Corrosion of Zn-Al coated carbon steel in conditions simulating deep geological storage of radioactive waste at 80°C

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For high-level and intermediate-level long-lived waste mainly issued from the nuclear industry and especially from the reprocessing of the nuclear spent fuel, the French National Radioactive Waste Management Agency (Andra) is currently studying a geological disposal site, called Cigéo, in eastern France. It is to be drilled in a very stiff clay (Callovo-Oxfordian claystone (COx) so called argillites) formation. A carbon steel casing will be inserted inside the horizontal tunnels and a specific cement grout (pH ~10) will be injected between the carbon steel casing and the claystone. The vitrified waste is set in a stainless steel container itself set in a carbon steel overpack that will be sled inside the carbon steel casing. A high temperature (max. 90°C) is expected at the overpack surface due to radioactive waste activity.

It is now envisioned to protect some specific parts of the carbon steel overpacks with Zn or Al based sacrificial coatings. Such metallic coatings were never studied in the particular conditions of the radioactive waste management described above. For that purpose, carbon steel electrodes were coated, using thermal spray, with Zn, Al or ZnAl15, 500 µm thick, coatings. The obtained coatings were thoroughly characterized by scanning electron microscopy and µ-X-ray fluorescence spectroscopy. Various mechanical methods were also used to quantify the adhesion of the coating to the substrate.

Uncoated and coated carbon steel (P285NH) coupons were immersed at 80°C in specific solutions simulating the electrolyte present in the pores of the cement grout after interaction with the surrounding claystone. Besides, coated samples were connected to uncoated samples to study the efficiency of the protection ensured by the sacrificial character of the coating. The galvanic current and the potential were followed with time using a potentiostat in ZRA mode. The experiments were performed for up to 6 months. The mineral layers formed on coated and uncoated coupons galvanically coupled or not, were thoroughly characterized by X-ray diffraction, µ-Raman spectroscopy and µ-X-ray fluorescence spectroscopy.

During the galvanic coupling experiments, the uncoated coupon remained the cathode, indicating that the galvanic protection remained effective, i.e. no inversion of polarity was observed between carbon steel and Zn, Al or ZnAl15. At the end of the experiments, the uncoated carbon steel coupons were mainly covered by a bilayer consisting of a thin magnetite (Fe_3O_4) film covered by an aragonite ($CaCO_3$) layer. Aragonite formed because these coupons behaved as cathode. The steel surface underneath did not show any significant degradation. In contrast, the coated coupons were mainly covered with Zn, Al or Zn-Al corrosion products even though some zones proved also covered with aragonite. This may indicate the presence of anodic and cathodic areas on the surface of the coatings.