The Selection of Magnesium alloys as Sacrificial Anode for the Cathodic Protection of Underground Steel Structure

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Abstract- *Various characterization 4 type of Mg sacrificial anodes (A,B,C and D from different products) have been conducted such as chemical composition, closed and opened potential, current capacity and efficiency test by galvanostatic method. On the basis of the results, the presence of impurities element gives detrimental effects of electrochemical properties and anode efficiency. The presence of high concentration of impurities for Cu, Fe and Ni have cathodic effect to Mg anode such as anode A and B , where the indication of galvanic corrosion take place in Mg anode. Mg anode A and B were lower current capacities, current efficiencies and consumption rates than Mg anode C and D. Mg anode A and B have a lower performance compared to Mg anode C and D Mg anode A and B are not eligible become a standard sacrificial anodes to protect steel structure in soil.*

Keywords — *Magnesium sacrificial anode, cathodic protection, steel structures, chemical composition, closed potential, current capacity, current efficiency, consumption rate, galvanostatic*

I. INTRODUCTION

Corrosion of industrial metal is one of the major problems that has ever challenged the industrial processess. The destructve attack of a material due to corrosion contribute the main cause of plant shutdown, waste of valuable resources, loss of product, reduction in efficiency, and costly maintenance [1]. Several technique have applied for checking the potency of corrosion. Furthermore, Cathodic protection is one of several techniques that are applied particulary in many industries to reduce corrosion attack. Sacrificial anode cathodic protection is used mainly to protect marine structures, oil pipelines and the other indutrials structures. With this system, electric current is applied by the employment of dissimilar metals with the driving voltage being created by the potential generated between the two metals in the electrolyte [2]. Generally, sacraficial anode which used are zinc (Zn), Aluminium (Al) and magnesium (Mg) with the different properties and applications [3]. One of properties on sacraficial anodes is potential. Those anodes generate negative potential vs reference electrode Ag/AgCl in electrolyt. The more negative potential take places, the more material is active, which folllowing the potential anodes :

- Sacrificial anode of Mg : -1.5 Volts
- Sacrificial anode of Al : -1.1 Volts
- Sacrificial anode of Zn : -1,05 Volts

The high potential difference between sacrificial anoda and protected steel structure contributes the protection of steel structure from corrosion process. The anode of Zn, Al and Mg used for protecting steel structure, which generate a potential difference of -1.60; -1.65 and -2.05 volts vs the reference electode of Ag/AgCl respectively as shown in Figure 1.

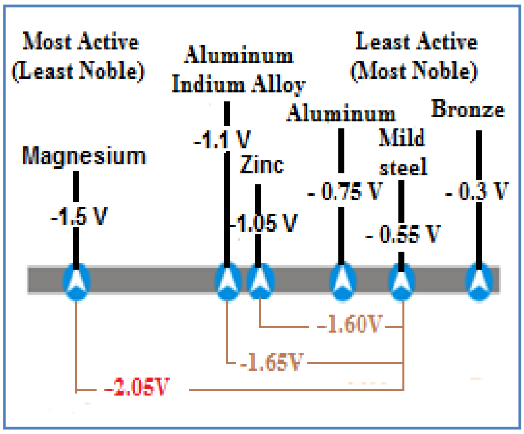


Fig. 1 potential difference between Zn, Al ,and Mg anode and steel structure vs reference electrode of Ag/AgCl [2].

Furthermore, sacrificial anode of magnesium alloy used to minimize corrosion of steel structure in higher resistivity soil because the magnitude of potential difference between Mg anode and steel structure is more higher than that between the other anodes (Zn and Al) and its structure [4-8]. Eventhough, Mg anode has lower current eficiency, generally that anode applied to corrosion protection of steel structure depending on its chemical composition[9]. Moreover, chemical composition of Mg anode can influence to electrochemical properties of anode such as potential, current capacity, current eficiency and consumption rate[9,10]. On the other hand, the effect of Ni, Fe

and Cu as the impurities in anode decrease the level of corrosion protection [11]. These impurities can act as local galvanic cell in matrix which decrease electric open circuit (EOC)[12].
There is corrosion problem of steel structure, even though cathodic protection of Mg anode had been set as corrosion control. This problem occurs due to the high impurities (Fe,Cu and Ni) in Mg anode[13]. The objective of this work is to elucidate the perfomance of Mg alloy anodes with various elements including the impurities element.

