CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 3, 2016 Chemical Technology

Galyna Kotsay

POZZOLANIC ACTIVITY DIAGNOSTICS OF FLY ASH FOR PORTLAND CEMENT

Warsaw University of Technology, Branch at Plock, Poland
17 Lukashevicha St., PL-09400 Plock, Poland; kotsayg@pw.plock.pl

Received: October 29, 2015 / Revised: December 22, 2015 / Accepted: May 30, 2016

Abstract. The work deals with the analysis and evaluation of different methods of pozzolanic activity determination in order to rationally use ash in cement. The most optimum diagnostic method has been suggested. The possibility of increasing fluidal fly ash activity has been established using the synthetic nanosilica.

Keywords*:* pozzolanic activity, fly ash, microsilica, synthetic nanosilica.

1. Introduction

The construction industry in Europe uses about 18 million tons of fly ash per year, out of which about 14 % fly ash was used to produce blended cements [1]. The requirements for fly ash are present in the European standards EN 197-1 [2], EN 450-1 [3] where ashes are classified depending on SiO_2, CaO, Al_2O_3 content, losses while burning and fractional composition. Such classification is typical of fly ash obtained via conventional method of coal combustion. However, fluid method at 1073–1173 K is also used in power engineering in order to decrease emissions of sulfur and nitrogen oxides. Such ashes are characterized by greater losses while burning due to unburned coal (> 5 %). The result is the increase of water consumption of binding material and corresponding decrease in the properties of cement wares. According to the data of the Society of Cement Producers in 2010 in Poland the usage of conventional fly ash was 1850.0 thousands tons; at the same time the fluid fly ash was used in the amount of 23.5 thousands tons [4].

Fly ash belongs to synthetic pozzolanes, which react with calcium hydroxide and form structurally active calcium hydrosilicates or hydroalumosilicates. They increase strength, density, corrosion resistance, and durability of cement stone [5-7]. Pozzolanic activity of the ash depends on chemical, mineralogical and fractional compositions. One of the problems appeared while using fly ash is its unstable chemical and mineralogical composition. For instance, SiO_2 content varies from 23 to 70 %, CaO – from 18 to 50 %, SO_3 – from 2 to 11 %, MgO – from 2 to 9 % [5, 6]. The most unstable chemical composition is typical of fly ash obtained from lignite. Therefore it is necessary to control the reactivity of mineral additives because using fly ash with low activity may decrease the strength of buildings and even destroy them.

There are many methods for pozzolanic activity determination through the investigations of chemical and physical properties of the materials. The most common method is physic-mechanical method according to EN 450-1 [3]. The essence is the determination of the coefficient of pozzolanic activity *via* compression strength. However, it is well-known that the strength depends on cement stone structure and porosity. Fly ash contains different amount of unburned coal affecting the increase of stone porosity and decrease of strength. Therefore the determination of the coefficient of pozzolanic activity by means of the above mentioned method does not allow to estimate evenly the reactivity of the additive itself.

Among standard chemical methods to determine cement pozzolanic activity the Fratiniego method is widely used according to EN 196-5 [8]. The essence is complexometric determination of calcium cations concentration (expressed *via* CaO) bounded by mineral additive, cement composite alkalinity and comparison of calcium cations concentration till saturated state under the same conditions. According to the standards the mentioned method may be applied for pozzolanic cement.

To estimate the reactivity of pozzolanic additives other methods are also used. For example, the method according to ASTM C 379-65T [9] is the determination of amounts of silicon and aluminium oxides capable to react with 0.5 N solution of NaOH at 353 K. However, NaOH has the strongest action (sodium anomaly) relative to hydroxides action on amorphous silicon dioxide [10].

Thertefore, at equal concentrations of hydroxides they may be placed in the following row according to the strength of their action: NaOH > KOH > LiOH > NH_4OH > $Ba(OH)_2$ > $Sr(OH)_2$ > $Ca(OH)_2$. Calcium hydroxide has the weakest reactivity with amorphous phases of silicon and aluminium oxides, hence it is pointless to correlate the reactivity of mineral additives with NaOH and $Ca(OH)_2$.

Chapellea method is also used among the chemical methods [11]. The essence is the determination of pozzolanic activity *via* boiling 1 g of the material in saturated solution of calcium hydroxide. The difference between $Ca(OH)_2$ content in the saturated solution and solution with pozzolanic additive is the measure of pozzolanic activity. However the dilution degree of $Ca(OH)_2$ at 373 K is 2.3 times less compared with that at 293 K, therefore the pozzolanic reaction does not proceed completely.

