Composition of raw mixes for portland cement clinkers using andesic basalt rock

Gulistan Orazimbetova[1*], *Umid* Turdialiev[1], and *Laura* Biniyazova[1]

[1]Andijan Machine Building Institute, Andijan, Uzbekistan

Abstract. This article studies, calculation of compositions of raw mixes and development of clinker production technology on the basis of using local raw materials of Karakalpakstan, is an effective solution to the problem of covering the needs of the construction industry of the autonomous republic in cement. As well as component composition of raw mixes with different values of saturation coefficient (SC), silicate (n) and alumina (p) modules, calculated chemical and mineralogical composition of clinker on the base of new raw mixes. Some properties of clinkers and Portland cements based on them have been studied. Keywords: limestone, andesibasalt, brown ironstone, barchan sand, raw mixes, firing, clinker, general construction, sulphate-resistant, Portland cement

1 Introduction

The northernmost territory of Uzbekistan, the Republic of Karakalpakstan, which occupies a vast territory, is characterised by a variety of climatic and geographical conditions[1-2]. Due to the drying up of the Aral Sea, salinization of soils and invasion of barchan sands are observed. This region is located far enough away from the main cement producers in Uzbekistan that its transportation cost increases (http://uza.uz/ru/politics/karakalpakstan-analiz-prodelannoy-raboty-i- plany-na-perspekt-15-12-2017) [3]. The emergence of new local producers would eliminate this transport surcharge, making cement more competitive [4-6].

The rapid pace of construction requires the production and output of new, more efficient types of cement based on the extensive use of local raw materials, which is an urgent task in the building materials industry [7-9].

2 Methodology

Determination of the phase composition of raw materials using modern methods of analysis.

Chemical analysis of raw materials, raw mixes and fired products was carried out in accordance with the requirements of GOST 5382-91 "Cements and materials for cement production. Methods of chemical analysis". [10].

* Corresponding author: mohim@inbox.ru

Compositions of raw mixes and clinkers for the production of general purpose and sulphate resistant cements are calculated by a special program using S.D. Okorokov's formulas in accordance with O'z DSt 2801:2013 "Portland cement clinker. Technical conditions". [12]. For grinding of raw mixtures we used a laboratory ball mill at the loading "grinding agent : grinding material = 3,5 : 1". Grinding fineness of the raw mixtures was determined in accordance with the requirements of GOST 310.2-76 "Cements. Test methods" [13].

The quality of raw materials for clinker production has been assessed in accordance with the requirements of O'z DSt 2950:2015 "Raw materials for the production of Portland cement clinker. Technical specifications"[14].

The clinkers were fired at the optimum temperatures determined by the reactivity of the raw mixesxx[15].

3 Results and discussion

Compositions of raw mixes and clinkers based on the tested raw materials were calculated by a special industry programme. The formulas of S.D. Okorokov [15-17] were used in the calculations.

Table 1. Calculated chemical compositions of raw mixes

№	Material composition of raw mixes	Oxide content, % by mass								
		clause p.p.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
	Composition No. 1									
1	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	sl	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	vll.	vll.	1,25	1,17
	Raw mix	35,76	13,10	4,61	2,35	41,42	2,29	0,00	0,24	0,23
	Composition No. 2									
2	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	sl	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	vll.	vll.	1,25	1,17
	Raw mix	35,88	12,91	4,55	2,33	41,58	2,30	0,00	0,24	0,22
	Composition No. 3									
3	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Barchan sand from the Dusshebulak deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99

	Raw mix	36,32	14,33	3,21	1,69	42,00	2,53	0,01	0,20	0,19
	Composition No. 4									
4	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Barchan sand from the Dusshebulak deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Raw mix	36,51	14,74	2,74	1,47	42,19	26,0	0,01	0,18	0,17
	Composition No. 5									
5	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Barchan sand from the Dusshebulak deposit	16,54	37,02	6,56	16,94	14,61	2,51	2,19	1,55	1,45
	Raw mix	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Composition No. 6									
6	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0.76	49,81	2,84	sl	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	vll.	1,25	1,17
	Barchan sand from the Dusshebulak deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Raw mix	35,90	12,95	4,51	2,31	41,59	2,30	0,00	0,24	0,22

