Civil and Environmental Research, Vol.4 2013
Special Issue for International Congress on Materials & Structural Stability, Rabat, Morocco, 27-30 November 2013

Validity of water industry wastes in cement industry

M. Teresa Blanco-Varela[1], N. Husillos Rodríguez[1], S. Martínez Ramírez[2].
1Instituto de Ciencias de la Construcción Eduardo Torroja (IETCC-CSIC), Department of Cements and Recycling Materials, Madrid, Spain
2Instituto de Estructura de la Materia (IEM-CSIC), Madrid, Spain

Abstract. This paper examines the validity of several water industry wastes to be reused in different stages of cement production. The wastes considered are: a drinking water treatment plant sludge (DWTP), a sewage sludge (SS) and a spent activated carbon. Different procedures of drying of wastes using a novel dry spray system or subjected to thermal drying or stabilization and dried with lime are analysed.

The spray drying process was successfully used with the DWTP sludge (but not with SS). The material was not found to be suitable as a supplementary material in blended cements. Despite this, the spray dried sludge did show good potential as partial or full substitute for clay as a raw material in cement clinker manufacture.

A novel thermally drying process (Turbo-drying RINA-JET) was applied to produce dried sewage sludge. The dry sludge consisted of 56 % organic matter and has a high calorific value (8291 J / g), making it valid as an alternative fuel. The ash (35% of dry SS) contains Ca, Fe, P, Si and Al as main inorganic elements which are incorporated into the clinker phases. The burnability of the raw mixture containing this SS sludge was better than in the control raw mix.

Furthermore, the paper describes an industrial process for stabilising sewage sludge (SS) with lime and evaluates the viability of the stabilised product, referred to as "Neutral", as a raw material in the production of Portland cement clinker for the cement industry. The proposed process for sewage sludge treatment has a number of advantages over traditional treatments. In the Basic plant design, the chemical energy in the reagents generates sufficient thermal energy for the moisture to evaporate. This makes the process more energy-efficient than others. The validity of the "Neutral" product as a starting material in raw mixes for the production of cement clinker by substitution of limestone is demonstrated.

Regarding the validity of spent activated carbon as an alternative to pet coke as fuel in Portland cement kilns, the carbon differed substantially from the coke, having lower calorific value (18 % less). However, the qualities of the spent coke were still sufficient for the intended use. The ash fraction of the spent activated carbon was mainly composed of anhydrite and quartz (SO_3 = 14.1 %) and it is included into the clinker phases during the burning. The SO_3 from the ashes promotes a very large growth in alite crystals in the clinker.

1. Introduction

The water industry produces a variety of wastes, dominated mainly by sludge from sewage treatment and drinking water purification. Other waste products such as activated carbon and sand are also produced from drinking water treatment processes but in much lower volumes.

The disposal of these wastes is becoming increasingly difficult due to the large volumes produced and the shortage of current disposal options. The limited availability of suitable agricultural land for sludge application, coupled with the risks of contamination of surrounding surface, water and ground water bodies has made it necessary to consider other possible sludge management and disposal techniques which will reduce the volume of sludge produced and thus the associated handling and transport costs during sludge disposal.

Consequently, the need to find a new destination for these more concentrated sludge wastes has arisen, the cement industry being one of the most obvious candidates. This paper examines the validity of several water industry wastes to be reused in different stages of cement production.

2. Drying systems and characterization of sludge from drink and sewage treatment plants

The amount of solid phases in the sewage sludge ranges from 0.25 to 12% (wt) depending on the treatment process. Plants with thickening and dehydration processes can have as much as 25-30% (wt) of solids. Previous to be used in the cement plant, the sludge should be dry in order to handle easily and under sanitary conditions.

Studies have been carried out to determine the viability of drying sludge in cement plants with the residual heat from cement manufacture [1-2]. Dry fraction in sludge has several minerals and a wide range of organic matter (15-65% wt) depending on the water source. Drying process can have some technical problems since organic matter can burn and then, produce explosions.

