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Abstract: Currently, the main destination for sludge from Drinking Water Treatment Plants (DWTP) is its disposal in sanitary landfills. However, its chemical composition and physical properties make it suitable for use as a building material. In this work, the use of spray-dried DWTP sludge on the manufacture of cladding ceramic material for the production of tiles as an alternative to the final disposal of sludge is analysed. The work is based on an experimental study carried out on a laboratory scale. Clay and spray-dried DWTP sludge (average humidity of 3 wt.%) were mixed with different percentages of sludge (from 0 to 70 wt.%) to form a slurry to be extruded. Specimens were then fired up to 980 °C. Chemical and mineralogical composition of raw materials was analysed. Technical properties of the ceramic samples were determined. The results obtained showed that the DWTP sludge became a powder with low organic content and a high-micronised calcareous content (14.4 wt.% calcium oxide). The ceramic samples had a high open porosity, which increases with the increase in sludge addition percentage. They also had a high dilatometric coefficient. Taking into account these two properties, a possible application of this material would be the manufacture of glazed tiles. The resulting ceramic material does not pose any environmental problem, far surpassing the NEN-7345 leaching test and accelerated degassing tests (outgassing PSS-01-702 and offgassing PSS-01-729 standards of the European Space Agency).

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RECYCLING OF SLUDGE FROM DRINKING WATER TREATMENT AS CERAMIC MATERIAL FOR THE MANUFACTURE OF TILES

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ABSTRACT

Currently, the main destination for sludge from Drinking Water Treatment Plants (DWTP) is its disposal in sanitary landfills. However, its chemical composition and physical properties make it suitable for use as a building material. In this work, the use of spray-dried DWTP sludge on the manufacture of cladding ceramic material for the production of tiles as an alternative to the final disposal of sludge is analysed. The work is based on an experimental study carried out on a laboratory scale. Clay and spray-dried DWTP sludge (average humidity of 3 wt.%) were mixed with different percentages of sludge (from 0 to 70 wt.%) to form a slurry to be extruded. Specimens were then fired up to 980 ºC. Chemical and mineralogical composition of raw materials was analysed. Technical properties of the ceramic samples were determined. The results obtained showed that the DWTP sludge became a powder with low organic content and a high-micronised calcareous content (14.4 wt.% calcium oxide). The ceramic samples had a high open porosity, which increases with the increase in sludge addition percentage. They also had a high dilatometric coefficient. Taking into account these two properties, a possible application of this material would be the manufacture of glazed tiles. The resulting ceramic material does not pose any environmental problem, far surpassing the NEN-7345 leaching test and accelerated degassing tests (outgassing PSS-01-702 and offgassing PSS-01-729 standards of the European Space Agency).

Keywords: recycling spray-dried sludge; drinking water treatment plant; ceramic material; tiles; leaching; degassing tests

1. INTRODUCTION

Until the end of the 20th century, the most part of sludge from Drinking Water Treatment Plants (DWTP) was disposed by direct discharge into surface waters, stored (often indefinitely) in deep lakes and oceans (Wang et al., 1992). Nowadays, discharge to surface waters and oceans is prohibited in some developed countries, as Spain, for example, in accordance with the European Waste List 2014/955/EU (European Commission, 2014). Another usual practice, when the proximity of the collectors and the existence of a Wastewater Treatment Plant (WWTP) allows it, is to discharge into the sanitation network. This practice is not recommended since it can lead to an overload of solids in the wastewater treatment process.

In some places, the option of incorporation in agricultural soils is used as an improvement of sandy soils (Elliot et al., 1990). This alternative has a low degree of acceptance and requires transportation to specific disposal sites and regulatory permits (Elliot et al., 1990).

DWTP sludge is a poor candidate for incineration, due to their low organic content and low calorific value (approximately 1164 kJ kg^{-1} compared to 23260 kJ kg^{-1} of the sludge from WWTP) (Wang et al., 1992).

Finally, its disposal in sanitary landfills is becoming a usual practice in Spain and other countries. Since the DWTP sludge has been considered as inert and not harmful to human health (however, some studies deny this claim mainly due to its alum and lime content (EPA, 2011; Sotero-Santos et al., 2005; Tumeo, 1992)), the landfills have been frequently coated with only one layer of native clay, instead of synthetic coating and/or permeable zones for monitoring and collection of leachates. For these reasons, landfilling is perhaps the preferred option for the disposal of DWTP sludge.

DWTP sludge is largely made up of inorganic components, mainly aluminum hydroxides or iron hydroxides. Aluminum is a ubiquitous element that pollutes our environment, whose toxicity is demonstrated in some pathologies of renal failure and which is seriously considered responsible for several diseases of healthy subjects (Krewski et al., 2007). Due to its aluminum content DWTP sludge cannot be considered as inert.

A more rational and beneficial alternative from the sustainable point of view is to use the sludge as raw material for some productive process and solve the issue of its final disposal. In this context, we can mention the production of ceramic materials for building. It should be noted that ceramic products are manufactured in large quantities in Spain (for instance, 3.9 millions t year^{-1} of bricks and other structural ceramic products in 2014 (CIC, 2016). Therefore, even when small percentages of sludge produced in the DWTP are incorporated in these products, the potential use of sludge would be very important.

The process that follows this alternative is the solidification. Solidification can be defined as a disposal technique that either fixes or encapsulates the waste in a monolithic solid by using a solidifying agent (i.e., cement-silicate, lime, clays, bitumen, paraffin, organic polymers, fiberglass, etc.) (Ioannidis and Zouboulis, 2005).

In the literature, there are numerous works that analysed the addition of sludge, especially from WWTP, in ceramic products (for instance, Wolfe, 1990; Devant, 1997; Kizienivic et al., 2013; Benlalla et al., 2015).

With respect to applications using DWTP sludge, Migneault (1988) reported that some trials carried out in California using DWTP sludge (sun drying) in a brick factory, found that 10 wt.% sludge (with a moisture content of 25 wt.%) could be incorporated to the ceramic material (hereafter, wt.% means wet weight percentage). Other authors have obtained similar results for the manufacture of bricks, concluding that adding more than 10 wt.% sludge compromises the brick's compressive strength (Torres et al., 2012).

More recently, Hidalgo et al. (2017) analysed possible uses of DWTP sludge. Frias et al. (2013) studied the use of this kind of sludge for use as supplementary cementing material in cements. Besides, Husillos Rodríguez et al. (2011) proposed the use of spray-dried DWTP sludge for clinker production.

