DOCUMENTATION AND EXAMINATION OF HISTORIC BUILDING MATERIALS FOR THE PURPOSE OF CONSERVATION: CASE STUDY, PART OF THE WALLS AT THE CITADEL OF ANKARA

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THE DEGREE OF MASTER OF SCIENCE
IN
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Approval of the Graduate School of Natural and Applied Science.

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

DOCUMENTATION AND EXAMINATION OF HISTORIC BUILDING MATERIALS FOR THE PURPOSE OF CONSERVATION: CASE STUDY, PART OF WALLS AT THE CITADEL OF ANKARA

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The study aimed to identify deterioration problems, repair and conservation needs of andesites on the walls of the Ankara Castle. Decay forms of walls were documented by visual examination. Samples taken from the surface of the weathered andesites were examined for their basic physical, mechanical compositional and minerological properties. The bulk density and total porosity were determined as basic physical properties. The mechanical properties were expressed as ultrasonic velocity and modulus of elasticity (Emod). Compositional and mineralogical properties were determined by optical microscopy and XRD analyses.

Soluble salt content of the andesite samples was determined by spot tests of anions and electrical conductivity measurements.

Findings were evaluated in terms of the long-term weathering behaviour of andesites under the effect of the prevailing climate, air pollution problems of

Ankara, dampness problems of the structure, previous repairs with incompatible cement mortars.
The surfaces of Ankara Castle andesite blocks were heavily weathered. The results were compared with the physical and mechanical properties of fresh andesites from Gölbaşı-Ankara quarry. The surface of the andesite blocks at the Ankara Castle, had low bulk density and high porosity, low ultrasonic velocity and low Emod values. Thin section and XRD analyses supported those results by revealing the presence of physical and chemical weathering on feldspars and other main minerals of andesite, as well as the presence of amorphous minerals at the surface.

Keywords: Dampness, Andesite Weathering, Non-Destructive Testing

ÖZ

TARİHİ YAPI MALZEMELERİNİN KORUMA AMAÇLI DÖKÜMENTASYONU VE İNCELENMESİ: DURUM ÇALIŞMASI, ANKARA KALESİ DUVARLARININ BİR BÖLÜMÜ

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Bu çalışmanın amacı Ankara andezitlerinin bozulma sorunlarını, bozulmuşluk durumlarını ortaya koymak, koruma çalışmalarının kapsamını belirlemektir.
Çalışmada önce, örneklerin alındığı kale duvarlarında ve andezit taşlarında görülen bozulma türleri belirlenmiştir. Andezit taşlarının yüzeylerinden alınan örneklerin temel fiziksel özellikleri kapsamında birim hacim ağırlığı ve gözenekliliği, mekanik özellikleri kapsamında ise ultrasonik hız değerleri ve esneklik modülü (Emod) hesaplanmıştır. Çalışılan andezit örneklerin mineral bileşimleri ince kesitlerinin optik mikroskop ile incelenmesi ve XRD analizleri ile belirlenmeye çalışılmıştır.Örneklerin içerdiği çözünen tuzların miktarı elektriksel iletkenlik ölçümüyle ve tuzlara ait anyonların türü spot testleriyle belirlenmiştir.
Sonuçlar, andezitlerin karasal iklim şartlarında ve Ankara'nın hava kirliliği sorunlarına bağlı olarak uzun sürede gösterdiği dayanıklılık özellikleri ve çimento

içeren harçlarla yapılan yanlış onarımlar, kalenin ilgili bölümlerindeki drenaj ve nem sorunları sonucu ortaya çıkan bozulmalar açısından ve koruma çalışmalarının kapsamı açısından değerlendirilmiştir.
Elde edilen fiziksel ve mekaniksel test sonuçları Ankara kalesi duvarlarından alınan andezit örneklerin yüzeylerinin çok bozulmuş olduğunu göstermiştir. Sonuçlar, Ankara Gölbaşı yeni andezit örneklerinin fiziksel ve mekanik özellikleri ile karşılaştırılmıştır. Yüzey katmanlarının gözeneklilik değerlerinin yüksek ve birim hacim ağırlıklarının düşük olduğu, ultrasonik hız ve esneklik modülü (Emod) değerlerinin bozulmaya bağlı olarak azaldığı saptanmıştır. İnce kesit ve XRD analizleri de feldspar ve diğer ana minerallerdeki fiziksel ve kimyasal değişmeleri ortaya çıkarmış ve andezit yüzeylerinde amorf minerallerin oluştuğunu göstermiştir.

Anahtar Kelimeler: Nem Sorunu, Andezit Bozulması, Tahribatsız İnceleme

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INTRODUCTION

Weathering defined as the process of alteration of rocks occurs under the direct influence of atmosphere and hydrosphere (Sounders et al., 1970). In a broader sense, weathering covers all physical, chemical and physico-chemical changes of the rocks under the influence of natural and man-made environmental conditions. Some rocks are suitable to be used as building stones. Weathering and durability characteristics of building stones are important subjects to be understood both in engineering and cultural heritage conservation studies.

Durability here is a term that is used to describe the performance of stone under weathering conditions.

There are many factors that cause the weathering of building stone, such as dampness, soluble salts, atmospheric pollution agents and biodeterioration agents. In the weathering process, more than one factor or all factors are involved and responsible of the changes. The dampness, which may be in different forms such as rising damp, rain penetration and condensation is the main decay factor.

The climatic conditions due to daily and seasonal thermal and humidity fluctuations as well as precipitation and wind effects may produce important physical weathering cycles, such as wetting-drying, freezing-thawing and salt crystallization (Arnold & Zehnder, 1989; Camuffo et al., 1997; Caner-Saltık, Schumann & Franke, 1998; El Hady, 1994; Fitzner, 1994).

1.1 Climatic Characteristics of Ankara

Climatic conditions, namely relative humidity, temperature, precipitation and wind induce weathering cycles in stone and other building materials as heating-cooling, wetting-drying, freezing-thawing, salt crystallization etc.

The climatic features of Ankara is of semi-arid region. The meteorological data for 28 years (1975-2003) are given in Table 1.1 (BDSMS, 2003). Summers are hot. The hottest months are July and August. The average temperature and relative humidity during summer are around 22 ºC and 49 % , respectively (Fig. 1.2 and Fig.1.4). Winters are cold, the coldest month being January. During winter times, the average temperature and relative humidity are around 1.5 ºC and 73 %, respectively (Figs. 1.2 and 1.4). The relative humidity is much higher in winter times than in summer times. The highest temperature fluctuations are observed in July, August and September with an average of 14.1 ºC and the lowest fluctuations are observed in December and January with an average of 7.1 ºC (Fig. 1.3).

Figure 1.1 shows the average monthly precipitations and wet days in the period of 1975-2003. The seasonal precipitation distribution is quite regular, maximum rainfall being in autumn and minimum being in August and September. The winter periods (December-February) have the higher precipitation with an average of 39.7 mm. The precipitation in winter is more likely to be due to the snowfall, the average snow-covered days being 8. The highest precipitation was recorded in April with an average of 53.6 mm, with 13 wet days. The lowest precipitation occurs in the summer periods (June-August), with an average of 21.6 mm. The lowest precipitation was recorded in August.

Table 1.1 The average of twenty-eight-years meteorological data of Ankara weather station between1975-2003 (BDSM, 2003)

PARAMETERS monthly mean values	JAN.	FEB.	MAR.	APR.	MAY.	JUN.	JUL.	AUG.	SEP.	OCT.	NOV.	DEC.	Annual Avr.	Annual Sum.
Temperature (° C)	0,3	1,8	5,9	11,2	15,9	19,9	23,3	22,8	18,5	12,9	6,6	2,3	**11,8**	
Relative Humidity (%)	74	70	64	61	58	53	47	47	50	61	70	76	**60**	
High Temperature (° C)	4,2	6,5	11,6	17,0	22,0	26,3	30,0	29,7	25,9	19,8	12,3	6,1	**17,6**	
Low Temperature (° C)	-3,0	-2,2	0,8	5,7	9,5	12,9	15,9	15,7	11,7	7,3	2,2	-0,8	**6,3**	
Difference Between High and Low Temperature (° C)	7,2	8,7	10,8	11,3	12,5	13,4	14,1	14	14,2	12,5	10,1	6,9	**11,3**	
Max. Temperature (° C)	16,6	19,9	25,7	30,3	33,0	37,0	40,8	39,0	35,2	32,2	22,8	18,0	**29,3**	
Min. Temperature (° C)	-21,2	-21,5	-19,2	-6,7	-1,6	5,0	6,8	7,2	2,8	-3,4	-8,8	-14,6	**-6,3**	
Min. Relative Humidity (%)	28	15	14	15	17	14	14	12	9	14	21	23	**14,4**	
Above Ground Low Temperature (° C)	-4,1	-3,3	-0,6	4,2	7,9	11,2	14,3	14,0	9,8	5,6	0,9	-2,0	**4,8**	
Min. Above Ground Temperature (° C)	-21,4	-23,0	-20,6	-7,6	-4,2	2,0	4,6	5,0	0,2	-5,6	-10,5	-17,2	**-8,2**	
Summer Days	-	-	0,0	2,1	8,7	19,4	28,7	27,9	18,8	5,9	-	-	**13,9**	**111,5**
Tropic Days	-	-	-	0,1	0,7	5,9	15,9	15,6	5,4	0,7	-	-	**6,3**	**44,3**
Frosty Days	21,2	18,4	11,9	1,7	0,0	-	-	-	-	0,7	8,3	17,7	**9,9**	**79,9**
Winter Days	5,9	3,2	0,4	-	-	-	-	-	-	-	0,1	3,0	**2,5**	**12,6**
Severely Frosty Days	3,6	2,0	0,4	-	-	-	-	-	-	-	-	0,4	**1,6**	**6,4**
Precipitation (mm)	41,3	33,0	34,9	53,6	50,6	33,8	17,6	13,6	14,5	31,4	36,7	44,8	**33,8**	**405,8**
Daily Max. Precipitation (mm)	27,9	26,9	22,1	29,4	27,0	88,9	62,6	35,6	32,2	29,0	36,0	36,7	**37,9**	
Wet Days	11,3	10,2	10,2	12,7	12,3	8,8	4,6	3,1	3,5	7,4	8,7	11,4	**8,7**	**104,2**
Number of Snow Covered Days	9,4	7,4	5,4	1,1	0,1	-	-	-	-	0,0	2,1	6,2	**3,9**	**31,7**
Max Snow Depth (cm)	30,0	30,0	20,0	7,0	-	0,1	-	-	-	0,5	4,1	3,3	**11,9**	**95,9**
Day of Hoarfrosty	7,9	6,8	4,0	1,1	0,0	-	-	-	0,0	1,2	5,6	7,1	**3,7**	**33,7**
Day of Hail	0,1	0,2	0,4	0,8	0,9	0,3	0,0	0,1	0,1	0,1	0,2	0,1	**0,3**	**3,3**
Wind Speed (m/sn)	1,7	1,9	2,0	1,9	2,0	2,0	2,3	2,2	1,8	1,6	1,6	1,7	**1,9**	
Speediest Wind (m/sn)	22,0	20,2	18,1	20,2	22,2	24,1	16,8	17,7	17,7	18,6	19,4	18,7	**19,6**	
Direction of Speediest Wind	SSE	SW	ENE	SSE	SSE	S	ENE	WNW	SE	SW	SSW	SSW	**S**	
Day of Gale	0,2	0,2	0,3	0,4	0,3	0,1	-	0,0	0,1	0,1	0,2	0,1	**0,2**	**2**

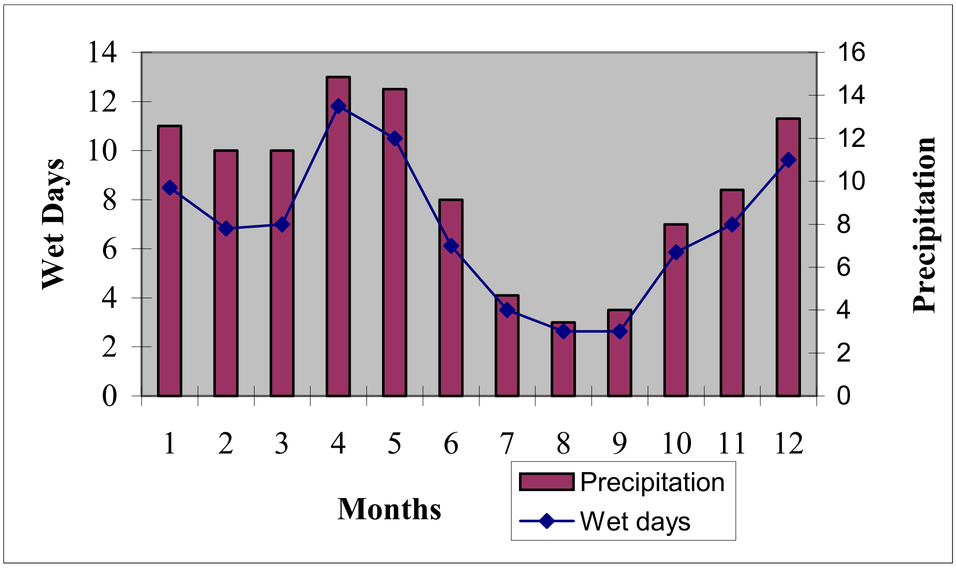


Figure 1.1 Monthly means of average precipitation and wet days for the period 1975-2003 (BDSMS, 2003)

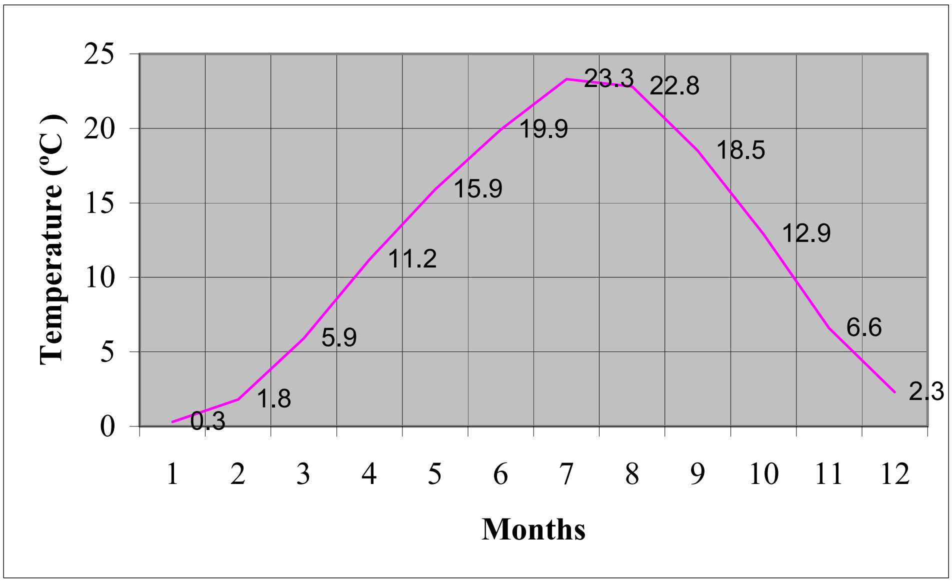


Figure 1.2 Monthly means of average temperature for the period1975-2003 (BDSMS, 2003)

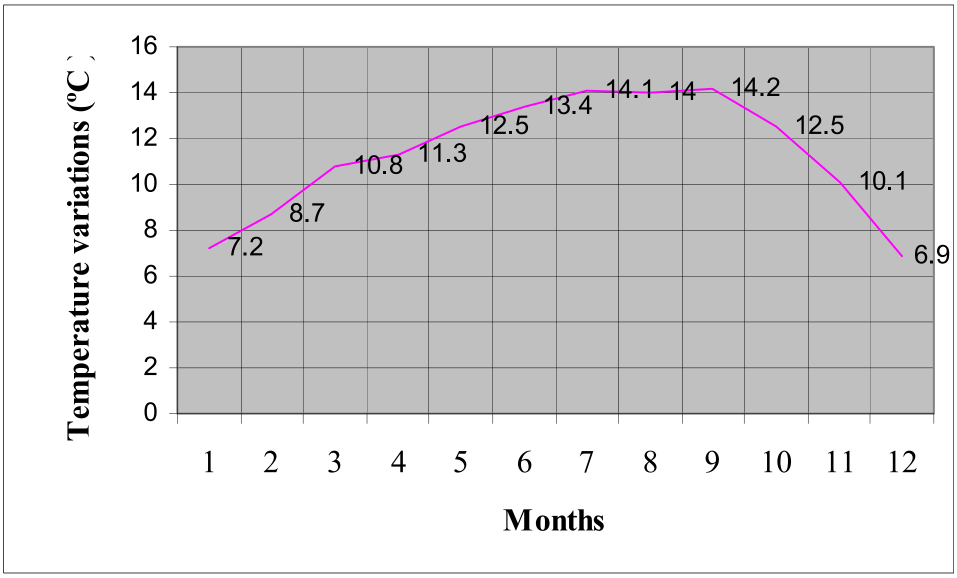


Figure 1.3 Monthly means of temperature fluctuations for the period 1975-2003 (BDSMS, 2003)

Meteorological data may give some idea about the weathering cycles of the stone and other building materials in Ankara as follows:

1)In the months of November, December, January, February and March, the average relative humidity is much higher than the yearly average (60 %) with a value of 70.8 %. This indicates the long duration of high humidity conditions and the risk of condensation under daily temperature fluctuations.

