UTILIZAÇÃO DE RESÍDUOS DE PRODUÇÃO DE PAPEL E CELULOSE PARA FABRICAÇÃO DE MATERIAIS DE CONSTRUÇÃO AMBIENTALMENTE LIMPOS

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RESUMO
O objetivo deste estudo é desenvolver compósitos e tecnologia para a produção de materiais de construção que resultarão no uso de maior porcentagem de resíduos de produção de papel e celulose - de resíduos da Caustificação: dregs, grits e lama de cal, originados de uma fábrica de celulose, utilizando cal residual como ligante. Os teores de dregs variaram entre 0 e 45 %, os de grits de 0 à 45 %, os de lama de cal de 0 à 30 % e a cal residual variou entre 10 e 25 %. No terceiro dia de cura os materiais desenvolvidos atingiram valores de 5,89 MPa, no 7º dia - 7,95 MPa, no 14º dia - 9,35 MPa, no 60º dia - 18,52 MPa e no 180º dia, 19,34 MPa. Por meio dos métodos XRF, XRD, SEM, EDS e LAMMA, determinou-se que os valores das propriedades mecânicas (resistência à compressão axial) podem ser explicados pela dissolução das superfícies das partículas sólidas dos componentes em um ambiente alcalino e pela síntese de novas formações, especialmente carbonatos amorfos e parcialmente cristalinos. Os resultados indicam que os resíduos da produção de papel podem ser utilizados como componentes alternativos na produção dos materiais de construção sem a aplicação de materiais naturais tradicionais.
Palavras-chave: Resíduos de produção de celulose, Poluição ambiental, Novos compósitos.

PAPER AND CELLULOSE PRODUCTION WASTES UTILIZATION FOR FABRICATION OF ENVIRONMENTALLY CLEAN CONSTRUCTION MATERIALS

ABSTRACT
The objective of this study is to develop composites and technology for the production of construction materials that will result in the use of highest percentage of paper and cellulose production wastes - dregs, grits and lime mud, with the lime production waste as a binding component. The concentration of these wastes, used as raw materials, varied in the following percentages: dregs 0-45%, grits 0-45%, lime mud 0-30% and lime waste production 10-25%. On the 3rd day of curing the developed materials reached values of 5.89 MPa, on the 7th day - 7.95 MPa, on the 14th day - 9.35 MPa, on the 60th day - 18.52 MPa and on the 180th day, 19.34 MPa. Through XRF, XRD, SEM, EDS and LAMMA methods, it was determined that values of mechanical properties (axial resistance strength) can be explained by dissolving the solid particles surfaces of the components in an alkaline environment and synthesizing new formations, especially amorphous and partly crystalline carbonates. Results indicate that the waste of cellulose production can be used as alternative components in the production of the construction materials without the application of traditional natural materials.
Keywords: Cellulose production wastes, Environment pollution, New composites.

1. INTRODUCTION

The management of industrial wastes, in an economically and environmentally acceptable manner, is one of the most critical issues facing modern industry. This is due to the increased difficulties in locating disposal works and complying with stringent environmental quality standards imposed by legislation (Bajpai, 2014). The actual world production of paper is approximately 400 million ton per year, with an estimated increase to 500 million ton (Bajpai, 2013). Approximately 300 kg of sludge is produced per ton of paper (Monte *et al.*, 2009), i.e. approximately 150 million ton annually with little industrial utilization.

Cellulose is the most abundant polymer on Earth, representing about 1.5 x 1012 t of annual biomass production (Wegner, 2012). Brazil has 220 cellulose production companies located in 540 municipalities of 18 states, with revenues totaling 4.7 billion dollars. They exported 13.98 million t in 2012. This activity has an average growth of 7.5% per year over the last 40 years in Brazil (BRACELPA, 2013).

In the work of Wenzl (1970), there is a detailed description of the kraft method and the process of waste production through sulfite cooking and the use of alkaline reagents. Pulp and paper mill industries are always associated with the disposal problem of highly contaminated sludge. Ang *et al.* (2012) informed that, in Australia, grits are normally disposed of in landfills. By-products of pulp, paper, and associated products at the North-American industry (Naik, 2002) are mainly sludge from liquid waste treatment plants. The sludge is usually lagooned, landfilled, or subjected to land cultivation. The chemical composition of typical sludge is composed of Mo (4.2 ppm), Zn (70 ppm), Ni (1.1 ppm), Pb (5.3 ppm), Hg (0.1 ppm), Cr (4.2 ppm), Cu (7.0 ppm).

