Characterization using XRD of puzzolanic materials from residual sludge from water treatment

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Abstract. The goal of this work is to do mechanical and chemical characterization of puzzolanic materials using compressive strength measurements and X-Ray Diffraction (XRD). These materials are composed of red clay and aluminous sludge produced by the treatment of potable water at Planta Algodonal, Ocaña, Norte de Santander, Colombia. Ceramic bricks were sintered to 1100°C and ten were characterized in their physically, mechanically and chemically properties. The results showed that the relationships with which the Colombian standards according to NTC 4017 (100KGF/cm²) for non-structural bricks are maintained for those containing 10% (105Kgf/cm²) and 20% (102.9Kgf/cm²) of sludge with respect to clay.

1. Introduction
The pozzolans are commonly siliceous materials or aluminosilicates which are capable of improving the properties of different products; this makes them useful in the formation of clay pieces which are subjected to a sintering process [1]. In Colombia, red and black clays are commonly used as raw materials for the formation of masonry products. In addition, sand is used as a complement. In recent years the study of materials has focused on the incorporation of industrial by-products or pozzolanic, considered waste [2], for the production of more environmentally friendly materials, one of these aluminosilicates is the sludge from the potable water treatment plants (PTAP).

In PTAPs during the water purification process, a quantity of coagulant, commonly aluminium sulphate, is added, thus generating the formation of sludge considered waste. These sludges are mostly composed of inorganic substances, feldspars, silts, fine sand [3] and are characterized by having a high concentration of silicon oxide and aluminium oxide. Approximately in PTAP, there are approximately 0.3% to 1% of these sludges compared to the total volume of treated water. Some researches around the world had found interesting properties in these sludges that allow them being part of glass-ceramics [4] and even used as coagulants [3]. In Colombia, there is no currently any regulation for the final disposal of sludge, which is why PTAPs discharge them further downstream from the watercourses from which they initially acquire their waters [5]. In Colombia the reuse of pozzolan materials mainly covers the construction sector, but in the case of sludge produced by water treatment, the reported information scarces, being thus used as additives for the production of Clinker, cement Portland, fertilizer in agricultural soils and as a raw material in recovery of aluminium [1,3,6-8]. For the manufacture of masonry units in Colombia, the Colombian Technical Standard (NTC) [9] must be taken into account, according to which the specimens created can be classified into units for structural and non-structural construction. In this study the compressive strength of non-structural type...
pozzolanic materials was evaluated before and after chemical attacks with hydrochloric acid and sodium hydroxide, followed by X-Ray Diffraction (XRD) characterization of the crystalline phases present in the formed units.

2. Methods
The elaborate units are composed of 100: 0 90:10 80:20 70:30 60:40 50:50 40:60 30:70 20:80 10:90 and 0:100 red clay from the alluvial fan of the City of Bucaramanga and residual sludge from drinking water treatment plan in the PTP Algodonal, located on the road to the Batallon Santander in the municipality of Ocaña. The specimens manufactured were solid cubic units of 5cm×5cm×5cm, which had a sintering process following the heating rate described below: 0-105°C (120min) 105°C-600°C (120min) 600°C-1100°C (180min), finally allowed to descend to room temperature.

Once elaborated, the materials were characterized mechanically, chemically and structurally. In the first one it is necessary to evaluate the resistance to the compression presented by the units according to the criteria of the NTC 4017, chemically an evaluation of the corrosion that the units present, for that they were submitted to an acid medium and an alkaline means, using 20% hydrochloric acid and 20% sodium hydroxide respectively for one hour followed the evaluation of the mechanical strength presented by the material after the characterization of the clay, sludge and mixtures 90:10 and 80:20.

By X-ray diffraction, these were taken on a BRUKER D8 ADVANCE powder diffractometer with DaVinci Geometry (40kV, 40mA, Cu Kα λ=1.5406Å) of “Laboratorio de Difracción de Rayos X” of the “Universidad Industrial de Santander, Parque Tecnológico Guatiguara”.

3. Result and discussion

3.1. Mechanical characterization
Results from the compressive strength for the units of different clay: sludge mixtures, are presented in Table 1, Compressive strength test. It is observed that as the concentration of sludge in the unit increases, the mechanical resistance decreases considerably. So that the mixtures 90:10 and 80:10 meet the quality standards described by the standard for non-structural materials [9] with values of 105Kgf/cm² and 102Kgf/cm² respectively, being 100Kgf/cm² the minimum value given by the norm.

