

Durability of Hydrophilic and Antimicrobial Zeolite Coatings under Water Immersion

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Gravity-independent water separation within the condensing heat exchangers onboard manned spacecraft is achieved by using hydrophilic fin surfaces that promote the wetting and wicking of the condensate on the fin. It is also important for the fin surfaces to be antimicrobial to prevent the bacteria growth that may thrive in the moist environment of the fin surface. For practical and economical reasons, the coating must also be durable under wet conditions. Ag-exchanged zeolite A (Ag-ZA) coatings have been shown to have excellent hydrophilicity and are highly antimicrobial. In this study we show that Ag-ZA coatings are highly durable under wet conditions, maintaining their hydrophilic and antimicrobial properties even after submersion in water for 8 weeks. The durability of the hydrophilic and antimicrobial properties of Ag-ZA coating make it a preeminent candidate for use in condensing heat exchangers onboard manned spacecraft. © 2005 American Institute of Chemical Engineers AICHE J, 52: 1157–1161, 2006

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Introduction

Condensing heat exchangers (condensers) are crucial to the environmental control systems onboard manned spacecraft, which regulate the temperature and humidity of the cabin.^{1–3} Condensers function by transferring heat from drawn-in air to a coolant, which circulates through the condenser. As the air cools, condensation forms on the air-side fin surfaces of the condenser. Because of the zero- or microgravity conditions of space, the fin surface must be hydrophilic to achieve effective water separation. A hydrophilic surface allows the condensate to wet and wick across the surface, allowing the use of vacuum to sip the water through the “slurper” holes.¹ If the surface is hydrophobic, then the condensate can form as a droplet, and may cause bridging across the air passageways if the droplets are strongly attached to the fin surface. This bridging increases pressure drop and subsequently leads to an increase in fan power consumption. If the droplets are not strongly attached, they may become entrained in the air stream, causing fog or rain to develop in the cabin.

Currently, the most commonly used hydrophilic and anti-

microbial coatings are sol-gel-based inorganic oxides such as silica and alumina.^{2,3} The process for applying this type of coating begins with preparation of a slurry that contains the components of the coating including the binder, hydrophilic agent, and antimicrobial agent. The slurry is then applied by wash-coating or dip-coating, followed by air knifing, drying, and sintering. This method of application presents several limitations for the coating. The air-knifing step can often cause problems for small wavy fins (such as 28 fins/in.) because excessively strong air knifing may leave some fins uncoated, whereas weak air knifing may lead to clogged fins. Another limitation is that drying and sintering steps must be performed at high temperatures (300–600°C), which often adversely affect the mechanical properties of the condenser alloy.

Because of the constantly wet environment on the fin surface, an antimicrobial agent is needed.^{2,3} The currently used sol-gel coatings include an antimicrobial agent, such as silver oxide, which is added to the coating in the initial slurry preparation step. However, this agent tends to be hydrophobic in nature, making it the center of competition between the coating's hydrophilic and antimicrobial properties. Furthermore, the antimicrobial agent functions in killing microbes by its natural dissolution in water, which limits the durability of the coating. This lack of durability decreases the service life of the entire coating because, after the

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antimicrobial agent is depleted, the coating must be stripped off and a new coating must be applied.

We have been interested in using hydrophilic and antimicrobial zeolite coatings for use on the condensing heat exchangers onboard manned spacecraft. In previous studies, we have shown that zeolite A (ZA) coatings are produced by a simple one-step in situ crystallization process at a relatively low temperature of 65°C.⁴ Zeolite A is a crystalline aluminosilicate with a silicon-to-aluminum ratio $\cong 1$. Each framework aluminum in zeolite A bears a negative charge, which is usually counterbalanced by a sodium cation. Previous studies have proved that zeolite A is extremely hydrophilic, giving the coating the ability to wet and wick water very effectively. The microporosity of the zeolite is believed to substantially contribute to the coating's extremely hydrophilic properties arising from the capillary effect. Previous studies have also shown that the sodium cations in the pores of the coating can be exchanged by silver cations. This provides the coating with antimicrobial function and does not significantly decrease the hydrophilicity of the coating.⁵ We have also previously suggested that if the silver ions are depleted from the coating, they can be easily replaced with an additional silver ion exchange, which gives the coating a regenerative antimicrobial function.

