

Development of an Anti-corrosion and Anti-pollution Stone Material

Yuning Lu, Xiang Lin, Pei Zhao, Yanhao Zhang, Enyao Li and Su Zhao *

Institute of Materials Science and Engineering, Shenyang Jianzhu University,
Shenyang 110168, Liaoning.
Email:zpljh123@163.com

Abstract. Stone is a non-renewable resource. In order to implement sustainable development in the field of building materials, it is necessary to carry out feasible protection for the existing stone. At present, the performance of the protection materials is relatively single. How to give consideration to both waterproof and anti-corrosion and anti-pollution properties is the focus of this study. Using tetraethyl orthosilicate (TEOS) as silicon source and adding appropriate modifier (silicone oil), the modified silicon stone protective material was prepared by sol-gel method. The ratio ranges of water, ethanol, hydrochloric acid and TEOS were determined by experiments, which were 1:1, 1: 1 ~ 1: 2, 1: 10 ~ 1: 20 respectively, the reaction temperature was 60°C, and the reaction time was 3.5h. Under the experimental conditions, adding modifier hydroxyl silicone oil (0.2%) can improve the anti-corrosion and stain resistance of stone protection materials.

1. Introduction

Entering the 21st century, China's stone industry ranks first in the world for many years. Stone resources belong to non-renewable resources. From the perspective of circular economy, no matter whether the resources are abundant or not and whether the utilization of resources is efficient or not, the final result will be the exhaustion of resources. How to protect the existing stone and slow down the loss of natural resources caused by environmental pollution and acid rain corrosion are the biggest problems currently facing the stone field [1].

At present, organic silicon protective materials have been tried to be applied in the field of material protection [2-3]. Its mechanism of action is through dehydration condensation reaction with silanol groups (Si-OH) on the stone surface, and a hydrophobic film is formed on the stone surface. Organic silicon protective materials can be prepared by sol-gel method. However, the biggest defect of stone protective materials prepared by sol-gel method is that they are easy to crack in the drying process of stone pores [4-5], so modification is needed. In this paper, silicone oil modifier is introduced to increase the pore diameter of the protective layer to make it evenly distributed, and to increase the toughness of the protective layer to prevent cracking, so that it has the effects of waterproof, anticorrosion and stain resistance.

2. Experiment and Test Methods

2.1. Stone Processing

Two commercially available white and yellow sandstones were cut into cuboids with a size of 5x5x2cm³, soaked in distilled water for 12 hours, cleaned with an ultrasonic cleaner for 30min, and then coated with stone protection materials after naturally drying for 24 hours.



2.2. Preparation Method of Organic Silicone Stone Protective Material

A proper amount of tetraethyl orthosilicate, a certain amount of modifier and absolute ethyl alcohol were added into a three-necked flask, the temperature was increased after full stirring, a small amount of hydrochloric acid solution was added dropwise after reaction for a certain time, then distilled water was added dropwise, and a constant temperature hydrolysis condensation reaction was carried out for a certain time to obtain transparent hydrolysate. Finally, the solid content was determined to prepare a modified silicon protective agent with a certain concentration.

2.3. Performance Test Methods

2.3.1. Contact Angle Test. Contact angle can quantitatively reflect the hydrophobicity of stone surface. Static contact angles of stone samples before and after sealing were measured by surface contact angle measuring instrument (GW360A), and compared with hydrophobic performance grade, with hydrophobic grade ranging from grade I to grade v [6], as shown in table 1.

Table 1. Relationship between Surface Hydrophobic Effect and Contact Angle

Hydrophobic capacity grade	Contact angle $\theta/^\circ$	Hydrophobic effect
I	$\theta \leq 30^\circ$	Fully moist
II	$30^\circ < \theta \leq 90^\circ$	Obvious wetness
III	$90^\circ < \theta \leq 110^\circ$	Slightly moist
IV	$110^\circ < \theta \leq 130^\circ$	Good hydrophobicity
V	$\theta > 130^\circ$	Very good hydrophobicity

2.3.2. Acid Resistance Test. Weighed the treated stone sample to M_0 , soaked it in sulfuric acid solution with PH=5 for 48h, the liquid level should be 50mm higher than the surface of the sample, then took out the sample and washed it with deionized water for three times, and dried it, weighed it to M_1 , dried it at 60°C , and calculated the mass change rate W of the stone sample:

$$W = \frac{M_1 - M_0}{M_0} \times 100\%$$

The acid corrosion is reflected by the mass change rate. The larger the mass change, the more serious the corrosion and the smaller the mass change rate, the better the acid resistance [7].

