

Performance Efficiency of High-Potential Mg Anodes for Cathodically Protecting Iron Water Mains

R.A. GUMMOW, *CORRENG Consulting Service, Inc.*

The service life of Mg anode cathodic protection systems installed on iron water mains has, in some instances, been significantly less than design calculations would predict. Testing of high-potential Mg alloys from various suppliers using the ASTM G97-89 test method indicates that efficiencies are widely variable and that the life of a Mg anode could be as much as 90% less than calculated, depending on the source of the Mg. 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. Municipalities are advised to conduct tests for alloy composition, microstructure, and backfill composition on anodes from industry suppliers in order to ensure anode quality and maximum system life.

Hundreds of kilometers of iron water distribution piping are cathodically protected annually in Canada with high-potential Mg anodes installed by the Auginode method that was developed in the mid-1970s.¹ This technique involves augering a hole above the water line to expose its surface. The line is then cleaned prior to stud-welding the anode lead to the pipe (Figure 1).

The installed anode usually is a 14.5-kg (32-lb) high-potential Mg anode casting surrounded by a sulfate-rich backfill, all of which is contained in a wettable cardboard tube. At typical current outputs of 45 to 90 mA, the service life is calculated to be from 34 to 17 years, respectively, at a utilization factor of 0.85 and a nominal efficiency of 50% of the Faraday calculated capacity. This current output range corresponds to a soil resistivity range of 2,000 to 4,000 Ω -cm. Unfortunately, in many instances the actual service life—as determined by measuring the pipe-to-soil potential profile over the piping route—has indicated a lesser system life than was anticipated. In one instance the efficiency of commercial Mg anodes was reported as being 30 to 35%.² There can be many reasons for the shortfall between calculated life (based on a 50% efficiency) and realized life, even though the anode current outputs are within the nominal range.

Faraday's Law and Calculating Efficiency

The electrochemical efficiency of Mg typically is assumed to be ~50% of theoretical, which is considerably less than the 85 to 90% for Zn and Al galvanic anodes. The theoretical weight loss is calculated using the following Faraday relationship:

$$W = M t I_{\text{corr}}/nF \quad (1)$$

where W = anode weight loss (g), M = atomic weight of the metal (24.3 g for Mg), n = number of electrons given up by an atom in the oxidation reaction ($n = 2$ for Mg), F = Faraday's constant of 96,500 coulombs per equivalent weight, t = time (s), and I_{corr} = corrosion current (A).

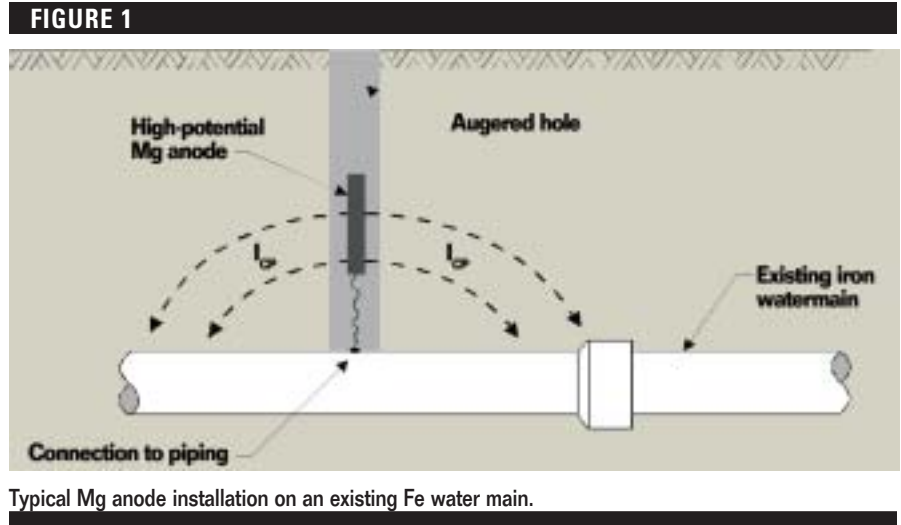
The percent efficiency on a weight basis is determined by comparing the theoretical weight loss from Faraday's equation to the actual weight loss:

$$\% \text{ Efficiency} = W_{\text{theoretical}}/W_{\text{actual}} \times 100 \quad (2)$$

Efficiency Testing

The efficiency of Mg anodes usually is determined using the ASTM G97-89³ test method, which involves cutting and machining five 12.7-by-152-mm specimens from an anode casting. The specimens are placed in separate containers with a calcium sulfate (CaSO_4)/Mg hydroxide [$\text{Mg}(\text{OH})_2$] electrolyte, connected in series with coulometers and powered at a constant current density (CD) of $42 \mu\text{A}/\text{cm}^2$ ($39 \text{ mA}/\text{ft}^2$) 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 potentials also are measured at the end of the test period. Table 1 tabulates typical results obtained by various laboratories for high-potential Mg anodes.