In this study, we are concerned with the durability of silver-exchanged zeolite A (Ag-ZA) under wet conditions similar to the environment on the fin surfaces of condensers. We show that the antimicrobial agent in the silver-exchanged zeolite A coating does not readily leach out into water, in contrast to the currently used sol-gel coatings which require dissolution for the antimicrobial agent to take effect. This property makes the antimicrobial function of the coating very durable, because the antimicrobial function is directly related to the concentration of silver ions held within the coating. We also show that the coating remains very hydrophilic after long periods of exposure to wet conditions. The durability of the hydrophilic and antimicrobial properties of the coating under wet conditions give the coating a long service life, and make it very promising for use onboard manned spacecraft.

Experimental

Preparation of zeolite A-coated coupons

SS-304-2B (McMaster-Carr, composition: $\sim 70\%$ Fe, 18–20% Cr, 8–12% Ni, 0.3–0.8% C, 2% Mn, 1% Si, 0.03% S, 0.045% P) coupons with dimensions 2×3.5 cm were cleaned in a 1.3 wt % solution of Alconox detergent (Alconox Inc., New York, NY) for 1 h at 80°C. The coupons were then rinsed and wiped clean under running deionized (DI) water with gloved hands. The clean coupons were then stored in a 50-mL centrifuge tube until coating deposition.

The ZA-coating process began with the preparation of a synthesis solution with molar composition of $10 \text{ Na}_2\text{O}:0.2 \text{ Al}_2\text{O}_3:\text{SiO}_2:200 \text{ H}_2\text{O}$. The typical synthesis solution was prepared by first combining 0.432 g of aluminum powder (200 mesh, 99.95+%, Aldrich) and 133.2 g of double deionized (DDI) water in a 250-mL wide-mouth polypropylene bottle and stirred for about 10 min. Next, 32.0 g of sodium hydroxide (pellet 97+%, Aldrich) was added under a fume hood, with the cap loosely fastened to allow for the escape of gases. After stirring for a minimum of 30 min, 8.0 g of Ludox[®] LS30

colloidal silica (30 wt %, silica, Aldrich) was added dropwise to the stirring solution. The synthesis solution was stirred until it became clear. Polypropylene balls (2 cm diameter) were slit with a razor blade and clean SS-304-2B coupons were individually inserted into the slits. The assemblies were then floated in the ZA synthesis solution, and cooked at 65°C for 11–12 h. After the coupons were removed from the synthesis solution, they were washed thoroughly under DI water and blown dry with compressed air. The coated samples were analyzed by X-ray diffraction (XRD, Siemens D-500 diffractometer using Cu-K_α radiation) to verify the formation of ZA.

Silver ion exchange

The ZA coating obtained its antimicrobial properties by exchanging the sodium ions in the pores of the zeolite with silver ions. This was performed by placing the ZA-coated coupons into slit polypropylene balls and floating them in a 500-mL polypropylene bottle with about 300 mL of 0.01 M AgNO_3 solution. The solution was gently stirred for about 6 h at room temperature, and the bottles were kept in darkness so that the AgNO_3 does not decompose as a result of light irradiation. The coupons were then washed thoroughly under DI water and then soaked in DI water for 1 h to remove any impurities that may have formed on the coupons' surface. Scanning electron microscopy (SEM, Philips XL30-FEG operated at 20 keV) images were used to show that there was no structural difference between the zeolite A coatings before and after silver ion exchange. Elemental analysis of the coating by EDAX was used to confirm the complete exchange of sodium with silver.