The development of sustainable, innovative systems to maximize recovery of useful materials is the main object of many studies. Foelkel (2008) considered that with further energy efficiency improvements and use of forest waste – sawdust - part of the lignin may also be used for energy bioproducts in an Integrated Forest Biorefinery (IFBR) which produces higher value-added products, carbon fibers and other valuable materials. H. Tran and D. Sanchez found that several pulp mills in North America achieve a target pH of below 12.5 for the dregs. In Finland, dregs neutralize the acidic effluent of bleach plants, which enables the possibility of its use for neutralizing more sewer effluents. Slacker grits in most mills receive only basic washing or are not treated at all. The research of Castro *et al.* (2009) assesses the incorporation of grits and dregs in cement clinker production. The results show that such incorporation could be an effective process for waste management – economically and environmentally. Demir *et al.* (2005) used short cellulose fiber waste of the Kraft pulp as organic pore-forming additions in the quantity of 2.5 to 5%, mixed with raw brick-clay. After sintering this mix at 900 °C, an environmentally safe brick-clay, with acceptable mechanical properties, was obtained.

A laboratory aerobic incubation study performed by Cabral *et al.* (2008) demonstrated that the use of dregs and grits could be a valid and less expensive option to improve soil fertility, when compared to the use of commercial agricultural limestone. Maciel *et al.* (2015) experimentally found that the amount of dregs/grits with lime mud and ash introduced into the soil must be less than 1.2 t / ha because of the larger concentration of Na transferred to the soil solution, different from literature recommendations. It has been estimated by Griffith *et al.* (2003) that 10% of the US Kraft lignin production produces enough carbon fiber to replace half of the steel in all US passenger vehicles. Industrial by-products of Kraft process work well in highway applications as one of the components of natural soils is strengthening (Stroup-Gardiner and Wattenberg-Komas, 2013). A study carried out by Naik (2002) on sand durability containing residual solids from pulp and paper mills has revealed that the addition of residual solids in concrete can enhance its strength and durability properties.

Lime production waste (LPW) is a quick-lime with high content of poorly burnt carbonates and other impurities, such as sand, clay, and organic materials (Garcia, 2008). LPW is usually used (Bhatty and Gajda, 2004) for the neutralization of acid soils or by the cement industry. Correa and Mymrin (2007) used LPW as a waste concrete binder. Mymrin (2012) also used LPW as a binder of different types of industrial wastes: natural rock cutting and polishing wastes, phosphor-gypsum,

wood ash, paper production pulp, municipal wastewater sludge, ferrous slag, asbestos tiles, porcelain production wastes, etc. Al-Sayed *et al.* (1992) informed that LPW increases the mechanical properties of the asphalt. Arce *et al*. (2010) used LPW for the paint waste immobilization. Marinkovic *et al.* (2010) used a LPW for the manufacture of bricks.

2. OBJECTIVE

The main objective of this study was to develop some compositions of construction materials with maximum contents as raw materials of three main types of pulp and paper production wastes – dregs, grits and lime mud - with complete compliance with the mechanical and environmental demands of Brazilian national norms; and to study the physicochemical processes associated with the strengthening of the developed materials in order to improve their mechanical and chemical properties and predict the behavior of materials during their application.

3. MATERIALS AND METHODS

3.1. Materials

For the conducting of this research, the representative samples of three types of by-products of the Kraft process causticizing reaction were selected in a pulp mill in the state of Espirito Santo, Brazil, particularly the Green liquor clarifier – Dregs, lime slacker - Grits and white liquor clarifier - lime mud (LM). As a binder component of these three materials, lime production waste from a lime production (LPW) plant in the city of Curitiba, Brazil, was used.

3.2. Research methods

The study of the raw and final materials was conducted by various complementary methods. Chemical compositions were studied by XRF method on Philips/Panalytical, model PW2400; mineralogical composition were determined by XRD method on Philips diffractometer, model PW1830, with generator settings of 40 kV, 30 mA with monochromatic wavelength Cu-Kα, at 2Θ range of 2 – 70°, step size (2Θ°) of 0,02° and scan step time of 0.5s. for semi-quantitative analysis. The results obtained were interpreted by Super-Q X'Pert High Score software (database PDF-2). Morphological structures were studied through scanning electron microscopy using FEI Quanta 200 LV. EDS chemical microanalyses were performed on an Oxford X-ACT (Penta FET-Precision), as well as micro-mass analyses through laser micro-mass analyzer LAMMA-1000 (model X-ACT). Leaching and solubility tests of liquid extracts were performed by atomic absorption spectrometry (AAS) on a Perkin Elmer 4100 spectrometer. Particle size distribution of the raw materials was determined on the Granulometer CILAS 1064, Brazil. Uniaxial resistance strength of the samples was conducted by testing performed on a EMIC universal testing machine, model DL10,000. The linear shrinkage of test samples was determined using DIGIMESS digital calipers. Exceptionally, water absorption coefficients were determined by complete water immersion and specific apparent gravity. The values of mechanical properties and standard deviations were obtained from an average of 10 sample measurements.