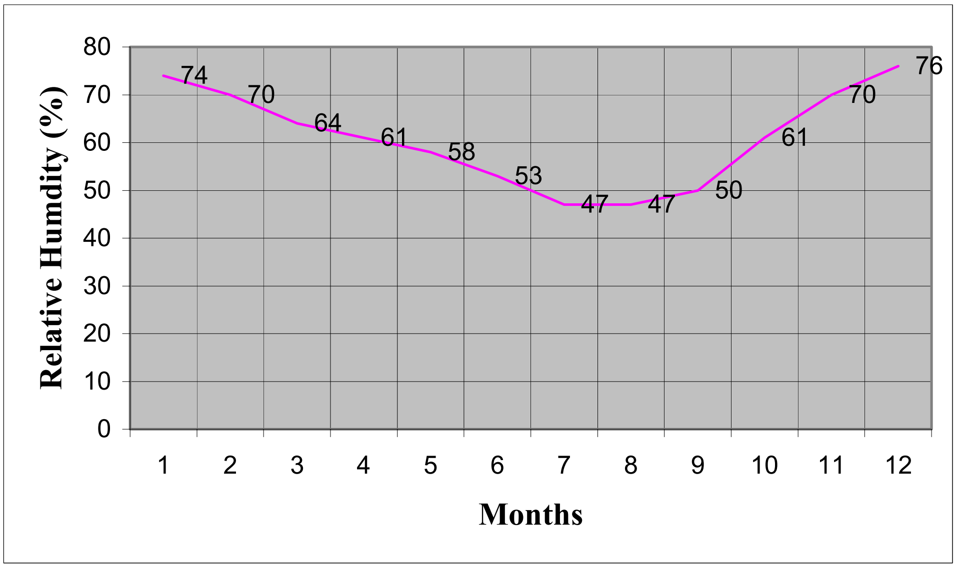


Figure 1.4 Monthly means of average relative humidity for the period 1975-2003 (BDSMS, 2003)

2) Wind Speed and direction has a significant role in Ankara's climate. When the wind speed values are smaller than 1 m/s, the situation is classified as calm. In Ankara the monthly means of wind speed is in the range of (1.6-2.3) m/s throughout the year with an average of 1.9 m/s (Fig. 1.5). The prevailing wind direction is SSW in winter with an average speed of 23.3 m/s. The prevailing wind direction is SSE in spring times with an average of almost 20.2 m/s .

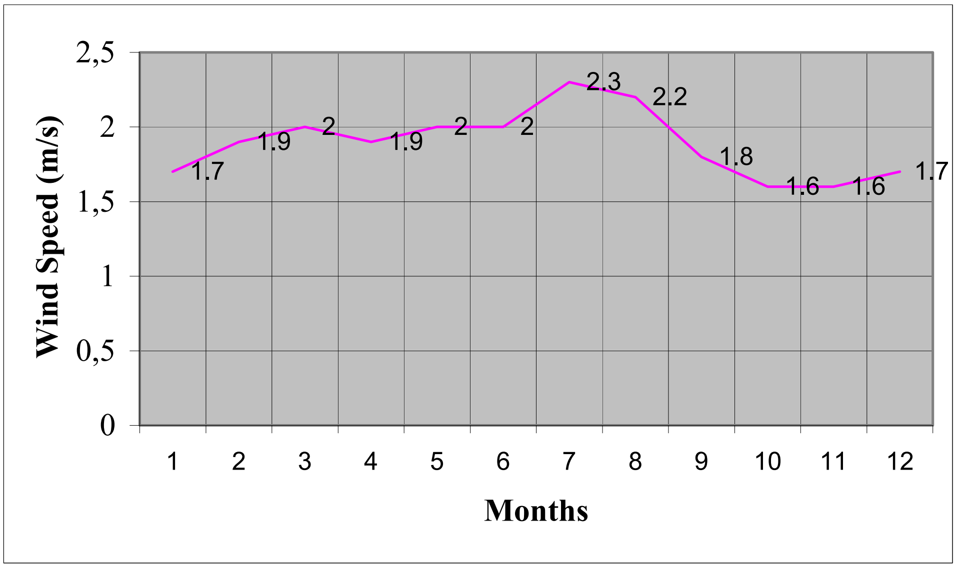


Figure 1.5 Monthly means of average wind speed for the period 1975-2003 (BDSMS, 2003)

3) Freezing-thawing cycles are expected to happen in 80 days/year when the ambient temperature drops to 0 ºC or below. The most damaging freezing-thawing cycles occur for about 6 days per year when the air temperature drops to –10 ºC or below (Table1.1). The prevailing wind direction as SSW and SSE and its speed should be affective on weathering cycles by accelerating water penetration inside the stone, during rainfall. On the other hand, it may provide the drying of wet surfaces.

1.2 Deterioration of Stone by Soluble Salts

The salts that damage the stone are either originally present in the material itself, derived from the decomposition of the material or come from the external sources such as jointing materials, backing materials, the soil, the atmosphere and the use of harmful methods of cleaning and preservation.

The common soluble salts in building stones are sulfates, chlorides and nitrates of sodium, potassium, calcium and magnesium elements. Phosphates of alkaline elements are also observed.

The damage by soluble salts depends on their types and amount in the stone material as well as the physical and mechanical properties of the stone itself. Pore size distribution and capillary system as physical properties, compressive and tensile streghts as mechanical properties influence the salt damage. The change in microclimatic conditions such as variations in relative humidity, temperature and air currents, induce salt crystallization cycles. The number of salt crystallization cycles is directly proportional with the degree of damage.

Salt damage occurs by production of internal pressure through several mechanisms. Internal pressure generated by salt solution in the capillaries is proportional with the concetration of the salt. Saturated solution of halite (NaCl) may built up a pressure of 200 MPa in the capillaries that can easily exceed the strength of the stone (Winkler, 1987). Another source of internal pressure can be generated by the growing cycles in the pores (Caner-Saltık et al., 1998). Still another source of internal pressure is the volume change of salt crystals in the pores through hydration, e.g. thenardite (Na_2SO_4) hydrates into mirabilite ($Na_2 SO_4.10H_2O$) with a considerable amount of volume increase (Nord and Tronner, 1996).

1.3 Air Pollution in Ankara Affecting Stone Deterioration

About three decades ago, Ankara was one of the most polluted cities in Turkey. Sulphur dioxide, the major pollutant in the atmosphere, was mainly due to the combustion of high sulphur containing coal used for domestic heating. According to the measurements of "Institute of Health Protection-Ankara", average sulphur dioxide concentration reached to 600$\mu g/m^3$ in winter times (Böke, 1987; Caner, et al, 1988) (Fig. 1.6). But still, sulfur dioxide concentration in winter times may have increased considerably.

Data collected by the Institute of Health Protection-Ankara, indicates considerable amounts of nitrogen oxides in the atmosphere (Fig. 1.7 and Fig. 1.8), although the determinations were done for limited period. The nitrogen gases in the atmosphere are mainly introduced by the exhaust gases of motor vehicles.

Pollutants other than the major gases mentioned above are particulate materials. Seasonal concentrations of atmospheric particulate materials as determined by neutron activation analysis reach to considerable amounts in winter times (Sabuncu et al, 1986).

Climatic conditions of Ankara atmosphere, with high average relative humidity values in winter months and high relative humidity values during the nights through the year even in summer times, must favor adsorption of both nitrogen oxides and sulphur dioxide on andesite and marble surfaces.

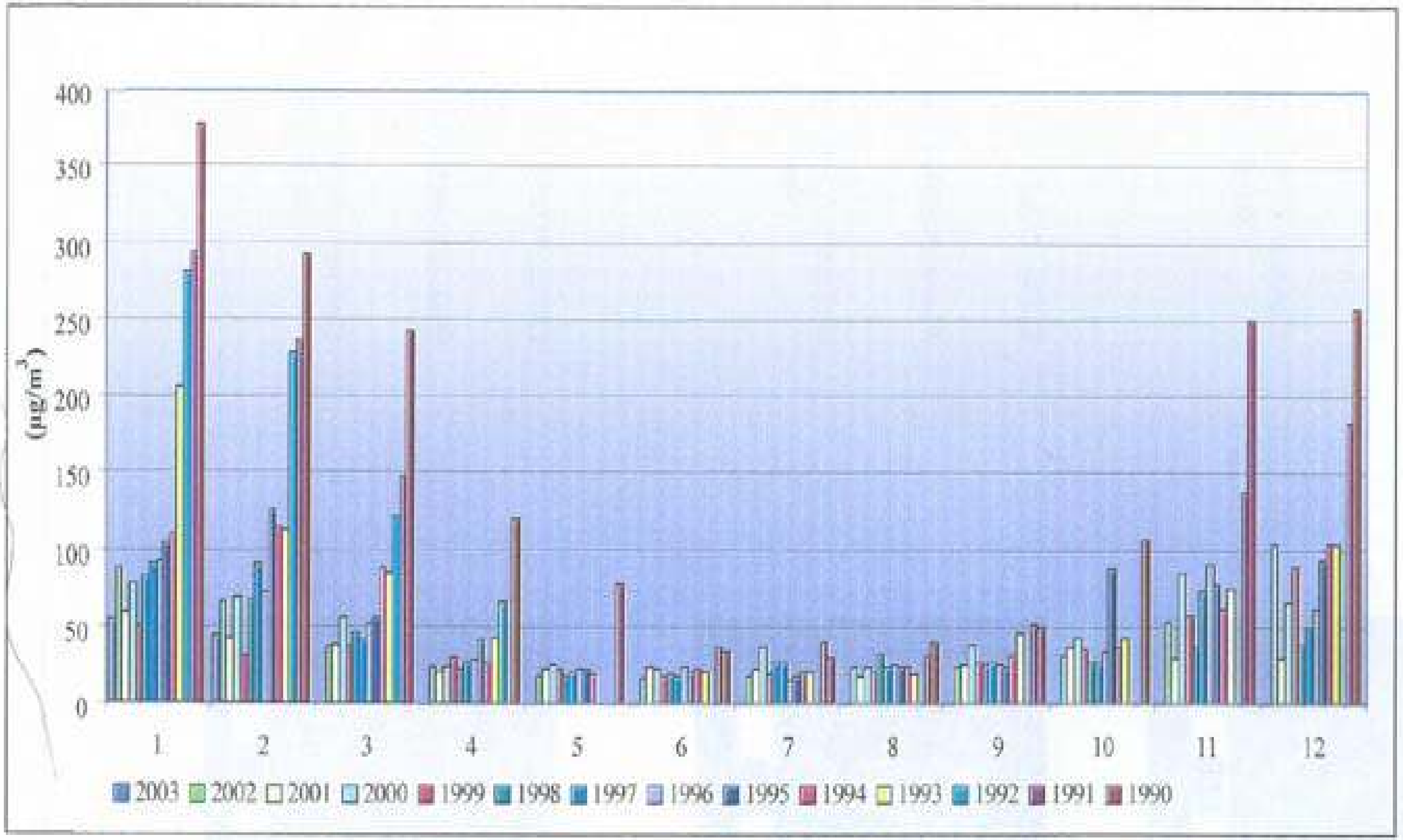


Figure 1.6 Average SO_2 concentrations in Ankara atmosphere (1990-2003) (IHP, 2003)

Nowadays, Ankara is not considered as a polluted city due to the usage of natural gas. Sulphur dioxide reaches to the stone surfaces by dry and wet deposition phenomena, dry deposition being the accumulation of airborne pollutants on stone surface by wind and turbulance and wet deposition consisting of the incorporation of pollutants by falling precipitation on the stone surfaces. Both of these processes were detected on the marble surfaces of the Temple of Augustus (Caner et al, 1988) and on travertine surfaces of several buildings in Ankara such as Anıtkabir, Maltepe Mosque, Hacettepe University and Yüzüncü Yıl Çarşısı (Böke, 1987). Besides forming a strong acid as nitric acid, nitrogen oxides play catalytic roles in the oxidation of sulphur dioxide and its pollution reactions with the stone (Al Badavi, 1988; Böke, 1987). That is why the traffic which is the main source of nitrogen oxides emission should be kept away from the monuments as much as possible.

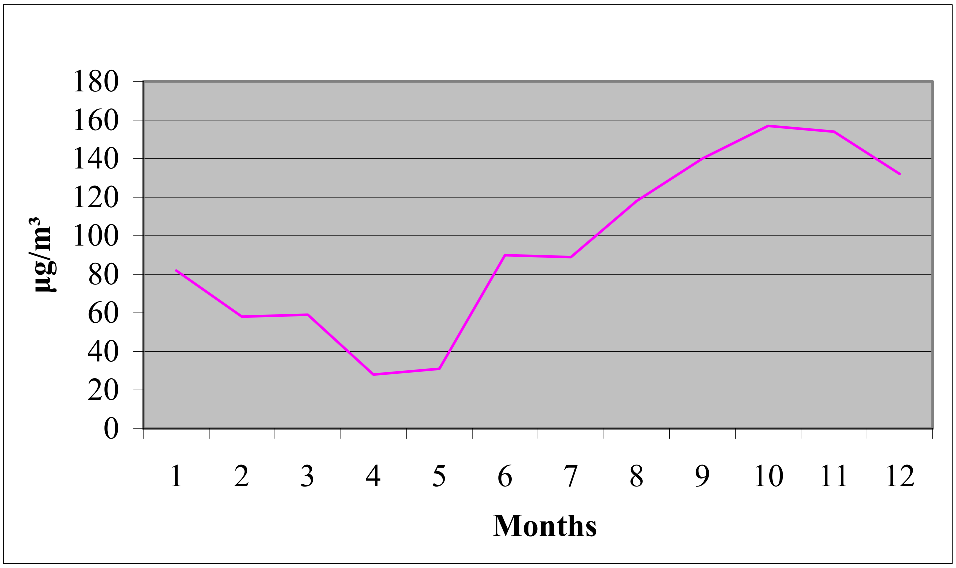


Figure 1.7 Average NO_2 concentrations in the Ankara atmosphere in 2003 (IHP, 2003)

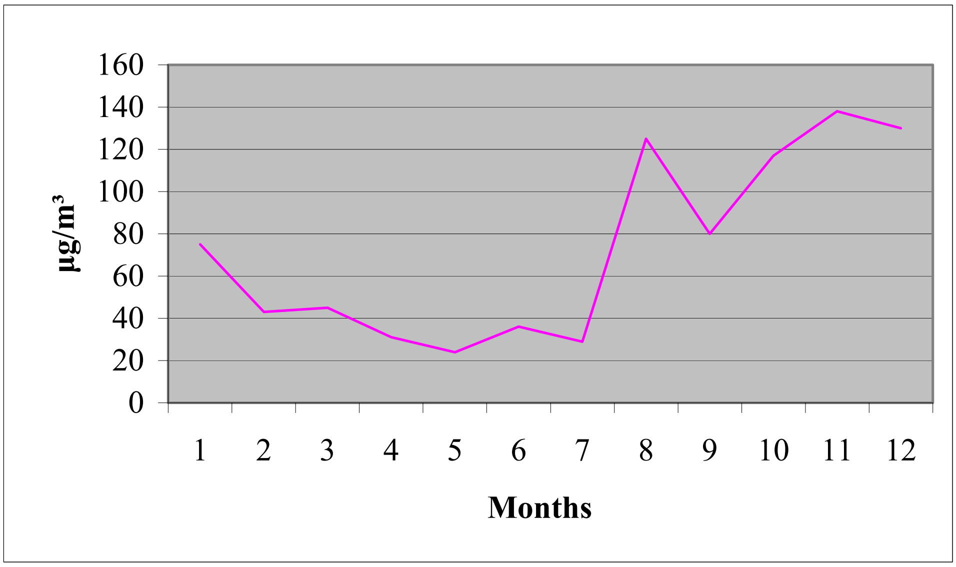


Figure 1.8 Average NO concentrations in the Ankara atmosphere in 2003 (IHP, 2003)

1.4 Previous Studies on Andesites

Andesite is a fine grained volcanic rock, particle size being less than 0.1 mm. Its colour is variable as the shades of grey, purple, brown, green and almost black. Only the phenocrysts are recognizable in hand specimen; these are white tabular plagioclase feldspars, plates of biotite mica or prisms of hornblende or augite. The microscope shows the groundmass to consist of plagioclase (oligoclase-andesine) with one or more of the minerals hornblende, biotite and orthorombic or monoclinic pyroxene. Andesite groundmass is composed chiefly of oligoclase or andesine feldspar. Orthoclase and quartz are absent or present in amounts less than five percent. Andesites are usually named according to the dark minerals present, such as hornblende andesite, hypersthene andesite, etc. In some andesite the groundmass is partly glassy and in rare types completely so.

