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Tuffs and kaolins areas evaluation for use as pozzolanic materials

Various tuffs and kaolin's were evaluated for use in cement as pozzolanic additives. These materials were analyzed for chemical and mineralogical composition, reactive Si content and also were used for the production and testing of blended cements. The JOMEN tuffs, that seem to exist in significant reserves, already appear to be problematic due to their low reactive SiO_2 content. The kaolin samples that were studied included those from the KORTHPULA, VIG and DEJAI areas. The search for suitable tuffs materials is now focused on the JOMEN area. The KORTHPULA kaolin had a high reactive silica content and could be considered as a potential pozzolanic additive. About the kaolins, the above conclusions were based on spot surface samples; the suitability of the kaolins as pozzolanic additives will need to be verified based on samples of core drilling that is planned for the near future.

Key words: *tuff, kaolin, pozzolanic additives, cement.*

INTRODUCTION

Pozzolanic materials are natural substances of siliceous or silica-aluminous composition or a combination thereof. Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water they react at normal ambient temperature with dissolved calcium hydroxide ($Ca(OH)_2$) to form strength-developing calcium silicate and calcium aluminate compounds [5-7]. Pozzolanic materials like Kaolin and Tuffs consist essentially of reactive silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). The remainder contains of iron oxide (Fe_2O_3) and other oxides. Various tuffs and kaolins were evaluated for use in the cement as pozzolanic additives [2-4]. Evaluation of these materials included:

a) Chemical and mineralogical analyses.
b) Determination of reactive SiO_2 content.
c) Production and testing of blended cements (Blaine, H_2O%, strength).

Ignition loss is usually determined by tests in a laboratory furnace. [1,8].

Tuffs:

Almost all of the examined tuff areas were rejected due to either quality of the material and/or potential local and mining conditions/problems (including low reserves availability). The JOMEN tuffs, that seem to exist in significant reserves, already appear to be problematic due to their low reactive SiO_2 content [8]. However, if there are formations in the vicinity different than those already examined, further testing is recommended.

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The search for suitable pozzolanic materials for the BEZHAN and PUKE areas should continue only after the investigation of geological and local mining conditions is completed

Kaolins:

Minerals of the kaolin group differ in content of SiO_2 as well as by the crystallographic structure and optical properties [8]. The kaolin samples that were studied included those from the KORTHPULA, VIG and DEJAI areas that were closer to the plant. The KORTHPULA kaolin had a high reactive silica content that satisfies the EN 197-1.

However, since the laboratory cement produced with that had a high water demand due to the presence of clays, further testing is needed when used for concrete manufacturing. The cement produced with the VIG kaolin had a satisfactory strength and a low water demand. Hence, if the reactive silica of the VIG kaolin content exceeds that required by the EN 197-1 it could be considered as a potential pozzolana [6,9,11].

MATERIALS AND METHODS

Materials used in this study were selected tuffs and kaolin's samples from different areas closer and far from the plant. The methods used for analyzing all these samples are X-Ray fluorescence and Wet Chemical Analysis [8]. Samples were prepared for measurement in the X-Ray Fluorescence apparatus in the form of tablets as follows. Upon arrival at the laboratory samples initially is made the determination of moisture and then pass on crusher to reduce the fines below 5 mm. Then we mix the sample well and weight respectively 12 g and 6 g of the same material and put in the Polab-APM apparatus for sample preparation in the form of tablets. After preparing the samples in the form of tablets we clean them with air and then introduce to the XRF measurement apparatus and make measurements of each material according to the respective calibration curves. Once the measurement is finished we take the results for each element and based on these results we judge on the quality of each material. For the wet chemical analysis we have followed the European Standard EN 196-2 [8].

RESULTS AND DISCUSSION

I. Tuffs

Tuff samples from the areas listed in the following table along with their XRF chemical analyses, were evaluated for use in cement as pozzolanic additives. The reactive silica content of selected tuff samples determined according to EN 197-1 is also reported [1,6]. The chemical analysis and the reactive silica content are presented in table 1.

