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Removal of Na_2SO_4 on historical buildings with bentonite clay

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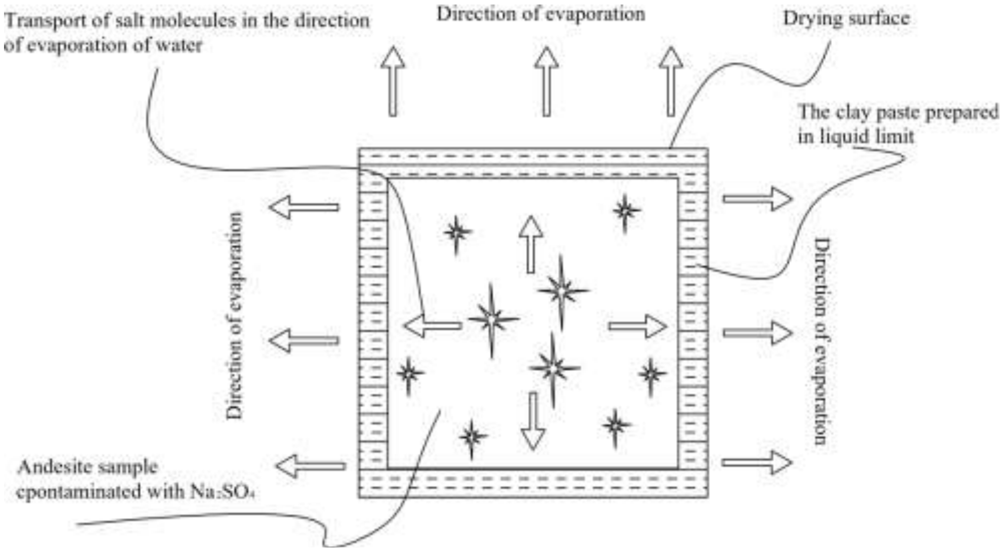
ABSTRACT
Andesite is usually an important material used in the construction of historical buildings. Due to different reasons, the historical building stones are affected negatively over time by the influence of some harmful salts. Because of different environmental and chemical effects, salt crystals may accumulate within pores of the stones. Also, one of these polluting salts is sodium sulphate. The main causes for damage in the stones may be the crystallization pressure of salt crystals growing in confined pores and corosive effects. Cleaning of these salts is the necessary for durability and also will provide more beautiful appearance to such structures. This study is carried out on the cleaning of andesite contaminated with sodium sulfate (Na_2SO_4) salt by bentonite clay. The main purpose of study is to try removing the sodium sulfate within andesite by the clay brought to liquid limit as paste and to apply the historical buildings. As a result of the experimental studies, it is observed that the salt impregnated by the andesite is significantly removed by the clay paste. After desalting, X-ray flourescence (XRF) analyzes for clay pastes and petrographich analyzes for cleaned andesite are carried out and it is provided approximately 56 % salt removal by deselination.
Keywords: *Andesite, clay paste, sodium sulphate, salt removal, X-ray analysis*

Graphical Abstract



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I. Introduction

Historical artifacts must be preserved to convey to future generations. Over time, it is known that a significant part of the porous rocks used in historical buildings is exposed to salt attack. Salt attack (or salt weathering) is explained as the damage caused by soluble salts crystallizing within the pores of stone, in which salts diffuse into the pores by means of rising, falling and penetrating humidity [1].

As the water in the stone evaporates, the salt will be left behind and the salt amount in the stone will increase more and more. So, when a salt-rich solution penetrates into the pores, the salt crystallization takes place and nucleation and growth of salt crystals within the pore spaces can induce alteration and degradation of the stone [2,3]. The stone deterioration depends on the shape of crystals, the degree of saturation of the salt, the pore size of stone and the force of repulsion between the salt and the walls of pores [4,5]. Cyclic wetting and drying is an important driver of salt attack decay. Each cycle may produce only tiny changes, but cumulatively they result in the progressive decay of the masonry material [6].

