CZY WARTO ZAWSZE STOSOWAĆ ANODY MAGNEZOWE?

WHY ARE YOU STILL USING MAGNESIUM ANODES?

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Streszczenie

Czas pracy systemów ochrony katodowej z anodami magnezowymi jest w wielu przypadkach krótszy niż wskazują na to obliczenia. Testy wysokopotencjałowych stopów magnezu, pochodzących od różnych dostawców, wykonane zgodnie z ASTM G97-89, wskazują na bardzo zróżnicowaną efektywność. Zgodnie z literaturą, na wydajność anody ma wpływ szereg czynników, takich jak: gęstość prądu, anodowa reakcja utleniania, charakterystyka środowiska anodowego oraz skład chemiczny i mikrostruktura stopu. Dla zapewnienia odpowiedniej jakości i maksymalizacji czasu pracy, zaleca się wykonywanie badań składu i mikrostruktury stopu anody oraz składu zasypki. Jednak nawet przy ciągłej kontroli jakości wydajność może być niska z uwagi na czynniki zewnętrzne. Z perspektywy efektywności anody cynkowe w zasypce byłyby lepszym wyborem w niektórych aplikacjach.

Summary

The service life of magnesium anode cathodic protection systems have been in many instances, less than design calculations would predict. Testing of high potential magnesium alloys from various suppliers using the ASTM G97-89 test method indicates that efficiencies are widely variable. The literature shows that various factors such as anode current density, anode oxidation reaction, anolyte chemistry, alloy chemical composition, and alloy microstructure can affect anode efficiency. Utilities are advised to conduct tests for alloy composition, microstructure, and backfill composition on anodes from industry suppliers in order to ensure anode quality and to maximize system life. But even with constant quality control efforts the efficiency can still be low owing to operating factors. From an efficiency perspective packaged zinc anodes would be a better option under some application conditions.

1. Introduction

Magnesium anodes were marketed to the pipeline industry after the end of World War II, when new uses for magnesium were being explored. They have become the dominant galvanic anode for cathodically protecting coated pipelines, primarily because of their higher driving potential compared to zinc anodes, which were the only galvanic anode available prior to the introduction of the magnesium anode. There are two different alloys from which to choose: a standard potential AZ63 alloy and a high potential M1 alloy with typical alloys composition and characteristics as shown in Table 1 [1].

Tab. 1. Composition and Performance Parameters of Magnesium Anode Alloys

Element	High-potential	AZ-63 or H1 Alloy		
		Grade A	Grade B	Grade C
Al	0.010% max	5.3 - 6.7%	5.3 - 6.7%	5.0 - 7.0%
Mn	0.50 - 1.30%	0.15% min	0.15% min	0.15% min
Zn	---	2.5 - 3.5%	2.5 - 3.5%	2.0 - 4.0%
Si	0.05% max	0.10% max	0.30% max	0.30% max
Cu	0.02% max	0.02% max	0.05% max	0.10% max
Ni	0.001% max	0.002% max	0.003% max	0.003% max
Fe	0.03% max	0.003% max	0.003% max	0.003% max
Other (total)	0.30% max	0.30% max	0.30% max	0.30% max
Mg	remainder	remainder	remainder	remainder
Use	soil/fresh water			
Nominal potential	-1.75 V_{CSE}	-1.55 V_{CSE}		
Efficiency	50%			
Capacity	1100 A-h/kg (500 A-h/lb)			
Consumption Rate	7.97 kg/A-yr (17.5 lb/A-yr)			

The high potential alloy has a nominal open circuit potential of -1.75Vcse whereas the standard potential alloy has a nominal open circuit potential of -1.55Vcse, which provides a driving potential to the -0.850Vcse polarized potential criterion of 0.900V and 0.700V respectively. Zinc on the other hand at a nominal potential of -1.100Vcse gives only a 0.250Vcse driving potential and therefore magnesium has a considerable driving voltage advantage. However, in terms of efficiency, magnesium, at a nominal 50% efficiency, is at a distinct disadvantage to that of zinc at 85-90%. Choosing a magnesium anode therefore results in a significant waste of a material resource.

