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LIGNIN IN LIME FOR WATER REPELLENT MORTARS

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ABSTRACT

Lignin is a constituent of all plants, including annual plants and wood, and is second in the natural abundance in the organic world after cellulose. Lignin has long laboured under the label of "waste material". However lasting recent years there has been an explosion of research into lignin-based products and processes which add significant value to a material that was and continues to be considered as a low-value fuel for pulping boilers.

This study concerns the evaluation of hydraulic lime based water proofing mortars with lignin as a water repellent. The lignin used in the experiments was extracted from the black liquor waste from a paper pulp mill. 50% (by volume) sulphuric acid was used for the extraction. XRD, FTIR, and SEM were used for the characterisation of the lignin and mortar samples. The mechanical strength of mortars containing the lignin addition was improved. Capillarity tests clearly showed the water absorbing nature of lime mortar is reduced considerably after curing for 90 days.

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1. INTRODUCTION

Lignin is the third most abundant natural polymer present in nature after cellulose and hemicelluloses [1]. Always closely associated with cellulose in woody tissue, it is probably combined with some of the cellulose, carbohydrates or other constituents. As a biopolymer, lignin is unusual because of its heterogeneity and lack of a defined primary structure. Its most commonly noted function is the support through strengthening of wood (xylem cells) in trees. Structural studies have shown that lignin is a major polymer component composed of repeating phenyl propane units which are linked to the phenolic oxygen para to the propyle side chain and in part by other linkages. Lignin can be separated from polysaccharides by pulping reactions that convert the organophillic lignin into degraded derivatives soluble in the aqueous pulping liquor. Different methods of extraction of lignin from wood are done mainly soda process using sodium hydroxide solution and the Kraft process using sodium sulphide and sodium hydroxide. These processes liberate the phenolic groups and make the lignin alkali soluble.

The estimated amount of lignin on earth is 300 billion metric tonnes with an annual biosynthetic production rate of 20 billion metric tonnes. Thus, lignin is expected to play an important role as a raw material for the world's bio based economy for the production of bio products and bio fuels. For years lignin has been viewed as a waste material or a low value by-product of pulping with its utilisation predominantly limited to use as a fuel to fire the pulping boilers [2]. But the increasing demand for use of waste materials into various industrial applications requires investigation of applications of lignin in established chemical industry subsectors such as polymers, resins, adhesives, etc. Lignin utilisations have been reported relating to a multitude of applications such as binders in mortar and construction systems, metal sequestration in solutions and *in vivo*, biodegradable plastic additive, basis of gel formation, polyurethane copolymers, etc. [3, 4].

Pulp industry faces new challenges due to the wood and energy costs and the lower trends in the price of pulp [5]. The separation of lignin from the kraft pulp and its valuable use in other chemical or energy applications is a promising solution of using the kraft pulp by-products in an efficient way [6]. In this present work the application of lignin extracted from black liquor, (a by-product of Kraft pulp process in a paper pulp mill situated in Portugal) as a water repellent in hydraulic lime mortars is studied. The lignin separation from the black liquor was done using an acidification method [7].

2. EXPERIMENTAL PROCEDURE

A) Lignin extraction using acidification method

This method consists in acidifying the black liquor with H_2SO_4 (concentrated solution of 50%) for the precipitation of lignin. The black liquor was diluted with sufficient pure distilled water to bring it's viscosity into a range suitable for the extraction process. The pH is noted and the 50% acid solution is added until the pH reaches around 2.0. The lignin in the black liquor starts to precipitate in the acidic environment. After the total precipitation, the lignin was washed to remove the acid. To obtain a dried and fine material the lignin was dried at 40ºC and disaggregated manually using a sieve of mesh size 500 microns.

B) Characterisation of lignin

An X-ray diffraction study was performed using a RIGAKU-Geiger flex diffractometer to identify the crystalline phases in extracted lignin. The X-ray power was set at 40 kV and 30 mA using a continuous scan mode of speed $3°2\theta$ min^{-1}. The organic content determination of the lignin samples was done using a standard method of analysis of loss on ignition of solid waste (EN 12879:2000). The chloride and sulphate contents of the lignin were determined by the Argentometric method (CHLORIDE, 4500-Cl^-; Standard Methods Committee, 1997) and the Gravimetric method (SULFATE, 4500-SO_4^{-2}; ignition of residue, Standard Methods Committee, 1997), respectively. Fourier transform infrared spectroscopy (FTIR) was carried out using a Perkin Elmer Spectrum 100 spectrometer within the wave number range 650 to 4000 cm^{-1}. Spectra were generated from an average of 4 acquisitions. Samples were dried over night in an oven at 80ºC to remove moisture before grinding to a fine powder using an agate pestle and mortar for analysis.