Leaching

Samples of Ag-ZA were immersed into DDI water for periods of 1, 2, 3, 4, 6, and 8 weeks. Ten samples were used for each leaching time. After the samples had been leached for the appropriate times, they were rinsed under running DI water, dried with compressed air, and stored in 50-mL centrifuge tubes until further testing was performed.

Testing hydrophilicity and silver content

The hydrophilicity of the leached samples was determined by contact-angle measurements using VCA-Optima (AST Products Inc., Billerica, MA). This was performed by placing the coated coupon on the sample stage, and dispensing a 0.6- μL droplet of DDI water that remained suspended from the tip of an automatic syringe. The sample was then raised to make contact with the water droplet, and then lowered so that the contact angle could be measured using VCA-Optima image analysis software. The coating is considered to be hydrophilic if the water contact angle is $<30^\circ$. Twelve measurements were made on each sample and 10 samples were used from each period of leaching. The data are reported as averages with error bars corresponding to the standard deviation between measurements.

The amount of silver remaining after leaching was determined by atomic absorption (AA) and EDAX. When determining the silver concentration with AA, the equipment was first calibrated with a blank sample and 0.50, 1.00, 2.00, 3.00, and 4.00 mg Ag/L silver standards. Next, the Ag-ZA coating was

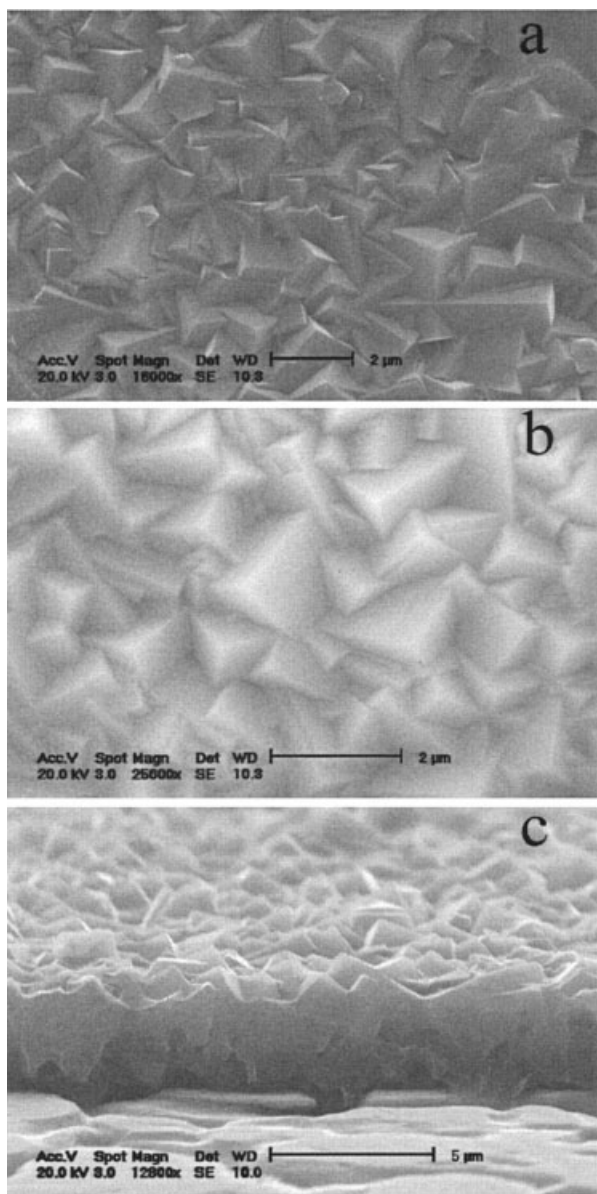


Figure 1. SEM images of coatings on SS-304-2B substrate.

