

Volume Synthesis of Calcareous Deposit on Carbon Steel in Natural Seawater: Effect of Two-Step Applied Potential Waveform

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In seawater, cathodic protection (CP) of metallic structures leads to the formation of calcareous deposits. This phenomenon depends on a lot of parameters, which have given origin to numerous researches for several years: applied potential, substrate nature, flow rate, temperature, pH, pressure or seawater composition influences have been extensively studied in artificial and natural seawaters. Recently, a new method based on an innovative adaptation of cathodic protection technique has been developed in order to synthesise in volume the calcareous structures in natural seawater. Our objective, in the context of the Research National Agency (ANR) EcoCorail project, is to favour conditions to a rapid 3D deposit growth, predominantly composed of CaCO₃. This calcareous conglomerate could be used as “natural cement” linked with sand, shells, marine sediments, etc. to create a natural concrete. This method needs to apply more cathodic potentials than those used in CP, corresponding to the range of potential of hydrogen evolution, in order to prevent the cathode blocking, and to induce pH increased far away from the electrode.

The influence of applied potential and temperature on properties of calcareous deposit has previously been studied [1]. It was shown that brucite is predominantly observed (> 90at%) with high deposition rate for high cathodic potentials (–1.2; –1.3V/Ag/AgCl) and acts as an aragonite’s growth inhibitor. A temperature decrease deactivates hydrogen evolution and reduces the pH favouring aragonite formation. For less negative potentials (–1.0; –1.1V/Ag/AgCl), deposit growth is very low. In all experiments, calcite is only present at very small ratio, typically lower than a few percent.

The present study focuses on the influence of the two-step applied potentials on the deposition and structure of calcareous formed. Experiments are designed to form volume calcareous deposits on immersed carbon steel grids in natural seawater with deposition time varied from 2 to 30 days. In order to simulate a natural environment, experiments are led with natural seawater directly pumped from the sea into a 0.9 m³ tank at the Marine Station of Luc-sur-Mer (Channel coast of France). The temperature is fixed at 20°C. Four different series were carried out with a first step of applied potential E₁ fixed at –1.3V/Ag/AgCl. The second step of applied potential (E₂) is fixed successively at –1.1V; –1.0V; –0.9V or open circuit potential–OCP for each experiment. Different periods for both steps were tested.

Two-step potential waveform influences the chronoamperometric curves. Deposit weights, structures and microstructures are followed using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction. XRD patterns analysed using the combined analysis methodology allow the quantitative determination of phase fractions, cell parameters, atomic positions and mean anisotropic crystallite sizes for each phase. Our results show that the two-step potential waveform permits to maintain a high rate of calcareous deposition and so favours to form rapidly the 3D calcareous deposits. The second step E₂ (especially at –0.9V; OCP) plays an important role to increase significantly the proportion of CaCO₃ present in the deposit to about 30-50at%.

References:

[1] Volume synthesis of calcareous deposit on carbon steel in natural seawater: effect of applied potential and temperature, D. Nguyen Dang, B. Kabbadj, S. Gascoïn, B. Riffault, R. Sabot, M. Jeannin, D. Chateigner, O. Gil, Eurocorr2015, Graz – Austria, September 2015.