J. Int. Environmental Application and Science, Vol. **18**(4): 139-144 (2023)
Research Paper

Behaviour of Sille Stone Against Acid Rain

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Received December 4, 2023; Accepted December 24, 2023

Abstract: The structures in which human activities are carried out and we are in at any time are reacting with the increasing acid rain and acids caused by different reasons. Building materials lose their chemical and physical properties as a result of reactions with acids. Sille stone, which has quarries in the Sille district of our Konya province, is a building material that has been used since ancient times. The resistance of this building material, which is still preferred in building construction in today's conditions, against acid rain, although it has been encountered in various historical artifacts carried from different cultures and civilizations until today, was discussed in this study. The pH value of rainwater varies between 5.6 and 6 and shows acidic properties. It has been observed that the pH value of acid rains fell below 5 and decreased to 3 in some places in the world. Sulfuric acid, nitric acid, carboxylic acid and their mixtures, which are frequently encountered in acid rain, were used in this study. 7x7x7 samples were taken from the stone quarries in Sille district. 1 molar concentration of citric acid was prepared in order to examine the behaviour of Sille stone as a result of the reaction of these stones in seasonal acid rains. The samples were kept in natural environment, in water and in acidic environments by varnishing and by without varnishing. In this way, the protected on of stone against acid rains was also analysed.

Keywords: *Acid rain, Nitric acid, Sille stone, Coat protection.*

Introduction

Palta (2020) examined the effect of boric acid on self-compacting concrete. They produced the concrete themselves. 6 samples were obtained by adding a reference sample and 0.5%, 1.0%, 1.5%, 2.0%, 2.5% boric acid by weight to the concrete water, respectively. Diffusion Table, V-Funnel, L-Box, U-Box tests from Fresh Concrete Tests were performed on these 6 samples produced. Compressive strength and bending strength experiments were carried out to compare the changes in the mechanical properties of the obtained samples. Additionally, SEM and XRD analyses were performed to observe structural characterization changes. When SEM images were examined, boric acid accelerated the formation of C-S-H gels by binding C-H to itself over time, and with the effect of this, an increase in compressive strength was achieved over time. Thus, with the addition of boric acid, a new C-S-H gel was formed, and the structure was made more impermeable and durable. With the addition of 2.5% boric acid, the gaps and pores began to increase significantly. Micro crack formation was also observed. As a result of this situation, the increase in compressive strength decreased compared to the control sample. In the XRD analysis, when looking at the XRD peaks, especially after the 0.5% Boric acid additive rate, the dominant peak intensities seen at approximately 30º started to increase effectively. The low peak intensity of 0.5% Boric acid additive ratio can be associated with the decrease in particle size and pores. It can be said in the SEM image of the sample with 0.5% boric acid that the particles are smaller compared to other samples. SEM and XRD analysis results support the increase in compressive strength, especially in the concrete sample with 0.5% Boric acid added. When a general evaluation was made, it was seen that Self-Compacting Concrete could be produced by adding boric acid.

Reddy studied three different regions in the northeastern United States in 1988. The aim of this research is to examine the effects of dry and wet deposition states of acid on stone separately. As a result of the experiments and observations, it was revealed that the stagnation on the stone surface is proportional to the amount of precipitation. In other words, the amount of precipitation that falls on the stone will increase the dissolution on the stone surface proportionally. This research has shown that the result is proportional to the hydrogen ion arriving on the stone surface (Reddy, 1988).

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Charola (1987) have studied limited the pollutants that cause acid rain to only sulphur oxides. He limited the stones he examined to quartz, which is a stable mineral form. As a result of his research, he attributed the deterioration of calcareous stone to two main reasons. The first is the chemical dissolution of calcite, and the second is the damage caused by the salts formed during dissolution crystallising again in the stone pores. The first case explains the deterioration in the surface details of buildings and monuments, and the second case explains the causes of structural damage to the stone.

In 2005, Tecer examined the effects of SO2 and NOx resulting from environmental pollution on carbonate rocks. He examined the results of the effects of air pollutants on historical structures whose main component is $CaCO_3$. Effects of Sulphur Dioxide, Nitrogenizes, Carbon Dioxide, Acid Rain, and Particulate Matters on carbonate rocks are examined in the study.

Bravo (2005) had experiments to observe the dissolution that occurs when limestone is exposed to acid rain. As a result of the studies, it was determined that 85% of the precipitation in this region is acidic and the limestone building material in this region is dissolved by acid rain and as a result, it erodes over time and loses its shape and resistance.

