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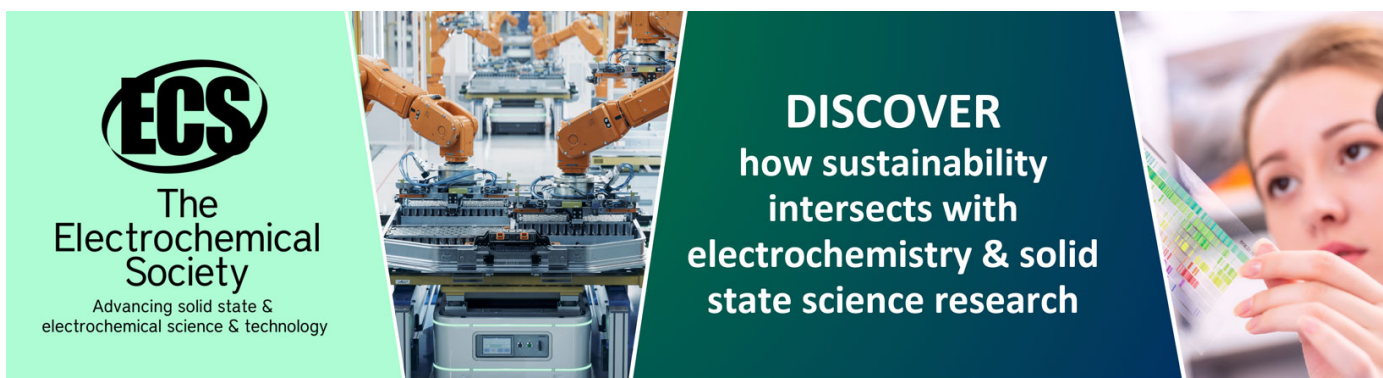
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Development of New Cementitious Caterials by Alkaline Activating Industrial by-Products

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Abstract. The alkaline activation of aluminosiliceous industrial by-products such as blast furnace slag and fly ash is widely known to yield binders whose properties make them comparable to or even stronger and more durable than ordinary Portland cement. The present paper discusses activation fundamentals (such as the type and concentration of alkaline activator and curing conditions) as well as the structure of the cementitious gels formed (C-A-S-H, N-A-S-H). The durability and strength of these systems make these materials apt for use in many industrial applications, such as precast concrete elements (masonry blocks, railroad sleepers), protective coatings for materials with low fire ratings and lightweight elements.

1. Introduction

Portland cement-based concrete is today's construction material *par excellence*. It owes this pre-eminence to its mechanical strength, good value for money ratio and performance in general. Nonetheless, Portland cement manufacture raises certain energy and environmental issues, for it calls for temperatures of up to 1400-1500 °C and the extraction of raw materials (with the concomitant destruction of natural quarries), and entails the emission of GHGs such as CO₂ and NO_x. Moreover, concrete is subject to certain durability problems, including the aggregate-alkali reaction and attendant expansion, chloride-induced corrosion in reinforcing steel, retarded ettringite formation, thaumasite formation and so on [1].

One possible way to solve these problems while contributing to better environmental balance (via the re-use of industrial by-products or waste, reducing the cost and potential for pollution inherent in their storage) is to add mineral or industrial by-products to Portland cement clinker. The result is different types of common cements listed in European standard EN 197-1:2000, which specifies the

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maximum amount of addition allowed for each cement type.

Another possible, more innovative option is the development of less expensive alternative cements, more respectful of the environment (lower CO₂ emissions, use of industrial by-products, etc.), with performance comparable to or even higher than ordinary Portland cements (OPC). The so-called **alkaline cements** [2-5] feature all these properties.

Two key characteristics of alkaline cements are: (i) they don't have clinker contents (free OPC); and (ii) they use alkaline activators. Two major alkali activation models in place can be distinguished by their starting conditions: **1st model**: activation of **calcium- and silicon-rich** materials (Me₂O-MeO-Al₂O₃-SiO₂-H₂O system) as the activation of *blast furnace slag* under relatively moderate alkaline conditions [2-5]; **2nd model**: activation of materials comprising primarily **aluminium and silicon** (Me₂O-Al₂O₃-SiO₂-H₂O system) also called geopolymers as the activation of metakaolin or fly ashes [3, 6-8].

