



# The role of Ce(III)-enriched zeolites on the corrosion protection of AA2024-T3

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## ABSTRACT

The present work demonstrates that the addition of Ce-enriched zeolite microparticles to hybrid sol–gel formulation confers protection to the coating. After two weeks of immersion the integrity of sol–gel film remains unchanged. These properties are due to the fact that the Ce(III) loaded zeolite microparticles are released in response to the adsorption of ionic species involved in the corrosion process of AA2024-T3 substrate. Zeolite adsorption of  $\text{Cu}^{2+}$  cations from intermetallic dissolution and  $\text{Cl}^-$  anions from the solution is shown to take place, enhancing the protective properties of the coating. The microparticles and coatings characterization were carried out by SEM/EDS and the protection properties of the modified coatings were assessed using EIS and localised electrochemical impedance spectroscopy (LEIS) measurements.

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## 1. Introduction

Ion-exchanger materials are one of the recent approaches to corrosion self-healing coatings. Natural and custom synthesized ion-exchange clays (bentonites [1–3], hydrotalcites [4–6]) and zeolites [7–9]) have been used as inhibitor reservoirs. The exchangeable species can be inorganic, organic or a mixture of both with corrosion inhibiting properties.

Ion exchangers are a class of functional materials that display ion exchange properties owing to the existence of fixed ionic sites bonded to their framework [10]. The framework is held together by chemical bonds or lattice energy and can be called polyions. Oppositely charged ions move throughout the framework and can be replaced by ions of similar charge [11]. Due to well-defined compositions and tunable structural features, minute tailoring of their specific properties is possible [12,13]. Synthetic zeolites are the most abundant inorganic ion exchange materials for technical applications [10,12–14].

Zeolites are crystalline aluminosilicates with IA and IIA elements such as sodium, potassium, magnesium, and calcium. They are a subset of the molecular sieve family [12,13]. The unit structure of

the zeolite is  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, i.e. Si or Al bonded with four oxygen atoms. The tetrahedra are linked to each other by sharing oxygen atoms. Each four-valent silicon cation is coordinated by four oxygen anions and the charges are balanced [15]. However, also each three-valent aluminium cation is coordinated by four oxygen anions, and thus, one negative charge from the oxygen atoms remains unbalanced [10,12,14]. Therefore, the aluminium cation position in a zeolite introduces a negative charge in the framework that requires extra cation to balance it [10,12,14]. This negative charge is compensated by an extra cation that is “trapped” in the channels and cavities of the respective zeolite. Since such extra cations are only weakly coordinated by the zeolite framework, they can be easily exchanged against other cations, provided the latter are small enough to fit into the channels of the zeolite [14]. The number of active sites often scales with the number of aluminium atoms in the framework [14]. The aluminium content is the main factor for their unique properties, such as cation exchange capacity, the ability to catalyze reactions, hydrophobicity and hydrophilicity which affect the adsorption of polar and apolar molecules into the zeolite. Thus, besides structure, the silicon to aluminium ratio determines the zeolite performance [14,16].

In our previous work [9] we demonstrated that 1 wt% of cerium(III)-enriched zeolite microparticles ( $\text{Ce}_y\text{Na}_z\text{Al}_{58-b}\text{Si}_{134-c}\text{O}_{384}\cdot z\text{H}_2\text{O}$ ) when used as reservoirs for Ce(III) improve the protective performance of the coating

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