2. Faraday's Law and Calculating Efficiency

The theoretical efficiency of magnesium can be calculated using the following Faraday relationship.

$$W = M\, t\, I_{corr}/nF \tag{1}$$

where:

W – weight loss at anode (gm),
M – atomic weight of the metal (24.3gm for Mg),

n – number of electrons given up by an atom in the oxidation reaction (n=2 for magnesium),

F – Faraday's constant of 96,500 coulombs per equivalent weight,

t – time (seconds),

I_{corr} – corrosion current (amperes).

The percent efficiency on a weight basis is determined by comparing the theoretical weight loss from Faraday's equation to the actual weight loss.

$$\% \text{ Efficiency} = W_{theoretical} / W_{actual} \text{ x } 100 \tag{2}$$

3. Efficiency Testing

The efficiency of magnesium anodes is normally determined using ASTM G97-89 standard test method [2], which involves cutting and machining five 12.7mm diameter x 152mm long specimens from an anode casting or extrusion. The specimens are placed in separate containers with a $CaSO_4/MgOH_2$ electrolyte, connected in series with coulometers, and powered at a constant current density of 42 $\mu A/cm^2$ (39 mA/ft^2) for 14 days. The weight loss during the test period is compared to the theoretical weight loss calculated based on coulometer measurements. The open and closed circuit potential is also measured at the end of the test period. Typical test results obtained by various laboratories for high potential magnesium anodes from a variety of suppliers are tabulated in Table 2.

The variation in electrochemical efficiency among these tests results is quite significant, ranging from 4.8–57.7% and for 60% of the test results the efficiency is than 45%. This illustrates extremely inconsistent quality, depending on the source of the magnesium anode alloy and demonstrates the essential need to conduct the ASTM test on each batch of anodes. It is interesting to note that the open circuit potential generally becomes increasingly electronegative as the efficiency increases and only one anode potential was more negative than the nominal -1.75Vcse. But even at the best efficiency almost 50% of the purchased anode material is being wasted.

Tab. 2. Typical Results from ASTM G97-89. Testing on High Potential Magnesium Anodes [3]

| Anode Supplier	Average Efficiency [%]	Average Open Circuit Potential [Vcse]	Life vs. Calculated @ 50% Efficiency [%]
A	51.5	-1.72	+3.0
B	57.7	-1.77	+15.4
C	22.9	-1.58	-54.2
D	37.7	-1.52	-24.6
E	56.6	-1.78	+13.2
F	45.7	-1.69	-8.6
G	17.0	-1.64	-68.0
H	11.2	-1.62	-77.6
I	39.1	-1.69	-21.8
J	52.2	-1.72	+4.4
K	49.3	-1.67	-1.4
L	41.6	-1.65	-16.8
M	12.1	-1.55	-78.0
N	11.0	-1.55	-78.0
O	4.8	-1.53	-90.4

4. Electrochemical Dissolution of Magnesium

The reason for the efficiency variation and the relatively low efficiency compared to the theoretical value is not well understood, probably because of the large number of factors that can affect the efficiency. It has generally been considered that magnesium corrodes according to the following equation:

$$Mg^o \rightarrow Mg^{++} + 2e^- \tag{3}$$

However, there is some evidence that the electrochemical dissolution of magnesium can produce an intermediate monovalent magnesium ion (Mg^+) according to the following reaction:

$$Mg^o \rightarrow Mg^+ + e^- \tag{4}$$

Research by Song et al [4] has concluded that, in sodium chloride and sodium sulfate solutions, magnesium is initially oxidized to an intermediate species (Mg^+) and then the monovalent magnesium ion chemically reacts with water to produce hydrogen and Mg^{++} according to the following reaction:

$$Mg^+ + H_2O \rightarrow Mg^{++} + OH^- + 1/2H_2 \tag{5}$$
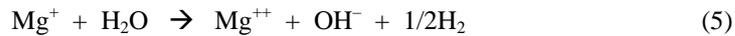
If the initial oxidation reaction produces a monovalent ion then 'n' will equal 1 instead of 2 in the Faraday equation, which will double the weight required to produce an equivalent current.

