from 290° to 320° is by 2% eventhough the values of $\phi_m$ for the two treatment temperatures remain same as 0.585. The probable cause for such an observation is the same as explained in the case of Neyveli II lignite.
5. In the case of South Gujarat lignite there is a gradual increase in values of $\phi_m$ as the treatment temperature increases. The corresponding increase in slurriability is also gradual.

6.1.1 Testing of Correlations and Determination of Frankel and Acrivos Parameters.

Correlation plots for all the hydrothermally treated lignites were obtained using the values of volume fraction of solids at maximum packing ($\phi_m$) and values of $\phi_m/\phi$ and $(\sqrt{\overline{\mu_r}} - 1)^{-1}$. The plots are shown in Figs. 6.21 - 6.34. The Frankel and Acrivos parameters for all the treated lignites are shown in Table 6.3. An inspection of the plots indicates that except for Kutch lignite, good correlation is obtained. Comparing the $\phi_m$ and K values for the feed and hydrothermally treated lignite at 320°, the following general observations can be made.

a) As the value of $\phi_m$ increases from the feed to hydrothermally treated ones, the corresponding K value also increases. But the magnitude of this increase in the value of K is not constant but differs from lignite to lignite.

b) Generally the values of K for all the feed lignites are lower than those for the treated lignites.
Fig. 6.21 Correlation plot for Neyveli I
HTT 200
Fig. 6.22 Correlation plot for Neyveli I
HTT 230
Fig. 6.23 Correlation plot for Neyveli I
HTT 260
Fig. 6.24 Correlation plot for Neyveli I
HTT 290

$[\sqrt{\mu_x} - 1]^{-1}$

Slope: 0.202
$K = 4.947$
Fig. 6.25 Correlation plot for Neyveli I
HTT 320
$[\sqrt{\mu_x - 1}]^{-1}$

Slope: 0.221
$K = 4.518$

Fig. 6.26 Correlation plot for Neyveli II
HTT 260
Fig. 6.27 Correlation plot for Neyveli II
HTT 290

Slope: 0.128
K = 7.800
Fig. 6.28 Correlation plot for Neyveli II
HTT 320
Fig. 6.29. Correlation plot for Kutch

HTT 260
Fig. 6.30 Correlation plot for Kutch HTT 290

Slope: 0.197
K = 5.079

[\sqrt{\mu_r - 1}]^{-1}
Fig. 6.31 Correlation plot for Kutch
HTT 320
Fig. 6.32  Correlation plot for South Gujarat
HTT 260

\[ \left[ \sqrt[\mu_x]{} - 1 \right]^{-1} \]

Slope: 0.255
K = 3.921
Fig. 6.33 Correlation plot for South Gujarat
HTT 290
Fig. 6.34 Correlation plot for South Gujarat

HTT 320
### TABLE 6.3

**FRANKEL AND ACRIVOS PARAMETERS FOR HYDROTHERMALLY TREATED LIGNITES**

<table>
<thead>
<tr>
<th>LIGNITES</th>
<th>NEYVELI I</th>
<th>NEYVELI II</th>
<th>KUTCH</th>
<th>SOUTH GUJARAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREATMENT TEMPERATURE</td>
<td>FEED</td>
<td>200</td>
<td>230</td>
<td>260</td>
</tr>
<tr>
<td>Slope</td>
<td>0.366</td>
<td>0.162</td>
<td>0.096</td>
<td>0.159</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>0.415</td>
<td>0.469</td>
<td>0.460</td>
<td>0.458</td>
</tr>
</tbody>
</table>
c) As predicted by Botsaris et al. the value of K is found to be different for each slurry in contrast to the report by Chong et al\textsuperscript{93}. as between 0.75 and 1.0 for all slurries.

d) The observations of Botsaris et al. show that the static / agglomerating stability of the slurries will increase as the K values decrease. Based on the above observation, it can be concluded as below:

In the case of Neyveli I, it is seen that among the treated lignites the K values steadily decrease from 6.160 to 4.521. This indicates that the aggregate stability increases as the temperature of treatment increases.

The opposite of the above is found to be true in the case of Neyveli II since the K values increase as the treatment temperature increases. In this case, the aggregate stability is predicted to decrease as the temperature of treatment increases.

