Quality evaluation of cement raw materials from Lar region, south Iran

Rajabzadeh.M.A.[1], Askarizadeh.V.[2]

[1] Assistant professor, Department of earth sciences, Shiraz University

[2] MSc in economic geology from Shiraz University, vajihegeology@yahoo.com

Abstract

In Lar region, south Iran, carbonate rocks mainly limestone are exploited as CaO source from Asmari-Jahrom, Asmari and Bangestan formations which are exposed extensively near Kurdeh village in the area. Clay stone and Mishan marl formations near Gardaneh-Narenji situated 10 kilometers from Kurdeh village are also exploited for their Al2O3 and SiO2 as cement raw materials. The representative samples of the formations were analyzed using wet chemistry and XRF methods. The chemical results, in respect to authorized cement raw material standards, indicate that MgO is the most important impurity in limestone. The maximum MgO content is detected in Asmari-Jahrom samples and its minimum content is recorded in samples from Bangestan formation. Clay materials collected from Dangz Plain contain 0.8% chlorine which is more than the respective standard limits (0.6%). This may have undesirable effects on the annealing (burning) process. The mean value of aluminum is between 6 and 7.5% and silica varies between 20 and 30 Wt. % in the samples. Marl samples from Mishan formation contain 35.5% SiO2 and 8% Al2O3 on an average. The Cl content in these samples is less than that of clay materials taken from Dangz plain. Mixing of marl with other raw materials can also reduce the chlorine concentration in clay materials and consequently, the chemical composition of the final product will be improved. Mechanical measurements including compressive strength, autoclave expansion, Blain, Fineness and free lime content were conducted before and after adding 2% silica so as to determine the effects of raw materials on cement product quality. In general, the addition of 2% silica leads to elevation the compressive strength (77 kg/cm2) of cement materials.

Introduction

Portland cement is hydraulic cement composed primarily of calcium silicates which hardens into a solid mass when combined with water[1]. The chief chemical components of portland cement are calcium, silica, alumina and iron. Calcium is derived from limestone, marl or chalk, while silica, alumina and iron come from the sands, clays and iron ore sources[2]. The main chemical compound constituents of Portland clinker are: Tricalcium Silicate (C_3S), Dicalcium Silicate (C_2S), Tricalcium Aluminate (C_3A), Tetracalcium Aluminoferrite (C_4AF) and Gypsum (CSH_2).

Physical properties including fineness (blaine), soundness (autoclave expansion), compressive strength, setting time and free lime content, affect cement behavior and can be used in classification and comparison of Portland cement types[3]. Cement raw materials with greater fineness have a faster rate of strength gain[4] and adding of Cu to the materials causes to decreasing their setting time and kiln temperature[5]. The raw mix composition is one of the important factors which affect cement quality. The paper presents the effect of raw materials composition on cement product quality in LAR area, South Iran. Due to geological setting of Lar region in Southeast of Fars province, South Iran, it is proposed that the studied area is suitable for cement industry development.

Geological setting

Lar is located 300 km southeast of Shiraz, Capital of Fars Province, and South Iran. Geological formations near Kurdeh village provide the raw materials for cement production (Fig. 1)[6]. The study area is located within 54º 15' and 54 º 30’ east longitudes and 27º45' and 28º north latitudes. Huge exposures of limestone, shale and marl are seen in the area, thus the area could be considered as one of the high potential region for cement production in south Iran. The numerous parallel anticlines and synclines strike in E-W direction constitute the major structures and the plains are covered by alluvial and fluvial recent sediments. The main lithostratigraphy from base to top is composed of Eocene-Miocene Asmari-Jahrom limestones overlain by lower Miocene Mol- chehel members then by Mishan formation to top (upper Miocene age). The sequence is followed by Aghajari formation (Mio- Pliocene age) overlain by upper Pliocene Bakhtiari conglomerates. Besides the formations, salt domes (Infracamberian age) that are surrounded by radial fault systems are present in the Lar region.

Chemical analyses

Limestones: The representative limestone samples from Asmari-Jahrom formation (255samples), Asmari formation(110samples) and Bangestan formation
(400 samples) were collected and analysed using wet chemistry and XRF methods. The results show that the mean MgO quantity ranges in E. Core (0.12-2%), PE. Core (0.26-1.9%), PW. Core (0.24-1.37%), G. Core (0.18-1.8%), H. Core (0.17-1.73%) (Fig.2), The results are summarized in table 1. Comparison of results reveals that average MgO quantities are 1.04% in Asmari-Jahrom formation, 0.488% in Asmari formation and 0.311% in Bangestan formation.

Clay materials: 18 clay samples were collected from 6m. Holes boring in Dangz plain which is coverd with hollocene age sediments. Cl% of samples was titrated. Averages of Cl% in samples are calculated at ranging value from 0.2% to 0.8% (table2).

Marls: 8 holes are boring in Gardane–Narenji reservoir. 10 samples were collected from each holes. Average quantities of elements are summarized in table3.

