Qatar Univ. Sci. J. (1996), 16(2): 315-323

THE MINERALOGY AND CHEMISTRY OF CEMENT AND CEMENT RAW MATERIALS IN THE UNITED ARAB EMIRATES

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معادن وكيميائية الأسمنت ومواد الأسمنت الخام في دولة الإمارات العربية المتحدة

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لقد تم دراسة المواد الخام والكلنكر والأسمنت من عدة مصانع أسمنت بدولة الإمارات العربية المتحدة وذلك باستخدام المجهر المستقطب والأشعة السينية والمجهر الماسح الإلكتروني والتحليل الكيميائي. لقد دلت الدراسات المعدنية والكيميائية على جودة الخامات المحلية لصناعة الأسمنت، كما أن الدراسات الجيولوجية المتوفرة تدل على وجود خامات محلية صناعية من الحجر الجيري والماري (الطفلة) والجبس واكاسيد الحديد والتي يمكن أن تحل محل الخامات المستوردة والمماثلة لها .

Key words: Cement, Clinker, Raw Materials, Mineralogy, Chemistry, United Arab Emirates.

ABSTRACT

The raw materials, clinkers and cements from different cement factories in the United Arab Emirates have been investigated using polarizing microscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM), and chemical analyses. The chemical and mineralogical analyses indicate that the local raw materials are suitable for cement industry. Geological review shows that there is a good potential for industrial-grade local occurrences of limestone, marl, gypsum and iron oxide, that may be used in place of imported similar commodites.

INTRODUCTION

Cement industry of the United Arab Emirates has been established and expanded very rapidly in the last twenty years. During that period, nine cement companies have been established (Fig. 1) with facilities to grind about nine million tons of cement annually (Table 1). Today, the industry comprises seven production sites. Two grinding plants are now out of production: Jebel Ali and Um Al-Quwain.

Limestone and sand, and in some cases gypsum and marl, are the only major raw materials which are supplied from local resources. The major raw materials are mixed with imported iron ore, bauxite and gypsum. For the cement industry about 100,000 tons of gypsum, 120,000 tons of iron ore and 180,000 tons of bauxite are imported annually (1, 2).

The objective of this study is to compare cements, clinkers and raw materials from the different cement factories in the United Arab Emirates by means of mineralogical and chemical investigations. Recommendation for the possible use of local raw material will be discussed through a geological review of the current situation.

Potential of raw materials in the United Arab Emirates

In U.A.E., bauxite, iron oxide and gypsum are usually imported from India and Australia. Table 2 shows the average quantity of raw materials used by the cement industry in the year 1992.

Limestone deposits are widespread in a substantial part of the country. Large tonnage is available from the Ruus al Jibal area, notably from the Musandam Limestone Group in the northeastern part of the Emirates (Ras al Khaimah, Fig. 1). Limestone from this source is used as the feedstock for large cement works at Ras al Khaimah (Union, Gulf and

Table 1

Cement industry of the United Arab Emirates

Emirate	Company		Cement capacity
Ajman	Ajman Cement Co.	(ACC)	0.750Mtpa
Abu Dhabi	Al Ain Cement Co.	(AACF)	0.780Mtpa
Fujairah	Fujairah Cement Co.	(FCC)	0.79Mtpa
Ras Al-Khaimah	Gulf Cement Co.	(GCC)	1.240Mtpa
	Union Cement Co	(UCC)	1.270Mtpa
Dubai	National Cement Co.	(NCC)	2.00Mtpa
	Jebel Ali Cement Co.	(JACC)	0.1Mtpa*
Sharjah	Sharjah Cement Co.	(SCC)	1.33Mtpa
Um Al-Quwain	Um Al-Quwain Cement Co.	(UQCC)	0.50Mtpa*

*Out of operation
Source: (2)