(a) Top view of ZA; (b) top view of silver-exchanged ZA (Ag-ZA); (c) cross-sectional view of ZA.

dissolved in 1.5 mL of 1.0 M HNO_3 and then brought to 10 mL with 0.1 M HNO_3 . The solution was then diluted 200-fold with 0.1 M HNO_3 such that the expected concentration would be between 0.00 and 4.00 mg/L, fitting within the standard curve. The diluted solution was then examined by AA, and the silver concentration was measured and back-calculated to find the silver amount within the coating. After the mass of silver was determined, it was divided by the mass of the zeolite within the coating such that all of the samples were normalized. The data are reported as the mass percentage of Ag within the coating. Elemental analysis by EDAX was carried out on the same samples before the coating was dissolved to confirm that the silver-to-aluminum ratio was $\approx 1:1$.

Antimicrobial testing

The antimicrobial function was tested following published protocols.⁶ *Escherichia coli* (JM 109) was spread on a Luria-Bertani (LB) agar plate and incubated at 37°C for 24 h such that individual colonies could be found. An individual colony was dabbed with a sterile toothpick, placed into a sterile test tube containing LB medium, and incubated at 37°C overnight. The bacteria were then centrifuged down at 4°C for 15 min at 3000 rpm, after which they were resuspended in Butterfields Buffer (BFB) until an optical density at 540 nm between 0.1 and 1.0 was taken.

Teflon® rings were placed into small petri dishes containing 6.5 mL BFB. Ag-ZA coupons were placed onto the Teflon® rings and 0.5 mL of the bacterial suspension was placed on the coupon. They were then incubated at 37°C for 0, 4, and 24 h. Three samples were used for each incubation time, and the previous procedure was repeated for nonexchanged ZA controls. After incubation, the Teflon® stands were removed and the petri dish was gently swirled. Each coupon was scraped with a sterile cell spreader (Fisher Scientific) three times along the major axis and three times along the minor axis. The cell spreader and the coupon were rinsed with 3 mL BFB, bringing the volume within the petri dish up to 10 mL. They were then serially diluted to have the appropriate number of colony-forming units (CFUs) for bacterial plating. Aliquots of 100 μL were spread across an LB agar plate and then incubated at 37°C for 20 h. The CFUs were counted visually and back-calculated to find the number of surviving CFUs. The antimicrobial testing was performed for every period of leaching.

Results and Discussion

The SEM images of ZA coating on stainless steel (SS-304-2B) substrates before and after a silver ion exchange are displayed in Figure 1. The ZA coatings display complete and even coverage with a thickness of 4–6 μm . There are no distinguishable differences between the two fully intergrown polycrystalline coatings.

Silver ions were used as the antimicrobial agent for the coating, and were added to the coating by exchanging sodium ions, which were initially held within the pores of ZA, for

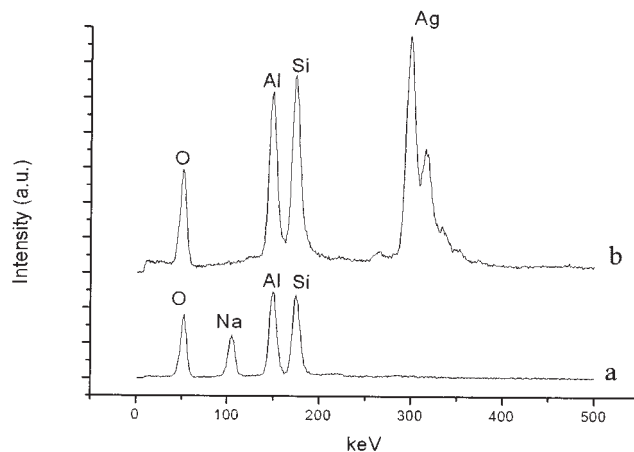


Figure 2. Semiqualitative elemental analysis by EDAX of (a) ZA and (b) Ag-ZA coating on SS-304-2B.

