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Types of Waste for the Production of Pozzolanic Materials – A Review

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1. Introduction

Currently there are large volumes of materials considered as wastes or by-products produced by industrial activities. In most cases, these wastes have not possibility of reuse, or low economic value for the companies that generate it. This adds to the cost of its management and disposal. Current production models have associated inefficient practices such as:

1. Resource consumption. Materials and energy.
2. Waste generation
3. Economic costs

It is important to realize that the generation of wastes is an inherent part of productive systems. The quantities and characteristics of the waste generated depend on the technologies used by companies. Sometimes companies need to restructure their productive systems in order to treat the waste they generate and many times its elimination is not easy, especially in sectors where production technologies are very matured. In this context, one of the possibilities for the recovery of these materials is their reuse and recycling in the construction sector. The construction sector annually consumes large volumes of materials, which clearly gives this sector potential to absorb and give value to the large quantities of wastes produced in the industry. On the one hand, this situation can achieve the environmental protection demanded by Society, and on the other hand allows to the companies to operate more sustainable productive systems. The reuse of waste may enable the attainment of a “sustainable construction” procedure, which can be defined as a set of constructive actions which take into account technical, economical, environmental and social aspects.

The development of new urban projects and the construction of new buildings need to consume huge quantities of materials, such as paving block, bricks, tiles, cement, aggregates, etc. The manufacture of these materials involves the consumption of natural raw materials and energy. Taking into account these conditions, the development of new sustainable materials is a very effective line of work for the modernization of the construction sector. One of the most acceptable possibilities in this area is the development of pozzolanic

materials based on wastes, which can be a real alternative to conventional construction materials. Currently, pozzolanic materials are frequently used in the construction sector. In civil engineering soil stabilization technique uses these materials as binders. In building the use of pozzolanic materials is also very important as structural elements, building enclosure, etc. In both applications the most useful pozzolanic additive is Ordinary Portland Cement (OPC), one of the main current construction materials, with an annual production estimated in 2010 at 3,300,000 Tons (USGS, 2011). This material is an import economic factor, used as an indicator of the development and economic activity of countries (Daugherty, 1973).

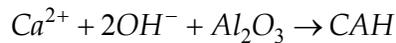
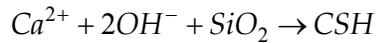
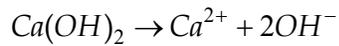
OPC is currently under discussion, not only for its cost but also for its environmental effects during manufacture. Thus, the production of 1 Ton of OPC supposes the consumption of 1.5 Tons of quarry material, energy consumption of 5.6 GJ/Ton and an emission of nearly 0.9 Ton of CO₂, representing 5 % of total anthropogenic CO₂ emission (Reddy et al., 2006; O'Rourke et al., 2009; Juenger et al., 2011; Billong et al., 2011).

Currently, other Alternative Hydraulic Binders (AHB) based on pozzolanic materials are being developed. The American Concrete Institute in its report ACI 232.1R-00 defines pozzolanic material as "siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties".

Some industrial wastes, usually coming from the combustion process, such as fly ash and bottom ash, have pozzolanic properties. The pozzolanicity of these materials is set in the ASTM C 593 and ASTM C 618 standards, and depends mainly on the amount of Ca, Si and Al oxides present, the ratio between them and their reactivity (Pacheco-Torgal et al., 2008; Ravikumar, 2010; Billong et al., 2011). The addition of pozzolans to OPC or their use together with lime allow the partial substitution or in certain applications full substitution of OPC. This supposes a reduction in waste, in energy consumption and in CO₂ emission, lower production cost and sometimes improved engineering properties. This converts the AHB into a potentially competitive material with OPC both in developed and in developing countries (Singh and Garg, 1999; Shen et al., 2007; Ercikdi et al., 2009; Billong et al., 2011; Kinuthia and Nidzam, 2011).