A number of water-soluble salts can be diffused into pores and cracks in stone by transporting with water. These crystals, which are formed as a result of the evaporation of water, accumulate in the surface of stone and capillary pores [7-9]. During the formation of salt, this crystallization carries out on the surface of the stone due to the increase of the molecular volume and the formation of hydrate salt by taking water into the crystal salt, which is called flowering [10,11]. The crystallization occured in the pores of the stone wall is also called "lower flowering” [12,13]. Thus, it becomes very important to prevent the crystallization of these salts which are effective in the degradation of the historical tissues, or to remove the salts formed in this way by appropriate methods.

The use of paper clay, clay and mixtures of different materials to reduce the damage caused by the resulting crystal salt structures is known for a long time. In addition, the different cleaning methods such as washing with water, cleaning with sand, using laser or using absorbent gel can be applied. However, since the nature of the salt problems is complex in historical buildings, the effect of the methods used is not yet clear [14,15]. In cleaning applications, adsorption and absorption properties of clay materials are also utilized. In addition to these properties, the chemical properties of the salt to be removed and the void fraction, the void network structure, the capillarity, the water absorption etc. properties of the stone to be cleaned are effective in the cleaning applications [16-18]. Many studies in the literature (*in situ* and laboratory applications) have investigated the efficiency of cleaning using different materials [19-22].

In this study, the cleanability of salt-contaminated stone samples with bentonite clay having high plasticity (CH) property with high water retention and ion exchange capacity was investigated. First, to ensure contamination, the stone samples were immersed in saturated Na_2SO_4 solution. Then, the paste prepared with bentonite clay in liquid limit was wrapped around the contaminated stones. After a certain period of time, the dried 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. In addition, petrographich analyzes were also made for cleaned stones.

Experimental work

The bentonite clay used in the study was obtained from Turkey General Directorate of state Hydraulic Works/Erzurum District Office and the andesite samples were obtained from Erzurum Kanber Village Stone Quarry. Some physical properties of bentonite clay were analyzed in soil mechanic laboratory in the R & D laboratory of 12. Distinction of General Directorate for Highways in Turkey. Also, the mechanical and physical properties of original andesite were determined in the R & D laboratory of General Directorate for Highways in Turkey. $Na_2SO_4.10H_2O$ used in the experiments was of reagent grade. According to EN 12370:1999 standard, the saturated Na_2SO_4 solution was used at 20 ± 5 ° C for the contamination of andesite samples. Bentonite clay was used for the cleaning of andesite contaminated with Na_2SO_4. Some properties of the bentonite clay, andesite and Na_2SO_4 salt used in the experiments were given in Tables 1-4, respectively.

Table 1
Some physical properties of bentonite clay.

Test Name	Value / Class	Test Standard
Liquid Limit (w_L)	378	[23]
Plastic Limit (w_P)	54	
Plastisity Index (I_p)	324	
Unified Soil Classification	CH	
Density ($g.cm^{-3}$)	2.5	

Table 2
Some mechanical and physical properties of original andesite.

Sample Test Name	Andesite (pink) Value		Test Standard
Friction Wear Strength ($cm^3/50\ cm^2$)	24.8	15.9	[24]
Unit Volume Weight (tm^{-3})	23	23	
Pressure Resistance (N/mm^{-2})	69.8	105.5	
Water Absorption (w/w, %)	4.5	3.0	[25]

Table 3

- Physical properties of original andesite[26]

Sample No	Specific gravity	Actual volume (cm^3)	Particle volume (cm^3)	Pore volume (cm^3)	Visible porosity (%)	Dry weight (g)	Unit volume weight (g/cm^3)	Dry density (g/cm^3)
7	2,60	68,34	59,15	9,19	13,45	153,85	2,19	2,25
8	2,60	70,64	61,75	8,89	12,58	160,61	2,21	2,27
9	2,60	68,74	56,57	12,16	17,70	147,15	2,08	2,14
16	2,60	67,05	57,73	9,31	13,89	150,17	2,18	2,24
17	2,60	65,22	50,95	14,27	21,88	132,53	1,98	2,03
18	2,60	65,51	56,20	9,31	14,21	146,18	2,17	2,23

Table 4
Some properties of sodium sulphate [27]

