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# Structure formation processes of composites on the base of ink rejected sludge

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## HIGHLIGHTS

- Ink sludge was characterized as principal raw material for construction material production.
- Flexural strength after 90 days is 7.15 MPa and after 180 days – 11.75 MPa.
- Water absorption value near 8% and dilatation near 5%.
- Studies by the XRF, XRD, DTA, TG, SEM, EDS and LAMMA methods.
- Utilization of these industrial wastes has high environment efficiency.

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## ABSTRACT

New composites of construction materials were developed and characterized based on ink sludge (IS) waste (50–60 wt.%) in combination with wood ash (15–30%) and lime production waste (15–25%). IS contains NiO (2.4%) and ZnO (1.1%). The materials uniaxial compression strength reached on the 3rd day 3.9 MPa, on the 7th day 4.8 MPa, and on the 180th day 11.7 MPa. Studies by the XRF, XRD, DTA, TG, SEM, EDS and LAMMA methods explain the strengthening of materials by synthesis of mainly amorphous carbonates. Comparison of leaching and solubility of raw materials with final products show that IS can be successfully used for improvement of the mechanical properties of the developed composites as an environmentally friendly construction material. New materials can be economically attractive because of only cheap industrial wastes utilization as raw materials. At the end of service as construction material, it can be used as an inert demolition waste.



## 1. Introduction

The objective of recycling and reutilizing of solid wastes is to use raw materials more completely, thus minimizing pollution problems and treatment costs [1]. The treatment of water for human consumption normally generates a great amount of wastes in the form of sludge. The common practice is their discharging directly onto the soil as landfills [2]. There is an extensive scientific and technical literature on environmental and economical methods of ink waste sludge reuse often based on the sludge utilization as raw materials for ceramics production [3,4]. In accordance with the classification of Dondi et al. [5], industrial sewage sludge was attributed to the category of fluxing and plastifying wastes.

Many alternatives have been studied and developed for industrial and municipal wastes utilization [6]. The Civil Engineering Department of the Federal Technological University of Paraná, Brazil, has wide experience in this field. New composites and technologies were developed for 77 types of industrial rejects utilized as raw materials. Among them, galvanic sludge recycling into ceramics [7], utilization of concrete rejects [8], different types of ashes, metallurgical slag, etc. [9].

This research proposes alternatives for the reutilization of ink waste. This solution will allow the improvement of ink waste management, minimization or prevention of environmental pollution and reduction of final production costs.

Therefore, objectives of this research were the next:

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1. Study of the possibility to utilize ink waste as a raw material for civil construction.
2. Study the physicochemical processes of new composites' structure formation for optimizing their mechanical and chemical properties.
3. Develop waste less technologies or to adapt current ones for production of new composites at laboratory level.

These objectives are in line with the 3-rd paragraph (Less Chemical Syntheses) of the Twelve Principles of Green Chemistry: "Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment" [10].

## 2. Materials and methods

### 2.1. Materials

Industrial sludge was supplied by an enterprise that produces inks, varnish and special decorative printing paper; wood ash was supplied by the Filtroil enterprise; and lime production waste (LPW) was supplied by the Cal de Rio Branco lime manufacturer, all of them located in the metropolitan region of Curitiba, Paraná State, Brazil.

The enterprise that produces inks has approximately 5 tones monthly of industrial ink waste sludge (IS) which is currently being disposed at an industrial landfill. This sludge cannot be discharged into domestic sanitary sewers, since they are classified as Class IIA – Non Inert, according to Brazilian Standard [11]. Their investigation and incorporation into Portland cement requires a detailed study of their compositions and changing their physicochemical properties at heating [12].

"Water content in the ink waste sludge is 64.45%; after burning of dry sludge at 1000 °C for 1 h the analyze demonstrate 56.85% of ash content".

### 2.2. Methods

The raw materials and the newly developed ceramics were analyzed by various methods. Chemical composition was studied by X-ray fluorescence (XRF) on Philips/Panalytical PW 2400, mineral composition by X-ray diffraction (XRD) on Philips PW 1830, morphological structure by scanning electron microscopy (SEM) on Jeol JSM-6360 LV, chemical composition micro analyses by energy dispersive spectroscopy (EDS) on Jeol JSM-5410 LV and laser micro-mass analyzer LAMMA-1,000, solubility and lixiviation of metals from liquid extracts by method of atomic absorption analysis (AAS) on Perkin Elmer 4100 spectrometer, granulometric composition by laser diffraction particle size distribution analysis on LA-950 Horiba analyzer, mechanical resistance by uniaxial compression strength on EMIC universal testing machine, water absorption (WA) on Instrutherm BD-200, thermal analyses (DTA and TG) with velocity of heating 10 °C per minute, and linear shrinkage on Mitutoyo caliper.

