ISSN: 0067-2904
GIF: 0.851

The Engineering Properties and Geochemical Relationship For The Volcaniclastic Rocks Of The Muqdadiya Formation In Hemrin Area, NE. IRAQ

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Abstract
Volcaniclastic rocks of Al Muqdadiya Formation (Pliocene) in Injana area, southern Hemrin anticline, NE of Iraq, were studied (petrographically, physically, mineralogically and geochemically , as well as the engineering properties) to assess the suitability of volcaniclastic rocks to use them in industry as refractories. The results show that the physical and engineering properties change with the temperature change. The bulk density and the specific gravity increase by increasing temperature while the apparent porosity, water sorption and the linear shrinkage decrease. On the other hand the compressive strength increase by increasing temperature. The volcaniclastics have very low thermal conductivity.
The petrography, mineralogy and geochemistry of these rocks show that there are positive and negative correlations between the major oxides as well as the minerals that make it suitable for refractory industry.

Keywords: Volcaniclastics, Engineering properties, Geochemical relationship, Refractories.

الخواص الهندسية والعلاقات الجيوكيميائية لصخور الرماد البركاني لتكوين المقدادية في منطقة حمرين شمال شرق العراق

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الخلاصة:
تمت دراسة صخور الفتات البركاني في تكوين المقدادية (البليوسين) في منطقة انجانة جنوب طية حمرين المحدبة بتروغرافيا ،فيزيائيا ،هندسيا، معدنيا وجيوكيميائيا لغرض تقييم مدى ملاءمة هذه الصخور في صناعة الحراريات. أظهرت النتائج ان الخواص الفيزيائية والهندسية تتغير بتغير درجه الحرارة، حيث تزداد كثافة الصخور بارتفاع الحرارة كذلك الوزن النوعي . أما المسامية الظاهرية و امتصاص الماء و الانكماش فقد تناقص . بالمقابل مقاومة الانضغاط تزداد بزيادة درجة الحرارة. بالنسبة للتوصيل الحراري فهي رديئة التوصيل. لقد تبين من خلال دراسة الخواص البتروغرافية والمعدنية والجيوكيميائية ان هناك علاقات ايجابيه واخرى سلبية بين الاكاسيد الرئيسية لهذه الصخور بالاضافة الى المعادن التي تجعلها ملائمة لصناعة الحراريات.

Introduction

The Volcaniclastic term was defined as all clastic sediments and rocks, regardless of depositional process, whose particles are predominantly of volcanic origin. [1]. Volcaniclastic consists of clay-size to sand-size particles of igneous rock material that have been blown into the air by an erupting volcano. The term is used for the material while it is in the air, after it falls to the ground and sometimes after it has been lithified into rock. The terms "volcanic dust" and "volcanic ash" are both

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used for the same material, however "volcanic dust" is more appropriately used for powder-size material. [2].

The study area is located in Hemrin area at Dyala Governorate northeast of Iraq where the Muqdadiya Formation is exposed there on both sides of the Southern Hemrin anticline at longitudes between (44°,34',00"- 44°,44',00") E, and latitudes (34°,28',00"- 34°,35',00") N (Figure-1). It is situated to the NE extremity of the Arabian platform, in the Hemrin-Makhul subzone within unstable shelf of Iraq (Foot Hill zone) in Hemrin area [3].

The Muqdadyia Formation (Pleistocene) is one of formations exposed in this area on the two sides of Southern Hemrin anticline and parallel to the anticline axis, while the Injana Formation represents the core of this anticline Figure-1.

Methodology

The tested samples were gathered by the cooperation between the Iraqi geology survey institute and a staff from department of geology, college of science, in university of Baghdad. The tests were applied on twenty two samples.

Tests include:

1. The physical properties for coarse-grained and fine-grained volcaniclastics.
2. Study the mechanical properties.
3. Mineralogy and Geochemical analysis.
4. Analyze the results.

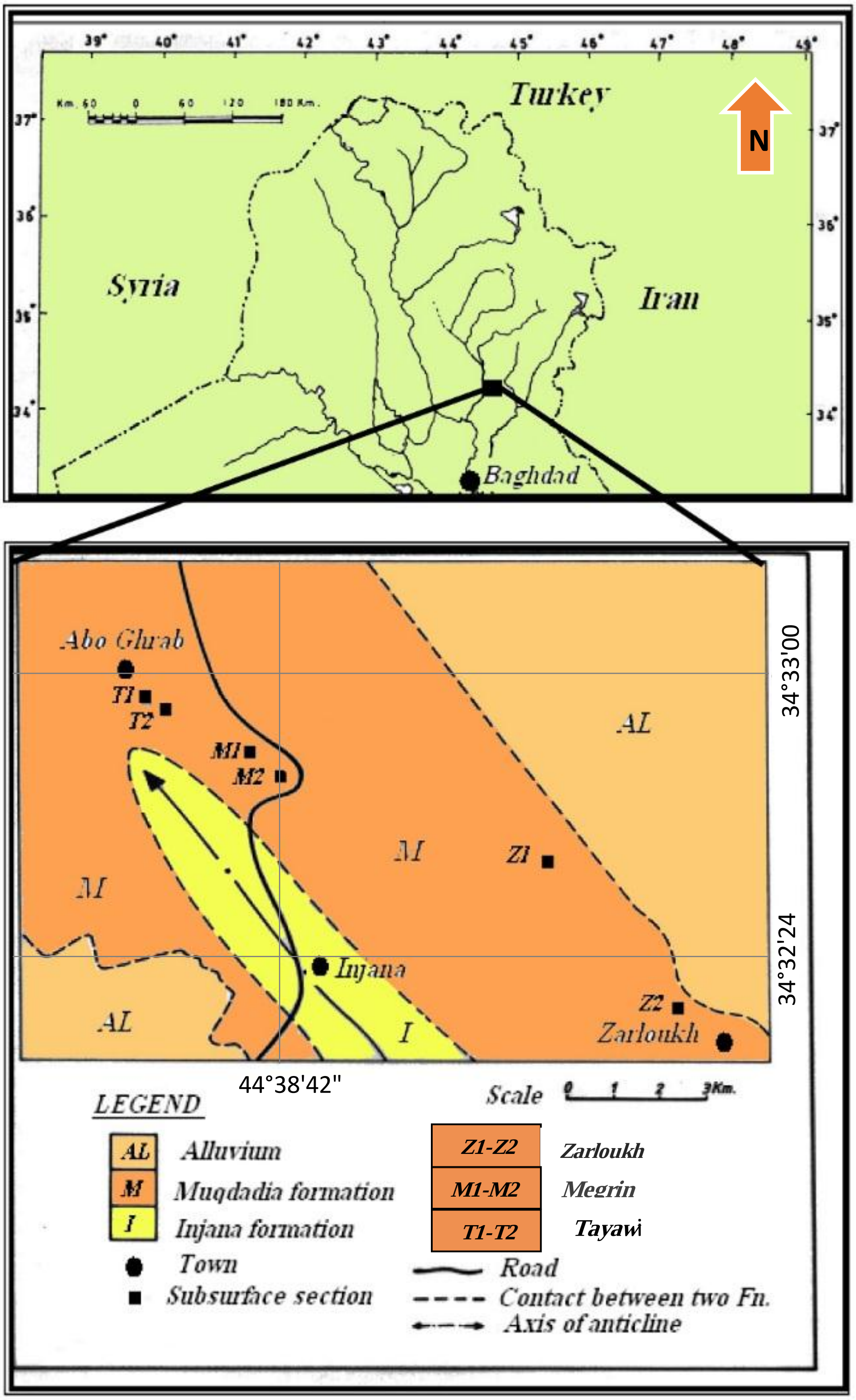


Figure 1- Location and geological maps of the studied area (modified after[4]) .

