

Correlation Between Strength and Phase Composition of Autoclaved Lime-Fly Ash Material

Gennady I. Ovcharenko and Daniel I. Gil' Miyarov
Department of Constructional Materials, Polzunov Altai State Technical University,
46 Lenina Avenue, 656038 Barnaul, Altai Region, Russian Federation

Abstract: The phase composition of the pressed stone of lime-fly ash mixture after autoclaving for 8.50 and 100 h at 0.8 MPa isotherm with no addition or with 1 and 2% Na₂SO₄ is represented by gel-like C-A-S-H, aluminum substituted tobermorite, hydrogarnet katoite. Adding of 1 and 2% Na₂SO₄ makes no qualitative change in phase composition but significantly increases the rate of phases formation. Thus, 2% Na₂SO₄ contributes to a substantial increase in the synthesis of Al-tobermorite but reduces the C-A-S-H phase formation. Katoite hydrogarnet content remains unchanged. Strength of the stone is always directly proportional to the content of a gel C-A-S-H phase. Its content is proportional to the number of Al-tobermorite in non-additional mixtures but does not correspond to the content of tobermorite in compositions with addition of 2% Na₂SO₄.

Key words: Lime-fly ash mixture, Na₂SO₄ addition, autoclave processing, phase composition, strength of the stone, correlation between the strength and phase composition

INTRODUCTION

The main law of the strength formation of silicate autoclaved materials have been discussed, since, the beginning of the 50 sec of the 20th century when Kalousek and Adams (1951) had found its direct dependence on the quantity of generated 11.3 angstrom tobermorite (Crennan *et al.*, 1977; Matsui *et al.*, 2011). Then, Taylor (1990) objected Kalousek and Adams (1951) noting that the strength of any material is a function of its density and for autoclaved materials, it also depends on presence of gel phase in them. The effect of a gel phase on the strength had been previously mentioned in the researches of P.I. Bozhenov for whom Taylor referred. However, both P.I. Bozhenov and Taylor have not reported quantitative relationships in those years. It was only 1977 when Taylor (1990) published the study (Ray, 2002) proving a direct link of strength of lime-silica material with a number of C-S-H gel being formed. Taylor (1990) stated a brief review of these issues in the last lifetime edition of "Chemistry of cement" (Chan and Mitsuda, 1978; Durack and Weiqing, 1998; Hauser *et al.*, 1999) also specifying differences in opinion on this issue, particularly in the extent beneficial to crystallize a gel phase.

When using various aluminosilicate materials including it in the form of CHP acidic ashes as well as portland cement as the silica component, phase formation of autoclave materials becomes more complicated. Even

the qualitative composition of the phases had caused discussions. It was only in the 2000's when the publications of Ray (2002) in conjunction with D.S. Klimesch (Holt and Raivio, 2005) were issued and as well of Japanese researchers Huang *et al.* (2012) which allowed to interpret and quantify unambiguously the phases being formed in such systems. The issue of the interrelation of the phase composition and strength of autoclavestone composed of lime-aluminosilicate raw materials remained open. Therefore, the aim of this study was to establish such an interrelation.

For this, it was necessary to establish a reliable quantitative composition of phases of autoclave stone composed of aluminosilicate raw materials on the basis of the CHPash to use an addition that promotes redistribution of the main phases in order to disclose interrelations between the phase composition and strength of stone.

It follows from that the addition of Al₂O₃ or SO₃ in lime-silica autoclave composition accelerates crystallization of C-S-H gel phase and formation of larger amount of tobermorite. Furthermore, it is known that the presence of alkali in autoclave synthesis significantly accelerates the hydrate formation. By definition, alumina is present in the aluminosilicate raw material. Therefore, Na₂SO₄ was selected as an activator additive. Sodium sulphate contains the required group of SO₃ and alkaline, released in hydrothermal reactions will accelerate the synthesis and crystallization of hydrated phases.

Corresponding Author: Gennady I. Ovcharenko, Department of Constructional Materials,
Polzunov Altai State Technical University, 46 Lenina Avenue, 656038 Barnaul, Altai Region,
Russian Federation

MATERIALS AND METHODS

In experiment, we used electrostatic precipitator ash provided by burning coal (Coal Ash-CA) of Kuznetsk basin brand G at Novosibirsk CHP-5 with the composition of unburned coal of 3.29% (Table 1, recalculated on ignited product). Granulometrically ash particles range from 1.5-250 μ with an average diameter of 70.5 μ. Calcium lime contained about 92% of active CaO and MgO and by main indicators was consistent with first grade lime according to GOST 9179-77. In some mixtures, we used curing activator of Na₂SO₄ with 98% content of the main substance.