B) Lime lignin mortar preparation

All the samples were prepared with a Natural Hydraulic lime NHL 3.5. The grain size of the sand used in the mortar preparation ranged from 0.010-2.18 mm. Lime lignin mortars were prepared by adding different amounts of lignin (1%, 3% and 5% by weight of lime) in the dry condition. The mortars were prepared with 18% water (in terms of the total weight of the sample mixture). The lime to aggregate ratio was taken as 1:3 and the water content was kept constant in all the samples. In order to investigate chemical changes lime / lignin mixes were manufactured containing 10, 20, 30, 40 and 50% lignin for FTIR analysis. This ensured that peaks associated with the lignin phase were not obscured by the very intense carbonate peaks which dominated the spectra.

Mortar workability was measured with the flow table method and expressed as a spread diameter in mm according to EN 1015-3. The water content was selected to have a minimum spread value of 120 mm ±10 mm. The density was observed from geometrical measurements. The mortar samples for mechanical tests were prepared with the standard dimensions 16cm x 4cm x 4cm. After 24 hours, the blocks were removed from the moulds and were stored in a curing chamber at a temperature of 20ºC and a relative humidity of 65% RH. The mechanical strength measurements of the samples were done after a curing period of 90 days. The mechanical strength was evaluated by compression and flexural tests carried out according to EN 1015-11:1999, on three samples of each composition, using a standard universal testing machine (Shimadzu). The prisms were first mechanically tested in three-point bending mode, after which each part was tested in compression. Scanning electron microscopy (SEM) was used to compare the microstructure of Lignin added lime mortars. The capillarity tests were conducted following the standard EN 1015-18.

3. RESULTS AND DISCUSSION

From the organic content analysis it was observed that the extracted lignin had approximately 81.3% organic content. The sulphate content was around 10.2% and the Chlorine around 0.2 %. An XRD pattern of the extracted lignin is shown in

Figure **1** indicating the presence of thenardite (Na_2SO_4) in the extracted lignin. This suggests that part of lignin reacted to form sodium ligno sulphonate; the remaining fraction is unlikely to be crystalline and was therefore not detected.
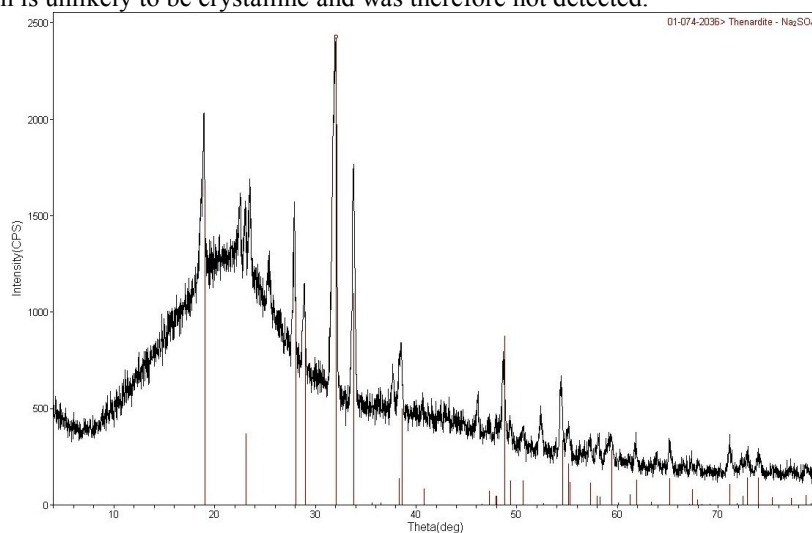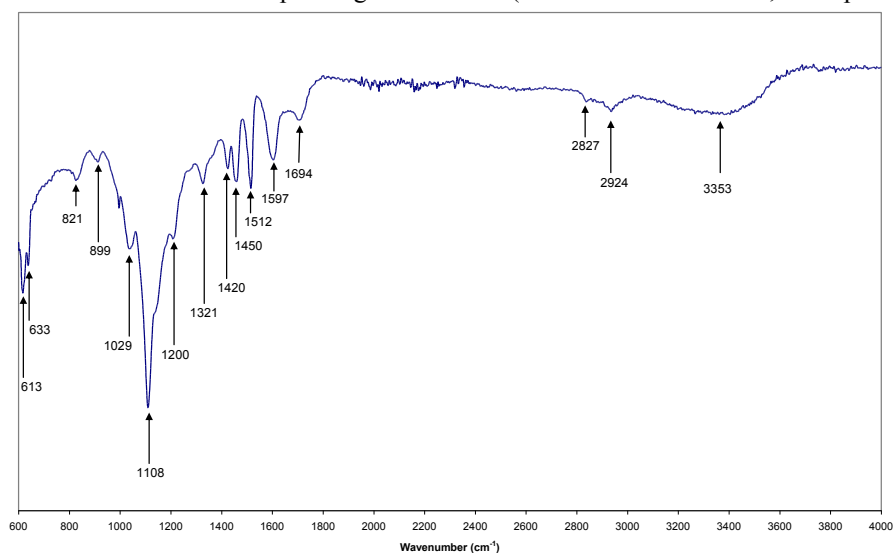

