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A new concept for corrosion inhibition of magnesium: suppression of iron re-deposition

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Abstract: In our recent work (Höche et al. 2015) we proposed that non-faradaic dissolution of Fe impurities and subsequent re-deposition of thin film of pure ("in statu nascendi") iron enlarges cathodically active sites at Mg surface. The effect drastically accelerates corrosion of impurity containing Mg. In this work we assumed that if Fe re-deposition is prevented, the area of cathodic sites can be drastically decreased and hence corrosion of Mg can be suppressed. In this prove of concept work we used strong Fe^{3+} complexing agents in order to remove dissolved iron from corrosion sites and prevent iron re-deposition.

All used iron complexing agents efficiently lowered the corrosion rate of Mg. Direct correlation of complex stability with its inhibiting efficiency was established. It was shown that cyanide, salicylate, oxalate, methylsalicylate and thiocyanate efficiently reduce hydrogen evolution and suppress critical dark area formation.

Keywords: Magnesium corrosion • cathodic corrosion inhibition • iron complexing agents • hydrogen evolution

1. Introduction

It is well known that magnesium is prone to corrosion not only due to its electrochemical potential but also due to its susceptibility to noble impurity elements. Most common is iron which is incorporated along the entire processing chain. Fe-rich particles are typical initiation points of corrosion since they force microgalvanic corrosion induced anodic dissolution of magnesium [1,2].

Williams et al. [3] showed the occurrence of active persistent cathodes on the anodically polarized bare magnesium mainly related to Fe-rich particles. Birbilis et al. [4] have shown the enhanced catalytic response by measuring enhanced cathodic currents of magnesium previously held at anodic conditions. It was pointed out that enrichments of noble metals on the Mg surface, with higher exchange current density such as iron, are more favourable sites for the cathodic reaction. Recent publication from Lebouil et al. [5] presented a description starting from initial impurity related reactions towards film formation and its spatial extension. The review of Thomas et al. [6] also stated that the amount of impurities influences the hydrogen evolution rate (HER) which indicates a direct link. Recent studies of Fajardo et al. [7] by galvanostatic experiments proved the impact of impurities even at very low concentrations. Curioni et al. [8] showed that the highest corrosion current is

expected close to the corrosion forefront, which indicates that suppression of propagation of dark area efficiently improves corrosion properties. Recent SVET studies by Williams et al. [9] showing circular expansion of mentioned dark area, also confirm the highest dissolution at the interface to unaffected magnesium and they clearly show cathodic current contribution over the entire dark film slightly decreases with distance to the interface. The occurrence of transition metal elements like iron on the corroded surface was shown by Cain et al. [10]. Very interesting contribution was given by Salleh et al. [11]. Their results state that iron particles entrapped under corrosion products still can sustain HER at high rates which fits to previous mentioned results. Frankel et al. [12] give a detailed overview on the topic. Thus, dark area suppression is one of the keys to inhibit corrosion of magnesium.

A lot of approaches to inhibit corrosion of magnesium have been developed during the last two decades. Eaves et al. [2] showed efficient inhibition by arsenates at acidic conditions. However, with a few exceptions, most of the reported inhibitors aim at supressing anodic dissolution of Mg. Mesbah et al. [13] used decanoate and heptanoate as anodic inhibitors. Their inhibiting mechanism based on Mg salt precipitation at the surface (partially protective film). Frignani et al. [14] applied anionic surfactants which apart from adsorbing on the surface also form sparingly soluble salts blocking Mg oxidation. 8-hydroxiqyinoline that forms sparingly soluble complex with Mg was also shown to inhibit Mg dissolution [15-17]. 5,10,15,20-Tetraphenylporphyrin showed high corrosion inhibition efficiency of 90% by forming chelate complexes with Mg which can precipitate as a film on AZ91D alloy [18]. Nevertheless, the anodic inhibition concept has not reached adequate efficiency level and mechanistic understanding. For example, 1,2,4-triazole and its derivatives were shown to inhibit corrosion of Mg alloys [19-21] but the inhibiting mechanism have not been explained. The environmentally friendly derivatives of lactobionic acid were found to provide 75 to 93% inhibiting efficiency to AZ91 but again, their inhibiting mechanism was not explained while the criteria for selecting said species was set as being good inhibitors against corrosion of ferrous and not-ferrous metals and having the ability to chemisorb on the metal surface [15].