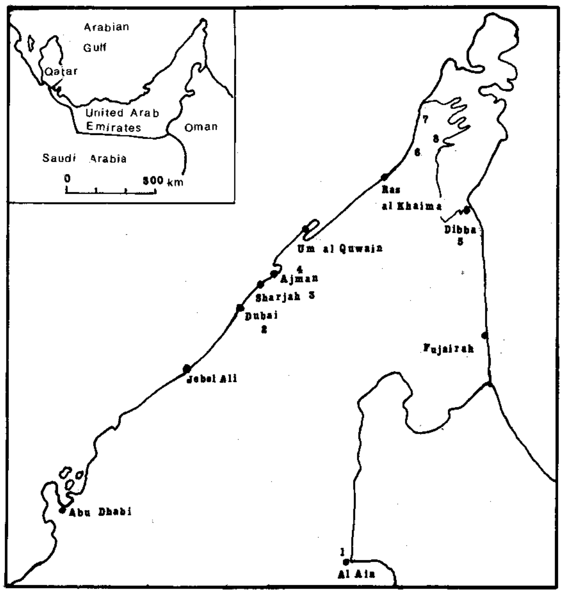

Fig. 1: Location map of the cement factories in the United Arab Emirates. 1: Al Ain Cement Factory, 2: National Cement Factory, 3: Sharjah Cement Factory, 4: Ajman Cement Factory, 5: Fujairah Cement Factory, 6: Gulf Cement Factory, 7: Union Cement Factory, 8: White Cement Factory.

Table 2

Quantity of raw material used in teh cement industry in the U.A.E. in the year 1992

Factory	Local raw material			Imported raw material			
	Limestone	Marl	Gypsum	Silica	Bauxite	Iron ore	Gypsum
	tons/year				tons/year		
Al Ain	820,000	450,000	40,000	50,000	–	18,000	–
Fujairah	500,000	140,000	–	–	–	15,000	20,000
Gulf	1,200,000	–	–	250,000	40,000	20,000	40,000
Union	1,200,000	–	–	250,000	40,000	20,000	40,000
White cement	240,000	–	–	15,000	27,000	–	15,000
Ajman	Imported clinker from Ras al Khaimah		–	–			10,000
National	Details uncertain						
Sharjah	Details uncertain						

White Cement Factories). Good quality limestones do also occur in the Hawasina Series southwest of Dibba (3). The softer and less pure dolomitic and cherty limestones of Maestrichtian age which occur a Jebel Faiya (4, 5) are used as feedstock for the Sharjah Cement Factory. In Abu Dhabi Emirate, huge reserves of limestone and marl exist in Jebel Hafit area at Al Ain (6, 7), where part of the Tertiary sequence provides the feedstock for the Al Ain Cement Factory.

Table 3

Types of studied samples

Sample No.	Type	Cement Factory	
RC-1	O.P.C. Clinker	Fujairah	(FCI)
RC-2	O.P.C. Clinker	Ajman	(ACC)
RC-3	O.P.C. Clinker	Dubai	(NCC)
RC-4	S.R.C. Clinker	Ajman	(ACC)
RC-5	O.P.C. Clinker	Union	(UCC)
RC-6	S.R.C. Clinker	Dubai	(NCC)
RC-7	O.P.C. Clinker	Al Ain	(AACF)
RC-8	S.R.C. Clinker	Al Ain	(AACF)
RC-9	Limestone	Gulf	(GCC)
RC-10	Limestone	Fujairah	(FCI)
RC-11	Limestone	Union	(UCC)
RC-12	Silica sand	Dubai	(NCC)
RC-13	Iron oxide	Fujairah	(FCI)
RC-14	Bauxite	Dubai	(NCC)
RC-15	Bauxite	Union	(UCC)
RC-16	Bauxite	Fujairah	(FCI)
RC-17	Iron oxide	Al Ain	(AACF)
RC-18	Iron oxide	Union	(UCC)
RC-19	Limestone	Al Ain	(AACF)
RC-20	Marl	Al Ain	(AACF)

O.P.C.: ordinary portland cement
S.R.C.: sulfate resistant cement

Gypsum occurs in recoverable quantities in the Tertiary rocks of the Lower Fars Formation and in the Cambrian rocks of the Hormuz series in the islands of Sir Bani Yas, Dalma, and Sir Abu Nu'air as well as in Jebel Dhanna and Jebel Ali (8). The largest deposits of gypsum, however, lies at Jebel Hafit area in Al Ain. It is exposed in the Oligocene and Miocene sequences of limestone, sandy limestone and marl. This occurrence is estimated to contain 3 million tons of gypsum (8).

Iron materials are found in small zones as siliceous hematite and hematite schist within the metamorphic unit near Dibba. Small magnetite bearing bodies are found within the gabbros near Fujairah (8). Hematite and limonite deposits were also described to occur on Sir Abu Nu'air island. However, these occurrences have limited potential for cement industry (8). Larger deposits are found in the form of specular hematite in Dalma Island.