The methodology for preparation of samples included selection, weighing, hydration and homogenization of mixtures' components (Table 1), compacting and hardening in open air. Compacting of the mixtures was performed in cylindrical forms under 10 MPa pressure to produce samples 20 × 20 mm in size and were stored in an open-air environment. They were then tested at the ages of 3, 7, 14, 28, 60, 90 and 180 days.

### 2.3. Calculations

Water resistance coefficient ($C_{WR}$) was calculated on the 28th day using [13] the equation:

$$C_{WR} = R_W/R_D, \quad (1)$$

where $R_W$ is uniaxial compressive strength after 24 h in water and $R_D$ is uniaxial compressive strength after 24 h in open air (Table 2).

Water absorption ($W_A$) tests were performed with specimens on the 28th day, in accordance with the ASTM [14], which uses the following equation:

**Table 2**
The substantial compositions of initial mixtures of raw materials under study.

| N° | Compositions (wt.%) | | |
|---|---|---|---|
| | Ink sludge | Wood ash | LPW |
| 1 | 55 | 30 | 15 |
| 2 | 55 | 25 | 20 |
| 3 | 60 | 15 | 25 |
| 4 | 55 | 20 | 25 |
| 5 | 50 | 25 | 25 |

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

where $M_{SAT}$ is the mass of the saturated specimen after 24 h in water and $M_D$ is the mass of the specimen after oven-drying at 100 °C for 24 h.

## 3. Results and discussion

### 3.1. Characterization of the raw materials

The chemical compositions of all the three raw materials under study (Table 1) are fundamentally different. The main element of ink sludge is $TiO_2$ (64.0%), of LPW – CaO and MgO (total 91.3%) and of wood ash – $Al_2O_3$, CaO and $SiO_2$ (total 83.4%). Besides, ink sludge contains NiO (2.4%) and ZnO (1.1%) and ash contains 1.7% of *F*. Calcination loss of the raw materials is estimated at 42.4% for ink sludge due to high organic content and up to 51.9% for LPW because of high water and $CO_2$ values.

Visual overview of X-ray diffractograms (Fig. 1) indicates a high content of amorphous substances in all three initial components. Ink sludge has very simple mineralogical composition (Fig. 1): Rutile – $TiO_2$ and Kaolinite–$Al_2Si_2O_5(OH)_4$. On the contrary, the wood ash under study demonstrates very rich mineral composition, including someone very rear minerals, such as alumina, calcium and fluor oxide $11CaO_7Al_2O_3CaF_2$ and alumina, calcium and ferric oxide $CaAl_2Fe_4O_{10}$.

Diffractogram of LPW used (Fig. 1-C) shows the absence of the peaks of lime CaO free from coincidence with the peaks of other minerals. The presence of peaks of Calcite $CaCO_3$ and Dolomite $CaMg(CO_3)_2$ confirms too low calcination temperature of limestone as raw material for lime production; the peaks of Portlandite $Ca(OH)_2$ indicate an insufficient insulation of burnt lime from atmospheric moisture during its storage.

In accordance with Brazilians standards [15], total content of polluters (chemical impurities) in the lime used for construction goals as binder material must be no more than 12%. The chemical composition of the material used in this research as binder (LPW) contains almost 10% of such elements and almost 52% of water and $CO_2$. The XRF and XRD (Fig. 1) analysis results confirm correct classification of the binder component used: not lime but lime production waste (LPW). That is why this product cannot be sold as construction binder material and must be classified as industrial waste. Usually it is used for acid soils neutralization or is rejected to industrial waste dump.

The thermo-graphic characterization of each of the three initial components by deciphering DTA and TG curves demonstrate the

**Table 1**
Chemical compositions of the raw materials used, determined by XRF analysis.

| Raw materials | Chemical composition (wt.%) | | | | | | | | | | | | C.L. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $TiO_2$ | $SiO_2$ | $Al_2O_3$ | $SO_3$ | Cl | $Fe_2O_3$ | CaO | $Na_2O$ | MgO | NiO | ZnO | F | |
| Ink sludge | 64.0 | 13.3 | 13.8 | 1.9 | 1.3 | 1.3 | 0.7 | 0.1 | 0.1 | 2.4 | 1.1 | – | 56.9 |
| LPW | 1.1 | 7.6 | 0.5 | 0.1 | – | 0.3 | 54.9 | – | 36.4 | – | – | – | 51.9 |
| Ash | 3.5 | 21.9 | 33.7 | 0.7 | 1.0 | 3.5 | 27.8 | 2.0 | 1.6 | – | – | 1.7 | 2.87 |

*Note:* C.L. – calcinations loss.