საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 19(193), №2, 2025
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Materials Science

Energy-Efficient Green Technologies of Reduction of Emission and Footprint CO_2 of Cement Production Using Natural Sorbents

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(Presented by Academy Member Ramaz Khurodze)

Abstract. Clinker ovens in cement factories emit approximately 0.89 t/t.cl. of CO_2 to the atmosphere, which generates greenhouse effect and carbon footprint promoting a global warming. In order to prevent the developed countries are implementing “Carbon capture and utilization” projects. Cement factories in Georgia previously used diatomite (5 mass %) as a pozzolan, while currently, they make use of clinoptilolites from Khekordzula or Tedzami deposit (5-40 mass %), which are also known as natural CO_2 sorbents. The problem of functional application of diatomite/clinoptilolite is that their high humidity complicates their grinding process and needs preliminary drying, which respectively increases energy expenses and cement self-cost. Another problem is associated with particle size (fractional composition) – grains with 3-5 mm in size are not used as sorbents as well as pozzolanic additives. Cement production using energy-efficient green technologies based on the local raw materials is a top-priority of our research, since clinoptilolite stocks in Georgia comprise approximately 300.0 mln tons, and diatomite – roughly 20.0 mln tons. Both materials can replace clinker in cement composition, which reduces the self-cost of the final product. At Georgian Technical University, we have studied the potential for targeted, combined application of small fractions of diatomite/clinoptilolite. Thermodyna-mic calculations of Gibbs energy of natural ($\Delta f G^0_{298}$ = -36735 kj/mol) and dehydrated ($\Delta f G^0_{298}$ = -31857 kj/mol) clinoptilolite has been made. Temperatures and pressures of dehydration onset (T = 94.7°C, P = 460 mm Hg Torr), physical (T = 97.2°C; P = 293 mm Hg Torr) and hemosorptive (T = 99.7°C, P = 706 mm Hg Torr) capture of CO_2 in the disperse system “Clinoptilolite – CO_2“ have been determined. The research sets a goal of validation of energy-effective green technologies of cement production developed at GTU and applied in the factories, using the results of experiments conducted in the modern accredited laboratories. © *2025 Bull. Georg. Natl. Acad. Sci.*

Keywords: clinoptilolite, diatomite, thermodynamic, pozzolan, cement

Introduction

In 2023, the worldwide cement production reached 4.0 bln tons, while in Georgia – 3,0 mln tons, which aggravates global ecological and economic problems. Clinker ovens of a cement factory when releasing 1 ton of clinker emit into atmosphere with flue gases 0.89 ton/t.cl. of CO_2 [1], which generates "greenhouse effect" and „carbon footprint" promoting global warming [2]. To prevent this issue, alternate technical and ecological projects are being developed worldwide according to "Carbon capture and utilization" (CCU) programs [3].

Georgian cement factories had used 5 mass % diatomite [4] as a pozzolanic mineral supplement (MS) in the process of cement production for Enguri HPP construction (in the 1960s-70s), while nowadays clinoptilolites (CPT) from the Khekordzula ($XKCPT_{nat}$) or Tedzami ($TZCPT_{nat}$) deposits (with 5-40 mass % (pieces 5-40 mm in size)) are utilized for cement production (different types according to assortment taken in [5]). At the same time, both materials are well-known natural CO_2 sorbents. The problem of diatomite and CPT application is that they need drying, since due to high structural porosity of diatomite and CPT (within 30 mass %) their "quarry humidity" sometimes reaches 20 mass % and more. The mentioned circumstance makes their grinding more difficult, increases energy expenses for drying and cement self-cost.

Receipt of competitive cements using energy-efficient green technologies based on the local raw materials is a toppriority for Georgian economy. Taking into account natural reserves of CPT and diatomite, as well as their low hardness (CPT hardness according to Mohs is 3-5, while diatomite is a loose amorphous rock) they are easily grinded. In cement composition, diatomite and CPT (priced at about 15$ per ton) can replace the most energy consumable and expensive component – clinker (priced within 100 $ per ton), which reduces cement self-cost. The problem also is that fractions lower than 3-5 mm in size are not used as MS sorbent with a purpose of reduction of CO_2 quantity and footprint in exhaust flue gases.