Latest progress in magnesium corrosion research based on theoretical approaches from Flis-Kabulska et al [22] delivers the evidence of chemical active iron at the corrosion forefront. In our recent work Höche et al. [23], we proposed that initial cathodic process on Fe-rich particles and anodic dissolution of Mg around it leads to detachment of iron particles from the metallic substrate by undermining or hydrogen bubbles. Chemical dissolution of detached Fe-rich particles occurs with the formation of Fe(II) and Fe(III). These species can be reduced to metallic Fe chemically (e.g. by adsorbed atomic hydrogen) or electrochemically that leads to deposition of thin metallic Fe film or Fe patches increasing total cathodic area. Accelerated HER takes place on the freshly deposited Fe due to the increased reactivity of pure metal ("in statu nascendi"). This mechanism points out the straightforward way for corrosion inhibition: if redeposition of dissolved iron is prevented, corrosion rate should decrease. In this work we used several different iron complexing agents to verify the aforementioned assumption.

2. Material and methods

For the experiments commercial purity magnesium 99.95% (ppm: Fe-220, Ni-2, Cu-5) was used. Impurity content was measured by spark emission spectroscopy. Bare material was cut into pieces, ground, polished and rinsed with ethanol. Roughly 24 hours hydrogen evolution tests were performed using eudiometers (NS45/27 from Neubert Glas, Germany). The immersion solution contained 0.5%

sodium chloride with or without 0.05M solution of iron complexing agent. Finally, the samples were observed by classical optical microscopy. Metrohm 691 pH meter equipped with Mettler Toledo LabExpert Pt 1000 pH was used for regular pH measurements. The following chemicals were used Potassium Cyanide, Ref. 1.04967.02 from Merck; Sodium Salicylate, Ref. 71945, 5-methylsalicylic acid, Ref. 146161 and Sodium Thiocyanate, Ref. 251410 all from Sigma-Aldrich and Di-potassiumoxalat monohydrat, Ref. 4264.3 from Carl Roth. pH of all 0.05M solutions of iron complexing agents was adjusted by NaOH or HCl for the final value varying between 7.5 (for KCN) to 5.9, see **Table 1** for more details.