Similarly, for Kutch lignite the aggregate stability may decrease as the temperature of treatment increases. In the case of South Gujarat lignite, the aggregate stability is not affected as the temperature of treatment increases.
6.2 Rheology of Hydrothermally Treated Lignite-Water Slurries.

The experimental conditions followed during the rheological studies are as below.

1. The water slurries of the treated lignites were prepared using samples dried in a current of nitrogen at 30°.

2. No dry grinding or adjustment to vary the particle size distribution was attempted during the rheological studies, and during the preparation of slurries using treated lignites. The particle size of the treated lignite samples were the same as indicated in chapter 5 under 5.4.

3. All the rheological test runs were conducted at 25°, the temperature being controlled using Haake constant temperature bath / circulator.

4. The mixing time during slurry preparation prior to rheological measurements was maintained as 1 min which is the same as the time followed during the studies of raw lignite slurry rheology.

5. The solid loadings of the treated lignite water slurries were maintained the same for better comparison of the flow behaviour of the treated LWS with that of raw LWS. The effect of hydrothermal
treatment temperature on the flow behaviour of treated LWS can also be compared if the solids loading of the slurries are maintained the same.

The following experiments were conducted.

1. Study of the variation of shear stress / viscosity with shear rate for Neyveli I LWS treated at 200, 230, 260, 290 and 320°. (Figs. 6.35 and 6.36). The solids loading was maintained as 42% by weight for all the above slurries.

2. Studies were conducted on the variation of shear stress / viscosity with shear rate for others as below:

<table>
<thead>
<tr>
<th>Lignite</th>
<th>Treatment temperatures</th>
<th>Solids loading(wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neyveli II</td>
<td>260, 290, and 320°</td>
<td>40.0</td>
</tr>
<tr>
<td>Kutch</td>
<td>260, 290, and 320°</td>
<td>45.0</td>
</tr>
<tr>
<td>South Gujarat</td>
<td>260, 290, and 320°</td>
<td>48.0</td>
</tr>
</tbody>
</table>

The flow curves and viscosity curves are given in Figs. 6.37 - 6.42. The best fit model to the flow curve with its specific constants were determined using computer.

The rheological data for the treated LWS are furnished in Table 6.4. The data output from the Haake viscometer system RV20 were not furnished since the corresponding rheograms and viscosity curves were presented. The following conclusions are made.
Fig. 6.35  Rheograms for hydrothermally treated Neyveli I LWSs.
Fig. 6.36 Viscosity curves for hydrothermally treated Neyveli I LWSs.
Fig. 6.37 Rheograms for hydrothermally treated Neyveli II LWSs.
Fig. 6.38 Viscosity curves for hydrothermally treated Neyveli II LWSs.
Fig. 6.39 Rheograms for hydrothermally treated Kutch LWSs.
Fig. 6.40. Viscosity curves for hydrothermally treated Kutch LWSs.
Fig. 6.41 Rheograms for hydrothermally treated South Gujarat LWSs.
Fig. 6.42 Viscosity curves for hydrothermally treated South Gujarat LWSs.
<table>
<thead>
<tr>
<th>Treatment Temperature °C</th>
<th>Feed 200</th>
<th>Feed 230</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>M</td>
<td>m</td>
<td>Hi</td>
<td>o^</td>
<td>o^-</td>
<td>3</td>
<td>S</td>
<td>X</td>
<td>o^</td>
<td>o^-</td>
<td>3</td>
<td>S</td>
<td>X</td>
<td>o^</td>
<td>o^-</td>
<td>3</td>
<td>S</td>
</tr>
</tbody>
</table>

