CLAY NANOTUBE PROTECTIVE COATING WITH CONTROLLED RELEASE OF HEALING AGENTS

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Halloysite clay tubes are aluminum-silicate hollow cylinders with a length of ca 1 μm, an outer diameter of 50 nm and a lumen of 15 nm [1-2]. These nanotubes were used for loading and sustained release of corrosion inhibitors. We demonstrated that the nanotubes are entrapping anticorrosion agents in the inner lumen and release them in the coating defect points where they are exposed to humid environment. Inhibitors may be kept inside the tubes doped into paint infinitely long. The inhibitors are released in the coating defect spots with initial bust to suppress the corrosion process, following by 20-50 hours curing [3-5] Longer release was achieved through tube openings stopper formation. A sustain corrosion protection in simulated sea water over 6 months was demonstrated [6-7]. Mechanisms of slowing release from halloysite were studied in terms of nanopore controlled release. The self-healing effect in the metal coating doped with inhibitor loaded halloysite nanotubes was studied in-situ with the scanning vibrating microelectrode technique monitoring of corrosion spots anodic activity. Two response mechanisms are analyzed: induced release in the coating defects and pH-sensitive polyelectrolytes shell formation which is more permeable at higher pH at the corrosion spots. Doping of paint with 5 % of halloysite nanotubes not only adds anticorrosion functionality but also increases the strength and hardness of the coating.

This work is based on our pioneering in halloysite nanotube studies and on results on their loading with corrosion inhibitor triazoles. Assembly of the stoppers at the tube's ends has further perfected these nanocontainers. In this research, we focused on novel coating material with integrated nano and micro features, and it is available in thousands of tons which is unique for nanotechnologies. All suggested processes are "green"; occur in aqueous solutions and under mild conditions. Now, when the most efficient chromate based anticorrosion coatings are forbidden because of their cancer effect, development of smart nanocontainers for efficient environmentally friendly chelate agents (e.g., benzotriazole, mercaptobenzimidozole, hydroxyquinoline) is especially important.

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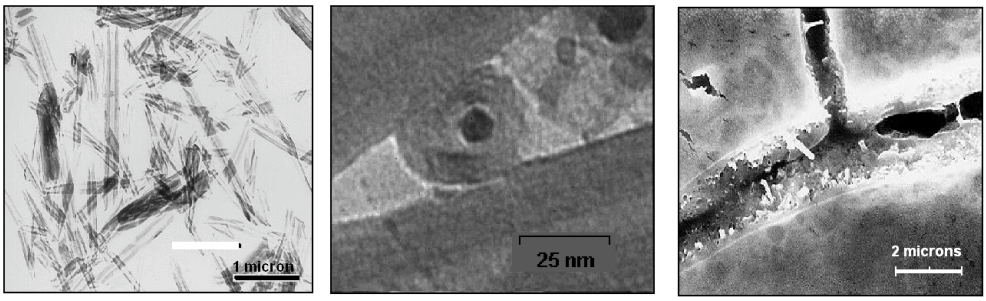
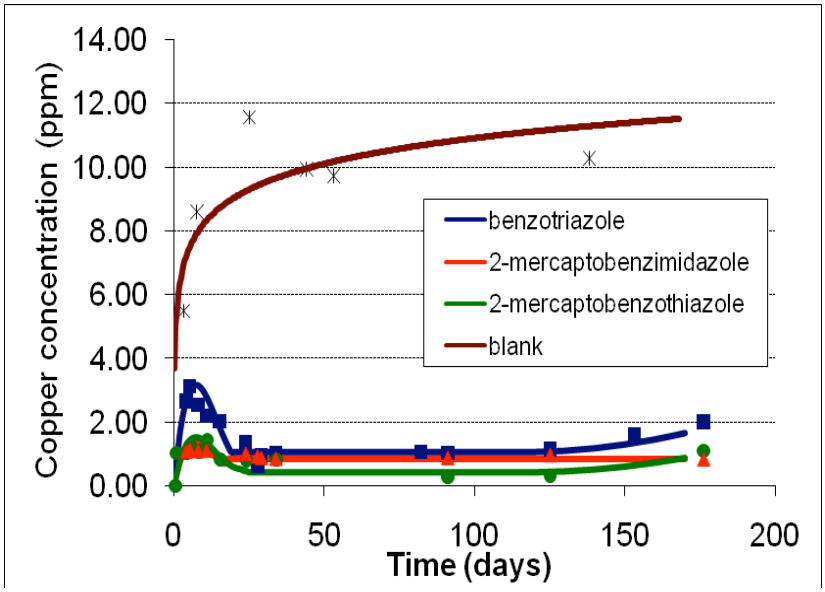


a **b** **c**

TEM images of halloysite in water (a), ammonium molibdate loaded in the tube, cross-section (b), and SEM image of cracks in the paint doped with halloysite (c).



Corrosion development on copper coated with halloysite composite (red) as compared with usual paint (pink).

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