Theoretical evaluation on possibility of using basaltoid as aluminosilicate component in raw mix for Portland cement clinker synthesis

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ABSTRACT
Theoretical evaluation of possibility on using basaltoids as aluminosilicate component for the Portland cement clinker synthesis was conducted on the base of mathematical calculations (by given LSF and module values of raw mix) and also analysis of diagram for system $CaO-SiO_2-Al_2O_3$, taking into consideration aluminosilicate minerals chemical composition average as basaltoids rock have shown that under certain conditions fluoride additives open a possibility of obtaining Portland cement clinker.
For the first time it was established that by using basaltoids as aluminosilicate component in raw mix (and additives fluor containing mineralizer) for obtaining Portland cement clinker is possible to synthesize Portland cement (high alit, alit and normal compositions) at temperatures 1250-1300^oC, that is low 200-250^oC comparing with traditional technology clinker burning.
Reduction of clinker obtaining temperature was stipulated by the low temperature on beginning of basaltoids fusion, strong destroy action of crystalline lattices by fluorine ion in the raw mix, as well as CaF_2 catalytic action on stage of carbonate component decompositions, that expressing in forming of intermediate unstable compound as carbonate spurrite other fluor containing phases. Developed physics-chemical bases of new direction for technologies of Portland cement are developed by using non-traditional aluminosilicate rock as basaltoid with together CaF_2 additive.

1. INTRODUCTION
In the world of cement industry as aluminosilicate components are mainly used different clay rocks (clay, loamy clay, loess, argillite, shale slate). At resent years, an interest increases in prospecting the new types of aluminosilicate minerals, capable to substitute (completely or partly) clay rocks for the composition of raw mix for obtaining Portland cement clinker. In works A.A.Pashenko, E.A.Myasnikova [1, 2] were shown a possibility for making Portland cement by using basalts of Ukraine.

The study was done by V.V.Timashev and other scientists [3] and have shown that clayely component in cement raw mix was possible on usage of porous basalt, perlitte and volcanic tuff.

1.1 Main objective of the study is a theoretical motivation for suitability and possibilities on using volcanic derived alkaline basaltoids as aluminosilicate component of raw mix for obtaining Portland cement. Decision of this problem was realized on the base of analysis for the three component (ternary) CaO-SiO_2-Al_2O_3 system diagram and corresponding methods of drawing and their calculations.
Analysis for CaO-SiO_2-Al_2O_3 system diagram was determined the area of basaltoid (except for alkalis), after the fixing chemical compositions content number for basaltoids from 7 deposits (refer to below shown Table) on the diagram and corresponding geometric constructing, which has shown that basaltoids chemical compositions get through the content of Portland cement clinker.

Table

The average chemical composition of basaltoid, (Mongolia)

N	Deposit	Content of oxides, weight %						
		SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O
1	Orkhon (Bulgan aimag)	5305	16.4	6.8	4.8	9.16	2.22	4.60
2	Khairtiin ovoo (Bulgan aimag)	52.71	17.0	5.69	3.22	9.33	1.0-6.0	2.40-5.30
3	Artsatiin am (Bulgan aimag)	44.8-47.8	8.2-18.5	7.5-10.41	2.36-6.3	8.55-9.72	1.0-2.7	3.4-5.4
4	Khukh-Tolgoi (Khuvsgul aimag)	49.9	8.15	7.15	6.35	10.57	-	-
5	Sain Eriin ovoo (Arkhangai aimag)	48.52	15.25	7.70	6.63	11.23	-	-
6	Sainshand (Dorno-Gobi aimag)	46.2	12.99	6.65	4.17	12.38	2.69	1.72
7	Zuun-Tsagaan (Dorno-Gobi aimag)	53.92	14.26	5.8	5.4	6.5	-	1.35

Thereby, it is possible to confirm that under certain ratio the Portland cement clinker would be made of basaltoid and limestone. However, basaltoid contains approx. 5-8 weight % alkalis, so questions arise on reducing contents of alkalis (Na_2O+K_2O) in synthesized clinker. For deciding this problem by the simplest way is a using the additive fluorite calcium.

2. RESULTS AND DISCUSSION

Evaluation on possibility of using basaltoid as aluminosilicate component for obtaining raw mix of Portland cement clinker was conducted not only by the calculation method, accepted for the cement

technologies, but also on the base of analysis for $CaO-SiO_2-Al_2O_3$ system diagram.

On the first stage, it is considered the possibility for obtaining Portland cement clinker from basaltoid, which contained three main oxides as CaO, SiO_2 and Al_2O_3 on the second stage, with consideration for contents of admixtures (Na_2O, K_2O, MgO, TiO_2, P_2O_5, Mn_2O_3), that amount is limited by technical recommendations and rates [5], contents of main oxides and carried on the system diagram $CaO-SiO_2-Al_2O_3$ (see the figure) allow to outline the area of basaltoid on this diagram. Hereinafter, connecting top of triangle, corresponded 100% CaO contents, as with the mid position for the basaltoid area, so conducting a tangent from the given top to the area basaltoid, convinced that all get through the area Portland cement clinker (area I in the Figure). Thereby, Portland cement clinker will be obtained under certain ratio of basaltoid and limestone.