The variation in electrochemical efficiency among these tests is quite significant, ranging from 4.8 to 57.7%. Test results for anode suppliers K to O were obtained in 2003 because of concerns about the quality of Mg from offshore sources. It is apparent from the foregoing statements that the life of a Mg anode system, compared to that calculated at 50% efficiency, could be reduced by as much as 90% depending on the anode supplier. It is interesting to note that the open-circuit potential generally becomes increasingly electronegative as the efficiency increases. The reason for the efficiency variation and the relatively low effi-



Typical Mg anode installation on an existing Fe water main.

TABLE 1

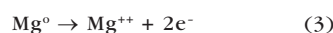
TYPICAL RESULTS FROM ASTM G97-89 TESTING ON HIGH-POTENTIAL Mg ANODES

Anode Supplier	Avg. Efficiency (%)	Avg. Open-Circuit Potential (V_{SCE})	Life vs Calculated @ 50% Efficiency (%)	Ref.
A	51.5	-1.72	+3	4
B	57.7	-1.77	+15.4	4
C	22.9	-1.58	-54.2	4
D	37.7	-1.52	-24.6	2
E	56.6	-1.78	+13.2	5
F	45.7	-1.69	-8.6	6
G	17.0	-1.64	-68.0	7
H	11.2	-1.62	-77.6	7
I	39.1	-1.69	-21.8	8
J	52.2	-1.72	+4.4	8
K	49.3	-1.67	-1.4	9
L	41.6	-1.65	-16.8	9
M	12.1	-1.55	-75.8	9
N	11.0	-1.55	-78.0	9
O	4.8	-1.53	-90.4	9

ciency compared to the theoretical value is not well understood—probably because of the large number of factors that can affect the efficiency.

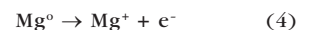
Electrochemical Dissolution of Mg

It has generally been considered that Mg corrodes according to the following equation:



There is some evidence, however, that the electrochemical dissolution of

Mg can produce an intermediate monovalent Mg ion (Mg^+) according to the following reaction:



Recent research by Song, et al.,¹⁰ has concluded that, in sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) solutions, Mg is initially oxidized to an intermediate species (Mg^+). Then, the monovalent Mg ion chemically reacts with water to produce hydrogen and Mg^{++} according to the following reaction:

FIGURE 2



14.5-kg high Mg casting reclaimed from a water main cathodic protection system.

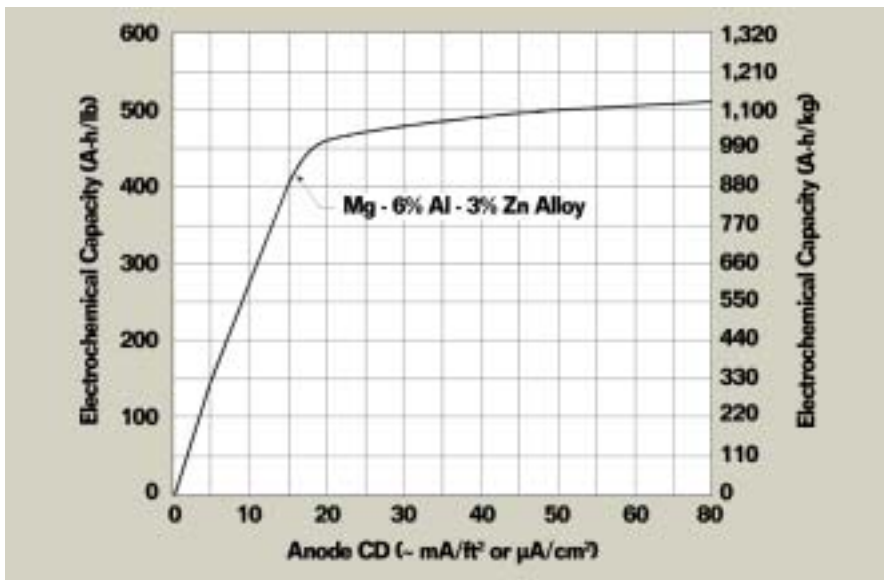
dency of Mg to corrode along the grain boundary, a Fe-Mn-rich impurity phase that is cathodic to the Mg grain. This causes the grain to separate from the parent Mg. Typically, Mg corrodes to produce a severely pitted appearance; Figure 2 is a photo of a typical 14.5-kg (32-lb) Mg casting reclaimed from a water main cathodic protection system ~1 year after installation.