3. Results and discussion

In this communication the first results on the corrosion inhibition efficiency of some iron complexing agents for commercial purity magnesium are presented. Since 1 mol of evolved hydrogen is produced when 1 mol of magnesium dissolves, hydrogen evolution measurements allow direct correlation with inhibiting efficiency. **Fig. 1** presents the normalized hydrogen evolution rate (HER) and **Fig. 2** visual appearance of the samples immersed in either 0.5% NaCl solution or NaCl solution mixed with iron complexing agent. The sample exposed to pure NaCl solution shows close to exponential increase of hydrogen evolution, the sample is heavily attacked by corrosion and covered by $Mg(OH)_2$ precipitates. Addition of KCN significantly improves the situation. KCN shows excellent suppression of hydrogen formation fully correlated with the surface appearance: three corrosion hotspots occurred while general formation of dark area was strongly suppressed. Note, that even at the very beginning of the immersion test the inhibiting efficiency is rather high probably combing from both adsorption and iron complexing mechanisms, **Fig.1 inset**.
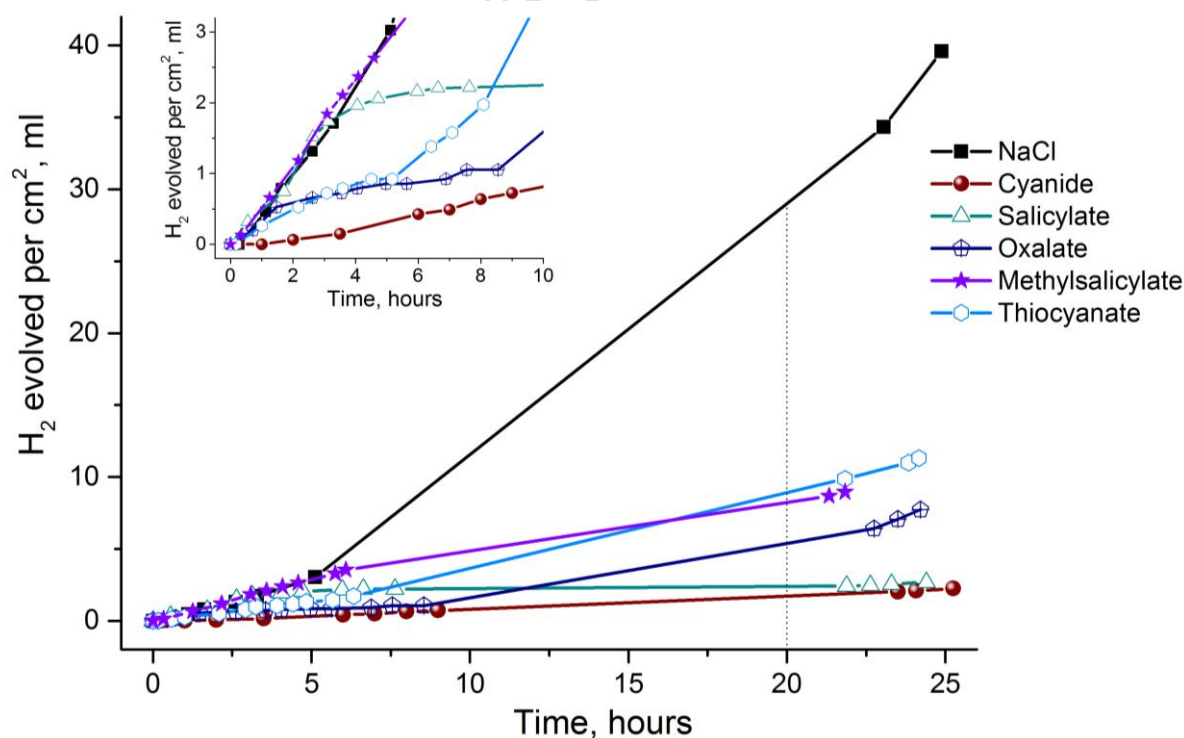

Figure 1. Normalized hydrogen evolution measured for commercial purity Mg containing 220 ppm Fe in 0.5% NaCl in the presence of iron complexing agents.

