

## **Volume synthesis of calcareous deposit on carbon steel in natural seawater: effect of applied potential and temperature**

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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 rise to many researches for several years. The influence of various parameters such as applied potential, substrate nature, flow rate, temperature, pH, pressure or seawater composition have been extensively studied in artificial and natural seawater. 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 structures synthesis, predominantly composed of CaCO<sub>3</sub>. 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, in order to prevent the cathode blocking, and to induce pH increased far away from the electrode.

This study focuses on the influence of applied potential and temperature on the calcareous deposit formed on carbon steel electrodes in natural seawater. In order to simulate a natural environment, a large-scale experiment with natural seawater directly pumped from the sea into a 0.9 m<sup>3</sup> tank is operational at the marine station of Luc-sur-Mer (Channel coast of France). Experiments are designed to form volume calcareous deposits on immersed carbon steel grids using -1.0, -1.1, -1.2 and -1.3V/Ag/AgCl applied potentials and 7.5, 20 and 27°C temperatures. Potential and temperature influences on chronoamperometric curves, deposit weights and microstructures are followed using SEM,  $\mu$ -Raman spectroscopy 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. It is shown that brucite, aragonite and calcite crystals are formed with condition dependent phase ratio. Brucite is predominantly observed for more cathodic potentials (-1.2; -1.3V) and acts as an aragonite's growth inhibitor. A temperature decrease favours aragonite formation for less negative potentials (-1.0; -1.1V), while calcite is only present at very small ratio, typically lower than few percents.