In order to produce rapid-hardening pozzolane cement and extend the opportunities of MS application for energy-efficient green technologies through recovery (utilization) of chilled clinker heat, relevant studies have been conducted at the GTU since 1978, results of which have been patented (see [6,7]), presented in the USSR Authorship certificates №№814921, 890683, 114-3713, 1158528, 1313821) and have been practically implemented in Heidelbergcement LLC and EuroCement LLC [8]. The opportunity of granulation of small fractions of diatomite (amorphous SiO_2) and CPT has been studied as well. It has been established by the carried-out thermodynamic calculations (TDC): for diatomite $\Delta_f G^0_{298}$ $SiO_{2amorph}$= -852.22 kj/mol, Gibbs energy of Khekordzula natural – CPT_{nat}, ($\Delta_f G^0_{298}$ = -36735 kj/mol) and dehydrated – CPT_{deh} ($\Delta_f G^0_{298}$ = -31857 kj/mol) clinoptilolites; temperatures and pressures of CPT dehydration onset (t = 94.7°C and P = 460 mm. Hg Torr), physical (T = 97.2°C; P = 293 mm Hg Torr) and chemisorptive (T = 99.7°C, P = 706 mm Hg Torr) CO_2 capture in the disperse system "CPT – CO_2" [9].

The research goal is validation of energy-efficient green technologies of heat recovery developed in GTU and used in factories, reduction of CO_2 emission and footprint of cement production, via experiments conducted in the accredited laboratories.

Materials and Methods

Research materials are as follows: natural raw materials of two types and functional opportunities – natural sorbents for carbon dioxide and puzzolanic mineral supplements (MS) to cement: in particular, diatomite ($SiO_2 \cdot nH_2O$) and CPT {$(Na,K)_6[Al_6Si_{30}O_{72}]$ 24 H_2O}, which have amorphous and crystalline structure, respectively, which includes nanopores 0,4-3,0 nm in size, as well as types of cement (according to classification given in [5]) with pozzolane additions on their basis.

An increase of puzzolane MS share (without strength reduction) in cement composition is one of the methods of integrated approach ensuring reduction of energy expenses and environmental emission of CO_2

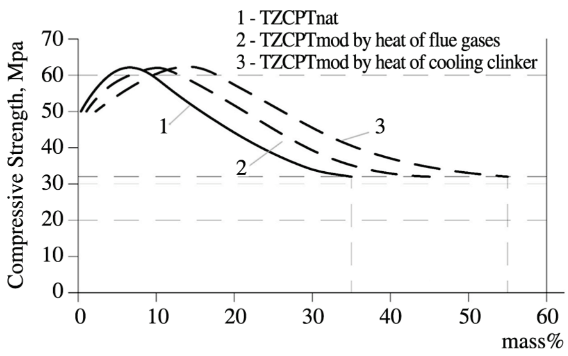

Fig. 1. Dependence of cement strength on MS amount.

traces, i.e. energy-efficient green technology [1, 10]. It is known [4], that entry of natural CPT into cement composition in the amount up to 7 mass % increases its strength above 62.5, and decreases it when entering more than 7 mass %. This dependence (Fig. 1) can be explained by the fact that small amounts of CPT during cement hardening stimulate formation of crystallohydrate ettringite [11]. GTU has developed and cement factories of Georgia have already applied two energy-efficient green technologies of natural sorbent CPT dehydration:

1. CPT delivery to the drying drum, with heat recovery of flue gases, and with simultaneous capture of CO_2 present into gas composition by means of CPT (Evrocementi LLC) [7,12]; 2. CPT delivery during clinker cooling process: 2.1 – either to the refrigerator (Heidelbergcement LLC); 2.2 – or else to the clinker conveyor with heat recovery of hot clinker (1000 → 50°C) (Evrocementi LLC) [6,7].

In this research, in addition to the results presented, a thermodynamic calculation (TDC) of the anticipated processes using approximation method [9] was implemented. A complete chemical analysis, differential-thermal and X-ray phase analyses of CPT were performed. Physical-mechanical tests of cement samples with diatomite and CPT selected in the process of their practical implementation at the cement factories were conducted performed according to ASTM standards [13].

Experimental part. Hypothesis: sorption reaction $Ca(OH)_2$ (CH) in CPT, i.e. "puzzolanization" with rehydro-liming will promote the formation of water-resistant nano-sized compounds with fibrous-acicular-lamellar habits, such as tobermorite CSH, stratlingite C_2ASH_8, ettringite C6AsH32, which will lead to their interlacement, self-nano-reinforcing to 3d-structures of solidifying cement and to drastic enhancement of its strength [14].

For the innovative application of a natural clinoptilolite (CPT_{nat}), it is necessary to know its behavior when heated: a) in the range of 25→200°C, which is attained in the cement mill during grinding; b) in the range of 25-400°C, which is the temperature of dispersion medium [CPT – flue gases] when dried in the drying drum; c) in the range of 25-700°C, which is an average temperature of a mixture [CPT – clinker] during the cooling process.