2.3.3. Pollution Resistance Test. The physical standard for making stain-resistant experiments with white marble [2]: Prepared solutions of different proportions with ink and distilled water and dropped them onto the white marble, then let it stand for 5 minutes, rinsed with distilled water, air dry, and graded them after comparing with the evaluation standard. Table 2 for stain resistance rating.

Table 2. Pollution Resistance Grade Table

Pollution resistance grade	1	2	3	4	5	6
V (ink) / V(distilled water)	1:0	1:2	1:4	1:6	1:8	1:10

3. Results and Discussion

3.1. Determination of Material Proportion

On the premise of fixed catalyst hydrochloric acid dosage, solvent ethanol dosage and other reaction conditions (constant temperature 65°C , stirring reaction time 2.5h, constant TEOS dosage, modifier hydroxyl silicone oil dosage 0.1%), the ratio of reaction materials was determined by single factor experiment.

3.1.1. Effect of Water on Hydrophobicity. The mass ratio of water to ethyl orthosilicate was 1:2, 1:1, 2:1, and 3:1. The influence of water content on hydrophobicity was discussed with reference to contact angles of different proportions. The contact angle is shown in Figure 1.

As shown in Figure 1, the effect of water content on hydrophobicity increases first and then decreases, reaching the best effect when the mass and TEOS are 1:1. This is because water is an important reactant in hydrolytic condensation, too little will affect the progress of the reaction, and too much water will affect the solubility of the final product, thus reducing the waterproof effect of the product.

3.1.2. Effect of Ethanol on Hydrophobicity. The mass ratio of ethanol to TEOS was 1:2, 1:1, 2:1, and 3:1. The influence of ethanol content on hydrophobicity was discussed with reference to contact angles of different ratios. The contact angle is shown in Figure 2.

As shown in Figure 2, the amount of ethanol has an effect on the hydrophobicity of both sandstones, reaching the best effect approximately around 2:1 of ethanol mass and TEOS. This is because when ethanol is used as a blending agent, the reactants cannot be completely dispersed when the amount is small, thus affecting the full progress of the reaction, and too much ethanol will evaporate with the increase of temperature, taking away some reaction products and reducing the reaction performance.

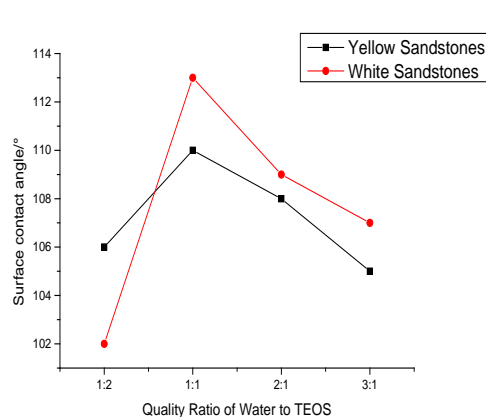


Figure 1. Relationship between Water Content and Contact Angle

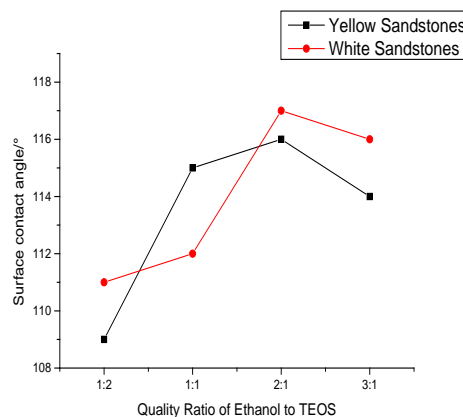


Figure 2. Relationship between Ethanol Content and Contact Angle

3.1.3. Effect of Hydrochloric Acid on Hydrophobicity. The mass ratio of hydrochloric acid to TEOS was 1:4, 1:10, 1:20 and 1:30. The influence of hydrochloric acid content on hydrophobicity was discussed with reference to contact angles of different ratios. The contact angle is shown in Figure 3.

As shown in Figure 3, the influence of hydrochloric acid as a catalyst on the hydrophobic property fluctuates slightly, and the contact angle changes of the two stones are not different, but the amount of hydrochloric acid has an influence on the reaction time, so the amount of hydrochloric acid in this experiment is generally between 1:10 and 1:20.

To sum up, under the experimental conditions, the ratio range of water, ethanol, hydrochloric acid and TEOS is: 1:1, 1:1 ~ 1:2, 1:10 ~ 1:20.