	Composition No. 7									
7	Limestone from the deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Brown glandular rock Hujakul	16,54	37,02	6,56	16,9	14,61	2,51	2,19	1,55	1,45
	Barchan sand from the Dusshebulak deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Raw mix	35,95	13,94	3,28	2,53	41,43	2,55	0,14	0,25	0,24
	Composition No. 8									

8	Limestone from the Dusshebulak deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Brown gland ular rock Hujakul	16,54	37,02	6,56	16,94	14,61	2,51	2,19	1,55	1,45
	Barchan sand from the Dusshebula k deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Raw mix	36,07	13,74	3,23	2,49	41,59	2,55	0,13	0,25	0,24
Composition No. 9										
9	Limestone from the deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Brown gland ular rock Hujakul	16,54	37,02	6,56	16,94	14,61	2,51	2,19	1,55	1,45
	Raw mix	34,89	13,07	3,36	4,81	39,81	2,63	0,50	0,41	0,38
Composition No. 10										
10	Limestone from the deposit	42,31	2,85	1,43	0,76	49,81	2,84	Sl.	-	-
	Andesibasalt of the Berkuttaou site	8,79	55,30	17,69	8,92	6,88	Sl.	Sl.	1,25	1,17
	Brown gland ular rock Hujakul	16,54	37,02	6,56	16,94	14,61	2,51	2,19	1,55	1,45
	Barchan sand from the Dusshebula k deposit	5,06	92,68	2,73	1,95	Sl.	2,55	0,13	1,01	0,99
	Raw mix	35,22	13,65	3,19	3,99	40,31	2,63	0,38	0,36	0,33

The calculations (Table 1.) are based on the chemical composition of the raw material samples taken for the process tests. Further analysis of the calculated data in Table 1. has shown, that on the base of two-component raw mixes with limestone of

Dusshebulak deposit and andesibasalt of Berkuttau site (compositions № 1 - № 2, table 1) we can not produce conditioned clinker for common building cements, because silicate module index in raw mixes (n=1,88) does not correspond to O'z DSt 2801:2013 requirements (n=1,90- 3,50).

Three-component raw mixes (formulations №3-6 of table 1) with additional addition of barchan sand of Dusshebulak deposit were designed to increase silicate module parameter of raw mixes based on limestone of Dusshebulak deposit and andesibasalt of Berkuttaum site. By indices KN (0,90-0,92) and modulus characteristics (n = 1,90-3,50; p = 1,87 -1,96) the given raw mixes completely correspond to the requirements O'z DSt 2801:2013. The mass fraction of andesibasalt in the composition of the raw mixes is (3.89- 18.91)%. The mass fraction of limestone changes accordingly (from 80.89 to 83.69)%. Mass fraction of barchan sand of Dusshebulak deposit is (0.20 - 8.94)%.

When introducing to the compositions of raw mixtures based on limestone of

Dusshebulak field, andesibasalt of Berkuttau area, barchan sand of Dusshebulak field the fourth component - brown iron rock "Hujakul" (compositions № 7 № 8 of Table. 1.6) raw mixes for indicators KN (0,90-0,92) and modular characteristics (n = 2,40; p = 1,30) are fully consistent with the requirements of O'z DSt 2801:2013. The mass fraction of andesibasalt in the composition of the raw mixes is (8.88- 9.14)%. The mass fraction of limestone varies accordingly (from 80.16 to 80.56)%. Mass fraction of barchan sand of Dussebulaksky deposit is (4.70-4.75%)%. Mass fraction of brown ferruginous rock "Khujakul" (5.86-5.95)%.