Antonyraj and Augustin [5] attributed the low faradic efficiency of magnesium to a combination of the formation of a monovalent magnesium and 'chunk' effect. The 'chunk' effect refers to the tendency of magnesium to corrode along the grain boundary, which is a Fe-Mn rich impurity phase that is cathodic to the magnesium grain. This causes the grain to separate from the parent magnesium.

Fig. 1. A 14.5kg High Potential Magnesium Casting Reclaimed from
a Cathodic Protection System after 1 year of Operation

Typically, magnesium corrodes to produce a severely pitted appearance as shown in the photo of a 14.5kg (32lb) high potential magnesium casting reclaimed about 1 year after installation. The corrosion pattern is non-uniform which tends to support the possibility of a 'chunk' effect.

5. Anode Current Density

As with any anode, the consumption rate and therefore its electrochemical capacity is also a function of the anode current density. Figure 2 compares the electrochemical capacity for an AZ63 magnesium anode alloy with anode current density in a gypsum/Na_2SO_4 backfill as determined by Robinson [6]. This indicates that the electrochemical capacity falls off dramatically as the anode current density approaches zero which is attributed primarily to the increasing significance of self corrosion current as the current density decreases, especially below 20mA/ft^2.

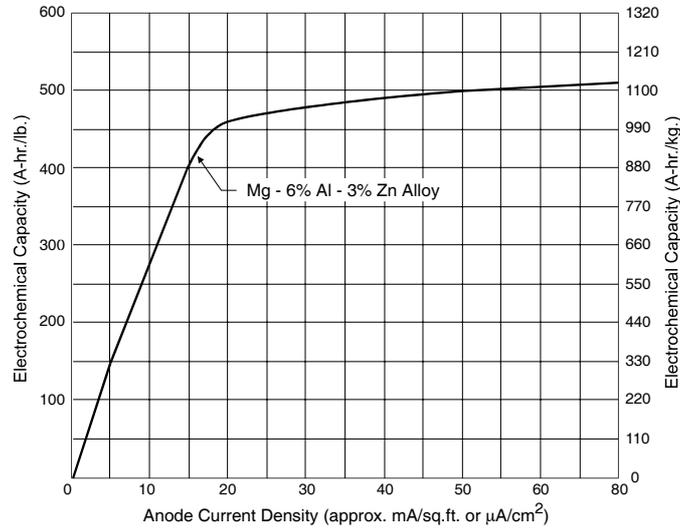Fig. 2. Electrochemical Capacity of AZ63 Magnesium Alloy vs. Anode Current Density
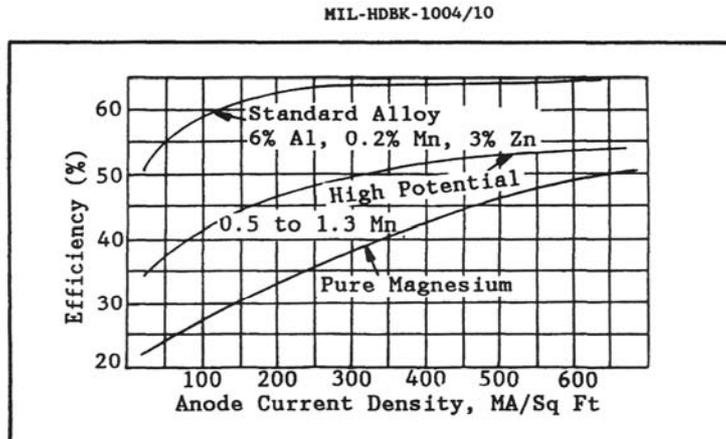(redrawn from Ref. [6])

MIL-HDBK-1004/10

Fig. 3. Efficiency vs Current Density for Magnesium Alloy Anodes
(Note that 1mA/ft^2 is approximately equal to 1μA/cm^2 [7])

The 50% efficiency typically used in system life calculations equates to an electrochemical capacity of 1100A-hr/kg (500A-hr/lb), which is justifiable if the anode current density is 50μA/cm^2 (50mA/ft^2) or more. Yet the average current density range on a 14.5kg anode, at an average current output of 45-90mA, is 14-28μA/cm^2 (14-28mA/ft^2) respectively, resulting in corresponding current capacities of 847-1045A-hr/kg (385-475A-hr/lb). Thus a calculated life based on 1100A-hr/kg (500A-hr/lb) is under-conservative and leads to a longer calculated life than should be expected in actual practice.