In the literature, the research works related to andesites are rather scarce. Majority of the previous works related to weathering generally involve granitic rocks and some sedimentary rocks. Kossev (1970), correlated the physical and mechanical properties of different rocks including andesites. Hoek and Brown (1980a) studied on the analyses of the Paguna andesites in New Guinea to relate the strength of andesite samples for different weathering grades. Kurti (1979) carried out some petromechanical tests such as uniaxial compressive strength, modulus of elasticity, density and porosity on different andesites in relation to water reservoirs constructed in Hungary. Saito (1981) studied the relationship between physical and mechanical properties of weathered igneous rocks, including andesites to define a quantitative measure of degree of weathering. Fookes et al. (1971) in New South Wales, Australia have carried out systematic studies on granites and granitic gneisses to establish the grades of weathering for engineering purposes. There are some studies on Ankara andesites in relation to their physical, mechanical and engineering properties. Nathaniel (1972) examined some Ankara andesites and found their compressive strength and modulus of elasticity. Taqieddin (1972) investigated Ankara Andesites for engineering purposes and found their porosity and compressive strength. Özdoğan (1973) also investigated Ankara andesites for engineering purposes and he found their modulus of elasticity. Karpuz (1982,) studied Ankara andesites and he grouped them four districts. Ayday (1989) also studied Ankara andesites and he found their bulk density and ultrasonic velocity. The results of all previous studies of Ankara andesites are summarized in Table 1.2.

Table 1.2 Previous studies on Ankara andesites.

LOCATION	BULK DENSITY g/cm³		POROSITY		COMP. STRENGTH MPa			Emod MPa		ULTASONIC VEL.m/s	
	1	5	1	4	1	4	3	2	3	1	5
Yenimahalle				10.26		48.94	63.74	31245	10885		
Çubuk	2.42		5.71	10.26	34.62	140.33	132.68	35045	16799	4397	
Esertepe	2.37		7.42		40.40					4127	
H.Gazi				11.14		48.54	49.23	25419	9238		
Gölbaşı	2.25	2.57	7.84		33.34					4270	3127
Keçiören				11.14		45.80	45.80	30655	7373		
Çubuk											
Solfasol								30905			

Karpuz,1982 (1) Özdoğan,1973 (2) Nathaniel,1972 (3) Taqieddin, 1972 (4) Ayday, 1989 (5)

Ankara andesites are found in four different districts of Ankara and they are grouped accordingly (Karpuz, 1982, Karpuz and Pasamehmetoglu, 1992; 1997).

a)-Çubuk region andesites: fine to medium grained

b)-Esertepe region: medium grained

c)-Hüseyin Gazi region: medium to coarse grained

d)-Gölbaşı region: fine grained

Those andesites were further grouped according to their degree of weathering and porosity as given in Table 1.3 (Karpuz, 1982, Karpuz and Pasamehmetoglu, 1992; 1997).

Five degrees of weathering were identified as :

I)- Fresh

II)- Slightly Stained

III)- Completely Stained

IV)- Weathered

V)- Decomposed

The porosity of andesites increses with weathering

Table 1.3 Effective porosity and degree of weathering of some Ankara andesites (Karpuz, 1982)

Mass Grade	Material Description	Porosity (%)	
		Çubuk+Esertepe Districts	H.Gazi District
I	Fresh	0-2.22	0-10.60
II	Slightly Stained	2.22-4.62	0.60-14.31
III	Completely Stained	4.62-6.62	14.31-17.21
IV	Weakened	6.44-10.06	17.21-21.46
V	Decomposed	> 10.06	> 21.46

According to Karpuz (1982), generally the andesites of Çubuk district are more weathered than those of other localities. Çubuk and Esertepe andesites have less porosity than porphyritic and finely crystalline types. Increase of porosity of Esertepe and Çubuk andesites in early stage of weathering is mainly due to an increase of crack-shaped pores which does not much contribute to an increase of porosity. The pores in porphyritic and finely crystalline types are closely related to the progress of alteration in the groundmass, having less crack-shaped pores when compared to the others (Saito, 1981). The different porosity produces different physical and mechanical properties upon weathering.

The porosity of Hüseyin Gazi and Gölbaşı districts are considerably high in comparison that of Çubuk and Esertepe districts. As the pores in the structure of rock material increases, its deformability also increases but its strength decreases. (Karpuz, 1982, Karpuz and Pasamehmetoglu, 1992; 1997). High porosity increases the deformability and decreases the strength of the fresh rocks. Thus, it causes weakening of the rock due to weathering processes.
The products of weathering of andesitic rocks are phyllosilicates, geoethite, gibbsite and halloysite. In the first weathering layer surface, an absolute accumulation of gibbsite was observed; further away from the surface, the gibbsite is redissolved, and replaced by alluvial phyllosilicate clay (Mulyanto and Stoops, 2003).

1.5 The Location of Ankara Castle and Gençkapı Gate on Ankara Castle

The whole Castle consists of an inner circle (İç Kale), an outer circle (Dış Kale) and a northern part. The inner circle is located at the top of the hill and apart from the Turkish modifications or repair work. It is mostly Byzantine. This inner circle (wall) is called the castle and it is the oldest part in the whole circuit. It is approximately square; 350 by 150-180 m. The northern side reaches a height of 135 m from the river Hatib. The west and south sides are built over a mildy sloping land and they are more or less rectilinear and construction is more regular. There is a large gate in the middle of south side which is the principal entrance (Gate C or Zindan Kapı). There is a large postern on the western side which is situated between the towers 12 and 13 (Gençkapı) (Figs. 1.9 and 1.10). There is a group of structures descend down the level of the river and they are constructed to defend the narrow valley. There seems to have been an underground passage opening to the north at the bottom of the ravine. Most of this part is Turkish and stands on earlier foundations. The outer circle follows a curvilinear path and it is at a distance of 100-150 m from the south and west sides of the castle. This circle is later than the inner one and it is also Byzantine. However, in this part the Turkish restorations are frequent (Jerphanion, 1928, Mamboury, 1933).

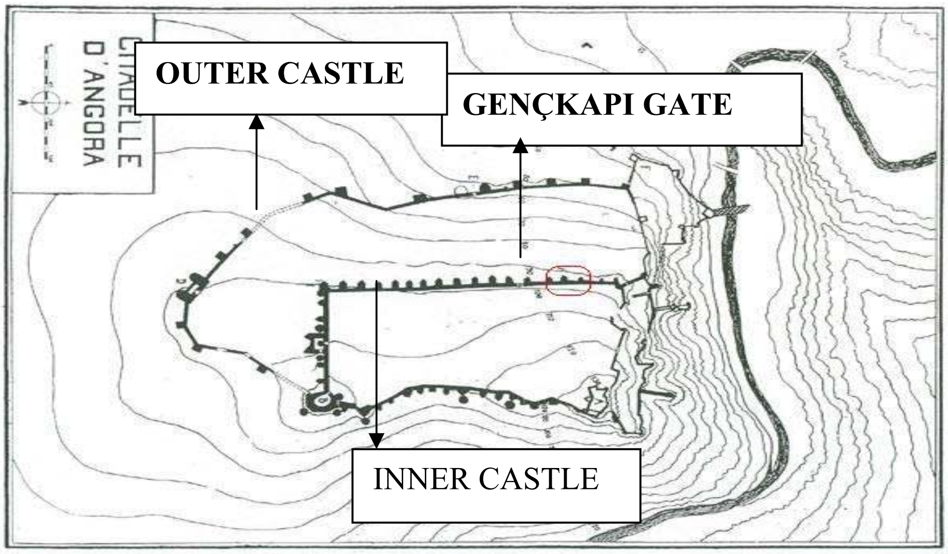


Figure 1.9 A map of Ankara Castle and position of Gençkapı Gate.
Redrawn after Jerphanion, 1928

Figure 1.10 A general view from Gençkapı Gate

1.6 The History of Ankara and Ankara Castle

Archaeological studies show that Ankara was continually settled since ancient times (Idil, 1997). Some artifacts belonging to Palaeolithic era were discovered in Ankara region. The remains of small palaces belonging to the Chalcolithic era and Bronze age unearthed in Ahlatlıbel and Koçumbeli indicate the existence of principalities in the prehistoric ages. It is known that later, Ankara and its vicinity were captured by the Hittites who settled in the city (Idil, 1997). Some settlements were found in the city centre that belonged to the Hittite period. It is believed that these were the remains of some Hittite military garnisons (Idil, 1997).

However, according to the legend, the town was founded by the Phrygian king Midas. Therefore, the first important settlement in Ankara was during the Phrygian times. The numerous tumuli indicate the existence of a Phrygian settlement in Ankara between 750-500 B.C (Idil, 1997).

The Tektosages, a tribe of the Galatians, who in 278-277 B.C. came to Anatolia from Europe in three branches and settled in the area made Ankara their capital (Idil, 1997). Apparently, the Galatians lived both in big and important centers like Ankara and fortresses and villages outside the town.They earned their living by raising sheep and pillaging. Galatians had their own system of administration. In 183 B.C., Ankara was placed under the rule of the Pergamon Kings. During the time of the Galatians Godman and Goddess Cybele were worshipped by the inhabitants of the Ankara castle and its vicinity. The Roman emperor Augustus, in 25 B.C. included Galatia under Roman rule and Ankara became the capital of Galatia, a Roman province. Due to its strategic location at the junction of the roads connecting the eastern border of the Roman Empire to Europe, Ankara, under Roman rule, developed fast and became a major militiary base where the emperors and armies rested (Idil, 1997). In the early 3$^{th.}$ Century A.D. emperor Caracalla repaired the walls of the castle and built a bath at the foot of the castle. In the second half of the century, due to the turbulance in the Roman Empire, the development of the city came to a halt and a new era for the city began (Idil, 1997). In 362 A.D. emperor Julia spent some time in Ankara and set new regulations to improve the administration of the city. When the Roman Empire split in 393 A.D., the city was acquired by the Eastern Roman Empire (Idil, 1997).

Under Byzantine rule, Ankara lived through a period of peace until the 7 th. Century A.D. In 838 A.D. Arab invasions began. Ankara was captured by Harun-el- Resit and in 839 El-Mutasıh invaded the city. Byzantine emperor Michael III, in 859, repaired the city walls which had been damaged during the Arab invasions (Idil, 1997).

The Seljuk Sultan, Alpaslan, defeated the Byzantine army in Malazgirt in 1071 and in 1073 Ankara came under Turkish rule. In 1101, during the crusades, it was recaptured by the Byzantine and for a while served as the eastern border fortress of the Byzantine Empire (Idil, 1997). In 1127, Ankara was captured by the Danismenlid's and in 1169 Kılıçarslan captured the city and succeeded in uniting the Seljuk state in Anatolia. The reign of Alaaddin Keykubat was the golden age (1219-1237) of the Seljuk. During this time Ankara was reconstructed extensively. In 1250, Keyhüsrev repaired the castle (Idil, 1997).

In 1304, Ankara came under the rule of Mongols. During the islamic era, the name of Ankara was changed to "Ergünü" and " Angora".

In 1356, the city was captured by the Ottomans. During the expansion of the Ottoman Empire, upon the establishment of state rule, Ankara became the center of the Anatolian States (Idil, 1997).

Ankara Castle is the symbol of the city. There are conflicting views about when the castle walls were originally built and to which era the surviving walls belong, but in design at least the inner walls are typical of Byzantine fortifications (Idil, 1997). The castle and city walls in certain parts are Roman in style. Under the Romans, Ankara expanded beyond the inner walls downhill towards the plain, in the form of an open city similar to the ancient Greek city states but subsequently the outer walls were constructed as protection against the Persians and Arabs. Most of the walls must have been built during Byzantine era and even later.

Ankara Castle consists of two sections: the inner castle and the outer castle. The inner walls were probably built after the town was recaptured by emperor Heraclius from the Sasani king Hüsrev II in 630 A.D. The castle was badly damaged later during the Arab attacks and it was restored in 859 A.D. by the Byzantine emperor Michael III. At a later, unknown date the outer walls were added .The castle, as we see today, dates to Seljuk period (Idil, 1997). It was restored during the Ottoman period as well. Today, Many Ottoman houses built in the previous century are seen along the narrow streets in the castle. The inner castle is almost rectangular and it is constructed of local andesite and elements brought from ancient structures (ıdil, 1997). Towers of the inner castle are pentagonal and its main entrance is in the South (Idil, 1997). The tower in the east is round and it is called the eastern fortress. Akkale (White Fortress) tower faces the Bent stream and it is located on the highest point in the north (Idil, 1997).

1.7 Aim and Scope of the Study

The aim of the study is to examine decay problems and the types of andesites in Ankara Castle. The visual examination of the castle gave an impression that Gençkapı region has the typical weathering problems that represent the problems of Ankara Castle andesites in general. Therefore, Gençkapı region was selected to be studied in detail.

CHAPTER II

MATERIALS AND METHODS

In this study, decay problems of Ankara Castle andesites were studied by in situ and laboratory analyses. In situ analyses involved recording the visual decay forms. After that, representative samples were collected from andesites as well as from other materials that are in touch with andesites such as marble, mortar and soil. Gölbaşı quarry andesites were also examined for comparison. Laboratory analyses involved determination of basic physical and mechanical properties, mineralogical and raw material composition of those representative samples.

Basic physical property examination included the bulk density, total porosity determinations. Analyses of basic mechanical properties were carried out by measurement of ultrasonic pulse velocity to estimate modulus of elasticity (Emod).

Raw material composition and mineralogical properties of selected samples were determined by combined interpretation of various analyses such as petrographic analyses of thin sections, X-ray powder diffraction (XRD), analyses electrical conductivity measurement and spot tests for soluble salts.

2.1 Mapping of Visual Decay Forms

The method developed by Fitzner et al. (1992, 1995, 1997) was adapted for the mapping of visual decay forms of stones at Gençkapı part of Ankara Castle. The decay forms and their distribution on the walls were documented by mapping the individual weathering forms on the photographs.