3.3. Calculations

The water resistance coefficient (C_{WR}) was determined from the uniaxial compressive strength of the TSs on the 28th and 90th day, which were saturated after a total immersion in water for 24 hours (R_{SAT}), and the strength of the dry TSs (R_D), following the standard in GOST 9479-84 (1985), was calculated with the following equation:

$$C_{WR} = R_{SAT}/R_D. \quad (1)$$

Water absorption coefficient (C_{WA}) tests were also performed on the 28th and 90th day of curing, following the standard in NBR (2003), which uses the equation below:

$$C_{WA} = [(M_{SAT} - M_D)/M_D] \times 100 \quad (2)$$

Where M_{SAT} = the mass of the test specimen saturated after total immersion in water for 24 hours
M_D = the mass of the test specimen.

3.4 Test Specimen (TS) Preparation

The materials were mixed and homogenized in selected compositions (Table 1), hydrated, and compacted in a cylindrical mold into 20 × 20 mm dimensions under a pressure of 10 MPa. The curing process occurred in the open air during 3, 7, 14, 28, 60, 90 and 180 days. The average values of the TSs mechanical properties and their deviations were obtained from ten (10) measurements. Therefore, the total quantity of the prepared TSs reached 850 pieces.

Table 1 - Substantial composition of the TSs

wt. %	Compositions									
	1	2	3	4	5	6	7	8	9	10
Dregs	25	30	25	30	30	30	35	35	30	25
Grits	25	30	30	30	35	30	25	35	30	35
ML	25	15	20	20	15	25	25	15	30	30
LPW	25	25	25	20	20	15	15	15	10	10

4. RESULTS AND DISCUSSION

4.1. Characterization of raw materials

4.1.1 Particles size distribution of raw materials

The particles size distribution of raw materials of the wastes from the Kraft process under study is showed bellow (Figure 1). Dregs and lime mud (84%), particularly, have a particles grain distribution from 0.0017 and 0.013 mm. 34% of the grits' particles have sizes between 0.01-0.1 mm, 20% - 0.1- 1 mm, and 20% - 1 – 3mm. The BET specific surface area of the LPW is near 1,000 cm^2/g.

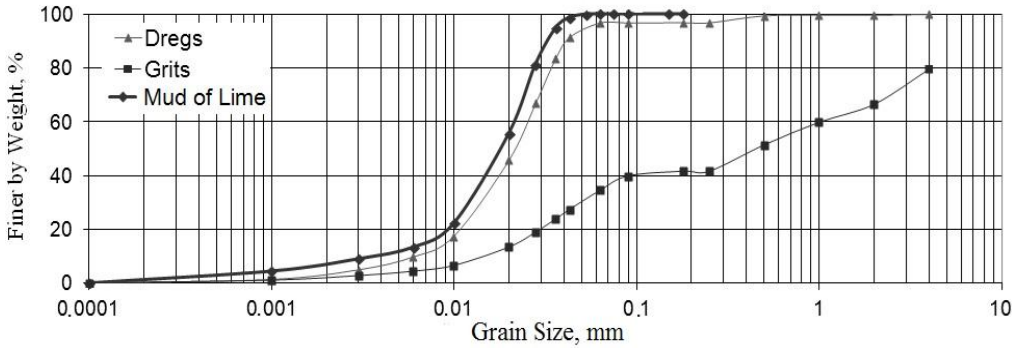

Figure 1 – Grain size distribution of the wastes from the Kraft process under study

4.1.2 Chemical composition of raw materials

The predominant element in the chemical composition of the raw materials (Table 2) studied by the FRX method is CaO, which varied between 37.4 and 54.5%. LPW has also 25.2% of MgO because it was produced from dolomite $CaMg(CO_3)_2$. 4.5% of Na_2O and 2.8 and 3.5% of SiO_2 respectively. All raw components have very high (24.1 – 46.8%) values of calcination loss (C.L.) because all of them have significant quantities of carbonates, and Kraft process wastes also show

high contents of organic materials from wood as the main raw material for pulp and paper production.

The CO_2 recalculation of 10.52%, which was measured by a calcimeter, compared with that of the initial dolomite $CaMg(CO_3)_2$ shows the presence of almost half (44.0 %) of the amount of carbonates contained in LPW. The total levels of dolomite and the impurity content (Table 1) is 26.21% of under-fired material, which is more than twice the quantity allowed (12%) by the Brazilian standard NBR 6453 (2003). Therefore, it cannot be sold as a construction material and must be classified as industrial lime production waste (LPW); usually used for acid soil neutralization, or sent to industrial waste dumps.