Physical properties

Portland cements are commonly characterized by their physical properties for quality control purposes. Their physical properties can be used in classification and comparison Portland cements**.** In this study, physical tests including compressive strength, autoclave expansion (soundness), blaine (fineness), setting time, free lime percent performed on cement samples before and after adding 2% SiO_2 . The obtained results compared with standard values and summarized in table 4.

Compressive strength: compressive strength is carried out on a 50 mm (2-inch) cement mortar test specimen. The test specimen is subjected to a compressive load (usually from a hydraulic machine) until failure[3]. Table(5) shows ASTM C 150 compressive strength specifications[1].

Soundness: soundness refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion. The typical expansion test places a small sample of cement paste into an autoclave (a high pressure steam vessel) [3]. The standard autoclave expansion test is:ASTM C 151: Autoclave Expansion of Portland Cement[1] .

Fineness: fineness, or particle size of Portland cement, can be measured by several methods: Fineness of Portland Cement by the Turbidimeter. Fineness of Hydraulic Cement by the (No. 70) and (No170) Sieves, Fineness of Hydraulic Cement by Air Permeability Apparatus (Blaine) [3].

Setting time: setting tests are used to characterize how a particular cement paste sets. Normally, two setting times are defined: Initial set; occurs when the paste begins to stiffen considerably. Final set; occurs when the cement has hardened to the point at which it can sustain some load. Common setting time tests are the Vicat needle and the Gillmore needle, however the Vicat needle test is more common[3]. Table 6 shows ASTM C 150 specified set times[1].

Results

-Due to well distribution of limestone formation and clay materials with desirable quality in the Lar region, therefore the various types of Portland cement could be easily produced in the area at large scale.

-The MgO content in all profiles of Asmari-Jahrom formation. Except for H and E cores increases with depth, thus the quality of limestone decreases downwards.

-Results on Asmari-Jahrom samples show that P and E Cores limestone have the best quality among the other rock samples.

-C_3S and C_2S minerals in cement generally composed of SiO2 and these minerals play an important role in the cement strength gain. Therefore, we expect that adding of SiO2 to raw mix materials causes an increase in cement's strength. Comparison of obtained results from analyses before and after adding silica reveals that the addition of 2% SiO2 exceeds strength to 77.7 kg/cm2 in 28 days of test curing time. The others physical properties do not differ in samples after and before silica addition.

Table 1: Chemical analyses of Limestones

Oxides Sam.	**Fe2O3 %**	**CaO %**	**Cl %**	**K2O %**	**SO3 %**	**SiO2 %**	**Al2O3 %**	**MgO %**	**Na2O %**	**L.O.I %**
As-Ja.Fm.	0.13	53.5	0.00	0.03	0.15	0.8	0.24	1.04	0.28	41
As. Fm.	0.300	53.9	0.00	0.075	0.110	3.00	0.700	0.488	0.05	43.5
Bg.Fm.	0.360	54.406	0.00	0.05	0.037	0.681	0.286	0.311	0.048	43.5

Table 2: Cl percent of clay material from Dangz plain

Cl%	**samples no.**	**Cl%**	**samples no.**	**Cl%**	**samples no.**
1	0.1	7	0.3	13	0.3
2	0.1	8	0.3	14	0.4
3	0.2	9	0.2	15	0.5
4	0.2	10	0.2	16	0.4
5	0.2	11	0.3	17	0.8
6	0.2	12	0.3	18	0.4

Table 3: Chemical analyses of Mishan marl samples from Gardane-Narenji

samples oxides%	T-1	T-2	T-3	T-4	T-5	T-6	T-7	T-8
SiO2	34.58	34.87	33.57	35.43	35.21	36.15	35.33	35.46
Al2O3	7.76	7.82	8.22	8.43	7.9	8.45	8.27	8.24
Fe2O3	3.95	3.99	4.35	4.6	4.45	4.57	4.58	4.53
CaO	24.67	20.81	21.24	24.47	22.79	21.67	22.36	24.72
MgO	4.41	5.02	5.08	4.9	4.67	5.12	5.47	5.16
SO3	0.35	0.41	0.75	0.24	0.6	0.6	0.6	0.6
Na2O	0.80	0.71	0.78	0.81	0.84	0.89	0.9	0.8
K2O	1.03	1.13	1.12	1.08	1.04	1.11	1.11	1.1
Cl	0.13	0.09	0.09	0.08	0.11	0.1	0.11	0.1

Table 4: Physical properties of cement samples before and after silica addition

Physical properties	Com.srength			Autoclave expansion	Setting time		Blaine	Fineness		Free lime%
	3day	7day	28day		initial	final		4900	900	
standard	>100	>175	>315	<0.8	>45	<300	>2800.			<2
Avg. Before SiO2addition	236	298	345.6	0.26	116	220	3270.3	4.28	0.44	1.5
Avg.After SiO2addition	253.5	324.6	423.3	0.234	112	215	3122.5	4.6	0.48	1.35

Table 5: Portland cement Mortar Compressive Strength Specifications in MPa (psi)