Anode CD

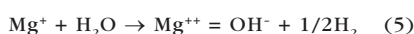
As with any anode, the consumption rate—and therefore its electrochemical capacity—is a function of the anode CD. Figure 3 compares the electrochemical capacity for an AZ63 Mg anode alloy with anode CD in a gypsum/ Na_2SO_4 backfill as determined by Robinson.¹² This indicates that the electrochemical capacity falls off dramatically as the anode CD approaches zero; this phenomenon is attributed primarily to the increasing significance of self-corrosion current as the CD decreases, especially below $\sim 20 \mu\text{A}/\text{cm}^2$ ($20 \text{ mA}/\text{ft}^2$).

The 50% efficiency typically used in system life calculations translates into an electrochemical capacity of 1,100 A-h/kg (500 A-h/lb), which is justifiable if the anode CD is $50 \mu\text{A}/\text{cm}^2$ ($50 \text{ mA}/\text{ft}^2$) or more. Yet the average CD range on a 14.5-kg anode, at an average current output of 45 to 90 mA, is 14 to $28 \mu\text{A}/\text{cm}^2$ (14 to $28 \text{ mA}/\text{ft}^2$), respectively, resulting in corresponding current capacities of 847 to 1,045 A-h/kg (385 to 475 A-h/lb). Thus, a calculated life based on 1,100 A-h/kg (500 A-h/lb) is overly optimistic and leads to a longer calculated life than should be expected.

FIGURE 3



Electrochemical capacity of AZ63 Mg alloy vs anode CD. (Redrawn from Reference 11.)



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 re-

quired to produce an equivalent current. Antonyraj and Augustin¹¹ attributed the low faradic efficiency of Mg to a combination of the formation of a monovalent Mg and the “chunk” effect. The “chunk” effect refers to the ten-

Electrolyte Resistivity and Anode Backfill

Martin¹³ conducted efficiency tests on AZ63 Mg anodes in mixtures of sand, NaCl, Na_2SO_4 , and biocarbonates of varying resistivity. He demonstrated that the efficiency was a function of both CD and resistivity (Figure 4).

Note that an efficiency of nearly 80% is possible if the electrolyte resistivity is 100 Ω-m (10,000 Ω-cm), but the electrolyte resistivity of the typical gypsum, bentonite, Na₂SO₄ backfill supplied in the packaged anode is ~50 Ω-cm (0.5 Ω-m). The efficiency at low CDs is improved as the electrolyte resistivity increases, probably because of a lower self-corrosion rate at the higher resistivities. Martin developed the following formula to determine the self-corrosion rate (CR_{self}) as a function of resistivity:

$$CR_{self} = 10^{(-0.305 - 0.0217 p)} \quad (6)$$

where CR_{self} = self-corrosion rate (kg/m²/y) and p = electrolyte resistivity (Ω-m).

For a backfill resistivity of 50 Ω-cm, a self-corrosion rate of 0.4 kg/m²/y is predicted, equating to ~15 mA on a 14.5-kg anode.