Table 2 – Chemical composition of the raw materials under study by FRX method

waste	Oxides contents %										
	CaO	MgO	Na_2O	Fe_2O_3	SO_3	P_2O_5	MnO	K_2O	SiO_2	Al_2O_3	C.L.
Dregs	37.4	5.1	4.5	0.5	1.6	0.2	0.3	0.3	2.8	0.5	46.8
Grits	50.8	0.3	4.5	0.4	1.7	0.5	-	0.3	3.5	0.4	37.6
ML	54.5	0.5	0.7	0.1	0.2	0.4	-	-	0.2	0.1	43.3
LPW	48.4	25.2	-	0.2	-	-	-	-	1.9	0.2	24.1

4.1.3 Mineralogical composition of the raw materials

Mineralogical compositions of the raw materials under study were determined by the XRD method and showed the presence, in dregs, of Calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$ and quartz SiO_2; in grits, there was also Pirssonite $CaNa_2(CO_3)_2(H_2O)_2$; ML consists only of calcite; and LPW has the most complicated composition: initial lime CaO, portlandite $Ca(OH)_2$, calcite $CaCO_3$, magnesite $MgCO_3$ and quartz SiO_2, with large quantities of amorphous materials. Therefore, the results of the XRD analyses strongly confirm the results of XRF. Rather different mineralogical compositions of the raw materials under study were determined by XRF, XRD, DTA and TG analyses, according to Martins *et al*. (2007): “dregs and lime mud contain Calcite and Gipsite $CaSO_4 \cdot 2H_2O$. The slacker grits contains Calcite, Portlandite, Pirssonite, Larnite and Brucite. The Calcite phase, present in the dregs and in the lime mud, has small amounts of magnesium replacing calcium”. The DRX patterns of the raw materials are showed bellow (Figure 2).

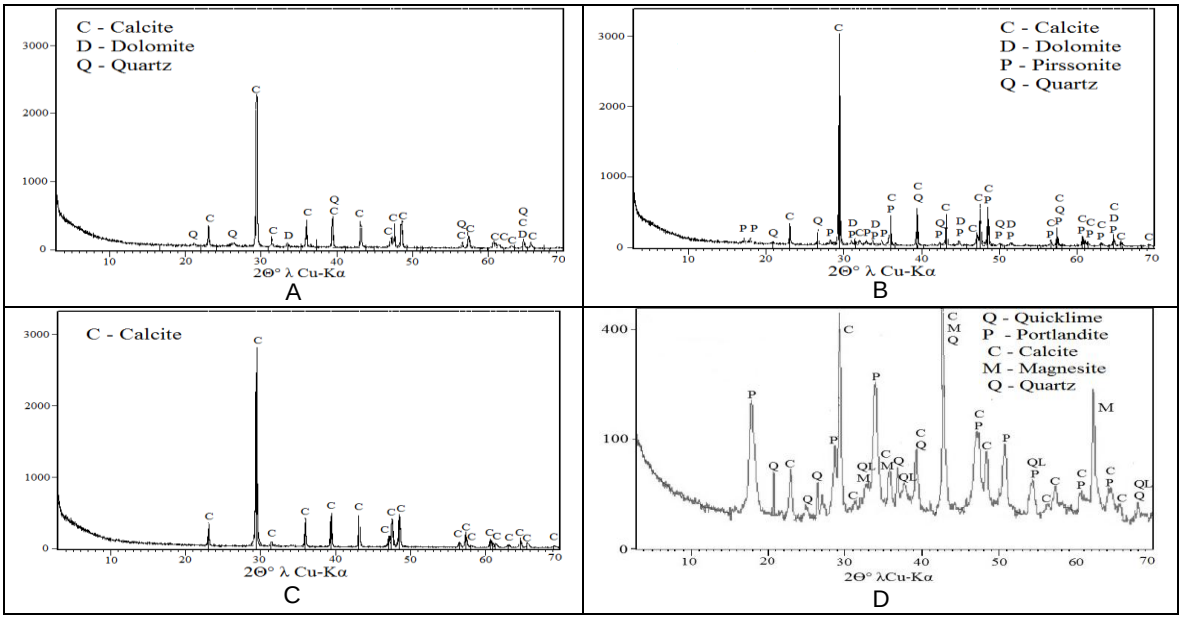

Figure 2 – DRX patterns of the raw materials: A – dregs; B – grits; C - lime mud; D – lime production waste

Taylor and McGuffie (2007) have identified, through the quantitative Rietveld XRD method, components in dregs, grits and lime mud that were unreported in the pulp and paper literature: the diopside $CaMgSi_2O_6$, the pargasite $NaCa_2Mg_3Fe_2Si_6Al_3O_{22}(OH)_2$, vermiculite $Mg_{1.8}Fe_20.9Al_{4.3}SiO_{10}(OH)_2{\cdot}4(H_2O)$ and a new component in lime mud $Ca_4Na_2(PO_4)_2(SiO_4)$. Such difference in mineralogical compositions at the present research can be explained by regional differences of raw materials, technological processes and, partially, the different methods available for each case. This may be one of the most important difference is the use of LPW after firing of local dolomite in the present study, but not a calcite, used in compared research.