Figure 1. XRD of the extracted lignin

Typical FTIR spectra obtained from the extracted lignin and 50% lignin/lime mixture is shown in **Error! Reference source not found.** and

  respectively. The wave number of each peak is shown and assignments are made to these peaks in the corresponding tables. (Tables 1 and 2, respectively).

Peak Position	Vibration	Source	Reference
613 w	(616-619) C-S stretching	Lignin	[8]
633 vw			
821 w			
899 w	(895) Glycosidic bonds	Polysaccharides	[9]
1029 m	(1037) guaiacyl unit	Lignin	[10]
1108 vw	(1113) syringyl structures	Lignin	[10]
1200 vw	(1150-1200) SO_4^{2-} Thenardite	Lignin	[11]
1321 m	(1324) syringyl structures	Lignin	[10]
1420 m	(1425) aromatic skeletal vibrations	Pectins, lignins, hemicelluloses	[12], [9]
1450 s	(1462) asymmetric vibration of CH_2	Lignin	[10]
1512 s	(1505) C=C aromatic symmetrical stretching	Lignin	[9]
1597 s	(1595) quadrant aromatic stretch		[12]
1694 w	(1711) non-conjugated carbonyl stretching	Lignin	[10]
2827 vvw	(2850) Asymmetric vibration CH_3	Lignin	[10]
2924 vvw	(2934) C-H stretching	Lignin	[10]
3353 vvw	(3417) O-H stretching vibration in aromatic and aliphatic OH groups	Lignin	[10]

Figure 2. FTIR Spectrum of extracted Lignin.

Table 1. List of wave numbers of peaks in the FTIR Spectrum of extracted lignin
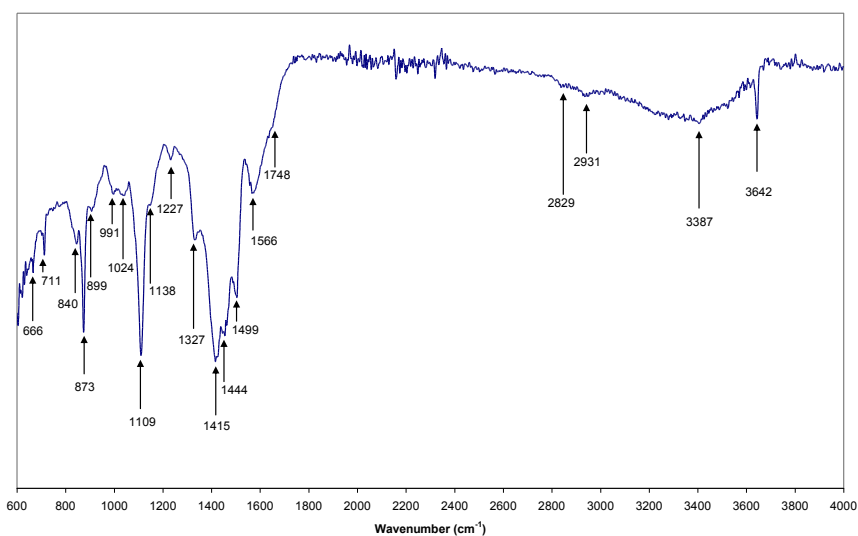
Figure 3. FTIR Spectrum of Lignin/lime mix (50%).