The process of drying DWTP slugde can be done in an spin-dry atomiser that consist of a crosscurrent of the sludge with warm air [3]. The material generated by spray drying DWTP sludge is a readily handled powder which had a rounded form and a particle size similar to that observed in Portland cement, and a BET specific surface (3.29 m^2/g) one order of magnitude higher. Atomized sludge contained 12–14% organic matter, 2–

4% moisture, muscovite (25.9%), quartz (11.6%), calcite (16.7%), dolomite (3.1%) and seraphinite (4.6%), anortoclase (2.3%) and 35% amorphous material. With reference to the heavy metal content in this atomized sludge, the concentration of Cd, Co, Cu, Ni, Pb, Sb and Zn was much lower than the minimum values reported by Cyr for sewage sludge ashes (SSA) [4], while As, Ba, Cr were much lower and vanadium higher [5].

Sewage sludge can not be dried from the above procedure since its high density produces blocking of the system. However, the sewage sludge can be dried using the novel RINA-JET system [**6,7**]. This process involves the turbulent circulation of hot air, combustion gases or hot inert gases at low pressures which creates an intense drying action with minimum heating of solid particles. The operating temperature can be varied and dry sludge can be re-circulated to control the final product humidity.

During the sewage sludge drying process, approximately 81% of the energy invested in the drying process is extracted in the dried sludge product. The RINA-JET process offers the potential to use waste heat sources to greatly reduce the energy footprint of the dried sludge fuel.

Dry sewage sludge is a powder with mean particle size of 369 μm and the diameter of 90% of particles is lower than 850 μm being its BET specific surface 0.63 m^2/g rather similar to that of industrial very fine cements.

From the chemical composition point of view, the main component is organic matter (56%wt) and also contains CaO (7.6%), P_2O_5 (6.43 %) and Fe_2O_3 (7.58 %) as well as SiO_2, MgO, SO_3, Na_2O etc., in low proportion.

Of the trace elements present, the most important were Cr and Zn. X-ray diffraction data reveal calcite and quartz as the only significant crystalline phases present in sludge. According to the EN 12457 leaching test results of the dried sludge, the material cannot be considered as an inert waste and, due to soluble Ni levels, would only qualify for disposal to hazardous waste landfills [8]

Another novel procedure for sewage sludge drying consists on the stabilization with CaO and re-use of the product obtained as a raw material in the preparation of Portland cement raw mixes has been published [9]. The use of CaO for sludge treatment is a method widely referenced in the literature [10-13]. Its use is limited, however, to stabilizing sludge on a small scale. Adding a sufficient proportion of CaO (20–30%) to the sludge and thoroughly mixing the two induce CaO hydration reactions and organic matter degradation. Both processes are exothermal, in turn favouring evaporation of part of the water in the sludge [14]. The lime stabilisation process was evaluated in a pilot industrial plant treating 6 t/day. A weight reduction of about 58% was attained during the industrial scale trials designed to stabilise sewage sludge with lime. The result of the chemical reactions and water evaporation taking place in the lime/sewage sludge mixture is a dry, powdery stable, homogeneous, and innocuous product (hereafter Neutral), eligible for deposit in class II landfills. It consists of portlandite (49.8%), calcite (16.6%), inorganic oxides (13.4%) and organic matter + moisture (20.2%). Neutral particle size is even smaller (90% of the Neutral particles had diameters of under 40 μM) than raw meal cement particles

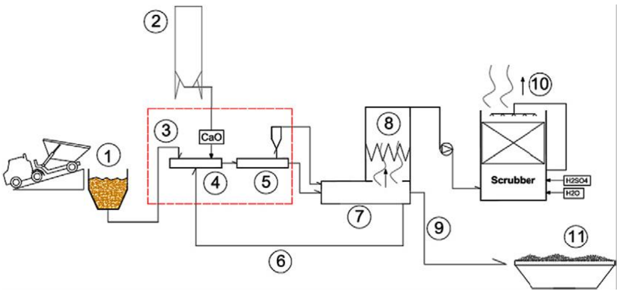

Fig. 1. Sludge treatment plant. (1) Incoming hopper; (2) lime silo; (3) sludge input; (4) pre-mixer; (5) intense mixing unit; (6) product re-circulation; (7) post-homogenization unit; (8) fabric filter; (9) Neutral output; (10) emissions to atmosphere; (11) shipping containers. [9]