4.1.4 Morphological structure of raw materials

The morphological structure of all raw materials under study (dregs, grits, ML and LPW), analyzed through the SEM method, shows (Figure 3) different particle sizes and shapes, and widely varying pore shapes and dimensions. All of the particles of the initial components are not chemically linked, but have only mechanical contact between them. The SEM images of the dregs demonstrate (Figure 3 – A and B) that the material has dispersed particles of irregular shapes, distributed without structure and without linkage to many visible pores, also of different configurations and sizes. Grits (Figure 3 – C and D), in contrast, show very smooth and ice-like forms with deep pores between them, which are a strong characteristic of amorphous particles. The morphology of the LPW particles at 10,000 fold magnification (Figure 3 – E) have crystal-like forms of cubic or rhombic edges with a large network of irregular pores; some points of the LPW (Figure 3 – F) are represented as formless small particles.

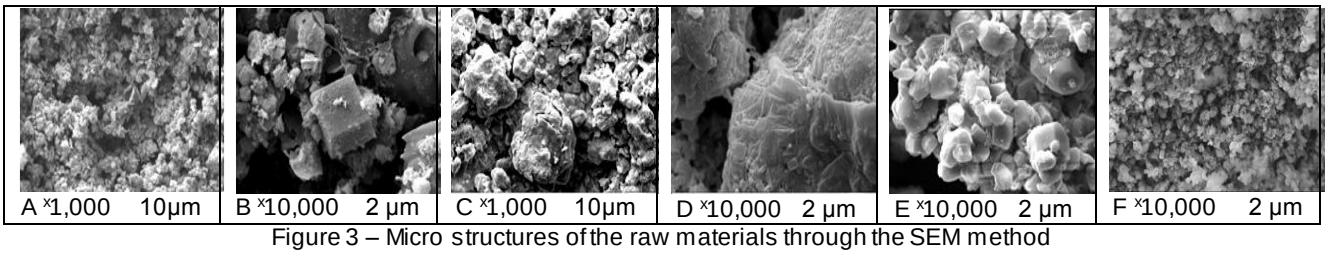

Figure 3 – Micro structures of the raw materials through the SEM method

4.2 Mechanical properties of the composites

4.2.1 Axial resistance strength

The analysis of test samples (TSs) for the axial strength (Figure 4) shows that they are dependent mostly on dry LPW and hydrated CaO content (Table 1) in the compositions studied. The maximum number of hydrated CaO is contained in the LS (54.5%) and grits (50.8%), and the minimum, in dregs (37.4%).

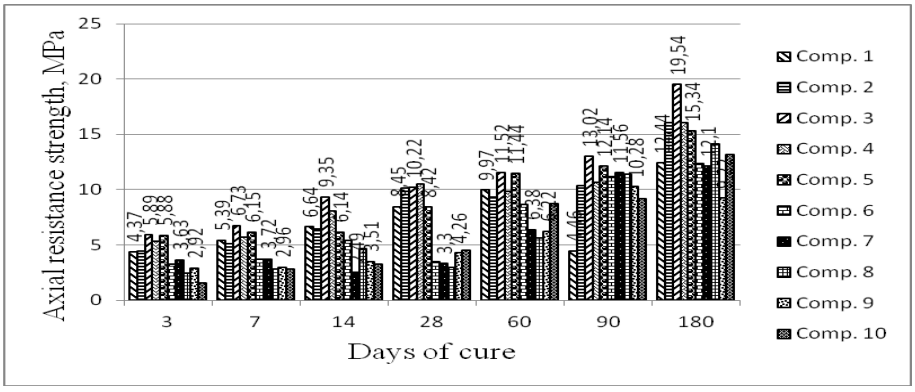

Figure 4 - Changes of uniaxial resistance strength in the TSs hydration and cure

The lowest values of the resistance strength in almost all ages are shown by the TSs of composition 9, with the lowest RPC content (10%). The composition 10 with the same LPW content has 5% more (35%) grits and 5% less dregs. That is the only visible reason for the resistance increase in composition 10, in comparison with the composition 9 from 9.22 till 13.16 MPa on the 180th curing day.
The increase of LPW content to 15% (compositions 6, 7 and 8) leads to significant (from 9.22 till 12.10 MPa) growth in the resistance of composition 7; but the resistance of composition 8 in comparison with composition 10 did not increase significantly because of the 15% decrease of LC and 10% more dregs in content. A higher resistance of TSs of composition 6, in comparison with composition 7, can be explained by the 5% higher content of grits and correspondingly 5% lower content of dregs.
Future increase of LPW to 20% shows the dominated influence of grits (composition 5) with 35% content when compared with 30% in the composition 4. The resistance values of TSs 5 were lower than the values of TSs 4 in all ages, maybe because of 5% more quantity of LS. Only at the age of 180-days, the resistance of composition 5 jumped to 6.2 MPa until 19.34MPa. So. The sharp jump in strength does not seem to be a gradual increase in strength due to the smooth process of the synthesis of carbonates; it is more peculiar to the process of syneresis of the gel group of amorphous calcium hydro-silicates CSH.
The highest (25%) LPW content in the compositions 1, 2 and 3 leads to the TSs strength increase, but it (16.05 MPa) does not reach the strength of composition 5 because of 5% less content of grits. The standard deviation values of the uniaxial compression strength of the obtained experimental data never exceeded 5.6 % of the average means.

