

Compact controllable electrochemical cell for corrosion protection based on micro-sacrificial anodes

S. Hild, C. Weidlich, K.-M. Mangold
 Email: hild@dechema.de
 Funded by AiF – PRO INNO II (KA0331101FK6)
 Period: 01.07.2006 - 30.06.2009



Aims

Corrosion problems are encountered in long standing water installations of zinc-plated steel.

The aim of this project is to reduce the concentration of iron in drinking water and to protect the installations against further corrosion. To achieve this aim magnesium is dissolved electrolytically to form magnesium ions as well as active magnesium particles. These particles are expected to act as micro-sacrificial anodes providing cathodic protection of the ambient steel inside the pipes.

A compact electrochemical cell will be designed consisting of four magnesium rods which are polarised pairwise and alternating as anodes and cathodes.

The project is performed on behalf of *perma-trade Wassertechnik GmbH* in Leonberg, Germany.

Results

Electrochemical dissolution of magnesium

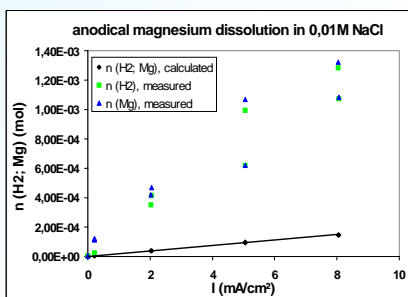
The formation of magnesium-particles and the evolution of hydrogen was investigated.

Pure Magnesium and commercial magnesium-alloys were dissolved anodically in artificial drinking water by applying different galvanodynamic polarisation routines. However the different polarisation routines did not show any influence on the composition and appearance of the particles (Tab. 1).

Tab. 1: Amount of dissolved magnesium obtained by different polarisation routines.

Different polarisation routines magnesium-alloy, Q = 81As			Mg dissolved	Particles not quantified
routine				
galvanostatic	15mA 90min		12.33 mg	
ramp I	15mA 200s 180min		11.33 mg	
ramp II	15mA 200s 180min		9.90 mg	
ramp III	15mA 200s 180min		10.32 mg	

Further anodical dissolution-experiments were carried out with pure magnesium in 0,01M NaCl solution. The electrochemical magnesium dissolution was investigated concerning the reaction mechanism and the formation of hydrogen.



During magnesium dissolution, hydrogen is formed anodically. Hydrogen and magnesium outvalue the expected concentrations. The evolved hydrogen was transported to a GC by a constant nitrogen flow and measured directly (Fig. 1).

Fig. 1: Anodical magnesium dissolution in 0,01M NaCl. Experimental and theoretical values for magnesium and hydrogen.

Characterization of the magnesium particles

The particles consist of magnesiumhydroxide and elemental (metallic) magnesium. Their size varies between 100µm and a few millimeters (fig. 2).

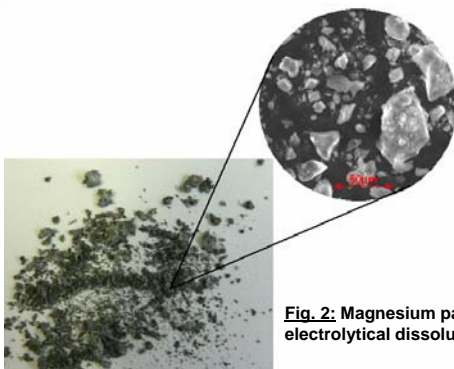


Fig. 2: Magnesium particles resulting from electrolytical dissolution of pure magnesium.

Figure 3 illustrates that the corrosion of magnesium in NaCl solution follows lamellar structures. Figure 4 shows that elemental magnesium is distributed irregularly within the magnesiumhydroxide matrix. Its size varies between 100nm to 200µm in diameter. Elemental magnesium is capsuled inside hydroxide particles.

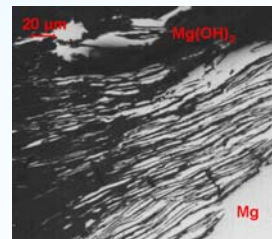


Fig. 3: Cross-section of a corroded magnesium anode (micrograph).

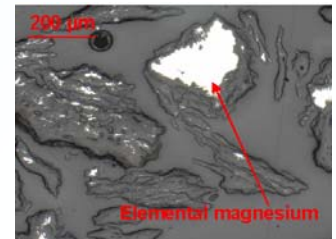
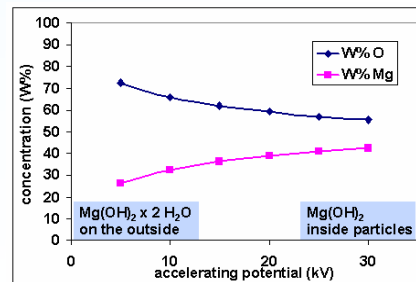


Fig. 4: Cross-section of magnesium particles (micrograph).



A depth profile obtained from EDX measurements (figure 5) shows that the content of magnesium decreases inside the particles. The rate of magnesium to oxygen inside the particles equals the rate in Mg(OH)₂. On the outside the higher oxygen concentration indicates the existence of water inside the hydroxide matrix.

Fig. 5: Depth profile of magnesium particles obtained from EDX measurements.

The elemental magnesium inside the particles is active thus the particles can be used as micro-sacrificial anodes. This could be demonstrated by the evolution of hydrogen during the anodic dissolution of the particles.

Corrosion protection of steel by magnesium particles

Corrosion protection of unalloyed steel (St37) by magnesium particles was demonstrated (fig. 6). In the vicinity of the particles the formation of rust was found to slow down significantly.

Immersion tests in buffer solution (pH 9) for 66 hours showed less corrosion on samples with magnesium particles (fig. 7).

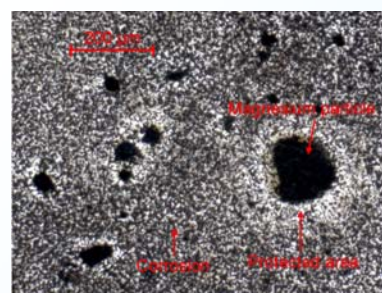


Fig. 6: Corrosion protection of unalloyed steel caused by magnesium particles (micrograph).

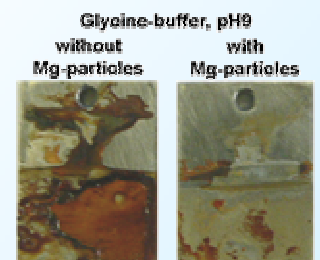


Fig. 7: Unalloyed steel in agitated buffer solution (pH9) without (left) and with (right) magnesium particles after 66h immersion.

Conclusion

- Electrochemically active magnesium particles can be produced by anodic dissolution of pure magnesium and magnesium-alloys.
- Variation of the polarisation routines did not show any effect on the particle size.
- The effect on corrosion protection was demonstrated. However the area protected by each particle is rather small.
- Due to their large size, the magnesium particles are not attached to the inner surface of the pipes but are carried away with the water flow. The travel distance within the pipes is not yet determined.
- Considerable amounts of gaseous hydrogen forms during the electrolysis and the dissolution of the particles. Its amount must not be neglected in technical systems.
- The formation of magnesiumhydroxide residue might be problematic in technical systems, however commercialization is still intended.