II. EXPERIMENTAL

A. *Preparation of specimen*

The specimen of Mg alloy anodes were manufactured (length 11 mm and diameter 1 mm), where they were cut with milling machine as shown in Figure 2.

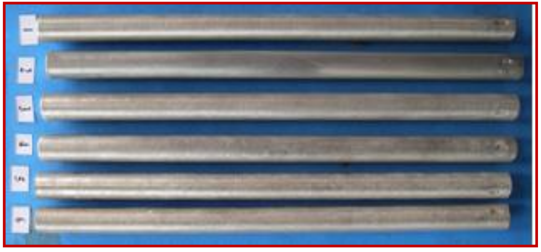


Fig. 2 Sacrificial anode of Mg before experiment.

B. *Preparation of specimen*

Galvanostatic method was carried out to evaluate the properties and perfomance for sacrificial anode of Mg in saturated calcium sulphate and magnesium hydroxide ($CaSO4-Mg[OH]2$) solutions. That solutions used as simulated medium in backfill (75% of gypsum ($CaSO4.2H2O$)- 20% of betonite-5% of sodium sulphate ($Na2SO4$), which applied around Mg anode[14]. The aims of galvanostatic experiment are to calculate closed-circuit current potential, capacity, current efficiency and comsumption rate of anode through impressed current and to ensure the perfomance of anode before installing in the field.
Furthermore, direct current with constant current density of 0.039 mA/cm2 applied in test cell which connected in series as shown in Figure 3. Each test cell consiting of three spesimens of anode had been weighted, where closed potential of specimen measured two times each day in 14 days exposures. Total current-hour (Ah) flows through cell which obtained from copper coulometer cell corresponded to precipitated copper weight (0.843 Ah/g x precipitated copper weight). After that, each specimen cleaned, rinsed with water, dried and weighted. Current capacity of Mg anode (A.h/kg) calculated based on total current-hour (Ah) which flows through cell per unit of weight loss (kg) from each specimen.

Fig. 3 Galvanostatic experiment for anode of Mg

The current capacity assessed by weight loss during the galvanostatic test was evaluated as issued by the ASTM G97 standard [15]. Thus, the actual current capacity of the anodes, CC, is obtained according to the following equation:

$$CC = \frac{Ah}{g} = \frac{Ah}{(M_{Mg_1} - M_{Mg_2})} \times 1000$$

where M_{Mg1} is the initial mass of magnesium anode and M_{Mg2} is the final mass (mass in grams). The theoretical current capacity, evaluated for this alloy, is CC_{Th} = 2.205Ah/g.

The anode efficiency is defined as the ratio between actual and theoretical values of current capacity, and it is evaluated by the following expression:

$$E\% = \frac{CC}{CC_{Th}} \times 100 = \frac{CC}{2.205} \times 100$$

Consumption rate for each anode, in grams per ampere year calculates, using the following equation :

$$\frac{8760}{Current\ capacity\ (Ah/g)}$$

III. RESULT AND DISCUSSION

A. *Chemical composition of Mg sacrificial anode*

The chemical composition for various specimens of sacrificial anode analized by using atomic absorption spectroscopy (AAS) as shown in Table *1*

TABLE I
CHEMICAL COMPOSITION OF VARIOUS MG SACRIFICIAL ANODES

Element	Composition (Wt.%)			
	Type of anode			
	Mg A	Mg B	Mg C	Mg D
Mn	0.303	0.311	0.805	0.594
Al	0.016	0.0001	0.008	0.008
Zn	0.004	0.004	0.073	0.008

Fe	0.021	0.025	0.019	0.001
Cu	0.003	0.002	0.002	0.010
Ni	0.002	0.002	0.009	0.002
Mg	*balance*	*balance*	*balance*	*balance*

Both chemical composition and alloying elements are essential parameters for the perfomance of Mg sacraficial anode, where considered to be controlled the impurities (Fe,Cu and Ni) and main alloying elements (Mn, Zn and Al) contents in Mg anode before applying in the field. Furthermore, the content for impurities elements of Fe and Ni in Mg anode A;B and C were higher than anode D. The presence of impurities gives dentrimental effects of electrochemical properties and anode eficiency. The presences of impurities of Cu, Fe and Ni have cathodic effect to Mg anode, where galvanic corrosion takes place in Mg anode.