The weaker complexing agents, oxalate and thiocyanate showed intermediate corrosion inhibition performance with HERs following the cyanide's trend but at lower efficiency also correlating with the visual appearance of sample surfaces that evidences certain degree of dark area formation and corrosion spots. Interesting, that HER for oxalate and thiocyanate starts slowly but increases after several hours of immersion. This cannot be explained by lower stability of formed iron complexes at alkaline pH, because pH sharply increases to 10 and 10.3 during the first hour of immersion (**Table 1**). More likely, this trend can be explained by the fact that oxalate also forms medium stability complexes with Mg^{2+} which can enhance active dissolution of magnesium, and deplete the complexing agent available for Fe (note that amount of dissolved Fe is roughly 5000 times lower than the amount of dissolved Mg). This explanation, however, is not satisfactory for SCN since it does not form stable complexes with Mg. Hydrogen evolution trends measured for salicylate and methylsalicylate differ from other discussed complexes. During the first three hours (for salicylate) and five hours (for methylsalicylate) no inhibiting effect of salicylates can be seen as hydrogen evolution curves for both complexing agents follow the curve of non-inhibited sample, **Fig.1 inset**. Intensive corrosion at the beginning virtually stopped after first three hours of immersion in salicylate containing solution. This can probably be explained by the fact that the most stable $Fe^{III}Sal_3$ are formed at higher pH while lower stability complexes $Fe^{III}Sal_2$ and $Fe^{III}Sal$ are formed at neutral pH [24]. Unfortunately, no data for stability of methylsalicylate complexes at different pH could be found.
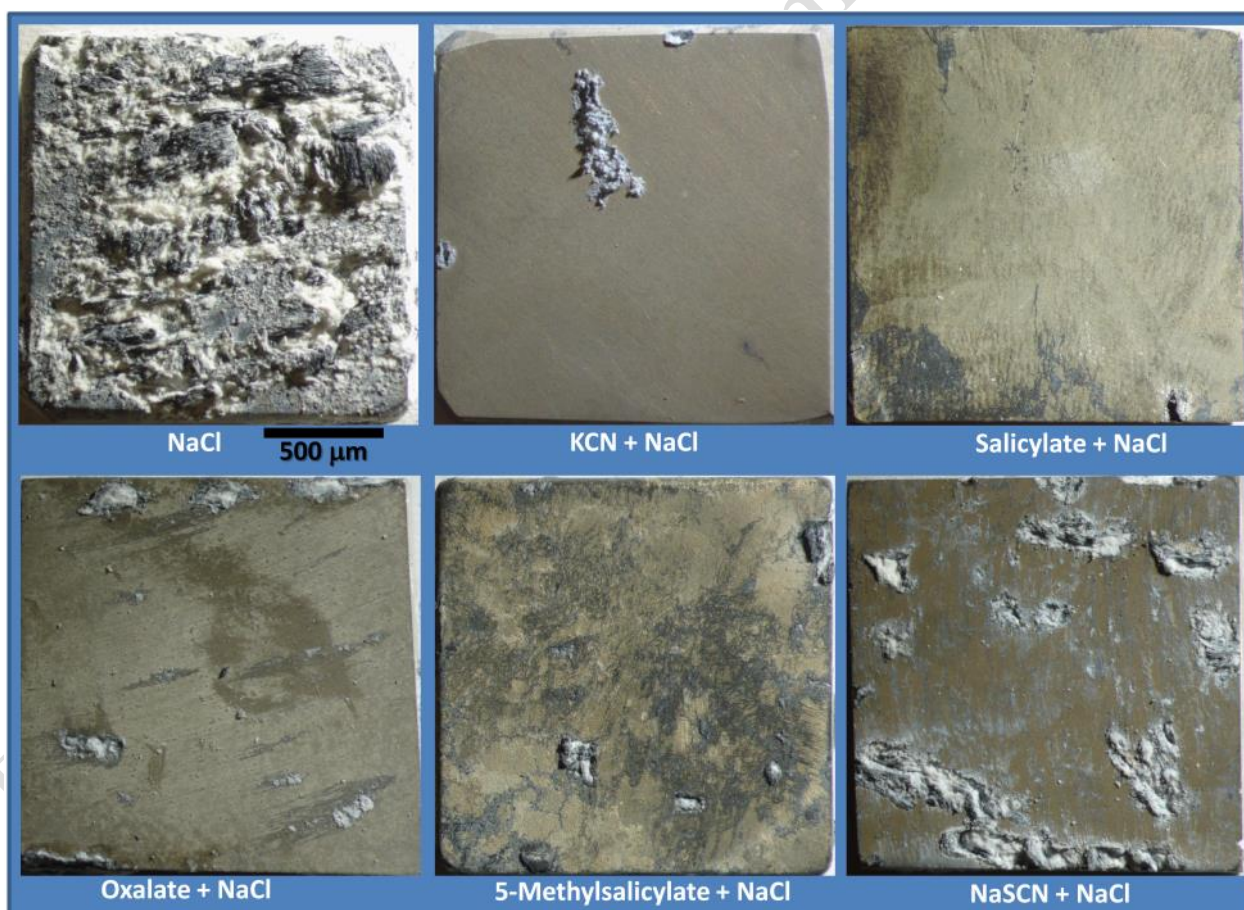