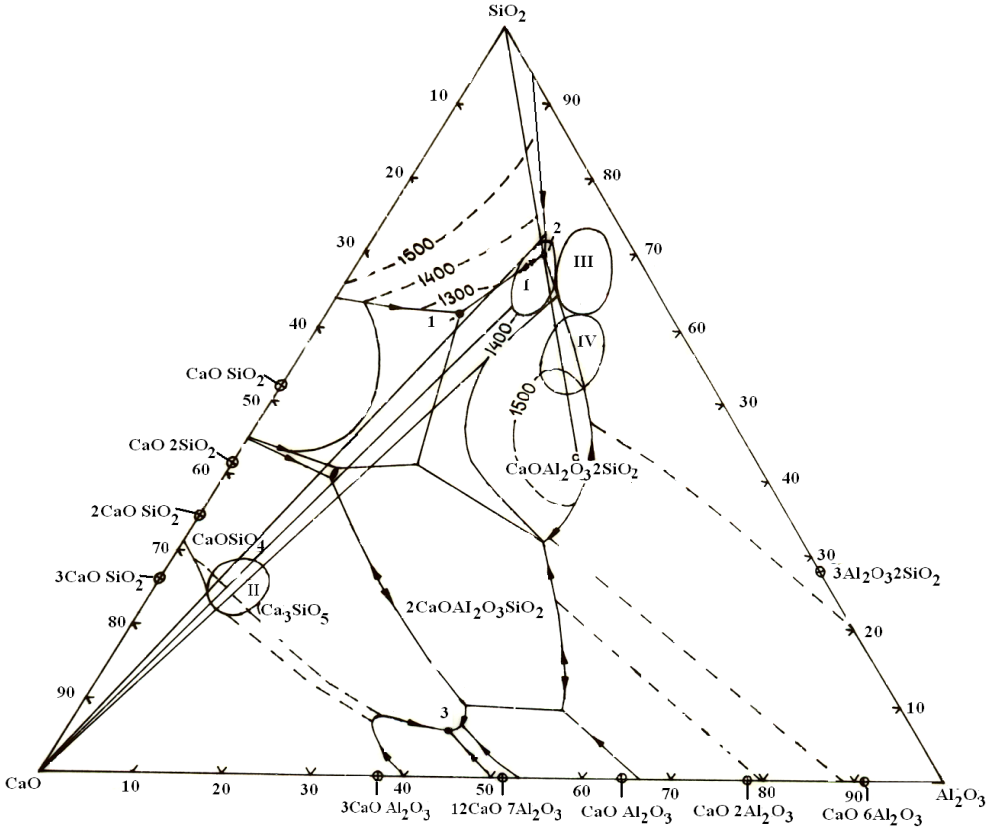

Figure. System diagram $CaO-SiO_2-Al_2O_3$, I- Basaltoid area, II- Portland cement area, III- Clays area, IV- Basalt rock area

Considered diagram (see the Figure) that helps to reveal and possible differences, which may take place on burning of cement raw mix that containing basaltoid, comparing to raw mix with clay and basalt.

For this a line will conduct, connecting the top of SiO_2 and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (anorthite). Herewith it appears that area of basaltoid (area I) is

located on the left of this line, the area of clays (area III) on the right; the area of basalts (area IV) inhere on the right by greater its part and smaller on the left. This signifies that liquid phase in basaltoid appears at the 1170^{o}C temperature, corresponding to triple eutectic 1, so then liquid phase in the clay (eutectic 2) can appear at the temperature 1345^{o}C. Known that eutectic compounds fusion for Portland cement composition appear at the temperature 1335^{o}C (eutectic 3).

As to basalts, their compositions, lying on the right of the lines, connecting the top of SiO_2 and anorthite, will behave as a clay for the same way, the liquid phase will appear at the temperature 1345^{o}C; In compositions, lying on the left of the specified line, a melt will appear in the same way as basaltoid, at T=1170^{o}C, when heating basaltoid, that melt amount of basaltoid will get approximately 2 times more, than the basalt with only difference, but full melting of basaltoid will occur at 1350^{o}C, and basalts at 1450-1550^{o}C.

Such position just only for pure compositions, if they are consisted of only CaO, SiO_2 and Al_2O_3. Natural limestone and basaltoid contain sufficiently much amount of other oxides, main of them was mentioned above. It's impossible to count up of their total influence nor on the temperature reduction of fusion appearance, nor on the last production viscosity reduction, but in analogy with the Portland cement clinker liquid phase, temperature, appearing of decrease from 1335 to 1275^{o}C under the influence of admixtures (that is by 60^{o}C), it's possible to expect, in case of using basaltoid, which is containing more impurities in the clay, fusion appearance will lower by 60^{o}C for the impurity of raw mix, so basaltoid containing mixture melting must start, as from 1100^{o}C.

