

# Effect of silane matrix on corrosion protection of zeolite based composite coatings

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*In the present work, the comparison of the anti-corrosive properties of various types of zeolite based coatings, with different silane matrix on AA6061 aluminum substrates, are reported. High hydrophobicity, good adhesion and resistance to corrosion were observed for silane modified with the addition of SAPO-34 zeolite filler.*

*Electrochemical impedance spectroscopy (EIS) tests were performed on all samples in a 3.5% (w/w) NaCl solution at increasing immersion times. All composite films showed good durability. Depending on the type of silane used as a matrix, the composite coating evidenced high stability up to one year of immersion.*

**Keywords:** Aluminium - Aluminium alloy - Corrosion - Coating - Material properties

## Introduction

Hybrid materials play a very important role in the field of anti-corrosion coatings with the ability to combine, in a synergistic way, complementary properties [1]. High degree of homogeneity, good level of interaction with the metal substrate and high degree of hydrophobicity, capable of limiting the interaction of the metal substrate with the outdoor environment inhibiting the corrosion process should be the main features that should have such coatings [2-3].

Silanes have long been used in the industrial field as coupling agents or for pre-treatment of metal substrates due to their easy applicability, durability and versatility combined with low costs. Zeolites are alumino-silicates with a crystalline structure, which possess a high chemical reactivity associated with the presence of external silanol groups. This reactivity promotes a variety of applications of zeolite coatings in industrial field [4-6]. The reactivity of these groups allows the superficial interactions with various reagents such as silanes [7]. The proposed addition of zeolite as filler inside a silane matrix promotes the electrochemical stability of the coating on the electrolyte solution in order to improve its active protective action [8]. The research in the coatings industry is also moving towards the use of additives and materials capable of producing a self-healing effect. In this concern, the zeolite coating offers great potential of applications due to its intrinsically environmental selectivity. Aim of the present work is to evaluate the effect of the addition of SAPO-34 zeolite crystals in various silane matrices (differing by functional groups) on mechanical and anti-corrosion performances of the composite coating.

## Experimental Part

Strips of commercial aluminium 6061, with size 20x40x2 mm, were cut from bars. The sample surface was mechanically polished with emery paper up to grade 500, then degreased in a diluted alkaline solution (0.1 N NaOH) for 60 s, washed in distilled water and finally with acetone.

Hydrolysis was performed in the presence of distilled water and ethanol (ethanol/water/silane 90/5/5 % v/v). The solution was then magnetically stirred, at 25 °C, for 24 h. Four types of silane compounds were used:

- N-propyl-trimethoxy silane S3 (Sigma Aldrich, ≥97%, MW 164.27)
- Octyltriethoxysilane S8 (Sigma Aldrich, ≥97,5%, MW 276.49);
- (3-Aminopropyl)triethoxysilane SA (Sigma Aldrich, ≥98%, MW 221.37);
- Dimethyl-dimethoxy-silane S2 (Sigma Aldrich, ≥95%, MW 120.22);

The pH of the solutions was chosen in order to ensure an optimal ratio between the speed of the hydrolysis of the silane and the natural tendency to self-condensation of the same [9]. By additions of acetic acid, the pH value of the baths was brought to 4.2 for S2 and S3, and 5 for S8.

High silica zeolite SAPO-34 powder, synthesised in laboratory as described in [10] (mean crystals size about 3 µm) were added to the silane/ethanol solution. The new solution was dispersed at first in an ultrasonic bath for 15 min and then magnetically stirred for 15 min before the dip coating procedure.

A bi-layer procedure was used [11] to develop the composite coating. After the first immersion in the silane solution for 1 min, the sample was cured at 80 °C for 20 min to allow cross-linking reactions to form aluminium-siloxane bonds (Me-O-Si) at the metal interface. Then, a second immersion was performed in the silane/zeolite solution for 1 min followed by the final curing procedure for 12h at 80 °C. The details of the types of coatings are given in table 1. The thickness of the composite coatings was about 15 microns.