Petrology of volcaniclastic rocks

The type of volcaniclastic rocks in the present study were defined as unique sedimentary facies; this sediment was generated by exceptional processes [4]. The base of classification of volcaniclastic rocks will be different from the normal sedimentary rocks. The sedimentological study for the volcaniclastic units were according to framework of the volcaniclasts, the degree of mixed grains and/or grain-size variation, and from these bases it can be divided into two main facies [4].

1. Non-reworking sediments (tuffstone facies) represents primary sedimentation from the eruption cloud. This type of rocks is important in the present study.
2. Reworking sediments (rocky tuffstone & tuffaceous rock), represents secondary sedimentation from suspension load and\or bed load. This type of rocks is not important in the present study.

The studied sections are located in three sections (Magarin, Tayawi and Zarloukh), which represent the lower part of the Muqdadiya Formation as a succession alternate from the tuffstone, rocky tuff and tuffaceous rocks. The distribution of the volcaniclastic unit showing increase thickness from 50cm in Tayawi (T1, T2) to 2-5m in Magarin (M1, M2) and 8m in Zarloukh (Z1, Z2) Figure-2,Figure-3,Figure-4 &Figure-5.

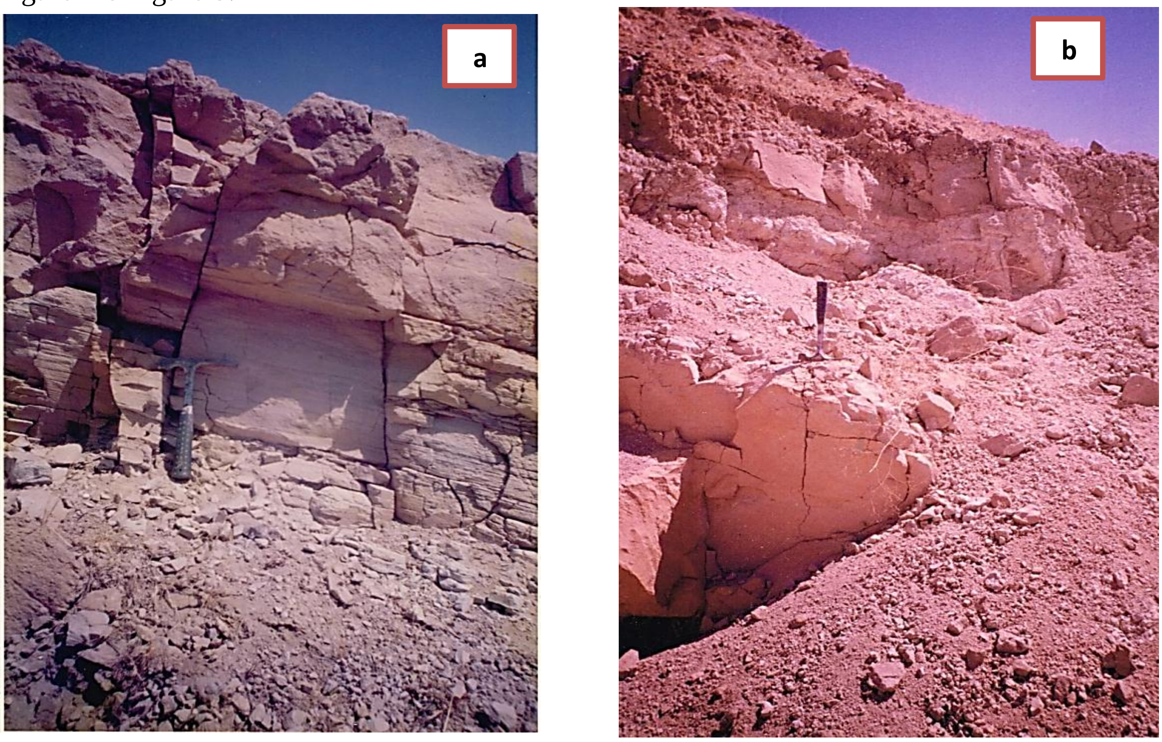


Figure 2- a. Megrin I section and b. Zarloukh section.

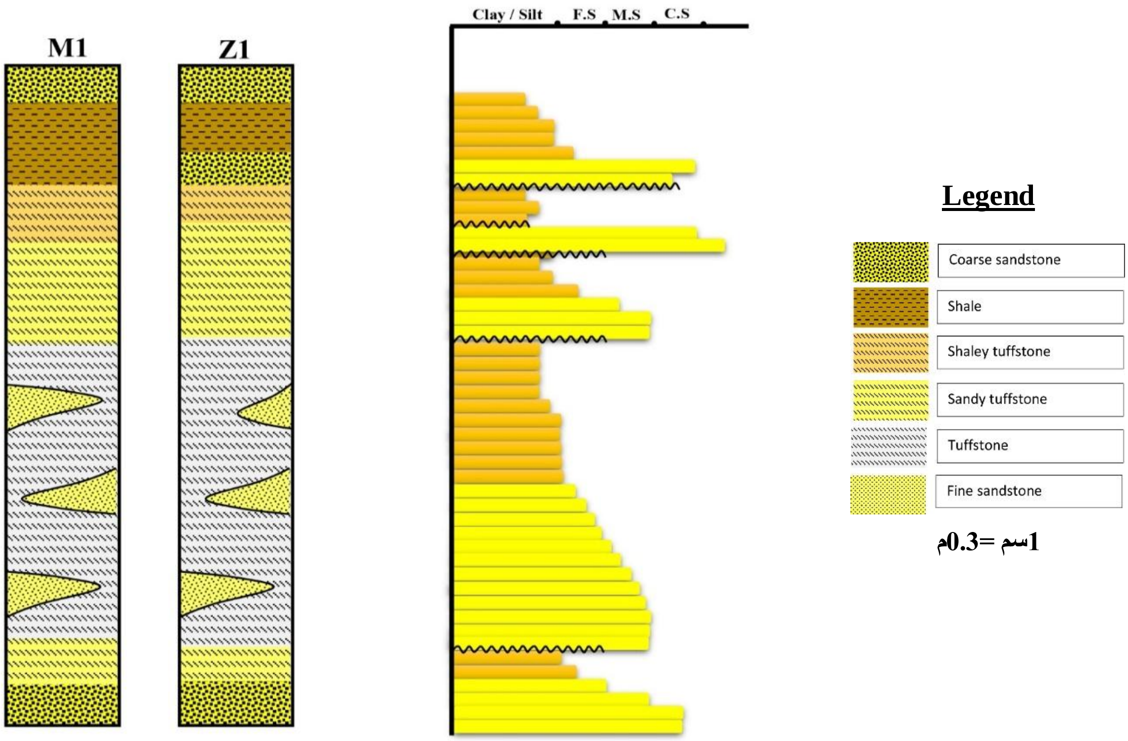


Figure 3- Lithologic section of the studied areas, Zarloukh [Z1] and Megrin [M1] (modified after[4]).