Method of study

The laboratory study was carried out on eight clinker samples and twelve rock samples representing the different local and imported raw materials (Table 3). Clinkers and raw material analyses have been carried out at the Central Laboratories of the Egyptian Geological Survey and Mining Authority, Cairo, at Al Ain Cement Factory, and at the National Cement Factory of Dubai. Cement analyses were carried out at Ajman Cement Company. Mineralogical studies include X-ray diffraction (XRD), polarizing microscopy, and sacnning electron microscopy SEM). X-ray diffraction analysis was carried out using a Phillips X-ray diffractometer (Type PW 1710). Scanning electron microscopic study was carried out on 2 cement clinker samples (RC-1 and RC-8) using SEM model JEOL, JSM-T20, with accelerating voltage 19 kV, magnification of 35X up to 10000X and resolution of 200A. Chemical analysis was carried out for 4 clinker samples and 12 raw material samples, using X-ray fluorescence equipment, model Phillips (Type PW 1404). The concentrations of the analysed elements were determined by using software Kernl X-44. Major elemental analysis was done on beads, which were prepared by mixing 1 gm of the sample with 6 gms flux ($Li_2B_4O_7$) and 0.35 gms ammonium iodide. The mixture is fused at about 1150°C using a bead machine model Perl X-1 and a Pt crucible.

MINERALOGICAL STUDY

Microscopic investigation

Microscopic investigation of clinkers indicates the presence of five principal constituents (Fig. 2-8): alite (C_3S), belite (C_2S), celite (C_4AF), felite (C_3A), as well as minor isotropic and black residue (glass, calcite and lime). Most of the constituents are nonmetallic, very fine-grained and show high refractive indices. Alite occurs usually as phenocrysts. Celite occurs as a reddish brown gel with strong pleochroism. Crystals of free CaO may exist as inclusions in the C_3S or as crystal aggregates. C_3A and C_4AF and glass make up the large part of the intestital materials. Alite makes up the major constituent in all of the studied samples. Belite and celite are the second major components whereas felite is mi-

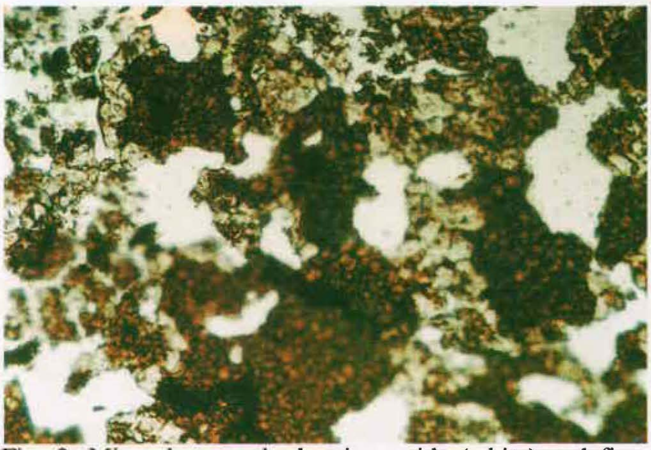

Fig. 2: Microphotograph showing voids (white) and fine-grained alite. 25 X

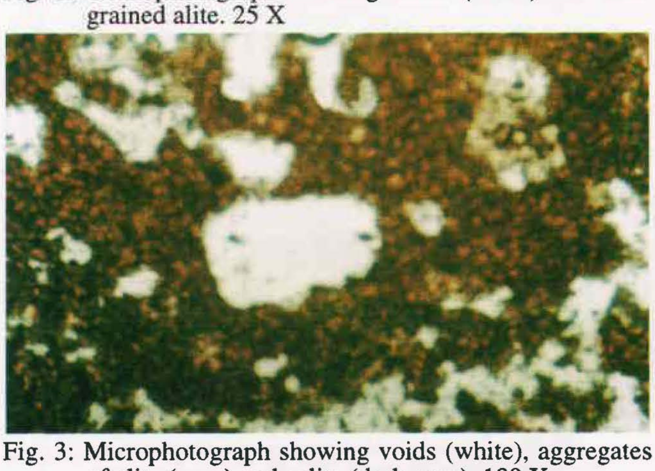

Fig. 3: Microphotograph showing voids (white), aggregates of alite (grey) and celite (dark grey). 100 X

