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RESEARCH ARTICLE

Effects of Sodium Chloride (NaCl) On Historical Bridges and Treatment with Bentonite

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Abstract

In this study, the effects of bentonite clay were investigated in the cleaning of the andesite stone samples used in the restoration of historical Çobandede Bridge and some historical buildings contaminated with sodium chloride salt. The stones of historical buildings are exposed to harmful salt effects for various reasons. Especially in regions where terrestrial climate dominates, the sodium chloride salt sprinkled on the icy roads for thawing may infiltrate over time into soil and then arrives at the historic bridges' stones. In this way, because of capillarity of the stones and ionic osmos, the salt accumulates in the pores of the stones and the hygroscopic nature of NaCl damages the historic bridges' stones on the road route. This physically damages the stone and reduces the life of historic bridges. Therefore, the removal of salt entering the structure of the stone is very important to increase the durability of the stones. In order to model this situation, a sum of bentonite clay paste prepared in liquid limit was implemented to artificially polluted andesite stone samples. The clay pastes applied to the stones were removed from the stones surfaces after a certain period of time and analyzed. X-ray Fluorescence Spectrometry (XRF) analyzes showed that bentonite clay gave positive results for sodium chloride removal from historical building stones exposed to NaCl salt.

Keywords: Sodium chloride damage, historical bridge, clay paste, stone cleaning, andesite stone

1. Introduction

NaCl salt is used to reduce the risk of icing on roads where terrestrial climate dominates within the boundaries of General Directorate for Highways 12th District. In 2016, the amount of salt consumed in the region is around 4141 tons and during last six years approximately 25000 tons NaCl salt were consumed [1]. The Historic Çobandede Bridge is one of the bridges on the existing road route exposed to the NaCl effect (Figure 1). NaCl, used for the problem of ice, exudes into the soil over time and reaches to the historical structure with the effect of capillarity. For this reason, rock salt (NaCl) used in icy roads can be one of the most harmful factors in stone decay. Crystallization, which is caused by free solubilizing salt such as NaCl, normally causes the surface of the stone to powder [2].

The salts carried by the water move within the wall accumulate in the pores near the surface in the period of drying the wall (evaporation of the water), crystallizing in the capillaries between the loosened granules [3]. It must prevent the formation of salts which are harmful to the stone or should be tried to be cleaned [4]. It is a known technique to use clay, paper clay and other materials obtained by mixing the various materials with water to reduce the salt content objects damages by salt. However, the outcome of most interventions is unpredictable because of the inherent confusion of salt problems in historical structures [5].

In cleaning applications, adsorption and absorption properties of clay materials are utilized. In addition to these properties, the chemical properties of the salt to be removed and the void fraction of the stone

to be cleaned, the void network structure, the capillarity, the water absorption etc. properties are effective in the cleaning application. Many studies in the literature (in situ and laboratory applications) have investigated the efficacy of cleaning using different materials [6-9].

Figure 1. The Çobandede Bridge (Erzurum 2019)

In this study, the cleanability of salt-contaminated stone samples was investigated with bentonite clay having high plasticity (CH) property with high water retention and ion exchange capacity. First, stone samples were contaminated with NaCl salt by dipping method. Then the paste prepared with bentonite clay in liquid limit was wrapped in contaminated stones. After a certain period of time, the clay paste was separated from the stone surfaces and a series of XRF analyzes were carried out to determine the effect of the clay paste on the cleanliness.

1. Testing process

2.1. Test specimens and properties

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The bentonite clay used in the study was obtained from Erzurum State Water Works Directorate and the stone sample was obtained from Erzurum Kanber Village Stone Quarry. Stone samples were contaminated with sodium chloride (NaCl) salt. Some properties of the bentonite clay, stone sample and NaCl salt used in the experiments are given in Tables 1, 2 and 3, respectively.