2. Chemical principles of the pozzolanic reactions

Pozzolanic reactions take place when significant quantities of reactive CaO, Al₂O₃ and SiO₂ are mixed in presence of water. Usually CaO is added as lime or cement meanwhile Al₂O₃ and SiO₂ can be present in the material to develop cementation gels to be added as cement or, for example, with a pozzolan. In this process the hydration of the CaO liberates OH⁻ ions, which causes an increase pH values up to approximate 12.4. Under these conditions pozzolanic reactions occur: the Si and Al combine with the available Ca, resulting in cementitious compounds called Calcium Silicate Hydrates (CSH) and Calcium Aluminate Hydrates (CAH) (Dermatas and Meng, 2003; Nalbantoglu, 2004; Guney et al., 2007; Yong and Ouhadi, 2007; Chen and Lin, 2009). A simplified qualitative representation of these reactions is summarized below:



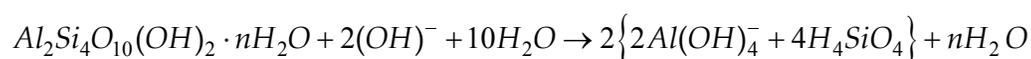
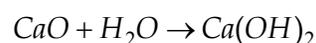
These compounds are responsible for improving the mechanical properties of the mix, due to the increasing development of pozzolanic reactions over time; some authors point up this may take place over years (Wild et al., 1998).

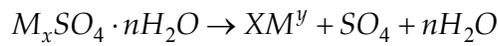
Where these oxides are not available in sufficient quantities in the materials to be cemented, they must be incorporated with the binder. In these cases it is particularly advantageous to use stabilizers which, like OPC, are rich in SiO_2 and Al_2O_3 as well as in CaO (Wild et al., 1998; Degirmenci et al., 2007) or for example the use of lime and pozzolan mixes. When these oxides are present in the material which needs to be cemented it is not necessary to add them as a binder. This situation is most usual in the stabilization of clay soils where oxides are present in the clay matrix. They are naturally rich in Si and Al oxides which become soluble at high pH conditions and then become available for the development of the pozzolanic reactions. The improved mechanical capacities achieved in each case depend on the amount, reactivity and concentration of the oxides, the size and shape of the particles and also on the curing conditions (Misra et al., 2005; Yarbasi et al., 2007; Göktepe et al., 2008).

One adverse effect related to the pozzolanic reactions is caused by the presence of sulfate (SO_4^{2-}). It may often appear both in industrial wastes and in natural soils, provoking the formation of a highly hydrated and expansive mineral called ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). The mechanics of the formation of ettringite are not yet well established (Mohamed, 2000), although the conditions for its formation are well known (Ouhadi and Yong, 2003) and are:

1. High pH,
2. presence of soluble Al,
3. presence of soluble Ca,
4. presence of soluble sulfate and
5. availability of water.

It is also known that the rate of ettringite formation is accelerated by high temperatures (Rajasekaran, 2005) and that given the right conditions for rapid formation, appears even in few seconds. Mohamed (2000) determined the total time of formation of ettringite in a natural soil as 48 hours. In their experiments Ouhadi and Yong (2003) and (2008) established the formation of this mineral over one month in one case, and in another experiment 48 hours after the mixture of the soil with lime. From a chemical point of view, the reactions involved in the formation of ettringite are (Ouhadi and Yong, 2008):



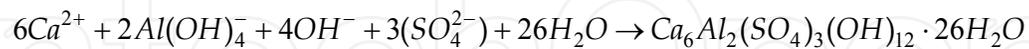


where

$$x = 1, y = 2$$

or

$$x = 2, y = 1$$



As can be seen, ettringite has 26 H₂O molecules in it, which is why it is very expansive during its formation and can cause the destruction of the cemented materials. This is the case, for example, of the well documented cases of premature concrete deterioration or the expansivity of stabilized soils (Collepari, 2003; Ouhadi and Yong, 2008; Thomas et al., 2008).

3. Interesting wastes for the production of pozzolanic materials

As explained previously, the most interesting waste substances for the production of pozzolanic materials are these that contain appreciable amounts of reactive Ca, Si or Al oxides. Although the majority of them are obtained in combustion processes, there are also other possible origins for the pozzolans. The composition and the quality of wastes with potential pozzolanic properties can vary from high reactivity to none, depending on: (1) the original materials and (2) the production processes. Apart from them, other wastes with no pozzolanic activity can be added as a target during the production of pozzolanic-based materials, to reach up to as much as 90% of the total mass of the final product. In the following sections of this chapter the main available pozzolanic wastes useful as binder materials are reviewed.

3.1 Fly Ash (FA)

Fly ash is the finely divided residue resulting from the combustion of coal in electric power generating stations. Its pozzolanic properties are well documented (Temimi et al., 1998; Senol et al., 2006; Samaras et al., 2008 among others) and it is usually employed in Portland Cement production. The large available quantities of this waste makes it necessary to dump it, causing environmental effects. Standard ASTM C 615 classifies it as F class or C class based on its reactivity and chemical composition.