The mentioned process for sewage sludge treatment has a number of advantages over traditional treatments. In the basic plant design, the chemical energy in the reagents generates sufficient thermal energy for the moisture to evaporate. This makes the process more energy-efficient than others, in which thermal energy is obtained from fossil fuels. The system is compact enough to be built inside typical wastewater treatment plant facilities, reducing the need for transport and the associated energy consumption.

3. Atomized DWTP atomized sludge as an addition to Portland cement.

The rounded shape of the atomized sludge together with its mean particle size (but similar to the Portland cement) would initially make the atomized sludge compatible with cement for the use described.

According to Husillos et al. [5], replacing cement with atomized sludge (I 42.5 N/SR cement, 90/10 to 70/30 cement-DWTPS blended cements) altered setting behaviour (and in the 70/30 blend even caused a false set) and occasioned a substantial decline in the slump of standardized mortars, which was not directly proportional to the replacement percentage.

Calorimetric studies (Figure 2) show that replacing 10% of the cement with atomized sludge lengthened both the induction period (by 6 h) and the time when maximum heat release was recorded. Replacing 30% of the cement with sludge altered the heat flow curve significantly, and three exothermal signals were recorded lengthening the induction period by over 12 h.

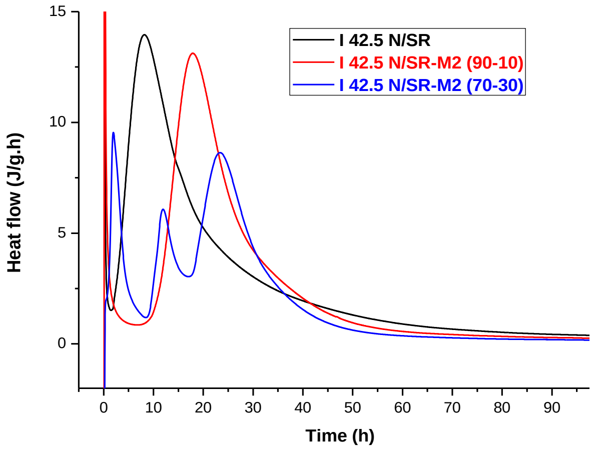

Fig. 2. Conduction calorimetry curves showing heat evolution in the three pastes.[5]

X-ray diffraction and FTIR spectra for 70/30 pastes hydrated for six hours (after the first peak), 15 hours (after the second peak) and 24 hours (at the beginning of deceleration), show the absence of characteristics portlandite signals, which indeed a substantial retardation of silicates hydration, possibly due to a reaction between the fatty acids and the Ca^{2+} and OH^{-} ions in the medium, which would inhibit portlandite nucleation. High alkali atomized sludge content could also contribute to delay the calcium silicate hydration process [14].

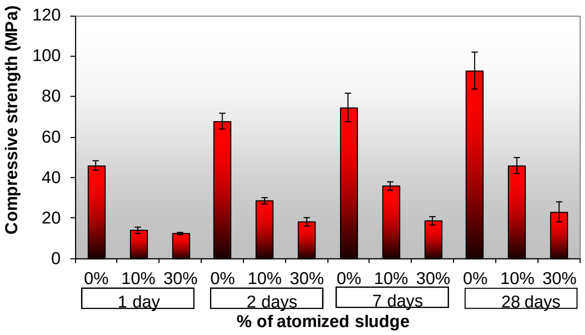

Fig. 3. Compressive strength of Cement/DWTP sludge pastes

Finally, the mechanical strength of the pastes declined substantially, even when only 10% of the cement was replaced with atomized sludge, (Figure 3).