Salt	Solubility $mol.L^{-1}$ (25°C)	Density (gcm^{-3}, 20°C)	Molar Mass ($gmol^{-1}$)	Molar Volume (cm^3mol^{-1})
$Na_2SO_4.10H_2O$	1.96	1.46	322	220

To calculate the mass changes of the andesite samples, the following equation was used.

$$D_M = \frac{Ms - Mo}{Mo}\ x\ 100 \quad (1)$$

here;
D_M: The Mass change after each test (%, w/w)
M_0: The beginning mass of the andesite (g)
Ms: The mass of the andesite after cycle (g)

To obtain test samples, the andesites in block size were cut into cubes (4x4x4 cm). These samples prepared were immersed in Na_2SO_4 solution in the tank. The tank was closed to prevent evaporation. The andesite samples were keep waited for 2 hours in the temperature of 20 ± 5 °C. Then the samples were taken from the solution and were allowed to stay in drying oven at 105 ± 5 °C and was left to the desiccator for 2 hours. This process is called a salt-contaminated cycle. According to EN 12370, the stone sample should be contaminate with saturated salt solution for 15 cycles. In the experiments, each orijinal andesite is contaminated with saturated Na_2SO_4 solution for 15 cycles. A general rule of a thumb is that more than about 0.5 % by weight of salt is considered cause for concern and reason for considering salt removal. So, the contamination experiments are made for 3 cycles as the condition mentioned above is provided (Table 5).

After each salt-contaminated cycle and drying process, the andesite samples are weighed on a precision scale of 0,0001 g and visible changes in the samples (fragmentation, cracks, surface erosion, decay etc.) are recorded (Fig. 1a). The andesite samples are allowed to stand for 24 hours in deionized water at an ambient temperature of 20 ± 5 ° C in order to remove salts on the surface (Fig. 1b).

Fig. 1. Andesite samples (a. after salt contamination cycle, b. in deionized water)

The bentonite clay used with the purpose of desalination was mixed with water to reach liquid state. It was keep waited in the desiccator for 24 hours to ensure homogeneity of the mixture. This mixture was called clay paste. All surfaces of each sample taken from deionized water were coated with clay paste (avarage 81.3 g) to be 3-4 mm thick. The samples coated with clay were allowed to wait until forming of shrinkages crack (10 days) in a dark room with a medium temperature of 20 ± 5 C. This process was considered to be a clay-paste cycle. Experiments were repeated three times and mean values were used in the evaluations. In this study, 3 clay-paste cycles were treated for each sample. After this process, the dried clay pastes were taken completely from the stone surface. These pastes taken were dried at 105 ± 5 ° C and then powdered for XRF analyzes. In addition, the petrographich analyzes for treated samples were carried out.

II. Results and discussion

Weights of original andesite, the average weights of the samples contaminated with the Na_2SO_4 and mass change values are given in Table 5.

Table 5

Weight of andesite samples and mass change values

Sample No	7	8	9	16	17	18
Original weight (g)	153.85	160.61	147.15	150.17	132.53	146.18
1. Cycle weigh (g)	154.51	161.32	148.27	150.92	133.90	146.88
2. Cycle weigh (g)	154.86	161.72	148.99	151.33	134.69	147.32
3. Cycle weigh (g)	155.17	162.01	149.61	151.61	135.47	147.65
D_M^*(w/w, %)	0.85	0.87	1.67	0.96	2.22	1.01

* The Mass change after each test

After salt removal, the cumulative values of XRF analysis for each component were used to determine the amount of the salt cleaning. The component types and the average compositions are given in Table 6 for original stone, original clay and treated clay samples.

Table 6

XRF analysis results for clay paste cycles after cleaning process.

