

## THE CALCAREOUS DEPOSIT FORMED UNDER CATHODIC POLARIZATION OF A GALVANISED STEEL ELECTRODE AS METALS REMEDIATION DEVICE OF SEAWATER

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### Introduction

The contamination of coastal waters by trace metals is an important worldwide concern. Although metals are natural part of the environment, their release to coastal waters may significantly affect the productivity and diversity of lagoon ecosystems. This is particularly true in New Caledonia, where soils are highly enriched in nickel and subjected to intense mining extraction and strong erosion due to tropical rainfall. In this context, a novel use of the calcareous deposit formed under the cathodic protection of a metallic structure is proposed to trap metallic contaminants in seawater. The goal of the study is to attempt to trap nickel inside the deposit present under their ionic form in seawater.

### Methods

The calcareous deposit is formed by imposing a small cathodic current density to force reduction of dissolved oxygen and water at a commercial galvanised steel working electrode. Whatever the current density is, the working electrode's potential reaches potential in the water reduction range giving rise to H<sub>2(g)</sub> bubbling. This reaction induces pH increase at the interface and thus calcium and magnesium precipitation. A voluminous deposit grows then with polarization time.

Electrodepositions are performed in artificial seawater containing different amounts of NiCl<sub>2</sub> ( $7 \times 10^{-6}$ ;  $3 \times 10^{-4}$  and  $3 \times 10^{-3}$  mol/L) (Figure 1). Two litre of electrolyte, *i.e* a large volume, is used in order to avoid the electrolyte impoverishment during the deposit formation.

The calcareous deposit is analysed by scanning electron microscopy (SEM),  $\mu$ -Raman spectroscopy (surface and cross section) and by X-Ray diffraction. Ni content in the deposit was also analysed after dissolution in HCl 37% and quantification by ICP-OES.

### Results

DRX analyses reveals that the deposit is a mixture of aragonite CaCO<sub>3(s)</sub> and brucite Mg(OH)<sub>2(s)</sub>. Ni is trapped in this deposit mainly as  $\beta$ -Ni(OH)<sub>2</sub>. Ni is competing with Mg for hydroxide formation.  $\mu$ -Raman spectroscopy and SEM results demonstrate that the surface of the deposit consists of a pure CaCO<sub>3</sub> (aragonite) layer, indicating that Ni is internalized in the deposit.

Ni content seems to increase with the initial concentration of NiCl<sub>2</sub> in the electrolyte since the higher the NiCl<sub>2</sub> concentration in the electrolyte, the greener the deposit (Figure 1). 14 to 26% in weight of Ni initially present in the electrolyte is trapped in the deposit after seven days of polarization.



**Figure 1.** Optical microscopy pictures of the working electrode after 7 days of polarization with different  $[\text{NiCl}_2]$  content in the artificial sea water

### Conclusion

Ni dissolved in seawater can be trapped in a calcareous deposit formed under cathodic polarization of a commercial galvanised steel working electrode. Current densities needed are very low and a very large electrode like wire grid can be used. This electrochemical method is thus a promising and cheap clean-up device for remediation of contaminated seawater.

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