Peak Position	Vibration	Source	Reference
666 vw	(603, 670)	Gypsum	[13]
711 w	(712) CO_3^{2-}	Calcium carbonate	[14]
840 vw, 873 s	(876) CO_3^{2-}	Calcium carbonate	[14]
899 vw	(895) Glycosidic bonds	Polysaccharides	[9]
991 vw			
1024 vw	(1037) guaiacyl unit	Lignin	[10]
1109 vw	(1113) syringyl structures	Lignin	[10]
1138 vw			
1227 w	(1217) guaiacyl unit	Lignin	[10]
1327 w	(1324) C-O stretching vibration in S units	Lignin	[10]
1415 vw	(1429) CO_3^{2-}	Calcium carbonate	[14]
1444 w	(1445)	Esterified pectins	[9]
1499 m	(1505) C=C aromatic symmetrical stretching	Lignin	[9]
1566 m			
1748 w shoulder		Esterified pectins	[9]
2829 vvw			
2931 vvw	(2934) C-H stretching	Lignin	[10]
3387 vvw			
3642 m	(3640) OH-	Calcium hydroxide	[15]

Table 2. List of wave numbers of peaks in the FTIR Spectrum of Lignin/lime mix (50% lignin)

On comparing the FTIR spectra obtained from mixes containing smaller fractions of lignin, between 1 and 40% showed correspondingly weaker intensity peaks assigned to the lignin (

Figure 4). Most absorption bands observed have been assigned to the corresponding functional group for the vibration. The majority are in agreement with those previously reported. The main peaks associated with lignin remain after mixing with lime although the recorded spectra are dominated by those from the lime matrix at wave numbers 873, 992 and 1406 cm^{-1}. Especially noteworthy is the absence of a weak peak from lignin at 1694 cm^{-1} assigned to non-conjugated carbonyl stretching in lignin [10]. (

Figure 4). A similar observation has been made for hemp fibres treated with calcium hydroxide where as in the present measurement the appearance of a peak at 1444 cm^{-1} and the presence of a shoulder at 1748 cm^{-1} was associated with the esterfication of pectins [9].
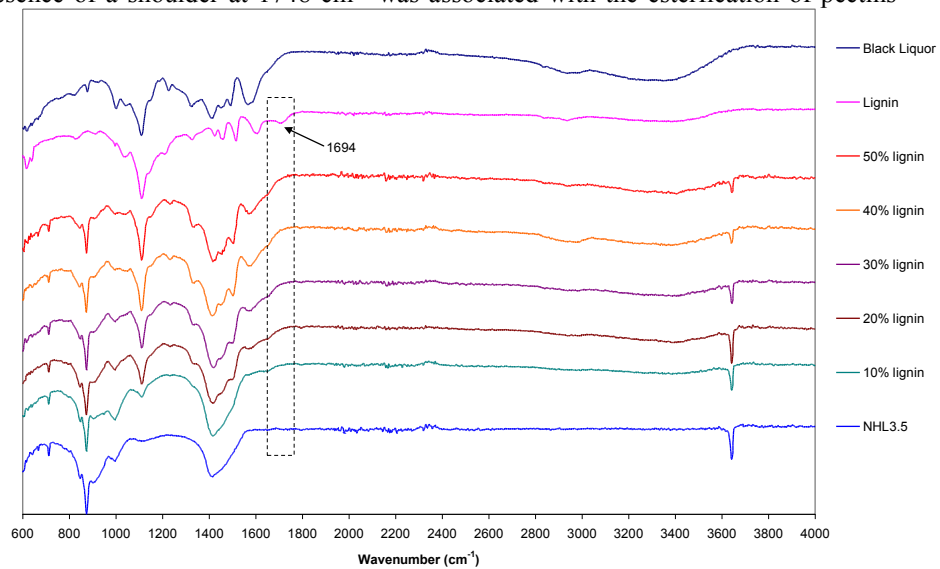
Figure 4. Comparison Spectra