In Fitzner’s mapping, the decay forms were classified into three groups. They are namely “detachment”, “discoloration and deposits on stone surfaces” and “stone loss”.
The degree of the damage was classified into five groups. They are; “most severe decay”, “severe decay”, ”medium decay”, ”slight decay”, “most slight decay”.
The damage categories were as follows;

1)- Loss of stone material (most severe (V) and severe decay (IV);
 a)- Break out (V)
 b)- Stone taken out (V)
 c)- Alveolar weathering (IV)

2)- Detachment of stone material (medium decay (III));
 a)- Flaking to crumbling (III)
 b)- Multiple flakes (III)

3)- Discoloration and deposits on stone surface (most slight (I) and slight decay (II));
 a)- White staining (I)
 b)- White-to-grey staining (I)
 c)- Grey-to-dark grey staining (I)
 d)- Black staining (I)
 e)- Salt deposition (II)
 f)- Microbiological colonization (II)

2.2 Samples Collection and Description

Samples were collected from the scales of north and west walls of Gençkapı, Ankara Castle (Fig. 2.1), in addition, three original Gölbaşı andesite samples from the quarry. Descriptions of the samples and their nomenclature are given below together with their photographs (Fig 2.2). Samples were collected with maximum care, with a scalpel avoiding to give damage to the walls. They were then placed in polyethylene bags and then labelled.

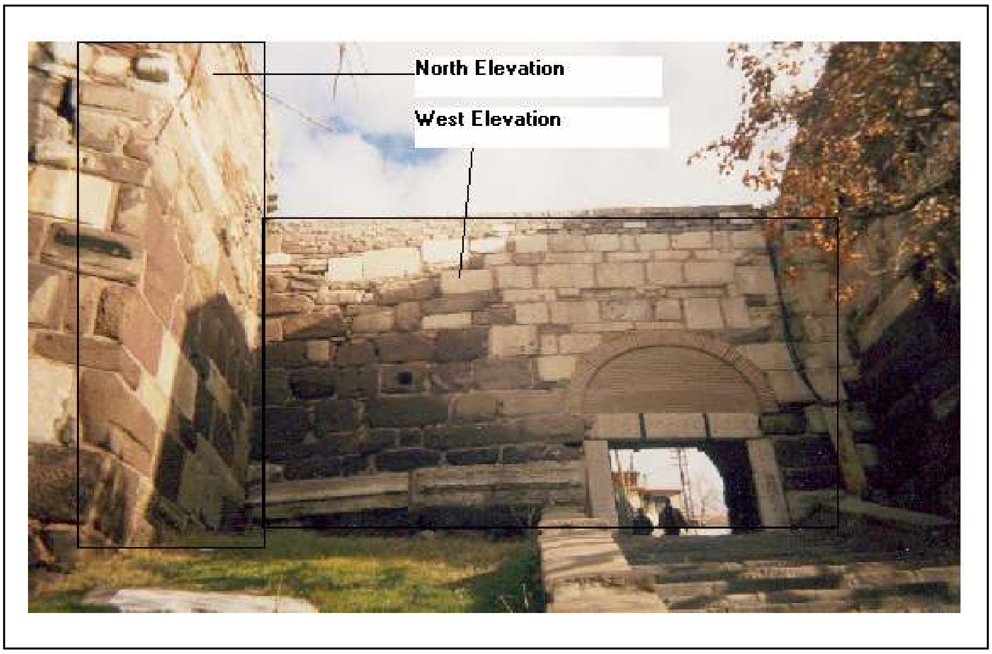


Figure 2.1 Thesis working area on the Ankara Castle wall

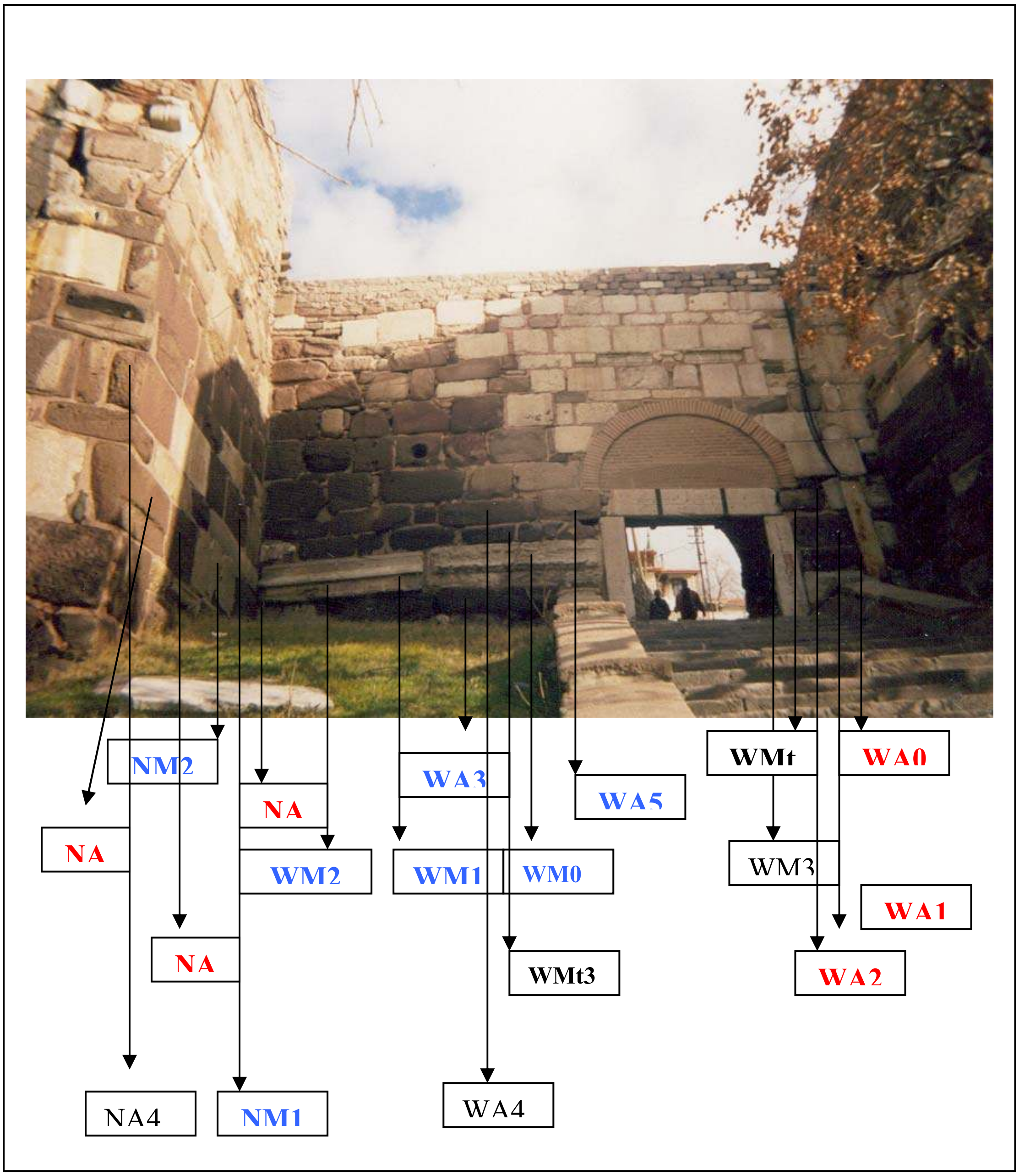


Figure 2.1 Samples location on the Ankara castle wall

Nomenclature is as follows :

W A 3 (Sc)

Location of the sample on the wall
Stone Type
Stone Number
Weathered layer (scratched in situ)

The first letter represents the location of the sample on the wall, e.g "W" represents the sample from the west elevation of the Gate. "N" represents the stone samples from the north elevation of the Gate . "Q" represents the stone samples from the Gölbaşı quarry andesite.

The second one or two letters show the sample type, e.g "A": andesite, "M": marble and "Mt ": mortar , "SO": Soil, "S": Salt .

The first number is the sample number. Letters a and b correspond to different parts of the sample analyzed. The locations of the samples on the walls were given in Figure 2.1

For the weathered andesites: "S", "I" and "C"represent stone surface, interior and crack surface, respectivately. And "Sc", "So" and "Sa" represent scale, soil and salt, respectively.

The complete description of the andesite samples taken from the Ankara Castle are given below:

Table 2.1 Description of the Samples

Code: WA3

Place: West Elevation

Colour : 2,5 YR – ¾ Dark Reddish Brown

Table 2.1 (continued)

Code: WA5

Place: West Elevation

Colour: 10 R – 4/2 Weak Red

Code: WA1

Place: West Elevation

Colour : 10 R – 3/2 Dusky Red

Code: WA2

Place: West Elevation

Colour : 7,5 R – 4/2 Weak Red

Table 2.1 (continued)

	Code: NA1 Place: North Elevation Colour: 10 R – 2,5/2 Very Dusky Red
	Code: NA2 Place: North Elevation Colour : 7,5 R – 3/2 Dusky Red
	Code: NA3 Place: North Elevation Colour : 10 R – 2,5/2 Very Dusky Red

Table 2.1 (continued)

	Code: NA4 Place: North Elevation Colour : 10 R – 3/6 Dark Red

2.3 Laboratory Analyses

The laboratory studies involved the analyses of the collected andesite, marble and mortar samples, for their basic physical properties as bulk density and porosity, basic mechanical properties as modulus of elasticity and the qualitative and quantitative analyses of soluble salts as well as mineralogical and petrographical analyses done by examinations of thin sections in optical microscope and XRD analyses.

2.3.1 Determination of Basic Physical Properties

The basic physical properties analysed were bulk density and total porosity. In the analyses each sample was divided into two parts and they were dried in the oven at 45 ^{o}C to constant weight and their dry weights were recorded (M_{DRY}). Later, the samples were immersed in distilled water for 24 hours and they were left under vacuum in a chamber at 0.132 atm (100 torr pressure) for about 30 minutes to let water enter into finest pores. Each sample was then taken out and weighed as it is and as immersed in water for Archimedes weight (M_{ARC}). All weights were measured with the sensitivity of 0.1 mg. The calculation of porosity and bulk density were done by using the following equations (Teutonico, 1988; TSE, 1987);

Total Porosity = $N=[(M_{SAT} - M_{DRY}) / (M_{SAT} - M_{ARC})] \times 100$ (%)

Bulk Density = $\delta = (M_{DRY}) / (M_{SAT} - M_{ARC})$ (g / cm^3)

Where;

Density (δ) is the ratio of the mass to the real volume of the sample. Porosity (N) is the fraction of the total volume of a porous material occupied by pores or more simply, the empty spaces or voids in the mass and it is expressed by the percentage of volume. (Teutonico, 1988).

2.3.2 Determination of Basic Mechanical Properties

Basic mechanical properties of the samples were studied by the measurements of ultrasonic pulse velocity which then were used to determine modulus of elasticity together with bulk density values.

2.3.2.1 Ultrasonic Velocity Measurement

This test is intented to determine the velocity of propagation of ultrasonic waves in andesite samples. The degree of fissuring and porosity of rock materials affect ultrasonic pulse velocity values (I.S.R.M., 1981). Longitudinal (p) velocities are measured. To calculate the velocity of the waves, the impulse is imported to the sample and the time is measured which is related with the pathlength of the wave which is the thickness of the sample.

$V = I / t$

Where:

V: Velocity (m/s)

I: Distance traversed by the wave (m)

t: Travel time (s)

In the measurements, PUNDIT-PLUS, instrument was used with its probes, transmitter and receiver of 220 kHz for all samples. A thin film of vaseline was applied to the surface of the transmitter and receiver to have good contact with the sample.

2.3.2.2 Determination of Modulus of Elasticity

The modulus of elasticity (Emod) is defined as the ratio of stress to strain and shows the deformation ability of a material under the effect of external forces (Timoshenko, 1970). The modulus of elasticity of andesites in this study was determined by using ultrasonic pulse velocity and bulk density of the samples through the following equation (ASTM, 1990; RILEM, 1980).

$$Emod = D \times V^2 (1+ \gamma dyn)(1-2 \gamma dyn) / (1- \gamma dyn)$$

Where;

Emod: modulus of elasticity (N/m^2)

D: bulk density of the sample (kg/m^3)

V: wave velocity (m/s)

γdyn: Poisson's ratio: The ratio of the lateral strain to the longitudinal strain

In this equation, poisson's ratio differs from 0.1 to 0.5. For this study, poisson's ratio of 0.166 for Çubuk region Ankara andesite samples were used (Özdoğan, 1973).

2.3.3 Quantitative Determination of Soluble Salts by Electrical Conductivity Measurements

Salt analyses were carried out in all samples. The soluble salt content of the samples was determined quantitatively by means of electrical conductivity measurements. Two sub-samples were prepared for each sample. Approximately 1 gram of dried and powdered sample was mixed well with 50 mL distilled water. The solution was then filtered to get a clear salt extract solution. The electrical conductivity of this solution was measured by using a conductometer 'Metrohm AG Konduktometer E382 '. As the last stage, the conductivity of the standard solution (0.01 N KCl) was measured. The percentage of salt in the sample was calculated using the following formula (Black, 1965).

$$EC = [(0.001411 \times R_{STD})/R_{EXT}] \text{ mhocm}^{-1},$$

where "EC" is the electrical conductivity in mhocm^{-1}, " R_{STD}" is the cell resistance with standard solution (0.01 N KCl) and "R_{EXT}" is the cell resistance with extract solution.

SC = 640 x EC   mg/L ,

where, ”SC” is the salt concentration in mg/L, and “EC” is the electrical conductivity in mhocm^{-1} calculated above.

$$SA = [(SC \times V_{EXT}) / (1000 \times M_{DRY})] \times 100 \quad \%,$$

Where “SA” is the amount of salt in the sample as weight percent, ”V_{EXT}” is the volume of the extract solution in mL, which was 50 mL in this experiment, and “M_{DRY}” is the dry weight of sample in mg.

2.3.4 Qualitative Analysis of the Soluble Salts by Spot Test

The salt extract solutions were concentrated by evaporation in oven at 40 ºC for about six hours to increase the concentration of the salt ions. The most common soluble salts in the porous building materials are sulphates, chlorides, nitrates, nitrites and phosphates of sodium, potassium and magnesium elements. The qualitative spot tests indicate their presence.

The presence and absence of an ion was designated with a cross (+) and with a minus (—). The proportionate number of plusses shows the relative abundance of an ion. “— “ shows the absence of ion, “+ —” shows ion at the limit of perceptibility. ”+” shows the presence of ion, “++” shows ion in notable abundance and “+++” shows ion in a high quantity. The tests for individual ions are given below (Teutonico, 1988).

The Spot Test of Phosphate (PO_4^{3-}) Ions

To determine phosphate, one or two drops of the test solution is placed on filter paper followed by a drop of ammoniummolibdate ($(NH_4)_2MoO_4$) solution. To accelerate the reaction, the paper is held over the hot wire gauze. After drying it, a drop of benzidine solution is added. Then the paper is developed over ammonia. In the presence of phosphates, a blue fleck or a ring is formed.

The Spot Test of Sulphate (SO_4^{2-}) Ions

A few drops of test solution is placed in a tube. One or two drops of dilute hydrochloric acid (2 N HCl) and one or two drops of a 10 % solution of barium chloride ($BaCl_2$) are then added. If a white precipitate forms, then sulphate is present in the sample (Teutonico, 1988). The reaction is as follows:

$SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4\,(s)$

The Spot Test of Carbonate (CO_3^{2-}) Ions

A few drops of test solution is placed in a tube. One or two drops of 4 M HCl is then added to the solution. Bubbles of gas (CO_2) in the solution indicate the presence of carbonate ions (Teutonico, 1988 ; Feigl, 1958). The reaction is as follows:

$CO_3^{2-} + 2HCl \rightarrow CO_2\,(g) + Cl^- + H_2O$

The Spot Test of Chloride (Cl^-) Ions

In determination of chloride, a few drops of test solution is placed in a tube. One or two drops of dilute nitric acid and then one or two drops of silver nitrate solution (0.1 N $AgNO_3$) are added. The formation of white precipitate shows the presence of chloride in the sample (Teutonico, 1988). The reaction is as follows:

$Cl^- + AgNO_3 \rightarrow AgCl\,(s) + NO_3^-$

The Spot Test of Nitrite (NO_2^-) Ions

A drop of the test solution is added on a spot plate. One drop of sulfanilic acid and α-naphthylamine solution are then added. Red color on the spot plate indicates the presence of nitrite ions (Teutonico, 1988; Feigl, 1958).