In the estimated mineralogical composition of clinker for the production of sulfate resistant cement on the basis of a three-component raw mix using limestone from Dusshebulak deposit, andesibasalt from Berkuttau site, brown iron ore "Hujakul" (composition № 3 of Table 1) the aluminum oxide content (Al_2O_3 = 5.17%) does not meet the requirements O'z DSt 2801:2013 (Al_2O_3 - not more than 5%). Therefore, in order to produce sulphate-resistant clinker, a fourth correcting component must be added to this raw mix. Dushebulak barkhan sand was used as a correcting component. The calculated chemical and mineralogical composition of clinker on the basis of four-

component raw mix based on limestone of Dusshebulak field, andesibasalt of Berktau area, barkhan sand of Dusshebulak field and brown iron ore "Hujakul" completely corresponds to the requirements of O'zDSt 2801:2013 for the content of tri-calcium aluminate (C_3A=3.59%), tri-calcium silicate (C_3S =47.99%) and aluminium oxide (Al_2O_3 =4.47%). At the same time the mass fraction of andesibasalt from the Berkuttaou site, is 5.24%. Limestone consumption is 75.17% Mass fraction of barchan sand of Dusshebulak deposit is 2.44%. Mass fraction of brown ferruginous rock "Hujakul" is 17.15%.

Based on the calculated data outlined in Table 1, the optimum compositions of raw material mixtures based on the raw material components of the Republic of Karakalpakstan were selected for further testing.

The material compositions of the optimum raw mixes are shown in Table 2.

Table 2. Component composition of optimum raw mixes with different pH values, silicate (n) and alumina (p) modules

№	S/C number	KN	Modular features		Material composition of c/c, %			
			n	p	Limestone	Andesibasalt	Brown glandular .breed	Barchan sand
1	*№ 5*	0,92	2,40	1,93	82,24	13,87	-	3,89
2	*№ 8*	0,92	2,40	1,30	80,56	8,88	5,86	4,70
3	*№10 SSPC*	0,88	1,90	0,80	75,17	5,24	17,15	2,44

Three component raw mixes and clinker on the basis of 82,24 % Dushebulak limestone, 13,87 % Berkuttau andesibasalt and 3,89 % Muynak barkhane sand fully correspond to requirements of O'z DSt 2801 on chemical mineralogical composition and modular characteristics. Four component raw mixes and clinker based on 80,56% Dussebulak limestone, 8,87% Berkuttau andesibasalt, 5,86% Khujakul brown ironstone and 4,70% Dussebulak barkhan sand fully meet the requirements of O'z DSt 2801 in terms of chemical-mineralogical composition and module characteristics.

Using 75.17% Dussebulak limestone 5.24% Berktau andesibasalt, 17.15% Khujakul brown ironstone and 2.44% Muinak barkhane sand as raw materials, it is possible to form the raw mixes for sulfate-resistant clinkers (Composition № 10, Table 1with chemical and

mineralogical composition and module characteristics corresponding to O'z DSt 2801 requirements.

Table 2. Calculated mineralogical composition of optimum clinker compositions based on new raw mixes

№	Material compositi on	Mineralogical composition, in %								
		FRO M_3 S	C_2 S	C_3 A	C_4 AF	KN	n	p	K total raw material consumption, per 1t clinker	Liquid phase
1	Raw mix No. 5	61,54	14,80	10,35	9,24	0,92	2,40	1,93	1,5677	28,87
2	Raw mix No. 8	61,37	15,32	6,79	11,83	0,92	2,40	1,30	1,5642	28,69
3	Raw mix № 10	49,52	23,08	2,59	18,73	0,88	1,90	0,80	1,5438	33,70

The composition of raw mixes for clinker burning was calculated with a special program in accordance with "Cement Plant Technological Design Guidelines"[18-19]. Some properties of clinkers and Portland cements based on them are given in table 3.