Table 1. Some properties of bentonite clay

Test Name	Value / Class	Test Standard
Liquid Limit (w_L)	378	[11]
Plastic Limit (w_P)	54	
Plasticity Index (I_P)	324	
Soil class	CH	
Density (g/cm^3)	2.5	

Table 2. Initial geometries of test models

Sample Test	Andesite (pink) Value	Andesite (Grey) Value	Test Standard
Friction Wear Strength experiment ($cm^3/50 cm^2$)	24.8	15.9	[12]
Unit Volume Weight (t/m^3)	2.3	2.3	
Pressure Resistance (N/mm^2)	69.8	105.5	[13]
Water Absorption (Weight) (%)	4.5	3.0	

Table 3. Some properties of NaCl [14]

Sample	Resolution mol/L (25 °C)	Density g/cm^3 (20 °C)	Molar Mass g/mol	Molar Volume cm^3/mol
NaCl	6.15	2.165	58.44	78

2.2. Test method

According to EN 12370:1999 standard, saturated solution prepared at $20 \pm 5^\circ C$ with NaCl salt was put into a container for the contamination of stone samples. Stones in block size taken from stone quarry were cut into $4 \times 4 \times 4$ cm cubes and stone samples were obtained. The stone samples prepared were immersed in NaCl solution. The container was closed to prevent evaporation. These stone samples in the container were waited for 2 hours in an environment with a temperature of $20 \pm 5^\circ C$. At the end of the waiting period, the stone samples taken from the solution were allowed to stay in drying oven at $105 \pm 5^\circ C$ and then was left to the desiccator for 2 hours. This process is called a salt crystallization cycle. Three salt crystallization cycles were performed for each sample.

Table 4. Weight change and sample damage (NaCl, 3 cycles)

Numune Numarası	130	131	132	133	134	135
Porozite (%)	14	21	14	20	15	15
Weight(g)						
Initial	157.6	133.9	143.5	131.1	153.3	147.9
1.Cycle	158.8	135.9	144.6	133.0	154.8	149.5
2.Cycle	160.1	137.9	145.7	134.9	156.2	151.1
3.Cycle	161.1	139.6	146.7	136.5	157.3	152.5
D_k^* (%)	+2.31	+4.24	+2.31	+4.17	+2.60	+3.11

*Mass change after the test

After each cycle, stone samples were weighed on a precision scale of 0.0001 g and visible changes in the samples (fragmentation, cracks, surface erosion, decay etc.) were recorded. In order to determine the maximum damage that can occur to the six stone samples 15 salt crystallization cycles have been applied and 3 salt crystallization cycles have been applied in order to carry out the salt removal operation on another six stone samples. The mass values obtained as a result of salt crystallization cycles are given in Table 4. When the schedules were examined, it was observed that as the result of salt crystallization cycles progressed, sample masses increased due to salt penetrated into the surface and into the body of the stones.

Since the forth salt crystallization cycle in the salt crystallization cycles for the NaCl salt, it has been found that they are become dust the surface of the andesite stone samples in powder form. Moreover, in the eighth salt crystallization cycle it has been observed that in the stone surface, they have flaked from the surface in thin layers. Since the thirteenth salt crystallization cycle erosion has begun to occur in the corners. As a result of the completed fifteen salt crystallization cycles, the reactions occurring in all the samples are almost the same (Figure 2).

Figure 2. Damage condition on sample surfaces (NaCl, 15 cycles)

No surface loss was observed on the surface of the artificially contaminated stone, which was formed by three salt crystallization cycles (Figure 3).

Figure 3. Damage condition on sample surfaces (NaCl, 3 salt crystallization cycles)

Because of contamination on andesite samples, thin section analyzes were carried out to observe the salt effect in the samples. A total of two images of each sample, with two nicholas and one nicholas, are shown in Figure 4. When these forms are examined, no mineralogical differences were observed in the microscopic examinations between the original sample and the contaminated samples as a consequence of three and fifteen salt crystallization cycles. In other words, any alteration in minerals such as plagioclase, amphibole, biotite etc., mineral transformation etc. not observed. However, in the contaminated samples, macroscopically, there was an increase in the void ratio and a slight amount of color change in the rocks [15].