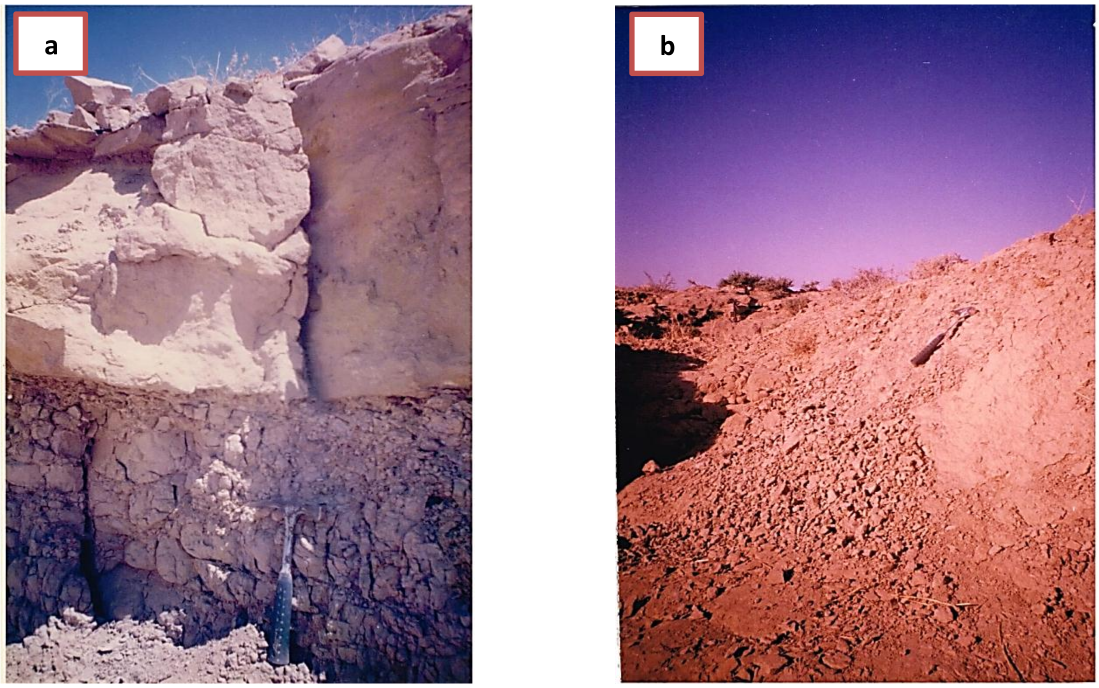


Figure 4- a. Megrin II section and b. Tayawi section.

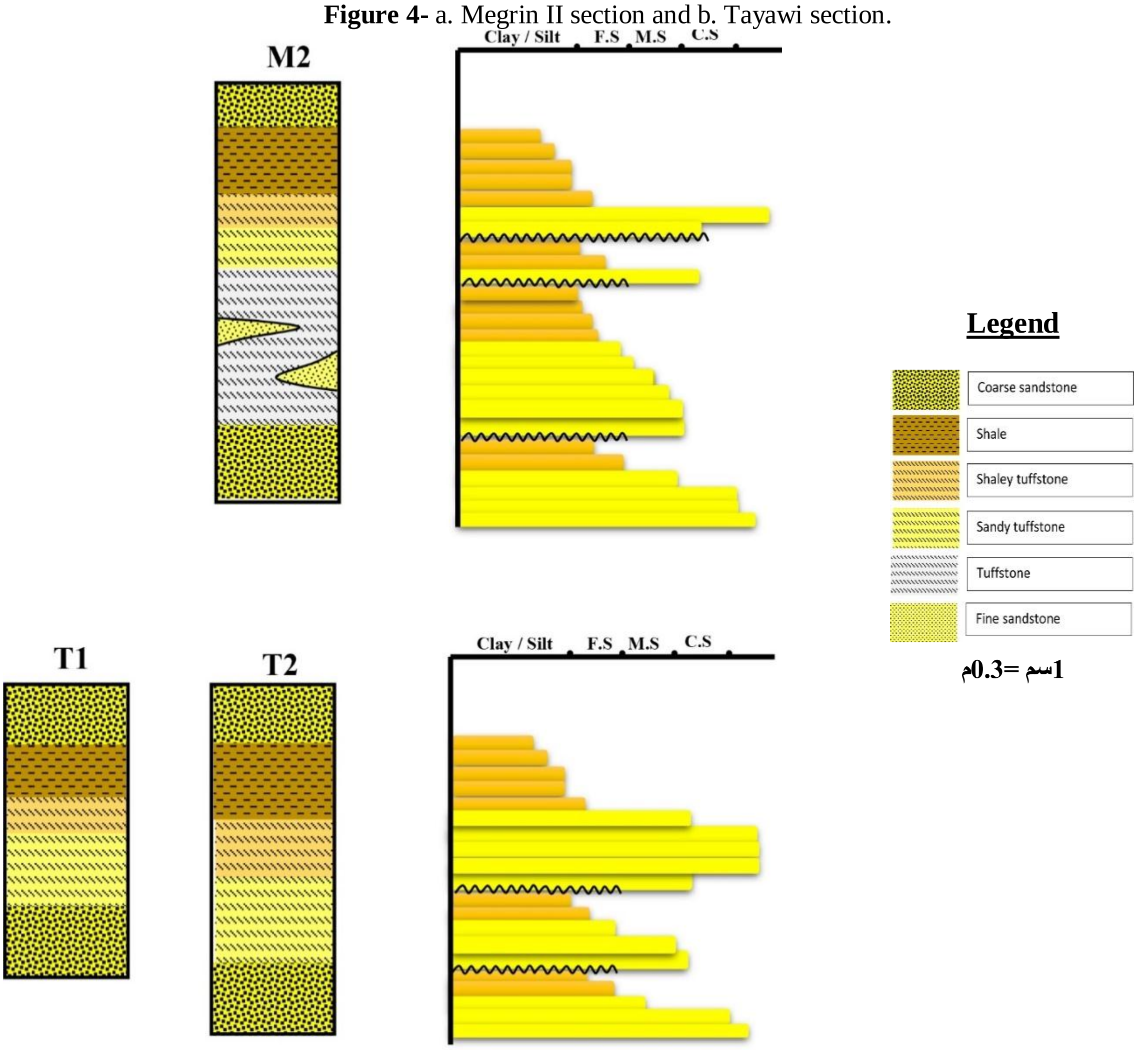


Figure 5- Lithologic section of the studied areas, Megrin [M2] & Tayawi [T1,T2] (modified after[4]).

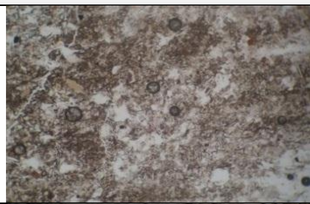
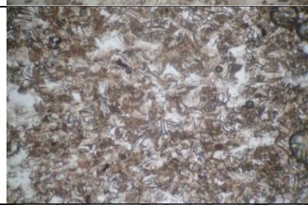
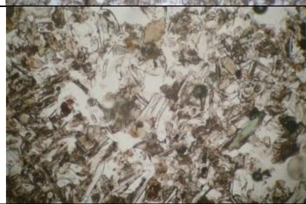
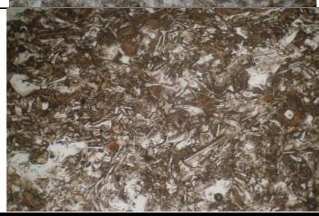
Petrographic analysis:

The volcaniclastic rocks were described as hand specimens and then under the microscope. The requirements of this stage of the study was:

1. Field description; this stage is represented by the all field observation and old geological reports, to determine the suitable type of the rocks for the present study.
2. Make about 10 thin sections to describe the studied rocks

In general, the volcaniclasts of Muqdadiya Formation are characterized by light colour rocks ranging between gray to beige with low specific gravity. The characterizations of the suitable rocks for this study are the purity (volcanic glass more than 90%), not altered, good bedding and thickness in addition to the large distribution. According to these properties seven selected samples were described in hand specimen and thin section Table -1.