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Contact angle measurements were performed by depositing 1  $\mu$ l of distilled water on the coated surfaces at room temperature (20 °C). The drop was observed by a micro CCD camera and a suitable PC image analysis script written in Matlab 2012.

Qualitative and quantitative adhesion tests (respectively peel and pull-off tests) were performed on the zeolite modified silane coating. The purpose was to have more information specific about the interfacial interaction between

Code	Silane matrix	Pre-treatment	Zeolite [%]
S3	N-propyl-trimethoxy silane	S3	–
S8	Octyltriethoxysilane	S8	–
SA	(3-Aminopropyl) triethoxy silane	SA	–
S2S3	S3+Dimethyl-dimethoxy silane	S3	–
ZS3	SAPO-34 + S3	S3	80
ZS8	SAPO-34+ S8	S3	80
ZSA	SAPO-34 + SA	S3	80
ZS2S3	SAPO-34 + S2S3	S3	80

**Table 1 - Tables summarizing coating types**

*Tabella 1 - Elenco dei rivestimenti realizzati*

the aluminium substrate and the bilayer composite coating. To have a statistical significant distribution of data an average of 5 replicates for each batch were performed.

Tape peel tests (according to ASTM D3359) were carried out to assess the coating adhesion to the substrate. A square grid was realized with 20 mm long cuts at a distance of 2 mm each other's. A tape was placed over the grid and rubbed with the eraser end of a pencil to ensure good contact. The tape was removed and then the samples were evaluated using a polarized light microscope. The removed grid area was rated according the ASTM specifications, from 0B (low adhesion) to 5B (high adhesion) to evaluate qualitatively the detachment of the coating from the substrate. The pull-off adhesion strength of the composite coatings on Al6061 substrate was measured according to ASTM D4541. The test was performed by securing a loading fixture perpendicularly to the surface of the coating with an adhesive. After the adhesive is fully cured, a portable testing apparatus (Positest AT-M by Defelsko) is attached to the loading fixture and aligned to apply tension normal to the test surface. The failure load was set when the plug of material is detached.

The electrochemical characterization was carried out by electrochemical impedance spectroscopy test (EIS) by using a PAR Versastat 4 potentiostat equipped with a frequency response analyser. The set-up has been constituted by a three-electrode system and the tests were carried out at room temperature in a 3.5% NaCl solution. The coated sample was the working electrode with an exposed

surface of 1 cm<sup>2</sup>, an Ag/AgCl as reference electrode and a platinum wire as counter electrode. All tests were carried out after 15 minutes of immersion in the solution. Impedance measurements were carried out in open circuit conditions by imposing an amplitude of voltage of 10 mV in a frequency range between 0.05 Hz and 1 MHz. The tests were performed at increasing immersion time with the purpose to evaluate the coating degradation during ageing in chloride solution.

## RESULTS AND DISCUSSION

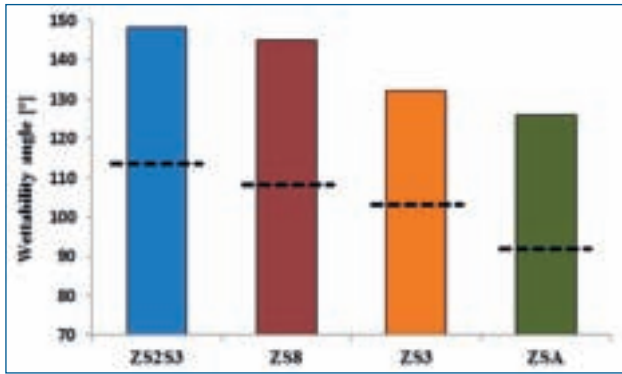
### *Wettability tests*

Figure 1 shows contact angles measured on hybrid coatings with 80% wt of SAPO-34 zeolite. Furthermore, each contact angle was compared with that observed on the film of the respective pure silane film (dashed lines).