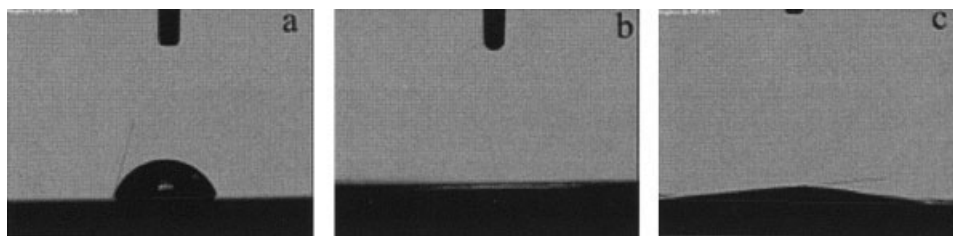


Figure 3. Water contact angles on (a) bare SS-304-2B; (b) the same substrates coated with ZA, and (c) Ag-ZA after 8 weeks of submersion in water.

silver ions. The silver ion exchange was performed by submerging the ZA-coated sample into 0.01 M AgNO_3 , and the semiquantitative elemental analysis (Figure 2) shows a complete exchange of the sodium ions for silver ions.

The durability of Ag-ZA was tested by submerging the coated samples in DDI water in weekly increments of time for up to 8 weeks. Tests were then run on the zeolite-coated samples to determine whether there was a decline in hydrophilicity, silver ion concentration, and antimicrobial effectiveness.

Water contact angles were used to test the hydrophilicity of the coatings. ZA was extremely hydrophilic, usually bringing the contact angle completely to 0° . After the silver ion exchange, the coating became slightly less hydrophilic than the nonexchanged coating, but it remained in the realm of hydrophilic coatings (water contact angle $< 30^\circ$). The slight decline in hydrophilicity in the Ag-ZA samples is attributed to the small amount of silver oxide, which is known to be hydrophobic, that formed on the surface during the ion exchange. Figure 3 shows the relative increases in hydrophilicity between the coated samples and the bare substrate, and how well water wets across the coated samples.

After submersion in water, Ag-ZA samples displayed no significant changes ($< 3^\circ$) in hydrophilicity with water contact angles staying $< 10^\circ$ throughout the entire 8-week period (Figure 4). Note that a coating is considered to be hydrophilic and adequate for space application if it has a water contact angle that is $< 30^\circ$.² This durability of the hydrophilic function of the coating would be very effective for maintaining the wetting and wicking properties needed for the condensing heat exchangers onboard manned spacecraft. Although Figure 4

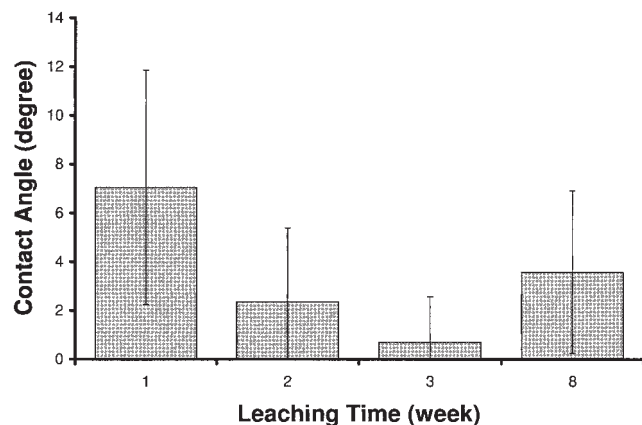


Figure 4. Water contact angles on Ag-ZA coating after submersion in water for various times.

shows some fluctuations in contact angle, it should be realized that these contact angles are all very small ($< 8^\circ$) and thus the minor change of several degrees of contact angle should not be overinterpreted. It does seem, however, that a slight increase in hydrophilicity is generally observed as the leaching time increases. This occurs likely because the silver oxides that may have formed during the silver exchange are soluble in water and are gradually washed off the surface of the coating.