Table 1- Petrographic description of volcanoclastic rocks

	description	Photo	Thin Section
Z1	Fine grained Laminated tuffstone (silt size). With very few fine Quartz grains associated with the glass shards.		
Z2	medium grained massive tuffstone. The Pumice and bone shaped shards.		
M3	Very fine graind tuffstone (clay size). With Conchoidal fracture.		
M4	Coarse graind tuffstone. With Obsidian and Y-shaped shards		
M5	Fine graind tuffstone. With altered part of this unit, and contained of sand lens in some parts.		
M6	medium grained massive tuffstone. With the Pumice and bone shaped shards.		
T 7	Very fine graind tuffstone (clay size). With Conchoidal fracture.		

These samples will be examined in the laboratory to study the engineering properties for the purpose of determining their importance and the possibility of industrial use.

Water Content

The volcaniclastic samples have a water content = 12.5% which is low [5]. Because the study area has arid climate with lack of water resources. And due to fine grains and small pores.

Drying and Firing:

At the Department of Geology, Collage of Science, University of Baghdad, samples of the volcaniclastic rocks were dried at 105^{o} C, , then followed by the process of firing at 950^{o} C , The samples were left in the kiln for 24 hours to cool and give enough time for the new minerals to crystallize and growth.(figure - 6).

The firing temperature of the volcaniclastic rock affect the internal surface pores at 950^{o} C, because it influences the bonds between the particles .It has a glazed view because of the sintering process, also its microstructure contains minimum pores.

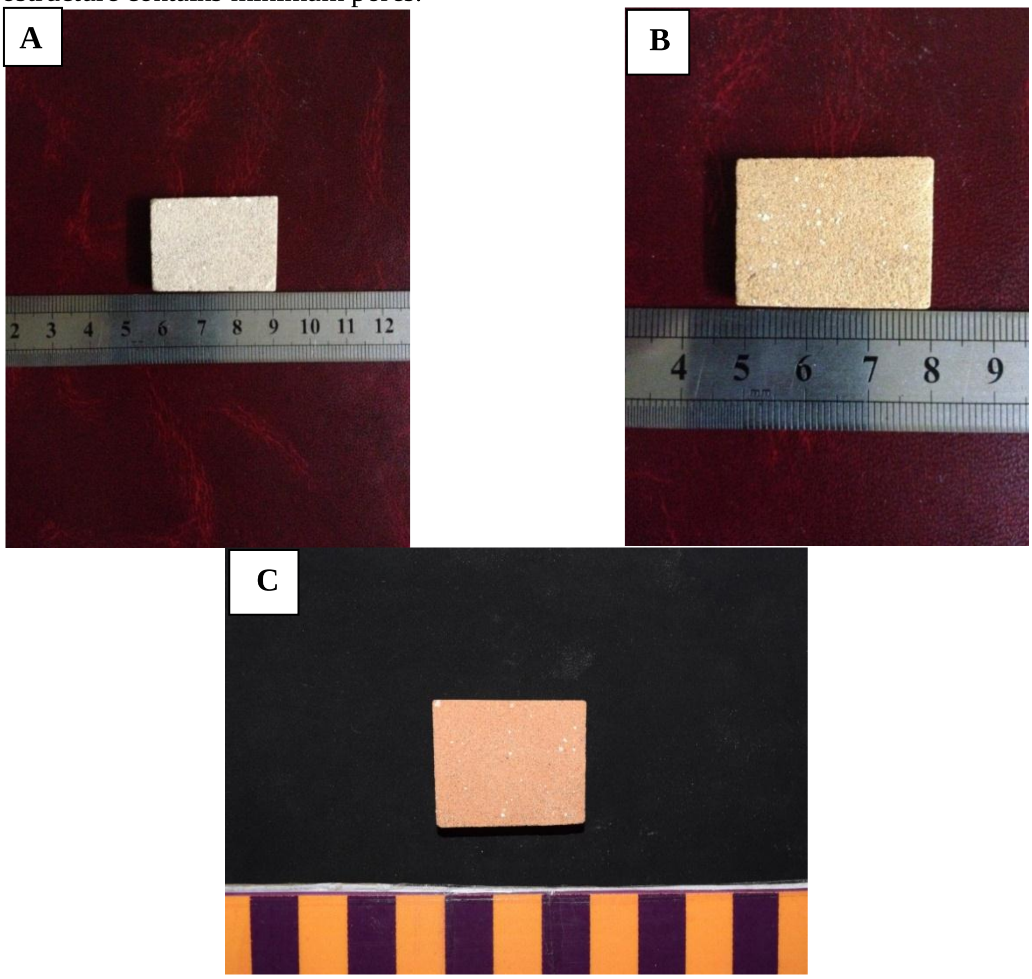


Figure 6- A-Sample before drying; B-Sample after drying at 100^{o} C; C-Sample after firing at 950^{o} C.

Bulk Density

Samples of volcaniclastic rocks from different sites were tested according to the ASTM C20 -97. [6]. The result shows that the density increases after firing from (0.9 to1.8 g/cm3) due to decrease in volume. Bulk density is a useful property of refractories, which defines the material present in a given volume. An increase in bulk density of a given refractory increases its volume stability, its heat capacity, as well as resistance to slag penetration. In general, the higher the density, the lower the porosity.The density and porosity of a refractory will influence its heat capacity i.e. higher density leads to higher heat capacity and the highly porous insulating the low heat capacity. The density and porosity of a refractory will influence its Permanent Linear Change (PLC) at high temperatures (higher porosity refractory = higher PLC). Some fine porosity can increase the toughness of a refractory by terminating propagating cracks.

Water Absorption

Tests were carried out on samples according to (ASTM C20-97). [6]. The results show that the water sorption of volcaniclastic rocks decreases after firing from (32.8%) to (14.3%). The decrease in absorption refers to the decrease in porosity while firing.

Porosity

The apparent porosity (***n***%) was calculated using formula (1) according to the (ASTM C20-97).[6].

$$n\% = \left(\frac{W - D}{V}\right) * 100 \qquad (1)$$

Where:

D : weight of the absolutely dry specimen [g].

W : weight of the same specimen saturated in water [g].

V : volume of the specimen [cm3]

The result shows that volcaniclastic rocks sample have an apparent porosity decreases after firing from (48.9%) to(25.3%).

Specific Gravity

Test was carried out according to the the (ASTM C20-97).[6]. The specific gravity increases after firing from (1.7) to (2.4). Since coarser and denser particles are deposited close to source, fine glass shards are relatively enriched in ash fall deposits at distal locations.

Shrinkage (PLC):

The shrinkage test was carried out according to the (ASTM C 356-87).[7]. The result shows that the volcaniclastic rocks shrink when dried to (17%) and after firing to (8.6%). Insulating refractory bricks produced using volcaniclastics as pore agents would record little to medium change in dimension due to:

- water loss
- The changes in the allotropic forms, which cause a change in specific gravity
- A chemical reaction, which produces a new material of altered specific gravity
- The formation of liquid phase
- Sintering reactions

The shrinkage value (8.6%) fell within the recommended range [8].

Particle Size Distribution:

The grain size distribution shows that in Zerloukh sections the samples have a maximum peak refers to very fine sandstone and ranges from (34.045% -47.95%) , while in Megrin sections the maximum peak refers to fine sandstone ranges from (22.76%%-50.336) .Also in some sites of Megrin the maximum peak refers to fine silt with value of (30.62%).The grain size distribution of the volcaniclastics show that they have three patterns of distribution:

1. The sandstone samples which have a unimodal shape and S-shaped curve.
2. Sandstone samples of Tuffaceous Sandstone show contrast in the pattern of grain size distribution which ranges from unimodal in the samples where the normal sedimentary clastics prevail the volcaniclastics, to bimodal when the two types are almost equal.
3. The Tuffstone samples show pattern of irregular distribution, this pattern ranges from unimodal to polymodal, where the shape of curve approaches straight line. Figure -7.

