한국부식학회지
J. Corros. Sci. Soc. of Korea
Vol. 29 No. 4. August, 2000
<연구논문>

흡수식 냉방기 설비용 금속 소재에 대한 유기계 및 무기계 부식 억제제의 복합 효과에 대한 평가

백 광 기 · 안 명 호
현대중공업 산업기술연구소

Evaluation of Combined Effect of Organic and Inorganic Inhibitors on The Metals used in Absorption Chiller System

Kwang-Ki Baek · Myung-Ho Ahn
1 Cheonha-Dong, Hyundi Heavy Industries Co., Ltd., Ulsan, KOREA 682-792

To develop "environment-friendly" inhibitors for the metals used in the absorption chiller system, inhibition efficiencies of six different combinations of inhibitors were evaluated in 64wt.%LiBr solution at 160oC. Double and triple combinations of inhibitors, such as lithium molybdate (Li_2MoO_4, inorganic), lithium hydroxide (LiOH, inorganic), and benzotriazole (BTA, organic) were evaluated for their efficiencies in corrosion inhibition of copper and mild steel.

Results from weight-loss tests showed that the double inhibitor combinations were less effective for copper than for mild steel, whereas the triple inhibitor combination of 0.2wt.% LiOH+0.02wt.%Li_2MoO_4+0.05wt.%BTA was most effective and it showed much better performance than any other double inhibitor combinations including the commercial products. This formula, of which inhibition efficiency was predicted to be about 83% for copper and 96% for mild steel, can replace the commercial grade inhibitors containing Lithium Chromate (Li_2CrO_4).

Keywords : Corrosion inhibitor, LiBr solution, Lithium Hydroxide(LiOH), Lithium molybdate (Li_2MoO_4), Lithium Chromate(Li_2CrO_4)

1. Introduction

In the absorption chiller system, a concentrated lithium bromide (LiBr) solution is used as the absorption fluid, of which concentration approaches up to 65%. The metallic components of the system, such as copper and mild steel, are subjected to severe corrosion under LiBr environment if proper corrosion inhibitor(s) is not employed in the system. The corrosion products usually reduce the thermal transfer efficiency of the metallic components, thus cause a poor performance of the system. A corrosion inhibitor is a chemical substance of various origin, of which addition to an environment usually resulted in effective prevention of the corrosion reaction of the metal.

In the absorption chiller system, various inorganic inhibitors, such as chromate, molybdate, nitrate, phosphate, have been used. In some case, organic inhibitors, such as citrate, urea, BTA and its derivatives, have also been tried and used [1-2]. Current industry standard for usage of inhibitors in the absorption chiller system is a mixture of lithium chromate (Li_2CrO_4) and lithium hydroxide (LiOH) [1], whereas the organic inhibitors, such as BTA, were later proposed for the same application [2]. However, there are only a few studies on the synergistic effect of applying two or three different inhibitors at the same time [3-7]. This kind of approach is especially needed considering the current trends to restrict or prohibit usage of Li_2CrO_4 due to its toxic nature, which have propelled the need for the utility industries to come up with the more environmentally-acceptable inhibitors for the absorption chiller system.

In this study, therefore, the conventional weight-loss measurements were used to study the inhibition effectiveness of lithium molybdate (Li_2MoO_4), LiOH, and BTA, either separately or in combinations since both Li_2MoO_4 and BTA are far environmentally benign compared to Li_2CrO_4. The objective of this work was to investigate systematically the ability of 6 different combinations of inhibitors (Li_2MoO_4, LiOH, and BTA) to suppress corrosion of common metallic components of absorption chiller systems, thus to find the optimized combination of these inhibitors which are more environmentally friendly than the current standard.

2. Experimental Procedure

64wt.%LiBr solutions were prepared with high-purity water, and all inhibitors were commercial grade reagents which were used without further purification. Each flask heated by an electric mantle contained around 1,000 c.c. of 64wt.%LiBr solution, and a condenser was used to prevent loss of water vapor.