However pectin and lignin are both very important non-cellulosic substances occurring in hemp fibres. In our studies using lignin extracted from black liquor from the paper industry the same features were witnessed. Thus we would associate these observations with the esterification of lignin in addition to/or rather than pectin.
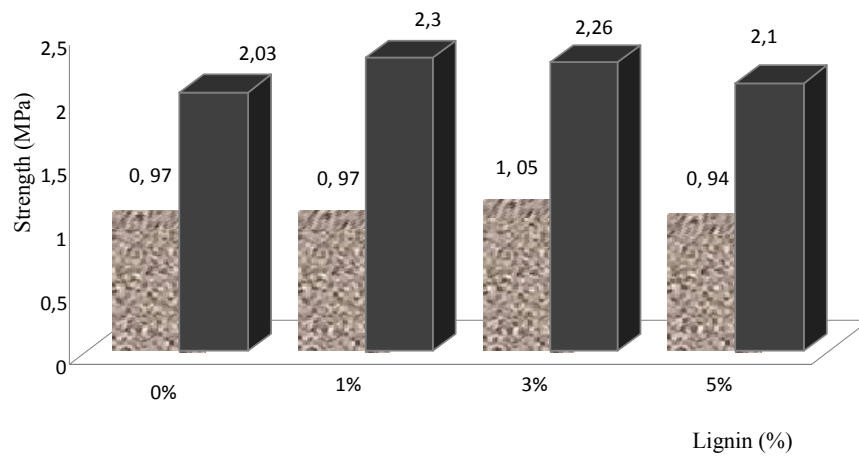

Figure 5. Flexural (grey coloured bars) and Compressive (black coloured bars) strength of lime lignin mortars cured for 90 days. (The standard deviations are in the range 0.020-0.030 and 0.006-0.035, for the flexural and the compressive strength values, respectively)

The mortars were prepared with three different compositions and one reference (without lignin). The workability and density of the mortar samples were maintained. There are slight variations in the flexural and compressive strength on adding lignin as additive. The strength values improved for 1% and 3% lignin added lime mortars. (
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The capillary absorption curves for lignin added lime compositions are shown in Figure **6**. The coefficient of capillarity for each composition is marked in Table 3.
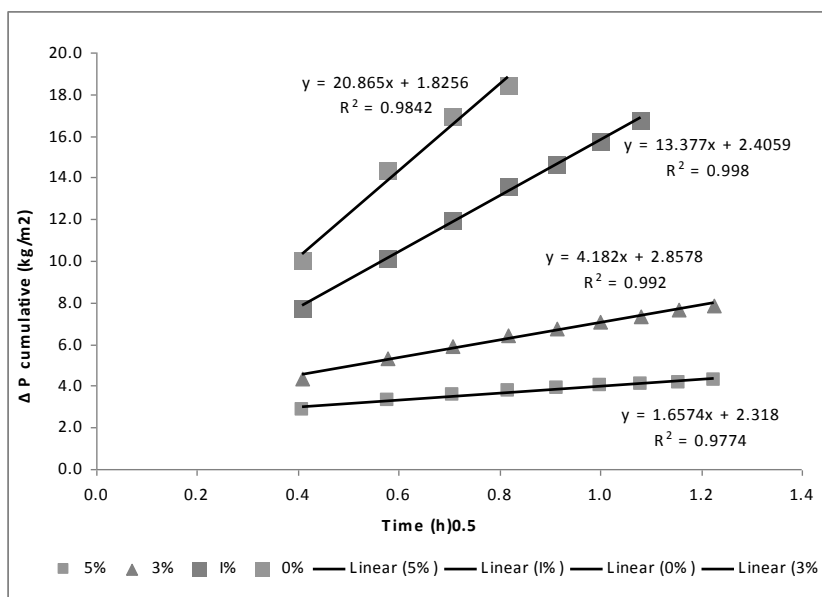

Figure 6. Curves of Capillary absorption for lignin added lime mortars cured for 90 days.