To determine the activity of acid mineral additives it is necessary to quantitatively define their capability to bond $Ca(OH)_2$ under the normal conditions and the rate of the process as well. The above mentioned methods do not estimate the reaction rate of pozzolanic materials with calcium hydroxide. So the determination method according to [12] is of great interest. The essence is determination of the amount of calcium hydroxide bounded with mineral additive for 30 days. The more active is the additive the greater amount of calcium hydroxide it reacts with. Thus, having the information about the reactivity of the additives it is possible to develop the cement composites.

Since fly ash is characterized by changing phase state and hence by different pozzolanic activity, its determination is an important parameter for fly ash quality necessary for cement production. Thus, the aim of the work is to choose the optimal method of pozzolanic activity determination and to diagnose the reactivity of mineral additives.

2. Experimental

We used two types of fly ash for the experiments: fluidal and conventional ones. The ashes were obtained via burning of hard coal at heat power plant in Żerań, Poland. The chemical composition of the fly ash is determined according to the European standard EN 196-2 [13] and specific surface – according to PN-EN 196-6 [14], [15]. The mentioned values are represented in Table 1.

The application of high-active synthetic nanosilica for the activation of fly ash was grounded in the previous investigations [16, 17]. Experimental investigations of the pozzolanic activity were carried out according to the European standards EN 450-1 [3], EN 196-5 [8] and special method [12].

To determine the pozzolanic activity in accordance with EN 450-1 it is necessary to determine the coefficient of pozzolanic activity of fly ash equal to the ratio between the compression strength of cement stone formed from 75 % of CEM I 42.5R cement and 25 % of fly ash and compression strength of cement stone formed from 100 % of CEM I 42.5 R cement. The ash is considered to be active if the coefficient of pozzolanic activity for 28 days is ≥ 75 %, and for 90 days – ≥ 85 %.

To determine the activity in accordance with EN 196-5 it is necessary to determine the concentration of calcium cations (expressed *via* CaO) bounded by mineral additive in the system cement – pozzolan – water in comparison with the concentration of calcium cations in the saturated solution. To carry out the investigations we used CEM I 32.5R cement, a mineral additive (10 % relative to the cement mass) and distilled water (water/cement = 5). The prepared sample was kept in the thermostat at 313 K for 8 days. Then 50 ml of the solution were taken off the filtrate and the general alkalinity was determined via titration using 0.1 N HCl. After the solution neutralization by 1 N NaOH till pH = 12.5 we determined CaO amount *via* titration by 0.03 mol/l solution of disodium salt of ethylenediaminetetracetic acid (EDTA). The obtained values of hydroxide ions and calcium oxide concentrations were compared with the concentration of calcium oxide in saturated state at 313 K and expressed as the function $C_{CaO} = 350/((C_{OH-})-15)$.

To determine the pozzolanic activity of the mineral additives in accordance with [12] it is necessary to determine the amount of bounded calcium hydroxide (expressed *via* CaO) by one gram of the additive from the limewater. For the experiments we used the mineral additive dried till the constant mass (2 g) and saturated solution of $Ca(OH)_2$ (100 ml). The solution of calcium hydroxide was titrated by 0.05 N HCl every 2 days for 30 days. After the sampling of solution of calcium hydroxide (50 ml) for titration we added 50 ml of the limewater to the cylinder. According to this method not only pozzolanic activity but also the degree of pozzolanic activity in time was determined.

Table 1

Chemical composition and specific surface of the mineral additives

Mineral additives	Chemical composition, %						Specific surface, m^2/g
	SiO_2	Fe_2O_3	CaO	SO_3	Loss on ignition	Other oxides	
Fluidal fly ash	43.4	3.7	10.9	0.3	19.0	22.7	0.3270
Conventional fly ash	70.8	3.5	4.2	4.0	7.6	9.9	0.3630
Synthetic nanosilica [18]	93.0	1.0	1.0	–	5	–	173

3. Results and Discussion

According to the standards the investigated fluidal fly ash cannot be used as an additive to cement due to the high content of unburned carbon particles (Table 1). For the fluidal fly ash the losses while burning are 4 times higher compared with the standard requirements [2]. The conventional fly ash belongs to the category C and may be used for the cement production if its strength meets the standard requirements.