The foregoing electrochemical capacity versus current density relationship is for the standard potential anode, but most natural gas utilities use high potential anodes. The electrochemical capacity is unfortunately worse for high potential magnesium as shown in Figure 3 [7]. For most high potential magnesium anodes, the anode current density is less than 20 μA/cm^2 when the soil resistivity is in the 4000 to 5000 Ω-cm range.

6. Electrolyte Resistivity and Anode Backfill

Martin [8] conducted efficiency tests on AZ63 magnesium in mixtures of sand, sodium chloride, sodium sulphate, and bicarbonates of varying resistivity and demonstrated that the efficiency was a function of both current density and resistivity as shown in Figure 4.
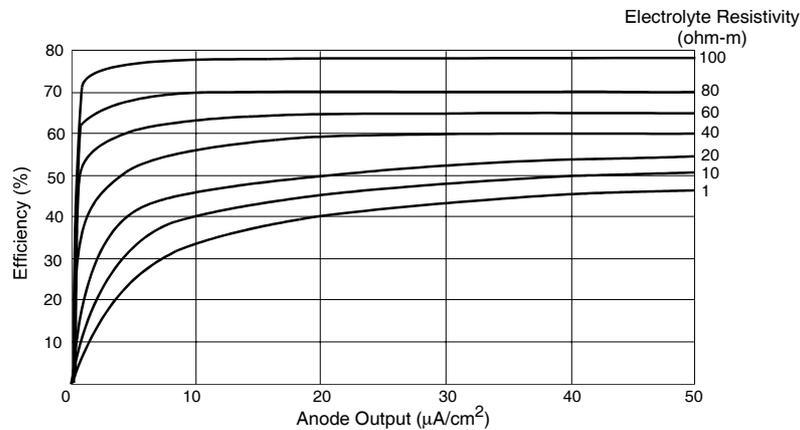

Fig. 4. Magnesium Anode Efficiencies vs. Current Density and Electrolyte Resistivity
(redrawn from Ref. [8])

Note that an efficiency of almost 80% is possible if the electrolyte resistivity is 100ohm-m (10,000ohm-cm), but the electrolyte resistivity of the typical gypsum, bentonite, Na_2SO_4 backfill supplied in the packaged anode is about 50ohm-cm (0.5ohm-m). The efficiency at low current densities is improved as the electrolyte resistivity increases, probably due to a lower self-corrosion rate at the higher resistivities. Martin developed an equation for the self-corrosion rate (CR_{self}) as a function of resistivity as follows:

$$CR_{self} = 10^{(-0.305 - 0.0217\,\rho)} \qquad (6)$$

where:

CR_{self} – is self-corrosion rate (kg/m^{2}y), ρ is electrolyte resistivity (ohm-m).

For a backfill resistivity of 50ohm-cm, a self-corrosion rate of 0.4kg/m^{2}y is predicted which equates to about 15mA on a 14.5kg anode.

Martin also found that chloride ions caused pitting attack and reduced efficiency while sulphate ions increased efficiency. The select backfill surrounding prepackaged magnesium anodes has a low resistivity (approximately 50ohm-cm) because it is composed of a high concentration of sulphate ions from ionization of the gypsum (CaSO$_4$) and sodium sulphate (Na$_2$SO$_4$), which together account for about 85% of the backfill. In addition the solubility of MgSO$_4$, the corrosion product formed on magnesium in sodium salt solutions, is high, which promotes corrosion activity.

It is often stated that the select backfill improves the anode efficiency but it can be argued that very low resistivity backfill actually increases the self-corrosion rate, which reduces the anode current capacity. The main advantage of the select backfill is to prevent anode polarization and to improve corrosion uniformity.