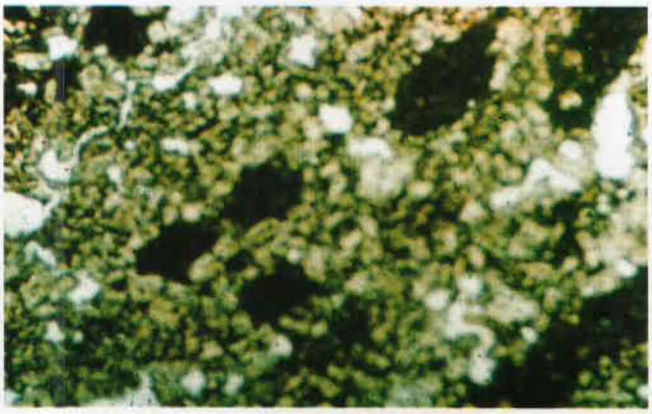

Fig. 4: Microphotograph showing nets of free lime (dark grey) and alite (grey). 25 X

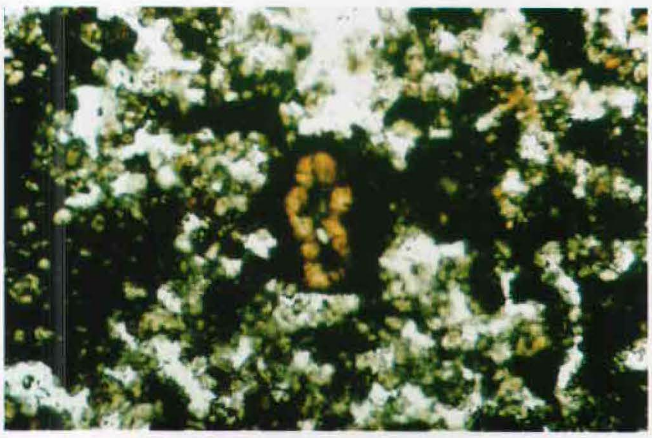

Fig. 5: Microphotograph showing alite (grey) with reaction rim of free lime (black). 25 X

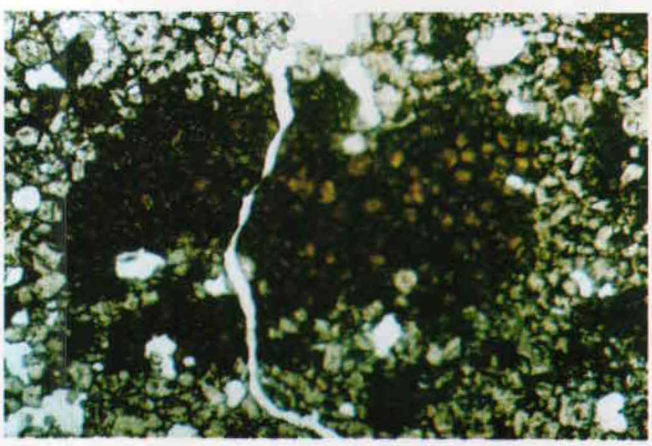

Fig. 6: Microphotograph showing aggregates of celite (dark grey) and alite (grey).

nor. Most of the investigated clinkers show high void percentage in the ground mass (Figs. 2, 3). Nets of free lime (Fig. 4), reaction rims (Fig. 5) and crystal aggregate (Fig. 6) textures are common. The homogenous distribution of free lime in the ground mass (Fig. 4) refers to high CaO-contents in the clinker.

The scanning electron microscope (SEM) appears to have better potentials for the examination of cement clinker since these are often fine-grained that they cannot be resolved properly with the polarized light microscope. The obtained SEM-microphotographs (Figs. 7, 8) show alite with well developed external shapes and hexagonal outlines. The alite crystals are larger than other existing phases.