The ash was mixed with powdered lime with Blaine specific surface area of about 6.000 cm²/g with a ratio of 20% basing on active CaO and MgO. In some mixtures with tempering water, Na₂SO₄ was added as hardening activator in an amount of 1 or 2% by weight. The raw material mixture was moistened, sealed in plastic containers and ensilaged at 60°C for 2 h to full lime hydration. After that, from that mass, we formed cylinder samples of diameter and height of 50 mm at specific pressing pressure of 20 MPa which were treated in an autoclave at 0.8 MPa with isothermal exposure of 8, 50 and 100 h correspondingly. Samples strength tests were produced after their drying at 100°C to constant mass. Number of samples for test was chosen to ensure measurement error of not more than 3-5%. Some samples were taken out of those ones for analysis by methods of X-Ray Fluorescence (XRF) and thermal analysis including Differential and Thermal Analysis (DTA), Differential Thermo Gravimetric analysis (DTG) and Thermo Gravimetric analysis (TG). The X-ray diffraction analysis was performed on a DRON-3 (Russia) with CuKα radiation at tube voltage of 40 kV and current of 25 A. The thermal analysis at rate of 10°/min was conducted using derivatograph Netzsch STA 449C (Germany) in a closed crucible and helium flow to create not-oxidative environment and eliminate the effects of burning coal residues in the ash. Granulometric composition of the ash of micron field range was determined using SALD-2101 Laser Diffraction Particle Size Analyzer (SHIMADZU, Japan).

Table 1: Chemical composition of the ash provided by Novosibirsk CHP-5

Materials	CHP-5 ash
SiO ₂	61.87
Al ₂ O ₃	23.73
Fe ₂ O ₃	5.00
CaO	4.38
MgO	1.29
SO ₃	0.33
Total	99.98

RESULTS AND DISCUSSION

It shows that with increasing isothermal hold up time from 8-100 h, strength without additional of lime-ash compositions is steadily increasing from 20-45.5 MPa. When injected with 1 and 2% Na₂SO₄ there is an inflection in strength at 50 h of autoclaving or composition strength decrease in proportion to additions at isotherm of 100 h. At this, the samples with the addition of 2% sodium sulphate gain the main strength after the first 8 h of heat treatment in the autoclave and then there is no substantial increase observed. Compared with the addition-free composition, the addition of 1 and 2% of sodium sulfate increases strength by 1.3 and 1.6 times, respectively at isotherm autoclaving of 8 h.

The composition of the formed hydrothermal synthesis products in the addition-free mixture according to XRF is presented by the following main phases: 8 h isotherm (X-ray pattern 1)-residual portlandite Ca(OH)₂ (4.91; 2.63; 1.80), the residual quartz ash of SiO₂ (4.27; 3.35; 2.28; 1.80), synthesized tobermorite (11.48; 5.41; 3.08; 2.98; 2.79), calcite (3.04; 2.28; 1.93). In addition to these phases, there are reflections of hydrogarnets: katoite-5.10; 2.79; 2.28; 1.67 and ferrous hydrogarnet-3.08; 2.74; 1.62. Probably, the presence of C-S-H phases (1 and 2) peaks are 3.07 and 2.80 but reflections for these phases are absent at small angles (12.5 and 9.80×10⁻¹⁰ m). Increasing the isotherm up to 100 h in the addition-free composition (X-ray pattern 2), we observe portlandite disappearance, the proportion of silica is reduced, the proportion of tobermorite is increased but not all peak intensities of tobermorite change proportionally the peak of 5.41 decreases, the one of 2.98 remains unchanged and the peaks of 11.60 and 3.08 increase. Instead of the 2.79 peak, the peak of 2.76 appears. The significant deviation of 11-angstrom peak of 11.30-11.60×10⁻¹⁰ m should be noted. The peaks of katoite transform to reflections of ferrous hydrogarnet 5.045; 3.08; 2.755; 1.62-1.63, although, certain sources attribute the peak of 2.76 as well to katoite. Besides of 1.1 nm of tobermorite and perhaps xonotlite (3.07-3.08; 2.83; 2.70), there are no peaks of other calcium hydrosilicates.