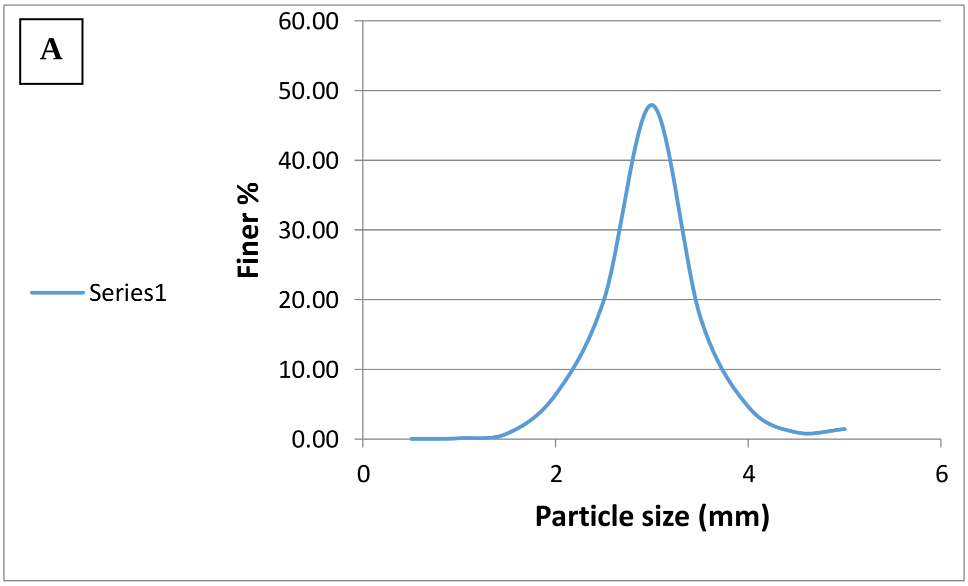


Figure 7- A: Grain size distribution in Zerloukh.

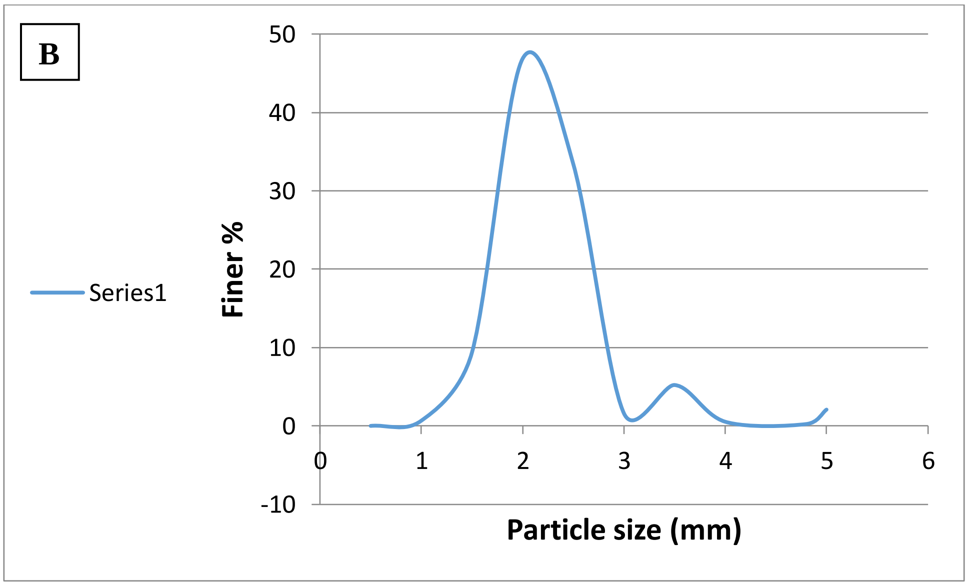


Figure 7- B: Grain size distribution in Megrin.

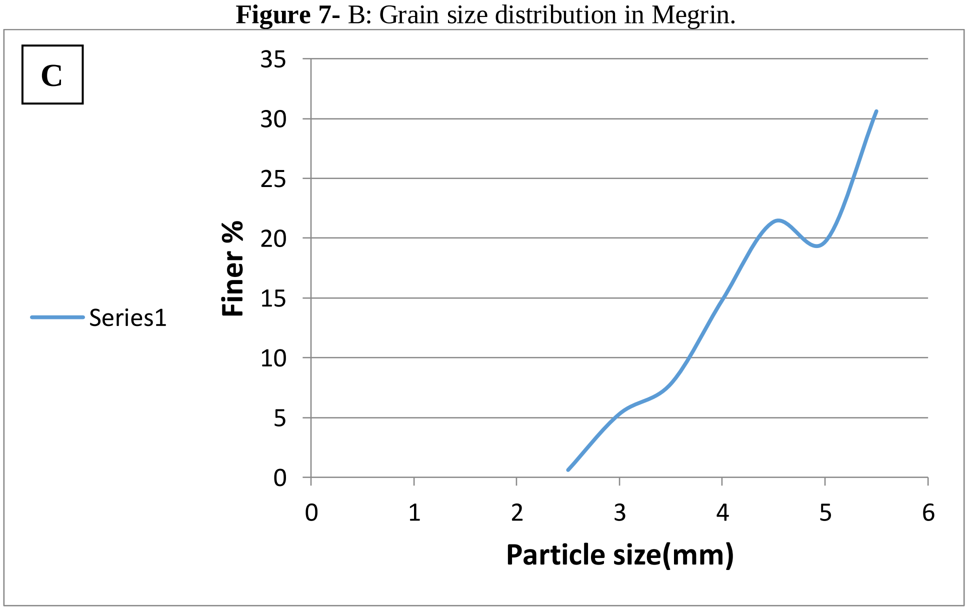


Figure 7- C: Grain size distribution in Tayawi.

The particle size destribution is an important factor for the refractory industry because it affects the porosity and bulk density; as the grain size increases the apparent porosity increases and therefor the bulk density decreases. Also the particle size affects the strength whereas the strength decreases as the size of the particles increases due to the increase of the apparent porosity.

Compressive Strength

The compressive strength tests were carried out at the Department of Building Research, Ministry of Building and Housing on three samples from the three sites, Figures - 8,9,10 and11. The strength increases from (9.5Mpa) to (12.3Mpa) after firing which is moderately weak, according to the Description of strength for rocks [9].

This value reflects the advantage of volcaniclastics to use them in refractories. The compressive strength of a refractory material is an indication of its stability for use of refractories in construction and it's resistance to crushing, which mostly happens during transport. The strength is a combined measure of the refractory for the strength of grains and also of the bonding system, it's important to realize that refractories are not very strong by any standards or comparisons. However refractories do not need to be very strong, for they do not generally serve a major structural load – bearing function.

Figure 8- Compressive strength test machine.

Figure 9- Rock sample during test.

Figure 10- Failure of rock sample.