The Spot Test of Nitrate (NO_3^-) Ions

In the determination of nitrate, a drop of the test solution is placed on a spot plate. One drop of sulfanilic acid and α-naphthylamine solution are added. Then, small quantity of zinc powder is added. If a red color occurs, nitrate is present in the sample (Teutonico, 1988; Feigl, 1958).

2.4 Determination of Mineralogical and Petrographical Analyses of Andesites

Mineralogical and petrographical properties of andesite samples were determined by combined interpretation of thin section analyses and XRD analyses.

2.4.1 Thin Section Analyses

To prepare the thin sections of the samples, they were firstly placed in plastic molding boxes of 1.5x3x1 cm. Then, they were saturated with the polyester (ESKIM–extra POLYESTER) mixed with accelerator and hardener under vacuum of 0.132 atm (100 torr) pressure. Following their hardening, the molded samples were removed from boxes and cut into 1 mm slices to be fixed and reduced to 30 μ thickness on glass slides. Thin sections of the samples were examined by using NIKON AFX-2A optical microscope equipped with a photographic attachment.

2.4.2 X-Ray Diffraction Analyses

XRD analyses were carried out on powdered samples of andesites and dried salt extracts. Before the analyses, exterior surfaces, crack surfaces and relatively interior parts of the samples were ground into fine powders by using agate mortar.

The instrument used was a Philips type PWI352/20 X-ray diffractometer. Analyses were done using CoKα X-ray with Ni filter, adjusted to 35kV and 14mA. The XRD traces were recorded for the 2θ values of 6° to 75°. Mineral phases were identified in XRD traces.

CHAPTER III

EXPERIMENTAL RESULTS

Results of visual anlayses and laboratory analyses are given in this section.

3.1 Mapping of Visual Decay Forms

Visual analyses was done according to procedure given in section 2.1. It showed that, the stone walls of Gençkapı Gate had some deterioration forms as material loss, alveolization, detachments as scales, discoloration and salt deposition on the stone surfaces
(Fig. 3.1-3.2). The most severe decay was found especially on the marble stones on the west elevation (Fig. 3.1). In the upper part of the north elevation, alveolar weathering and salt deposition were observed (Fig. 3.2).
Rain water was not drained properly in the castle walls. Seasonal rising damp in the lower parts of the walls due to the improper site grading and continual rain penetration in the upper parts due to the faults of drainage system were observed at the site. The lower parts of the Gençkapı Gate had damp zones where dampness stayed for a long period of time. Duration of dampness in the walls affected the severe stone decay.

Figure 3.1 A view from west elevation at Gençkapı Gate; material loss and detachment as scales on marble surfaces

Figure 3.2 A view from north elevation at Gençkapı Gate; salt depositon and alveolar weathering on the andesite surface

3.2 Results of Bulk Density and Porosity Determinations

Bulk density and porosity values of samples have shown some differences in comparison to each other (Table 3.1)

Bulk density of Ankara Castle andesite samples varied in the range of 2.22-2.34 gr/cm^3, the average being 2.28 gr/cm^3. The porosity values of the same samples were in the range of 3.24-10.47 %, with an average value of 6.16 % (Fig. 3.3)

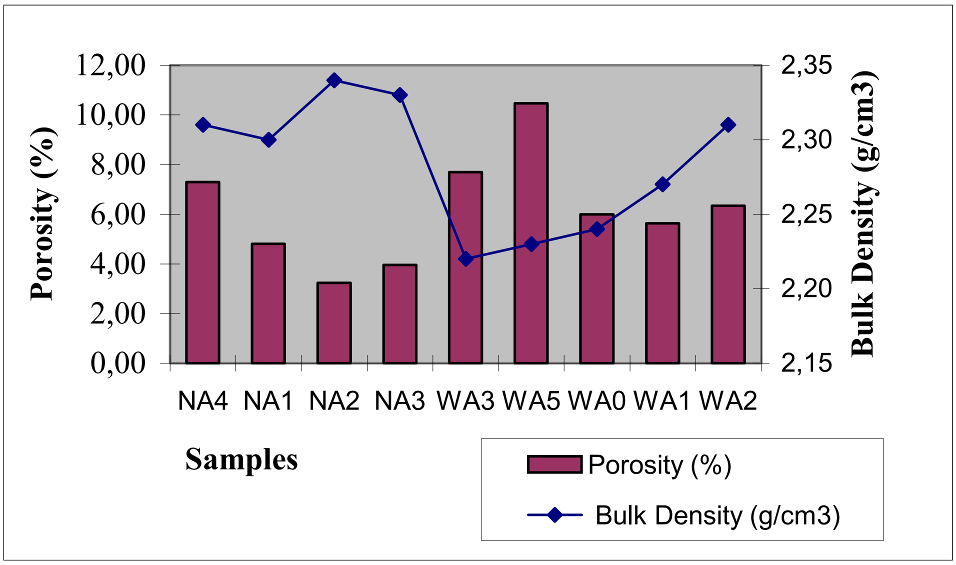


Figure 3.3 Bulk density and porosity values of Ankara Castle andesite samples

The average porosity and bulk density of Gölbaşı quarry andesite samples were 12.56 % and 2.54 gr/cm^3, respectively (Fig. 3.4).

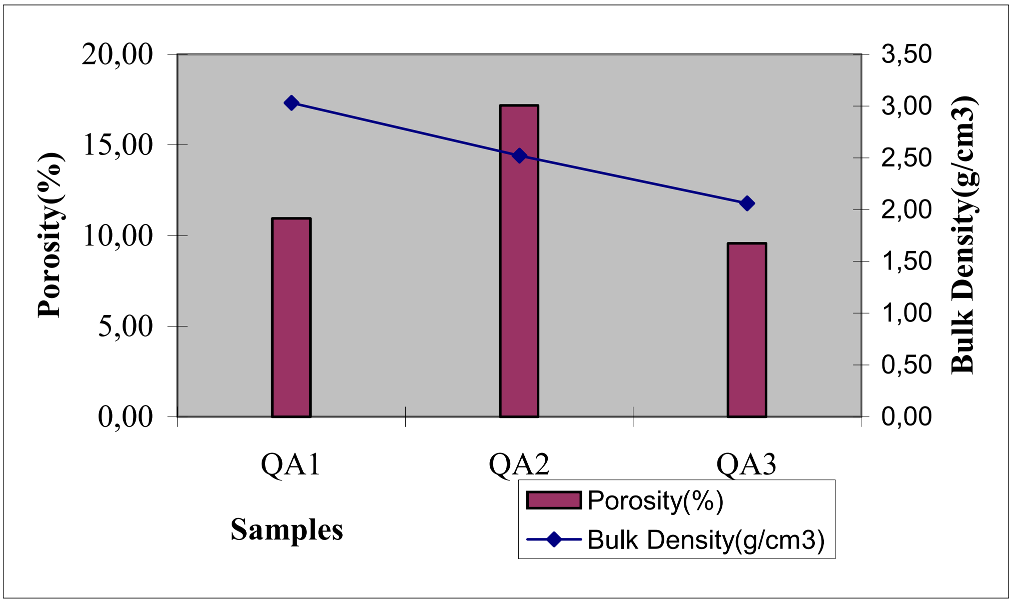


Figure 3.4 Bulk density and porosity values of Gölbaşı quarry andesites

Table 3.1 Bulk density and porosity of andesite, marble and mortar samples studied

Sample	M dry(g)	M sat(g)	M arch(g)	Porosity (% v)	Bulk Density (g/cm^3)
NA4a	15.52	16.02	9.03	7.16	2.31
NA4b	15.45	15.43	9.23	7.44	2.31
NA4 (Average)				**7.30**	**2.31**
NA1a	14.12	14.42	8.20	4.80	2.32
NA1b	13.03	13.30	7.68	4.82	2.27
NA1 (Average)				**4.81**	**2.30**
NA2a	5.06	5.13	2.95	3.26	2.35
NA2b	4.32	4.38	2.54	3.21	2.32
NA2 (Average)				**3.24**	**2.34**
NA3a	16.15	16.42	9.52	4.01	2.31
NA3b	15.57	15.84	9.11	3.91	2.34
NA3 (Average)				**3.96**	**2.33**
WA3a	2.29	2.37	1.34	7.62	2.21
WA3b	2.32	2.40	1.35	7.77	2.23
WA3 (Average)				**7.70**	**2.22**
WA5a	2.91	3.05	1.75	10.17	2.22
WA5b	2.62	2.74	1.56	10.76	2.24
WA5 (Average)				**10.47**	**2.23**

Table 3.1 (continued)

Sample	M dry(g)	M sat(g)	M arch(g)	porosity (% v)	Bulk Density (g/cm^3)
WA0a	1.48	1.52	0.86	5.81	2.23
WA0b	1.92	1.97	1.11	6.16	2.25
WA0 (Average)				**5.99**	**2.24**
WA1a	1.23	1.26	0.72	5.71	2.26
WA1b	0.79	0.81	0.46	5.55	2.28
WA1 (Average)				**5.63**	**2.27**
WA2a	4.23	4.33	2.53	6.57	2.30
WA2b	3.15	3.24	1.87	6.11	2.31
WA2 (Average)				**6.34**	**2.31**

Table 3.1 (continued)

Sample	M dry(g)	M sat(g)	M arch(g)	porosity (% v)	Bulk Density (g/cm^3)
QA1a	20.12	20.95	14.21	12.40	2.98
QA1b	15.45	15.92	10.97	9.50	3.12
QA1 (Average)				**10.95**	**3.03**
QA2a	16.45	17.45	11.76	17.51	2.89
QA2b	8.25	8.72	5.93	16.83	2.96
QA1 (Average)				**17.17**	**2.93**
QA3a	9.45	9.92	5.44	10.41	2.11
QA3b	13.26	13.82	7.44	8.71	2.08
QA3 (Average)				**9.56**	**2.06**

Table 3.1 (continued)

Sample	M dry(g)	M sat(g)	M arch(g)	Porosity (% v)	Bulk Density (g/cm^3)
NM1a	7.42	7.50	4.70	2.45	2.62
NM1b	6.42	6.48	4.03	2.50	2.70
NM1 (Average)				**2.48**	**2.66**
NM2a	3.56	3.59	2.24	2.19	2.61
NM2b	4.77	4.81	2.98	2.22	2.60
NM2 (Average)				**2.21**	**2.61**
WM2a	5.79	5.83	3.71	1.85	2.71
WM2b	2.93	2.95	1.87	1.89	2.73
WM2 (Average)				**1.87**	**2.72**
WM1a	6.25	6.33	3.90	3.16	2.59
WM1b	4.10	4.15	2.57	3.29	2.57
WM1 (Average)				**3.23**	**2.58**
WM0a	6.65	6.72	4.19	2.71	2.60
WM0b	5.74	5.80	3.59	2.77	2.63
WM0 (Average)				**2.74**	**2.62**
WM3a	8.79	8.82	5.47	0.84	2.65
WM3b	6.27	6.29	3.92	0.89	2.68
WM3 (Average				**0.87**	**2.67**

Table 3.1 (continued)

Sample	M dry(g)	M sat(g)	M arch(g)	Porosity (% v)	Bulk Density (g/cm^3)
NMt1a	15.34	16.17	9.01	11.60	2.13
NMt1b	15.04	15.86	8.79	11.59	2.15
NMt1 (Average)				**11.60**	**2.14**
NMt4a	16.15	16.77	9.26	8.35	2.10
NMt4b	12.59	13.09	7.10	8.26	2.15
NMt4 (Average)				**8.31**	**2.13**
NMt2a	16.00	16.82	9.27	10.95	2.10
NMt2b	15.57	16.38	8.98	10.86	2.12
NMt2 (Average)				**10.91**	**2.11**
WMt3a	18.30	19.26	10.38	11.27	2.14
WMt3b	18.07	19.02	10.59	11.38	2.17
WMt3 (Average)				**11.33**	**2.16**
WMt1a	3.97	4.16	2.34	9.79	2.14
WMt1b	4.16	4.35	2.41	10.43	2.18
WMt1 (Average)				**10.11**	**2.16**

3.3 Results of Quantitative and Qualitative Analyses of Soluble Salts

All materials analysed contained considerable amounts of soluble salts, especially in the north elevation of the Gençkapı Gate, because of continuous water penetration due to the lack of a well-designed drainage system in the upper part of the wall. The soluble salt content of the samples was found in the range of 0.27 to 11.11 % by weight. The results were given in Table 3.2.

The average soluble salt content of the andesite samples were 5.6 % by weight, whereas marbles and mortars they were 1.4 and 8.7 %, respectively.

Soluble salt content of mortar and andesite samples were higher than the marble (Figs. 3.5, 3.6 and 3.7).

The samples from north elevation of the Gençkapı Gate had higher soluble salt content in comparison to the ones from west elevation (Table 3.2).

Ground soil samples were also analyzed for their soluble salt content and the types of anions. The average soluble salt content of the soil was 1.25 % (Table 3.2).

Phosphate, sulphate, chloride, nitrite and nitrate ions were in considerable amounts, whereas, carbonate ion was not detected in the samples.

The phosphate ion was determined in notable quantities in almost all samples. Its source could be the soil.

Sulphate ion was also determined in almost all samples with the exception of WA1 and WA2 andesite samples which were located on the west part of the Gençkapı Gate. The sources of sulphate ions might be cement mortar repairs and soil.

Chloride ion was found in almost all stone samples except marble sample, WM2 for which soluble salt content was the lowest (0.27 %).

Nitrate ion was found in almost all andesite samples except WA3. Nitrite ion was found in all mortar and andesite samples. The sources of nitrate and nitrite ions might be the soil or decomposition of nitrogeneous organic matters and atmospheric pollutants (Teutonico, 1988; Schaffer, 1972).