In the presence of 2% Na₂SO₄ activator for 8 h of treatment (X-ray pattern 3), there is an intermediate phase composition reached compared with 8 and 100 h without additive composition except of a significant increase in the peak of 2.76. It can be referred to katoite or ferrous hydrogarnet. The 100 h exposure in the presence of 2% Na₂SO₄ (X-ray pattern 4) differs only slightly from the 100 h exposure in a system without the activator, except of even larger decrease of quartz proportion and outlined supplements.

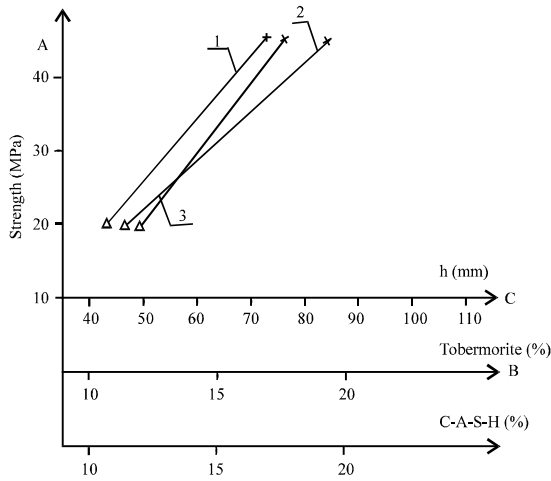


Fig. 1: Correlation of lime-ash stone strength with its phase composition; 1: Change in the intensity of the peak of aluminum substituted tobermorite according to the RFA data; 2: Change in content of aluminum substituted tobermorite according to the DTG data; 3: Change in content of C-A-S-H according to the DTG data. Δ: 8 h of isothermal exposure; x: 100 h of isothermal exposure; A: Strength (MPa) B: tobermorite, % content of tobermorite phase in the sample; C: A-S-H % content of C-A-S-H phase in the sample and C: h tobermorite peak intensity according to the RFA data (mm)

Analysis of the mixture thermogram based on the ash of Novosibirsk CHP-5 at 8 h of isothermal exposure. shows the effect of weight loss (DTG curve at approximately 95°C which is associated with removal of moisture adsorption. There we see presence of hydrogarnets that are noted with little effect at 373°C. A large weight loss at 447°C corresponds to residual portlandite $\text{Ca}(\text{OH})_2$. In the 700-780°C interval, there occurs decomposition of calcium hydrosilicates, calcite and probably of C-A-S-H phase, dehydration of which is accompanied by a pronounced effect at 741°C. Taylor (1990) also attributed this effect to amorphous hydrosilicate phase (Kalousek and Adams, 1951). Tobermorite phase having significant deviations of XRF reflections from 11.3, represents aluminum substituted tobermorite with other impurities and thus, loses weight at 180°C being much smaller than 240°C (Ray, 2002).

At increasing the isothermal exposure to 100 h, a differential curve of weight loss, DTG (Fig. 1), represents a significant increase in endo effect at 86°C and the

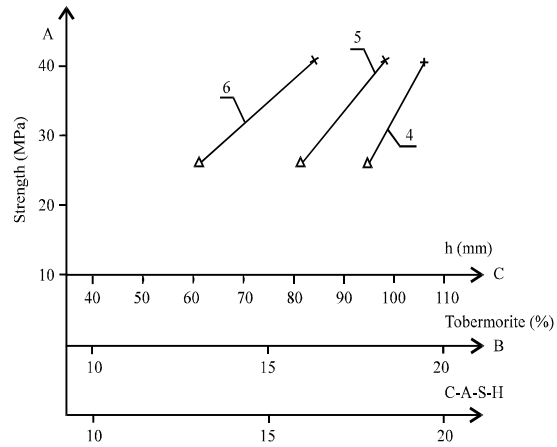


Fig. 2: Correlation of lime-ash stone strength with its phase composition at addition of 1% Na_2SO_4 ; 4: Change in the intensity of the peak of aluminum substituted tobermorite according to the XRF data; 5: Change in content of aluminum substituted tobermorite according to the DTG data; 6: Change in content of C-A-S-H according to the DTG data. Δ: 8 h of isothermal exposure; x: 100 h of isothermal exposure; A: strength (MPa); B: tobermorite, % content of tobermorite phase in the sample; C: A-S-H: % content of C-A-S-H phase in the sample; C: h-tobermorite peak intensity according to the RFA data (mm)