However, the possibility of fly ash usage considerably depends on its pozzolanic activity. That is why the determination of pozzolanic activity will allow to use it rationally for the production of cement and concrete.

In accordance with EN 450-1 the coefficient of pozzolanic activity (CPA) was determined for the fluidal and conventional fly ashes for 28 and 90 days (Fig. 1). The increase of the conventional ash CPA by 8 % (compared with that of the fluidal fly ash) is connected with lesser content of unburned coal in the coal (Table 1). The result is the decrease of cement stone porosity and the increase of compression strength.

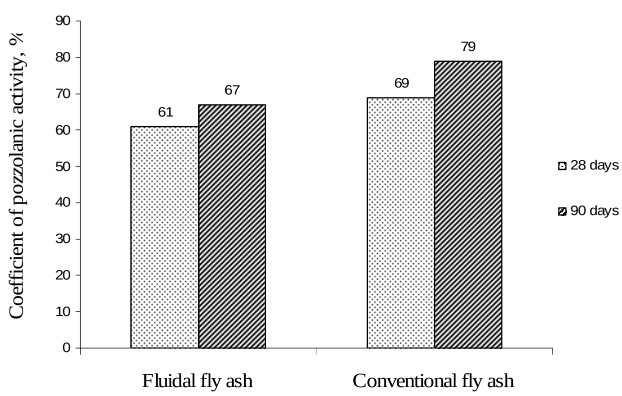

Fig. 1. The coefficient of pozzolanic activity of cement mortar with fluidal and conventional fly ash for 28 and 90 days

The obtained values of CPA do not meet the standards because they are less than 75 % for 28 days and 85 % –for 90 days. CPA values are more dependent on porosity than additives activity, which does not allow to estimate the pozzolanic activity of additives.

The results of investigations according to EN 196-5 are represented in Table 2.

In the saturated solution the concentration of calcium hydroxide (expressed *via* CaO) is inversely proportional to the solution alkalinity. The exchange of cement for the fluidal fly ash in the amount of 10 % increases the filtrate alkalinity and decreases CaO content compared with the filtrate of the check sample. At the same time the introduction of conventional fly ash slightly changes the filtrate alkalinity and CaO content is the same as in the check sample. If we compare the pozzolanic activity of cement till achieving the saturation state of CaO we observe that the fluidal fly ash has ΔC_{CaO} = =0.8 mmol/dm^3 at filtrate alkalinity of 61.5 mmol/dm^3, and the conventional fly ash also has ΔC_{CaO} = = 0.8 mmol/dm^3 at the alkalinity of 58.7 mmol/dm^3. It means that pozzolanic activity is the same for both cement samples (with fluidal and conventional fly ashes).

The CPA determined in accordance with EN 450-1 is higher by 8 % for the conventional ash than CPA for the fluidal fly ash. Thus, the values of pozzolanic activity determined by the above mentioned standard methods do not correlate with each other, so it is impossible to evaluate the role of ash in cement mortar.

For example, the pozzolanic activity of cements with such high-reactive mineral additives as microsilica and synthetic nanosilica determined in accordance with EN 196-5 shows higher content of CaO in the filtrate compared with the check sample cement due to the decrease in alkalinity. However, the ΔC_{CaO} values of filtrates obtained from cement with microsilica and check sample are equal; the introduction of the synthetic nanosilica leads to double increase of ΔC_{CaO} value compared with microsilica (Table 2). Thus, the estimation of pozzolanic activity of cements with mineral additives according to EN 196-5 depends on alkalinity of cement mortar, which complicates the analysis and evaluation of the mineral additives reactivity.

Table 2

The investigation results of pozzolanic activity of cement with mineral additives

Cement with mineral additives	Concentration hydroxide ions C_{OH-}, mmol/dm^3	Concentration of CaO in the filtrate C_{CaO}^*, mmol/dm^3	Concentration CaO in the saturated solution[1] C_{CaO}, mmol/dm^3	$\Delta C_{CaO} = C_{CaO} - C_{CaO}^*$, mmol/dm^3
Cement, contr.	57.3	7.2	8.3	1.1
Cement + 10 % fluidal fly ash	61.5	6.7	7.5	0.8
Cement + 10 % conventional fly ash	58.7	7.2	8.0	0.8
Cement + 10 % synthetic nanosilica	51.4	7.3	9.6	2.3
Cement + 10 % microsilica	48.5	9.3	10.4	1.1