Fig. 7: Scanning electron microphotograph showing hexagonal crystal of alite. Ordinary portland cement clinker, Fujairah. 1000 X

Fig. 8: Scanning electron microphotograph showing alite (grey), free lime and calcite (white). Sulphur resistant clinker, Al Ain. 1000 X

Table 4

X-ray diffraction data of the studied samples

Sample No.	Major Minerals	Minor Minerals	Trace Minerals
	Clinkers		
RC-1	Alite	calcite, belite	celite, felite
RC-2	Alite	calcite, belite	celite, felite
RC-3	Alite	calcite, belite	celite, felite
RC-4	Alite	calcite, belite	celite, felite
RC-5	Alite	calcite, belite	celite, felite
RC-6	Alite	calcite, belite	celite, felite
RC-7	Alite	calcite, belite	celite, felite
RC-8	Alite	belite	celite, felite
	Raw materials		
1. Carbonate			
RC-9	Calcite	---	---
RC-10	Calcite	dolomite	illite
RC-19	Calcite	---	quartz, illite
2. Bauxite			
RC-14	Gibbsite, Hematite	quartz	calcite
RC-15	Gibbsite Kaolinite	quartz	calcite
3. Marl			
RC-16	Gibbsite Calcite	hematite	kaolinite
RC-20	Calcite	montmorillonite	kaolinite
4. Silica sand			
RC-12	Quartz	calcite	montmorillonite
5. Iron oxide			
RC-13	Hematite	kaolinite + gibbsite	calcite
RC-17	Hematite Kaolinite	quartz + gibbsite	illite
RC-18	Hematite	---	quartz

X-RAY DIFFRACTION

Clinkers

The results of X-ray diffraction analysis of the samples of clinkers and raw materials are given in Table 4. All clinker

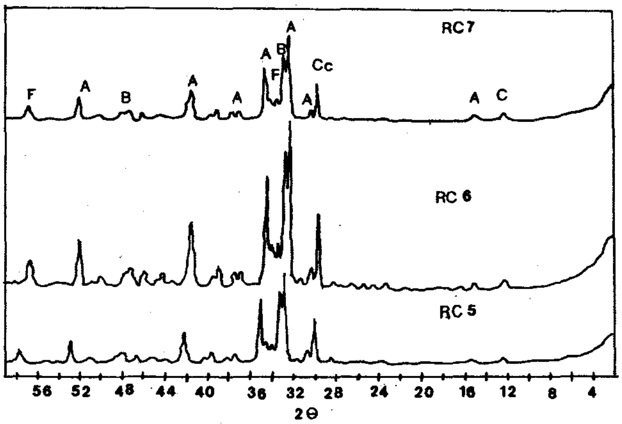

Fig. 9: Representative X-ray charts for the investigated clinkers. A: Alite (C3S), B: Belite (C2S), C: Celite (C4AF), CC: Calcite, F: Felite (C3A).

samples contain alite as a major mineral phase, calcite and belite are minor. Other phases are trace. Figure 9 shows representative patterns of the identified minerals.

Raw materials

The limestone samples show calcite as a major mineral with traces of kaolinite and quartz. The limestone from Fujairah Cement Company has dolomite beside calcite as a major mineral. The analysed bauxite samples have a major mineral composition of gibbsite ± hematite ± kaolinite ± calcite and quartz. The marl consists mainly of calcite, clay minerals and quartz. The silica sand contains mainly quartz, whereas calcite is minor and clays are trace. The iron oxides consist of hematite as a major mineral and quartz, gibbsite and kaolinite as minor minerals, whereas calcite and illite are found in trace amounts (Table 4).

CHEMICAL ANALYSIS

Raw materials

The analysed local limestone is almost pure calcite with small impurities of SIO_2 and MgO (Table 5). The analysed marl from Al Ain area show relatively high amount of SiO_2 - 23 wt. %), high CaO (33 wt. %) and moderate amounts of Al_2O_3 (6 wt. %). Imported bauxite contains high Al_2O_3 (46-51 wt. %), and Fe_2O_3 (12-20 wt. %) but low SiO_2 (2-3 wt. %). The imported iron oxide contains high Fe_2O_3 (81-96 wt. %) and the silica sand contains up to 91 wt. % SiO_2.

Clinkers

Analyses of representatives homogenous samples of clinkers from the Al Ain Cement Factory, National Cement Factory, the Ajman Cement Factory and Union Cement Factory are given in Table 6. The composition is relatively similar to standard clinker compositions. However it is slightly different from the cement composition due to the addition of gypsum to the later.

Cements

The results of cement analyses, mineral components and physical properties from different cement factories are given in Table 7, and displayed in Figures 10-13. The chemical composition and the physical properties of the analysed cement from the different cement factories in the U.A.E. indicate a good quality cement and are comparable to good quality cements reported by Taylor (9) and Lea (10).