**Table 6.4**

**RHEOLOGICAL DATA TREATED LIGNITE - WATER SLURRIES**

<table>
<thead>
<tr>
<th>Treatment Temperature °C</th>
<th>Feed 200</th>
<th>Feed 230</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
<th>Feed 260</th>
<th>Feed 290</th>
<th>Feed 320</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEST FIT</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td>Ostwald</td>
<td>Ostwald</td>
<td>Ostwald</td>
<td>Ostwald</td>
<td>Bingham</td>
<td>Bingham</td>
<td>Bingham</td>
<td>Bingham</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td>Herschel Bulkley</td>
<td></td>
</tr>
<tr>
<td>Low behaviour</td>
<td>HER-</td>
<td>HER-</td>
<td>HER-</td>
<td>HER-</td>
<td>OSTA-</td>
<td>OSTA-</td>
<td>OSTA-</td>
<td>OSTA-</td>
<td>BING-</td>
<td>BING-</td>
<td>BING-</td>
<td>BING-</td>
<td>HER-</td>
<td>HER-</td>
<td>HER-</td>
<td>HER-</td>
<td></td>
</tr>
<tr>
<td>Regression coefficient (R^2)</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>0.99</td>
<td>1.00</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td>1.00</td>
<td>0.99</td>
<td>0.99</td>
<td>1.00</td>
<td>1.00</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Yield stress (τ₀)</td>
<td>2.910</td>
<td>2.72</td>
<td>2.51</td>
<td>1.93</td>
<td>1.70</td>
<td>1.59</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.429</td>
<td>2.894</td>
<td>1.638</td>
<td>0.4218</td>
<td>4.557</td>
<td>3.615</td>
<td>2.823</td>
</tr>
<tr>
<td>Viscosity (η) Slope</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7.826</td>
<td>2.636</td>
<td>0.0233</td>
<td>0.0091</td>
<td>—</td>
</tr>
<tr>
<td>Low consistency number (K)</td>
<td>24.68</td>
<td>20.38</td>
<td>17.55</td>
<td>15.10</td>
<td>14.50</td>
<td>9.35</td>
<td>31.7</td>
<td>25.15</td>
<td>20.70</td>
<td>15.60</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>25.10</td>
<td>18.32</td>
<td>12.30</td>
</tr>
<tr>
<td>Low behaviour index (n)</td>
<td>0.63</td>
<td>0.60</td>
<td>0.59</td>
<td>0.57</td>
<td>0.50</td>
<td>0.42</td>
<td>0.34</td>
<td>0.33</td>
<td>0.28</td>
<td>0.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.70</td>
<td>0.68</td>
<td>0.59</td>
</tr>
</tbody>
</table>

213
1. The hydrothermally treated LWS of Neyveli I lignites were found to behave as yield, pseudoplastic lignites obeying Herschel Bulkley equation. Similar observations are reported with respect to low rank coals by Germane et al.\textsuperscript{131}. Hydrothermally treated South Gujarat lignites behave similarly. The above observations agree with those of Woskoboenko\textsuperscript{132} who has shown that flow behaviour of coal suspensions was highly influenced by prior drying and dewatering. The solids loading being the same, the hydrothermally treated LWS showed a gradual decrease in yield stress values with increase in the treatment temperatures. In the cases of both Neyveli I and South Gujarat lignites the flow consistency numbers (K) for the pseudoplastic slurries were found to decrease as the treatment temperature increases. Obviously, this indicates that much easier flow can be achieved for the slurries treated at higher temperature viz., 320°.

In the case of raw Neyveli I LWS, the value of flow behaviour index (n) reduced due to hydrothermal treatment. This reduction in the value of ‘n’ continues gradually as the temperature of treatment increases. The same phenomenon was observed with respect to raw and treated South Gujarat LWS. For Neyveli I LWS the reduction in the value of ‘n’ is from 0.63 (feed LWS) to 0.42 (LWS treated at 320°). For South Gujarat LWS
the reduction in the value of ‘n’ is from 0.70 (feed LWS) to 0.51 (LWS treated at 320°C). In the above cases, for raw and treated LWSs, the solids loadings remained same.

2) Both the untreated and hydrothermally treated Neyveli II LWS, behave as Ostwald liquids. Here again, there is a reduction in both flow consistency number and flow behaviour index, when the untreated LWSs are compared with treated ones. There is gradual decrease in the values of K and n as the treatment temperature increases.

3) Both the raw and hydrothermally dried Kutch LWSs, behave as Bingham plastics. Being Bingham plastics, they behave as a non-fluid gel when stationary, but become easily fluid once set in motion at shear stress beyond its yield point. Similar Bingham plastic behaviour with respect to hot water dried North Dakota lignite slurries are reported by Hauserman\textsuperscript{133}. The solids loading remaining same as 45% by weight the yield stress values decrease as the treatment temperature increases for the treated LWS. Higher solids loading will result in an increase in yield stress, and especially in the case of Bingham plastic slurries, Hauserman recommends the use of an additive to reduce the yield stress.