The clay has sufficient pore size and distribution with high adsorption and absorption capacity, large surface area and pore volume. The salts accumulated in the stone can be removed by taking advantage of these properties. With the purpose of cleaning artificially polluted

stone samples, bentonite clay was thoroughly mixed with the amount of water corresponding to liquid limit (w_L) and to keep homogenous the mixture in the desiccator for 24 hours. This mixture is called clay paste. A schematic representation of the cleaning application planned in the study is shown in Figure 6.

Figure 4. Photomicrographs (crossed polars light) for andesite samples (for original samples (a,b); 15 salt crystallization cycles (c,d); 3 salt crystallization cycles (e,f))

In order to ensure the workability of the clay paste, it was prepared at the liquid limit value of the clay. However, in salt removal applications in historical buildings with a large surface area, additional materials may need to be supported to prevent cracking due to surface tension.

Figure 5. Schematic representation of desalination

Figure 6. State of stone samples before clay paste application

In practice, it is stated that a very thin liquid cleaning paste application is effective in removing the surface with distilled water before applying the paste to the surface of the object to be cleaned [4]. Due to the water-soluble properties of the salts used in the experimental work, it is considered appropriate to clean the residues on the surface and to use pure water for the moisture content of the stone to be high. The samples to be applied clay paste in this way were stored in pure water at ambient temperature of $20 \pm 5^\circ \text{C}$ for 24 hours in order to model the application in the field and to clean the free salts in the stone surface (Figure 6).

Figure 7. Bentonite clay paste

All surfaces of each stone sample removed from pure water were wrapped with clay paste (Fig. 7) prepared in 3-4 mm thickness (Fig. 8). The stone specimens covered with clay paste were allowed to stand until crevices would be formed (10 days) in a dark room with a medium temperature of $20 \pm 5^\circ \text{C}$ and away from sun exposure. After the crevices have been formed, the dry clay paste has been separated from the stone surface using suitable materials. This process is considered to be a desalination cycle. In this study, 3 clay pastes were made for each stone sample.

Figure 8. Application of clay paste on andesite samples

The clay pastes which were completed their cycle time were taken losslessly from the stone surface. These clay pieces were dried at $105 \pm 5^\circ \text{C}$ and then powdered for XRF analysis. The values of the XRF analyzes were used to interpret the experimental results. The results can be examined in table 5.

3. Findings and Discussion

The composition type - % composition plot drawn using the data in Table 5 is shown in Figures 10-12 for each clay cycle. The XRF analysis

for the bentonite clay pastes used in the cleaning was followed by the sodium chloride (Na_2O) and chlorine (Cl) in the pastes as components.

Figure 9. First desalination cycle component - composition graph

The cumulative values of the XRF data were used to interpret the experiment results. The XRF analysis for the bentonite clay pastes used in the cleaning and the NaCl salt present in the paste were evaluated over sodium oxide (Na_2O) and chlorine (Cl). Figures 9-11 show that the Na_2O and Cl compositions in the clay paste increased by 10.52 % and 0.06 %, respectively, compared to the original clay sample, as a result of the first desalination cycle to remove the NaCl salt ions were removed from the samples to clay pastes.

Table 5. XRF analysis results for clay paste cycles after cleaning process.

Component	Original andesite	Original clay	Treated clay sample		
	Compositon (%)				
	1.cycle	2.cycle	3.cycle		
SiO ₂	64.29	52.93	48.06	51.12	52.39
Al ₂ O ₃	15.64	14.37	12.87	13.88	14.37
Fe ₂ O ₃	3.07	12.05	10.24	11.54	11.91
CaO	3.53	3.44	3.13	3.53	3.61
MgO	1.35	2.49	2.32	2.34	2.37
SO ₃	0.05	0.13	0.21	0.13	0.13
Na ₂ O	5.96	3.95	12.23	5.98	4.16
K ₂ O	1.99	1.23	1.13	1.23	1.28
Cl	0.0287	0.0302	0.08	0.04	0.03
I.L.*	3.12	5.53	5.08	5.29	5.46