Figure 2. *Visual appearance of tested samples after 20 h of immersion in solutions containing 0.05M of iron complexing agent and 0.5% NaCl.*

The bonding ability of each complex can be described by stability constant. In **Table 1** stability constants of Fe^{III} and Mg^{II} with the complexing agents are gathered. Although Fe^{II} is more likely to form at the initial stage of dissolution of Fe-rich impurity on magnesium, Fe^{III} is by far more stable at

alkaline pH characteristic for Mg corrosion. **Table 1** shows that cyanide forms highly stable complex with iron while magnesium cyanide immediately hydrolyses and does not exist in solution [25]. Thus, high inhibiting ability of cyanide cannot be ascribed to its interaction with magnesium. Thiocyanate forms much weaker complexes with Fe^{III} that reflects on its corrosion inhibiting performance. In general, direct correlation of inhibiting efficiency with stability constant of each iron complexing agent was found, while no correlation with stability constant of Mg complex could be deduced, **Fig. 3**. Note, that it was not possible to find stability constants for Mg-cyanide and Mg-methylsalicylate. In **Fig. 3**, we assumed that the *log $K_x Mg^{II}$ = 0* for the purpose of visualisation.

Table 1. Stability constants of Fe^{III} complexing agents and
*pH of the solutions used for hydrogen evolution tests shown in **Figure 1**.*

Complexing agent	pH of the testing solutions			Stability constants		
	Before immersion	1 hour of immersion	≈ 24 hours of immersion	log $K_{x\,Fe^{III}}$	log $K_x Mg^{II}$	Reference
CN⁻	7.5	n/a	10.5	K_6 43.9	n/a	[26]
Salicylate	5.9	10.5	11.3	K_3 36.8	K_1 4.7	[27]
Oxalate	6.0	10.0	11.2	K_3 20.2	K_2 4.38	[27]
5-Methylsalicylate	6.6	n/a	10.4	$K_?$ 9.77	n/a	[28]
SCN⁻	6.1	10.3	10.8	K_3 5.0	K_1 -0.9	[29]
NaCl	6.5	10.8	10.9	-	-	-

The values of the inhibiting efficiency (IE) presented in **Fig. 3** were calculated using the following equation:

$$IE = \frac{CR_0 - CR_{inh}}{CR_0}$$

where CR_0 is the corrosion rate in pure 0.5% NaCl and CR_{inh} is the corrosion rate in the presence of NaCl and inhibitor. The corrosion rate was determined as amount of H_2 (ml) evolved at 20 hours of immersion.

The approach presented in this communication can also explains the inhibiting effect of some previously reported inhibitors. E.g. 1,2,4-triazole [19-21] and benzotriazole [30] were shown to inhibit corrosion of Mg but the reason why it works was not explained. Since both 1,2,4-triazole and benzotriazole form iron complexes [31, 32] their inhibition performance might be related to slowing the rate of Fe re-plating. With no intention to question in any way the correctness of the inhibiting mechanism proposed for 5,10,15,20-tetraphenylporphyrin in [18] (formation of chelate complexes with Mg that precipitate on Mg surface) we would like to note that this complexing agent also forms stable complexes with iron [33] and high inhibiting efficiency of tetraphenylporphyrin well could be a synergistic effect of both mechanisms.