Table 1 - Tuffs chemical analysis and the reactive silica content

Location	Nr	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	SUM	SiO_2 react
GRAMSH	1	74.34	12.07	1.21	0.62	0.19	4.39	3.00	0.00	4.34	100.14	
	2	73.46	11.82	2.04	0.35	1.40	7.08	0.00	0.00	2.99	99.14	
	3	67.39	12.35	2.23	2.18	1.53	7.52	0.00	0.00	4.04	97.24	7.80
	4	69.92	13.64	2.54	0.30	1.83	8.12	0.00	0.00	3.86	100.22	
	5	72.55	12.26	2.16	0.46	2.17	6.76	0.00	0.00	3.42	99.79	
	6	70.44	12.95	2.42	0.42	2.27	7.50	0.00	0.00	3.70	99.70	
	7	56.81	18.58	3.88	1.74	0.77	5.55	3.37	0.00	7.66	98.37	
	8	54.36	20.81	4.78	1.26	1.06	4.11	2.34	0.01	10.02	98.73	
	avg	67.41	14.31	2.66	0.92	1.40	6.38	1.09	0.00	5.00	99.17	
VRAP	9	62.22	15.49	4.11	3.09	2.52	1.46	2.10	0.00	7.92	98.90	
	10	64.26	13.59	3.34	1.96	3.11	1.56	1.23	0.00	9.49	98.55	**47.45**
	11	63.14	13.34	3.73	1.92	3.64	1.41	0.93	0.00	9.28	97.39	
	12	62.16	13.98	3.82	2.59	3.55	1.43	0.86	0.00	9.56	97.94	
	13	70.03	12.36	2.13	1.60	1.51	2.42	1.11	0.00	9.11	100.27	
	14	66.03	12.88	2.64	1.96	1.97	1.94	0.96	0.00	11.14	99.53	
	15	66.95	13.07	2.53	1.68	1.68	2.10	1.90	0.00	8.97	98.87	
	16	66.78	12.97	2.35	2.30	1.30	2.20	1.78	0.02	8.59	98.28	
	17	68.58	12.82	2.33	1.62	1.19	2.23	1.97	0.00	7.99	98.75	
	18	67.57	13.62	2.59	2.15	1.06	2.04	2.46	0.00	7.27	98.76	
	avg	65.77	13.41	2.96	2.09	2.15	1.88	1.53	0.00	8.93	98.72	
JOMEN (GJIROKASTER)	19	40,08	7,94	3,85	16,50	7,53	2,57	0,00	0,13	22,16	100,76	
	20	57,70	15,36	5,17	1,16	5,98	5,06	0,00	0,03	7,86	98,33	
	21	55,12	14,16	5,91	3,26	5,62	4,89	0,00	0,02	9,95	98,92	
	22	62,17	13,20	5,95	1,25	3,78	4,81	0,00	0,04	6,81	98,00	
	23	46,26	11,84	4,90	9,70	6,46	2,52	1,76	0,06	16,29	99,78	
	24	51,43	14,16	5,67	5,75	4,57	3,02	1,82	0,05	12,17	98,64	4,60
	25	53,81	15,70	6,35	2,72	4,17	2,59	2,83	0,01	9,82	98,00	
	26	53,84	12,39	4,84	5,94	5,92	4,81	0,00	0,01	12,11	99,85	
	27	57,84	6,92	3,07	13,20	2,46	1,85	0,00	0,01	14,70	100,05	
	28	36,36	6,25	2,05	26,32	1,98	1,87	0,00	0,00	26,2	101,05	
	avg	51,46	11,79	4,78	8,58	4,85	3,40	0,64	0,04	13,81	99,34	
MUZINE (DELVINE)	29	84,52	6,27	2,96	0,20	0,73	1,52	0,00	0,00	4,28	100,49	
	30	69,17	12,30	5,80	0,02	1,40	3,77	0,00	0,00	6,13	98,58	3,46
	31	86,52	5,06	239	0,11	0,53	1,33	0,00	0,00	3,87	99,81	
	avg	80,07	7,88	3,72	**0,11**	0,89	2,20	0,00	0,00	4,76	99,63	