Some common observations can be listed as under:

1. The general flow behaviour (whether Ostwald, Herschel-Bulkley or Bingham) of the raw lignite-water slurry is not changed due to hydrothermal treatment.
2. But the rheological and flow parameters like yield stress, flow behaviour index, and flow consistency number are altered due to hydrothermal treatment, resulting in slurries having better flow characteristics and slurriabilities.

3. The reduction in yield stress value after hydrothermal treatment is mainly due to removal of hydrophilic groups (−COOH) from lignite structure, the presence of which in larger extent will create a net work structure in the slurry and thereby increase the yield stress.

6.3. Effect of Time of Shear on Shear Stress / Viscosity.

Parallel to the investigations on the thixotropic characteristics of untreated lignites as explained under 4.5, a series of experiments were done to understand the effect of hydrothermal treatment on thixotropic characteristics. The experimental conditions were the same as explained under 6.2 except for solids loading of LWS.

The solids loadings are selected depending on the rheological behaviour of individual lignites predicted in chapter-4. Wu et al.\textsuperscript{134} have found that the apparent viscosities of raw brown coal suspensions were too large to measure when the solid contents was greater than 45% by weight. As the LWSs become very thick beyond 45% the
solids loading was maintained at 45% by weight during the studies on thixotropy.

**List of Experiments:**

1. **Study on the Variation of Viscosity with Time at Different Shear Rates viz., 50, 100, and 150 s⁻¹.**
   The studies are conducted for
   a) Raw Neyveli I LWS and Neyveli I LWSs treated at 200, 230, 260, 290 and 320°, Figs. 6.43 - 6.48.
   b) Raw Neyveli II LWSs of 40% by weight solids loading, Fig. 6.49.
   c) Raw Kutch LWS and Kutch LWSs treated at 260, 290 and 320° with 45% by weight solids loading, Figs. 6.50 - 6.53.
   d) Raw South Gujarat LWS and treated South Gujarat LWS at 260, 290, and 320° with 45% by weight solids loading, Figs. 6.54 - 6.57.
   e) Singareni (Bituminous) CWS with 55% by weight solids loading, Fig. 6.58.

2. **Studies on Thixotropy by the Method of Hysteresis Loop.**
   The programmable rotational viscometer RV 20 was found quite adequate and sensitive to measure thixotropy of the LWS, subjecting it to a shear cycle as shown in Figs. 6.59 and
6.72. According to Mewis, the thixotropy is the major remaining problem in the field of theoretical rheology. The main reason is the lack of a perfect measuring method of thixotropy at present\textsuperscript{135}. The RV 20 Viscometer system could measure the phenomenon of thixotropy using a Rheocontroller RC 1 through which the entire shear cycle to measure thixotropy could be programmed precisely. The method was explained already in chapter 2 under 2.15.3.

In this method, the area of the hysteresis loops were used as a measure of the degree of thixotropy\textsuperscript{136}.

The experiments on thixotropy involving shear cycles are done for the following.

a) Neyveli I LWS (raw) with 40\% by weight solids loading, Fig.6.60

b) Neyveli I LWS (raw) with 45\% by weight solids loading and the same treated at different hydrothermal treatment temperatures, Figs. 6.61 & 6.66.

c) Raw Neyveli II LWS (40\% solids loading), Fig. 6.67

d) Raw and Treated Neyveli II LWS at different hydrothermal temperatures, Figs.6.68 - 6.71.

e) Raw Kutch LWS (45\% solids loading) and treated ones at different temperatures, Figs.6.73 - 6.75

f) Kutch LWS with increased solids loading of 50\% by weight, Figs.6.76 and 6.77.
g) Singareni CWS (Bituminous) untreated with solids loading of 58% by weight Fig. 6.78. This is done for comparison purposes.