In the present work, the use of spray-dried DWTP sludge on the manufacture of cladding ceramic material as an alternative to the final disposal of sludge is analysed. To this end, an experimental study has been carried out on a laboratory scale. This paper shows the process followed and the characterization of the ceramic pieces obtained, as well as their environmental evaluation. Based on these results, it is also proposed to use this additive in other possible added-value applications.

2. MATERIALS AND METHODS

2.1. Raw materials

Raw materials used in this research to obtain the ceramic pieces were basically clays and DWTP sludge. The clays chosen correspond to clays commercially used for the production of ceramic tiles, and came from the quarries of El Papiol and Piera (Catalonia, Spain). The sludge came from the Sant Joan Despí DWTP, which is currently the largest plant supplying the city of Barcelona and is one of the largest drinking water treatment plants in Spain (> 50,000 m^3 day^{-1}) (AGBAR, 2018). It is one of the most advanced DWTPs in Europe in terms of waste minimisation and reuse. Water from the Llobregat river enters the plant through grids and large particles (gravel and coarse sand) are removed by sedimentation. Then, the following stages follow in this order (Fig. 1): dispensing of aluminium salt coagulant, sedimentation of coagulated matter and decanting of clarified water, filtering through sand, underground water collection, ozone treatment, granular activated carbon filtering, ultrafiltration, reverse osmosis, remineralisation, chlorination, final pumping to the distribution network, and a relatively new sludge treatment. This plant produces about 17000 m^3 of sludge daily: 7000 m^3 from decanters draining and 10000 m^3 from cleaning of filters. Nowadays, thickening and dewatering by means of centrifugal decanters allow the sludge to be concentrated up to 65% humidity, and allow that 16900 m^3 per day of clean water returns to the Llobregat river. The dehydrated sludge (100 m^3 per day) go to a spray-drying process, in which the rest of water is evaporated, obtaining 25 m^3 per day of dried powder (< 5% humidity). This powder is currently reused as raw material in the cement industry.

Since this work was started before the commissioning of the new sludge treatment facilities in the Sant Joan Despí DWTP, the sludge was collected directly from the plant's discharge pipe (see Fig. 1). In order to obtain composite samples, it was collected at different times and poured into a 25-litre refrigerated tank where it was kept at 4ºC in the plant itself. This allowed the supernatant to be purged from its top and the sludge sedimented and concentrated on its bottom. This resulted in an easier to transport sludge, as the sludge treatment line at the DWTP results in an extremely diluted waste (5% solid matter). A total of 100 litres of sludge (average density 1.1 kg L^{-1}) were collected between weeks 18 and 22 (springtime) of 2008. No variations were observed in the composition of the sludge. The sludge was kept refrigerated to avoid bacterial activity and nematode proliferation.

Clays and sludge were transported in plastic containers to the laboratory.

A granulometric analysis was carried out on clay and sludge samples by X-ray absorption. The chemical composition of metals was studied by ICP-MS and oxides by X-ray fluorescence.

To observe the effect of temperature on the mineralogical composition of clay, three samples were dried and calcined at 105, 350 and 650 ºC. Later, they were analysed by X-ray diffraction. Like clay, three sludge samples were first dried and calcined at 105, 550 and 1000 ºC and then analysed by X-ray diffraction to determine the effect of temperature on its mineralogical composition.

2.2. Spray-drying of DWTP sludge

In order to spray DWTP sludge, first it is necessary to prepare a slurry, i.e. an appropriate sludge suspension. In our case, sodium polyphosphate was used as a deflocculant. Deflocculation tests were carried out for different moisture content of DWTP sludge (65, 70 and 75 wt.%) after filtration of the slurry to remove vegetable residues and other impurities that could block the holes in the atomising impeller. Viscosity of the slurry was measured by a ford cup viscometer according to DIN 53211 standard. Once the optimum viscosity of the slurry was determined, it was sprayed with a Niro Mobile Minor spray drier (Fig. 2), whose technical specifications can be seen in Table 1. The minimum sludge moisture content that allowed flocculation to achieve an optimum atomisation viscosity was 70 wt.%. In these conditions, a total of 20 liters of sludge were spray-dried obtaining 7 kg of atomized powder (5 wt.% moisture), at a rate of 3.5 kg h^{-1}.

2.3. Ceramic specimens

2.3.1. Sampling and characterization

Clay and spray-dried DWTP sludge (average humidity of 5 wt.%) were mixed with different percentages of sludge (0, 20, 30, 40 and 70 wt.%). To these mixtures, water was added in sufficient quantity to have an adequate rheology (plasticity) to make it extrusionable. An extruder (Verdés, model 050C) with worm drive, driven by a 2.2 kW electric motor, a variable speed reducer between 9-40 rpm, and a vacuum pump driven by a 0.55 kW electric motor were used for this purpose. The paste was extruded into strips of rectangular cross-section, 70x10 mm^2. The humidity of the paste was determined by gravimetry.

Once the test specimens had been formed, while they were still soft, two parallel lines were drawn with a cutter 10 cm apart on one side to measure the degree of shrinkage during the drying and firing processes. The specimens were dried in a RAYPA oven, model DO-40, at a temperature of 105 ºC for 24 hours. To determine the weight loss of the drying process, a

COBOS scale model D-6000 with a sensitivity of 0.1 g was used. Once dry, ceramic firing of the specimens was carried out in a FORMAGAS propane gas oven, model HG-150. The heating rate was 160 ºC h^{-1}, from the ambient temperature to the maximum cooking temperature (980 ºC), with an exposure time of the specimens at this temperature of 3 h. Finally, after cooking, the specimens were allowed to cool freely for approximately 12 h until the ambient temperature.

A sample of 10 specimens of ceramic pieces were characterized by the following tests/calculations: shrinkage, apparent density, weight loss, water absorption, saturation coefficient, suction, flexural strength, hardness, linear expansion coefficient, and porosity. The water absorption tests were carried out for 24 hours at room temperature, in one case, and for 5 hours during boiling in another case, according to the ASTM C373 standard (ASTM C373, 2018). The suction tests by partial immersion of the specimens in water were carried out according to the UNE 67-031-85 standard. The flexural strength was determined according to the UNE 67-100-85 standard, specific for ceramic tiles, using a servo-hydraulic machine INSTRON 8500 DIGITAL CONTROL, model 1342, with a plunger speed of 0.027 mm sec^{-1}. The hardness tests were carried out using a CARL ZEISS microdurometer, applying a load of 50 ponds for approximately 30 s. The mean values were obtained from 10 random measurements on the surface of the analysed sample. The linear thermal expansion test was carried out following the UNE-EN ISO 10545-8 (2014) standard, using an ADAMEL LHOMARGY DI-24 dilatometer with a heating rate of 8 ºC min^{-1}, between 20-100 ºC.