Component	Original andesite	Original clay	Treated clay paste		
			Composition (%)		
			1. Cycle	2.Cycle	3.Cycle
SiO_2	64.29	51.75	48.84	51.29	51.97
Al_2O_3	15.64	13.96	13.10	13.96	14.25
Fe_2O_3	3.07	11.73	11.33	11.76	11.88
CaO	3.53	3.41	3.80	4.70	4.88
MgO	1.35	2.44	2.18	2.31	2.35
SO_3	*0.05*	*0.13*	*2.41*	*0.63*	*0.18*
Na_2O	*5.96*	*3.95*	*8.72*	*4.99*	*3.97*
K_2O	1.99	1.25	1.23	1.28	1.30

Cl	0.0287	0.030	0.03	0.03	0.03
Loss on ignition	3.12	11.05	7.61	7.94	7.90

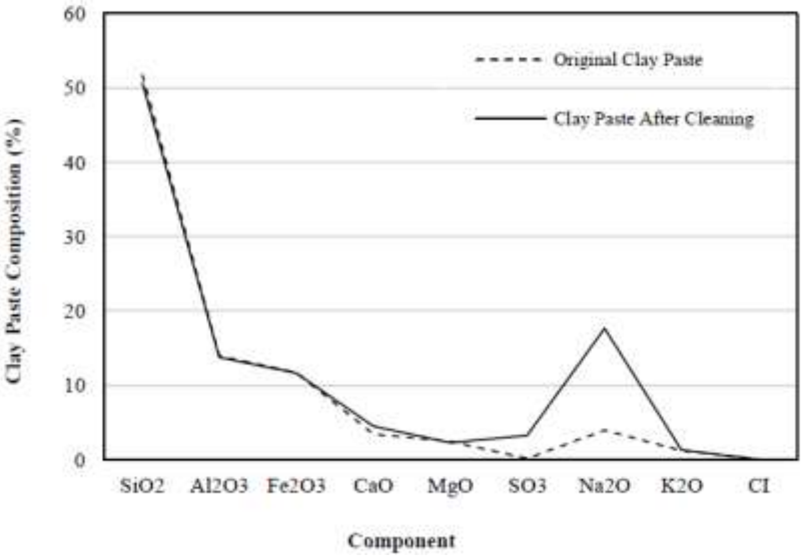

Fig. 2. Component - composition graph

While no significant change was observed in the amount of other components in the clay, it was observed that the amount of Na_2O and SO_3 increased significantly. This shows that the salt in the stone passes into the structure of the clay. When Fig. 2 is examined, it is seen that the amount of sodium sulphate salt decreases in the andesite before and after the cleaning application. From Na_2O and SO_3 values in Fig. 2, in the process of Na_2SO_4 cleaning, it is provided approximately 56 % salt removal.

The porosty - mass change graph is shown in Fig. 3 for each clay- paste cycle. From Fig. 3, as the porosity increases, it is seen that the mass change percentage increases. This situation is attributed to increasing of the total surface area in the andesite structure with increasing porosity. Thus, both the amount of salt accumulation and the amount of salt removal increase. The changes in the clay pastes and andesite samples as a result of each clay cycle are shown in Fig. 5.

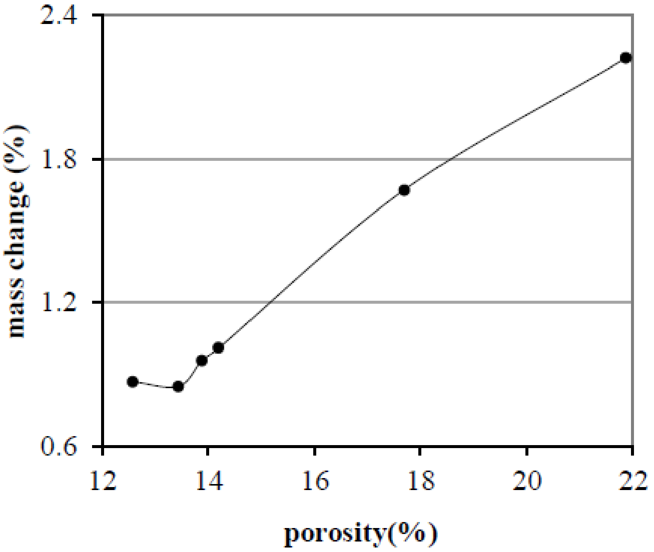

Fig. 3. Porosty - mass change graph

Fig. 4. Na_2SO_4 crystals after clay-paste cycles (a.Firstb.Secondc.Third)