The present summary addresses the most relevant aspects of alkaline cements, including composition of the prime materials, reaction mechanisms, characteristics of the reaction products, process variables (such as the type and concentration of alkaline activator and curing conditions), physical-mechanical properties as well as the structure of the cementitious gels formed (C-A-S-H, N-A-S-H). The durability and strength of these systems make these materials apt for use in many industrial applications, such as precast concrete elements (masonry blocks, railroad sleepers), protective coatings for materials with low fire ratings and lightweight elements.

2. Composition of prime materials

The materials most commonly used to manufacture alkaline cements and concretes are blast furnace slag and fly ash. As table 1 shows, the chemical composition of these materials in % of mass.

Table 1. Chemical composition (%) in mass.

	L.O.I.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SO ₃	Na ₂ O	K ₂ O	Other
Slag	0.77	37.42	11.47	0.66	10.62	32.71	2.96	1.47	1.19	0.73
Fly ash	2.19	54.42	26.42	7.01	1.79	3.21	0.01	0.59	3.02	1.34

L.O.I. = Loss on ignition.

Vitreous blast furnace slag, waste generated by the steel industry, is formed when the clayey acid gangue from the iron ore and the sulfur ash in the coke combine with calcium and magnesium in the limestone or dolomite used as fluxes. The vitreous blast furnace slag obtained when acid (SiO₂ and Al₂O₃) and basic (CaO and MgO) oxides combine at high smelting temperatures (1600 °C) and are then abruptly cooled to T < 800 °C is later ground and stored in silos for shipping. On average, slag has a 90-95 % vitreous content, with network-forming [(SiO₄)⁴⁻ (AlO₄)⁵⁻, (MgO₄)⁶⁻] and modifying (Ca²⁺, Al³⁺, Mg²⁺) cations [2]. Its minority crystalline phases form a solid solution of two melilite family

crystals, gehlenite and åkermanite, which crystallize in the tetragonal system.

Fly ash is an industrial by-product generated by coal-fired steam power plants. Before it can be used as a fuel in power plants, coal must be ground to a very fine powder. During combustion, the coal forms coarse ash (called “bottom ash”) and other much finer particles that are carried by smoke and collected in precipitators to prevent dispersal into the atmosphere. This is what is known as ***fly ash***. Fly ash particles are characteristically spherical and may be either hollow or filled with other smaller spheres. The ash best suited for alkali activation is type F fly ash ($[\text{CaO}] < 10\%$), which has a vitreous content of $> 50\%$ (the vitreous content can be determined by a chemical attack with HF acid [9-10] or thought a XRD-Rietveld analysis [11]). Its minority crystalline phases include quartz (5-13 %), mullite (8-14 %) and magnetite (3-10 %), they are basically inert to the alkali- activation process [9-11].

3. Results

A considerable number of variables are involved in alkaline activation, most prominently: the composition of the prime materials, type and concentration of the alkaline activator; liquid/solid ratio; curing temperature and time; and moisture conditions during initial curing. These variables have been amply studied in the literature because they affect the degree of reaction, the mineralogical composition and microstructure of the reaction products and ultimately the physical-mechanical properties of the material. This review focuses specifically on how the type and concentration of the activator, along with temperature and curing time, affect mechanical properties.

3.1. Effect of type and concentration of activator

The solubility of these materials varies depending on the pH of the activating solutions. Solubility is high in acid media, but the instability of the resulting hydrates prevents any cementitious structure from forming. By contrast, at basic pH > 11 the material dissolves and forms stable hydrates, with a gradual increase in the binding properties of the material. Therefore, the functions of the activating substance can be summarized as: i) to accelerate material solubility; ii) to stimulate the formation of stable, low solubility compounds; iii) to stimulate the formation of a compact structure.

The most widespread opinion around ***activator concentration*** is that the higher it is, the greater is mechanical strength. Nonetheless, this is not completely accurate: depending in part on the activator used, there may be certain threshold values above which strength does not rise significantly, or may even fall. Moreover, these high doses of alkalis may have adverse effects, increasing efflorescence, brittleness and so on. Nor should the economic factor be overlooked, for higher doses entail higher costs.

In any event, the thresholds apparently vary depending on the material. For materials rich in SiO_2 and Ca_2O , this threshold is in the order range of 3-6 % of Na_2O by mass with respect to the binder [2-4]. Much more basic concentrations are needed for materials rich in SiO_2 and Al_2O_3 , with Na_2O values in the range of 8-10 % [2-4].