It is possible to observe as the addition of the zeolite is able to raise the average value of the contact angle of 20-30° with respect to the unfilled silane film. High contact angles favour a better and easy sliding of the solution along the walls and therefore a lower residence time of the same on the treated surface. In the light of these considerations, the result is even more significant if we consider that the contact angle of the aluminium alloy used is equal to 60°. The best hydrophobic properties were observed for the samples containing the S2S3 and S8 silanes. These results can be justified considering that the nature and the steric hindrance of the organic chains of the different silanes plays a predominant role on the wettability performances of the coatings (the composite films have the same amount of zeolite). Furthermore, it can be considered a greater degree of crosslinking of the composite film (due to a greater flexibility of the chains during the siloxane crosslinking step) and, the steric hindrance of the methyl groups that can act as a shield for the metal substrate.

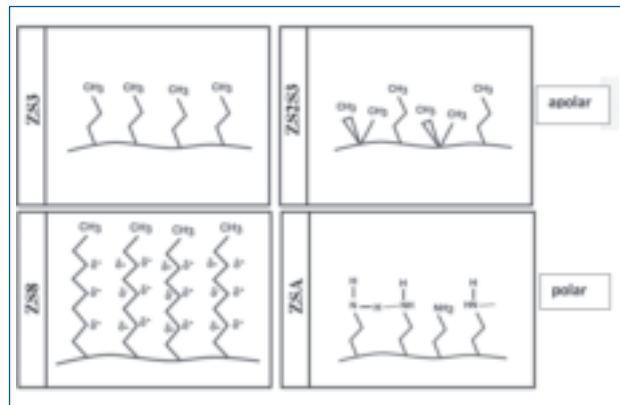
Figure 2 shows a schematic description of the hypothesized organic chain configurations. Based on this scheme, the hydrophilic or hydrophobic behaviour of each zeolite composite coating can be understood and it could be related with the presence of the specific silane matrix and its interaction with the zeolite filler.

The behaviour of the ZS8 system could be associated with a regular and orderly arrangement of the long carbon chains linked to the generation of induced dipoles along the same (Figure 2). The hydrophobic character of these coatings can be explained considering the high chemical affinity existing between the crystals of SAPO-34 zeolite and the matrix silane. The silanol groups, generated during the acid hydrolysis, are very reactive and capable of establishing interactions (initially via hydrogen bonds) with the hydroxyl groups present on the external walls of the zeolite crystals. After curing, these interactions are transformed into covalent bonds [12]. Some authors have shown that the hydrophobicity of the external surface of the zeolite may be increased through its functionalization of surfaces with silane molecules [13-14].



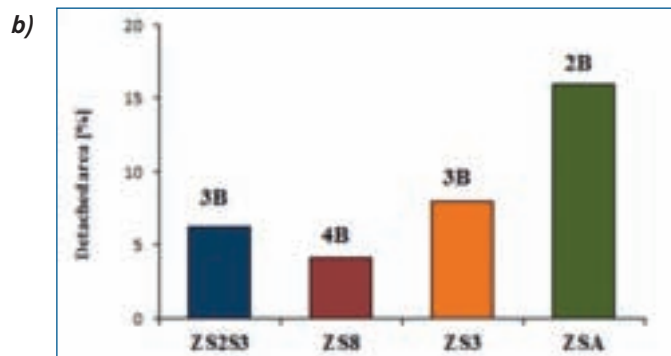
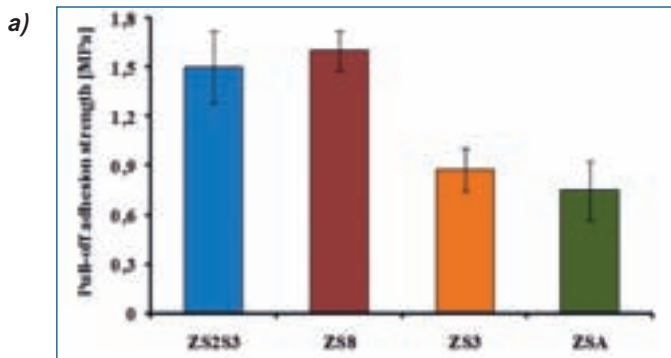
**Fig. 1 - Wettability angle, obtained with distilled water, on composite coatings varying silane matrix (the dashed lines refers to the pure silane coating).**

Fig. 1 - Angoli di bagnabilità, determinati con acqua distillata, dei rivestimenti composti in funzione della matrice silanica (le linee tratteggiate si riferiscono ai rivestimenti di solo silano).