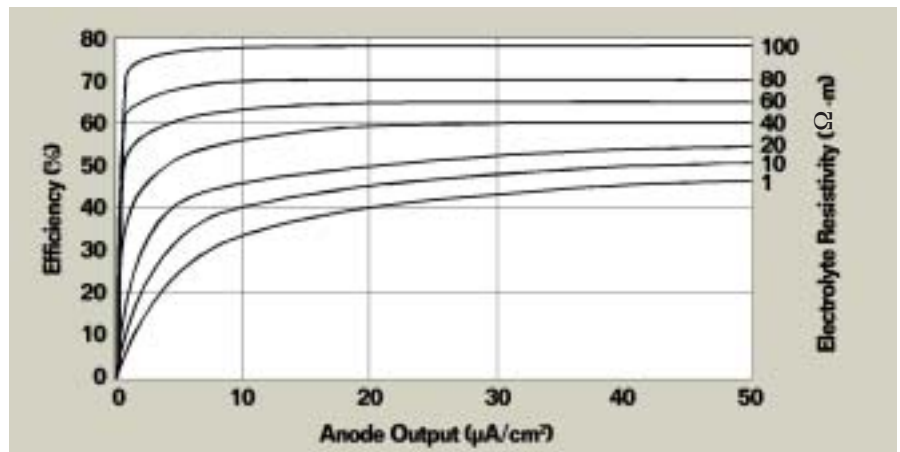
Martin also found that chloride ions caused pitting attack and reduced efficiency while sulfate ions increased efficiency. Even though the select backfill surrounding prepackaged Mg anodes has a low resistivity (~50 Ω-cm), it improves efficiency because it is composed of a high concentration of sulfate ions from ionization of the gypsum (CaSO₄) and Na₂SO₄, which together account for ~85% of the backfill. In addition, the solubility of MgSO₄—the corrosion film formed on Mg in sodium salt solutions—is high, which promotes corrosion activity.

Anode Chemical Composition

According to ASTM B843-93,¹⁴ the nominal composition of a high-potential Mg alloy anode (M1C [UNS M15102]) by weight percentage is:

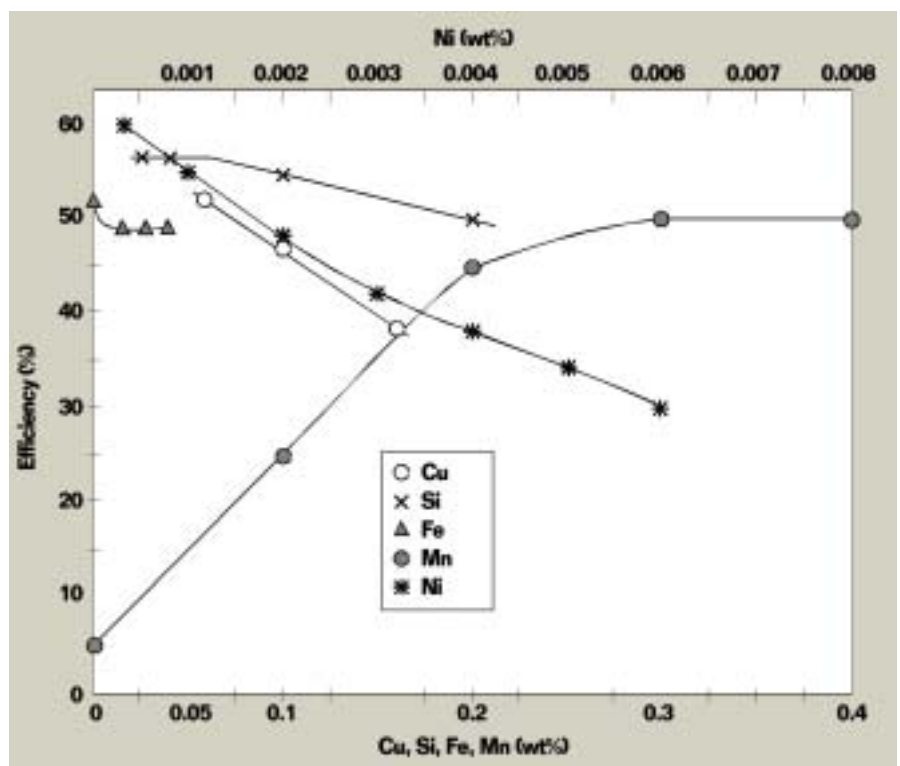
Al	0.01 max.
Mn	0.5 to 1.3
Si	0.05 max.
Fe	0.03 max.
Ni	0.001 max.
Cu	0.02 max.
Other, each	0.05 max.
Other, total	0.03 max.
Mg	Remainder

FIGURE 4



Mg anode efficiencies vs CD and electrolyte resistivity. (Redrawn from Reference 12.)