The present discussion focuses on the alkaline activators that the literature regards to be the most

effective in terms of mechanical strength and other properties, namely: NaOH, Na₂CO₃ and sodium silicate (waterglass). Some authors [12] have also reported that mixing the activators may have a beneficial effect on strength development.

As figure 1 shows, activator behaviour is very similar in the two systems (Slags and Fly Ash). At any given Na₂O concentration, the highest strength values are consistently obtained when the activator used is a sodium silicate solution (waterglass). In the opinion of a number of authors, waterglass contributes doubly to strength development, both by acting as an alkaline activator and giving rise to the formation of a more compact structure and cementitious gel richer in silica [13]. Variations in the SiO₂/Na₂O ratio are known to significantly modify the degree of polymerization of the dissolved species (monomers, dimers, trimers and so on), the optimal SiO₂/Na₂O ratio in a waterglass solution according to the literature is in the range of 0.75-1.25 [3,13]. While the presence of soluble silica in the system generates no essential change in the reaction mechanism, it does substantially lower the range of the long-term structural order. This plays a very significant role in determining the structure and properties of polymeric gels synthesized using these solutions.

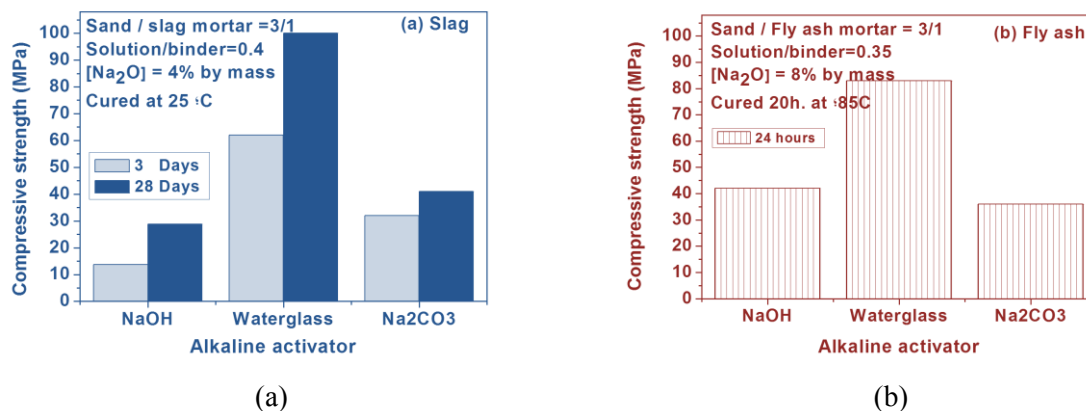


Figure 1. Variation in compressive strengths in mortars depending on the type of alkaline activator (prismatic specimens 4x4x16 cm): (a) slag mortars; (b) fly ash mortars.

As a rule, sodium carbonate activation yields lower early age strength than when the activator is NaOH or sodium silicate (waterglass). The explanation is associated with the formation of calcium sodium carbonates and/or bicarbonates, which lower the pH and therefore the degree of reaction of the starting material. This effect is attenuated at older ages, however, and some of these mortars eventually exhibit higher strength values than NaOH-activated materials (see figure 1). Briefly, then, the OH⁻ ions catalyze the dissolution of the vitreous phase of the material. Up to a certain threshold, the presence of soluble silicate ions may have a beneficial effect on mechanical strength, for it occasions the formation of initial gels richer in Si. The presence of carbonate ions may lead to the formation of calcium/sodium carbonates that acidify the system, lowering strength, particularly at early ages.