Units with relationships 70:30, 60:40 and 50:50 are too close to the minimum value of the standard, so, these could be used just as a non-structural material, together with aggregates that confer greater resistance to compression. Remaining ratios are well below the minimum value required by the units for which they are not suitable for the manufacture of non-structural materials.

| Mixture | Area [cm²] | Load of Break [Kgf] | Mechanical Strength [Kgf/cm²] |
|---------|------------|---------------------|-----------------------------|
| 100:0   | 25         | 2731.22             | 109.24                      |
| 90:10   | 25         | 2625.10             | 105.00                      |
| 80:20   | 25         | 2572.58             | 102.90                      |
| 70:30   | 25         | 2433.15             | 97.32                       |
| 60:40   | 25         | 2258.48             | 90.34                       |
| 50:50   | 25         | 2057.31             | 82.29                       |
| 40:60   | 25         | 1517.96             | 60.72                       |
| 30:70   | 25         | 1335.25             | 53.41                       |
| 20:80   | 25         | 1244.42             | 49.78                       |
| 10:90   | 25         | 802.58              | 32.10                       |
| 0:100   | 25         | 623.38              | 21.95                       |
3.2. Chemical tests

Based on the data obtained above, the chemical resistance to the units of ratios was evaluated: 100:0 (used as reference), 90:10 and 80:20, these are the mixtures that meet the requirements of the NTC, the results obtained are observed in Table 2.

During the attack with hydrochloric acid, the immersed material initially absorbs a large amount of acid, due to its porosity. After 5 minutes, the absorption process becomes slow, once the immersion time and curing time elapses, the material acquires a dark tone with respect to the initial one. The size does not change considerably since the material is minimally corroded by the acid [10], thus generating slight deformations in the tips of the cube due to small parts detached. In the case of the attack with alkali, after the immersion the specimen is corrodes since there is a high discoloration at the time of curing at room temperature; however, it does not generate a change in the size of the unit under test. Finally, the material after the curing time in the open air acquires mass, so that at a higher concentration of sludge in the specimen there is a higher degree of absorption of acid and base. The mechanical strength of the specimens was measured after 7 days of outdoor curing; For the 90:10 ratio it is observed that there is no significant change in the strength of the material while for the 80:20 ratio the change in mechanical strength is considerable. Therefore, this last mixture does not comply with the value stipulated by the standard.

| Mixture  | Initial mass [g] | Final mass [g] | Mass difference [g] | Area [cm²] | W [Kgf] | Mechanical Strength [Kgf/cm²] |
|----------|-----------------|----------------|---------------------|------------|---------|-------------------------------|
| 100:0 acid | 174.01          | 186.41         | 12.40               | 25         | 2783.55 | 111.34                        |
| 90:10 acid | 157.93          | 180.82         | 22.89               | 25         | 2672.49 | 107.02                        |
| 80:20 acid | 155.02          | 193.48         | 38.46               | 25         | 1232.78 | 49.31                         |
| 100:0 base | 174.32          | 183.25         | 8.93                | 25         | 2742.98 | 109.72                        |
| 90:10 base | 163.34          | 180.58         | 17.18               | 25         | 2668.74 | 106.75                        |
| 80:20 base | 151.42          | 170.63         | 19.21               | 25         | 2161.62 | 86.47                         |

3.3. Structural study

Mineralogical phases of the samples are analysed by XRD using de database PDF-2 [11] for clay (with and without sintering), sludge (with and without sintering) and mixtures of 90:10 and 80:20, Figures 1, 2 and 3 respectively. In the case of non-sintered clay, we observe the phases of Quartz (Q), Muscovite (M), Caolinite (C), Microcline (Mi), Albite (A), Cristobalite (Cr), Hematite (H) and Montmorillonite (Mo). Quartz, muscovite and kaolinite phases have the highest concentration in the sample, which is understandable since the silicon and aluminium oxides are the ones that are in the highest proportion.