Copper and mild steel, which are the common metallic components of most absorption chiller systems, were used as test coupons. They were prepared from mild steel of composition (wt.%) : 0.12%C, 0.65%Mn, 0.07%Si, 0.010%P, and 0.012%S ; and copper (99.9wt.%). All test coupons were prepared in tube form with the length of 40mm, thickness of 6mm. To determine the corrosion efficiency of each inhibitor combination, three coupons were tested separately for each condition after allowing the (stationary) coupons to corrode in the boiling 64wt.%LiBr solution at 160℃ for 200 hours. Prior to each experiment, the test coupons were degreased and rinsed by acetone, then dried and weighed before being immersed in the test solution. Microbalance was used to measure the weight of each coupon up to 0.1mg range. No attempt was made to remove the air-formed oxide film that may have existed on the metal surface prior to immersion. After boiling tests, corrosion products on each coupon was removed by using HCl solution for 5 minutes, followed by water and acetone rinsing and drying. Then, each coupon was reweighed for evaluation of the corrosion rate.

3. Results and Discussion

3.1 Selection of Inhibitor Combination

Based on previous potentiodynamic polarization experiments by the authors [3] and others [4-6], the presence of LiOH, Li_2MoO_4 and BTA, either individually or in different combinations made the corrosion potential of mild steel move in the noble direction, and better

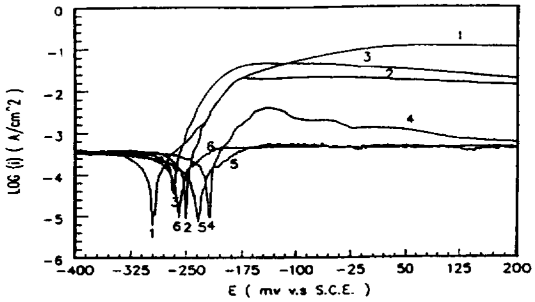

Fig. 1. Anodic polarization curves of mild steel in LiBr solution with or without various inhibitors [3] (1 : Blank, 2 : Li2CrO4 only, 3 : BTA only, 4 : LiOH only, 5 : BTA + LiOH + Li2CrO4, 6 : LiOH + Li2CrO4)

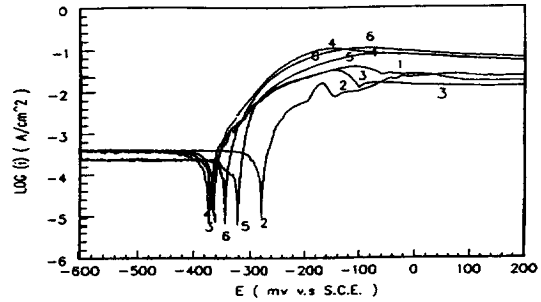

Fig. 2. Anodic polarization curves of copper in LiBr solution with or without various inhibitors [3] (1 : Blank, 2 : Li2CrO4 only, 3 : BTA only, 4 : LiOH only, 5 : BTA + LiOH + Li2CrO4, 6 : LiOH + Li2CrO4)

passive regions were observed with addition of corrosion inhibitors. The result, as shown in Fig. 1, suggested that the LiOH, which controls the pH of the solution, had positive effect on the corrosion inhibition of mild steel, whereas the addition of the Li_2CrO_4 (which will electrochemically behave like Li_2MoO_4), and BTA to the LiOH as an anodic and absorbent type inhibitor, respectively, even more improved the corrosion inhibition [3,4]. These results suggested that the some combinations of LiOH, Li_2MoO_4, and BTA would provide a good corrosion inhibition for mild steel.

In case of copper, however, either single or double combination of above three inhibitors were less effective than the triple combination regarding the degree of corrosion potential movement toward noble direction (Fig. 2), even though the current density of the single or double combination is slightly lower than the triple combination. Thus, the addition of Li_2MoO_4 and BTA to LiOH is probably more effective in terms of corrosion inhibition of copper [5-7]. Based on these observations, a total of six different combinations of inhibitors were selected as summarized in Table 1, and were tested. In these combinations, the concentration of LiOH was kept constant at

Table 1. Types and concentration of inhibitor combinations(wt.%)

Type \ Inhibitors	LiOH	Li2MoO4	BTA
A1	0.2	0.1	-
A2	0.2	0.2	-
B1	0.2	-	0.08
B2	0.2	-	0.15
C1	0.2	0.02	0.10
C2	0.2	0.02	0.05

Table 2. Corrosion data of blank test and two commercial inhibitors in 64wt.%LiBr solution (160°C, 200hrs)

Blank Test		Copper	Mild Steel
Weight Loss, mg/dm2		52.6	478.6
Commercial Inhibitor	Nominal Composition of Inhibitor (wt.%)	Weight Loss, mg/dm2 (Inhibition Efficiency, %)	
		Copper	Mild Steel
No.1	0.0057%LiOH+ 0.27%Li2CrO4	27.1 (48.6)	70.2 (85.3)
No.2	0.21%LiOH+ 0.20%Li2MoO4	20.0 (61.9)	52.3 (89.1)

0.2wt.% for all types based on previous observation that either higher or lower than the optimal concentration of LiOH would resulted in a higher corrosion rate due to either gel formation or lower pH of the solution [5-7].