3.2. Effect of temperature and curing time

Increasing the temperature during initial curing accelerates the reaction rate of these materials: this is known as **accelerated curing**. Curing enhances mechanical strength, particularly early age strength, improves durability, and limits product fluctuations and efflorescence. As in the case of Portland cement, higher temperatures may have both beneficial and adverse effects on mechanical strength development in alkaline cements. Figure 2 shows the effect of thermal pre-curing treatment (time and temperature) in alkali activated slag and fly ash mortars (prismatic specimens 4 x 4 x 16 cm, sand/binder ratio=3/1). Slag mortars were activated with a 4M NaOH solution, solution/ slag ratio = 0.4; the pre-curing process were 20h at two temperatures, 25° and 45 °C, with 95% of r.h. , to be later curing in a chamber (22° ± 1°C at 95% of r.h.). Fly ash mortars were activated with 8M NaOH solution, solution/fly ash ratio = 0.35; the pre-curing process lasted 5h, 12h, 24h and 7 days at 45°C, 65°C and 85°C at 95% r.h. The effect of pre-curing temperature is more relevant in alkali activated fly ash where time and temperature have a considerable impact on the mechanical behaviour. This could be explained by the fact that the solubility of Al and Si increases significantly with temperature but it is not so with calcium compounds. Nonetheless, in alkali activated fly ashes, after a certain threshold value, this rise tapers (see figure 2b). Mechanical strength grows exponentially with temperature [14], considerably reducing the time needed to reach high mechanical strength values.

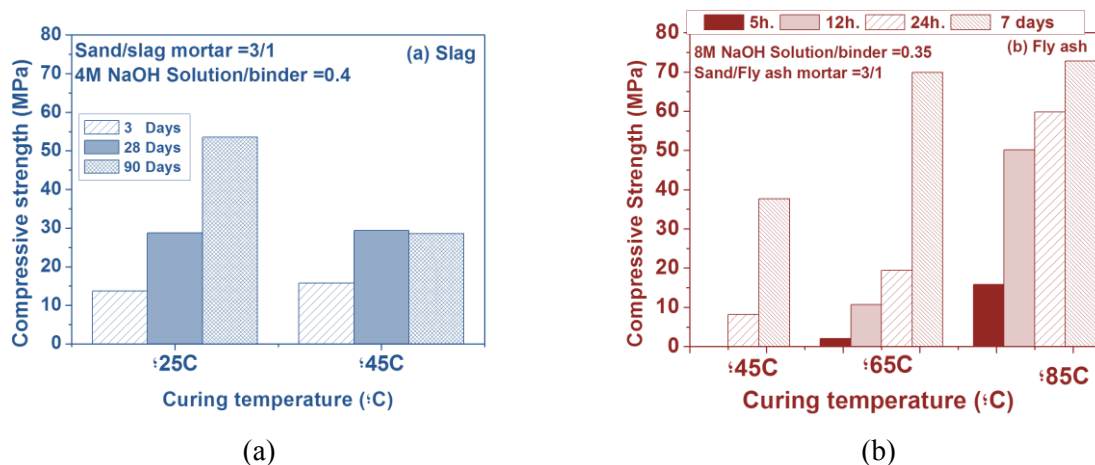


Figure 2. Effect of time and temperature on the mechanical strength in mortars (specimens 4x4x16 cm) of (a) slag activated with 4M NaOH; (b) fly ash activated with 8M NaOH.

3.3. Reaction products

The majority product forming in Portland cement hydration is a C-S-H gel to which the material primarily owes its mechanical properties. The secondary products include portlandite, ettringite, monosulfoaluminate, etc. In alkaline cements, the process is similar, inasmuch as the main reaction product is a gel with a different composition and structure than the one found in the OPC gel. The

secondary products also vary. The type of secondary product depends on the starting materials, type and concentration of the activator, curing conditions and so on. Table 2 compares the most common reaction products formed in these materials [2-5].

Research conducted on fly ash at the Eduardo Torroja Institute has shown that the uptake of small amounts of soluble Si in the system enhances the tendency of the tectosilicate structure to attain high range order in a short period of time. The transformation kinetics of zeolite precursors into crystalline phases (aluminosilicates) are accelerated under these conditions. Nonetheless, when the degree of soluble Si polymerization rises, the gels formed are apparently more amorphous. For both types of materials, then, the optimal $\text{SiO}_2/\text{Na}_2\text{O}$ ratio in a waterglass solution is in the range of 0.75-1.25 [2-5].

Table 2. Reaction products.