These results proved that the atomized sludge failed to behave like an active addition. The significant decline in paste performance and the setting alterations may be related to the organic matter in the atomized sludge. According to Albayrack et al. [15], the presence of fatty acids retards setting time and lowers strength by up to 50%. They attributed the steep decline observed in compressive strength to the fragility of the double bonds present in fatty acid structures, which are readily oxidized during the curing period by the oxygen dissolved in the water, causing microscopic fissures. Other authors observed longer cement setting and lower hydration rate in the presence of fatty acids, with intense alterations in initial ettringite formation. This has been explained by the hydrophobic effect of the acids when bonding to cement particles [16].

Studies realized on mortar or concrete carrying non-incinerated sewage sludge report that the presence of sludge reduces substantially the mechanical strength of concrete recommending additions of 10% or less and only for certain specific uses [17-19]. Given the higher content of organic material of this kind of sludge this results should be waited.

These studies demonstrate the unsuitability of dry DWTP sludge and sewage sludge as components of blended cements and further investigation should be done.

4. Dried sludge as prime material for cement raw mixes or as alternative fuel in clinker kilns

Because of the different composition of both atomized sludge and sewage sludge their recycling can not follow the same paths.

4.1.- Sewage sludge

The DSC/TG study of SS [8] shows two very strong exothermic signals in the 200-500 ℃ region with maxima at 298 and 424 ℃, due to the combustion of organic matter present in the sludge [20]. By integration of the two exothermic peaks in the thermogram given in Fig. 4, over the temperature range at which they occurred, the enthalpy of combustion was calculated to be 8291 J/g. The associated mass loss during this period was 55.74%.

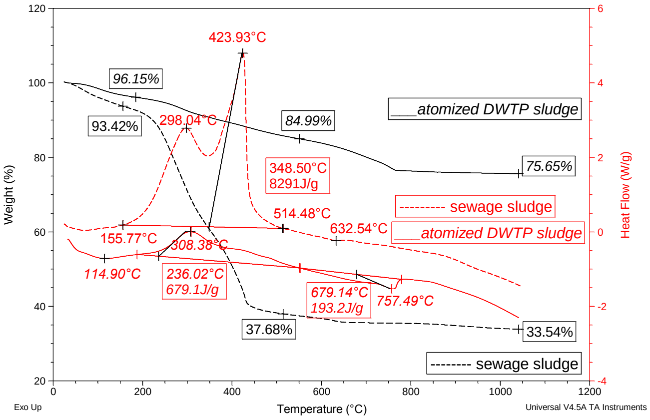

Fig. 4 DSC/TG of atomized DWTP sludge and SS.

The calorific value easily exceeds the minimum required for alternative fuels to be accepted by the cement industry of 6250 J/g [21], then the SS can be considered as an alternative fuel, for example in combination with pet coke. Since the dried sludge is a free flowing powder, feeding of the fuel to industrial scale kilns could be done via the same equipment used to feed pulverised coal to cement kilns.

Since the main components (CaO, Al_2O_3, Fe_2O_3, SiO_2) of sewage sludge ashes compare well with the proportions used in clinker raw meal, the sewage sludge can partially replace a number of raw materials normally used in cement raw meal. On a per weight basis, the ash content of dried sewage sludge is around 30 times higher than pet coke [22], then its effect has to be studied.

In fact clinkerization (at 1450 ℃ for 30 minutes) of a raw meal containing SS ash (14 % by mass) partially substituting to sand and limestone give rise to a clinker containing less alite and more belite than the reference clinker [8], which is thought to be related with the P_2O_5 contributed from the sludge component stabilising belite and partially restricting its conversion to alite [22].

According to the literature, P can be found in both alite and belite lattices but mainly in belite phases [23]. Due to the fact that the ionic radius of Si^{4+} in tetrahedral coordination is 0.26 Å and that of P^{5+} is 0.17 Å [24], the incorporation of P in alite and belite structures causes a contraction in the unit cell, which facilitates high levels of substitution of Si^{4+} for P^{5+} in belite phases [25].