Percentage in the sample of crystalline material is high: 83.1%. Clay after the sintering process presents the phases Quartz (Q), Hematite (H), Microcline (Mi), Illita (I), Mullite (Mu) and Albite (A). As can be observed due to the high temperature, there is a loss of the phases Muscovite (M), Cristobalite (C) and Montmorillonite (Mo), and at the same time the Illita (I) and Mullite (M) phases appear. All of the above causes the amount of crystalline material after the sintering process to decrease to 51.9%. Quartz should not be present in the sintered clay, since this phase at 870°C becomes tridimite and at approximately 1000°C becomes cristobalite. Kaolinite should be transformed to primary mullite at approximately 979°C [12], because it is a metastable phase and because of the heating rate used, this transformation was not carried out, thus taking form of quartz, which is corroborate in the quantitative analysis of XRD with an increase of concentration of this phase. The rest of the kaolinite, becomes amorphous. Expected transformations were not obtained even though the sintering process was carried out at temperatures reported in the literature. This could be due to the presence of microcline and albite in the clay, these two minerals are characterized by having a thermal effect of running, which causes that the phase transformations do not occur at the expected temperature but at higher temperatures. Sludge contains the Caolinite (C) phase and, to a lesser extent,
the phases Quartz (Q), Muscovite (M), Microcline (Mi), Albite (A), Magnesiohorn blende (Mg), Gibbsite (G) and Vermiculite (V). In the sintering process phases such as magnesium blende, some phosphates and sulphates are formed, which result from the combination of atoms in the crystalline lattice. Finally, in the diffractogram of the mixtures, a combination of the minerals present in the sludge and in the clay, is present, which is why there are small non-quantifiable quantities of the minerals Biotita, Paligorskita, Bernalita, Chabasita.
4. Conclusions
Sludge from the water purification process of the El Algodonal plant is useful as additive in non-structural building materials. The 90:10 and 80:20 mixtures comply with the parameters of mechanical resistance being that described by the Colombian Technical Standard of 100Kgf/cm² and 105Kgf/cm² and 102.9Kgf/cm² respectively. Absorption of acids and bases increases as the amount of pozzolan material increases in the sample, causing the material a decrease mechanical strength in 90:10 mixture after the attack with hydrochloric acid and sodium hydroxide, it complies with the mechanical resistance parameter described by the Colombian Technical Standard. The expected phase transformations were not metastable due to the presence of minerals such as microcline and albite. These minerals, when present, create a thermal phenomenon that raises the temperature at which a phase change occurs.

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References
[1] Torres P, Hernández D and Paredes D 2012 Uso productivo de lodos de plantas de tratamiento de agua potable en la fabricación de ladrillos cerámicos Rev. Ing. Constr. 27 145–154
[2] Seco A, Ramírez F, Miqueleiz L, Urmeneta P, García B, Prieto E and Oroz V 2012 Types of waste for the production of pozzolanic materials – A Review Review Industrial Waste ed Kuan-Yeow Show and Xinxin Guo (Croatia: InTech) Chapter 7 pp 141–150
[3] Ahmad T, Ahmad H and Alan M 2016 Characterization of water treatment plant’s sludge and its safe disposal options Procedia. Environ. Sci. 35 950-955
[4] Toya T, Nakamura A, Kameshima Y, Nakajima A and Okada K 2007 Glass-ceramics prepared from sludge generated by water purification plant Ceram. Int. 33 573-577
[5] Grajales S, Monsalve J and Castaño J 2006 Programa de manejo integral de los lodos generados en la planta de tratamiento de aguas residuales de la universidad tecnológica de Pereira Rev. Ing. Uni. Medellín 31 285-290
[6] Hernández D, Villegas J, Castaño J and Paredes D 2006 Aprovechamiento de lodos aluminosos generados en sistemas de potabilización, mediante su incorporación como agregado en materiales de construcción Rev. Ing. Unid. Medellín 5 119–132
[7] Mantilla G 2015 Validación de uso de lodos generados en plantas de tratamiento de aguas residuales tipo UASB como insumo en la recuperación de suelos agrícolas Esaica 1 18-23
[8] Gutiérrez-Rosero J A, Ramírez-Fajardo A I, Rivas R, Linares B and Paredes D 2014 Tratamiento de lodos generados en el proceso convencional de potabilización de agua Rev. Ing. Univ. Medellín 13 13–27
[9] ICONTEC NTC 4017 2005 Métodos para muestreo y ensayos de unidades de mampostería y otros productos de arcilla (Colombia: Icontec) pp 1–30
[10] Escoda L, Lledó M, Suñol J J, Roura P and Carda J 2003 Estudio sobre la resistencia química de baldosas cerámicas no-esmaltadas para pavimientos industriales Bol. Soc. Esp. Cerám. Vidr. 42 85–88
[11] ICCD 2012 PDF-2/inorganic+2016 (database) ed S. Kabekkodu (USA: International Centre for Diffraction Data) (http://www.icdd.com/products/pdf2.htm)
[12] Macías López M A 2006 Estudio de las transformaciones en estado sólido de las arcillas de san jose de cucuta utilizadas en la fabricación de baldosas mediante caracterización mineralogica por difracción de rayos-x de muestras policristalinas (Bucaramanga: Universidad Industrial de Santander)