**Fig. 2 - Scheme of functional groups of silane on the silane-zeolite interaction.**

Fig. 2 - Schematizzazione della interazione dei gruppi funzionali del silano sul sistema silano-zeolite

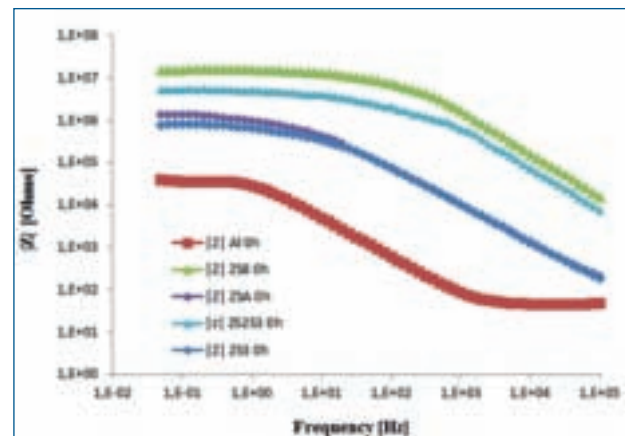


**Fig. 3 - Adhesion properties of coatings. a) pull-off strength; b) percentage of detached area by peel test.**

Fig. 3 - Proprietà di adesione dei rivestimenti: a) resistenza di pull-off; b) percentuale di area rimossa nel peel test.

### Adhesion tests

Figure 3 shows the adhesion performances of the coatings as measured by pull-off and peel tests. The pull-off adhesion strength histogram shows how the sample ZS8 had the best performances (pull-off strength ~1.58 MPa). Comparable results were found for ZS2S3 batch (~1.5 MPa). A confirmation of the degree of adhesion and resistance of the coating is provided by data on the peel test,



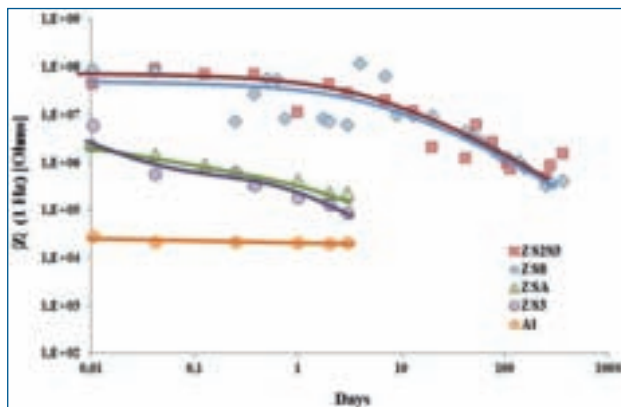
**Fig. 4 - Bode Plot s obtained for composite coated and bare aluminium after 15 minutes (0h) of immersion in 3.5% NaCl solution.**

Fig. 4 - Diagramma di Bode per i rivestimenti composti e il metallo nudo dopo 15 minuti di immersione (0h) in soluzione 3.5% di NaCl.

which show that these samples show the lowest percentages of detached area, respectively, with 4% and 6% (3B-4B index, according with ASTM D3359). The systems ZS3 and ZSA showed worse resistance and adhesion properties of the coatings. In particular, ZSA samples evidenced a detached area up to three times higher than that of the other specimens (2B index).

### Electrochemical tests

Figure 4 shows the impedance modulus trend in a large frequency range (Bode plot of the impedance modulus) for samples coated with the various silane matrices with equal content (80%) of zeolite filler. These curves have been realized, as described in the experimental part, after 15 minutes of immersion in the chloride solution (3.5% NaCl) to allow the stabilization of the open circuit poten-



**Fig. 5 - Evolution of 1 Hz frequency impedance for composite coated and bare aluminium samples at increasing immersion time**

*Fig. 5 - Andamento dell'impedenza a 1 Hz per i rivestimenti compositi e il metallo nudo all'aumentare del tempo di immersione*

tial. It is possible to observe how, with respect to the behaviour of the bare aluminium, all composite coatings are characterized by high impedance values in the whole range of frequencies. This phenomenon can be commented whereas the presence of the filler zeolite is able to reduce the diffusion rate of the electrolytic solution to the metal substrate due to its barrier action.

