HALLOYSITE NANOTUBES FOR SUSTAINED RELEASE OF CORROSION INHIBITORS

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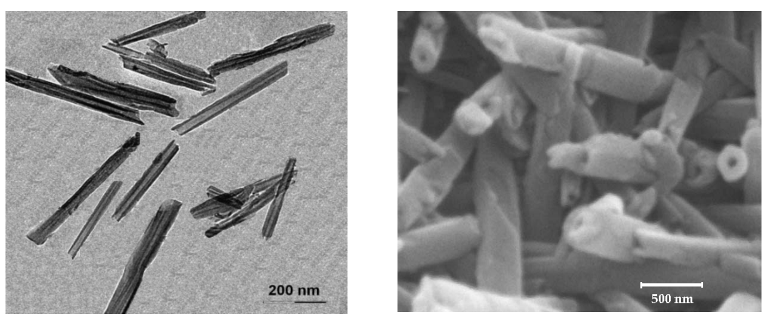
Halloysite clay nanotubes of different sizes were investigated as potential low cost alternative nanocapsules for self-healing protective coatings. Halloysite is alumina silicate clay with hollow cylindrical geometry. It occurs in a nature as hydrated mineral that has the ideal chemical formula of $Al_2Si_2O_5(OH)_4.2H_2O$ which is similar to kaolinite except for the presence of an additional water monolayer between the adjacent layers.



(A) *(B)*

Figure 1 TEM (A) and SEM (B) images of halloysite nanotubes

In Fig. 1 TEM, SEM and AFM images of the halloysite nanotubes are shown. Halloysite layer, which has a characteristic 7.2 A of thickness is structurally similar to the kaolinite layer. Empty tubular lumens of the tubes are clearly visible from TEM images. Hollow tubular structure of the halloysite nanotubes makes it very perspective for using as nanocontainers for encapsulating corrosion inhibitors and other active agents for active and passive corrosion protection. These tubes were utilized for producing self healing coatings.

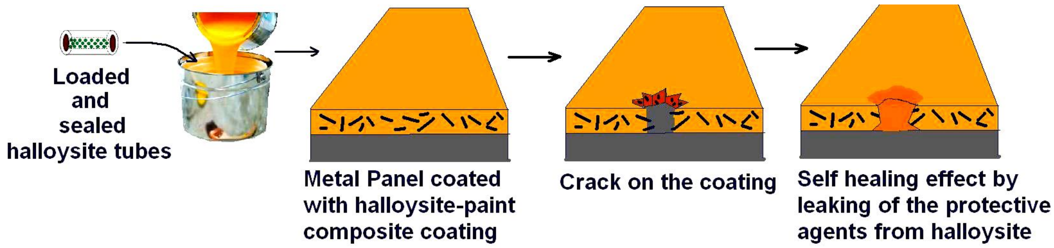


Figure 2 Schematic demontration of the self healing effect

Self healing effect is demonstrated in figure 2. First, halloysite nanotubes, loaded with desired substances for self healing effect, is added to the liquid paint and applied to the metal surface. Loaded substances stay in the halloysite lumen as long as no crack is occured on the paint. Once paint is cracked loaded agents leak to the corrosive environment and stop the corrosion process, either by healing the coating or by inhibiting the corrosion process. Both of these approaches were analyzed in the current work. First we demonstrate self healing process by using corrosion inhibitors.

Benzotriazole, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole was used as corrosion inhibitor for the protection of the metals. These inhibitors form two dimensional thin film with the metal ions on the metal surface, which insulates metal from the corrosive environment and protects it from corrosion.

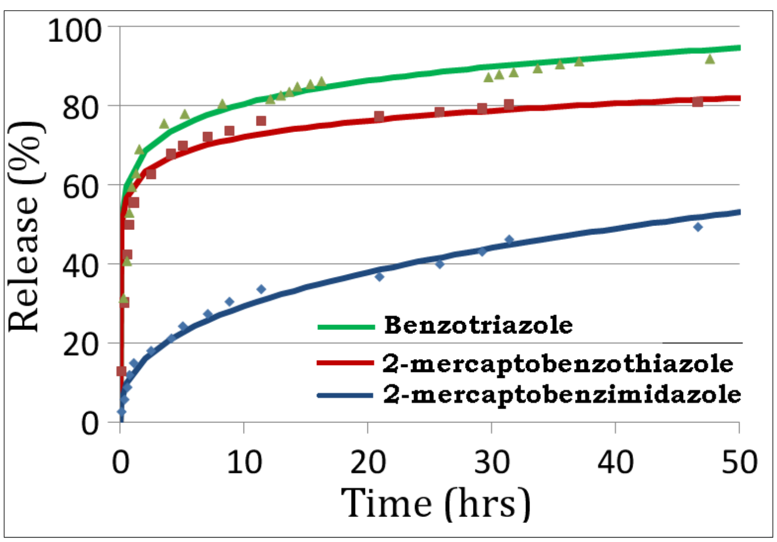


Figure 3 Release profiles of benzotriazole, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole from halloysite.