3.2 Ground Granulate Blast-furnace Slag (GGBS)

GGBS is a by-product obtained during the manufacture of pig iron in the blast furnace and is formed by the combination of iron ore with limestone flux. If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs. This process results in the formation of sand size fragments, usually with some friable clinker-like material known as GGBS. The physical structure and gradation of GGBS depend on the chemical composition of the slag, the temperature at the time of water quenching and the method of production. GGBS, when it is activated with small amounts of lime, has a high pozzolanic activity, and it has been widely used in various engineering applications (Wild et al, 1998; Binici et al., 2007; Oti et al., 2009 among others).

| OXIDES | CLASS C FA | CLASS F FA | GGBS | SILICA-FUME | RHA | PG | CW |
|--------------------------------|------------|------------|-------|-------------|-----|-------|-------|
| CaO | 14.8 | 2.39 | 41.99 | 0.8-1.2 | | 32.04 | 9.45 |
| Al ₂ O ₃ | 25.5 | 26.67 | 11.59 | 1-3 | | 0.88 | 14.16 |
| SiO ₂ | 47.4 | 54.45 | 35.35 | 85-95 | 99 | 3.44 | 52.36 |
| MgO | 2.7 | 1.12 | 8.04 | 1-2 | | | 1.97 |
| SO ₃ | 2.8 | 0.10 | 0.23 | | | 44.67 | |
| Fe ₂ O ₃ | | 6.91 | 0.35 | | | 0.32 | 6.22 |
| Na ₂ O | | 0.21 | | | | 0.13 | 1.02 |
| K ₂ O | | 2.03 | | | | | 1.85 |

Table 1. Oxide composition of the waste materials

3.3 Silica-fume

Silica-fume is an industrial waste produced from the smelting process for silicon metal and ferrosilicon alloy production. It contains high amounts of extremely fine and amorphous SiO₂ particles (see table 1). Silica-fume has been used in civil engineering works as a binder in combination with cement for soil stabilization giving great results (Taylor et al, 1996).

3.4 Rice Husk Ash (RHA)

Rice husk is a common agricultural by-product around the world. In many countries this husk is used as fuel for power plants, generating from its combustion large quantities of RHA. These ashes are rich in amorphous SiO₂ as is shown in table 1, having great pozzolanic properties (Behak and Perez, 2008; Seco et al., 2011a; Seco et al., 2011b among others).

3.5. Phosphogypsum (PG)

Phosphogypsum is a byproduct of the chemical reaction between sulfuric acid and phosphate rock to produce phosphoric acid. Nowadays large volumes of PG are dumped in tips, causing economic loss and environmental concerns. Some authors have used it, combined with cement, lime and fly ash, to stabilize soils in spite of its high sulfate content (Shen et al., 2007; Degirmenci et al., 2007).

3.6 Ceramic Wastes (CW)

Ceramic wastes include all the waste from bricks, tiles and other fired-clay based materials. These materials when ground up have pozzolanic properties, known since Phoenician times (Baronio and Binda, 1997). This is because they are produced from clay, and the thermal process leaves the Al and Si oxides in an amorphous state.

3.7 Sewage Sludge (SS)

Sewage Sludge is the generic name of all kinds of fresh or incinerated wastewater treatment wastes. Its composition and available quantities vary depending on its origin (industrial,

water treatment, tannery, etc.). The majority of these materials often have an appreciable content of heavy metals, making their use as construction material more difficult. Although the majority of the experiences of their use in construction is as a target in fired clay materials (Weng et al., 2003; Lin et al., 2005; Chen and Li, 2009) other authors have demonstrated the possibility of using them in the production of pozzolanic materials (Tay and Show, 1997; Cyr et al., 2007; Liu et al., 2011).

4. Construction materials based on pozzolanic wastes

This section includes a review of the most interesting construction materials created from pozzolanic wastes, such as soil stabilized layers, unfired bricks and blocks, and masonry mortars.

4.1 Soil stabilized layers

Wild et al. (1998) improved the strength properties of a soil with sulfates by stabilizing it with lime and GGBS. Nalbantoglu (2004) used C class fly ash as a binder to stabilize an expansive soil, reducing its plasticity and swelling capacity. Koliaş et al. (2005) demonstrated the benefits of soils stabilized with cement and fly ash compared with conventional flexible pavements. Degirmenci et al. (2007) showed the possibility of stabilizing soil with a mix of phosphogypsum, cement and fly ash. They improved the compressive strength as well as the Atterberg limits. Lin et al. (2007) demonstrated the improvement of the mechanical properties of a soil when it was treated with a mix of lime and sewage sludge, increasing the strength resistance and reducing the swelling capacity. Shen et al. (2007) showed the possibility of using a lime-fly ash-phosphogypsum binder for road base construction. Yarbasi et al. (2007) used silica-fume and fly ash to increase the durability of the tested samples of granular soils for road construction. Chen and Lin (2008) used a mix of cement and incinerated sewage sludge to improve the basic properties (strength and swelling) of subgrade soils. Samaras et al. (2008) demonstrated the potential use of a mix of sewage sludge, fly ash and lime as soil stabilizer.