It will not be surprising however, if some of the iron complexing agents do not fully follow the correlation presented in **Fig. 3**. E.g. the ligands that also form highly stable soluble complexes with Mg, e.g. EDTA [30] might not be as efficient because while they reduce iron re-plaiting they will also

accelerate dissolution of Mg. On the contrary, 8-hydroxiqyinoline that forms sparingly soluble complex with Mg at alkaline pH [15-17] might be more efficiently inhibiting Mg corrosion than it can be predicted from Fe-hydroxyquinolinate stability constant. In general, stability and solubility of both FeL and MgL complexes at neutral and alkaline pH might influence their inhibiting efficiency. The role Fe^{II} (its presence cannot be excluded in a system where atomic hydrogen is present) in iron complexation and re-plating is still not clear. Besides, in our future work we will also discuss the comparative ability of formed complexes to be electrochemically reduced on the surface of corroding magnesium.
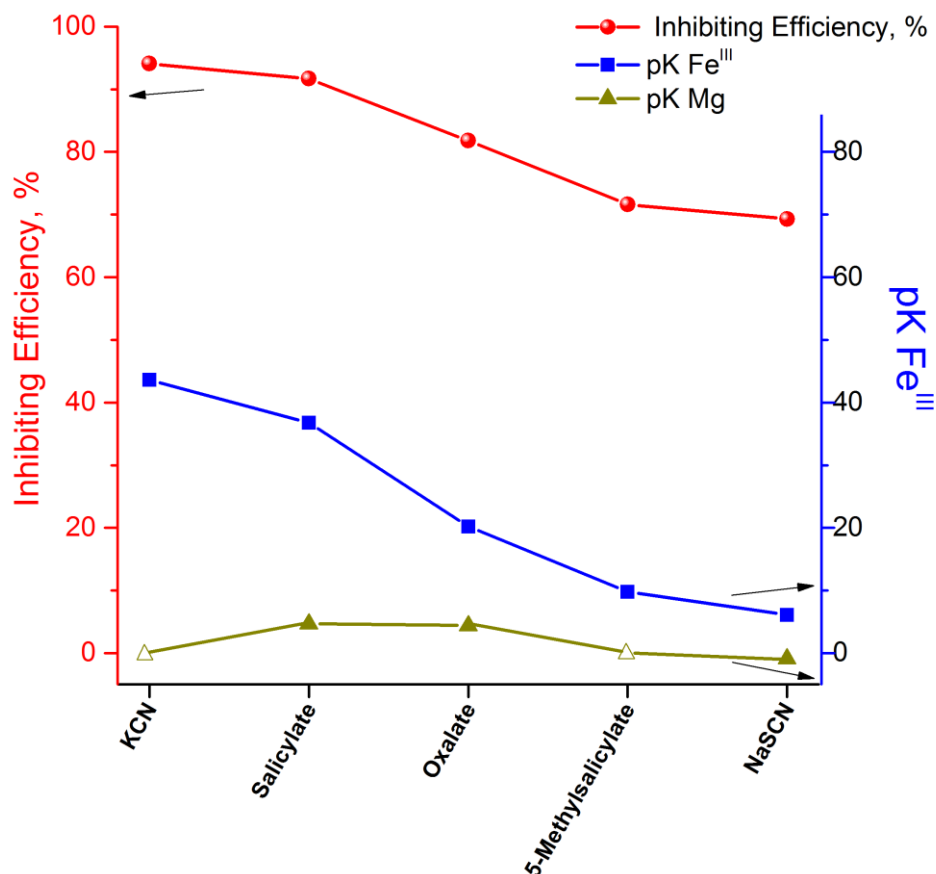

Figure 3. *Correlation of inhibiting efficiency and corresponding stability constants of iron and magnesium complexes.*

4. Conclusion

The efficient corrosion inhibition of commercial purity Mg containing high amount of Fe (220ppm) by iron complexing agents was shown. Hydrogen evolution measurements showed strong suppression of gas evolution during immersion in 0.5% sodium chloride solution. Inhibition efficiency directly correlates with stability constants of Fe^{III} complexing agents.

Acknowledgements

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