Table 5

Results of raw material chemical analyses (wt. %)

	Carbonate				Marl	Bauxite		
	RC-9	**RC-10**	**RC-11**	**RC-19**	**RC-20**	**RC-14**	**RC-15**	**RC-16**
SiO_2	0.56	6.79	1.26	3.96	22.97	3.10	3.32	2.26
TiO_2	0.04	0.12	0.03	0.14	0.47	4.95	4.21	3.19
Al_2O_3	0.03	0.18	0.20	1.28	6.09	46.71	46.71	50.83
Fe_2O_3	0.01	0.01	0.04	1.38	4.28	17.73	19.46	12.56
MnO	0.01	0.01	0.01	0.01	0.03	0.03	0.02	0.05
MgO	0.19	0.30	1.43	0.70	1.08	0.39	0.01	0.06
CaO	54.92	51.30	53.80	51.03	33.10	0.14	0.03	2.19
Na_2O	0.10	0.10	0.10	0.29	0.10	0.10	0.10	0.10
K_2O	0.01	0.01	0.02	0.19	0.69	0.11	0.10	0.05
P_2O_5	–	–	–	0.01	0.10	0.08	0.01	0.20
L.O.I.	42.93	40.10	41.70	41.01	31.40	25.49	25.48	28.64

Table 5 continued

	Iron oxide			Silica sand
	RC-13	RC-17	RC-18	RC-12
SiO_2	9.42	4.10	1.60	91.40
Ti_2O_3	0.14	0.65	0.50	0.12
Al_2O_3	2.89	3.50	0.51	3.27
Fe_2O_3	81.03	89.01	95.51	1.29
MnO	0.52	0.33	0.10	0.10
MgO	0.19	0.08	0.30	0.66
CaO	0.89	0.08	0.85	0.89
Na_2O	0.10	0.10	0.10	0.10
K_2O	0.06	0.04	0.01	0.67
P_2O_5	0.09	0.05	0.05	0.05
L.O.I.	5.49	2.97	0.74	2.40

Table 6

Results of chemical analyses of clinker

Sample	ACC	UCC	AACF	NCC	BS12-78	ASTM-81
SiO_2	21.5	21.9	21.53	21.3	21.19	22.2
Al_2O_3	3.7	4.7	3.58	3.92	5.36	4.7
Fe_2O_3	5.2	4.20	4.26	5.19	3.27	2.1
MgO	0.7	1.0	2.01	1.18	0.89	1.1
CaO	65.0	64.5	65.09	65.04	64.4	65.8
Na_2O	0.2	0.12	0.24	0.25	0.36	0.04
K_2O	0.35	0.25	0.84	0.28	0.58	0.19
wt. %*						
C3S	61.1	52.9	65.45	59.43	45	54
C2S	15.6	22.7	12.35	16.32	27	23
C3A	1.0	5.4	2.28	1.62	9	9
C4AF	15.8	12.7	12.96	15.78	10	6

* calculated according to Bogue formulae (21)
ACC: Ajman cement Company
UCC: Union Cement Company
AACF: Al Ain Cement Company
NCC: National Cement Company
BS12-78: British Standard
ASTM-81: American Standard

Table 7
Analyses and physical properties of ordinary portland cement from different cement factories in the U.A.E.

	UCC	GCC	NCC	FCI	SCF	ACC	AACF
wt. %							
SiO_2	21.39	21.67	20.80	19.84	21.80	21.79	21.11
Al_2O_3	5.38	5.28	5.35	5.83	5.18	5.39	4.78
Fe_2O_3	4.20	4.20	3.60	3.20	3.60	3.65	3.30
MgO	1.10	0.70	1.00	1.20	1.20	0.60	1.67
CaO	63.80	64.90	64.90	63.72	63.80	64.80	64.17
Na_2O	0.38	0.22	0.45	0.40	0.39	0.25	0.32
IR	0.15	0.10	0.20	0.20	0.10	0.10	0.50
Free Lime	0.67	0.56	0.67	0.67	0.67	0.50	1.10
Physical properties							
wt. %							
LSF	89.58	91.21	94.37	95.77	89.86	90.57	97.82
LCF	88.61	90.40	93.37	94.74	88.90	89.85	93.30
SR	2.23	2.28	2.32	2.19	2.48	2.41	2.61
AR	1.28	1.25	1.48	1.44	1.47		1.45
wt. %							
C_3S	44.47	50.51	55.49	54.73	46.24	48.48	56.66
C_2S	27.77	24.02	17.77	15.59	27.61	25.89	17.86
C_3A	7.15	6.88	8.08	10.03	7.63	8.10	7.09
C_4AF	12.78	12.78	10.95	7.73	10.95	11.10	10.03
% S.C.							
27.50	27.50	26.50	23.00	26.00	26.75	28.00	26.00
Initial	225	190	100	195	170	185	110
Final	265	225	145	250	225	225	175
90r	1.22	1.75	3.04	1.40	0.95	1.30	0.50
45r	10.56	8.85	19.00	12.50	10.15	8.82	5.40
SA m_2/kg	334	305	334	325	327	311	331
3 days	34.4	32.9	35.0	41.1	35.5	32.9	36.0
7 days	45.8	45.4	42.2	49.1	47.6	50.7	44.0
28 days	62.7	60.5	56.0	61.9	61.2	75.3	54.0