Table 3.2 Results of soluble salt ions and contents

SAMPLES	PO_4^{3-}	$S0_4^{2-}$	Cl^-	NO_2^-	NO_3^-	CO_3^{3-}	% Salt
NM1	+ -	+	++	+++	+	-	2.20
NM2	+ -	+	++	+	-	-	2.65
WM2	+	-	-	+ -	-	-	0.27
WM1	+	++	+	++	-	-	1.13
WM0	++	++	++	+	-	-	1.16
WM3	+ -	-	+	-	-	-	1.04
NA4	++	+	++	++	+	-	5.01
NA1	++	+	++	+++	++	-	11.11
NA2	+ -	+	++	+++	++	-	6.64
NA3	+ -	+	++	+++	++	-	10.20
WA3	++	+	++	++	-	-	3.63
WA5	+ -	++	+	-	+	-	2.03
WA0	+ -	++	++	-	+++	-	2.74
WA1	+ -	-	++	-	+	-	5.99
WA2	+ -	-	++	-	++	-	3.06
NMt1	+	+	++	+++	++	-	9.63
NMt4	++	-	+	+++	++	-	10.76
NMt2	++	++	++	+++	++	-	9.30
WMt3	+ -	++	++	++	-	-	7.55
WMt1	+	-	++	-	+++	-	6.05
WSO	+	-	++	+++	-	-	2.17
NSO	+ -	-	++	-	-	-	0,30
WS1	+ -	-	++	-	+	-	
WS2	++	-	++	-	+++	-	
WS3	-	-	++	-	++	-	

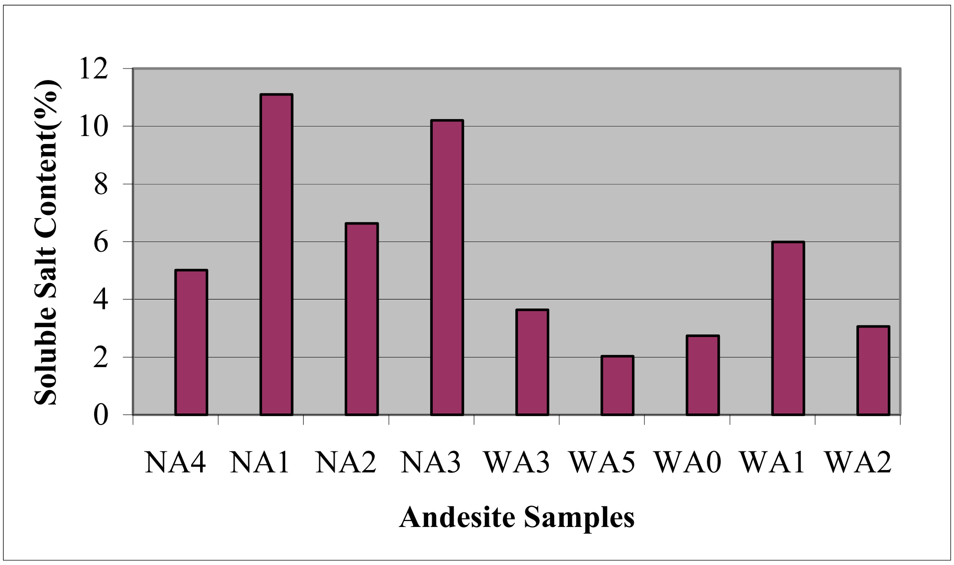


Figure 3.5 Distibution of soluble salts in andesite samples taken from north and west elevations of Gençkapı Gate

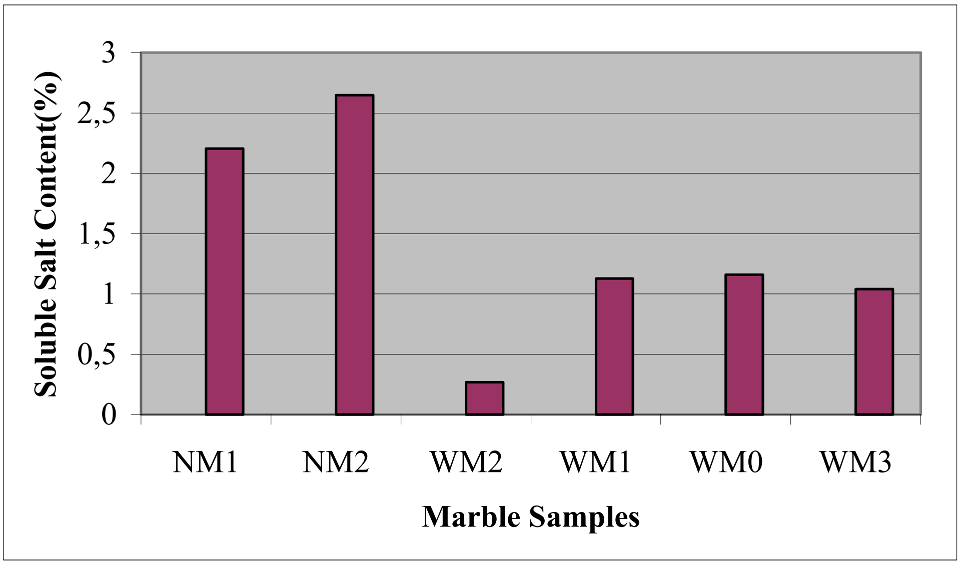


Figure 3.6 Distibution of soluble salts in marble samples taken from nort and west elevation of Gençkapı Gate

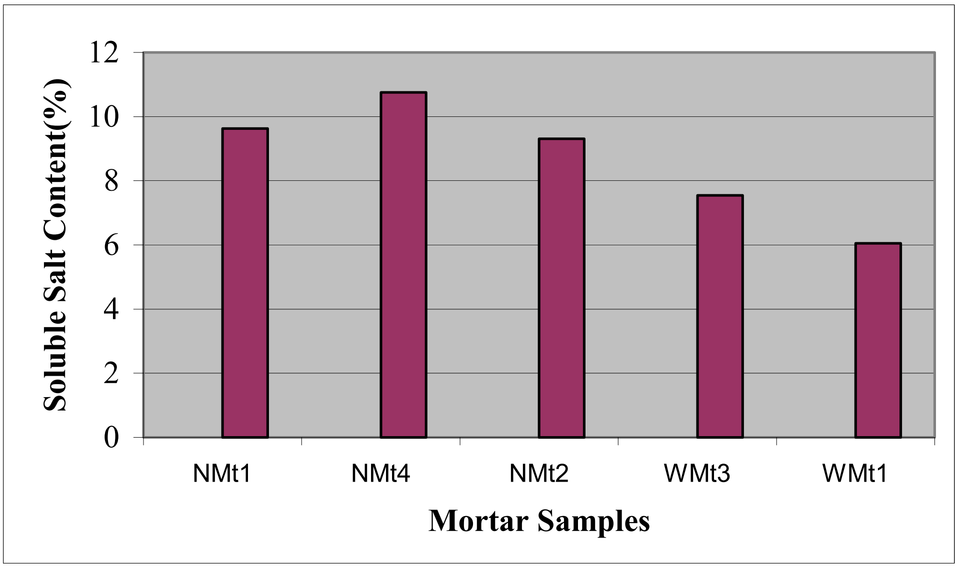


Figure 3.7 Distibution of soluble salts in mortar samples taken from nort and west elevation of Gençkapı Gate

XRD traces of extracted and dried soluble salts from andesite sample NA3 showed the presence of halite (NaCl), niter (KNO_3), sylvite (KCl), gypsum ($CaSO_4 . 2H_2O$), hexahydrite ($MgSO_4 .6H_2O$) and sodaniter ($NaNO_3$) minerals (Fig. 3.8).

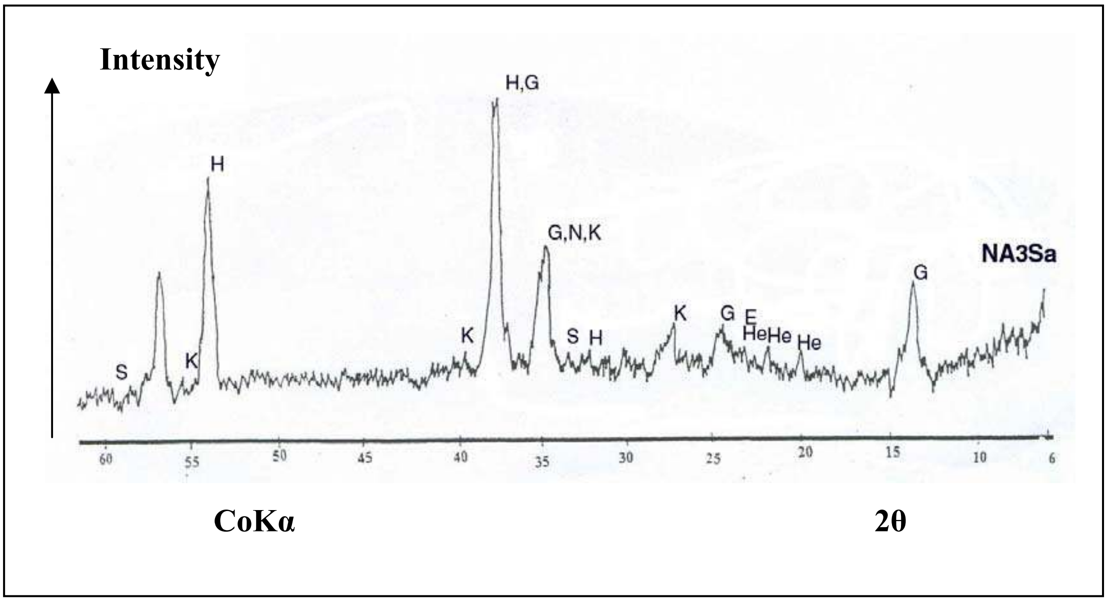


Figure 3.8 XRD pattern of salt sample extracted from andesite sample NA3: **H**:Halite (NaCl); **K**: Niter(KNO_3); **S**: Sylvite (KCl) ; **G**:Gypsum ($CaSO_4 .2H_2O$); **He**:Hexahydrite ($MgSO_4 .6H_2O$); **E**:Epsomite($MgSO_4 .6H_2O$); **N**:Sodaniter($NaNO_3$)

3.4 Results of Basic Mechanical Properties of Andesites

In this study, modulus of elasticity was the only mechanical property that was determined. Ultrasonic pulse velocity values and bulk density values were used to calculate modulus of elasticity (Emod) using the equation given in section 2.3.2.2. The results were given in Table 3.3 for Ankara Castle andesite samples and in Table 3.4 for Gölbaşı quarry andesite samples.

The ultrasonic velocities of Ankara Castle samples were in the range of 779 m/s-1246 m/s, average being 832 m/s (Fig. 3.9, Table 3.3)

The ultrasonic velocities of the Gölbaşı quarry andesite samples were found to be in the range of 2448-2721 m/s, average being 2539 m/s (Fig. 3.9, Table 3.4).

Emod of Ankara Castle samples were found to be in the range of 1269 MPa-3248 MPa, average being 1872 MPa (Fig. 3.11, Table 3.3). Emod of Gölbaşı quarry andesite samples were found to be in the range of 13520 MPa-16450 MPa, average being 15262 MPa (Fig. 3.12, Table 3.4).

Ultrasonic velocities and Emod values of Ankara Castle andesite samples were much lower than the Gölbaşı quarry andesite samples.

Table 3.3 Ultrasonic pulse velocity measurements and modulus of elasticity of Ankara castle andesite samples

Sample	Thickness (mm)	Time (s)	Velocity (m/s)	Bulk Density (g/cm³)	Mod.elast. (MPa)
NA4a	19.5	20.5	951	2.28	1926
NA4b	20.2	22.4	902	2.27	1725
NA4 (Average)			**927**	**2.28**	**1830**
NA1a	18.0	16.6	1084	2.35	2579
NA1b	15.2	16.3	933	2.38	1935
NA1 (Average)			**1009**	**2.37**	**2253**
NA2a	20.0	23.7	844	2.29	1523
NA2b	15.3	19.4	789	2.21	1285
NA2 (Average)			**817**	**2.25**	**1403**
NA3a	22.8	22.4	1018	2.30	2227
NA3b	17.8	23.7	752	2.38	1257
NA3 (Average)			**885**	**2.23**	**1631**

Table 3.3 (continued)

Sample	Thickness (mm)	Time (s)	Velocity (m/s)	Bulk Density (g/cm³)	Mod.elast. (MPa)
WA3a	18.6	21.3	873	2.25	1601
WA3b	20.5	18.3	1120	2.18	2554
WA3 (Average)			**997**	**2.22**	**2061**
WA5a	20.8	16.8	1238	2.26	3235
WA5b	23.3	18.6	1253	2.21	3240
WA5 (Average)			**1246**	**2.24**	**3248**
WA0a	16.8	25.3	664	2.23	918
WA0b	20.2	18.3	1104	2.25	2561
WA0 (Average)			**884**	**2.24**	**1635**
WA1a	15.5	26.3	589	2.24	726
WA1b	15.2	15.7	968	2.24	1960
WA1 (Average)			**779**	**2.24**	**1269**
WA2a	21.0	24.2	868	2.28	1604
WA2b	15.3	18.8	814	2.32	1436
WA2 (Average)			**841**	**2.30**	**1519**

Table 3.4 Ultrasonic pulse velocity measurements and modulus of elasticity of Gölbaşı quarry andesite samples

Sample	Thickness (mm)	Time (s)	Velocity (m/s)	Bulk Density (g/cm³)	Mod.elast. (MPa)
QA1a	4.50	19.7	2284	2.98	139991
QA1b	5.25	20.1	2612	3.12	19157
QA1 (Average)			**2448**	**3.03**	**16450**
QA2a	5.53	22.3	2480	2.89	15997
QA2b	4.86	20.1	2418	2.96	15575
QA2 (Average)			**2449**	**2.93**	**15815**
QA3a	5.20	19.2	2708	2.11	13925
QA3b	3.50	12.8	2734	2.08	15547
QA3 (Average)			**2721**	**2.06**	**13520**

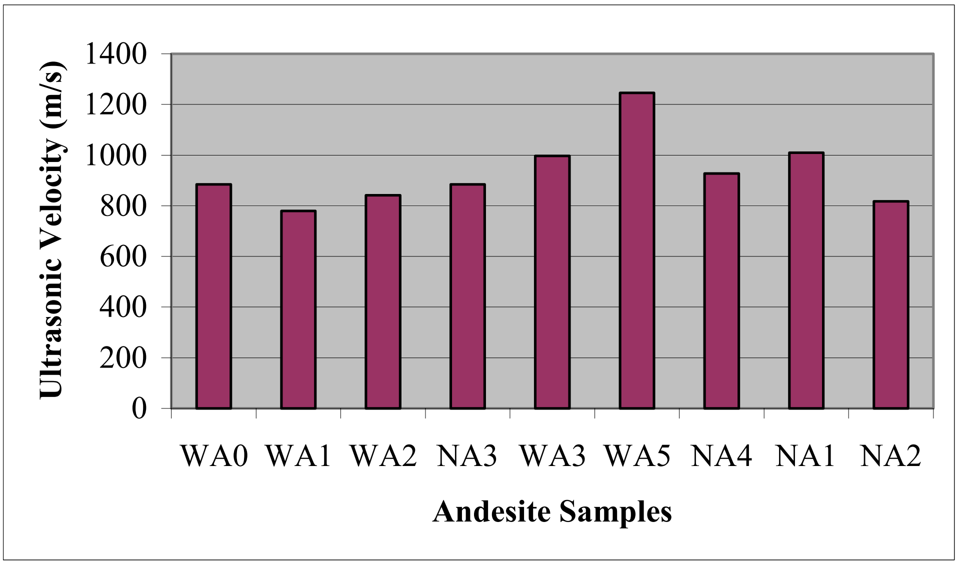


Figure 3.9 Ultrasonic velocity values of andesite samples taken from Ankara Castle