The highest impedance values were observed for the ZS8 and ZS2S3 batches while the worst behaviour was found for the ZSA and ZS3 ones. However, all the specimens were better than of the bare aluminium at least of a decade in the whole range of frequency. After 72h of immersion, in chloride solution, only samples ZS3 and ZSA showed appreciable reduction of impedance values while the remaining coatings (ZS2S3 and ZS8) kept unchanged their protective action, evidencing good durability.

The high hydrophobicity of such coating protects the metal surface from the chloride solution for several weeks. For these coating batches, a significant decrease of the properties was observed only after 365 days of immersion. The figure 5 compares the values of impedance module, at low frequency (1Hz) of composite coatings with bare aluminium, as a function of time of immersion in the aggressive solution. Good durability performances were observed for ZS8 and ZS2S3 samples, which highlight quite stable anti-corrosion performance for a long time. After over 365 days, the impedance value of the specimens and ZS8 ZS2S3 are higher by nearly two decades with respect to the value of the base metal. Instead, samples ZSA and ZS3 evidenced a progressive reduction of the impedance modulus already at few immersion days, observing after three days impedance values quite similar with bare aluminium.

Fluctuations of impedance values were observed for ZS2S3 ZS8 samples at long immersion times. This behaviour is due to a healing and passivation effect that slows

down the corrosion processes. The passivation mechanism could develop on the surface of the metal by the reaction of the zeolite with the -OH groups originating from cathodic processes thus generating SiO<sub>2</sub>- polar groups which would favour the formation of a silicon-aluminium-phosphate film with passivation properties [15-16]. The silicon-aluminium-phosphate has furthermore cation exchange properties, the excess of negative charge in the lattice may be compensated by the presence of protons or cations located in the network cavities stabilizing the structure [17].

## CONCLUSIONS

The silane-zeolite composite coatings represent an interesting alternative to the traditional coatings. This class of coatings, obtained by the sol-gel technique, showed good degree of homogeneity and high levels of adhesion to the substrate metal. High contact angles were observed (130°-148°) revealing a significant hydrophobic behaviour of the coated surfaces. These properties are related with the properties of the functional group of the silane matrix. All samples showed good durability in a NaCl electrolytic solution. The silane matrix influences significantly the durability performances of the coating. ZS2S3 and ZS8 samples evidenced highest hydrophobic and anticorrosion properties.

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## Effetto della matrice silanica sulla protezione dalla corrosione di rivestimenti compositi a base di zeolite

**Parole chiave:** Alluminio e leghe - Corrosione - Rivestimenti - Proprietà

All'interno del presente lavoro sono riportati i principali risultati inerenti alla valutazione delle proprietà anticorrosive di diverse tipologie di rivestimenti compositi realizzati su substrati di alluminio AA6061. I risultati hanno messo in evidenza, come mostrato in Figura 1, l'ottenimento di elevati valori d'idrofobicità per tutti i film silanici modificati con l'aggiunta della zeolite SAPO-34 nonché buoni livelli di adesione e resistenza a fenomeni corrosivi degli stessi (Fig. 3). Sono stati condotti, test di impedenza elettrochimica (EIS) su campioni immersi in una soluzione areata al 3,5% (w/w) di NaCl. Come evidenziato all'interno della Figura 5, i film compositi mostrano una buona durabilità in ambiente aggressivo. In funzione della tipologia di silano usata come matrice sono stati ottenuti rivestimenti compositi stabili, in soluzione aggressiva, fino a un anno. Sono stati inoltre schematizzati dei modelli strutturali al fine di comprendere meglio le proprietà di tali coating a parità di filler zeolitico. Le tipologie di rivestimenti sono state poi differenziate in funzione della natura chimica e all'ingombro sterico dei silani impiegati (Figura 2).