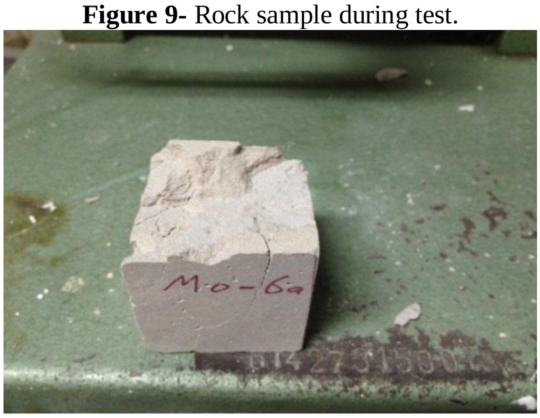


Figure 11- Rock samples after failure.

Thermal Conductivity test

The thermal conductivity test of volcaniclastic rocks was carried out at the Department of Materials Engineering, University of Technology by using the hot disk method. Figures -12, which shows that they have low thermal conductivity ranges between (0.22 W/m K) and (0.41W/m K). Volcaniclastics characterized by porous structure whereas these (pores) filled by air and act insulators which cause reduction in coefficient of heat transfer. Reasons for the decrease in thermal conductivity are the increase of the apparent porosity and the corresponding increase in density as the temperature is increased. This phenomenon resulted from increase in sintering process and the crystal growth due to crystallization. For effective thermal insulation, materials with high porosity (≥ 90%) and nanoscopic (˜100 nm) pores are required.This corroborates averment that porosity is the major determinant of low thermal mass which is important for heat energy efficiency, [10] .

Figure 12- Samples in the hot disk machine

Assessment of Geochemical analysis

The stability of the rock, especially that of mono-mineralic stone provides stable physical and chemical characteristics. This property is useful in the industrial and petrotechnological evaluation.For chemical analysis. X-Ray flouresence and X-Ray diffraction tests were applied on volcaniclastic rocks Table - 2, 3 and 4.

Table 2- Comparison of the oxides % in deferent sections within Zerloukh area.

Section	Oxide %	Sample No.	
		1	2
Zerloukh	MgO	3.77	2.99
	Al2o3	9.40	10.85
	Sio2	41.40	55.51
	P2O5	0.49	0.55
	SO3	0.18	0.23
	Cl	0.03	0.09
	K2O	0.91	1.40
	CaO	12.98	2.53
	TiO2	0.43	0.29
	V2O5	0.01	0.00
	Cr2O3	0.01	0.00
	MnO	0.06	0.04
	Fe2O3	3.26	2.17

Table 3- Comparison of the oxides % in deferent sections within Megrin area.

Section	Oxide %	Sample No.			
		1	2	3	4
Magarin	MgO	4.25	4.25	5.34	3.78
	Al2o3	9.80	10.22	10.74	10.98
	Sio2	43.51	47.09	46.48	51.26
	P2O5	0.51	0.54	0.52	0.55
	SO3	1.41	0.48	1.33	0.73
	Cl	0.03	0.03	0.10	0.04
	K2O	9.75	1.05	0.43	0.94
	CaO	9.71	8.30	3.90	5.08
	TiO2	0.44	0.44	0.38	0.36
	V2O5	0.01	0.01	0.01	0.00
	Cr2O3	0.02	0.02	0.01	0.01
	MnO	0.05	0.05	0.05	0.06
	Fe2O3	3.22	3.18	2.73	2.72

Table 4- Comparison of the oxides % in deferent sections within Tayawi area.

Section	Oxide %	Sample No.
		1
Tayawi	MgO	3.57
	Al2o3	11.03
	Sio2	49.54
	P2O5	0.53
	SO3	0.06
	Cl	0.04
	K2O	0.47
	CaO	3.91
	TiO2	0.33
	V2O5	0.00
	Cr2O3	0.00
	MnO	0.04
	Fe2O3	2.42

Geochemical relationship between oxides

The relationship between major oxides shows that there is strong and moderate positive correlation between SiO_2 and (Al_2O_3, P_2O_5, Cl and K_2O), which indicate that these oxides are derived from the same source and their source region is most probably detrital materials transported to the basin [11].
The correlation is strongly and moderately negative between SiO_2 and each of (CaO , Fe_2O_3 ,SO_3,V_2O_5, TiO , MgO, and Cr_2O_5); and weak with MnO. Figure -13 and14.On the other hand a strong and moderate positive correlation between MgO and (TiO_2, Fe_2O_3, SO_3,V_2O_5 and Cr2O3); and weak with (Al_2O_3, and CaO). The negative correlation is strong and moderate between MgO and (K_2O, $P_2O_3$and SiO2); and weak with(CL and MnO).Figure-15 and Figure -16.

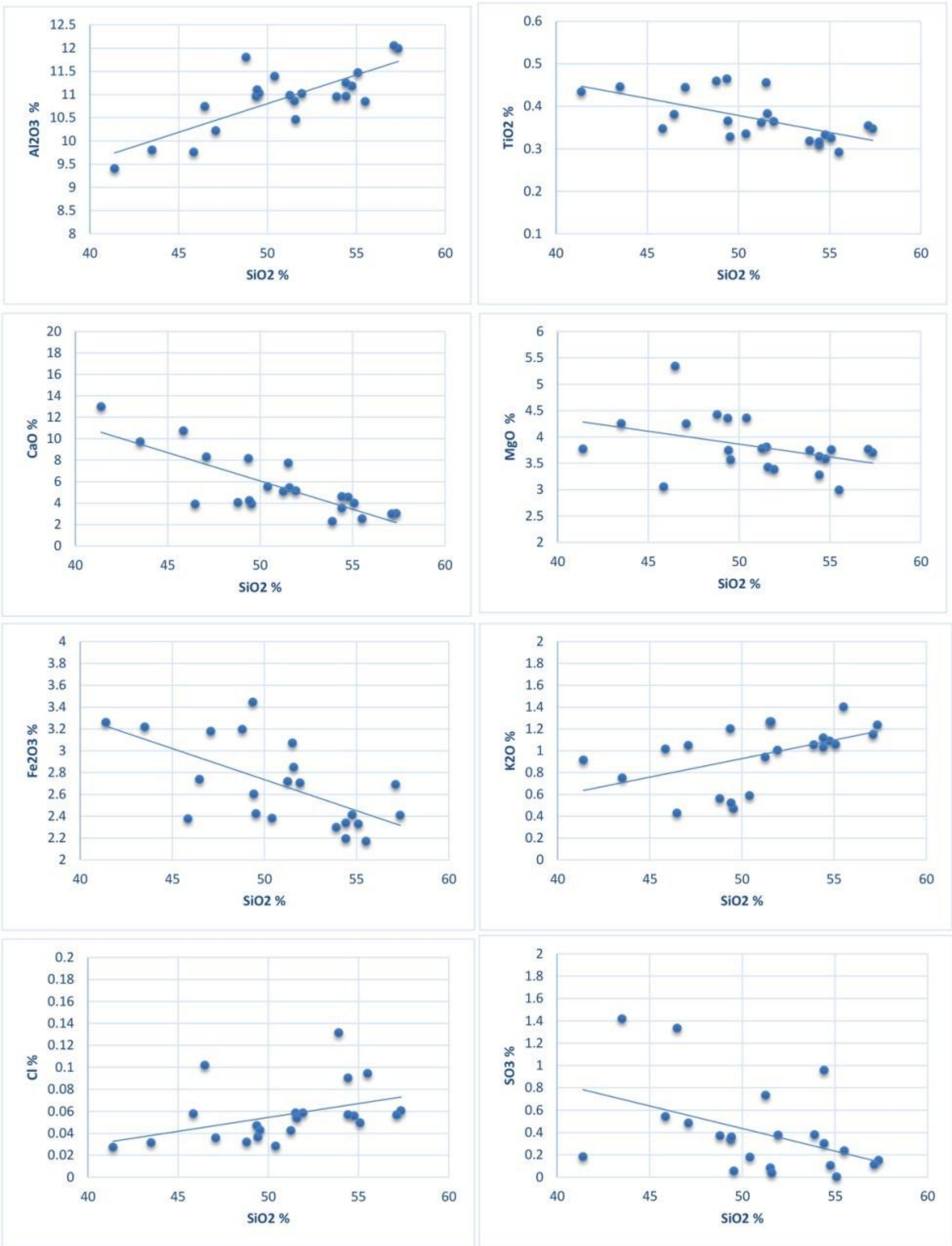


Figure 13- Relationship between SiO_2 and (Al_2O_3, TiO_2, CaO, MgO, Fe_2O_3, K_2O, Cl & SO_3) oxides