On the hand, the content of alloying elements of Al, Zn and Mn in anode A and B were lower than anode C and D. In addition, according to ASTM B 843-07, the content of alloying elements consiting of 5.3-6.7wt.% Al; 2.5-3.5wt.% Zn and 0.15-0.70 wt% Mn, has criteria as a good standard of Mg anode. However, anode A and B has no criteria according to ASTM B843-07, where the perfomance of those anodes indicated to decrease. On anode C and D, the content of Mn is higher than anode A and B, where the presence high content of Mn decreases local galvanic cell on Mg anode. The decrease of that cell contributes to increase the perfomance of Mg anode which show the parameter of current capacity, current eficiency and consumption rate.

B. Potential of Mg anode and The measurement of Total current-hour (Ah)

Closed-circuit anode potential was calculated 2 times a day in 14 days exposure by using voltmeter and Ag/AgCl reference electrode. The result of average closed potential is shown in Table 2.

TABLE III

THE RESULT OF AVERAGE CLOSED POTENTIAL ON VARIOUS MG ANODES

Anode	**Average potential (-V) vs Ag/AgCl**
Mg A	1.59
Mg B	1.58
Mg C	1.58
Mg D	1.54

TABLE IIIII

CHEMICAL COMPOSITION OF MG RAW MATERIAL FOR MAKING MG ANODE[7]

Element	Composition (wt.%) max.
Mg	99.80
Al	0.008
Zn	0.002.
Mn	0.017
Fe	0.003.
Si	0.072
Sn	0.002
Ni	0.001
Ca	0.002
Pb	0.003

The result of average anode potential showed that all Mg anodes have almost the same values. The presence of Mn for all Mg anodes can increase the magnitude of anode potential to become more negative compared to potential of raw material of Mg. The addition of higher content for Mn in anode C and D compared to anode A and B increase more negative anode potential up to -1,7 V which generate higher driving voltage and current to protect steel structure in soil (high soil resistivity : 4000-6000 ohm-cm). In addition, the addition of higher Mn content also fullfill the standard catagory of Mg high potential as shown in Table 4. However, the presence for impurities of Fe and Ni in anode C, and that of Cu in anode D were not able to reach more negative potential (-1.7 V). Therefore, those anodes only used to protect steel structure in soil due to more lower than 4000 ohm-cm.

TABLE IVV

ALLOYING ELEMENT, COMPOSITION AND ELECTROCHEMICAL PROPERTIES FROM STANDARD MG SACRAFICIAL ANODE[16]

Specification/composition (Wt.%)	**Mg standard**	**Mg high potential**
Aluminium (Al)	5,3 – 6,7	0,01 max
Zinc (Zn)	2,5 – 3,5	–
Manganese (Mn)	0,15–0,70	0,50 – 1,3
Silicon (Si)	0,30 max	0,05 max
Copper (Cu)	0,02 max	0,02 max
Iron (Fe)	0,003 max	0,03 max
Nickel (Ni)	0,002 max	0,001 max
Other Impurities	0,30 max	0,30 max
Magnesium (Mg)	remainder	remainder
Efficiency (%)	min. 50	min. 50
Potential vs CSE (Volt)	-1,50	-1,70
Current Capacity (A-hr/kg)	~ 1100	~ 1180
Consumption Rate (kg/A-yr)	7,96	7,96

Electric potential of anode is related to current output of anode, shown in the following expression[17] :

$$I(A) = \frac{E1 - E2}{R}$$

Current output anode (I) is defined as the potential difference between potential of Mg sacraficial anode (E1) and potential of steel protection (E2) vs Ag/AgCl (E2 = -0.850 V) which devided by resistance (R) of Mg anode. The less negative potential take places on Mg anode, the lower current output produced from Mg anode. Therefore, that anode is difficult to polarize steel structure, where protection potential can not be obtained. On the other hand, the essential requirement of Mg anode has to polarize steel structure, which certain potential is more negative than -850 mV vs reference electrode Ag/AgCl, thus corrosion on steel structure decreases significantly. The minimum potential of Mg anode which polarizes steel structure up to potential of -850 mV is -1.5 V. Therefore, potential of Mg anode can suppresses potential of steel structure which protected until reaching minimum protection potential .