In Fig. 4.a, it is observed that the salt crystals retained in the clay-paste accumulate intensely on the surface of the shrinkage cracks. From Fig. 4.b, it is shown that the salt crystals on the surface of the clay paste formed by the shrinkage crack are less than the first cleaning cycle, after the third clay cycle (Fig. 4c) and that the salt crystals on the surface of the dried clay paste are also very little. As a result of cleaning the samples contaminated with the Na_2SO_4, in the sample with the lowest porosity value of sample with number 8 as shown in Fig. 5, it is observed that the corner erosion has the lowest porosity value.

Fig. 5. Situation after the first clay paste cleaning cycle of sample 8 (a. Before cleaning aplicationb.The sample and clay paste c. After cleaning aplication)

The petrographic analyzes relating to some differences between original and contaminated samples are given in Fig. 6.

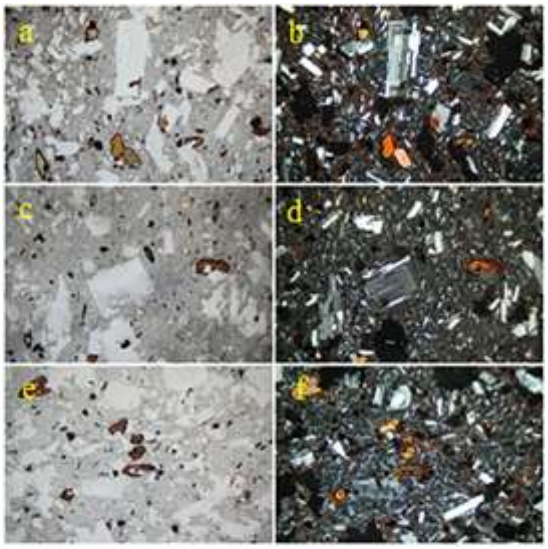

Fig. 6. Photomicrographs (crossed polars light) for andesite samples
(for original samples (a,b); 3 salt crystalization cycles (c,d); 15 salt crystalization cycles (e,f))

From Fig. 6, in particular, mineralogical differences are not observed in the microscopic examinations between the original sames (Fig. 6(a,b)) and the contaminated samples as a result of three (Fig. 6(c,d)) and fifteen salt crystallization cycles (Fig. 6(e,f)). In other words, any alteration in minerals such as plagioclase, amphibole, biotite etc., mineral transformation etc. is not observed. However, in the contaminated samples, macroscopically, there are an increase in the void ratio and a slight amount of color change in the rocks [28].

III. Conclusions

In this study, firstly, the andesite used in the historical artifacts is polluted with the Na_2SO_4 salt. After, the salt content in the contaminated andesite is removed by bentonite clay. The results obtained from the experiments can be given as follows:

- Salt migration takes place towards the evaporation direction of the water, that is, from andesite to clay.
- In the process of Na_2SO_4 cleaning, it is provided approximately 56 % salt removal.
- By XRF analysis of Na_2O and SO_3 values before and after desalting, it is observed that the salt contamination shows a nearly homogeneous distribution.
- The mass change percentage increases as the porosity of andesite sample increases
- There is no damage on the surface of the andesite after contamination with salt.
- From petrographic analyzes,any alteration for minerals in andesite is not observed and but in the contaminated samples, macroscopically, there are an increase in the void ratio and a slight amount of color change in the andesite.
- After desalting application, some damage was observed on the sample with the lowest porosity, so it is recommended to examine the properties of the historical building stones and to perform laboratory tests and pre-tests before the application.
- It is thought that the experimental studies managed by utilizing the adsorption and absorption properties of bentonite clay have carried out the migration of salts to a high degree.
- It was observed that the clay pastes brought to the liquid limit was completely attached to the surface of the stones and that the pastes was easily cleaned after drying.

This study is thought to be a suitable method for practically cleaning of many historic buildings or bridges. On historical stones which are likely to be affected by Na_2SO_4 salt, to obtain more realistic results on the subject, it is recommended to perform in-situ and laboratory studies.

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