As the reference for evaluation of the effectiveness of these six combinations, three additional corrosion tests were done for the mild steel and copper coupons. They are two tests with commercial inhibitors (No. 1 & 2) and the one without any inhibitor (blank test). The inhibitor efficiency of each case was evaluated by using the following equation :

$$I(\%) = 100 \times (Wo-Wi)/Wo \qquad (1)$$

where Wo and Wi are the average weight change of test coupons immersed in the LiBr solution for 200 hours without any inhibitor and with each mixture of inhibitors, respectvely.

3.2 Double Inhibitors Combination Tests

The effects of double combination of inhibitors ($LiOH/Li_2MoO_4$ and LiOH/BTA) on corrosion inhibition of mild steel are shown in Fig. 3. In case of $LiOH/Li_2MoO_4$, it is clear that Li_2MoO_4 which replacing toxic Li_2CrO_4 is effective for corrosion inhibition in LiBr solution at both low (A1) and high (A2) concentration. This is consistent with other study that corrosion rate of mild steel in LiBr solution reaches minimum at around 0.03wt.% of Li_2MoO_4, and then remained rather constant with increase of the Li_2MoO_4 concentration [5]. This can be attributed to the observation that the molybdates, which are efficient as anodic inhibitors like chromates, can easily form protective films composed of iron oxide containing molybdenum [5].

In case of LiOH/BTA, the corrosion inhibition efficiencies of mild steel were satisfactory

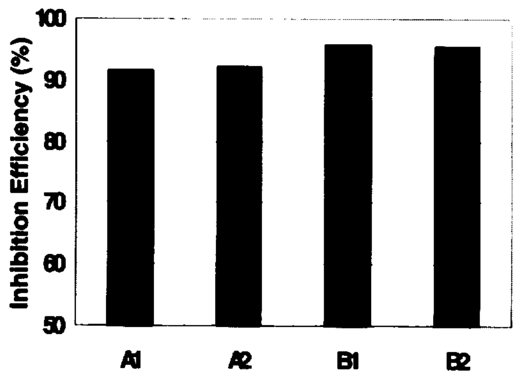

Fig. 3. Inhibition efficiency of double inhibitor combinations for mild steel in LiBr solution

at both low (B1) and high (B2) concentration. This is also consistent with the saturation effect of BTA concentration reported by others that at the concentration higher than around 0.05wt.%BTA, the corrosion rate of mild steel in LiBr solution was almost kept constant by forming passive film of Fe(II)-BTA of dark gray color [2,6].

The effects of double combination of inhibitors ($LiOH/Li_2MoO_4$ and LiOH/BTA) on corrosion inhibition for copper are shown in Fig. 4, indicating generally lower inhibition efficiency than that for mild steel, as expected from the higher passivation current for copper in the anodic polarization curve [3,7]. In case of $LiOH/Li_2MoO_4$, there is a sharp increase in the inhibition efficiency as Li_2MoO_4 concentration increases from 0.1wt.% (A1) to 0.2wt.% (A2). Considering the finding that addition of $LiOH/Li_2MoO_4$ promote the formation of protective, thin Cu_2O film on surface of copper in LiBr solution [5], this result indicates that at least a certain amount of Li_2MoO_4 should be present in the LiBr solution for this type of double inhibitor combination to work efficiently.

For LiOH/BTA combination, on the other hand, the corrosion inhibition efficiencies of

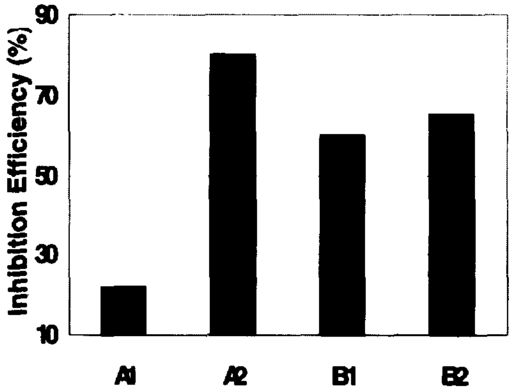

Fig. 4. Inhibition efficiency of double inhibitor combinations for copper in LiBr solution