7. Anode Chemical Composition Effect

The nominal composition of the standard and high potential magnesium anode alloys were shown in Table 1. Variation in the alloy constituents can affect the anode performance. Impurities such as Si, Fe, Ni, and Cu can significantly affect the electrochemical efficiency as indicated in Figure 5 [9], which contains the results of testing an AZ63 magnesium alloy in a saturated CaSO$_4$ solution at a current density of 38.7μA/cm^2. Manganese beyond 0.4% weight percentage actually improves the efficiency. Small percentage increases in the copper or nickel content can significantly lower the efficiency. At lower anode current densities (i.e. ≤38.7μA/cm^2) the effect is even more severe.
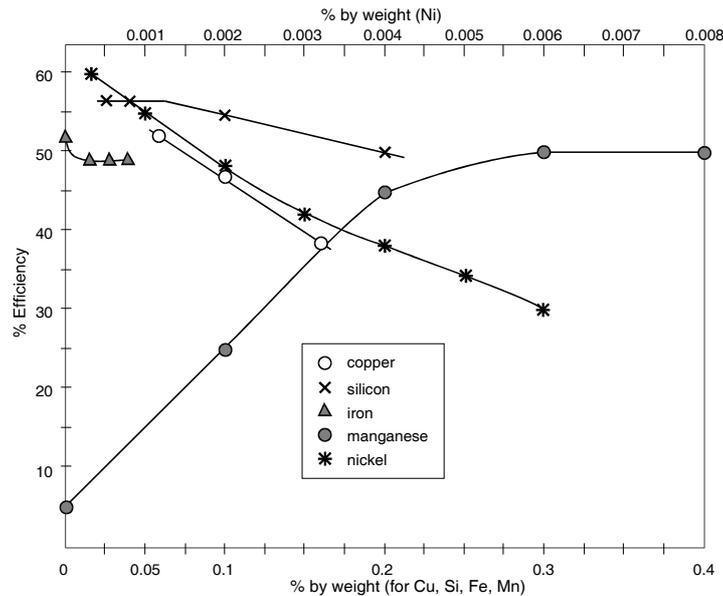

Fig. 5. Effect of Alloying and Impurity Elements on the Efficiency of AZ63 Magnesium Anode @ 38.7μA/cm^2 (36mA/ft^2) Current Density in a Saturated CaSO$_4$ Solution

8. Microstructure

It has been apparent that even when the metallurgical composition is similar and in accordance with the anode material standards, there can still be a wide variation in efficiencies for anodes from different suppliers. Genesca et al [10],[11] found that the microstructure (i.e. grain size and impurity solubility) was an efficiency factor. They found that, by heat treating a commercial anode alloy, the current efficiency could be increased by as much as 40% above the as-cast efficiency as shown in Figure 6.

When heated to 300ºC, water-cooled, and aged at 150ºC for 8 hours, a current efficiency of 64% was obtained. Microanalysis of the treated specimen indicated that the microstructure was finer grained (5-10μm versus 100μm for the cast magnesium) with very fine precipitates distributed in the matrix. This produced more general corrosion as opposed to pitting corrosion.
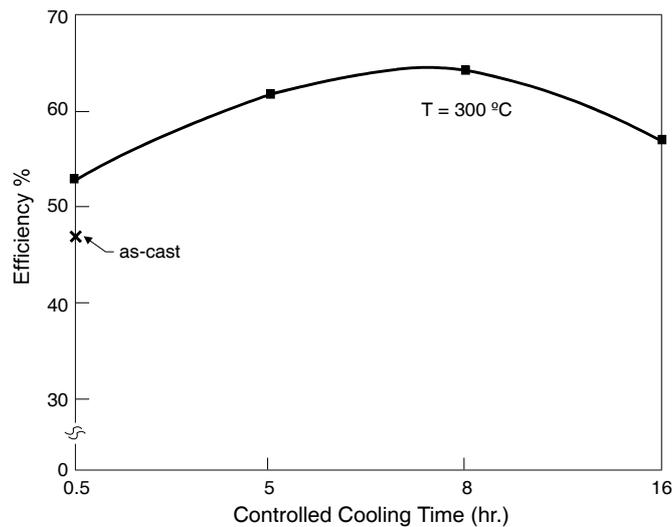

Fig. 6. Magnesium Current Efficiency as a Function of Treatment Time After Reheating at 300ºC
(redrawn from Ref. [10],[11])

9. Overprotection Implications on Material Efficiency

Magnesium anodes, because of their high driving voltage, can polarize well coated pipelines to potentials much more negative than -1000Vcse. Once the polarized potential encounters the hydrogen line an increase of 100mV requires about 10 times as much current as shown in Figure 7 [11].