4.2.2 Linear expansion change

A study of the coefficient of linear expansion (Table 3) shows its direct dependence on the amount of LPW as the hydraulically most active component of the mixtures, as well as on the length of the hydration of the TSs. It is also well visible a tendency to increase the coefficient values up to the 28th or 90th days with subsequent reduction to 180 days.

Table 3 - Expansion coefficient change during TSs hydration and cure

Composition	Expansion coefficient (wt.%) after cure time (days)						
	3	7	14	28	60	90	180
1	1.65	1.68	1.69	1.71	1.68	1.64	1.60
2	1.68	1.71	1.73	1.70	1.67	1.67	1.64
3	1.66	1.67	1.70	1.72	1.70	1.67	1.65
4	1.61	1.64	1.65	1.63	1.60	1.60	1.57
5	1.60	1.60	1.62	1.64	1.68	1.65	1.61
6	1.53	1.58	1.63	1.60	1.55	1.57	1.52
7	1.55	1.57	1.60	1.56	1.58	1.55	1.53
8	1.51	1.55	1.55	1.58	1.54	1.55	1.51
9	1.50	1.55	1.57	1.60	1.65	1.61	1.57
10	1.44	1.51	1.54	1.58	1.54	1.55	1.52

Initial expansion of the TSs can be explained by the exothermic reaction of lime hydration with formation of lime hydrated shells over the lime particles; the process of the synthesis of new formations also leads to the increase in TSs volumes. But after 14 days (compositions 2, 4, 6 and 7) or after 28 days (compositions 1, 3, 5, 8 and 10) or even after 60 days (composition 9) of cure, the process of the TSs volumes' shrinkage starts to prevail over the process of expansion. This

may occur due to the flow of shrinkage phenomena: 1. phenomenon of gel syneresis of new formations and 2. evaporation of water, which was not chemically bonded by the interaction with solid particles of the materials. The shrinkage process continued until 180 days and may continue for many years (Mymrin, 1987).
Standard deviations of shrinkage coefficient values were increasing with de increasing of average values, but all time are inside the meanings 0.03- 0.09%.

4.2.3 Density of the materials

The comparison between the values of density of the composites under study (Table 4) and their changes during the hydration and hardening of the TSs indicate the simultaneous occurrence of the following directly opposite processes: 1. adsorption of CO_2 from the air causes an increase in weight and therefore in the density of the TSs; but 2. the evaporation of hydration water, which has not engaged in chemical interaction with the LPW and other components of the TSs stored outdoors; this process leads to the decrease of the TSs weight and therefore is a decrease in density; 3. expansion of the TSs after 28 days of hydration (Table 3) also causes a decrease in their density. The values of standard deviation of the coefficient of density of all the samples have a tendency to increase with the increasing of average meanings, but do not exceed 0.15 g/cm^3.

Table 4 - Density change during TSs cure

Composition	Density (g/cm^3) after cure time (days)						
	3	7	14	28	60	90	180
1	1.97	1.80	1.75	1.72	1.78	1.79	1.82
2	1.99	1.82	1.79	1.8	1.81	1.82	1.84
3	1.87	1.86	1.86	1.85	1.88	1.87	1.86
4	1.98	1.81	1.75	1.76	1.76	1.78	1.8
5	1.74	1.74	1.72	1.73	1.75	1.78	1.79
6	1.73	1.73	1.70	1.68	1.71	1.71	1.80
7	1.77	1.73	1.69	1.65	1.65	1.66	1.67
8	1.82	1.79	1.71	1.64	1.64	1.66	1.68
9	1.81	1.77	1.70	1.61	1.64	1.64	1.66
10	1.84	1.82	1.71	1.72	1.69	1.74	1.75

4.2.4 Water absorption

The values of the water absorption coefficient (C_{WA}) on the 28th day varied (Table 5) between 14.8 and 12.0%, and on the 90th day – between 13.6 and 10.7 %. This decrease in water absorption is the result of the decreasing number of pores in the materials, particularly of open pores due to synthesis of a new formation in the result of the initial components' hydration and chemical interaction. The C_{WA} values have also common decreasing tendency with the decreasing of LPW content because of the incomplete LPW hydration during TSs producing and curing. The values of C_{WA} standard deviation of all compositions were within the confines of 0.4 – 0.7%.