	OPC	Alkaline cement					
		$\text{Me}_2\text{O}-\text{MeO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$			$\text{Me}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$		
Main product	C-S-H	C-A-S-H			N-A-S-H		
Secondary product	$\text{Ca}(\text{OH})_2$	Hydrotalcite $[\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}]$			Zeolites: HS, P, Na-CHA, Y, FAU		
	AF_m	C_4AH_{13}	CASH_8				
	AF_t	$\text{C}_4\text{AcH}_{11}$	$\text{C}_8\text{A}_2\text{cH}_{24}$				
	$\text{C}=\text{CaO}$	$\text{S}=\text{SiO}_2$	$\text{A}=\text{Al}_2\text{O}_3$	$\text{N}=\text{Na}_2\text{O}$	$\text{H}=\text{H}_2\text{O}$	$\text{c}=\text{CO}_2$	

The gel forming during the alkali activation of *blast furnace slag* is similar to C-S-H gel in which the Al_T is taken up into the structure of the material, replacing a Si tetrahedron in the bridging tetrahedron position. The presence of Al gives rise to longer linear chains as well as to the possibility of occasional inter-chain bonds “*cross-linked*” across Si-O-Si bonds to form plane-like structures (Q^3 nAl units). In other words, in this way C-A-S-H – type gels would form (see figure 3a).

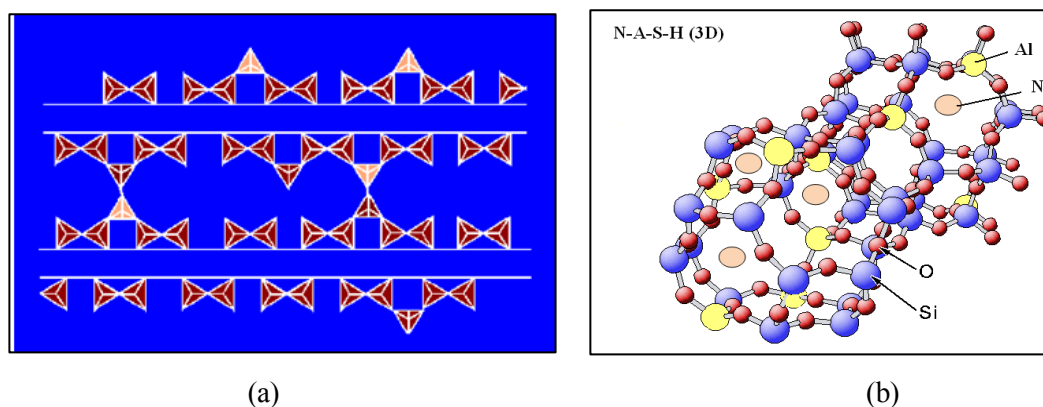


Figure 3. (a) Structural model for C-A-S-H; (b) structural model for N-A-S-H gel [4-5].

By contrast, the structure of the gels forming *during the alkali activation of silicoaluminous materials (with low Ca content)* varies substantially from the foregoing. This gel, a silicoaluminate alkaline inorganic polymer (N-A-S-H) characterized by a three-dimensional structure in which the Si is found in a variety of environments, with predominance of $Q^4(3Al)$ and $Q^4(2Al)$ units, may be identified as a “zeolite precursor”. The Si^{4+} and Al^{3+} cations exhibit tetrahedral coordination and are connected by oxygen bonds (see figure 3b). The negative charge on the AlO_4^- group is offset by the presence of alkaline cations (typically Na^+ and K^+). The initial, metastable, Al-rich compound that forms subsequently evolves into phases with a higher Si content [4,5,7].

4. Applications

In this section some applications (made by the authors of this paper) in the precast industry are shown. Figure 4 shows the railway sleepers manufactured with alkali activated fly ash concrete (without OPC) with no need for any significant material change in the normal manufacturing stream used at the factory. The most relevant modification was to increase the curing temperature from 50 to 85-90 °C. A tunnel was built for this purpose, in which pressurized water vapour was injected (see figure 4). Increasing the curing temperature in these materials does not cause the durability problems observed in Portland cement when cured at $T > 60$ °C. The sleepers manufactured demonstrated very good behaviour to static and dynamic test [15].



Figure 4. Photographs of industrial-scale manufacture of railway monoblock sleepers using alkali-activated fly ash concrete (with no OPC) [15].

Figure 5 (a) and (b) show alkali-activated fly ash-based inorganic materials usable as a fire-resistant coating for fibreglass or carbon fibre matrices. Despite their lower density, sheets of fibreglass- or carbon fibre-reinforced polymeric resin can develop strength similar to the values characteristic of steel. The main drawback to such materials is their low resistance to high temperatures and their combustibility when directly exposed to flame. The improvements achieved in fibreglass with an alkali-activated fly coating included the following: I) -The primary advantage obtained with the use of this type of coating is non-propagation of the flame; ii)-The resin ignites where the flame is applied but the flame does not propagate upwards. The flame disappears when the resin is consumed.