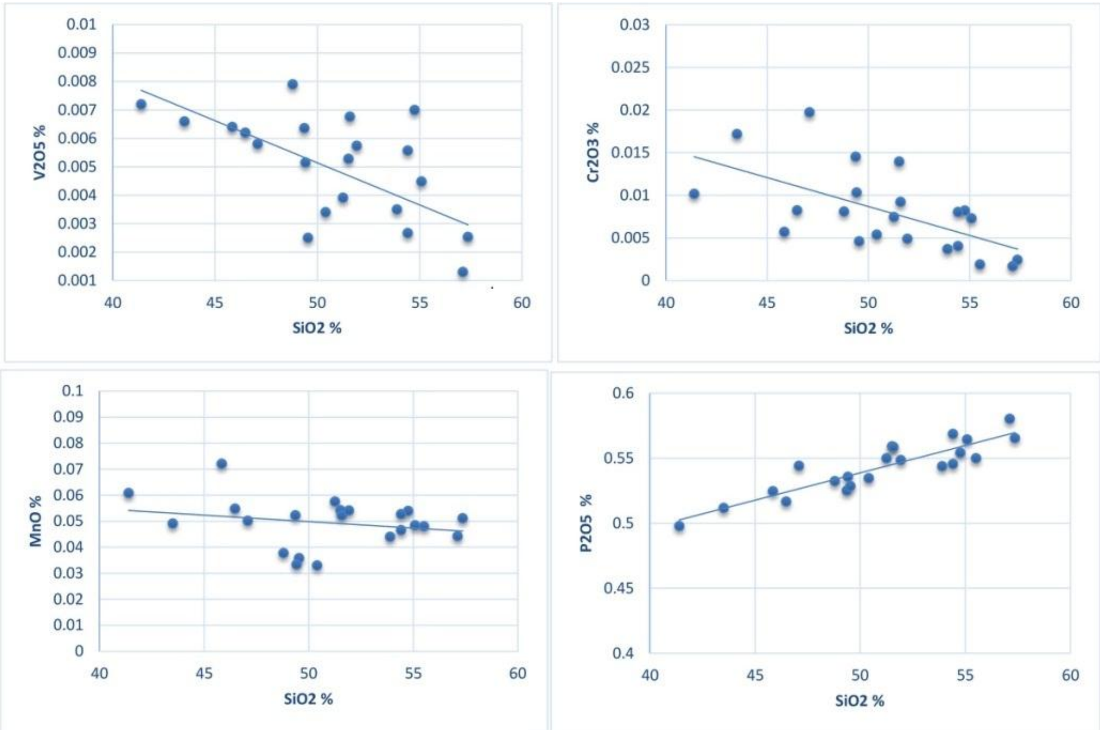


Figure 14- Relationship between SiO_2 and (V_2O_5,Cr_2O_3,MnO and P_2O_5)

