

Absorption technologies materials and coatings corrosion performance under high temperature lithium-bromide environment

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ABSTRACT

The aim of this study is the comparison of the behavior of different AHT construction materials when in contact with the working fluid (LiBr solution, molybdate inhibited) at the Absorption Heat Transformer operating conditions (or as close as possible to them). The corrosion behavior of the usually used metal alloys and those with application of a set of coatings that could improve the corrosion resistance of the tube materials was evaluated by means of Electrochemical Impedance Spectroscopy, EIS. Four different coatings were selected and deposited into the AHT tubes construction materials (Cu and Cu-Ni alloy). Corrosion tests were performed with the samples immersed in a solution of LiBr at a concentration of about 60 wt%, a temperature of 140°C, in an O₂-free atmosphere.

1. INTRODUCTION

The study and use of different absorption technologies employing higher temperatures than those used by single stage absorption chillers has been increasing during the last years. On the one hand, cooling absorption chillers tend to multi-effect cycles, including triple-effect because it is possible to use thermal potential of high temperature sources. On the other hand, absorption heat transformers are a very promising technology for recovering low quality industrial processes' waste heat that today is not being recovered [1]. In addition to these two examples, new cycles are being proposed, such as the hygroscopic cycle, where also high temperatures are employed.

The common working fluid used in the above-mentioned technologies is usually a LiBr solution, which has favorable thermo-physical properties, however it can cause serious corrosion damage in the structural materials. High temperature applications (> 150 °C) require special materials to maintain long life, and this is being one of the main barriers of these technologies to reach the market [2,3]. The commonly used corrosion inhibitors in single-effect chillers are degraded at such high temperatures so they cannot be used in this application. In addition, these corrosion events produce non-condensable gases, "killing" the absorption processes and therefore the performance of the machines.

2. EXPERIMENTAL SETTING AND RESULTS

2.1 Bare materials

The corrosion behavior of the materials has been assessed through Electrochemical Impedance Spectroscopy (EIS) analysis. Tests were performed with the samples immersed in LiBr molybdate inhibited solution at a concentration of about 60 wt%, a temperature of 140°C, in an O₂-free atmosphere (Ar gas was purged in the solution for the purpose). Four construction materials were tested as received: Cu (Cu-DHP EN 1172 CW024A R240), Cu-Ni alloy (Cu90Ni10 alloy), carbon steel (EN 10028-2 P265GH) and stainless steel (EN 1.4571). Bulk materials results showed that the Cu-Ni alloy and stainless steel are the ones with the best corrosion resistance in the working fluid, while Cu is the one with the worst corrosion properties. Carbon steel has also a better performance than expected due to the presence of molybdate in the working fluid.

2.2 Coated materials

Four different coatings based on sol-gel technique were selected and applied to the commonly used Cu and Cu-Ni alloys tubing materials. The main coating characteristics are summarized in Table 1. These coatings have a thickness of a few microns; therefore, they should not cause any heat transfer decrease in the heat exchangers. Nevertheless, other key parameters could be directly affected, such as the wettability of the tubes. Wettability is



Table 1: Coatings selected to improve the corrosion resistance of Cu and Cu-Ni alloy.

Coating	Type	Thickness	Curing Temp.	Curing time
Coating 1 (Tecnalia)	Hybrid: Inorganic part: SiO ₂ -ZrO ₂ Organic part: Acrylic-based	~5 µm	140°C	1 hr
Coating 2 (Tecnalia)	Inorganic: SiO ₂ network	~180 nm	350°C	1 hr
Coating 3 (Tecnalia)	Hybrid: Inorganic part: SiO ₂ -ZrO ₂ Organic part: Epoxy-based	~1,5 µm	180°C	1 hr
Coating 4 (Commercial)	Organic: epoxy-based	~3 µm	120°C	0.5 hr

a very important parameter, as higher wettability allows larger surface area of the heat exchanger to be used, thus optimizing both the heat and mass transfer. Adding a specific coating to the bare copper tubes could evidently change interaction between the LiBr solution and the respective surface, therefore affecting the wettability. This has been studied through wet drop tests performed on the coated samples. In these types of tests, the contact angle of a drop of solution over a flat surface of the tested material is measured. The lower the angle, the better the wettability of the material by the testing solution. The objective is to obtain coatings resistant to corrosion, without reducing the wettability of the substrate material.

The analysis performed on the tubing materials (Cu and Cu-Ni alloy) treated with the selected coatings showed that the corrosion resistance of Cu in LiBr solution increases when treated with Coating 2 (Tecnalia's development) and Coating 4 (Commercial product). In both bases the corrosion properties improve significantly, compared to the bare metal, achieving performance corrosion resistance near to Cu-Ni alloys and Stainless-Steel. Coating 1 (Tecnalia's development) also confers an added value in terms of corrosion performance, but small compared to previous ones. On the other side, the corrosion properties of Cu-Ni alloy in LiBr do not show any improvement when the material is treated with the selected coatings. Even more, in the case of Coating 2, a decrease in the corrosion resistance of the CuNi alloy is noticed: this could be since the high temperature during the curing step of the coating application procedure might affect the microstructure of the CuNi alloy, hence reducing its corrosion properties. All four coatings show improved wettability behavior compared to the bare Cu material, becoming the material more hydrophilic, reducing contact angles in 8.86, 16.93, 21.02 and 28.18% for coatings 4, 3, 2 and 1 respectively.

6. CONCLUSIONS

As a conclusion, the corrosion performance of Cu tubes in high temperature LiBr molybdate inhibited solution, improves considerably after treating the material with SiO₂ and epoxy-based coatings. These two coatings are therefore potential candidates for the further improvement of the corrosion properties of the Cu tubing material for this specific industrial application. Future works analyzing heat and mass transfer improvements related to the expected wettability ratio increase are considered.

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REFERENCES

- [1] R. R. S. A. K. Keith E. Herold, Absorption Chillers and Heat Pumps.
- [2] R. Sánchez-Tovar, M. Montañés and J. García-Antón, "The effect of temperature on the galvanic corrosion of the copper/AISI 304 pair in LiBr solutions under hydrodynamic conditions.," *Corrosion Science*, vol. 52, p. 722–733, 2010.
- [3] S. Jiangzhou and R. Wang, "Experimental research on characteristics of corrosion-resisting nickel alloy tube used in triple-effect LiBr/H₂O absorption chillers," *Applied Thermal Engineering*, vol. 21, pp. 1161-1173, 2001.