DOMNIE SHKODER	32	91,99	3,18	1,52	0,31	0,50	0,72	0,00	0,07	1,96	100,24	
	33	71,60	14,49	2,50	0,14	1,54	3,68	0,00	0,00	5,.32	99,28	
	34	*77,64*	11,58	1,91	0,16	0,75	1,48	0,00	0,00	5,31	98,82	
	35	66,92	17,79	2,61	0,10	0,88	2,09	0,00	0,00	7,78	98,16	**38,84**
	36	72,37	13,87	2,79	0,26	1,05	1,74	0,00	0,00	7,01	99,08	
	37	91,79	3,41	1,54	0,17	0,42	0,75	0,00	0,00	1,79	99,86	
	38	63,46	2,94	1,38	17,13	0,83	0,82	0,00	0,00	14,59	101,14	
	39	85,09	5,63	2,34	0,40	0,99	1,67	0,00	0,00	2,75	98,88	
	40	73,53	4,32	2,00	9,82	0,80	1,03	0,00	0,24	7,60	99,33	
	avg	77,16	8,58	2,06	3,16	0,86	1,55	0,00	0,03	6,01	99,42	
DUMREA (BELSH)	41	62,76	10,36	5,65	5,06	3,37	1,53	0,60	0,00	8,70	98,02	16,68
	42	71,39	8,30	4,15	3,11	2,33	130	0,54	0,00	7,75	98,86	
	43	56,45	11,98	6,50	5,17	4,49	1,80	0,43	0,00	11,05	99,85	
	avg	52,75	8,90	3,89	14,24	2,51	1,49	0,47	0,03	15,17	98,91	
CAKRAN	44	49,45	10,16	5,32	13,37	3,60	1,84	0,56	0,00	15,21	99,51	13,07
	45	44,13	10,63	4,53	16,79	3,26	1,76	0,47	0,10	18,35	100,02	
	46	50,33	5,66	2,01	20,64	1,30	0,84	0,00	0,10	20,67	101,55	
	47	41,57	6,22	2,25	27,17	1,58	1,02	0,00	0,08	20,18	100,07	
	48	40,52	5,90	1,97	27,69	1,36	0,93	0,00	0,02	20,95	99,34	
	49	58,11	10,88	2,64	9,20	1,35	2,36	1,60	0,00	13,70	99,85	
	50	29,30	5,84	1,94	35,01	1,54	0,96	0,00	0,09	26,05	100,73	
	51	70,95	12,82	1,94	1,45	0,80	3,19	2,14	0,00	6,79	100,09	
	52	38,06	8,91	4,86	23,56	3,96	1,72	3,00	0,03	15,44	99,54	
	53	29,33	5,83	1,94	35,13	1,54	0,95	0,00	0,09	26,02	100,83	
	54	58,34	11,51	2,24	6,31	1,20	2,57	1,66	0,03	16,68	100,54	
	55	45,91	19,02	4,06	10,38	2,85	039	0,00	0,03	17,85	100,49	
	56	22,78	6,29	1,88	38,67	1,41	1,08	0,00	0,05	28,05	100,21	
	57	63,37	11,31	2,44	6,75	1,22	2,78	2,20	0,00	10,98	101,05	
	58	59,98	11,87	2,82	7,47	1,62	2,35	1,41	0,01	11,18	98,72	
	59	69,12	12,41	1,67	1,49	0,62	3,16	2,09	0,00	7,66	98,21	
	avg	48,20	9,70	2,78	17,57	1,83	1,74	0,95	0,04	17,24	100,05	
BEZHAN	60	64,59	9,88	4,42	5,40	236	1,39	0,87	0,01	8,91	97,84	
	61	39,69	10,07	3,98	18,57	3,22	1,05	0,00	0,23	18,10	94,91	
	62	42,12	9,79	6,45	0,85	3,10	1,31	0,68	0,11	11,74	76,16	
	63	54,27	12,77	6,46	3,51	4,04	1,52	0,00	0,29	14,94	97,80	
	64	54,12	12,10	12,21	1,17	3,46	1,58	0,00	0,16	12,43	97,23	
	65	55,64	13,27	6,78	2,20	3,94	1,64	1,79	037	12,89	98,51	
	avg	51,74	11,31	6,72	5,28	335	1,42	0,56	0,20	13,17	80,35	
HELMES	66	19,54	5,07	1,90	42,24	3,25	0,25	0,00	0,02	36,74	109,01	
	67	15,07	4,22	1,70	45,08	4,97	0,04	0,00	0,04	40,85	111,97	
	68	44,47	7,88	7,25	10,34	15,72	0,00	2,09	0,01	11,79	99,55	
	69	16,75	2,82	0,99	48,62	1,87	0,00	0,00	0,01	40,25	111,31	
	70	3,91	1,16	0,50	46,36	0,37	0,03	0,08	0,04	36,85	89,30	
	71	59,37	11,47	8,67	1,71	5,19	0,93	2,54	0,03	7,58	97,49	
	72	49,18	8,18	7,49	6,91	12,96	0,88	0,00	0,00	12,46	98,05	
	73	22,86	3,05	2,92	29,78	3,25	0,17	0,06	0,00	30,27	92,36	
	avg	28.89	5.48	3.92	28.87	5.94	0.29	0.59	0,0I8	27.09	101.12	

Only two of the examined tuff samples, namely from the VRAP and DOMNIE areas, had a reactive silica content exceeding that required by the EN 197-1. Testing of a laboratory cement produced with the VRAP tuff showed a high late strength [6,9,10].