The silver ion concentration within the coating is extremely important for maintaining the coating's antimicrobial function. If the silver ions were to readily leach out into water, this would limit the life span of the coating's antimicrobial properties. Ideally, there would be a silver cation for every aluminum anion in the coating, and the theoretical maximum percentage of silver in the coating is about 40.3%. Figure 5 shows that silver concentrations after all of the leaching times remain very close to the theoretical maximum concentration. Elemental analysis by EDAX confirmed that the atomic ratio of silver to aluminum was roughly one to one, which implies that no significant amount of silver ions had leached out from the coating throughout the entire 8 weeks of submersion.

The durability of the antimicrobial effectiveness was examined by inoculating 500 μL of bacterial suspension on three samples of Ag-ZA for 24 h of incubation. One nonexchanged ZA sample was incubated for each set of exchanged sample as a control. The previous steps were repeated twice more, except that the bacteria were incubated on the coating for 0 and 4 h, instead of 24 h. After incubation, the bacteria were removed from the samples, plated, and incubated for 20–24 h for visual counting. These steps were carried out for each period of leaching.

Cell counts on the ZA controls showed more than 1×10^7

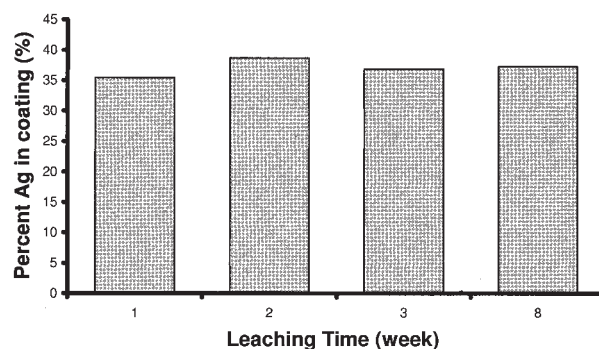


Figure 5. Percentage Ag (g/g) within the coating after submersion in water before antimicrobial testing.

Table 1. Surviving Colony-Forming Units (CFUs) Found after 0-, 4-, and 24-h Incubation on ZA and Ag-ZA Coating after Submersion in Water for Various Times*

	Log CFU Recovered after Incubation					
	0-h Incubation		4-h Incubation		24-h Incubation	
	Na-ZA	Ag-ZA	Na-ZA	Ag-ZA	Na-ZA	Ag-ZA
1 week leached	8.09 (0.07)	0 (0.0)	8.11 (0.16)	0 (0.0)	8.04 (0.03)	0 (0.0)
2 week leached	7.27 (0.02)	0 (0.0)	7.12 (0.08)	0 (0.0)	7.01 (0.26)	0 (0.0)
3 week leached	7.58 (0.01)	0 (0.0)	7.32 (0.03)	0 (0.0)	7.30 (0.06)	0 (0.0)
8 week leached	8.32 (0.03)	0 (0.0)	8.21 (0.02)	0 (0.0)	8.20 (0.09)	0 (0.0)

*Values in parentheses are SDs.

CFU, whereas the Ag-ZA samples had no surviving bacteria for 0, 4, and 24 h of incubation. Although the ZA controls have no antimicrobial agent, there was a slight decrease in CFU between the 0- and 24-h incubation period. This is possible because the hydrophilicity of the coating may allow some of the cells to adhere to the coating instead of being transferred to the buffer solution.⁷ No change was observed in the antimicrobial effectiveness of Ag-ZA throughout the entire 8 weeks of submersion (Table 1). This, along with the relative constant silver concentration within the coating, implies that the Ag-ZA coating will have an extremely long service life with respect to its antimicrobial function.

Conclusion

This study shows that Ag-ZA coating is durable under wet conditions. The silver ions in the pores of the coating are not readily leached out by water, leading to the highly effective antimicrobial function with a very long service life. Submersion in water also does not significantly affect the hydrophilic properties of the coating, allowing it to maintain the wetting and wicking properties needed for condensing heat exchangers for long periods of time. This study shows the high durability of Ag-ZA after 8 weeks in water, and future research will be done to show its durability after up to one year of leaching.

This high durability of Ag-ZA coating makes it a preeminent candidate for use onboard manned spacecraft.

Acknowledgments

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