FIGURE 5

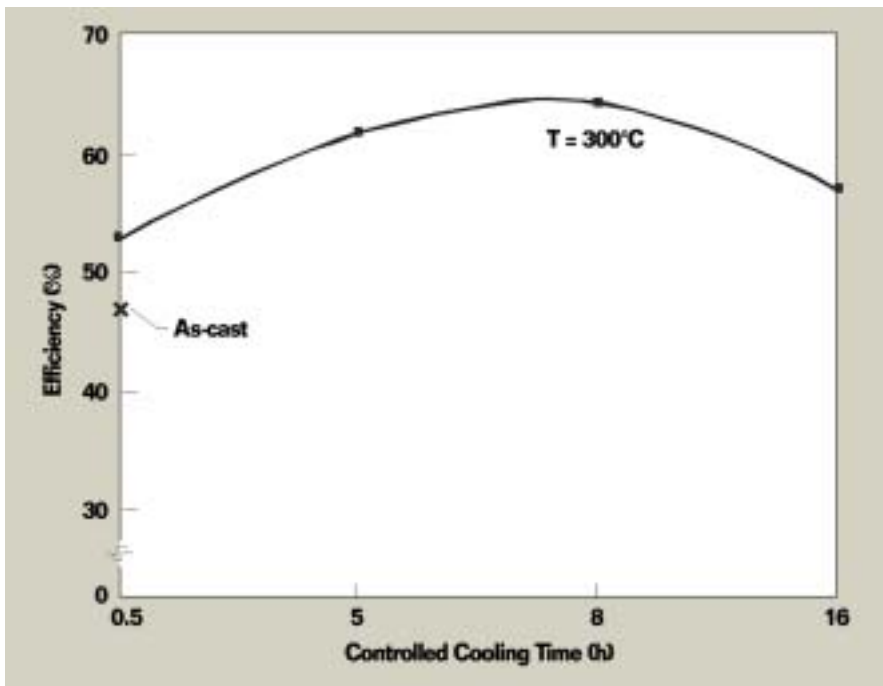


Effect of alloying and impurity elements on the efficiency of AZ63 Mg anode @ 38.7 μA/cm² (36 mA/ft²) CD in a saturated CaSO₄ solution.

Impurities such as Si, Fe, Ni, and Cu can significantly affect the electrochemical efficiency as indicated in Figure 5, which shows the results of testing an AZ63 Mg alloy in a saturated

CaSO₄ solution at a CD of 38.7 μA/cm² (36 mA/ft²).¹⁵ Mn beyond 0.4 wt% actually improves the efficiency. Small percentage increases in the Cu or Ni content can significantly lower the ef-

FIGURE 6



Mg current efficiency as a function of treatment time after reheating at 300°C. (Redrawn from Reference 12.)

efficiency. At lower anode CD's (i.e., $\leq 38.7 \mu\text{A}/\text{cm}^2$ [$\leq 36 \text{ mA}/\text{ft}^2$]), the effect is even more severe.

Microstructure

It has been apparent that even when the metallurgical composition is similar and in accordance with the anode material standards, there still can be a wide variation in efficiencies for anodes from different suppliers. Jurez-Islas, et al.,² claimed that the presence of Mn-rich particles (which are cathodic to Mg) at the grain boundaries were responsible for anode inefficiency. Genesca, et al.,¹⁶ 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 300°C, water-cooled, and aged at 150°C for 8 h, a current efficiency of 64% was obtained. Microanalysis of the treated specimen indicated that the micro-

structure was finer grained (5 to 10 μm vs 100 μm for the cast Mg) with very fine precipitates distributed in the matrix. This produced more general corrosion as opposed to pitting corrosion.

Conclusions

Results from efficiency tests conducted on Mg anodes using the ASTM G97-89 method indicate that the life expectancy of the anode, calculated on 50% of theoretical basis, can be reduced by as much as 90% depending on the source of the Mg. The electrochemical efficiency of Mg anodes, typically used to cathodically protect iron water mains, is compromised by a number of factors.

The anticipated (design) efficiency in the range of 50 to 60% of theoretical is significantly lower than that of either Zn or Al galvanic anodes. It may be caused by a combination of the formation of a monovalent rather than divalent Mg ion and, to a lesser extent, by a "chunk" effect.

Even if anodes tested in accordance with the ASTM G97-89 method show

50 to 60% efficiency, their actual efficiency will drop dramatically if the output CD decreases below $\sim 20 \mu\text{A}/\text{cm}^2$. This change occurs primarily because the self-corrosion current, estimated at 15 mA, becomes increasingly significant as the current output diminishes. The average CD on the 14.5-kg (32-lb) anode, used in the waterworks industry, is probably less than this value; hence, current efficiencies will be $< 50\%$.

The current efficiencies of high-potential Mg anodes also are 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 efficiency at various times among anode suppliers, the municipal 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 it will aid in the calculation of a more accurate anode service life.