Table 5 - Values of water absorption coefficient (C_{WA}) on the 28th and 90th days of hydration and cure

Water absorption %	Composition									
	1	2	3	4	5	6	7	8	9	10
28th day	14.8	14.3	13.4	12.7	12.9	12.9	12.3	12.5	12.0	12.2
90th day	13.6	12.6	12.0	11.2	10.8	11.1	11.3	11.6	10.7	10.5

4.2.5 Water Resistance of the materials

The values of water resistance coefficient (Cwr, Table 6) on the 28th hydration day varied between 0.59 and 1.15; they depend particularly on the LPW contents, therefore the lowest values (0.59 and 0.61) have composites 9 and 10, correspondingly, with 10% of LPW contents, and the highest values – compositions 3 and 1, with 25%of LPW contents.
Most of Cwr values are increasing on the 90th day of TSs age for 0.02 – 0.11 and the highest number (1.20) continues to belong to the TSs of composite 5. The standard deviation values of the Cwr of the obtained experimental data never exceeded 8 % of the average means.

Table 6 – Coefficient of Water Resistance (Cwr) on the 28th and 90th days of cure

Days of cure		Composition									
		1	2	3	4	5	6	7	8	9	10
28th	Dry	8.45	10.11	10.22	10.53	8.42	3.50	3.30	2.95	4.26	4.50
	Saturated	9.13	9.81	11.75	9.06	8.25	2.98	2.57	2.18	2.51	2.75
	Cwr	1.08	0.97	1.15	0.86	0.98	0.85	0.78	0.74	0.59	0.61
90th	Dry	4.46	10.34	13.02	10.63	12.14	11.15	13.56	11.36	10.28	9.17
	Saturated	4.10	8.79	15.84	9.35	12.75	9.48	10.98	8.86	6.48	6.60
	Cwr	0.92	0.85	1.20	0.88	1.05	0.85	0.81	0.78	0.63	0.72

4.3 Physico-chemical processes of structure formation

This study assessed the reasons for the changes in the developed materials mechanical properties due to the initial components' chemical interaction and changes in their mineralogical compositions, morphological structures and micro-chemical compositions of the new formations, which are responsible for these properties. They were studied on composition 3 because of the best mechanical properties after sintering at almost all sintering temperatures and, therefore, it expressed these processes more clearly.

4.3.1 Changes of mineralogical compositions during the cure

The mineralogical composition of the composite 3 on the 3rd day of hydration is presented (Figure 5) by the rest of non-hydrated lime CaO, portlandite $Ca(OH)_2$, periclase MgO, brucite $Mg(OH)_2$, calcite $CaCO_3$ and quartz SiO_2. The strongest mineral XRD peaks belong to the calcite, because all the raw materials used have calcite as the main mineral (Figure 2).

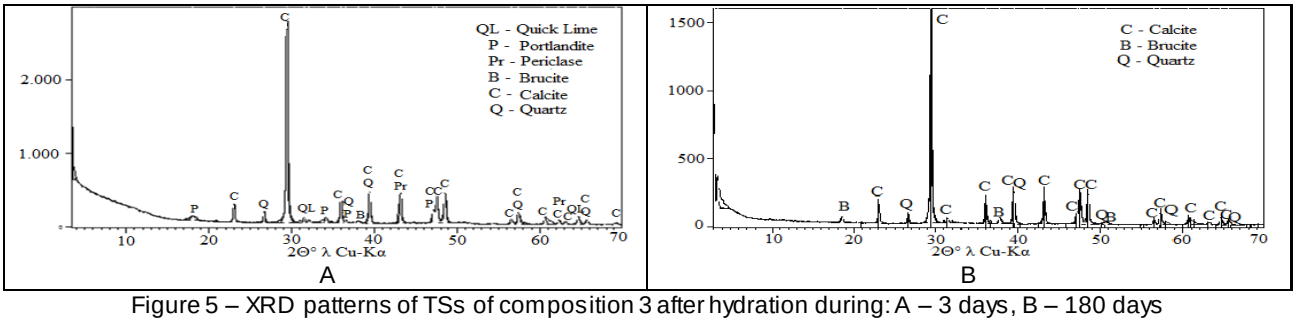

Figure 5 – XRD patterns of TSs of composition 3 after hydration during: A – 3 days, B – 180 days

On the XRD pattern of the same composite after 180 days of cure, the peaks of portlandite, periclase and brucite completely disappeared, which were transformed into carbonates on the open air. But the intensity of the calcite peaks, including the main one at 2Θ° = 29.5°, did not

increase. That means that these minerals were transformed into the non-crystalline amorphous carbonates.

4.3.2 Studying of the new formations of materials

The study of the morphological structures of new materials of composition 3 by the SEM method (Figure 6), at different magnifications, confirms complete absence of crystalline or crystal-like forms. It seems that all crystal structures determined by XRD methods (Figure 5) are covered by a layer of swelled rounded shape forms. The main difference between micro images of the 3rd and 180th days (Figure 6-A and C) is the particles size: 0.1 – 0.5 μm with several pores of different sizes and shapes among them on the 3rd day, which on the 180th day were mostly closed by new formations and the particles size was particularly enlarged up to 5 – 25 μm.