In Fig. 3 release profiles of three corrosion inhibitors; benzotriazole, 2-mercaptobenzothiazole and 2-mercaptobenzothiazole from halloysite are shown. Release rates of benzotriazole and 2-mercaptobenzothiazole are close to each other more than 80% being within 40 hours while release rate of 2-mercaptobenzimidazole is a bit slower (only 50% in 50 hrs).

Corrosion test was performed on copper wafers. For this purpose four copper wafers were coated with transparent polyurethane paint (this was chosen purposely in order to analyze corrosion process underneath the paint) on one side and acrylic latex paint on the other side. One strip was coated with pure acrylic paint while three others with acrylic paint containing halloysite loaded with abovementioned corrosion inhibitors. Halloysite was admixed with paint as a dry powder by means of simple mechanical mixing. Paint was artificially scratched and exposed to salty water with 30 g/L NaCl. Corrosion process was monitored by analyzing the copper concentration in the corrosive media.

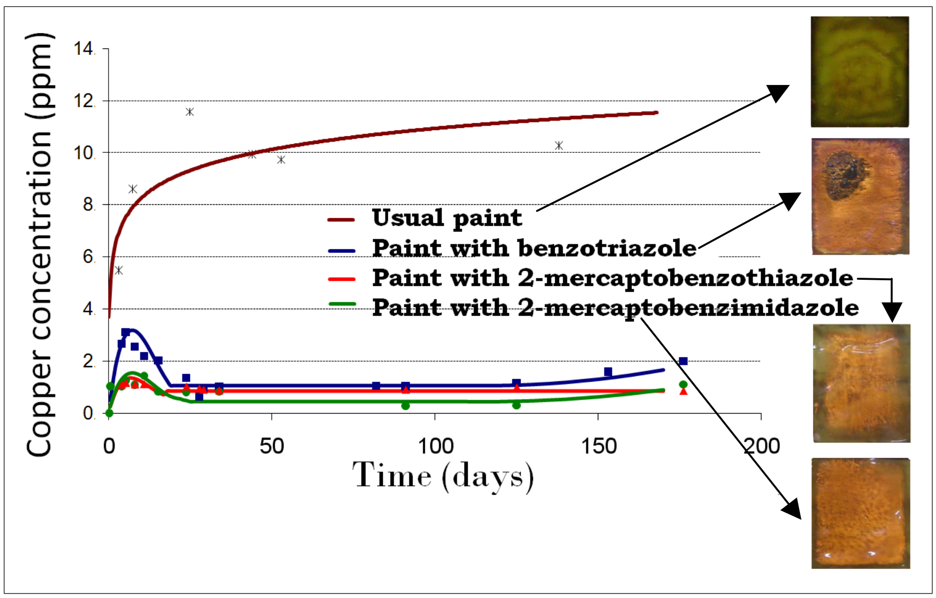


Figure 4 Results for the corrosion test by using halloysite paint composite coating loaded with three different corrosion inhibitors; benzotriazole, 2-mercaptobenzothiazole and 2-mercaptobenzimidazole.

Result for the corrosion test is displayed in figure 4. Concentration of the copper ions is constantly increasing in the corrosive environment indicating the strong corrosion process taking place. Green patina underneath the paint observed by light microscope is also indicating the strong corrosion process. However, by adding halloysite, loaded with corrosion inhibitors, significantly reduced the corrosion rate. Some corrosion process took place in the initial stage, which was stopped by the release of corrosion inhibitors from the scratches. Small corrosion spots that observed for these coatings are due to the initial corrosion process. Paint adhesion was checked after the corrosion test and best adhesion was observed for the paint with benzotriazole loaded halloysite. Results indicate that addition of inhibitor loaded halloysite into the paint significantly improved its anticorrosive performance.

Second approach for improving the coating quality was achieved by repairing the damage of the coating by leakage of the monomer and curing agent from halloysite nanotubes in the cracks. This idea was tested on epoxy coating. It is believed that during the curing process monomer of the epoxy resin do not mix with the hardener in the inner lumen of the tubes due to limited diffusion speed and remain unreacted. These agents (epoxy resin and curing agent) stay inside the tubes as long as there is no damage in the coating since all the openings are blocked. As soon as there is damage in the coating some of the tubes get exposed to air (or other external environment) and start releasing their content. Leaking monomer reacts with curing agent in the damage and repairs coating.

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(A) (B)

Figure 8 Epoxy coating; pure (a) and with 5 wt% halloysite (b), coated on A366 iron alloy and artificially scratched by knife. Repair of the coating was checked with 0.25 M $CuSO_4$ solution.

As soon as there is damage in the coating some of the tubes get exposed to air (or other external environment) and start releasing their content. Leaking monomer reacts with curing agent in the damage and repairs coating. In the figure pure epoxy coating (A) and epoxy with 5 wt% halloysite (B) is shown. Coating was applied to A366 iron alloy and artificially scratched by knife. Repair of the coating was checked by exposure of the damaged coating to 0.25 M $CuSO_4$ solution after 2 days. Self healing effect significantly blocked the diffusion of Cu (II) ions through the scratch; however, some electrical contact between solution and metal panel was observed.

References

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