The Gibbs energies of the CPT_{nat} dehydration process in the range of 25-700°C based on the equation $CPT_{nat} + H_2O(l_ig) = CPT_{deh} + H_2O(gas)$ were calculated according to equation [9]:

$$\Delta_f G_T^o = - 707738 – 596.78\ TlnT – 107.675 \cdot 10^{-3}T^2 – 5.16 \cdot 10^5\ T^{-1} + 1645.1011\ T \qquad (1)$$

where: $\Delta_f G_T^o$: (at 200°C = -1693; 400°C = -2277; 700°C = -2346; 740°C = -2468; 800°C=-2653) kj/mol.

Dehydration onset temperature equals to 94.7°C, when P = 460 mm Hg Torr.

Gibbs energy of CO_2 chemisorption process in CPT was calculated in analogy with the equation (1):

$$\Delta_f G_T^o = 837684 – 343.4\ TlnT – 78.3 \cdot 10^{-3}T^{-1} – 22.7 \cdot 10^5 T^{-1} – 168.4T \qquad (2)$$

The chemisorption onset temperature is t°C = 99.65^{0}C at a pressure of P=706 mm Hg Torr. From the differential thermal analysis DTA carried for CPT_{nat} containing 60 mass% of CPT (Fig. 2) it is seen that the dehydration peak t_{max}= 130°C, and the dehydration process itself starts after 90°C, which corresponds with

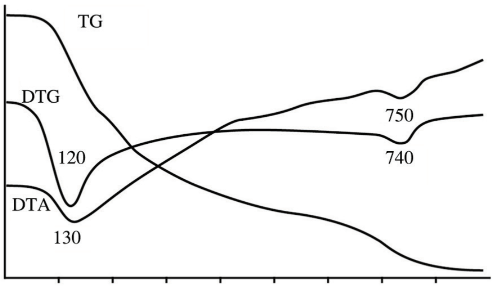

Fig. 2. Derivatogram of CPT.

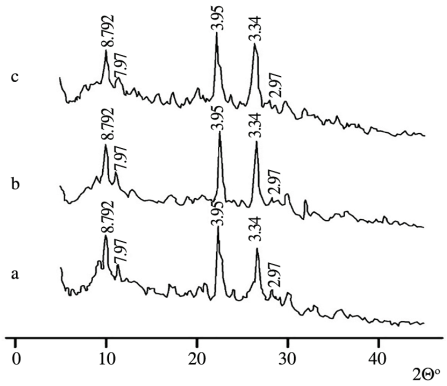

Fig. 3. Diffraction pattern of CPT.

the results of thermodynamic calculations (TDC), where t_{deh}=94.7°C. The second peak at 740°C likely demonstrates the onset of amorphization and CPT_{deh} break-down into β-crystobalite (β-SiO_2) and gibbsite $Al(OH)_3$. During dehydration, the water present in nano-sized pores (0.4-3.0 nm) of CPT releases space for $Ca(OH)_2$ (CH) sorption, i.e. "rehydro-liming" and "pozzolanization" [11,14]. This leads to the formation of stratlingite crystallohydrates (C_2ASH_8) and other calcium silicates, which further increases concrete structure resistance and its longevity:

$$CPT + 11CH = 2[CAS_2] + 2[C_2ASH_8] + 9[CS_2H_2] + 6[SH];\ \Delta f G^0_{298} = -8717 \text{ kj/mol.} \quad (3)$$

At the CPT_{nat} diffractogram (Fig. 3. a), CPT_{deh} peaks (2.98; 3.34; 3.96; 7.97; 8.792)Å repeat for 3.b, and 3.c, as well. The mentioned fact confirms that when heating CPT_{nat} up to 700°C, its dehydration with endo-effect at 130°C is the basis process.

The heat from flue gases and chilling clinker may be used for humiditying CPT drying and enhancement for $Ca(OH)_2$ (CH) activity to CO_2 adsorption and, therefore, cement strength.

The chemical composition of the considered CPT_{nat} (TZCPT/XKCPT) is as follows (in mass %): SiO_2 43.80/57.45; Al_2O_3 14.83/16.06; Fe_2O_3 6.87/3.75; CaO 12.89/5.89; MgO 2.45/1.70; MnO 0.44/ 0.01; R_2O 4.72/3.65; SO_3 0.02/0.22; LOi 14.06/11.56. The minerals entering the CPT composition are: volcanic glass, SiO_2; $Al_2O_3{\cdot}SiO_2{\cdot}nH_2O$; $R_2O(RO)Al_2O_3\ mSiO_2{\cdot}nH_2O$; $(Na,K)_6[Al_6Si_{30}O_{72}]24H_2O$. The new formations in the cement stone are: CO_2, CSH(B), C_2AH_8, C_4AHx, C_2ASH_8, C_3AsxH_{32}.