disappearance of residual portlandite $\text{Ca}(\text{OH})_2$ because of the formation of hydrate phases large number being a result of hydrothermal synthesis. For this, as additional evidence, the large weight loss may serve as evidence which is associated with the removal of moisture adsorption and with loss of water by the gel phase. Weight loss effect by hydrogarnet at 381°C is registered. The weight loss at effects of 185 and 727°C increases up to 2.4%.

The thermogram of samples hydration products on the basis of Novosibirsk CHP-5 ashat 20% of lime with 8 h of isothermal exposure with additional injection of 2% Na_2SO_4 (Fig. 2) differs only slightly from the thermogram being addition-free of lime-ash mixture at 100 h of isothermal exposure that indicates the activation of hydrothermal synthesis in the presence of sodium sulfate. However, with the activator additive, the proportion of C-A-S-H phase gets reduced if judging by the weight loss at 727°C endoeffect.

Estimation of interrelation between strength of the stone with its composition of hydrate phases variety (Table 2) shows that it increases in proportion to the

Table 2: Strength and quantitative characteristics of phase contents in stone

Mass composition	Isotherm of autoclaving (h)	Stone, strength (Mpa)	Peak intensity 11.5×10^{-10} m tobermorite (XRF) (mm)	Weight loss DTG			
				Weight loss DTG at 165-190°C (% tobermorite)	Weight loss DTG at 373-381°C (% hydrogarnet katoite)	Weight loss DTG at 439-447°C (% Ca(OH) ₂)	Weight loss DTG at 725-735°C (% gel C-A-S-H)
Base	8	20	48	1.5	0.8	1.1	1.7
Base	100	46	77	2.4	1.0	-	2.4
Base +1% Na ₂ SO ₄	8	26	96	2.3	0.8	0.4	2.0
Base +1% Na ₂ SO ₄	100	41	107	2.7	1.0	-	2.6
Base +2% Na ₂ SO ₄	8	31	60	2.3	0.9	-	1.5
Base +2% Na ₂ SO ₄	100	34	112	2.9	1.0	-	1.5

main XRF reflection of Al-tobermorite (11.5×10^{-10} m) to increase in weight loss both at the temperature range 180°C (tobermorite) and at 730°C (gel C-A-S-H) that indicates the correct classifying of that effects to hydrated phases. This pattern holds true for both addition-free and Na₂SO₄-activator systems. Base composition 20% of lime+80% of coal ash quantitative phase composition of autoclave stone, after its recalculation on corresponding compounds.

The interrelation between strength and phase composition of the stone of the studied compositions is shown in figures from which is obvious that the strength of Na₂SO₄ free compositions is directly proportional to the content of both the Al-tobermorite and gel phase of C-A-S-H. This interrelation becomes less pronounced but still maintained at 1% of sodium sulfate. However, with addition of 2% Na₂SO₄, this relationship is not observed anymore. At this, a considerable increase in Al-tobermorite in this composition according to both the data of XRF and DTG does not correspond completely to a slight increase in stone's strength. However, a small amount of C-A-S-H phase here fully agrees with the same slight increase in strength.

Thus, the strength of the autoclave stone made of lime-ash mixture is always proportional to the content of gel C-A-S-H phase. At the same time, the content of the latter can be or can be absolutely not proportional to the amount of Al-tobermorite. It is typical that initiating the synthesis of Al-tobermorite with the Na₂SO₄ addition, its crystallization is carried out at the expense of C-A-S-H phase. The content of katoite hydrogarnet remains practically unchanged at the 5-6% level.

The results obtained conforms with the most recent publications reporting the formation of the phase composition in the autoclave stone basing on lime-quartz and cement-aluminosilicate compositions with additions of alumina or sulphate-containing materials (Fig. 3).