Thereby, basaltoid not only provides the obtaining of Portland cement clinker, as well as in consequence of reducing temperature for liquid phase appearance must greatly lower the temperature of clinker burning, but consequently, shorten the heat amounts, consuming for Portland cement clinker synthesis. All stated would be, basaltoid does not interact with CaO completely if it in a temperature period of solid phase reaction till to the appearance of liquid phase. Considering, that melt appears at 1100^{o}C, it follows to expect only the partial reduction of basaltoid amount.

Possibility for obtaining Portland cement from basaltoids by using the $CaO-SiO_2-Al_2O_3$ diagram can be considered by the accounting of impurities. Consequently, amount of impurities in raw mix for comparing with basaltoid decreases by 5 times, but in clinker for comparing with raw mix increases by 24% or by 1.24 times. Counts, coming from taken ratio, show that total amount of impure oxides, with the exclusion amounts of Na_2O and K_2O, if it being in possible limits of requirements, present cement production raw mix [5, 6]. Maximum contents of alkalis in Portland cement clinker at the request of

standard specifications (SS) [5] must be not more 1.2 weight %, the burn obstruct and clinker would counted non-standard greater amounts.

Alkali amount in basaltoid was in range 5-8 weight %. At the recalculation by above specified ratio for the alkalis contents would be in range 1.14-2.48 weight % for cement clinker. If alkalis in small quantities for the natural limestone is present that takes into account, and usage of basaltoid as aluminosilicate component is impossible for the Portland cement production. Not ensure sufficient reducing on alkalis contents and their volatilisation for clinker burning, which as work [3] alkali volatility forms 15-25% in modern rotary kilns. One of the ways for reducing alkalis contents in clinker is essentially enlarge their volatility by putting additive, which promoting alkalis sublimation for burning the raw mix.

In the work [7] it is established that at the additive of fluoride calcium to raw mix by the amount 1.0-1.5 weight % ensures reduction of alkalis in clinker by 2.5-3.0 times. Consequently, it's possible to expect that in clinker, obtaining by using basaltoid and additives CaF_2 contents of alkalis will be decreased from 1.14-2.48% to 0.45-0.99% that wholly meets the requirements SS [5, 6].

Adding fluoride calcium to basaltoid containing raw mix would promote much more the temperature reducing and the amount increasing for liquid phase appearance, and reducing its viscosity, thereby can greatly lower temperature the completion of clinker obtaining.

Experimental results on using basaltoid as aluminosilicate component in raw mix were checked both in laboratory conditions, and pilot-scale test, which results were reported on international congresses on cement chemistry (New-Delhi, 1992 and Gothenburg, 1997) and in Russia and Mongolian scientific publications [8, 9, 10, 11, 12].

Experimental studies have shown possibility of low temperature syntheses of Portland cement clinker (LSF=0.93-0.88) from raw mix that containing carbonate calcium (CaO≥80%) and basaltoid as taking mineralizer of fluoride calcium as 0.7-1.0-weight %.

Studies have shown that grown up volatility of alkalis would increase clinker burning temperature, as well as amount of additive CaF_2, for example, for the CaF_2 additive by 1.0 weight % in clinker sample with LSF=0.93 evaporate approximately (1.8-2.5 weight.%) 50 weight % alkalis from "introduced" amounts of alkalis to 1300^{o}C burning, but alkalis sublimation is approximately to 60 weight % at 1350^{o}C burning.

Physics-chemical testing the basaltoid containing Portland cement have shown that cements, received in pilot-scale conditions satisfy acting in Russia and Mongolia to standards and their strengthening factors correspond to "400" and "500" mark of Portland cements [4].

CONCLUSION

1. Analysis of systems diagram $CaO-SiO_2-Al_2O_3$ have shown that using basaltoids allows to synthesize Portland cement clinker considerably low warm-up conditions, than on the traditional technology of cement.
2. Chemical composition proximity of basaltoid rocks is in average of traditional clays chemical composition, which is applied in cement production at present, is one of advantage for basaltoid.
3. Basaltoids meet the requirements, present to the chemical composition of aluminosilicate raw mix for the Portland cement clinker production, specified in standard specifications, with the exclusion of the total contents of alkalis. Additive fluoride mineralizer promotes the reducing of alkali contents in clinker; thereby it is opened way for obtaining qualitative clinker. Besides, the whole amount of impure oxides, that contained in basaltoid, provides an earlier appearance of liquid phase in basaltoid containing raw mix.
4. Sufficient constancy of basaltoid chemical composition within given deposit is an important qualitative factor for preparing the raw mix with stable chemical characteristics.
5. Broad prevalence and large resource of volcanic rock basaltoid deposits on territory of many countries in the world open a new possibility on mineral resources for cement industry.
6. It's established experimentally fluoride additive to basaltoid containing the raw mix powerfully reduces the beginning temperature for liquid phase appearance; at CaF_2 additive to the above specified mix liquid phase formation was started from 980^oC, but for crystalline basaltoid melting is started at 1060^oC.
7. Basaltoid is possessed a high reactivity in comparing to the clay and shale slate for usage of the raw mix; its reactivity considerably increased in presence CaF_2, CuO, ZnO, $CaSO_4$, and especially with their combinations: CaF_2+CuO, CaF_2+ ZnO, CaF_2+ $CaSO_4$.

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