To determine the open porosity, the results of the 5-hour boiling water absorption test (which were allowed to cool at room temperature and then weighed) were used, using the following equation:

$$p_o = \frac{w_{5h} - w_0}{\rho_w} \frac{100}{V} \qquad (1)$$

where p_o is the open porosity (%); w_{5h}, weight of the saturated specimen after boiling (g); w_0, weight of the dry specimen (g); ρ_w, water density (1 g cm^{-3}); V, geometric volume of the specimen tested (cm^3). The closed porosity (p_c) has been calculated as the difference between total porosity (p_t) and open porosity (p_o):

$$p_c = p_t - p_o \qquad (2)$$

2.3.2. Environmental evaluation

For the environmental evaluation of the ceramic specimens, a leaching test according to the NEN 7345 (1995) standard was carried out. This is a dynamic test where the sample is completely immersed in the leaching solution, which is replaced by a new solution every so often, during a period of 64 days (NEN 7345, 1995). This is one of the most severe leaching tests applied to construction materials; it is even more stringent than the current standard NEN 7375 that superseded it (Cusidó and Cremades, 2012). The test was performed in triplicate for three clay/sludge mixtures containing 0, 30 and 70 wt.% sludge. All specimens were fired at 980 ºC. The test samples were immersed in acidified water with HNO_3 at pH = 4 and the concentration of the relevant inorganic components was measured at different time intervals (NEN 7345, 1995). The extraction is carried out in eight stages. The first leaching fluid change takes place at 6 hours from the start of the test, i.e. 0.25 days; the second one the following day, and the rest at 2.25, 4, 9, 16, 36 and 64 days. The leachate obtained in each stage was filtered in a 0.45 µm filter and adjusted to pH = 2 with HNO_3 for metal determination. To determine F^- the selective electrode method was used, adjusting the pH between 5 and 6. The remaining anions (Cl^-, Br^-, SO_4^{-2}) were determined using ion chromatography without pH correction. In the case of metals, mass spectrometry (for As, Cd, Mo, Pb, Sb, and Se) and atomic emission spectrometry (for Ba, Co, Cr, Cu, Ni, Sn, V, and Zn) were used.

Secondly, the degassing tests developed by the European Space Agency (ESA) as standards PSS-01-702 and PSS-01-729 were conducted to check the safety of the ceramic product on site (ESA PSS-01-702, 1994; ESA PSS-01-729, 1991). These approved tests applied to the ceramic samples were carried out at the National Institute of Aerospace Techniques in Torrejón de Ardoz (Madrid, Spain). The tests were performed in triplicate for three clay/sludge mixtures containing 0 and 70 wt.% sludge.

A detailed description of the above mentioned tests used in other ceramic applications can be found in other works (Cusidó and Cremades, 2012; Luna, 2013; Williamson et al., 2006).

3. RESULTS AND DISCUSSION

3.3. Raw materials

The results of the granulometric analysis of the clay used can be seen in Table 2. This clay presents a portion of particle size too large to be considered a good brickwork clay (Kingery et al., 1976), but it can be acceptable for tile manufacture.

Table 2 also shows a similar analysis for the DWTP sludge used. The resulting powder has a yellowish ochre colour (Fig. 5). The sample corresponded to a wet sludge with a moisture content of 80 wt.%, but the analysis is expressed on a dry basis. The size of the sludge particles was between 1.5 - 50 µm, with a high concentration of particles in the medium sizes (slime fraction). Coarse granulometries of the clays are usually found from 44 µm onwards (Gippini, 1979; Newman, 1987). This suggests that this DWTP sludge can be used in the manufacture of building ceramics without grinding.

The content of heavy metals in clay and DWTP sludge is presented in Table 3. The limit values for the concentration of some heavy metals in soils according to Dutch legislation are also presented for comparison. In general terms, the content of heavy metals analysed in both clay and sludge is of the same order of magnitude. However, in the case of DWTP sludge, certain metals (Ba, Cd, Cu, Zn) exceed the reference values for uncontaminated soils, and others (Cr, Ni) are very close to their limit value. Therefore, they cannot be discharged into the soil without prior treatment.

Table 4 presents the chemical analysis of clay and DWTP sludge in terms of its composition as oxides. It is worth noting the high content of CaO (14.4 wt.%) in sludge compared to clay (2.6 wt.%). On the other hand, the SiO_2/Al_2O_3 ratio is 3.4 both in clay and sludge, which is higher than the average values found in pure minerals, ranging from 0.92 for chlorite to 2.64 for montmorillonite (Brownell, 1950). Therefore, it suggests the presence of free silica in crystallized or amorphous form, or other mineral phases rich in SiO_2. This is evidenced by observing X-ray diffractograms of dried samples (Figs. 3a and 4a). In the sample of clay burnt at 350 ºC (Fig. 3b), it is observed that no significant changes have occurred at this temperature. On the other hand, at 650 ºC (Fig. 3c) there is a decrease in the intensity of chlorite and quartz peaks, and the appearance of anorthite as a new crystalline phase. This transformation as the temperature increases is confirmed in other works (Martínez, 1980; Newman, 1987).

As far as DWTP sludge is concerned, in the diffractogram of its sample calcined at 550 °C (Fig. 4b), it can be seen that the first major phase is still quartz and the second phase is still calcite. However, in the diffractogram of the sample calcined at 1000 ºC (Fig. 4c), the absence of calcite and dolomite is evident. This is due to the decomposition of carbonates, which takes place between 800 and 900 ºC. Phases such as anorthite, diopside, gehlenite and wollastonite have also been formed, which is common in the firing of calcareous pastes (Albero, 2014). Free quartz remains the major phase, although as it is only stable up to 870 ºC, it would be tridimite, which is a polymorphic state of silica (Reed, 1995; Tiwari et al., 2016).

3.4. Characterization of ceramic samples

The results of moisture determination of the ceramic pastes and the extrusion pressure used are given in Table 5. In general, the higher the moisture content of the paste, the lower the extrusion pressure, and the higher the percentage of sludge in the mixture, the more water needs to be added in order to extrude the pieces. An example of the appearance and color of a ceramic specimen can be seen in Fig. 5.

The results of the tests carried out on the ceramic samples fired at 980 ºC are shown in Table 6.