*Ignition loss

Figure 10. Second desalination cycle component-composition graph

Figure 11. Third desalination cycle component-composition graph

This increase in the Na_2O and Cl ratios in the clay paste may be due to the adsorption and absorption properties of clay, as well as the internal structure between the rock and clay paste and the mechanism of salt transport. Observations made on stone samples as a result of each desalination cycles are shown in Figures 12 a-c. With increasing the cycle number of desalinations, the total amount of NaCl in the paste decreases. This means that the salt pollution on the stone sample is removed.

a. Andesite sample and clay paste state for first desalination cycle

b. Andesite sample and clay paste state for second desalination cycle

c. Andesite sample and clay paste state for third desalination cycle

Figure 12. Observations of the clay paste application

Since the transportation mechanism of the salt is parallel to the evaporation direction of the water, the salt in the stone is transported together with the water evaporating from the surface of the drying clay paste. It was observed that the salt crystals adsorbed in the clay paste accumulated intensively on the upper surface of the clay paste (Fig. 12.a). In the second desalination, the salt crystals on the surface of the clay paste with the shrinkage crack were less than the first desalination cycle, and the salt accumulation was observed to be mainly at the interface where the clay paste and the stone were contacted (Figure 12.b). No salt crystals were observed on the surface of the dry clay paste after the third cleaning cycle (Figure 12.c). Accordingly, the situation in which salt accumulation occurs at the stone interface with the paste is observed in Figure 13.

Figure 13. Salt particles on interfaces between clay pastes and stones' surfaces

As a result of the observations made in the 15 salt crystallization cycles, it was observed that the rate of physical damage increased due to the increase in the amount of salt in the stone samples. Considering this situation, it can be expected that an increase in the durability of the stone may occur because the amount of salt in the stone will decrease after the salt cleaning application.

4. Results

In this study, desalination experiments are carried out with bentonite clay in order to remove the NaCl salt in the andesite stone used in the historical Çobandede Bridge in Erzurum(Turkey) and its regions. The results obtained from the experiments are listed as follows:

- The results of XRF analysis of the clay pastes used to remove the NaCl salt are evaluated in terms of Na_2O and Cl. It is observed that the Na_2O and Cl components in the clay pastes increased by 10.52 % and 0.06 %, respectively, compared to the original clay sample. It has been determined that the amount of NaCl present in the threatened bentonite clay pastes has decreased.
- The pollution rate of stone (i.e. mass change) increases with the increasing stone porosity.
- From mass change and XRF data, it has been calculated about 44 % salt removal. For this study, it can be said that two cycles for desalination are sufficient. Also, desalination may increase as the number of cycles increases.
- As a result of the three salt crystallization cycles, any visible damage on the andesite stone is not observed.
- Since the fourth salt crystallization cycle for the NaCl salt, it has been found that they have become dust on the surface of the andesite stone samples in powder form.
- According to these results of the thin section analysis made, no difference is observed mineralogically in microscopic examinations between contaminated samples as a result of the original sample and three salt crystallization cycles. In other words, any alteration in minerals such as plagioclase, amphibole, biotite etc., mineral transformation etc. are not established. However, in the contaminated specimens, macroscopically an increase in the void ratio and a slight amount of color change in the rocks are observed.

- It has been found that salt transport is towards the evaporation direction of the water, that is, from stone to clay.
- Increase in durability of the stone can be expected by providing salt removal.
- The application of clay paste was achieved with liquid limit value of clay. However, additional materials may be needed to prevent problems due to surface tension when applying clay paste to large surface areas.

In order to achieve more realistic results related to the subject, continuing the experiments with field studies on more historical stone samples and historical bridges which are likely to be affected by NaCl salt is recommended for further studies.

Declaration of Conflict of Interests

The authors declare that there is no conflict of interest.

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