Table 3. Some properties of optimum clinker compositions and Portland cements based on them

Name of raw mixes	Sinterin g temper ature,° C	Quant ity of gypsu m, %	Norma density	Timing of setting	
				start, min	end, min
Raw mix No. 5	1420	4	0,25	01:50	03:05
Raw mix No. 8	1430	4	0,25	04:00	05:50
Raw mix No. 10 SSPC	1430	4	0,25	05:25	07:55

Raw mixes in calculated ratios of initial components were milled in a double chamber ball mill MBL to a fineness of 10-12% residue on sieve number 008[20]. Annealing of raw mixes in the form of pressed tablets 1.41x1.41cm in size was carried out in a laboratory silite furnace, the temperature in which was controlled by a thermocouple TPR with a secondary device. Firing of raw mixes was carried out at temperature 1420-1430° C and holding time 60 min. Completion of the process of clinker formation was judged by the amount of $CaO_{св}$, whose content was determined by ethylene-glycerate method. Tests for determining physical and mechanical properties of cements for compliance with the requirements of GOST 10178-85 were conducted in accordance with GOST 310.1-310.4.

According to the calculated data, the content of the main minerals in clinkers, depending on the values of the modular characteristics is C_3 S from 49,52 % to 61,54 %; C_2 S 14,80 - 23,08 %; C_3 A 2,59 - 10,35 % (Table 2).

Portland cement clinker must fulfil the requirements of O'z DSt 2801:2013 (Table 2 and Table 3) with regard to its chemical, mineralogical composition and modulus characteristics.

4 Conclusion

The optimum interval for clinker sintering (1420-1430)° C for three- and four-component raw mixes using Dusshebulak limestone, barkhan sand, Berkuttaum andesibasalt and Hudzhakul brown iron. By using new raw materials it is possible to form raw mixes for general construction and sulfate-resistant clinkers and with chemical and mineralogical composition and modular characteristics, fully compliant with the normative documents.

References

1. D.K. Kudainazarova, J. Vestnik KKO AS RUz **1,** 76-78 (2012)
2. U.Kh. Yeshimbetov, Journal of Economics and Finance **2,** 15-18 (2018)
3. N.K. Aimbetov, The role of the small business and entrepreneurship sector in the development of industrial production in Karakalpakstan **1**, 72-76 (2012)
4. Mineral raw material base of construction materials of the Uzbek SSR. Reference book (Tashkent. : Fan. 1967)
5. B.T. Taimasov, N.N. Zhanikulov, A.R. Kaltay, N. Nurmagambet, A. Kosymbekova. Integrated use of mineral raw materials **2**, 95-101 (2016)
6. I.V. Kalyuzhenov, E.S., Nurakov V.K. Klassen, Vestnik BSTU named after V.G. Shukhov **17**, 75-80 (2017)
7. P. Pulatov, E.M. Butaev, Journal Cement and its application p. 134- 136 (2011)
8. A.N. Zavaritsky, Eruption of rocks (Moscow: USSR Academy of Sciences Publishing House, 1956)
9. R.W. Le Maitre, (editor) Igneous Rocks: A Classification and Glossary of Terms, Recommendations of the International Union of Geological Sciences, Subcommission of the Systematics of Igneous Rocks (Cambridge, Cambridge University Press, 2002)
10. V.S. Gorshkov, V.V. Timashev, V.G. Savelyev, Methods of physico-chemical analysis of binders (M.: High school, 1981)
11. G. Orazimbetova, L. Ubbiniyazova, A. Nimchik, AIP Conference Proceedings **2432**, 050026-1- 050026-5 (2022) https://doi.org/10.1063/5.0089920
12. A. Nimchik, et.al., AIP Conference Proceedings **2432**, 050059-1- 050059-6 (2023) https://doi.org/10.1063/5.0089917
13. Effusive rocks. Great Soviet Encyclopaedia : in 30 vol. / Ed. by A. M. Prokhorov.3rd ed. (M. : Soviet Encyclopaedia, 1969-1978)
14. E.N. Ushakova, R.A., Shelepaev A.E. Izokh, V.P. Sukhorukov, A. A. Nikitin, Magmatic rocks: systematics, nomenclature, structures and textures (inaccessible). Geological Museum, NSU. Date of access: 11 September 2016 (Archived 12 September 2016)
15. G. Orazimbetova, IOP Conference Series: Materials Science and Engineering **883**, 012200 (2020)