- Shrinkage. In the case of 0% sludge addition, shrinkage during drying is less than shrinkage during firing. This may be due to the fact that the paste had a coarse grain size, with a high quartz content, which could have meant that during the drying process the coarse particles did not get together as much as in the cases where finer textured sludge was added. The total shrinkage in the cases of 20 and 30% sludge addition is less than in the case of 0% addition, despite its higher moisture content. This may be due to the reactions of calcium oxide in the DWTP sludge. For additions of 40 and 70%, the total shrinkage is greater, because in these cases the higher moisture content (greater shrinkage during drying) is not compensated by the re-expansion that takes place during firing.

- Apparent density. The apparent density of dry specimens (105 ºC) is decreasing as the percentage of sludge increases, due to the higher moisture content of the pastes, which is lost during drying. The same applies to fired samples (980 ºC), but in this case carbonates release CO_2 during firing. Although the change in volume (due to the re-expansion that occurs) is usually not significant, weight loss can be considerable (Tiwari et al., 2016).

- Weight loss. The first weight loss occurs during drying and is directly related to the moisture content of the ceramic pastes. The weight loss of dry samples is increasing as the sludge percentage increases due to the higher moisture content of the pastes. The second weight loss during firing is caused by the release of the constituent water, but above all by the decomposition of carbonates. For this reason, the higher the percentage of added sludge (rich in carbonates), the greater the weight loss.

- Water absorption. It occurs mainly due to the presence of hollow spaces or pores inside the fired pieces. Absorption increases with the percentage of sludge addition. This result coincides with other published works (Schmidt, 1981). ASTM C373 (2018) establishes a maximum water absorption rate of 22 % for 5 hours at boiling point for moderate climatic conditions. According to the results, the ceramic material obtained with sludge additions of up to 40 % may be used in regions that are not exposed to frequent frost cycles. In the case of 70 % sludge addition, the ceramic material obtained would not be suitable for use on surfaces exposed to the environment. Given their excessive absorption of moisture, in the case of frost, the pieces would break when the water freezes and expands in the pores.

- Saturation coefficient. It is defined as the quotient between the percentages of water absorption during 24 hours at room temperature and during 5 hours of boiling. In all cases, the coefficient exceeds the limit of 0.88 set by ASTM for moderate climatic conditions (ASTM C373, 2018). Even clayey material (0% sludge) would not be suitable for use on external surfaces exposed to the environment.

- Suction. It is the capacity of imbibition of water by capillarity by partial immersion of the ceramic piece in a short period. In no case the maximum suction limit of 0.45 g cm^{-2} min^{-1} established by the UNE 67-031 (1985) standard has been exceeded.

- Flexural strength. The results generally indicate that the higher the sludge percentage in ceramic pastes, the lower the flexural strength. The reason for this is the carbonate content of the DWTP sludge, which results in a larger volume of pores during firing. If the ceramic pieces obtained with the addition of sludge were intended for use as flooring, a maximum addition of sludge between 15 and 20 % would be recommended. For use in areas that do not withstand high traffic frequency, or in wall cladding, sludge additions could be significantly higher.

- Hardness. This parameter is of great importance when the ceramic material is used as a pavement, since it is a measure of its durability. The results show great variability, mainly due to the heterogeneity of the surfaces analysed. In all cases, the addition of sludge significantly reduces the hardness, but there is no clear trend.

- Coefficient of linear expansion. In general, the addition of sludge in ceramic pastes increases the coefficient of linear expansion of the material. This property could suggest that the DWTP sludge can be used as an additive to increase the expansion of the biscuit in the case of glazed ceramic manufacturing. Generally, the enamel has an expansion superior to the clays that make up the base or biscuit (Tiwari et al., 2016). The industry of these products currently uses calcareous pastes to make the expansion of enamel and biscuit more compatible (Tiwari et al., 2016). Difference in dilatation between the enamel and the biscuit leads to thermal stresses resulting in the well-known flaking in glazed ceramics.

- Porosity. It is a characteristic that plays a very important role in some properties of the ceramic material, such as thermal and acoustic insulation, mechanical resistance, water absorption, etc. It is noted that total porosity generally increases with the increase in sludge addition percentage, due to carbonate content as stated above. Open porosity is the main component of total porosity, as it gives a direct measure of mechanical strength and frost resistance. The increase in porosity by increasing sludge additions suggests that the ceramic product thus obtained should preferably be used in interiors not exposed to low temperatures.

3.5. Environmental evaluation

The results of the leaching test on ceramic specimens are presented in Table 7. The standard NEN 7345 sets a limit value (U_1) below which the ceramic material can be used without any environmental restrictions. As can be seen from Table 7, all concentrations of metals and ions in the analysed samples in the leaching test are below this limit. Thus, it can be deduced that this ceramic material manufactured by adding DWTP sludge has no environmental restrictions, and therefore its use will depend on physical and structural criteria.

The results of the outgassing and offgassing tests on ceramic specimens are presented in Table 8. The acceptance limits (PS-01-702 and PS-01-729 standards, respectively) for use of material and equipment in spacecraft are included in the table. In the outgassing test, the ceramic product made from 70 wt.% sludge has lower values than the product without sludge, and both are well below their acceptance limit. In the offgassing test, both the ceramic material made of 70 wt.% sludge and the material without sludge have no detectable content of the parameters analysed (CO and TOC).

Therefore, in terms of gas emissions, the ceramic material obtained by adding up to 70 wt. % of this DWTP sludge would not present environmental restrictions for use in the construction industry.

To complete this environmental assessment, it might be interesting to apply the life cycle assessment and carbon footprint analysis to the production of this ceramic product and compare them to those of the traditional treatment of DWTP sludge. The application of these methodologies, as described in many studies (for instance, Amores et al. 2013; He et al., 2018; Lundin and Morrison, 2002; Remy et al., 2013), is time-consuming and have not been undertaken in this paper, but will be the subject of further research.

4. CONCLUSIONS

Spray drying of DWTP sludge has allowed sludge to be used as a slurry, a process known in the ceramic cladding industry. By means of the atomising process, a powder with low organic content and a high-micronised calcareous content is obtained. Up to 100% of this powder could be added for tile manufacture if the moisture and extrusion pressure conditions necessary to prepare the slurry are controlled, but this would require further research.

The high open porosity of ceramic tiles obtained with the addition of DWTP sludge prevents them from being used outside as an uncoated material (enamel, glaze, etc.). However, its high dilatometric coefficient makes it possible to consider the applicability of this material as a thermal stress corrector between the biscuit and the enamel in the production of tiles.

The resulting ceramic material does not pose any environmental problem, far surpassing the NEN-7345 leaching test and accelerated degassing tests (outgassing PSS-01-702 and offgassing PSS-01-729 standards of the ESA).