6.3.1. Observations on Thixotropic Behaviour of Hydothermally Treated LWS.

Generally the viscosity - time curves are found to have an initial steep decrease in viscosity up to a finite time. Then the curve tends either to flatten or shows a slight increase in viscosity with further increase of time. In all our studies, the initial steep decrease in viscosity is found to be a linear behaviour as can be seen from the curves. Regression analyses were carried out for all the viscosity - time curves fitting the initial linear drops in viscosity with time with straight lines (\(Y = mX + c\)) and the slopes of those lines were determined.

The values of slopes \(d\eta/dt\) is obviously quite different from \(d\eta/d\ln t\) which was discussed under 2.15.4. Since the value of \(d\eta/dt\) is proportional to \(d\eta/d\ln t\), it can be considered to represent the coefficient of thixotropic breakdown time. The values of \(d\eta/dt\) for raw and hydrothermally treated Neyveli I and south Gujarat LWS are shown in Table 6.5.

For Neyveli II lignites the viscosity vs time curves were found irregular and hence the coefficients could not be calculated. For both raw and treated Kutch lignites, no
Fig. 6.43 Viscosity-time curves for different shear rates-Raw Neyveli I LWSs.
Fig. 6.44 Viscosity-time curves for different shear rates - Neyveli I LWSs - HTT 200.
Fig. 6.45  Viscosity - time curves for different shear rates - Neyveli I LWSs-HTT 230
Fig. 6.46 Viscosity -time curves for different shear rates- Neyveli I LWSs - HTT 260

VISCOSITY VS TIME
NEYVELI I LWS- HTT 260
SOLIDS LOADING: 45% BY WEIGHT
Fig. 6.47 Viscosity - Time curves for different shear rates - Neyveli I LWSs - HTT 290

Viscosity vs Time

Neyveli I LWS - HTT 290

Solids loading: 45% by weight

Apparent viscosity (mPa s)

Time (min)

52 (1/s), 100 (1/s), 150 (1/s)
Fig. 6.48 Viscosity-Time curves for different shear rates - Neyveli I LWS - HTT 320.
Fig.6.49 Viscosity-time curves for different shear rates- raw Neyveli II LWSs.
Fig. 6.50  Viscosity-time curves for different shear rates- raw Kutch LWSs.
Fig. 6.51 Viscosity-Time curves for different shear rates- Kutch LWSs- HTT 260
Fig. 6.52  Viscosity-Time curves for different shear rates- Kutch LWSs- HTT 290
Fig. 6.53  Viscosity-Time curves for different shear rates- Kutch LWSs- HTT 320
Fig. 6.54 Viscosity - Time curves for different shear rates - raw South Gujarat LWSs.
Fig. 6.55  Viscosity-Time curves for different shear rates- South Gujarat LWSs - HTT 260
Fig. 6.56 Viscosity-Time curves for different shear rates- South Gujarat LWSs- HTT 290
Fig. 6.57  Viscosity-Time curves for different shear rates- South Gujarat
LWSs- HTT 320
Fig. 6.58  Viscosity -Time curves for different shear rates- Singareni CWSs (bituminous)
Fig. 6.59 The shear cycle used in the thixotropic studies- Neyveli I LWSs
Fig. 6.60 Raw Neyveli LWS 40% by weight solids loading - Thixotropic studies.
Shear rate (1/s) →

Fig. 6.61 Raw Neyveli I LWS 45% by weight solids loading - Thixotropic studies.
Fig. 6.62 Neyveli I-HTT 200 - Thixotropic studies.
Fig. 6.63 Neyveli I-HTT 230 - Thixotropic studies.
Fig. 6.64 Neyveli I - HTT 260 - Thixotropic studies.
Fig. 6.65 Neyveli I-HTT 290 - Thixotropic studies.
Fig. 6.66 Neyveli I- HTT 320- Thixotropic studies.
Fig. 6.67 Raw Neyveli II (40% by weight - solids loading)- Thixotropic studies.
Fig. 6.68 Raw Neyveli II (45% by weight-solids loading)- Thixotropic studies.
Fig. 6.69  Neyveli II LWSs - HTT 260- Thixotropic studies.
Fig. 6.70 Neyveli II LWSs - HTT 290 - Thixotropic studies.
Fig. 6.71 Neyveli II LWSs-HTT 320-Thixotropic studies.
Fig. 6.72 The shear cycle used in the thixotropic studies-Kutch LWSs.
Fig. 6.73  Raw Kutch LWS (45% solids loading)-Thixotropic studies
Fig. 6.74 Kutch LWSs- HTT 260 & HTT 290-
Thixotropic studies.
Fig. 6.75 Kutch LWSs- HTT 320- Thixotropic studies.
Fig. 6.76 Kutch LWSs (50% solids loading) raw & HTT-260- Thixotropic studies.
Fig. 6.77  Kutch LWSs (50% solids loading) HTT 290 & HTT 320- Thixotropic studies.
Fig. 6.78 Singareni CWS (bituminous) - Solids loading 50% by weight. - Thixotropic
TABLE 6.5