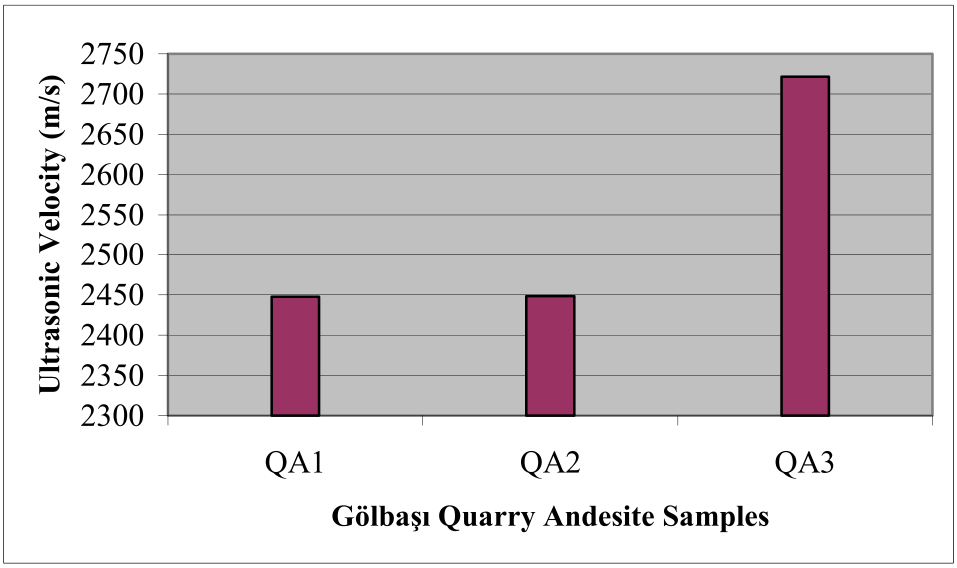


Figure 3.10 Ultrasonic velocity values of Gölbaşı quarry andesites

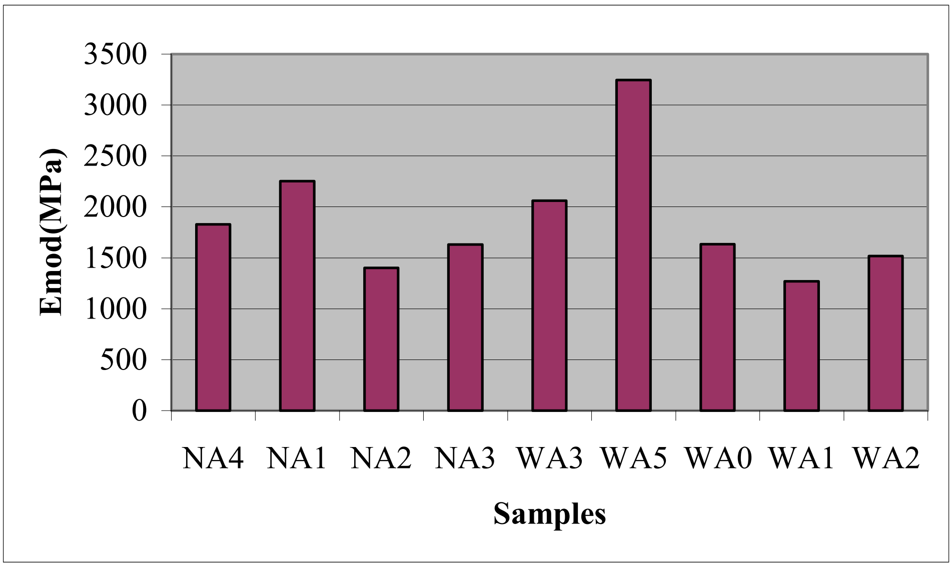


Figure 3.11 Modulus of elasticity values of Ankara Castle andesite samples

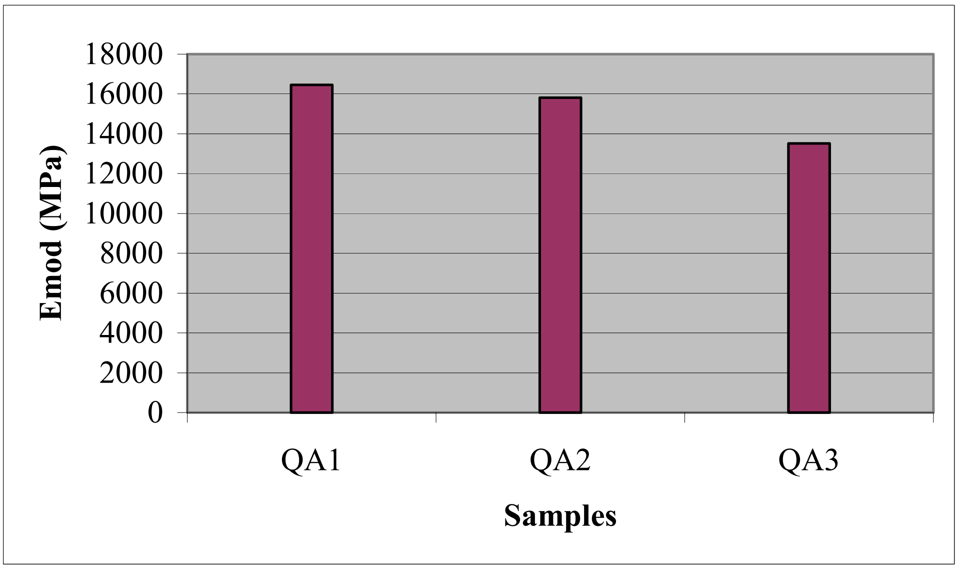


Figure 3.12 Modulus of elasticity values of Ankara Gölbaşı quarry andesite samples

3.5 Mineralogical Properties of Andesites

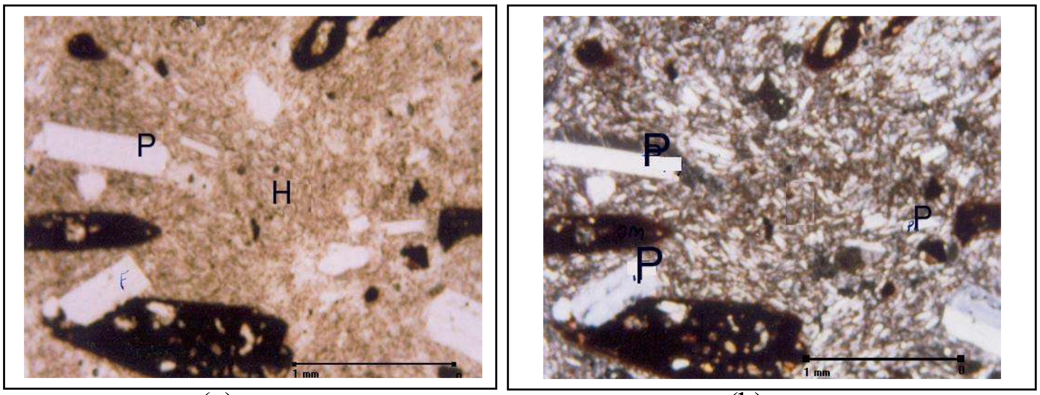
Mineralogical properties of andesite samples were studied by examining thin sections using optical microscope and XRD analyses of powdered samples.

3.5.1 Thin Section Analysis

Thin section analyses of two Ankara Castle andesite samples and a Gölbaşı quarry sample were done. Thin sections were examined to see the mineral phases and their transformations.

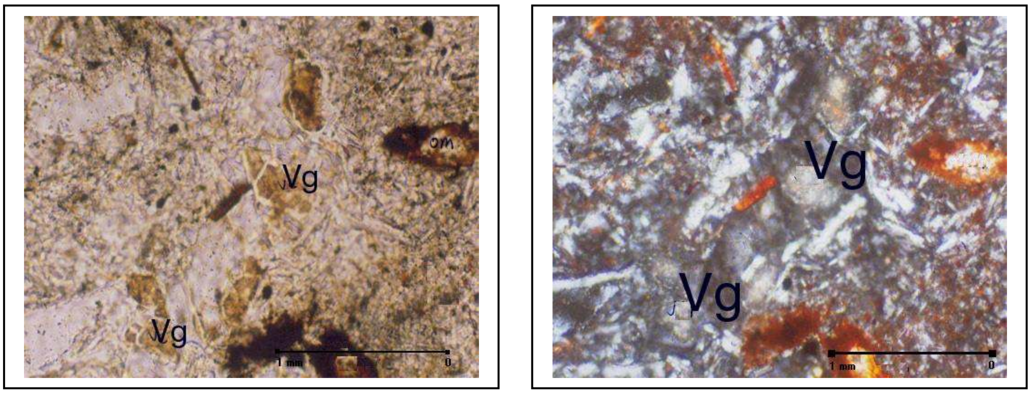
The petrographic analysis of thin sections revealed the major minerals of andesite structure such as plagioclase, hornblende, biotite as expected (Figs. 1.3 and 1.7). In the thin sections, some small volcanic glass fragments (Fig. 3.14) were also observed. In addition, secondary minerals, minerals that were formed by decomposition, including opaque amorphous formations and clay minerals were observed (Figs. 3.15 and 3.17). The scale bar that was put in the figures is 1 mm fort he magnification X 2.5 and 0.1 mm fort he magnification X 20.

In Ankara Castle samples, plagioglase minerals surrounded by secondary clay formations, hornblendes surrounded by weathered zone and chlorite formation in biotites were observed (Figs. 3.15 and 3.17). The results indicated that Ankara Castle andesite samples were weathered.



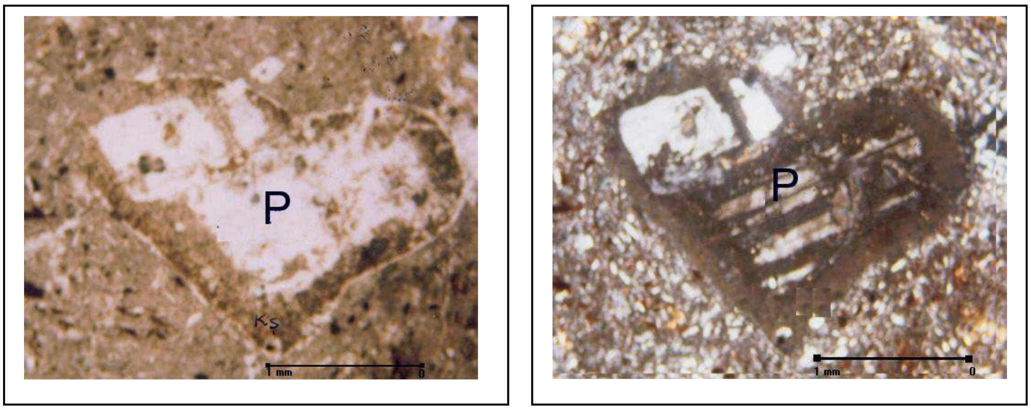
(a) (b)

Figure 3.13 General view of Gölbaşı quarry andesite sample QA1 in thin section; (a) single nicol, X2.5, (b) cross nicol, X2.5. H:Hornblende, P:Plagioclase



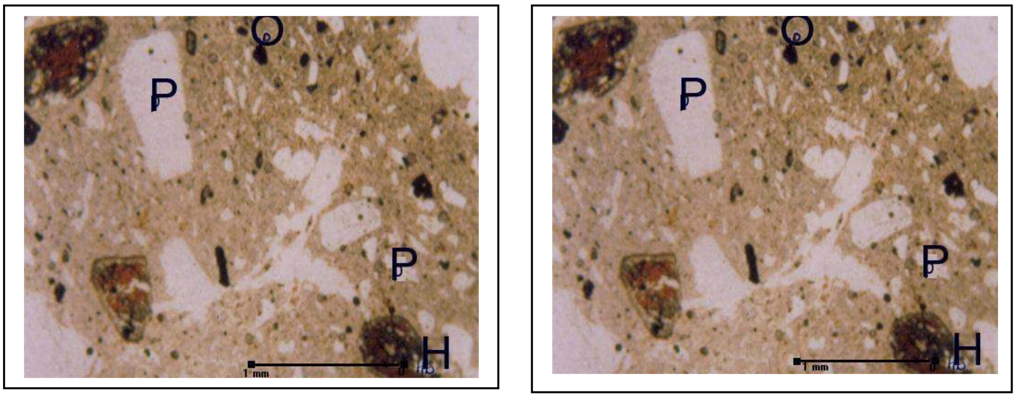
(a) (b)

Figure 3.14 General view of andesite sample WA1 in thin section; (a) single nicol, X2.5, (b) cross nicol, X2.5. Vg:Volcanic glass



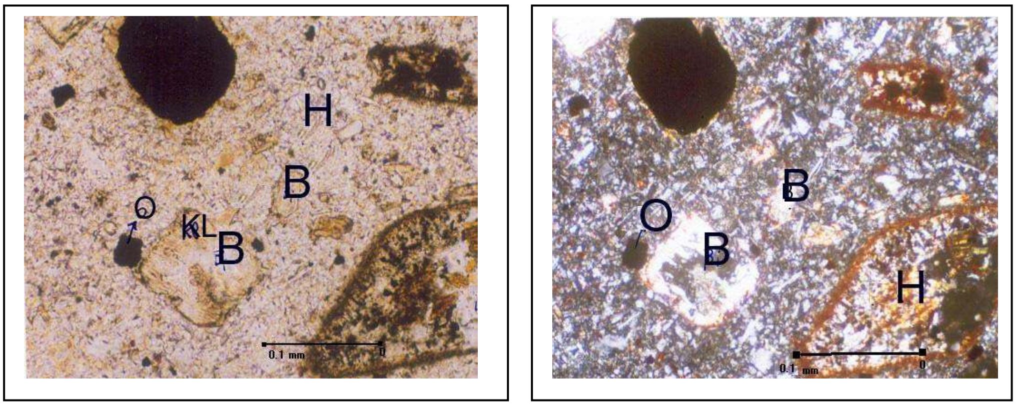
(a) (b)

Figure 3.15 Decomposition and clay formation around plagioclase in andesite sample WA1 as observed in thin section; (a) single nicol, X2.5, (b) cross nicol, **X2.5. P:Plagioclase**



(a) (b)

Figure 3.16 General view of andesite sample WA2 in thin section;
(a) single nicol, X2.5, (b) cross nicol, X2.5. P:Plagioclase, H:Hornblende,
(b) O:Opaque mineral



(a) (b)

Figure 3.17 Decompositon and weathered zone around hornblende, and in biotite as observed in andesite sample WA2;
(a) single nicol, X20, (b) cross nicol, X20. H:Hornblende, O:Opaque
(b) mineral, Kl:Chlorite

3.5.2 X-Ray Diffraction Analysis:

XRD analyses were carried out on powdered andesite samples a) scrached from the surface of the andesite blocks at the site, b) scrached from the exterior surface, crack surface and relatively interiors of andesite scales. Gölbaşı quarry andesite was also analysed to compare it with the Ankara Castle andesites.

XRD traces of the samples showed the presence of the main minerals of andesites such as plagioclase, biotite, hornblende and pyroxene (Fig. 3.18). XRD traces of the samples representing the weathered exterior surface of andesites (WA3S, WA4S and WA5S) showed the presence of amorphous weathering products indicated by the wide hump distributed between 2θ angles of 15˚-40˚. In addition, the presence of clay minerals (Ph: Phylosilicate) and goethite was also detected in those traces (Fig. 3.19). Exterior surface of scales (NA3ScS, WA3ScS) and their crack surfaces (WA3ScC) have also revealed the presence of amorphous phases, phylosilicates and goethite as weathering products of andesite.

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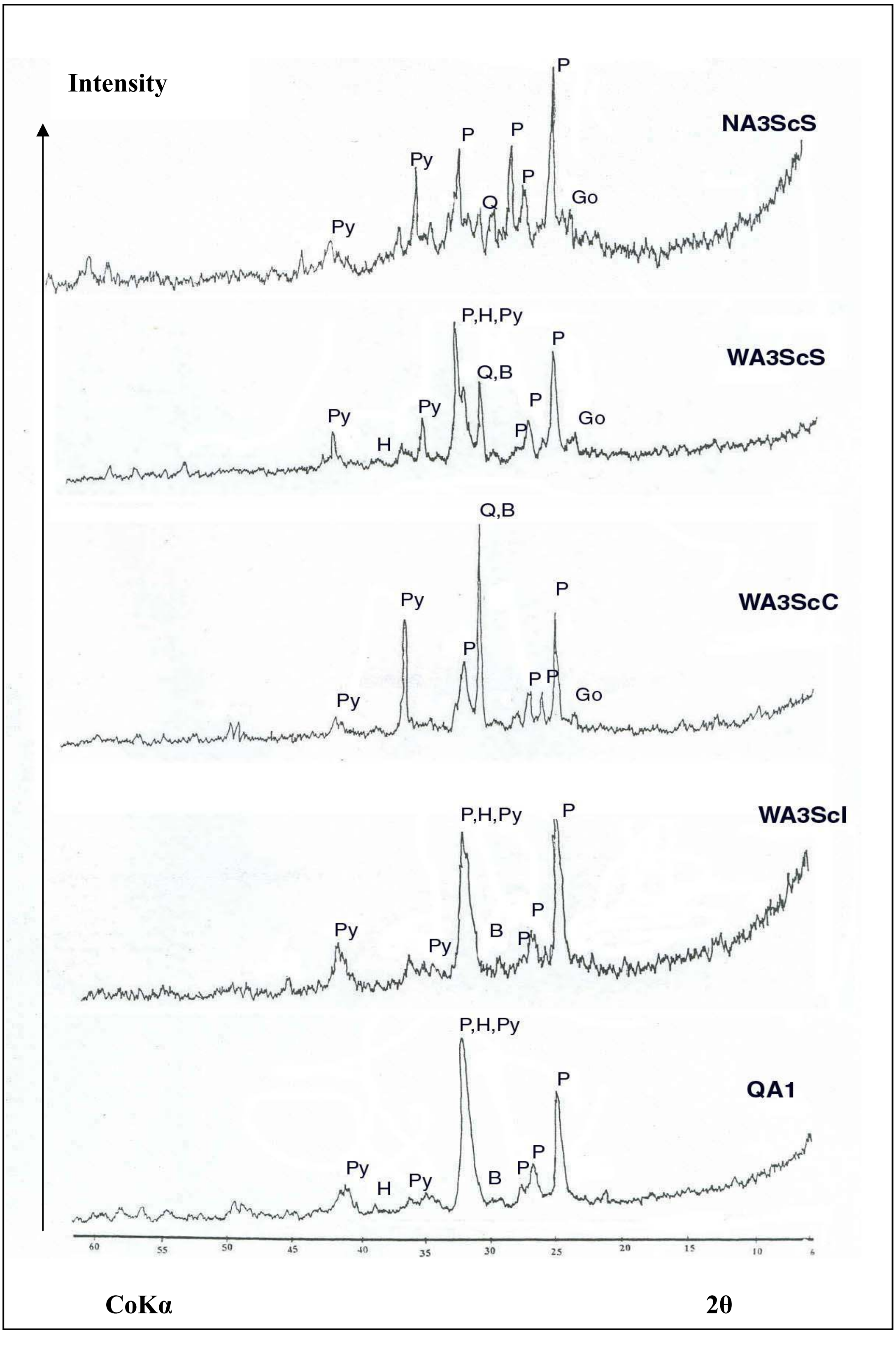