This alternative for the recycling of DWTP sludge can have a double environmental advantage: 1) space-saving in controlled landfills, and therefore less environmental impact (waste is reconverted into a raw material or added-value product), and 2) savings in virgin resources, by replacing part of the raw material (clay) with DWTP sludge in the manufacture of tiles.

Given these environmental advantages, the Sant Joan Despí DWTP, which is considered a clean production plant, decided to implement this sludge atomization technology at large scale. Currently, this plant produces 30 t day^{-1} of spray-dried powder (5 wt.% moisture) (AGBAR, 2018). The results could be extrapolated to other DWTP that treat calcareous waters, such as the majority of waters in the Mediterranean basins.

As regards spray-dried DWTP sludge, taking into account its characteristic colour, it could be useful as a colouring additive to achieve ochre colours in bricks or structural ceramic pieces. In addition, given its spray-drying sterilization process, we suggest that one of its possible applications could be for use in spa mud baths.

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LIST OF FIGURE CAPTIONS

Fig. 1. Schematic process diagram of the Sant Joan Despí DWTP. The asterisk (*) indicates the point at which the sludge samples were taken in this work.

Fig. 2. Spray drier used.

Fig. 3. X-ray diffractograms of clay: a) 105 ºC; b) 350 ºC; c) 650 ºC. Al = albite; An = anorthite; C = calcite; Cl = chlorite; D = dolomite; I = illite; Q = quartz.

Fig. 4. X-ray diffractograms of DWTP sludge: a) 105 ºC; b) 550 ºC; c) 1000 ºC. Al = albite; An = anorthite; C = calcite; Cl = chlorite; D = dolomite; Di = diopside; G = gehlenite; I = illite; Mi = microcline; Mo = montmorillonite; Q = quartz; W = wollastonite.

Fig.5. Picture of spray-dried DWTP sludge (left) and a ceramic specimen (right).

Table 1. Technical specifications of the spray drier used.

Specification	Description
Drying chamber	diameter 800x620 mm, cone 60º, inner plate AISI 316
Exhaust system	Cyclone diameter 140 CHE
Heater	7.5 kW, maximum hot air temperature 350 ºC
Dust collection	Single point under the cyclone
Feed pump	Variable control peristaltic pump, 0.1 kW
Control panel	Operation switches for fan, electric air heater and feed pump. Digital input air control. Digital output air temperature indicator. Valve and pressure gauge for sprayer impeller speed control
Fan	Centrifugal suction fan, three-phase motor 0.25 kW / 2900 rpm
Rate	Drying air flow rate: 80 kg h^{-1}
Temperatures	Maximum operating temperatures: - Air inlet: 350 ºC - Exhaust air outlet: 120 ºC
Drying capacity	Between 1 and 7 kg h^{-1} water
Sizes	Length x width x height: 1800 x 925 x 2200 mm
Weight	280 kg

Table 2. Granulometric analysis of clay and DWTP sludge.

Solid fraction	Clay (d.wt.%)*	DWTP sludge (d.wt.%)*
Sand (> 20 µm)	43.4	10.6
Silt (2 - 20 µm)	39.2	86.6
Clay (< 2 µm)	17.4	2.8

* d.wt.% : dry matter weight percentage

Table 3. Heavy metal content (in mg per kg of dry matter) in the clay and DWTP sludge used and some reference values of concentration levels for uncontaminated soils in Netherland.

Parameter	Clay	DWTP sludge	Reference value
As	0.23	n.d.	29
Ba	499	495	200
Cd	0.18	1.4	0.8
Cr	81	93	100
Cu	22.3	62	36
Hg	n.d.	0.08	0.3
Mn	583	575	-
Mo	0.07	n.d.	10
Ni	-	34	35
Pb	36	74	85
Se	n.d.	n.d.	-
Ti	4665	3163	-
Zn	98	195	140

n.d. = not detected

Table 4. Chemical analysis of clay and DWTP sludge (wt.%).

Parameter	Clay	DWTP sludge
SiO_2	59.4	53.7
Al_2O_3	17.3	15.8
Fe_2O_3	6.8	5.0
K_2O	2.9	3.2
CaO	2.6	14.4
MgO	1.5	3.6
Na_2O	1.1	0.4
TiO_2	1.0	0.7
P_2O_5	0.2	0.4
MnO	0.1	0.1
Residual, not identified	7.1	2.7

Table 5. Moisture content of the paste and extrusion pressure.

Sludge added (wt.%)	Moisture (wt.%)	Extrusion pressure (bar)
0	13.7	23
20	18.4	22
30	19.1	19
40	20.9	18
70	29.0	15

Table 6. Characterization of ceramic specimens (980 ºC) *.

Property	DWTP sludge added				
	0 wt.%	20 wt.%	30 wt.%	40 wt.%	70 wt.%
Shrinkage (wet –dry) (%)	0.67±0.09	1.68±0.05	1.49±0.04	2.80±0.10	4.01±0.07
Shrinkage (dry –fired) (%)	1.30±0.10	0.17±0.05	0.34±0.05	0.20±0.05	2.19±0.20
Total shrinkage (%)	1.96±0.07	1.84±0.07	1.80±0.07	2.90±0.20	6.10±0.10
Apparent density (105 ºC) (g cm^{-3})	1.92±0.02	1.85±0.01	1.76±0.03	1.77±0.05	1.48±0.04
Apparent density (980 ºC) (g cm^{-3})	1.90±0.02	1.69±0.01	1.59±0.03	1.60±0.02	1.30±0.04
Weight loss (wet – dry) (%)	12.8±0.3	16.5±0.2	17.9±0.7	20.0±0.7	27.0±0.9
Weight loss (dry – fired) (%)	4.9±0.2	8.7±0.1	11.0±0.4	11.4±0.4	18.8±0.2
Total weight loss (%)	17.0±0.3	23.8±0.3	27.0±0.7	29.0±1.0	41.0±0.8
Water absorption, 24h, room temp. (%)	12.4±0.2	19.8±0.3	23.6±0.4	22.6±0.5	37.0±1.0
Water absorption, 5h, boiling (%)	13.5±0.4	20.6±0.2	24.0±0.5	23.0±0.5	39.0±1.0
Saturation coefficient	0.92±0.010	0.96±0.006	0.97±0.005	0.97±0.03	0.96±0.07
Suction (g cm^{-2} min^{-1})	0.16±0.02	0.26±0.01	0.32±0.01	0.30±0.01	0.39±0.01
Flexural strength (kg cm^{-2})	87±11	58±3	40±5	49±3	34±3
Vickers hardness (kg mm^{-2})	150±130	25±9	19±5	43±19	30±16
Coefficient of linear expansion (K^{-1})	$5.5\cdot10^{-6}$	$6.2\cdot10^{-6}$	$8.0\cdot10^{-6}$	$5.6\cdot10^{-6}$	$6.2\cdot10^{-6}$
Open porosity (%)	26	35	38	38	50
Closed porosity (%)	7	4	4	5	4
Total porosity (%)	33	39	42	43	54

* Mean ± standard deviation values of all measurements are shown, except for the last four variables

Table 7. Results of the leaching test after 8 extractions (highest values of each triplicate) and leaching limit values set by the Netherlands Tank Leaching Test (NEN 7345) (all values expressed as mg m^{-2}).