Another effect of the increase of phosphorus in raw meal of cement was reducing the viscosity of the interstitial phase and thus affecting alite (larger) and belite (smaller) crystal sizes [8].

4.2.- Atomized sludge

The organic fraction of the atomized sludge burns at around 300 ℃, releasing 678 J/g sludge, the mass loss associated with this peak amounted to 7.83 wt% [26]. This calorific value does not achieve the minimum required for alternative fuels for the cement industry. However, DWTP atomized sludge as a prime material for clinker manufacture, should be studied.

The clinkerization of a raw mix with 12% atomized sludge at 1450 ℃ for 30 min gives rise to a clinker with over 75% silicates and 22% interstitial phase. The microstructural analysis showed no differences in silicate crystal size or composition between this clinker and the control.

Finally the organic fraction of both, the atomized DWTP and sewage sludge burns at around 300 ℃. Under laboratory DTA/TG experimental conditions, the organic matter continued to burn up to a temperature of 500 ℃. These combustion temperatures are high enough to guarantee the absence of spontaneous combustion and explosions in the raw meal mill.

5- Neutral as prime material for cement raw mixes.

The main component of Neutral is CaO and the main phase portlandite; in addition its specific surface is very high and consequently it should be a very reactive material, so that it could be used as substitute of limestone in the elaboration of raw mixes for the clinker Portland.

Studies on the burnability of raw mixes having a silica modulus of 2.25, alumina modulus of 1.54 and lime saturation factor of 103.32, being the dosage: Neutral, 63.95%; clay, 35.65%; and iron ore, 0.39% revealed that the Neutral raw meal exhibited an excellent burnability as when it was burned at 1400 ℃ for 30 minutes as if the temperature was 1500 ℃. Neutral raw mix burnability was even better than that showed by the control raw mix elaborated with limestone as source of CaO [9].

The mineralogical composition of the Neutral clinkers obtained at 1450 and 1500 ℃ was the same as any industrial clinker with high alite content [27]. Alite is the phase that, when hydrated, produces the C–S–H gel responsible for the binding properties, strength and durability of Portland cement. The mineralogy and crystal size and distribution in the clinker phases were similar in the clinkers prepared with Neutral and limestone. These findings lend support to the premise that Neutral is a technologically viable as a component of cement raw mixes.

Consequently, from mere waste, sewage sludge could be converted into a product, Neutral, usable as an alternative raw material in the cement industry where it could be used as raw mix component instead of quarry limestone [28]. The benefits obtained would be:

a) Energy savings are produced by replacing limestone with Neutral, since the energy needed to thermal decomposing of limestone is nearly triplet that of the Neutral product and that the combustion of organic matter present in Neutral would produce energy that offsets kiln fuel cost.

b) The Neutral product was inherently finer than the reference limestone, reducing the energy required for grinding of the raw mix.

c) Reduction of CO_2 emission in clinker production since less calcite is present.

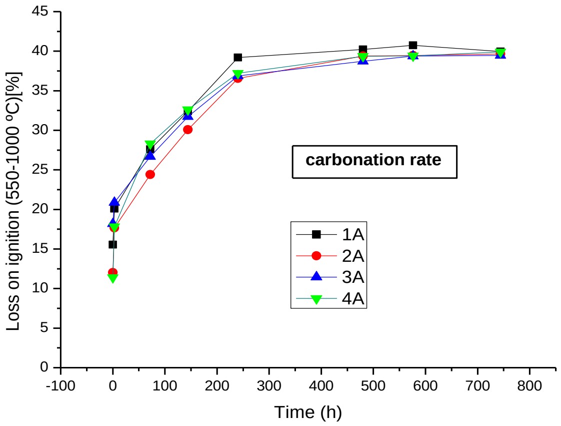

Fig 5. CO_2 content in Neutral versus time in open air at 21 ℃ and relative humidity of 95%

A negative characteristic of Neutral could be its possible carbonation when handling it. According to our results (Figure 5) Neutral is 10% carbonated after two hours and fully carbonated after 10 days exposed in open air at 21 ℃ and 95% of relative humidity.