Materials and Methods

Air pollution, which has become one of today's important environmental problems with the rapid increase in industrialization brought about by advanced technology, causes acid rain. Acid rain, or acid deposition, includes any form of precipitation with acidic materials, as sulfuric acid, nitric acid, citric acid which fall from the atmosphere to ground in wet or dry forms. Its shape may be rain, snow, fog, hail or even dust that is acidic form. Its effects directly each part of the planet so our life. It is harmful to aquatic life and vegetation. It effects the human health by causing the important diseases in human body. It also accelerates weathering in stone and metal structures. The aim of this study is related to weathering in stone structures as the stone structures are very popular as they have more advantages with compared to other structural materials. Sille stones are magmatic stones such as granite, kyanite and andesite found in volcanic lands (Tapur, 2019). Although Sille stone is referred to as andesite in many sources, Taşlıgil, in his article written in 2016, mentioned it as trachyte, which is also a stone of magmatic origin and has a silica content of 62% (Taşligil & Şahin, 2016). Sille stone is composed of cinder blocks formed by andesite blocks and andesite tuffs (Kazancı & Gürbüz, 2014). In order to examine the effect of acid rain on the Sille stone, the sample stones are taken from a geological heritage reserve located in the Sille district of Konya as seen in Figure 1. The changes in physical and chemical properties of Sille stone exposed to acid rain were examined. Additionally, it was aimed to reduce this effect and the Sille stones so the stones were covered with stone varnish. The change in strength and chemistry of Sille stones coated by stone varnish compared with unvarnished Sille stones was compared.

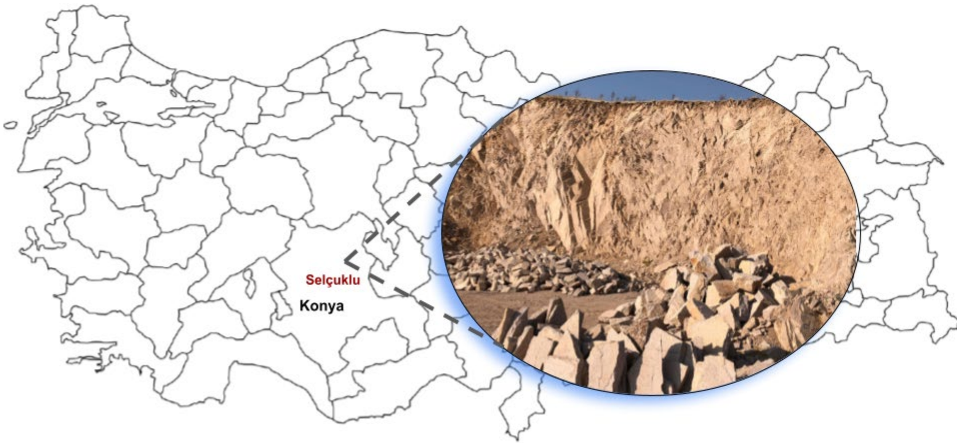


Figure 1. Sille stone Source

In this study, Sille stone samples are kept in water, in nitric acid (HNO_3) prepared as 1 molar, in the atmosphere environment, coated with stone varnish and uncoated for Sille stone for 6 months. Mechanical and chemical changes of Sille stones during seasonal transitions were analysed over a 6-month period.

Used materials
The main material of this study is Sille stone which is stated that the required sample size for the pressure test on TS1926 natural stones should be 7x7x7 cm^3. For this reason, in this study, which will last 6 months, the size of a sample of Sille stone will be a cube of 7x7x7 cm^3. Compressive strength test is performed on at least 5 test samples for each environment (TS 1926) and averaged their results. Additionally, 1 test sample is required for chemical experiments. In this case, 5+1 unvarnished and 5+1 varnished test samples are required for each environment. Tested material are given in Table 1.

Table 1. Tested materials

	varnished	unvarnished
References	5+1	5+1
Nitric Acid	5+1	5+1
Atmosphere	5+1	5+1
Water	5+1	5+1
Total	48	

Discussion and Results
Pressure Test
Compressive strength is the maximum stress that is measured on concrete under the effect of axial pressure load. The compressive strength of the concrete cube test provides an idea about all the characteristics of concrete. By this single test one can judge if the resistance of it is suitable or not to avoid breaking. The reasons why the most commonly used strength is compressive strength; the test applied to determine compressive strength is simpler than the tests applied to determine other types of strength. The compressive strength value has an important role in building designs. If the compressive strength is known, one can have an idea about the other strength values of the samples and make comments.