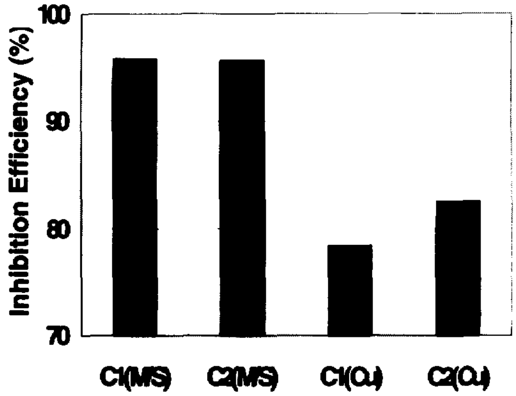

Fig. 5. Inhibition efficiency of triple inhibitor combinations for mild steel and copper in LiBr solution

copper were slightly increased to 65% as theBTA increase from low (B1) to high (B2) concentration. Even though the BTA was known to spread at the surface of copper and to form a protective film consisting of a Cu(I)-BTA polymeric network in the LiBr solution [8], the current concentration level seemed not so effective for the corrosion inhibition of copper. This difference in inhibition efficiency of BTA for mild steel and copper can be explained by the following [7] : BTA seemed to increases film stability by adsorbing on the surface of mild steel due to the existence of empty d-orbitals by a process of electron donation, involving the pair of electrons situated at the nitrogen atoms. By the same token, BTA is not so effective for the corrosion inhibition of copper because there is no empty d-orbitals for copper.

3.3 Triple Inhibitors Combination Tests

The effects of triple combination of inhibitors ($LiOH/Li_2MoO_4$/BTA) on corrosion inhibition of mild steel and copper are shown in Fig. 5. It shows that at a constant concentration of LiOH and Li_2MoO_4, the higher concentration (C2) of BTA yielded a slight increment of corrosion rate of copper when compared with the lower one (C1). However, the overall inhibition efficiencies for both copper and mild steel were satisfactory at both level, and showed much better performance than other double inhibitor combinations including the commercial products (No.1 & No.2) even though one-tenth concentration of Li_2MoO_4 was used for this formula. This means that variations in inhibitor concentrations seems to be less significant within a range of concentration for triple mixture of LiOH, Li_2MoO_4 and BTA, even though further experimental works are required to confirm this argument. This phenomenon, so called as "robustness", is good for this type of inhibitors to be used in the realistic case directly from the laboratory results. Based on these evaluations, the triple inhibitor combination of 0.2wt.%LiOH, 0.02wt.%Li_2MoO_4, 0.05wt.%BTA was proposed, of which inhibition efficiency would be around 83% for copper and 96% for mild steel.

4. Conclusions

The simultaneous addition of organic and inorganic inhibitors has been proved to be effective for corrosion inhibition of copper and mild steel in LiBr solution. Results from the weight-loss tests showed that the double inhibitor combinations were less effective for copper than for mild steel, whereas the triple inhibitor combination of 0.2wt.%LiOH+0.02wt.%Li_2MoO_4+0.05wt.%BTA was most effective and it showed much better performance than any other double inhibitor combinations including the commercial products. This formula, of which inhibition efficiency was predicted to be about 83% for copper and 96% for mild steel, can replace the commercial grade inhibitors containing Lithium Chromate (Li_2CrO_4).

References

1. R. H. Krueger, K. F. Dockus, and W. F. Rush, *ASHRAE Jr.*, 40(2), p. 67 (1964).
2. M. A. Babosa, *Ann. Univ. Ferrara, N.S., Sez. V, Suppl.*, **8**, 613 (1985)
3. M. -H. Ahn and K. -K. Baek, *Hyundai Technical Review*, **15**(2), 36 (1996)
4 M. Itoh, M. Aizawa and K. Tanno, *Boshoku Gijutsu*, **36**, 142 (1987)
5 K. Tanno, S. Saito, M. Itoh and A. Mitano, *Boshoku Gijutsu*, **33**, 504 (1984)
6. M. Itoh, A. Mitano, M. Aizawa and K. Tanno, *Boshoku Gijutsu*, **33**, 516 (1984)
7 T. -C. Wen and S. -M. Lin, *Jr. Chin. I. Ch. E.*, **22**(5), 311 (1991)
8 G. -G. Zhou, Y. Feng and N. Takenori, *Boshoku Gijutsu*, **39**, 361 (1990)