IR: Insoluble residue, LSF: Lime saturation factor
LCF: Lime combination factor, SR: Silica ratio
AR: Aluminium ratio, % S.C.: Percentage of saturation capacity
SA: Strength after

DISCUSSION

Portland cement is prepared by igniting a mixture of raw materials, one of which is calcium carbonate and the other is aluminium silicates. The most typical materials that fit these compositions are limestone and clay or marl; bauxite, iron oxide, silica sand may be used in adjusting the chemical composition. Gypsum is commonly used as a retarder.

Analyses of local raw material (limestone and marl) indicate their suitability for cement industry. The marl from Jebel Hafit in Al Ain area shows a very suitable composition and could be a good source for SiO_2, Al_2O_3 (Table 5). This marl could replace imported bauxite. However, it is poor in Fe_2O_3 and a source for iron should be added. The market study shows a need for crushed gypsum within the Emirates, which would replace imported gypsum used in cement manufacturing plants in some parts of the country (11). The total resources of argillaceous materials (claystone) which occur between the gypsum beds at Al Ain are quantitatively similar to the resources of gypsum (e.g. 3 million tons). These materials could be a possible feedstock for cement manufacturing, especially white cement. The analysed representative clinkers from the Emirates have normal composition which is comparable to the British and American standard clinker composition (Table 6). However, the Emirates clinkers have relatively lower Al_2O_3 and higher Fe_2O_3. The silica ratio (SiO_2 wt. %/(Al_2O_3 wt. % + Fe_2O_3 wt. %), the alumina ratio (Al_2O_3 wt. %/Fe_2O_3 wt. %) and the lime saturation factor LSF (CaO wt. %/(2.8*SiO_2 wt. % + 1.2*Al_2O_3 wt. % + 0.65*Fe_2O_3 wt. %) are important factors for chemical control of cement (12, 13, 14). The potential for C_3S formation is given by the lime saturation factor. Figure 10 shows that Al Ain, National and Fujeirah cements have the highest LSF and the highest C3S. However, C_2S is negatively correlated with LSF. The Union cement has the lowest LSF and C_3S but the highest C_2S. C_3S is responsible for much of the strength of concrete up to 28 days, so it is im-

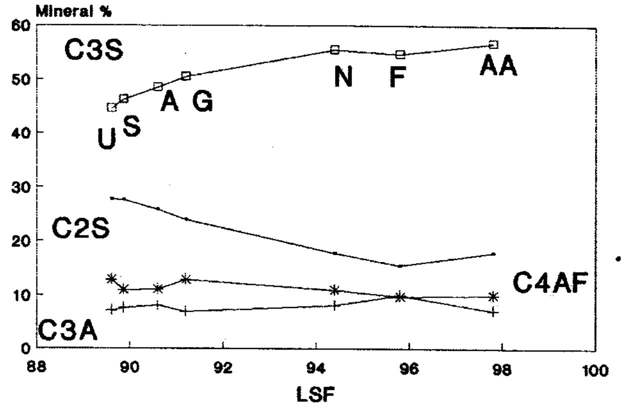

Fig. 10: Lime saturation factor (LSF) vs. Mineral wt % calculated according to Bogue [21] (C3S, C2S, C3A, C4AF). U: Union cement, F: Fujairah cement, AA: Al Ain cement.