The pressure test was prepared depending on TS 1926 conditions and its procedure. Test for compressive strength is carried out on a 7x7x7 cm^3 cube. So, Sille stone test samples were prepared as cube samples with dimensions of 7x7x7 cm^3. Before placing the sample on the compression device with adjusted loading speed, it was checked that the surface on which the sample would be placed was clean and smooth. The sample was carefully placed on the testing device in the centre of the loading bed so that the load would act exactly in the middle and axially. After the placement process was completed, loading was started and the maximum force withstood by the sample was measured from the device (Figure 1). The compression test was carried out with the compression device in the civil engineering laboratory of Necmettin Erbakan University.

Figure 1. The compressive strength test of the samples

Firstly, the compression is applied on unvarnished Sille stone, as it was originally removed from the its source and the compression strength was measured as 30.91 MPa. The compression test result of the Sille stone samples, which were varnished and kept for the varnish to dry, was measured as 25.61 MPa as seen in Table 2.

Table 2. Compressive strength of Sille stone, taken from the its source, with and without varnished

	Sample No	7*7*7 Cubic (KN)	Compressive strength (MPA)	Average (MPA)
Unvarnished	1	133,95	27,34	
	2	177,44	36,21	
	3	128,57	26,24	30,91
	4	162,26	33,11	
	5	154,98	31,63	
Varnished	1V	84,93	17,33	
	2V	154,36	31,50	
	3V	109,13	22,27	25,61
	4V	135,54	27,66	
	5V	143,44	29,27	

As can be seen from the Figure 2, the varnish prevents oxygen passing through from surface to insight of the stone. For this reason, the compression strength in varnished samples was lower than in unvarnished samples. As can be seen from the Figure 2, it was observed that the compressive strength is increasing in all environments with compared to the strength of the samples which as first came out of the quarry in varnished samples. This is a sign that the strength of quarried samples increases when exposed to oxygen. Applying varnish prevented oxygen from passing through in it. For this reason, the strength of varnished samples was lower with compared to strength of unvarnished samples.