Acknowledgments

The author wishes to thank Dave Raymond of the Regional Municipality of Ottawa-Carleton, Ontario, William Russell of Interprovincial Corrosion Control (Burlington, Ontario), and Terry May of Mesa Products (Tulsa, Oklahoma) for providing some of the efficiency test results reported in this article.

References

1. R.A. Gummow, "Corrosion Control of Municipal Infrastructure Using Cathodic Protection," NACE International Northern Area Eastern Conference (Ottawa, ON: NACE, Oct. 24-27, 1999).
2. J.A. Jurez-Islas, L. Martinez, Llongueras, "Solidification Techniques and Electrochemical Properties of Magnesium Based Anodes," CORROSION/93, paper no. 536 (Houston, TX: NACE, 1993).

3. ASTM G97-89, "Standard Test Method for Laboratory Evaluation of Magnesium Sacrificial Anode Test Specimens for Underground Applications" (West Conshohocken, PA: ASTM, 1989).

4. B. Baldock, S. Qian, Electrochemical Evaluation of the Properties of Magnesium Anodes, NRC Report B-5311.1, Region of Ottawa Carleton, Sept. 16, 1999.

5. S. Dontigny, N. Kadouin, Anode Testing: Magnesium and Zinc, CPI Corrosion Ltée, Project no. 2M03-011-C, City of Ottawa, Apr. 28, 2003.

6. B. Campillo, C. Rodriguez, J. Juarez-Islas, J. Genesca, L. Martinez, "An Improvement of the Anodic Efficiency of Commercial Mg Anodes," CORROSION/96, paper no. 201 (Houston, TX: NACE, 1996), p. 12.

7. Memorandum from Interprovincial Corrosion Control on Chinese Anode Efficiencies, Apr. 29, 1998.

8. Confidential Report by CPI Corrosion, Ltd. To Interprovincial Corrosion Control Co., Ltd., Oct. 7, 2002.

9. T. May, "Magnesium Anodes—A Quality Crisis," NACE International Eastern Conference (Columbus, OH: NACE, Sept. 21-24, 2003).

10. G. Song, A. Atrens, D. St. John, X. Wu, J. Nairn, "The Anodic Dissolution of Magnesium in Chloride and Sulphate Solutions," *Corr. Sci.* 39, 10-11 (1997): p. 2003.

11. A. Antonyraj, C.O. Augustin, "Anomalous Behaviour of Magnesium Anodes in Different Electrolytes at High Concentrations," *Corrosion Reviews*, Special Issue: Corrosion Resistance of Magnesium Alloys, M. Schorr ed., Freund Publishing House, Ltd. 16, 1-2 (1998): p. 136.

12. H.A. Robinson, "Fundamental Characteristics of Magnesium Galvanic Anodes," *Cathodic Protection—A Symposium* (Houston, TX: NACE, 1949).

13. B.A. Martin, "Magnesium Anode Performance," *MP* 26, 8 (1987): p. 16.

14. ASTM B843-93, "Standard Specification for Magnesium Alloy Anodes for Cathodic Protection" (West Conshohocken, PA: ASTM, 1993).

15. H.A. Robinson, P.F. George, "Effect of Alloying and Impurity Elements in Magnesium Alloy Cast Anodes," *Corrosion* 10, 6 (1954): pp. 182-188.

16. J. Genesca, C. Rodriguez, J. Juarez, B. Campillo, L. Martinez, "Assessing and Improving Current Efficiency in Magnesium Base Sacrificial Anodes by Microstructure Control," *Corrosion Reviews*, Special Issue: Corrosion Resistance of Magnesium Alloys, M. Schorr ed., Freund Publishing House, Ltd. 16, 1-2 (1998): pp. 95-125.

This article is based on a paper presented at the NACE Northern Area Western Conference, February 16 to 19, 2004, in Victoria, British Columbia.

R.A. GUMMOW is a consulting corrosion engineer with Correng Consulting Service, Inc., a subsidiary of Corrosion Service Co., Ltd., 369 Rimrock Road, Downsview, ON M3J 3G2, Canada. A NACE-certified Corrosion Specialist, Gummow has more than 40 years of experience in the application of cathodic protection (CP) to a wide variety of structures in many industries. He has a diploma in natural gas technology from Ryerson Polytechnical Institute and a degree in electrical engineering from the University of Toronto. A 41-year member of NACE, he has presented many technical papers and has instructed NACE CP courses for more than 25 years. He received NACE Technical Achievement Awards in 1989 and 1992 and the R.A. Brannon Award in 2004. *MP*