Metal or Ion	DWTP sludge added			NEN-7345 limit value U_1
	0 wt.%	30 wt.%	70 wt.%	
As	43.5	8.1	5.1	40
Ba	<0.02*	0.12	0.10	600
Cd	<0.002*	0.004	0.011	1
Co	0.08	<0.06*	<0.06*	25
Cr	1.11	5.6	21.0	150
Cu	0.12	0.16	0.12	50
Mo	2.6	4.6	2.7	15
Ni	0.45	0.40	0.41	50
Pb	6.0	6.7	7.6	100
Sb	0.06	0.1	0.07	3.5
Se	<0.001*	<0.001*	<0.001*	1.5
Sn	1.8	1.9	2.5	25
V	53.6	64.9	99.9	250
Zn	1.6	1.8	1.0	200
Br^-	<19.1*	<19.1*	<19.1*	25
Cl^-	35.5	101.3	33.4	20000
F^-	<9.5*	<9.5*	<9.5*	1500
SO_4^{2-}	65.4	2226.0	4436.2	20000

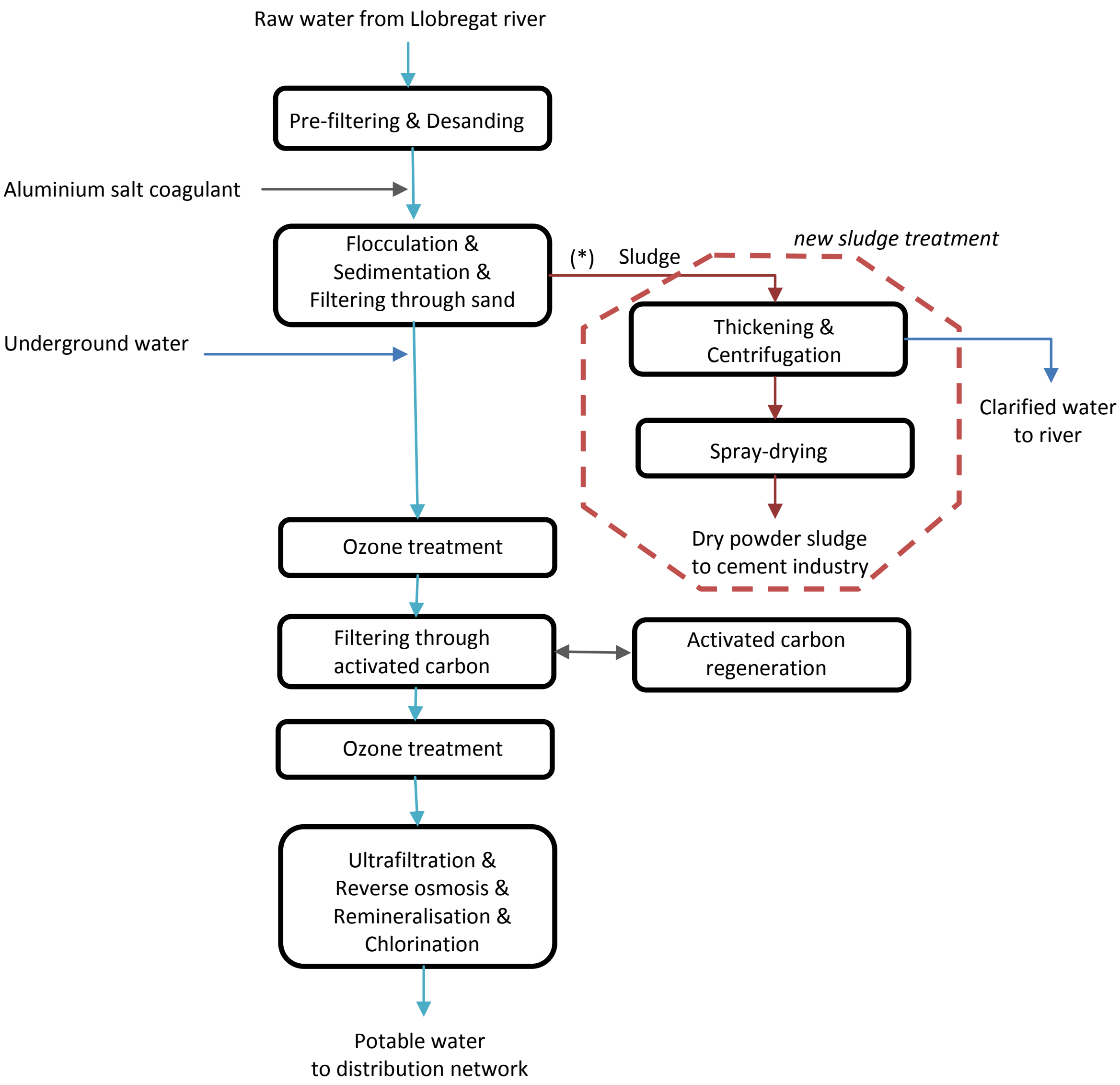
* Detection limit

Table 8. Results of the outgassing and offgassing tests (highest values of each triplicate) and allowed limits according to PS-01-702 and PS-01-729 standards, respectively.