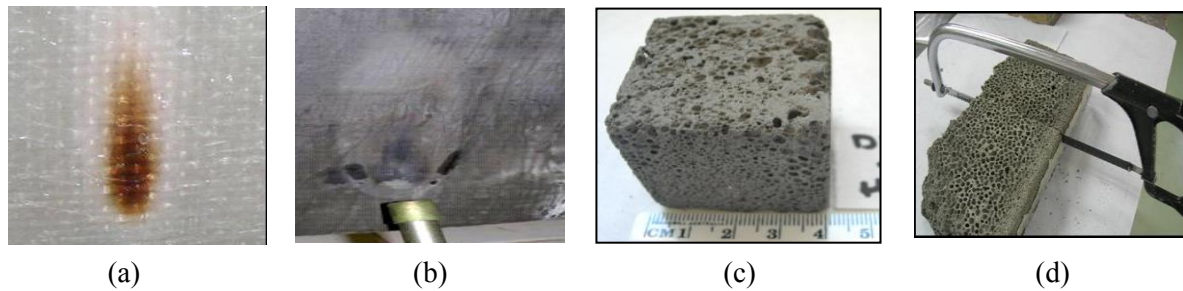


Figure 5. Photographs of fire protection test. (a) Fibreglass + epoxy resin, exposure time 8s; (b) coating *Material 1* exposure time 8m; (c) Lightweight materials evenly distributed pores; (d) Physical appearance of the panels manufactured.

Other possibility to manufacture lightweight materials is with alkali-activated fly ash, using a series of air-entraining admixtures to lower the density of this material (see figure 5 c and d). As a rule, they also provide acoustic and thermal insulation. The admixture can react very rapidly with the paste, the resulting material can have densities between 1000 to 500 kg/m³ and resistances between 10 to 3 MPa latter of cured in a kiln for 20 hours at 85 °C.

Finally, figure 6 depicts the elements precast (wall blocks and type 6 pavers) with a blend (12% OPC+88% BFS) alkali activated and cured at room temperature. Both 2- and 28-day materials met mechanical strength requirements. The only difference between these elements and the products made with Portland cement worth mentioning was their slightly lower density.

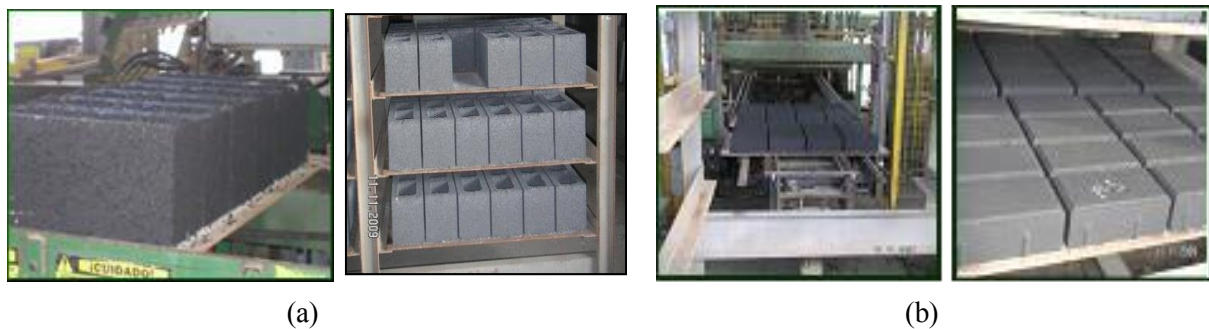


Figure 6. Production of (a) type 14 wall blocks; (b) type 6 pavers.

Of course, many others works by different authors [2-4, 16] about different applications in the precast industry, ceramics, porous materials and even biotechnologies [17] can be found in literature.

5. Conclusions

Alkali activation of aluminosilicates can be considered a very versatile technology that can be adapted to a variety of industrial applications. Particularly within the construction industry, alkali activation of slag and fly ash (industrial by-products) allows getting a material with the cementing features similar to the Ordinary Portland Cement. Besides, this process offers important economic and environmental benefits when compared with the traditional fabrication of OPC. The possibility to obtain different qualities of materials by modifying not only the binder composition but also the nature of the activator used and the pre-curing treatment deserves special attention.

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