Laboratory experiments on six specimens (contr. mix = CPT nat. 25°C): CPT-1 = 200°C in the mill; CPT-2 = CPT 95% + diatomite 5% granular, 200°C+CO_2; CPT-3 = 400°C + CO_2; CPT-4 = 400°C conveyor; CPT-5 = refrigerator 700°C – for 10 min; CPT-6 = refrigerator 700°C – for 15 min.) have been conducted through determining the activity index of cement of laboratory milling, when clinker composition is 60 mass % and that of prepared specimens – 40 mass %, according to the ASTM C 311-05 methodology [13]. Experimental results obtained for number of properties are given in Table.

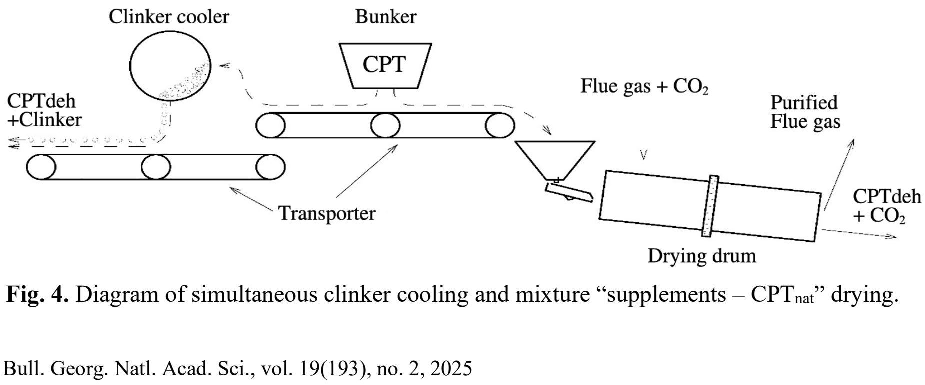

Fig. 4. Diagram of simultaneous clinker cooling and mixture "supplements – CPT_{nat}" drying.

Table. Strength activity index (ASTM C 311-05.)

Constituents	Control mix	Testmix					
		CPT-1	CPT-2	CPT-3	CPT-4	CPT-5	CPT-6
A. Strength,2 day, MPa	-	23.0	28.0	30.0	27.0	31.0	330
B. Strength,2 day, MPa	30.0	-	-	-	-	-	-
Activity index, %	-	76.7	93.3	00.0	90.0	103.3	110.0
C. Strength, 28day, MPa	-	48.0	50.0	56.0	54.5	62.0	64.0
D. Strength, 28day, MPa	54.0	-	-	-	-	-	-
Activity index, %	-	88.8	95.6	03.7	00.9	114.8	118.5

Results and Discussion

It is established that activity index of cement mixed with following additives is: with CPT-1 equals 76.7 in 2 sec, and 88.8 in 28 sec; with CPT-2–93.3 and 95.6, respectively; with CPT-3 = 100.0 and 103.7; with CPT-4 = 90.0 and 100.9; with CPT-5=103.3 and 114.8; with CPT-6 = 110.0 and 118.5. Thus, the cements mixed with obtained test mineral supplements are hydraulically active and pozzolanic ones (Table).

When heating CPT up to 700°C, the basic processes are: dehydration onset at 94.7°C (with maximum at 130°C), CO_2 chemisorption with CPT, with a process onset at 99.65°C, when pressure is 706 mm Hg Torr. Interaction of thermally-activated CPT's components with CH, i.e. "pozzolanization" reaction with rehydro-liming facilitates application of innovative nanotechnology – intense formation of nano-size water-resistant compounds with fibrous-acicular-lamellar habit: tobermorite CSH, stratlingite C_2ASH_8, ettringite C6AsH32, which leads to their interlacement, (3d) self-nano-reinforcing of solidifying cement structure and to enhancement of its strength, with the opportunity of reduction of clinker quantity in cement composition; emission and CO_2 traces from cement production [8, 9, 14].