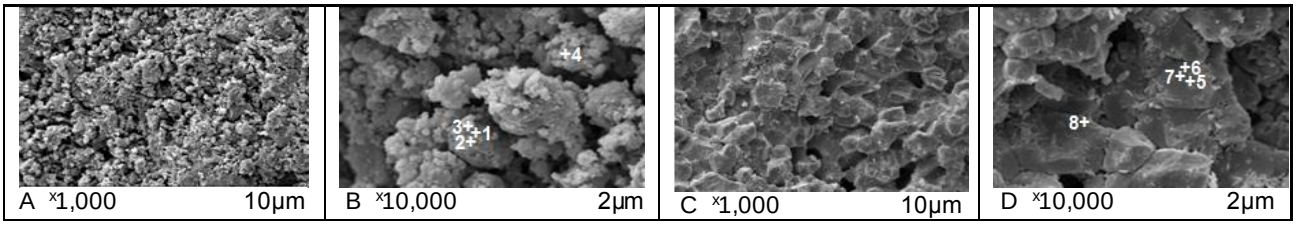

Figure 6 – Micro structures of the comp. 3 by the SEM method after hydration during: A and B-3 days, C and D-180 days

Micro-chemical compositions of new formations demonstrate (Table 7) very high levels of heterogeneity at the closest points (Figure 6-B and D). None of the minimum repetition of the chemical compositions was met during investigations of these TSs of composition 3.

Table 7 - Chemical elements of the new formations after the hydration of composite 3 during 3 days (points 1-4) and 180 days (points 5-8) by the EDS method

Points	C	Na	Mg	Al	Si	P	S	Ca	K	Fe	Total
1	24.2	-	9.2	0.6	7.0	-	0.2	58.8	-	-	100
2	35.3	4.35	-	0.9	3.3	0.5	-	54.7	-	0.88	100
3	34.3	0.28	0.32	0.2	1.1	0.3	-	63	-	0.45	100
4	41.5	5.29	0.51	0.4	0.5	-	4.7	45.5	0.9	0.79	100
5	22.7	0.26	-	3.3	6.9	2.2	6.3	57.4	0.9	-	100
6	49.2	-	7.18	-	0.4	0.4	0.3	42.6	-	-	100
7	0.34	20.9	21.2	0.9	-	0.6	-	51.7	3.2	1.15	100
8	16.6	-	21.1	-	-	1.2	-	12.3	8.3	40.5	100
Max.	49.2	20.9	21.2	3.3	7.0	2.2	6.3	63	8.3	40.5	-
Min.	0.34	0.26	0.32	0.2	0.4	0.3	0.2	12.3	0.9	0.45	-

This heterogeneity of the new formations of TSs of comp. 3 was confirmed by the results of the study using the Laser micro-mass analysis (LAMMA) method (Figure 7), because all peaks of the Isotopes' compositions of the three closest points a, b and c, similarly to the eds analysis, have different compositions and intensities. This means the main amorphous structure of new formations, responsible for the strengthening of newly developed composites.

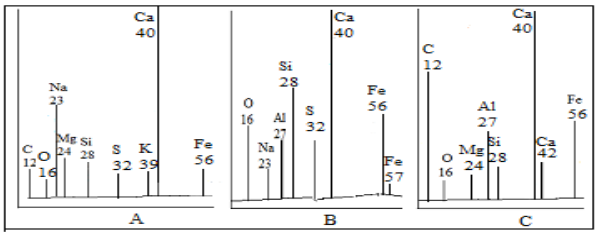

Figure 7 – Isotopes compositions of new formations of composition 3 at the 180th day by Laser micro-mass analysis (LAMMA) method

5. CONCLUSION

The results of this experimental research confirm the high efficiency of paper and cellulose production wastes (dregs, grits and mud of lime) utilization as the main components in composites with lime production waste for producing materials with mechanical properties that significantly exceed the demands of Brazilian technical standards.

The best values of axial resistance strength demonstrates the composite 3 with dregs, grits, lime mud and lime production waste contents of 25, 30, 20 and 25 wt.% correspondingly. It has 5.9 MPa on the 3rd day of hydration, 9.4 – on the 14th day, 11.5 – on the 60th day and 19.5 – on lime production waste; (1.65%), g/cm^3 density, this material has very low values of expansion coefficient (1.65%), 1.86g/cm^3 density, low values of water absorption (12.0% on the 90th day) and very high value of coefficient of water resistance (1.20).

The XRD, SEM, EDS and LAMMA methods determined that, during chemical interaction of the initial mixtures, the hydration in high alkaline environment (pH=12.5 - 13) led to a complete transformation of initial minerals portlandite, periclase and brucite in the mainly non-crystalline amorphous carbonates. The synthesis of these amorphous new formations may explain the synthesis of the materials' structures with high mechanical properties from the mixes of only industrial wastes.

The most important result of these research findings is the experimentally proven possibility of the use of the aforementioned vast volume of cellulose and paper production wastes on industrial scale, as valuable components of materials. Such utilization can significantly reduce the existence of wastes dumps, which pollute the world environment.

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