3.2. Determination of Reaction Conditions

3.2.1. Effect of Temperature on Hydrophobicity. The reaction temperature was chosen to be 50°C, 55°C, 60°C, 65°C, 70°C to discuss the effect of temperature on hydrophobicity. The contact angle is shown in Figure 4.

As shown in Figure 4, the influence of temperature on the hydrophobic property of both sandstones increases slightly first and then decreases, too low a temperature will lead to incomplete reaction, while when the temperature is higher than 60°C, the contact angle drops sharply, indicating that too high a temperature will lead to the condensation reaction to start earlier without complete hydrolysis, thus greatly reducing the hydrophobicity of the final product. Therefore, the experimental reaction temperature is chosen to be about 60°C.

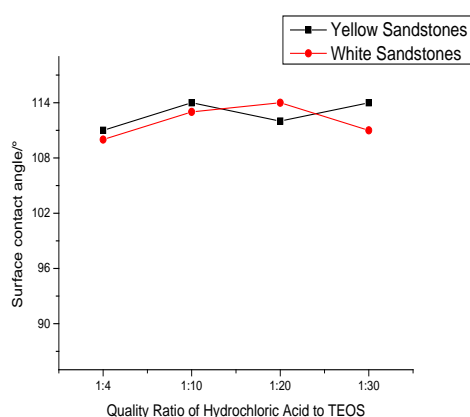


Figure 3. Relationship between Hydrochloric Acid Dosage and Contact Angle

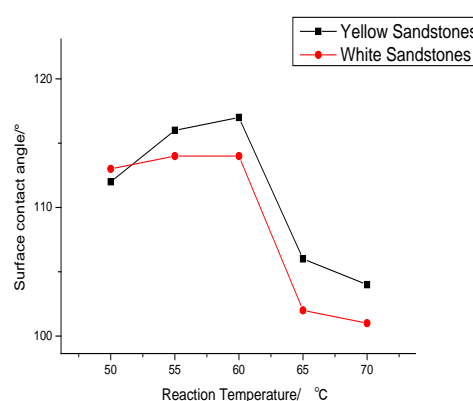


Figure 4. Relationship between Reaction Temperature and Contact Angle

3.2.2. Effect of Reaction Time on Hydrophobicity. The reaction time was chosen to be 2.5h, 3h, 3.5h, 4h, 4.5h, and the effect of reaction time on hydrophobicity was discussed. The contact angle is shown in Figure 5.

As shown in Figure 5, the contact angle continuously increases before the reaction time reaches 3.5h, and tends to be stable after reaching 3.5h, indicating that the reaction is complete at this time, so the reaction time is selected as 3.5h.

3.3. Determination of Modifiers

Hydroxy silicone oil and dimethyl silicone oil were selected as modifiers, and the dosages are 0, 0.1%, 0.2%, 0.3%, 0.4% and 0.5% respectively. The influence of modifier on hydrophobicity was discussed with reference to contact angles of different dosages. The results are shown in Figure 6.

As can be seen from Figure 6, the hydrophobicity of hydroxyl silicone oil is significantly better than that of dimethyl silicone oil. Hydroxyl silicone oil can undergo hydrolytic condensation reaction due to the presence of hydroxyl, and $-CH_3$, the outermost hydrophobic group of hydroxyl silicone oil, is successfully linked to the hydrophobic membrane and acts on the outermost side of the whole system, thus improving the hydrophobic capability. However, dimethyl silicone oil has no hydroxyl group that can undergo dehydration condensation and can only achieve common effect, so its hydrophobic ability is not strong.