Finally it is important to mention that organic matter present in Neutral produce its combustion at temperature above 200 ℃; this temperature is higher than the one produce in the cement mill. Then, spontaneous combustion and explosion are not been expected during the grinding process.

6. Activated carbon a an alternative fuel

Potabilization of water produces spent activated carbon. With a view to its valorisation the feasibility of using activated carbon as an alternative fuel to replace oil coke in portland clinker furnaces has been explored. This involved determining the composition, calorific value, ash and heavy metal content of the former. Since the ash generated by the use of activated carbon is taken up by the clinker, the possible effect of such uptake on clinkerization or the properties of the clinker obtained had also to be ascertained.

6.1 Activated carbon characterisation

Activated carbon differs substantially from the oil coke used as reference, with lower C, H, N and S contents and much higher ash content (one whole order of magnitude). In addition, its calorific value (6623Kcal/Kg) is 18% lower, although still sufficient for the proposed use. Lower N and S contents are beneficial in clinkerization, for the resulting NO_X and SO_2 emissions in the air around the furnace are also lower. The activated carbon contained 10.3% ash while the oil coke analyzed had only 0.81% ash, a full order of magnitude lower than activated carbon [29].

The carbon ash particles were very fine, with a mean diameter of 26 µm. The majority components in the activated carbon ash were Si, Al, Ca, S and Fe. The SO_3 content was very high, at around 14-15%, (Table 1). The most abundant crystalline phase, determined by XRD-Rietveld method, was anhydrite (22 wt%), followed by quartz (17 wt%), while 59 wt% was amorphous.

Table 1. Composition of activated carbon ash

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
	29.40	18.30	4.56	16.5	2.40	14.1
	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LI*
	1.11	1.29	0.64	0.17	0.98	5.95

*Loss on ignition at 1000 ℃

During the heat treatment to determine the ash content, 26% of the S was lost for the active carbon, while the remaining 74% was essentially in the form of anhydrite; however the heat treatment applied to oil coke to quantify this component induced a loss of over 99% of the S.

Given the high ash content in activated carbon, its effect on the clinker obtained was studied by preparing a raw mix in which it replaced the clay.

6.2. Activated carbon ash as a prime material in clinker manufacture

In order to evaluate the effect of active carbon ash on the clinker characteristics industrial prime materials and the carbon ash were used to manufacture raw mixes with the same chemical composition [(M_s= 2.30), (Mf= 1.50) and (LSF=98.00)]. Two raw mixes were batched. One (the reference) was made with industrial prime materials (limestone, 82.32; clay, 16.14; sandstone, 0.6; and Fe_2O_3 0.94 wt%) and the other with active carbon ash (ash raw mix) (limestone, 81.36; carbon ash, 10.93; sand, 6.30; Fe_2O_3, 1.38 wt%). The Fe_2O_3 used in both cases was a laboratory reagent. Wafers of raw mixes were then clinkerized for 30 minutes at three temperatures: 1 400, 1450 and 1500 ºC

Activated carbon ash demonstrated to be highly reactive with lime According XRD data; both clinkers contained a high and similar percentage of alite (72-73%) and the reference clinker a relatively low proportion of belite. The interstitial phase of both clinkers contained large amounts of ferrite and substantially smaller amounts of aluminates. The optical microscope study revealed that the 1 450 ℃ ash clinker contained 100-140 µm alite crystals which were much larger than the 30-60 µm crystals in the reference clinker [30]. The latter were automorphic crystals, i.e., with regularly shaped faces. The small, round belite crystals that ranged in size from 10 to 30 µm were smaller than the 20-45 µm crystals in the reference clinker [30] Summarizing the replacement of clay with ash in the raw mix introduce an additional amount of sulphur in the system and modifies the microstructure of the clinker obtained, as well as the composition of its majority phases. Alite dissolves more S and Al and its crystals are large, whereas belite solubilises more Mg and S and has small crystals.