Table 2 - VRAP tuff laboratory cement analysis

Nr	%VRAP	Blaine	H_2O%	In. Setting Time	Fin. Setting Time	1-d	2-d	7-d	28-d
1	0	3330	23.4	100	150	10.2	18.1	29.7	44.7
2	20	5000	30.6	180	230	13.5	21.8	36.0	49.3

Both of the above together with the SHKODER area tuffs have been rejected as potential quarries due to inadequate reserves and non-favorable mining conditions/problems. The GRAMSH, JOMEN/GJI-ROKASTER, MUZINE, DUMREA and CACRAN tuffs had a low reactive SiO_2 and could not be used as pozzolanic additives according to EN 197-1 [6]. Preliminary examination of the HELMES samples indicated that the quality of the raw materials from this area was rather low, since most of the samples had low a SiO_2 and a high carbonate content. Even though the reactive silica content in one of the JOMEN tuff samples came up low, the present investigation should focus on this area due to its considerable reserves and favorable mining conditions.

II. Kaolins

Kaolins from the Korthpula (react. SiO_2=41.6), Vig and Kaster areas were also examined as alternative pozzolanic sources. The strength of the respective laboratory cements was acceptable but the water demand of the cement produced with the Korthpula kaolin was high and that could cause problems in concrete [6 - 10].

Table 3 - KAOLINS laboratory cement analysis

Nr	Location	Blaine	H_2O%	In. Setting Time	Fin. Setting Time	1-d	2-d	7-d	28-d
1	-	3330	23.4	100	150	13.5	21.8	36.0	49.3
2	Korthpula	4430	33.4	140	200	10.9	15.8	26.5	35.8
3	Vig	4580	26.8	180	240	9.0	15.4	27.1	36.2
4	Kaster	4540	26.8	160	210	10.8	15.6	28.5	39.3

CONCLUSIONS

Tuffs: Almost all of the examined tuffs areas were rejected due to either quality of the material and/or potential mining conditions/problems and low reserves potential. The search for suitable pozzolanic materials is now focused on the JOMEN area due to its considerable reserves and favorable mining conditions despite its low reactive silica and additional tests and sampling is necessary. Further, it is recommended to clarify the potential of the areas of BEZHAN and PUKE.

Kaolins: The KORTHPULA kaolin had a high reactive silica content and could be considered as a potential pozzolana. However, the water demand of the respective blended cement was high and that could be a drawback when used for concrete manufacturing. The lab cement produced with the VIG kaolin had a low water demand and a satisfactory strength. Hence, the VIG kaolin could be used as pozzolana in case its reactive SiO_2 comes out higher than the min. limit of the EN 197-1. The above conclusions were based on spot surface samples; the suitability of the kaolins as pozzolanic additives will need to be verified based on samples of core drilling that is planned for the near future.

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IZVOD

TUFOVI I KAOLINI IZ RAZLIČITIH OBLASTI ZA UPOTREBU KAO POCOLANSKI MATERIJALI

Razni tufovi i kaolini bili su razmatrani za upotrebu u cementnoj industriji kao pocolanski aditivi. Ovi materijali su analizirani na hemijski i mineraloški sastav, sadržaj reaktivnog Si, a takođe, su korišćeni za proizvodnju i testiranje raznih mešavina cementa. Tufovi iz JOMENSKE oblasti, koji postoje u značajnim rezervama, problematični su zbog niskog sadržaja reaktivnog SiO_2. Uzorci kaolina, koji su proučavani, uzeti su iz oblasti KORTHPULA, VIG i DEJAI. Potraga za odgovarajućim tuf-materijalima je sada fokusirana na JOMEN oblasti. Kaolin iz KORTHPULA ima visok sadržaj reaktivnog Si i može se smatrati kao potencijalni pocolanski aditiv. Navedeni zaključci o podobnosti kaolina, kao pocolanskog aditiva iz ovih oblasti, na osnovu uzoraka sa površine zemljišta, moraće da se verifikuju na osnovu uzoraka uzetih sa većih dubina, koji su planirani za blisku budućnost.

Ključne reči*: tuf, kaolin, pocolanski aditiv, cement.*

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