When the polarized potential reaches about -1000mVcse, water molecules in the vicinity of cathode are hydrolyzed in the following reduction reaction.

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \qquad (7)$$

This is, of course, a waste of anode current, since there is no cathodic protection benefit in polarizing to a potential more negative than -1000mVcse. The result is a substantially reduced material efficiency, especially when the best electrochemical efficiency that can be

achieved is 50%. If the anode produces 10 times more current than is needed then the material efficiency is reduced to 5%. Zinc anodes would not have this problem because of their nominal potential of -1100mVcse.
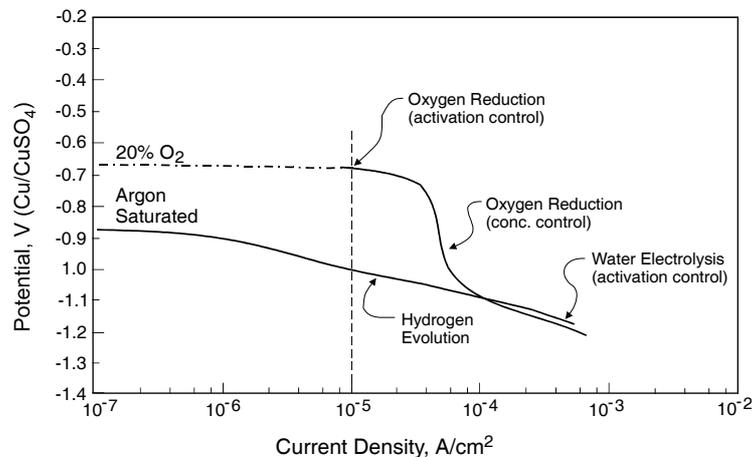

Fig. 7. Polarization Curves in Aerated and Deaerated Solutions of pH7

Adjustable resistors could be used to reduce the anode output current to maintain a -1000mVcse polarized potential but this would also reduce the anode current density and the 50% efficiency would still not be obtained.

10. Conclusions

The electrochemical efficiency of magnesium anodes, typically used to cathodically protect pipelines is compromised by a number of factors.

The anticipated maximum electrochemical efficiency of 50-60% of theoretical, which is significantly lower than for either zinc or aluminum sacrificial anodes, may be due to a combination of the formation of a monovalent rather than divalent magnesium ion and to a lesser extent by a 'chunk' effect.

Even if anodes tested in accordance with the ASTM G97-89 method show 50-60% efficiency, their actual efficiency will drop dramatically if the output current density decreases below about $20\mu A/cm^2$. This is primarily due to the increasing significance of the self-corrosion current as the current output diminishes.

The current efficiencies of high potential magnesium anodes are also affected by the chemical composition of the alloy. Weight percentages of Fe, Cu, Si and Ni, above the maximum values stipulated in ASTM B843-93, can reduce anode efficiencies. However, even when the chemical composition meets the ASTM specification, the efficiency can still be low as a result of a coarse microstructure.

Because of the substantial variation in current efficiency at various times among anode suppliers, the consumer should continually have anode samples tested for alloy composition, microstructure, and backfill composition. Not only will this ensure that the anode suppliers

maintain a high quality product but will aid in the calculation of a more accurate anode service life.

Magnesium anode efficiency could be improved by changing the select backfill to obtain a higher resistivity but this would require considerable testing to determine the optimum backfill composition.

For protecting many well coated and electrically isolated pipe lines, zinc anodes would be a much better choice than magnesium from a material efficiency point of view.

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