7. Conclusions

Validity of different water industry wastes in different stages of cement production has been demonstrated.

- Both sludge (atomized DWTP and sewage) can be used as prime material in the elaboration of raw meal for cement Portland clinkerization.
- Dry sewage sludge as well as active carbon can be used as alternative fuel. Ashes produced in their burning are incorporated in the clinker phases.
- It can also be concluded that sewage sludge stabilized with CaO (as Neutral product) can be used as prime material in clinker raw meal. Industrial validation of Neutral product in clinker production has been concluded.
- The unsuitability of atomized DWTP sludge and sewage sludge as components of blended cements has been demonstrated.

Acknowledgements: This study was conducted under the leadership of Aguas de Barcelona as part of a CENIT (National Strategic Consortia for Technical Research) project titled "Technological development of a self-sustainable urban water cycle" (SOSTAQUA), funded by the Spanish Centre for Technological Development in Industry (CDTI). The authors wish to thank E. Larrotcha, J. Flores (Agbar), M. Guillem and J. Puig (Molins) for their comments on the article preparation.

8. References

[1] Peña Cuesta, M., 2009. Secado de lodos de depuradora aprovechando el calor residual de los gases del horno en la fábrica de Cemex España S.A., Cemento-Hormigón 1, 321–334.

[2] Arauzo, I., Permuy Vila, D., 2009. La gestión de lodos y el protocolo de Kyoto. El secado térmico y la valorización en cementera. Cemento-Hormigón 1, 365–374.

[3] Patent nº ES2157752 (A1) "Procedimiento de obtención de un producto pulverulento a partir de la fracción de rechazo de una planta potabilizadora de agua, producto obtenido con tal procedimiento y utilización de tal producto". 2002 (http://lp.espacenet.com/publicationDetails/originalDocument?CC=ES&NR=2157752A1&KC=B1&DB=lp.espacenet.com&locale=es_LP).

[4] M. Cyr, M. Coutand, P. Clastres, Technological and environmental behavior of sewage sludge ash (ssa) in cement-based materials, Cement and Concrete Research 37(2007) 1278–1289.

[5] N. Husillos, S. Martínez Ramírez, M.T. Blanco Varela; M. Guillem, J. Puig, E. Larrotcha, J. Flores. "Re-use of drinking water treatment plant (DWTP) sludge: Characterization and technological behaviour of cement mortars with atomized sludge additions" Cement and Concrete Research 40 (2010) 778–786

[6] www.agbar.es

[7] Nuria Husillos Rodríguez "Valorización de residuos de estaciones de tratamiento de agua potable y residual en la industria del cemento" (2012), PHd Facultad C.Químicas, Universidad: Autónoma de Madrid.

[8] N. Husillos Rodríguez, S. Martínez-Ramírez, M.T. Blanco-Varela, S. Donatello, M. Guillem, J. Puig, C.Fos, E. Larrotcha, J. Flores. "Thermally dried sewage sludge as an alternative fuel in the cement industry" Journal of Cleaner Production . On line marzo 20013.

[9] N. Husillos Rodríguez, R.J. Granados, M.T. Blanco-Varela, J.L. Cortina, S. Martínez-Ramírez,M. Marsal, M. Guillem, J. Puig, C. Fos, E. Larrotcha, J. Flores."Evaluation of a lime-mediated sewage sludge stabilisation process. Product characterisation and technological validation for its use in the cement industry" Waste Management 2012, 32, 3, pp. 550-560.

[10] Vesilind, P.A., Hartman, G.C., Skene, E.T., 1986. Sludge Management and disposal for the practicing engineer. Lewis Publishers, INC., USA.

[11] Turovskiy, I.S., Mathai, P.K., 2006. Wastewater Sludge Processing, Wiley-Interscience, 354.