Parameter	Sludge added		Allowed limit
	0 wt.%	70 wt.%	
Outgassing test			
Weight loss of material (%)	0.054	0.031	<1
Volatile condensed matter (%)	0.000	0.000	<0.1
Loss of recovered mass (%)	0.009	0.021	<1
Offgassing test			
CO (μg g^{-1})	n.d.	n.d.	25
Total organic compounds (TOC) (μg g^{-1})	n.d.	n.d.	100

n.d. = not detected

Fig. 1.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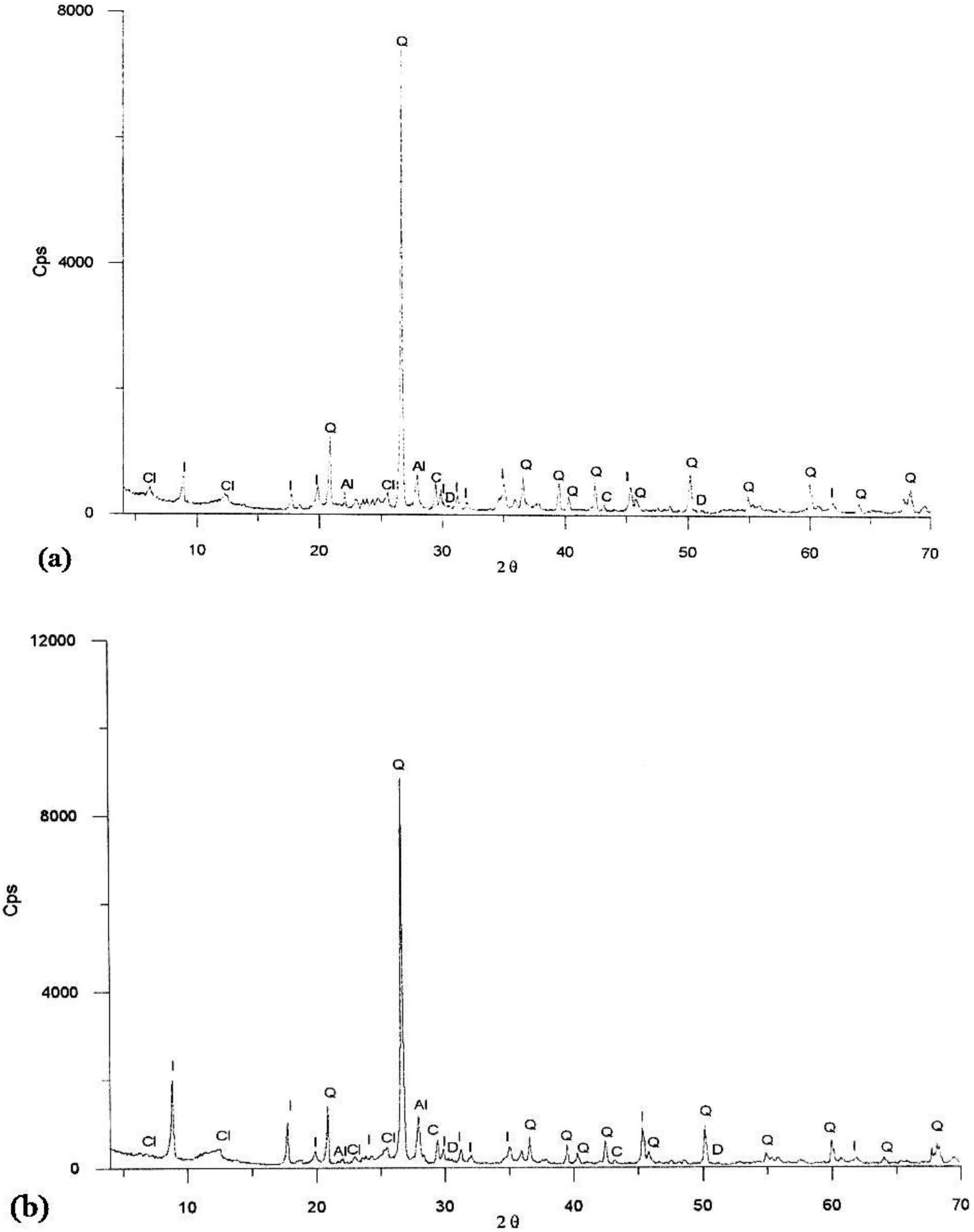
Pre-filtering & Desanding
Aluminium salt coagulant
Flocculation & Sedimentation & Filtering through sand
(*) Sludge
new sludge treatment
Thickening & Centrifugation
Clarified water to river
Spray-drying
Dry powder sludge to cement industry
Underground water
Ozone treatment
Filtering through activated carbon
Activated carbon regeneration
Ozone treatment
Ultrafiltration & Reverse osmosis & Remineralisation & Chlorination
Potable water to distribution network

Fig. 2.