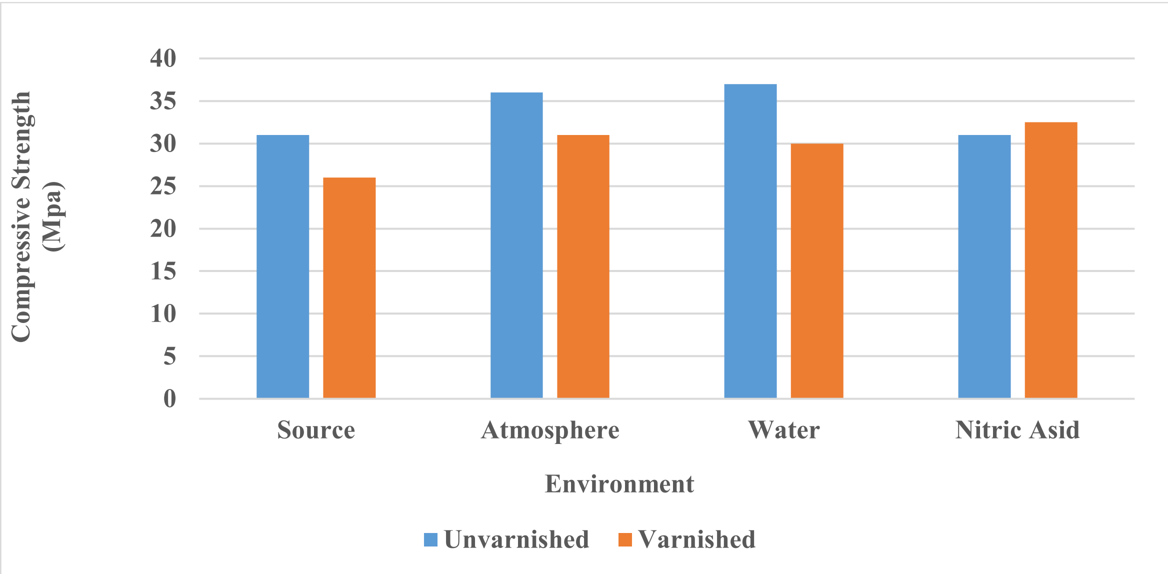


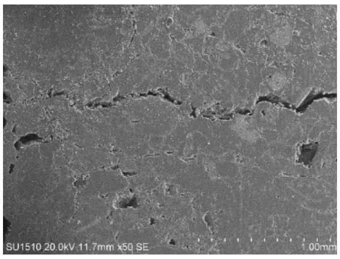
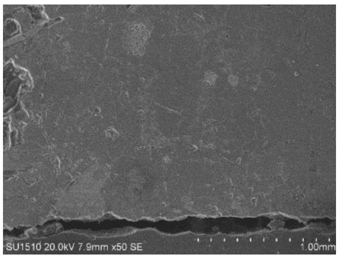
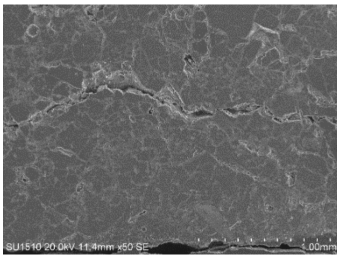
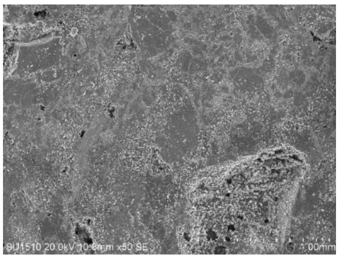
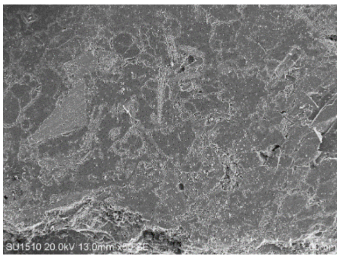
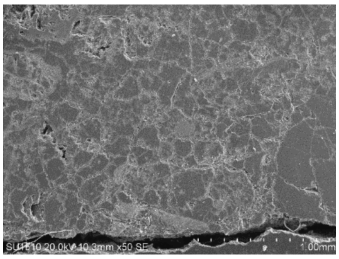
Figure 2. Compressive Strength of samples

Over time, physical and chemical transformation occur in Sille stone. It has been observed that the improvement in mechanical properties is slower in Sille stone samples varnished and kept in atmosphere, water and acid environments. However, it has been determined that Sille stone samples behave more stable over time. The physical transformation of the stone occurs when the quarried Sille stone turns into a lower energy state as the pressure on it decreases. Chemical transformation of the stone is the changes in compressive strength as a result of chemical reactions in Sille stone samples kept in different environments.

SEM analysis

Varnished and unvarnished SEM images of the samples tested in the most applicable atmosphere, water and nitric acid environments are given in Table 4.2. In general, applying varnish to the samples causes the cracks and pores on the material surface. When SEM images are examined, it can be said that the idea that small molecules, which were formed during the transformation, accumulate in the cracks and pores in the material is supported.

Table 2. SEM images of varnished and unvarnished Sille stone

	Varnished	Unvarnished
Atmospheric Environment		
Water Environment		
Acidic Environment		

Results

- The transformation began to negatively affect the sample by destroying it, and a decrease in compressive strength occurred in the 6th month.
- It has been observed that the improvement in mechanical properties is slower in Sille stone samples varnished and kept in atmosphere, water and acid environments. However, it has been determined that Sille stone samples behave more stable over time.
- It is thought that not varnishing the stones used in houses and buildings intended to be built using Sille stone at the beginning, but varnishing them after a certain period of time, will be effective in increasing the compressive strength. Determining this period clearly experimentally may be the subject of future studies.
- In order to examine the transformations in the chemical and physical properties of Sille stone in more detail, more detailed findings can be detected and evaluated by selecting a single aging environment and performing strength tests over a longer period of time and at shorter intervals.

Acknowledgment: *We thank the Necmettin Erbakan University for encourage given to this study. The authors would like to thank the Editor-in-Chief for editorial suggestions. A special thanks go to reviewers.*

Compliance with Ethical Standards Ethical responsibilities of Authors: *The author has read, understood, and complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors".*

Funding: *We express our greatest thanks to the Necmettin Erbakan University - Scientific Research Projects Coordination for financial support, which made the publication possible.*

Conflict of Interest: *The authors declare that they do not have any conflict of interest.*

Change of Authorship: *The author has read, understood, and complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and is aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.*

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