Note: [1] it is calculated according to the equation $C_{CaO} = 350/(C_{OH-} - 15)$, [8]

Table 3

Pozzolanic activity of the mineral additives according to [12]

Mineral additives	Pozzolanic activity, mg CaO/1g additive
Fluidal fly ash	149.3
Conventional fly ash	12.9
Synthetic nanosilica	454.1
Microsilica	223.2

One of less-known methods to determine the pozzolanic activity of the mineral additives is the method described in [12]. According to this method it is possible to determine not only the pozzolanic activity but the rate of additive reaction with calcium hydroxide as well. It is an important point while developing complex additives. It is known that ashes belong to pozzolanic additives and the increase in pozzolanic activity depends on glassy phase content [5]. However, according to [19] not every glassy phase has pozzolanic properties. As it was mentioned above, ashes are characterized by variable chemical and phase composition, therefore the application of additives has to be pre-diagnosed relative to pozzolanic activity.

The results of pozzolanic activity of the mineral additives investigated in accordance with the method [12] are represented in Table 3.

The investigated ashes are characterized by different pozzolanic activity. The activity of the fluidal fly ash is considerably higher compared with that of the conventional ash at smaller amount of SiO_2 and specific surface area (Table 1). To increase the ash activity we added the additive with high activity – the synthetic nanosilica. Its pozzolanic activity is 3 times higher than the activity of fluidal fly ash and two times higher than that of microsilica (Table 3).

The reaction between mineral additive and calcium hydroxide varies in time (Fig. 2). If we compare the synthetic nanosilica with other additives, its rate of reaction with calcium hydroxide is found to be the highest one. After 2 days the synthetic nanosilica binds 91.6 % of calcium hydroxide from the saturated solution of calcium hydroxide, after 4 days its activity is twice reduced (46.1 %) and remains without changes till the end of investigations. In its turn, the degree of microsilica activity after two days is 39.1 % and after 30 days is reduced to 14.1 %.

Pozzolanic activity of the fluidal fly ash after two days is the smallest value (6.2 % of bounded calcium hydroxide from the saturated solution). The reaction rate increases only after 4 days, the degree of pozzolanic activity is 17 % and slightly increases till the end of investigations.

It should be noted that the degree of pozzolanic activity for the conventional fly ash remains constant. On average its value is 1.4 % of the bounded calcium hydroxide. Therefore the ash in cement mortar may be as filler or pozzolanic additive while preactivation that demands the additional costs.

It is well-known that pozzolanic activity is not an additive property. One of the reasons may be different rate of the reaction with $Ca(OH)_2$. If we compare the degree of pozzolanic activity in time for synthetic nanosilica, microsilica and fly ash the highest rate is observed for synthetic nanosilica and the lowest one – for the fluidal fly ash. Using high-active additive in the mixture with fluidal fly ash we may increase the ash activity at the early stages of cement hydration. To study the effect of high-active additives on pozzolanic activity of the complex additive with fluid fly ash we developed the following compositions (Table 4).