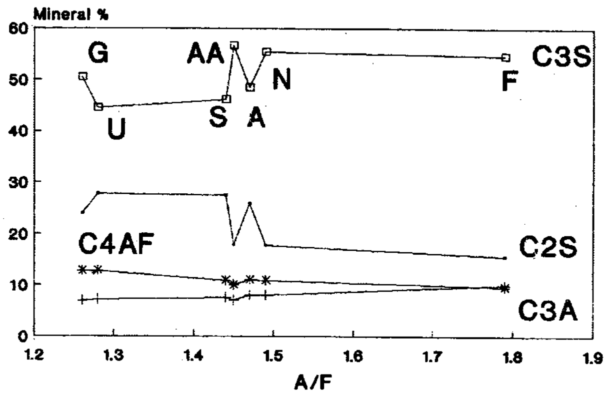

Fig. 11: Aluminium ratio (A/F) vs. Mineral %. Abbreviation as in Fig. 10.

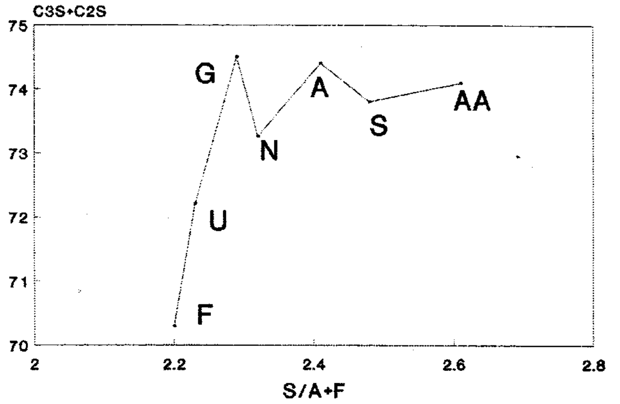

Fig. 12: Silica ratio (S/A+F) vs. calcium silicate (C3S, C2S). Abbreviation as in Fig. 10.

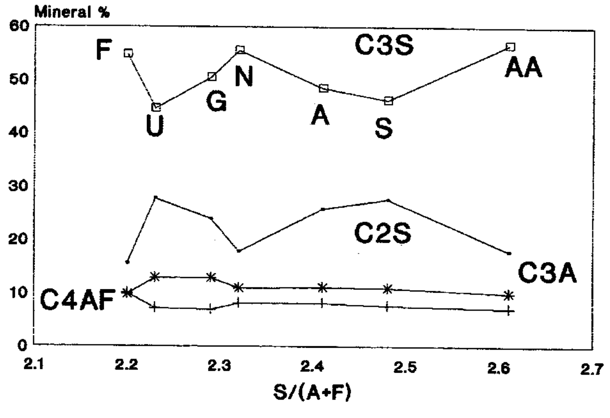

Fig. 13: Silica ratio (S/A+F) vs. Mineral %. Abbreviation as in Fig. 10.

portant to maximize the C_3S content. C_2S, however, is still an important strength-giving compound. It contributes to strength development at 28 days and beyond (15, 16, 17, 18, 19, 20). C_3A and C_4FA do not show a clear relation to LSF, but the higher the alumina ratio, the higher the C_3A % and the lower the C_4AF % (Fig. 11). The alumina ratio influence the characteristics of the molten flux (molten alumina, ferric oxide combined with lime). Both C_3A and C_4AF make little contribution to strength. C_3A influence the early hydration reactions which determine the setting behaviour of cement. C_4AF gives cement its grey colour. The silica ratio is a controlling factor that determines the possible amount of calcium silicates formed in the clinker (Fig. 12). The highest C_3S+C_2S is found in the Gulf cement, followed by Ajman, Al Ain, Sharjah, and National cements. The Gulf and Ajman cements show abnormality with respect to their calcium silicate % and the silica ratio. Either lower calcium silicate or higher ratio is expected in this case. The lowest silica ratio and lowest calcium silicate are observed in the Fujeirah cement, whereas C_3S is the highest, followed by Al Ain, National, Gulf and Ajman cements. The lowest C_3S and highest C_2S are observed in the Union cement and Sharjah cement. (Fig. 13).

CONCLUSION

The overall conclusion of this work is that there is a range of potential raw materials (gypsum, marl and limestone), suitable in chemical composition, for cement industry. These local raw materials should replace the imported ones. Microscopic and chemical study of clinkers and cements are essentials for the control of cement quality which should be monitored not only from the chemical point of view but also from the mineralogical point of view.

ACKNOWLEDGEMENTS

This work was financially supported by the United Arab Emirates University. The author is grateful to Hassan El-Etr for his support and encouragement to carry out this research.

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