[12] Metcalf, Eddy, Tchobanoglous, G., Burton, F.L., Burton, F., Stense, H.D., 2003.Wastewater Engineering: Treatment and Reuse, 4th Ed. Mc Graw- Hill, NewYork, USA.

[13] National lime association, using lime to stabilise biosolids. Fact sheet. 1999. www.lime.org.January.

[14] A.Palomo, A.Fernández-Jiménez, G. Kovalulchuck, L.M Ordoñez, M.C Naranjo, OPC-Fly ash cementititious systems: study of gel binders produced during alkaline hydration, Journal of Materials Science 42 (2007) 2958–2966.

[15] A.T. Albayrak, M. Yasar, M.A. Gurkaynak, I. Gurgey, Investigation of the effects of
fatty acids on the compressive strength of the concrete and the grindability of the cement, Cement and Concrete Research 35 (2005) 400–404.

[16] E.E. Hekal, M. Abd-El-Khalek, G.M. El-Shafey, F.S. Hashem, Mechanical and physicochemical properties of hardened portland cement pastes containing hydrophobic admixtures: Part 1. Compressive strength and hydration kinetics, ZKG International 52 (12) (1999) 697–700.

[17] S. Valls, E. Vàzquez, Stabilization and solidification of sewage sludges with portland cement, Cement and Concrete Research 30 (2000) 1671–1678.

[18] S. Valls, E. Vàzquez, Accelerated carbonation of sewage sludge-cement-sand mortars and its environmental Impact, Cement and Concrete Research 31 (2001) 1271–1276.

[19] S. Valls, A. Yagüe, E. Vázquez, C. Mariscal, Physical and mechanical properties of concrete with added dry sludge froma sewage treatment plant, Cement andConcrete Research 34 (2004) 2203–2208.

[20] Wang, J., Xue, Q., 2010. Study on microscopic characteristics and analysis methods of municipal sludge. Electron. J. Geotech. Eng. 15, 441e448.

[21] Ruiz Garcia M., 2009. Preparation of waste derived fuels and their evaluation in the cement industry. In: 1er Congreso Nacional de Pyme y Medio Ambiente (COPYMA) Estella, Navarra, Spain, June 2009. (in Spanish).

[22] Kolovos, K.G., Tsivilis, S., Kakali, G., 2004. Study of clinker dopped with P and S compounds. J. Therm. Anal. Calorim. 77, 759e766.

[23] Ghose, A., Barnes, P., 1980. Distribution of minor elements in cement clinkers d
macroscopic and microscopic variations. World Cement Technol. 11, 441e443.

[24] Lide, D.R. (Ed.), Handbook of Chemistry and Physics, 84th ed., vol. 12. CRC Press, New York, pp. 14e16.

[25] Halicz, L., Nathan, Y., Ben-Dor, L., 1984. The influence of P2O5 on clinker reactions. Cem. Concr. Res. 14, 11e18.

[26]N. Husillos, S. Martínez Ramírez, M.T. Blanco-Varela; M. Guillem, J. Puig, E. Larrotcha, J. Flores. "Evaluation of spray-dried sludge from drinking water treatment plants as a prime material for raw mix manufacture" Cement and Concrete Composites 33, (2011), 267-265

[27] Aranda, M.A.G., Blanco-Varela, M.T., De la Torre, A.G., Bruque, S., Zúñiga, F.J., 2003 Cuantificación mineralógica directa de cementos portland por el método de Rietveld. Cemento-Hormigón 850, 4–25.

[28] EU BREF, 2001. Draft Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries.

[29]Nuria Husillos Rodríguez; Sagrario Martínez Ramírez; María Teresa Blanco Varela; "Activated carbon as an alternative fuel. Effect of carbon ash on cement clinkerization" JACER 2013 (submitted)

[30]D.H. Campbell, "Microscopic examination and interpretation of Portland cement and clinker," Portland Cement Association (1986).