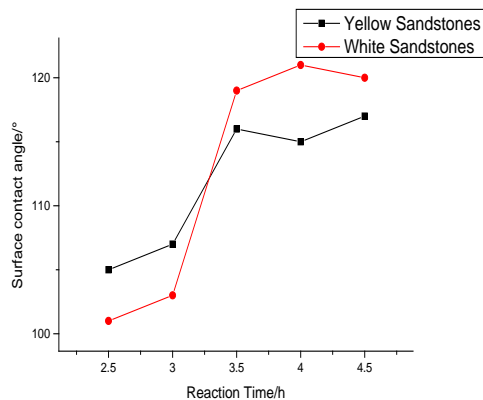


Figure 5. Relationship between Reaction Time and Contact Angle

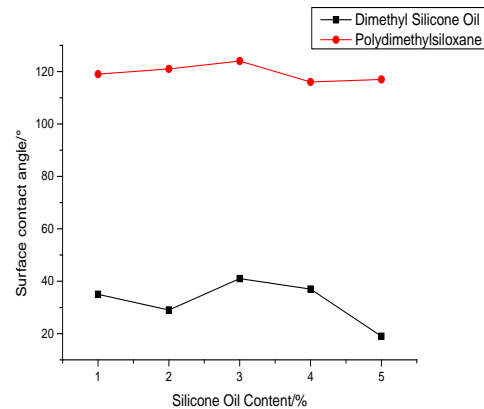


Figure 6. Relationship between Silicone Oil Content and Contact Angle

3.4. Relevant Performance Test

3.4.1 Acid and Corrosion Resistance Test. Stone protective materials before and after modification with hydroxyl silicone oil (content: 0.2%) were coated on the surfaces of two kinds of sandstones, and acid and corrosion resistance tests were carried out according to the method of 1.3.2. The results are shown in Table 3.

From Table 3, it can be seen that the mass change rate of the modified protective material sample is obviously reduced, indicating that the acid resistance is enhanced. The addition of hydroxyl silicone oil can increase more Si-O-Si bonds, and the increase of Si-O-Si bonds can weaken the oxidation ability of acid, thus improving the ability of stone sample surface to resist acid corrosion. Through comparison, it can be seen that the corrosion resistance of the protective material to the yellow stone is improved more obviously, because compared with the white stone, the main mineral composition of the yellow stone is CaCO_3 , and the existence of CaCO_3 causes the stone to be more easily corroded by acidic substances and damages the integrity. The corrosion resistance of the yellow stone sealed by the organic silicon protective material will be improved more obviously.

Table 3. Acid Corrosion Resistance Test Results

Stone type	Hydroxy silicone oil	Poor quality /g	Integrity
Yellow sandstone	No	-0.66	Incomplete
Yellow sandstone	Yes	-0.23	More complete
White sandstone	No	-0.22	Incomplete
White sandstone	Yes	-0.12	More complete

3.4.2 Pollution Resistance Test. Stone protective materials before and after modification with hydroxyl silicone oil (content: 0.2%) were coated on the surfaces of two kinds of sandstones, and the stain resistance was tested according to the method of 1.3.3. The results are shown in Table 4.

From Table 4, it can be seen that the stain resistance level of the modified protective material sample is increased from no stain resistance effect to Grade 5, and the stain resistance ability is greatly improved, because the surface of the stone sample sealed by the modified silicon protective agent forms a compact and smooth hydrophobic film, thus reducing the roughness of the surface of the stone sample, reducing the attachment points of water molecules and contaminated particles, and improving its stain resistance ability.

Table 4. Pollution Resistance Test Results

Stone type	Hydroxy silicone oil	Pollution resistance rating
Yellow sandstone	No	Five
Yellow sandstone	Yes	
White sandstone	No	Five
White sandstone	Yes	

4. Conclusion

(1) The ratio range of water, ethanol, hydrochloric acid and TEOS is determined by experiments, which are 1:1, 1: 1 ~ 1: 2 and 1: 10 ~ 1: 20 respectively.

(2) Under the conditions of 60°C temperature and 3.5h reaction time, the prepared modified stone protective material has better hydrophobic effect.

(3) Adding 0.2% modifier hydroxyl silicone oil can not only improve the hydrophobicity of stone protection materials, but also greatly improve their corrosion resistance and stain resistance.

5. References

- [1] Chen Weixu, Zhang Jiyu. Cherish the Stone Resources in China and Protect the Sustainable Development of Mines [J]. Journal of Fuzhou University (Philosophy and Social Science Edition), 2009, 23(02):35-37+48.
- [2] Su Jingliang, Wu Ge. Research and Application Progress of Stone Protective Agents [J]. Liaoning Chemical Industry, 2013, 42(04):349-351.
- [3] Liu Jia. Preparation of Modified Silicone Protective Agent and Its Application on Baodingshan Sand Rock [D]. Chongqing University of Technology, 2015.
- [4] SUPPLIT R, SCHUBERT U. Corrosion protection of aluminum pigments by sol-gel coatings [J]. Corrosion Science, 2007, 49: 3325-3332.
- [5] Zhao Qiang, Qiu Jianhui, Peng Cheng. Study on Application of Silicate Oligomer in Stone Protection [J]. Cultural Relics Protection and Archaeology, 2007(03):26-31.
- [6] Maria J. Mosquera, Desiree' M. de los Santos, Antonio Montes. New Nanomaterials for Consolidating Stone [J]. Langmuir 2008, 24(6), 2772-2778.
- [7] Sun Shunjie, Hong Yongshun, Zhang Lin. Study on Properties of Silicone Stone Protective Agent [J]. Stone, 2008(03):8-13.