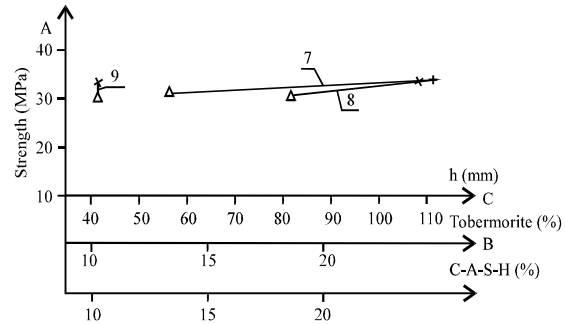


Fig. 3: Correlation of lime-ash stone strength with its phase composition at addition of 2% Na₂SO₄; 7: Change in the intensity of the peak of aluminum substituted tobermorite according to the XRF data; 8: Change in content of aluminum substituted tobermorite according to the DTG data; 9: Change in content of C-A-S-H according to the DTG data. Δ: 8 h of isothermal exposure; x: 100 h of isothermal exposure; A: strength (MPa); B: tobermorite, % content of tobermorite phase in the sample; C: A-S-H: % content of C-A-S-H phase in the sample; C: h-tobermorite peak intensity according to the RFA data (mm)

CONCLUSION

Autoclave materials on the basis of lime and quartz sand are prevailing in the construction. Siliceous component of the mixture can be replaced by raw aluminosilicate materials in particular when transferring heat power plants to a non-waste production. Thus, the issue related to the strength of such materials and its interrelation with the phase composition remains relevant.

Formation of phase composition of lime-ash autoclave materials has a certain specific character that differs from lime-quartz systems. The main patterns preserves: formation of gel C-A-S-H phase (instead of C-S-H) crystallizing in aluminum substituted tobermorite (instead of tobermorite). This process is actively modified by the presence of alumina and sulfate-containing

additions. Their presence speeds the Al-tobermorite crystallization by reducing the gel C-A-S-H phase. There is always constant amount of hydrogarnet katoite in the stone which is also involved in these processes.

The strength of autoclave stone basing on aluminosilicate raw materials and lime is always proportional to the content of C-A-S-H phase irrespectively to content of tobermorite. This can be explained by the high specific surface area of the particles of the solid phase of the C-A-S-H gel which "glue" the composite.

REFERENCES

- Chan, C.F. and T. Mitsuda, 1978. Formation of 11 Å Tobermorite from mixtures of lime and colloidal silica with quartz. *Cem. Concr. Res.*, 8: 135-138.
- Cremnan, J.M., S.A.S. El-Hemaly and H.F.W. Taylor, 1977. Autoclaved lime-quartz materials I. Some factors influencing strength. *Cem. Concr. Res.*, 7: 493-502.
- Durack, J.M. and L. Weiqing, 1998. The properties of foamed air cured fly ash based concrete for masonry production. *Proceedings of the Fifth Australasian Conference on Masonry, July 1-3, 1998, Gladstone, America*, pp: 129-138.
- Hauser, A., U. Eggenberger and T. Mumenthaler, 1999. Fly ash from cellulose industry as secondary raw material in autoclaved aerated concrete. *Cem. Concr. Res.*, 29: 297-302.
- Holt, E. and P. Raivio, 2005. Use of gasification residues in aerated autoclaved concrete. *Cem. Concr. Res.*, 35: 796-802.
- Huang, X.Y., W. Ni, W.H. Cui, Z.J. Wang and L.P. Zhu, 2012. Preparation of autoclaved aerated concrete using copper tailings and blast furnace slag. *Constr. Build. Mater.*, 27: 1-5.
- Kalousek, G.L. and M. Adams, 1951. Hydration products formed in cement mortar and concrete. *J. Am. Concr. Inst.*, 48: 77-81.
- Matsui, K., J. Kikuma, M. Tsunashima, T. Ishikawa and S.Y. Matsuno *et al.*, 2011. In situ time-resolved X-ray diffraction of tobermorite formation in autoclaved aerated concrete: Influence of silica source reactivity and Al addition. *Cem. Concr. Res.*, 41: 510-519.
- Ray, A., 2002. Hydrothermally treated cement-based building materials. *Past Present Future Pure Appl. Chem.*, 74: 2131-2135.
- Taylor, H.F.W., 1990. *Cement Chemistry*. 2nd Edn., Academic Press, London, UK., ISBN:9780126839005, Pages: 475.