4.2 Unfired bricks and blocks

Kumar (2002) studied fly ash-lime-gypsum bricks, observing that the resistance of these materials and durability make them available as low cost housing materials. Poon and Chan (2006) demonstrated the possibility of making paving blocks from concrete and ceramic wastes. Chindraprasirt and Pimraksa (2008) demonstrated that heavy metals were retained in a fly ash-lime unfired brick. Degirmenci (2007) demonstrated the possibility of producing adobes with phosphogypsum as stabilizer, obtaining good strength values, although this material was susceptible to water damages. Oti et al. (2009) demonstrated the increase in the strength and durability of unfired clay bricks with GGBS with lime or cement as binder. Wattanasiriwech et al. (2009) produced paving blocks with a ceramic waste that reached the standard requirements after a curing period of between 7 and 28 days. Oti et al. (2010) demonstrated that unfired clay bricks based on a clay soil stabilized with a mix of GGBS or lime comply with the thermal design requirements for masonry. Liu et al. (2011) analyzed the effect of water sludge waste in unfired brick production, demonstrating that by

combining it with cement it was possible to achieve all the performance criteria for unfired bricks.

4.3 Masonry mortars

Tay and Show (1997) created a waste-based mortar by incineration of municipal wastewater sludge. This material was useful as masonry mortar, replacing up to 30% of Portland Cement. McCarthy and Dhir (1999) stated that fly ash can be used to improve the properties of Portland Cement. Papayianni and Stefanidou (2006) observed lower strength and good durability of lime-pozzolan mortars compared with cement based ones. Rodriguez de Sensale (2006) demonstrated the increase of strength in cement mortars at 90 days curing age when rice husk ash was added. Cyr et al. (2007) analyzed mortars containing sewage sludge ash, discovering a long-term positive effect because of its slight pozzolanic activity. Zerbino et al. (2011) observed the possibility of replacing cement by rice husk ash by up to 25% in concrete without loss of resistance.

5. Conclusions

This review has aimed to improve our knowledge on the application of different industrial wastes in the construction field. Much industrial wastes can be absorbed by civil engineering and building construction, reducing at the same time both the consumption of Portland Cement and the environmental problems provoked by the dumping of wastes. There are industrial wastes with pozzolanic characteristics which can at least partially substitute Portland Cement without loss of resistance, and even increase other properties like durability. All of them have a potential use as a sustainable, green, and low cost binders. Nowadays these sustainable binders are being used in soil stabilization and in the building industry in the development of new sustainable construction materials. These new materials have demonstrated their capacity to reach all the technical requirements. Thus the potential for industrial waste utilization in the field of construction has a potential so far not fully exploited, that may transform current construction practices into new sustainable construction, socially and environmentally more responsible.

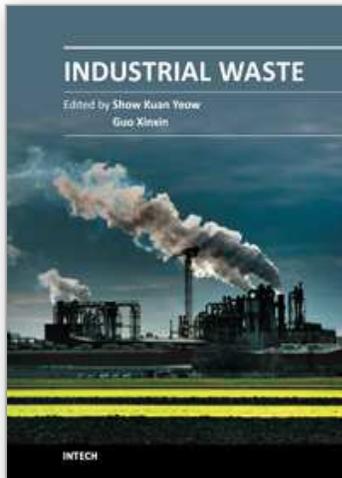
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This book is intended to fulfil the need for state-of-the-art development on the industrial wastes from different types of industries. Most of the chapters are based upon the ongoing research, how the different types of wastes are most efficiently treated and minimized, technologies of wastes control and abatement, and how they are released to the environment and their associated impact. A few chapters provide updated review summarizing the status and prospects of industrial waste problems from different perspectives. The book is comprehensive and not limited to a partial discussion of industrial waste, so the readers are acquainted with the latest information and development in the area, where different aspects are considered. The user can find both introductory material and more specific material based on interests and problems. For additional questions or comments, the users are encouraged to contact the authors.

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