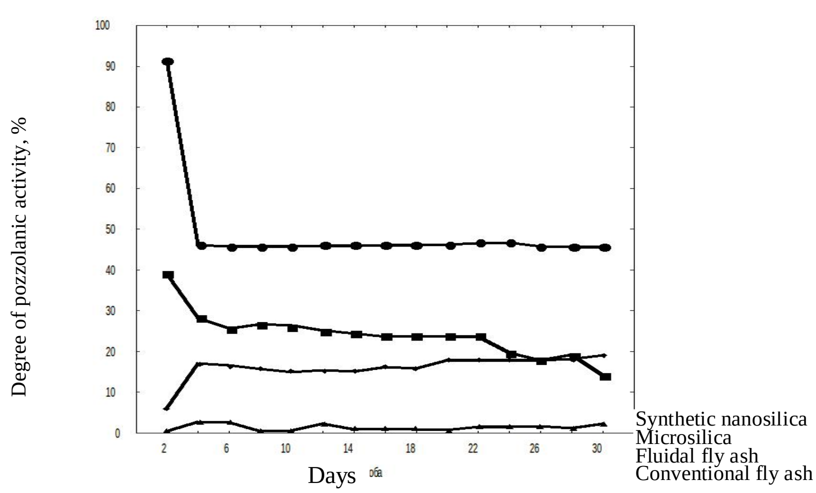

Fig. 2. Degree of pozzolanic activity of the mineral additives

Table 4

Composition of the complex additives and analysis of static pozzolanic activity

Composition of the complex additives, %			Pozzolanic activity, mg CaO/1g additive		R^2
Fluidal fly ash	Synthetic nanosilica	Microsilica	Experimental	Theoretical	
75	25	–	333.2	319.3	0.89
50	50	–	422.8	422.0	
25	75	–	449.4	464.4	
75	–	25	165.3	167.7	0.95
50	–	50	181.6	188.0	
25	–	75	220.7	228.7	

Note: R^2 – coefficient of determination

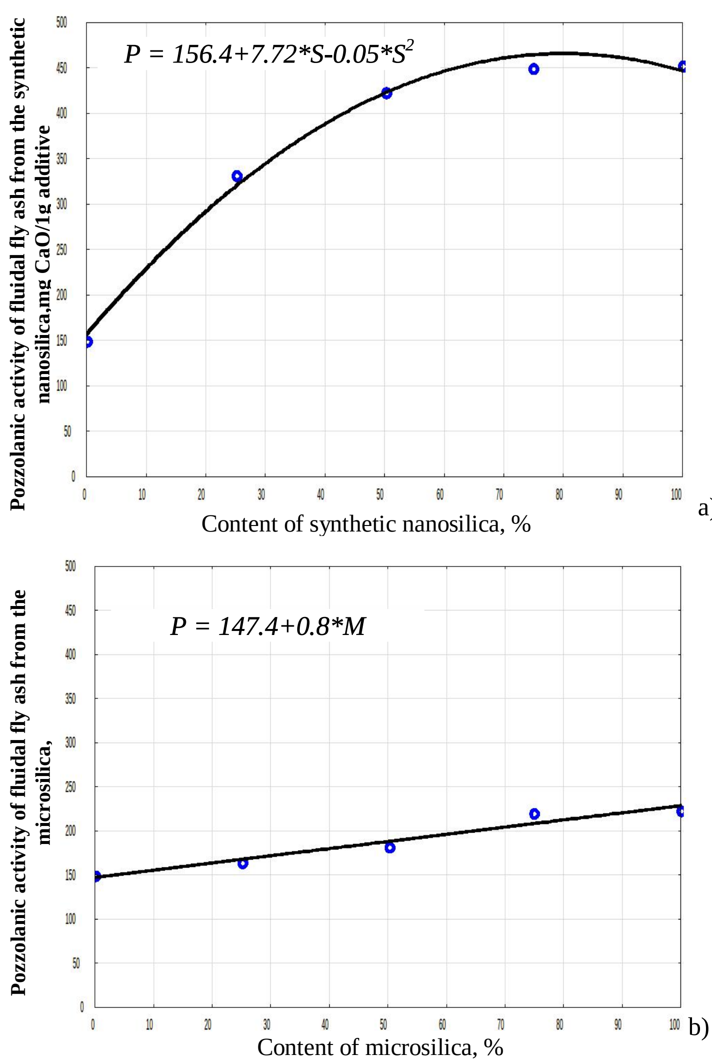

Fig. 3. Models of regression function for the dependence of pozzolanic activity on content of synthetic nanosilica (a) and microsilica (b). For the formula: P – pozzolanic activity; S – content of synthetic nanosilica; M – content of microsilica

High values of coefficient of determination of the regression equations indicate compliance between function data and empirical ones. The dependence of fluidal fly ash pozzolanic activity on the introduction of synthetic nanosilica and microsilica is represented in Fig. 3.

The evaluation of the reactivity of complex additives with calcium hydroxide according to the regression equations allow to estimate the change of pozzolanic activity at the introduction of high-active component. We found (Fig. 3) that introduction of 1 % of synthetic nanosilica instead of fluidal fly ash increases pozzolanic activity by 10 %. At the same time it is necessary to introduce 18 % of microsilica to achieve the same value.

The changes of pozzolanic activity for the complex additives with fluidal fly ash and synthetic nanosilica/ microsilica are different (Fig. 3). The pozzolanic activity of the complexes with synthetic nanosilica sharply increases till 50 %, the further exchange slightly changes the reactivity. The exchange of ash for microsilica proportionally increases the pozzolanic activity.