Conclusions

Thus, the drying of diatomite natural sorbents and CPT in the dryer drum, with heat recovery of flue gases and simultaneous capture of CO_2 presented, is an innovative energy-efficient green technology, which reduces emissions and CO_2 traces of cement production;

– Drying the same materials with heat recovery of chilling clinker, through their mixing with chilling clinker in refrigerator or conveyor, is an innovative energy-efficient green technology, that reduces CO_2 emissions in cement production;

– It is possible to enter, without strength loss, the offered mineral additives into cement composition in the amount of up to 40 mass % from clinker weight, which is justified from the economic standpoint, since it leads to reduction of clinker's share – the most expensive and energy-consuming component. This makes it possible to reduce atmospheric emission and traces of CO_2 by 40%, i.e. down to 0.351-0.384 t/t.cl., which is so important from environmental point of view.

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მასალათმცოდნეობა

ენერგოეფექტური მწვანე ტექნოლოგიები ცემენტის წარმოებიდან CO_2-ის ემისიებისა და კვალის შესამცირებლად ბუნებრივი სორბენტების გამოყენებით

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** საქართველოს ტექნიკური უნივერსიტეტი, ქიმიური ტექნოლოგიისა და მეტალურგიის ფაკულტეტი, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის რ. ხუროძის მიერ)

ცემენტის ქარხნის კლინკერის ღუმელებიდან ატმოსფეროში ემისირებული 0,89 ტ /ტ.კლ. CO_2 ქმნის სათბურის ეფექტს და ნახშირბადის კვალს, რაც ხელს უწყობს გლობალურ დათბობას. პრობლემის თავიდან ასაცილებლად ეკონომიკურად განვითარებულ ქვეყნებში მუშავდება პროექტები „ნახშირბადის დაჭერა და უტილიზაცია“. საქართველოს ცემენტის ქარხნებში პუცოლანის სახით ადრე იყენებდნენ დიატომიტს (5 მას.%), ამჟამად კი – კლინოფთილოლითს (5-40 მას.%), ხეკორძულას ან თეძამის საბადოებიდან, რომლებიც ასევე ცნობილია როგორც CO_2-ის ბუნებრივი სორბენტები. დიატომიტის/კლინოფთილოლითის ფუნქციონალური გამოყენების პრობლემას ქმნის მათი მაღალი ტენიანობა, რაც ართულებს დაფქვას, ზრდის ენერგიის ხარჯს და ცემენტის ღირებულებას, რის გამოც, ისინი საჭიროებენ წინასწარ გამოშრობას. კიდევ ერთი პრობლემაა დაკავშირებული მასალების ფრაქციულობასთან – 3-5 მმ-ზე მცირე ზომის მარცვლები არ გამოიყენება როგორც სორბენტი, ასევე როგორც პუცოლანური დანამატი. ჩვენი კვლევის მთავარ პრიორიტეტს წარმოადგენს ადგილობრივ ნედლეულზე დაფუძნებული ენერგოეფექტური და მწვანე ტექნოლოგიების გამოყენებით ცემენტის წარმოება – კლინოფთილოლითის მარაგი საქართველოში, დაახლოებით, 300,0 მლნ ტონაა, ხოლო დიატომიტის – დაახლოებით, 20,0 მლნ ტონა. ცემენტში კი ორივე მასალა ცვლის კლინკერს, რაც ამცირებს საბოლოო პროდუქტის ღირებულებას. ჩვენ გამოვიკვლიეთ დიატომიტის/კლინოფთილოლითის წვრილი ფრაქციის მიზნობრივი კომბინირებული გამოყენების შესაძლებლობა. განისაზღვრა: ბუნებრივი ($\Delta f G0298$=-36735 კჯ/მოლ) და დეჰიდრატირებული ($\Delta f G0298$=-31857კჯ/მოლ) კლინოფთილოლითის ჯიბსის თავისუფალი ენერგიის თერმოდინამიკური მნიშვნელობები; CO_2-ის დაჭერის მოსალოდნელ დისპერსირებულ სისტემაში, „კლინოფთილოლითი-CO_2”, დეჰიდრატაციის დაწყების ტემპერატურა (T = 94.7°C) და წნევა (P = 460 მმ Hg Torr), ასევე ფიზიკური (T = 97.2°C; P = 293 მმ Hg Torr) და ქემოსორბციული (T = 99.7°C, P = 706 მმ Hg Torr) პროცესების ტემპერატურები და წნევები. კვლევის მიზანი იყო სტუ-ში შემუშავებული და ქარხნებში გამოყენებული ცემენტის წარმოების ენერგოეფექტური მწვანე ტექნოლოგიების დადასტურება თანამედროვე აკრედიტებულ ლაბორატორიებში ჩატარებული ექსპერიმენტების შედეგების გამოყენებით.

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