Fig. 3.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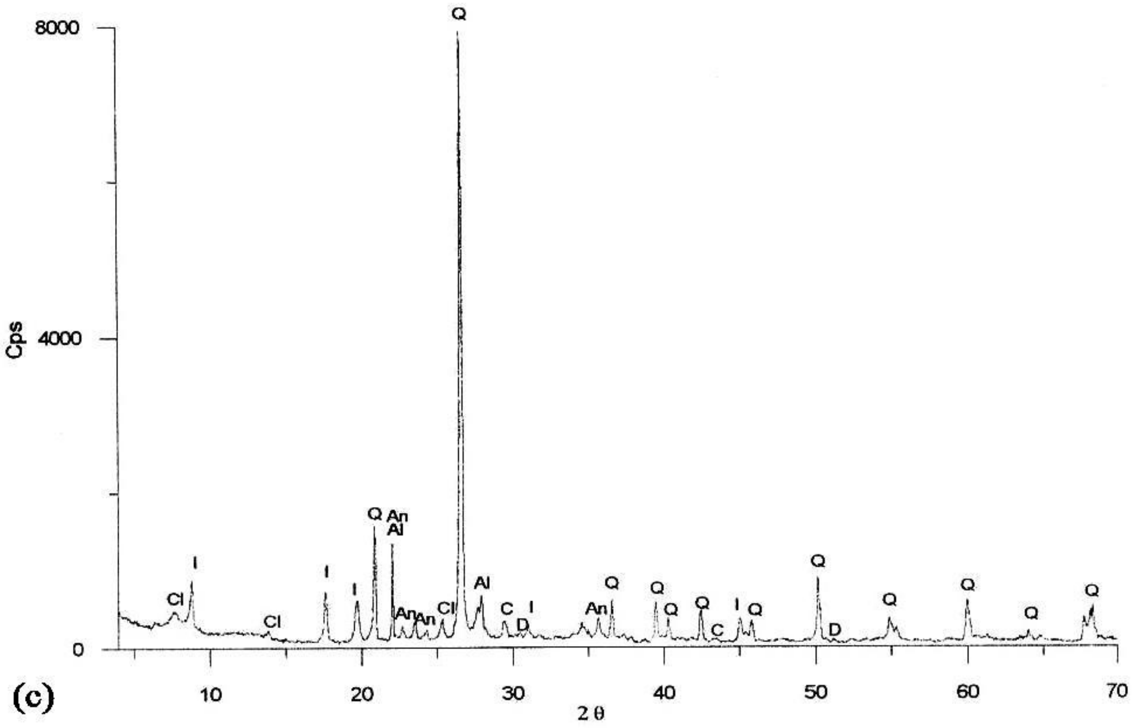
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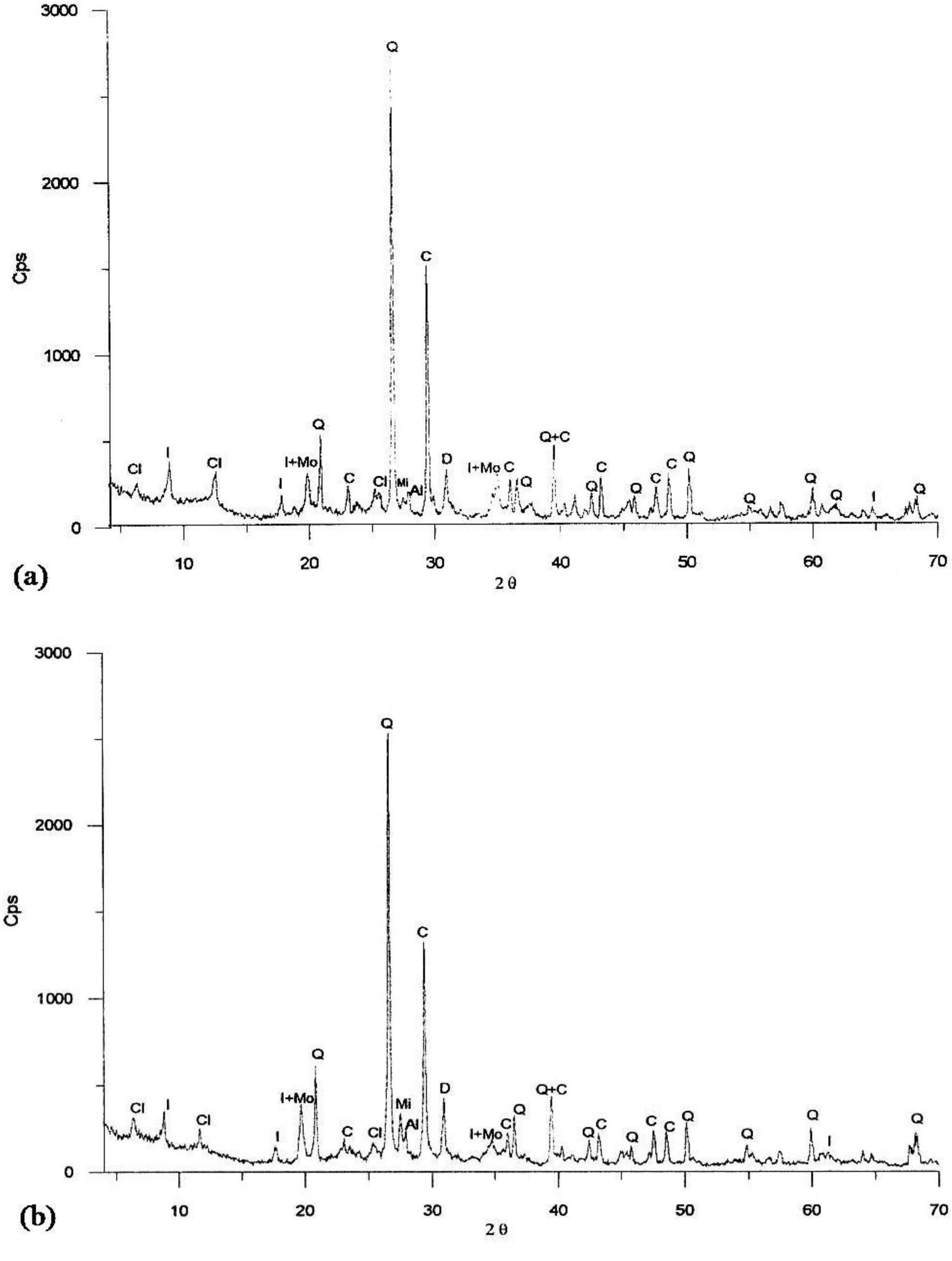
Fig. 4.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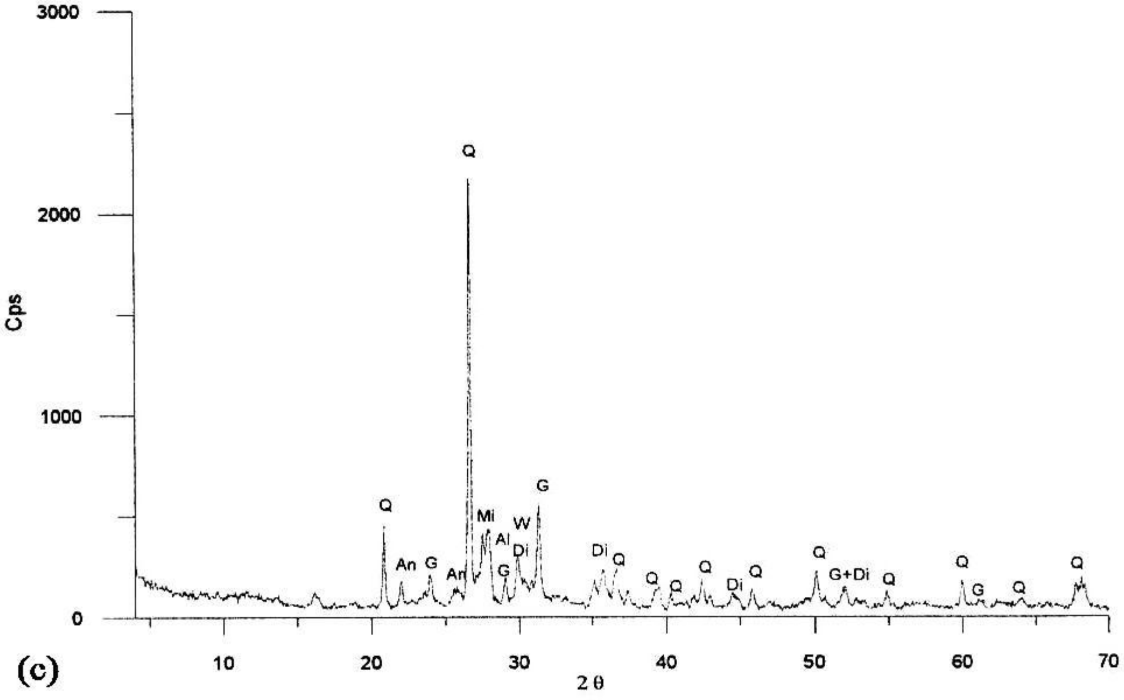
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Fig. 5.