Before using fly ash for the cement or concrete production it is always necessary to investigate pozzolanic activity since both fluidal and conventional fly ashes are characterized by variable phase composition. The choice of the optimal method for pozzolanic activity determination according to [12] allows to determine whether the ash is pozzolanic active or inert additive in cement mortars. Such investigations will prevent the worsening of physical properties of the building materials.

It should be noted that using chemical method of pozzolanic activity determination of the mineral additive in limewater according to [12] allows to shorten the diagnostics of pozzolanic activity from 30 to 4 days and in such a way to optimize the cement composition using emitted ash.

4. Conclusions

The determination of fly ash reactivity in the limewater according to the chemical method allows to rationally use this additive in the building industry. Moreover, this method allows to diagnose the reactivity of mineral additives in time in order to optimize the composition of the complex additives. According to the fulfilled investigations we established that pozzolanic activity of the fluidal fly ash with SiO_2 content of 54 % is higher compared with that of the conventional ash with SiO_2 content of 72 %. The ash pozzolanic activity may be enhanced using synthetic nanosilica in the complex additives. The exchange of 1 % of fluidal fly ash for synthetic nanosilica increases pozzolanic activity by 10 % while microsilica increases the activity by 1 %.

References

[1] ECOBA Statistics on Production and Utilization of CCPs in Europe (www.ecoba.org).
[2] EN 197-1. Cement, Composition, Specifications and Conformity Criteria for Common Cements, 2007.
[3] EN 450-1. Fly Ash for Concrete. Definition, Specifications and Conformity Criteria, 2009.
[4] Polish Association of Cement Producers (www. Polskicement.pl).
[5] Kurdowski W.: Chemia Cementu i Betonu. Stowarzyszenie producentów cementu, PWN, Warszawa 2010.
[6] Giergiczny Z.: Rola popiołów wapniowych i krzemionkowych w kształtowaniu właściwości współczesnych spoiw budowlanych i tworzyw cementowych. AGH, Kraków 2006.
[7] Sanytskyy M., Sobol Ch. and Markiv T.: Modyfikovani Kompozycijni Cementu. Lvivska Politechnika, Lviv 2010.
[8] EN 196-5: 2006. Methods of testing cement – Part 5. Pozzolanicity test for pozzolana cements.
[9] ASTM C 379-65T: 1965. Specification for Fly Ash for Use as a Pozzolanic Material with Lime. American society for testing and materials. West Conshohocken, PA: ASTM International.
[10] Yaschyshyn J.: Technologia skla. Fizyka i Chemia Skla. Lvivska Politechnika, Lviv 2008.
[11] Reverdy M., Brivot F., Pailler A., Dron R.: 7th ICCC Paris, 1980, **III**, IV-36.
[12] Butt J., Sychev M. and Timashev V.: Prakticum po Khimicheskoi Technologii Sviazuyushchikh. Vyshaya schkola, Moskva 1973.
[13] EN 196-2: 2013. Method of testing cement. Chemical analysis of cement.
[14] PN-EN 196-6: 1997. Method of testing cement. Determination of fineness.
[15] Gawlicki M.: Materiały budowlane. Podstawy technologii i metody badań. AGH, Kraków 2004.
[16] Kotsay G.: Chem. Chem. Technol., 2013, **7**, 335.
[17] Kotsay G., Kuzhnyetskyy M. and Pilarczyk S.: XIV Int. Sci. Conf. "Current issues of civil and environmental engineering", Lviv 2013, 189.
[18] Certyficate of quality silica WL-160, Lot no. 20111128.
[19] Shevchenko V. and Kotsay G.: Voprosy Khim. Khim. Technol., 2012, **6**, 122.

ДІАГНОСТИКА ПУЦОЛАНОВОЇ АКТИВНОСТІ ЗОЛИ ВИНЕСЕННЯ ДЛЯ ПОРТЛАНД ЦЕМЕНТУ

Анотація. *В роботі проведено аналіз і оцінку різних методів визначення пуццоланової активності золи винесення з метою її раціонального використання в цементах. Запропоновано найбільш оптимальний метод діагностики пуцоланової активності золи. Встановлено можливість збільшення активності флюїдальної золи з використанням синтетичного нанокремнезему.*

Ключові слова: *пуцоланова активність, зола винесення, мікрокремнезем, синтетичний нано-кремнезем.*