On comparing the lignin added samples with the pure lime samples a steep reduction in capillary water absorption in the samples made with lignin is observed. This indicates the water resisting nature of the kraft pulp extracted lignin. Water resisting admixtures consist of materials which reduce the hydraulic permeability of mortars and often confer water repellence to the exposed surfaces. The extracted lignin comes in the category of permeability reducers which lessen the overall porosity by blocking the normal interconnected capillary pores [16]. This indicates the usefulness of kraft pulp extracted lignin by acid method in the water repellent mortars

Table 3. Values of capillary absorption coefficient of lignin added lime mortars

% of Lignin	Capillary Coefficient kg/m^2/h
0	20.87
1	13.38
3	4.18
5	1.66

The micro structures of the mortars are shown in Figure 7.

Needle-shaped CSH phases are observed in clusters in the samples. SEM analysis shows that the surfaces of the quartz grains are covered with hydration products of the hydraulic binder, out of which grow the fibres and needles typical of CSH phases. The SEM pictures don't give any indication that the presence of lignin admixture changes the hydration behaviour and hydration products compared to admixture free hydrates. This confirms that the insignificant variations in the strength properties of lignin added lime mortars are solely due to the influence of the distribution of lignin in the lime matrix.
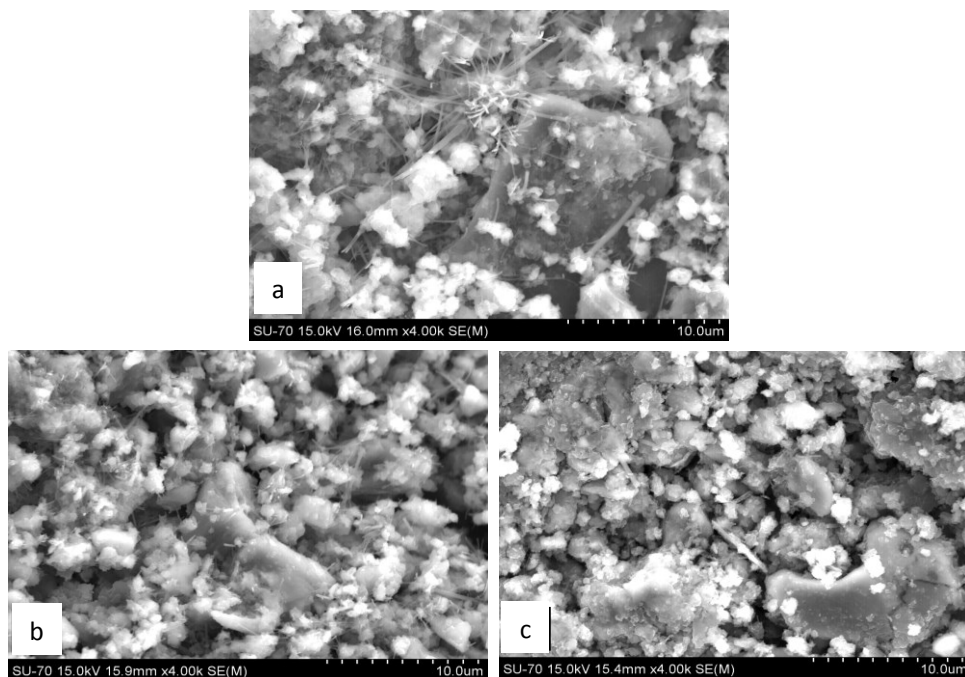

Figure 7. SEM of a) 0%, b) 3% and c) 5% Lignin added lime mortars cured for 90 days.

4. CONCLUSION

The following conclusions have been drawn from this study.

1. Lignin was extracted from black liquor using an acidic method. The presence of thenardite (Na_2SO_4) is suggesting that part of lignin was reacted to form sodium ligno sulphonate.

2. FTIR analysis of the 50% lignin / lime mixture indicated that the behaviour observed was very similar to that of esterification of pectin. It was suggested that the associated observations may indicate esterification of lignin.

3. The flexural and compressive strength of the NHL lime mortar after 90 days were maintained on addition of the extracted lignin.

4. A significant impact on the capillary coefficient of the lime mortars was observed on the addition of extracted lignin indicating the strong repellent action of the extracted lignin in the mortars.

5. The study shows that lignin extracted from Kraft pulp (black liquor) using acidic method can provide water repellent properties to a natural hydraulic lime mortar by an effective and simple way. However further detailed examinations are in progress to ensure the quality of the extracted lignin added mortars regarding other characteristics.

5. REFERENCES

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