Figure 3.18 Gölbaşı quarry and Ankara Castle andesite XRD results (**P**:Plagioclase; **H**: Hornblende; **B**: Biotite; **Q**: Quartz; **Py**: Pyroxene;G**o**:Goethite)

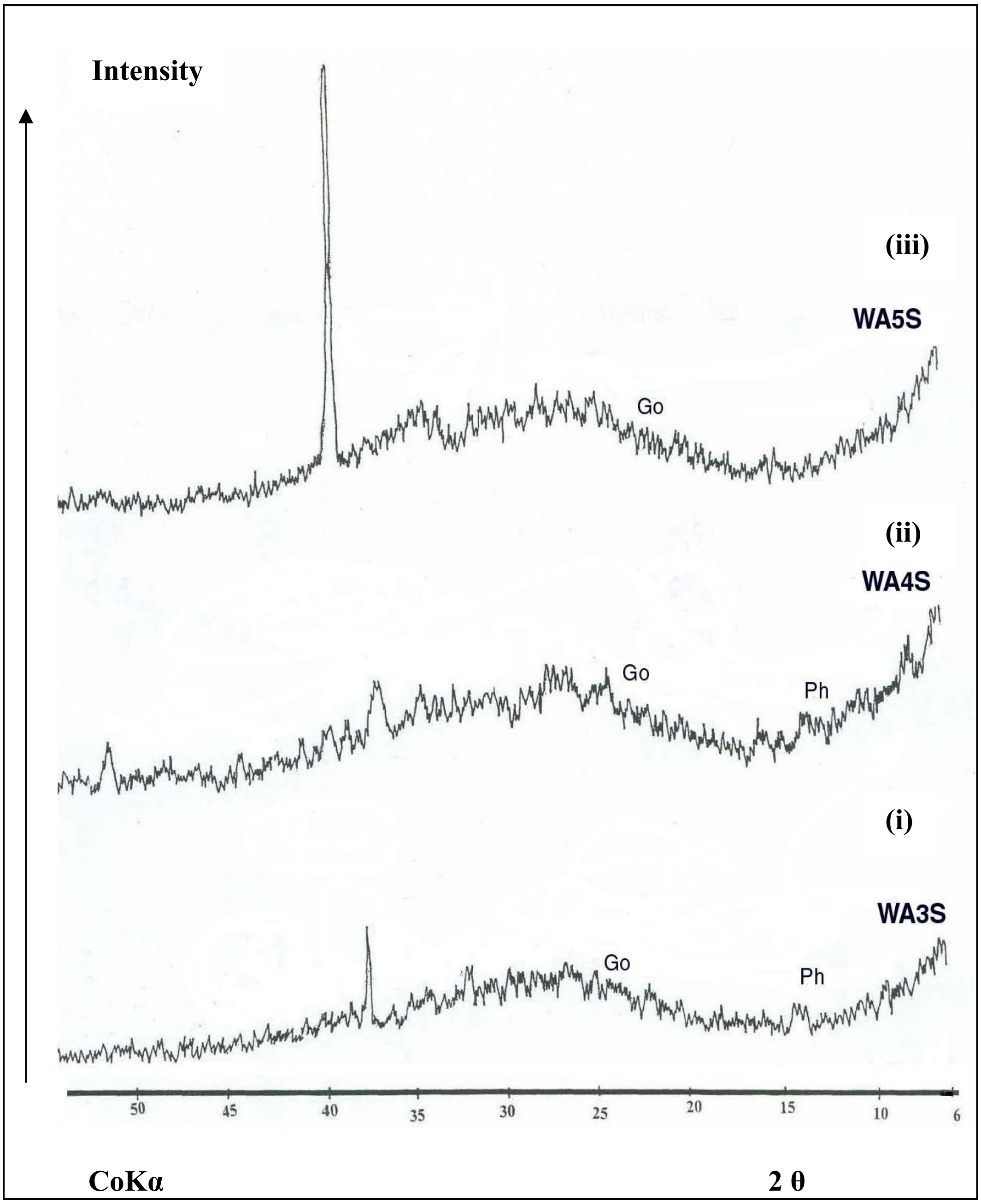

Figure 3.19 Ankara Castle andesite surface XRD results (**Ph**: Phyllosilicate, **Go**: Goethite)

CHAPTER IV

DISCUSSION OF THE EXPERIMENTAL RESULTS

In this chapter, the experimental results that were obtained by the examination of Ankara Castle andesites and Gölbaşı quarry andesites were discussed in terms of factors affecting the deterioration of Ankara Castle andesites, extent of deterioration in those andesites and their properties.

4.1 Factors that Affect Weathering of Andesites

The main factors that affect the weathering of Ankara Castle andesites were found to be the dampness, air pollution and soluble salts.

Ankara has a semi-arid climate. Meteorological conditions summarized in section 1.1 showed the existence of several physical weathering cycles on the Castle andesites. Precipitation as rain and snow, high average relative humidity in winter months that promoted condensation were the main sources of dampness.

Visual analyses by mapping of stone decay forms have shown that rain water was not drained properly andAnkara Castle walls got wet by rain penetration and rising damp. Material loss as scales, alveolization and salt deposition were the main forms of andesite decay at the site (Fig. 3.1, 3.2).

Changes in relative humidity and condensation were important variables which affected the adsorption of air pollutant gases sulphur dioxide and nitrogen oxides on stone surfaces in Ankara (Section 1.3, Fig. 1.6, 1.7). Climatic conditions of Ankara atmosphere with high average relative humidity in winter months and high relative humidity values during the night through the year even in summer times, favored adsorption of both nitrogen oxide and sulphur dioxide on stone surfaces (Fig. 1.4). The air pollutants must have contributed to acidic reactions with the stone and to the formation of soluble salts as sulphates and nitrates as well as to the formation of an amorphous layer on andesitic surfaces (Table 3.2, Fig. 1.6 and 1.8, Fig. 3.8, Fig. 3.19). Salt crytallization was another important decay factor that contributed to andesite deterioration in Ankara Castle. In this study, considerable amount of soluble salts were detected in the andesite scales. That proved the importance of salt crystallization in deterioration of Ankara Castle andesites. Soluble salts content was found to be in the range of 2.03-11.11 % in andesites (Table 3.2, Fig. 3.5). Common soluble salts were sulphates, chlorides, nitrates, nitrites and phosphates of sodium, potassium and magnesium (Table 3.2). XRD analyses of dried salt extract from an andesite scale (NA3) had shown that the main salt minerals were halite (NaCl), niter (KNO_3), sylvite (KCl), gypsum ($CaSO_42H_2O$), hexahydrite ($MgSO_4.6H_2O$), epsomite($MgSO_4.6H_2O$) and sodaniter($NaNO_3$) (Fig. 3.8).

The presence of large amount of sulphate containing ions and magnesium sulphate was also due to the use of portland cement as repair mortar. Portland cement containing mortars were incompatible with the andesite stone and caused its decay. Cement mortars are known to be incompatible, dangerous materials for historic structures due to their inherent physical and mechanical properties and soluble salt content (Arnold & Zehnder, 1989; Torraco, 1982).

The wind effect was also important in andesite weathering by promoting rapid drying out and salt crystallization. The deterioration factors dampness, soluble salts and wind acting together have led to alveolar weathering (Fig.3.2).

Therefore, together with dampness problems as continued rain penetration and condensation, acidic reactions and salts originating from air pollutants, salts originating from soil and from repairs with cement mortars had accelerated the weathering of andesites.

4.2 Extent of Deterioration in Ankara Castle Andesites

Visual examination of andesites at Gençkapı Gate revealed drastic deterioration as material loss, alveolization, detachment as scales, salt deposition and colour changes (Section 3.1). The extent of deterioration was examined by determination of basic physical, mechanical properties and mineralogical characteristics of samples taken from andesite surfaces.

Ankara Castle andesite samples were scales and powdered material scraped from the surfaces. They represented the most deteriorated parts of the andesite blocks.

In this study, some representative samples of mortar and marble taken from Gençkapı (Fig. 2.1) and some andesite samples from Gölbaşı quarry were also examined.

The basic physical properties obtained for the Ankara Castle andesite samples were bulk density and porosity. The majority of Ankara Castle andesite samples had the bulk density in the range of 2.22-2.34 gr/cm^3 and the porosity in the range of 3.24-10.47 % (Fig. 3.3). Since those samples were weathered, original bulk density of andesites must have been higher and total porosity must have been lower. Gölbaşı quarry andesite samples had the bulk density in the range of 2.06-3.03 gr/cm^3 and the porosity in the range of 9.56-17.17 % (Fig.3.4, Table3.1). Their bulk density and porosity values obtained in this study were found to be comparable with those values of Gölbaşı quarry andesites found before (Karpuz, 1982; Karpuz and Pasamehmetoglu, 1992; 1997).

Mechanical properties of Ankara Castle andesites were expressed by the modulus of elasticity, Emod, values which were obtained indirectly from ultrasonic pulse velocity and the bulk density measurement using a mathematical equation (Section 2.3.2.2). Since the Emod values obtained were not based on direct experimental measurements, they should be considered as approximate values.

For the majority of the samples, Emod values of Ankara Castle andesite samples were in the range of 1269-3248 MPa (Fig. 3.9). Emod values of Gölbaşı quarry andesite samples were found to be in the range of 13520-16450 MPa (Fig. 3.10).

The Emod values obtained for Gölbaşı quarry samples were comparable with those of andesite samples studied before (Nathaniel, 1972; Özdoğan, 1973; Karpuz, 1982; Karpuz and Pasamehmetoglu, 1992; 1997).

The Emod of Ankara Castle andesite surface samples as scales showed that they had much lower mechanical strength compared with some Gölbaşı quarry andesites.

Karpuz (1982, 1992 and 1997) investigated various andesites in Ankara region. The various stages of weathering of the rock material were given grades of weathering based on their physical and mechanical properties. As the degree of weathering increased, modulus of elasticity, bulk density and sonic velocity decreased while effective porosity increased. Medium-to-fine grained Çubuk and Esertepe andesites had less porosity than porphyritic and finely crystalline types. Increase in porosity of Esertepe and Çubuk andesites in early stages of weathering was mainly related with an increase in crack-shaped pores.

Bulk density and porosity values of andesite scales found in this study as well as their ultrasonic velocity and and Emod values showed that Ankara Castle andesite surfaces which were being detached as scales were heavily weathered and had low mechanical strength (Table, 3.4, Fig. 3.12).

The petrographical analyses of thin sections of Ankara Castle andesite samples indicated that most abundant mineral was plagioclase and they were heavily weathered. Biotites and hornblende also showed weathering (Figs. 3.13, 3.15). Opaque minerals and clay mineral formation on those samples observed in thin sections and XRD traces showing abundant presence of amorphous material at the surfaces of andesites approved that Ankara Castle andesite surfaces had also chemical weathering process (Fig.3.16, 3.17, 3.19).

4.3 Properties of Ankara Castle Andesites

Previous studies on Ankara andesites were related with their engineering properties. Quarry samples were extensively examined for their colour, physical and mechanical properties and weathering grades (Nathaniel, 1972; Özdoğan, 1973; Karpuz, 1982; Karpuz and Pasamehmetoglu,1992; 1997).

In this study, weathered andesite surface scales from Ankara Castle walls were examined. Therefore, the physical and mechanical properties obtained from those samples were for the weathered andesites. They did not represent the physical and mechanical properties of fresh quarry andesites. However, the results have shown that those unweathered Ankara Castle andesites must have had bulk densites higher than 2.22-2.34 gr/cm^3 and porosities lower than 3.24-10.47 %.

Andesites collected from Ankara Castle and those from Gölbaşı quarry were compared with each other in terms of colour, grain size, mineral composition, physical and mechanical properties. The andesites taken from Ankara Castle had similarities in colour with Çubuk and Esertepe region andesites that were studied before (Karpuz, 1982; Karpuz and Pasamehmetoglu,1992; 1997). Ankara Castle andesites had red to pink colour and Çubuk quarry andesites had light grayish purple colour. While Esertepe quarry andesites have grey colour. Gölbaşı quarry andesite samples had grayish colour (Karpuz, 1982; Karpuz and Pasamehmetoglu, 1992; 1997). Colour and grain size of Ankara Castle andesites were different from the Gölbaşı quarry andesite samples. Ankara Castle andesites were fine-to-medium grained, whereas Gölbaşı quarry andesites were fine grained.

Thin section and XRD results showed that Ankara Castle andesite samples had the common andesite minerals such as plagioclase, hornblende, pyroxene and biotite. In addition to those minerals some secondary minerals and decomposition products such as opaque minerals, clay minerals and some volcanic glass fragments were also detected. Since the minerological properties of Ankara quarry andesites were not yet studied, it was not possible to compare the minerological characteristics of Ankara Castle andesites with the other Ankara andesites.

CHAPTER V

CONCLUSIONS

In this study, deterioration problems of Ankara Castle andesites were examined for the purpose of their conservation. The results obtained were discussed to explain factors that affect their deterioration, extent of deterioration and the properties of Ankara Castle andesites.

Ankara Castle andesites showed the visual deterioration forms as material loss, detachment as scales, alveolization, salt deposition and colour change.

The main factors which affected the weathering of Ankara Castle andesites were dampness, air pollution and soluble salts.

Dampness problem was mainly due to rain penetration and condensation.

Air pollutants promoted acidic reactions with the stone and caused formation of soluble salts in the stone. Considerable amount of soluble salts in the range of 2.03-11.11 % were detected in Ankara Castle andesites. Common soluble salts were sulphates, chlorides, nitrates, nitrites and phosphates of sodium, potassium and magnesium. Salts originating from air pollutants, from soil and from repairs with cement mortars had accelerated the weathering of andesites.

Scales of weathered Ankara Castle andesites were heavily deteriorated. The deterioration factors caused changes in physical, mechanical and mineralogical properties of andesites. Their average bulk density, porosity and Emod values were in the range of 2.22-2.34 gr/cm^3, 3.24-10.47 % and 1269-3248 MPa, respectively.

The surfaces of Ankara Castle andesites contained large amount of amourphous weathering products that were detected by XRD analyses.

In the thin sections, opaque minerals and clay mineral formation were observed in plagioclase minerals of andesite scales. Alterations were also observed in biotites and hornblendes.

Ankara Castle andesites had pink colour and fine-to-medium grain size and major minerals as plagioclase, hornblende, pyroxene and biotite. Although the physical and mechanical properties of relatively unweathered andesites were not studied, their bulk densities should be higher than and porosities should be lower than the values obtained for the weathered andesites in this study.Although Ankara Castle andesites had similiraties with Çubuk and Esertepe quarry andesites, more studies are needed for the identification of their original quarries.

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