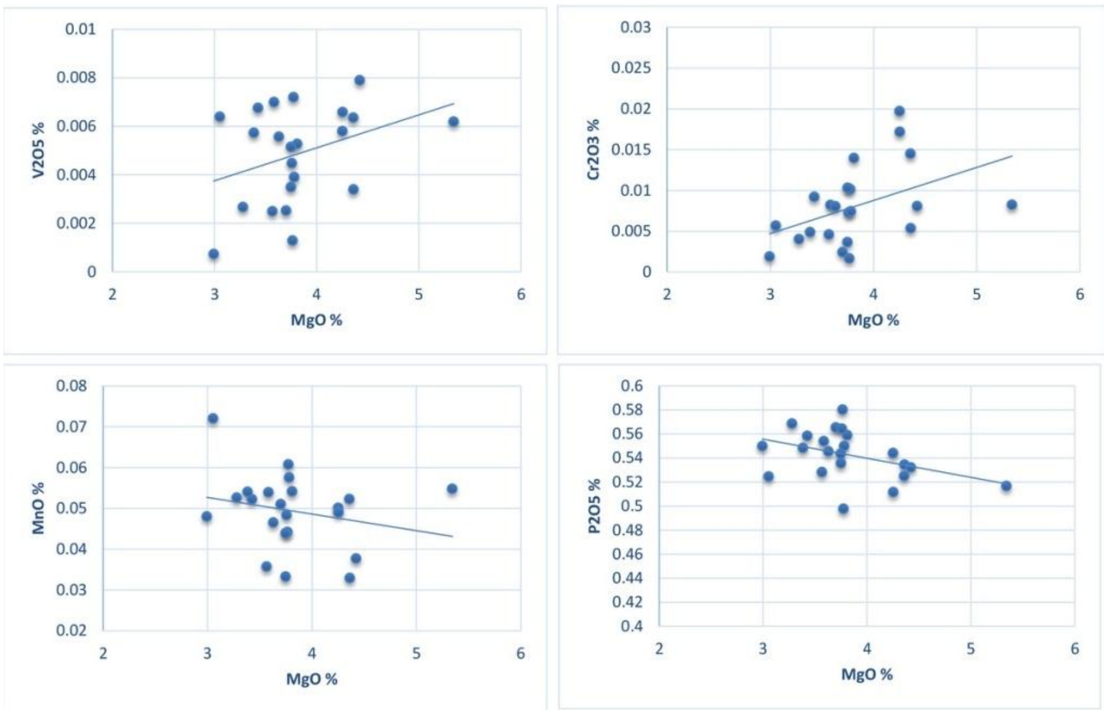


Figure 15- Relationship between MgO and (V_2O_5, Cr_2O_3, MnO & P_2O_5) oxides

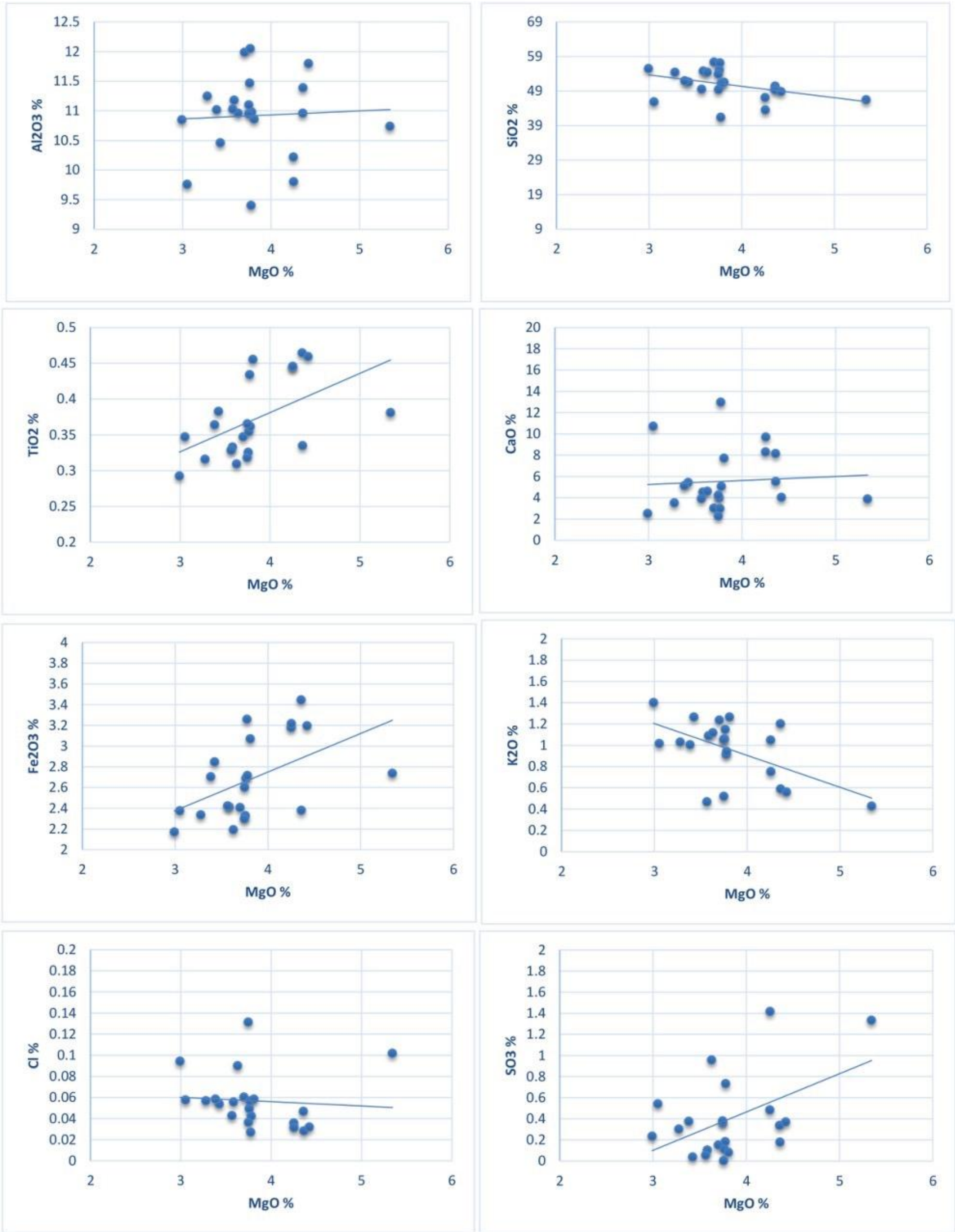


Figure 16- Relationship between MgO and (Al_2O_3, Sio_2, TiO_2, CaO, Fe_2O_3, K_2O, Cl & SO_3) oxides.

MgO is used as a basic refractory material for crucibles and as a principal fireproofing ingredient in construction materials. As a construction material, it has several attractive characteristics: fire resistance, moisture resistance, mold and mildew resistance, and strength.

Table 5- Final Results of tests in the study area

Test type			Results
Water content		W_c	12.5 %
Bulk Density (before firing)		γ	0.9g/cm^3
Bulk Density (after firing)		γ'	1.8g/cm^3
Apparent porosity (before firing)		n	48.9 %
Apparent porosity (after firing)		n'	25.3 %
Specific Gravity (befor firing)		G_S	1.7
Specific Gravity (after firing)		G_S'	2.4
Water Absorption (before firing)		A	32.8 %
Water Absorption (after firing)		A'	14.3 %
Compressive strength (before firing)		$\mathcal{P}$	9.5 Mpa
Compressive strength (after firing)		$\mathcal{P}'$	12.3 Mpa
Linear Shrinkage (after drying)			17 %
Linear Shrinkage (after firing)			8.6 %
Shear Strength Parameters	Friction Angle	ϕ	31.0^o
	Cohesion	c	9.5 Kpa
Thermal conductivity			0. 31 (W/m K)

Conclusions

a. The engineering properties of the volcaniclastics show low water content which mean low obvious change because the change in volume and the effect of water migration is low, as well as low destruction of cementation, it also influences the deformation parameters and mechanism of rocks. The bulk density increases by the increase of temperature which leads to volume stability, heat capacity and resistance to slag penetration ,and less heat conducting. The apparent porosity decreases by the increase of temperature, low apparent porosity prevents molten material from penetrating into the refractory, and the large number of small pores is generally preferred to a small number of large pores. Water sorption is low and this property would allow for minimal use of water of plasticity in the production of insulating refractory bricks. The presence of this quantity of water in the wet brick would reduce drying time, thereby quickening the production process. The compressive strength increases as temperature increases because the internal surface of pores in rock sample begins to sinter at high temperatures. The specific gravity increases after firing , which is important to consider the weight of a brick. Cost of bricks of higher specific gravity is more than that of lower specific gravity. The thermal conductivty increases with increasing in firing temperature and decreases with increasing in apparent porosities presented in specimens. Effective insulating materials require relatively low thermal conductivity in order to reduce the co-efficiency of heat transfer. Thus, reducing the pore sizes to nanoscopic level would increase the collisions between the gas molecules and the pore walls, that is Knudsen effect, and such an effect could be potentially used to reduce thermal conductivity, this is coincide with the volcaniclastiv rocks when fired.

b. Chemically; at temperature 350^o C, the chemical combined water which is part of the molecular structure of the rock started to be driven off, this water is not to be confused with pore water and water of plasticity, which escapes during early stages of drying.

The nature of the material comprising the studied sediments and the purpose of studying them was compared with other materials with the same specifications and used locally or globally. So it was noted the existence of convergence in the results which supports the possibility to use this material in the proposed type industries. An example of this material is (Jiuqiang Ceramic Fibre Module):- It is made of fold or pre-cut Sino-shine Blanket stack. This blanket stack is folded, then tightly compressed and banded to form the Bonded block. The Sino-shine Ceramic Fiber Module contains no any binders. A special equipment's were used for producing Sino-shine Ceramic Fiber Module to confirm the precise dimensions of Sino-shine Ceramic Fibre Modules. Sino-shine Ceramic Fiber Module can be connected with structures of kiln and furnace by Anchor. It’s easy to install and speed constructing lining of furnace.

Characteristics

1. Low bulk density
2. Low thermal conductivity
3. Resistance to heat-shock
4. Resistance to airspeed eroding
5. High mechanical strength
6. High safety within anchorEasy installation

Table 6- Technical Specifications **of** Jiuqiang Ceramic Fibre Module

Descriptions		JQ-COM	JQ-STD	JQ-HP	JQ-HA	JQ-ZA
Classification temperature (℃)		1260	1260	1300	1400	1430
Operating temperature(℃)		＜1000	1000	1150	1200	1350
Density（kg/m^3)		190-240	190-240	190-240	190-240	190-240
Compressive strength (Mpa)		0.5	0.5	0.5	0.5	0.5
The chemistry constitute (%)	AL_2O_3	44-45	45	47-49	52-55	39-40
	AL_2O_3+SiO_2	96	97	99	99	-
	AL_2O_3+SiO_2+ZrO_2	-	-	-	-	99
	ZrO_2	-	-	-	-	15-17
	Fe_2O_3	1.2	1	0.2	0.2	0.2
	Na_2o+K_2O	0.5	0.2	0.2	0.2	0.2
Dimensions (mm)		610×300×100-200（without Anchor）;300×300×175-250（With Anchor or without Anchor）;Other specifications according to the customer request				

Applications

Iron-steeling: heating furnace Carbonizing Furnace, Ladle Petro-industry: Heater, Reformer, Cracking Furnace All other industrial kilns such as heat-treatment furnace, ceramic kiln and kiln car

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