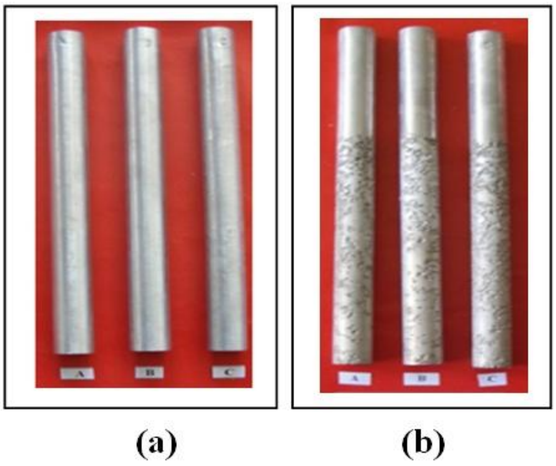
Total current-hour (Ah) which flows through cell, obtained from copper coulometer cell according to the number precipitated copper weight from cathode of copper rod as shown in Table 5.

TABLE V
TOTAL AVERAGE CURRENT-HOUR (AH) OF MG ANODE

Sample	Cathode weight of Cu (g)			Amp - hour (A.h)
	Before (M1)	After (M2)	(M2-M1)	
Mg A	3,1965	3,8149	0,6178	0,52
Mg B	3,0274	3,6421	0,5184	0,52
Mg C	7,8627	8,4926	0,6299	0,53
Mg D	8,7089	9,3110	0,6021	0,51

C. Visual observation of Mg anode

Visual observation on various specimens of Mg anode after exposure of 14 days through galvanostatic test showed that all specimen surfaces coated by white corrosion product from $Mg(OH)_2$ compound as shown in Figure 4.



(a) (b)

Fig.4 Mg Anode before (a) and after (b) experiment

D. Capacity and curret efieciency, and comsuption rate of Mg anode

On the basis of result, current capacities of A anode and B anode were lower than those of C anode and D anode as shown in Table 6. Furthermore, capacity of anode is more lower then teoritical Faraday capacity. According to the faraday law, 1 gram equivalent of metal is 96500 C [19]. From that law, teoritical capacity of Mg anode can calculate (1 Kg = 2205 Ah). It showed that 1 Kg of Mg anode dissolved electrochemically and all charges or currents flowed into protected steel structure, thus 1 Kg of Mg anode release 2205 electrons to that structure. Current capacity of anode is related to current output and consumed weight loss of anode. The lower current output of anode is released or the higher anode is comsumed, the lower the magnitude of current capacity take places. In previous description, current capacity of Mg anode depends on the amount of Fe, Ni and Cu as impurities elements and that of Al,Zn and Mn as alloying elements. In addition, the higher content of impurities element and the lower content of alloying elements take places in Mg anode, the lower current capacity released from anode.

TABLE VI
CAPACITY, CURRENT CAPACITY AND CONSUMPTION RATE OF VARIOUS MG ANODE

Anode	Current capacity (A.h/kg)	Current efciency (%)	Consumption rate (kg/A.y)
Mg A	353.4	16.02	25.72
Mg B	321.8	14.60	29.55
Mg C	1,155	52.36	7.61
Mg D	1,099	50.00	7.97

On the other hand, in Table 6, current eficiencies of A anode and B anode were lower than those C anode and D anode. In addition, current eficieny is defined as the percentage of ratio between efective current capacity and teoritical current capacity. The lower efective current capacity occurs in Mg anode, the lower current eficiency produced from anode. Moreover, current efficiency of anode depend on the amount of alloying and impurities elements. The higher impurities elements and the lower alloying elements occur in Mg anode, the lower current eficiency takes place in anode.

Furthermore, in Table 6, consumption rates of A anode and B anode were higher than those of C anode and D anode, which calculated in equation 3. Consumption rate is related to capacity and current efficiency. The lower current capacity and current eficiency take place in Mg anode, the higher consumption rate occurs in anode. Therefore the number of Mg anode per unit weight is higher to protect steel structure. On the other hand, consumption rate also is affected by impurities element such as Fe, Ni and Cu and alloying elements such as Al, Zn and Mn. The higher impurities element and the lower alloying elements occur in anode, the higher magnitude of consumption rate take places.

IV. CONCLUSION

The perfomance of magnesium alloys as sacraficial anode for the cathodic protection of underground steel structure has been evaluated and studied . The following things were obtained.

1. The presence of impurities gives dentrimental effects of electrochemical properties and anode eficiency. The presence of high impurities of Cu, Fe and Ni have cathodic effect to Mg anode such as anode A and B , where the indication of galvanic corrosion take place in Mg anode.
2. Mg anode A and B were lower current capacities, current eficiencies and consumption rates than Mg anode C and D.
3. Mg anode A and B have a lower perfomance compared to Mg anode C and D
4. Mg anode A and B are not eligible become a standard sacraficial anodes to protect steel structure in soil.

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