DATA ON COEFFICIENT OF THIXOTROPIC BREAKDOWN WITH TIME

<table>
<thead>
<tr>
<th>IGNITE</th>
<th>REAIDIMENT TEMPERATURE °</th>
<th>NEYVELI I</th>
<th>SOUTH GUJARAT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>200</td>
<td>230</td>
</tr>
<tr>
<td>HEAR RATE (s⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>62.1</td>
<td>50.0</td>
<td>52.1</td>
</tr>
<tr>
<td>100</td>
<td>121.2</td>
<td>281.3</td>
<td>213.6</td>
</tr>
<tr>
<td>150</td>
<td>104.6</td>
<td>189.9</td>
<td>87.3</td>
</tr>
</tbody>
</table>
thixotropy was found and hence the initial dip of the viscosity time curve was not present. Except for some irregularities, it can generally be concluded from the values of $d\eta/ dt$ that under the constant shear rate conditions, the coefficient of thixotropic breakdown with time decreases and tends to a least number as the treatment temperature increases. Also from the examination of the viscosity time curves shown in Figs.6.43 - 6.48 (Neyveli I) it is inferred that under constant shear rate conditions, the curves get flattened and finally become more or less parallel to the time axis as the hydrothermal treatment temperature increases. The curves corresponding to treatment temperatures of $290^\circ$ and $320^\circ$ are quite comparable with the viscosity time curves obtained for Singareni (bituminous) CWS of 55% solids loading as shown in Fig.6.58. The same observations were found true in the cases of Neyveli II and South Gujarat lignites also. For raw Kutch LWS (45% by weight solids loading), the viscosity time curves showed an increase in viscosity with time at constant lower shear rate condition ($50 \text{ s}^{-1}$). This behaviour can be compared very well with Fig. 4.28 wherein the Kutch LWS of solids content 46% by weight behaves as a rheopectic liquid at constant shear rate of $100 \text{ s}^{-1}$. Hydrothermal treatment tends to induce some thixotropy for Kutch LWS (45% by weight) observable at low constant shear conditions viz., 50 and $100 \text{ s}^{-1}$. Even this small variation is absent at higher
constant shear rate condition viz., 150 s$^{-1}$ and at higher treatment temperature viz., 320°. Thus Kutch LWS (45% by wt) does not show thixotropy after treatment at 320° at constant shear rate of 150 s$^{-1}$ (Fig.6.53).

**Study on Thixotropy by Hysteresis Loop Method - Observations.**

The area of the hysteresis loops obtained for raw and treated Neyveli I and Neyveli II LWS are shown in Table 6.6. The total shear cycle time was selected as 15 min. (Fig.6.59) since it was found by trial and error that this was quite adequate to achieve completion of thixotropic breakdown and equilibrium status thereafter. The problem faced during the test runs was due to the overlapping of the II and III loops probably due to drying of the slurry during this extended period of shear cycle. Again it was found that after the III loop, the area became negligibly small and overlap occurred as well, if the cycle period was extended beyond 15 min. since the equilibrium status could very well be achieved within 15 min. It was decided to compare areas of the loops obtained for different LWS within the thixotropic region, individually (loop wise) and as well as total area. The observations are as below:
# Table 6.6

## Results on Area of Hysteresis Loops

<table>
<thead>
<tr>
<th>Lignites</th>
<th>Neyveli I</th>
<th>Neyveli II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AREA (Pa/s)</td>
<td>AREA (Pa/s)</td>
</tr>
<tr>
<td></td>
<td>Raw (40%)</td>
<td>Raw (45%)</td>
</tr>
<tr>
<td>Loop I</td>
<td>1538</td>
<td>2973</td>
</tr>
<tr>
<td>Loop II</td>
<td>482</td>
<td>476</td>
</tr>
<tr>
<td>Loop III</td>
<td>229</td>
<td>135</td>
</tr>
<tr>
<td>Total Area</td>
<td>2249</td>
<td>3584</td>
</tr>
</tbody>
</table>
Neyveli I and Neyveli II LWS:

1. The total area of the loops increased as the solids loading of the slurry goes up indicating an increase in quantity of thixotropy.