Curing Time	Portland Cement Type				
	I	II	III	IV	V
3 days	12.4 (1800)	10.3 (1500)	24.1 (3500)	-	8.3 (1200)
7 days	19.3 (2800)	17.2 (2500)	-	6.9 (1000)	15.2 (2200)
28 days	-	-	-	17.2 (2500)	20.7 (3000)

Table 6: Specified Set Times by Test Method

Test Method	Set Type	Time Specification
Vicat	Initial	≥ 45 minutes
	Final	≤ 375 minutes

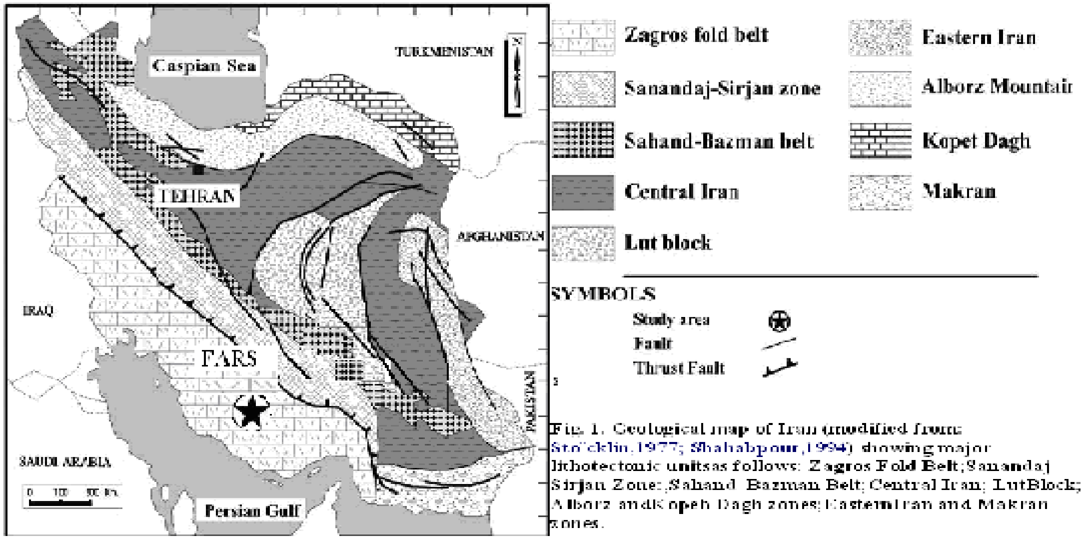

Fig. 1. Geological map of Iran (modified from: Sto'cklin,1977; Shahabpour,1994) showing major lithotectonic unitsas follows: Zagros Fold Belt;Sanandaj Sirjan Zone:,Sahand Bazman Belt; Central Iran; LutBlock; Alborz andKopeh Dagh zones;Easternlran and Makran zones.

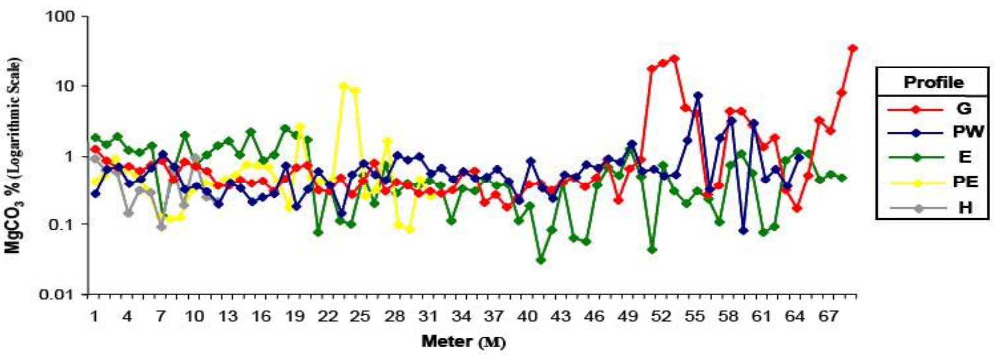

Fig.2: Variation of MgCO3 with depth in limestone cores

Refrences

1- Annual book of ASTM standards,section 4, Vol.04.02,1995

2-Evans, A. M., 2000,Principle of Ore mineral and Industrial mineral Geology:Shiraz University Publishers,Translators:Moore, F.,Modaberi,S., Moghadasi, J.

3.Muench,Steve."PortlandCement"(2007).[onlin].<http://guides.ce.washington.edu/ptc/Modules/03_materials/03-4_body.htm>.[12.6.2007]

4- Tsivilis, S., 1999, A Study of the parameters affecting the properties of Portland limestone cement: Cement and Concrete composite, V. 21

5-Suhua Ma, Xiaodong Shen, Xueping Gong , Baiqian Zhong,2006**,** Influence of CuO on the formation and coexistence of $3CaO{\cdot}SiO_2$ and $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ minerals, Cement and Concrete Research .Vol.36, Issue 9 .

6- Hezarkhani ,A.,2005, Hydrothermal evolution of the Sar-Cheshmeh porphyry Cu–Mo deposit,Iran: Evidence from fluid inclusions, Journal of Asian Earth Sciences 28 (2006) 409–422