2. The total area of the loops of treated LWSs were found to decrease as the hydrothermal treatment temperature increased indicating the downward trend of the quantity of thixotropy. Further, beyond the treatment temperature of 260° the area of the III loop became very small for Neyveli II and almost negligible for Neyveli I.

Kutch LWS

Eventhough there was no indication of the existence of thixotropy in the case of Kutch LWS (raw), the thixotropic studies involving one shear cycle with a total cycle time of 5 min were performed. The shear cycle is shown in Fig.6.72. Examination of hysteresis loops obtained under shear cycle conditions are shown in Fig.6.73 (raw Kutch LWS with 45% solids loading) shows an anti-clockwise hysteresis typical of a dilatant liquid. Examination of the hysteresis loops obtained for treated Kutch LWS (Figs 6.74 and 6.75) shows open anti-clockwise loop, with slightly increased area. Fig.6.76 shows the effect of shear cycle for the Kutch LWS with increased solids loading viz., 50% by weight. Closed but overlapping loops were obtained for raw Kutch LWS. But in the case of treated ones, open clock wise loops were obtained whose areas were found to increase as the treatment
temperature increased. Acceptable similarity exists when the open loops of treated Kutch LWS are compared with the open loops obtained for bituminous Singareni CWS. (Fig. 6.78).

6.4 Studies on Stability of Slurries Prepared From Hydrothermally Treated Lignites.

The static stability of the hydrothermally treated lignite-water slurries are evaluated and the softness of pack of the settled mass is determined. The procedure for the above is furnished under 2.16.

The following are the experimental conditions.

1. The slurries of the hydrothermally treated lignites are prepared keeping the time of stirring same for all the lignites as 1 min.

2. No change is made in the particle size distribution of the lignites obtained after hydrothermal treatment.

3. Additives are not used while preparing the slurries.

4. The temperature is maintained at 27°C. (ambient)

5. The solids loading (% by weight) used for raw and treated lignite-water slurries are as shown below:

Neyveli I LWS .. 45%
Neyveli II LWS .. 40%
Kutch LWS .. 48%
South Gujarat LWS: \(48\%\)

The results of the studies made are shown in Table 6.7.

**Table 6.7**

**RESULTS ON STABILITY OF THE HYDROTHERMALLY TREATED LIGNITE-WATER SLURRIES**

<table>
<thead>
<tr>
<th>Lignite</th>
<th>Treatment Temperature °C</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neyveli I</td>
<td>Raw</td>
<td>97.3</td>
<td>95.2</td>
<td>84.1</td>
<td>77.9</td>
<td>62.3</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>100.0</td>
<td>95.3</td>
<td>87.1</td>
<td>79.4</td>
<td>65.5</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>100.0</td>
<td>100.0</td>
<td>90.4</td>
<td>85.4</td>
<td>85.2</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>95.3</td>
<td>92.7</td>
</tr>
<tr>
<td>Neyveli II</td>
<td>Raw</td>
<td>99.5</td>
<td>95.3</td>
<td>90.6</td>
<td>85.3</td>
<td>80.4</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>95.4</td>
<td>90.8</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>100.0</td>
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It is seen that the static stability of the hydrothermally treated lignite-water slurries improve with the increase in treatment temperature. The treated Kutch lignite-water slurries show poor static stability compared to others. The treated Neyveli II LWS show maximum stability.

The studies on the softness of pack for the raw and treated LWSs show that only in the case of Kutch LWS the SOP values are ranging between 95% and 100% indicating that soft packs are formed due to settling. But in all the rest of the LWSs no soft pack formation is obtained.