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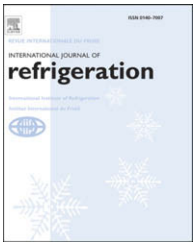

A basis for the development of new ammonia–water–sodium hydroxide absorption chillers

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ABSTRACT

Adding NaOH to ammonia/water improves the separation of ammonia in the generator and reduces both chiller driving temperature and rectification losses. In this paper the main disadvantages for the implementation of these new mixtures are addressed: a) few experimental data or reliable correlations of the fluid mixture properties exist; b) selection of an adequate system for separating the hydroxide; and c) evaluation of potential corrosion problems. Our results show that the separation of NaOH from an ammonia/water solution with a maximum approximate mass fraction of 0.05 (5% weight) is viable when reverse osmosis is used with membranes BW30 and SW30HR LE. Cycle simulation using experimental data to calculate the vapour–liquid equilibrium properties shows that the COP is approximately 20% higher than with a conventional ammonia/water chiller working under the same conditions and using a hydroxyl separation efficiency of 99% for NaOH, which is feasible according to the experimental tests.

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Mots clés : Système à absorption ; Ammoniac-eau ; Enquête ; Amélioration ; Additif ; Hydroxyde ; Sodium ; Simulation ; Performance ; COP

1. Introduction and objectives

Adding hydroxides to the conventional ammonia–water mixture in absorption refrigeration cycles has been proposed as a way to increase efficiency and reduce the driving temperature for ammonia–water refrigeration cycles.

Reiner and Zaltash (1991, 1992, 1993) investigated ternary ammonia–water fluids for absorption cycles in order to

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Nomenclature

E	electrical voltage (V)
i	electrical current density (μA)
J_W	permeate flux or solvent flux (L m^{-2} h^{-1})
K	permeability coefficient characteristic of each membrane (L m^{-2} h^{-1} bar^{-1})
ΔP	transmembrane differential pressure (bar)
$\Delta\pi$	osmotic pressure difference (bar)
R	retention coefficient (%)
Φ	osmotic coefficient (usually 0.93 for brackish water and 0.902 for sea water)
T	temperature (°C)
m_i	molality of all the solution components, ionic or non-ionic components (mole L^{-1})
C_i	concentration of component "i" in the solution (mg L^{-1})
MW_i	molecular weight of component "i"
TDS	total dissolved salts content in the solution (mg L^{-1})
COP	coefficient of performance

identify the best additives for the salting-in of both water and ammonia molecules. Their results show that LiBr, LiCl and $LiNO_3$ increase the boiling temperature relative to the standard binary solution and that LiOH and KOH decrease it. The increase in the boiling temperature is caused by preferential holding-in of the ammonia molecules in the liquid phase. The decrease in the boiling temperature, on the other hand, is caused by the shift in the phase equilibrium towards a more effective separation of ammonia molecules from aqueous solutions (i.e. salting-out). The advantages of these additives therefore derive from the fact that can affect the preferential holding (salting-in) of water and/or ammonia molecules. This leads to a higher concentration of ammonia leaving the generator of ammonia–water absorption systems, thus diminishing rectification losses and allowing the generator to operate efficiently. For low-temperature heat sources (such as solar energy or waste heat), it is highly desirable to significantly reduce the generator temperature with respect to that of conventional ammonia/water refrigeration cycles while retaining benefits such as evaporation at very low temperatures and ambient air heat rejection capability.

Ammonia is highly soluble in water generating NH_4^+ and OH^- ions. Adding sodium hydroxide to the ammonia/water mixture shifts the chemical equilibrium towards a more effective separation of ammonia molecules from the generator aqueous solution (Eqs. (1) and (2)). The hydroxide on dissolution in water produces hydroxyl (OH^-) ions that compete with those produced by the ionisation of the ammonia molecules in water. As ammonia is a much weaker electrolyte than the hydroxide, the resulting "common ion" effect tends to drive the ammonia ionisation equilibria backwards hence salting-out ammonia vapour from the solution.

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \tag{1}$$

$$NaOH \rightarrow Na^+ + OH^- \tag{2}$$

The effect is a reduction in the bubble point of the ternary mixture solution with respect to the conventional binary solution and an increase in COP for a given chiller capacity and operation conditions. The hydroxide increases also the ammonia concentration of the vapour stream, thus reducing the need for rectification. However, the presence of the hydroxyl ion in the absorber negatively affects the performance of the cycle because the common ion effect tends to prevent the absorption of NH_3 molecules by the weak solution. It is therefore necessary to modify the basic ammonia–water cycle with a separation system to retain the hydroxyl ions in the generator section as much as possible.

Thermophysical property data for ammonia–water–NaOH mixtures are very scarce. Brass et al. (2000) presented experimental data on the vapour–liquid equilibrium for temperatures close to the ambient temperature (303–318 K) and from 0.1 to 0.9 MPa. Salavera et al. (2005) presented experimental data at higher temperatures. In this paper we have correlated their vapour–liquid equilibrium data using the Electrolyte-NRTL model and used them to calculate the binary interaction parameters of the ammonia/water/NaOH mixture.

In this paper we present our experimental results using a laboratory-scale reverse osmosis membrane to separate the hydroxide from the weak solution. We also model the absorption cycle to calculate its performance using this separation system and experimental vapour–liquid equilibrium data and explore the use of electrochemical techniques for measuring the potential corrosion rate of the ternary mixture. The model implemented in the Aspen Plus process simulator (www.aspentech.com) has been used to calculate the performance of the refrigeration cycle including the E-NRTL model with experimental parameters rather than the default parameters included in the process simulator, as has been done in previous simulation works that have used these mixtures (Balamuru et al., 2000; Bruno et al., 2005). The main aim of this paper is to set a basis for the future development of ammonia/water/NaOH chillers in order to exploit their advantages over the currently used water/LiBr absorption chillers at low temperature for mainly solar energy and waste heat applications.

In the next section we briefly describe our procedure for calculating the interaction parameters of water/sodium hydroxide and ammonia/sodium hydroxide pairs later used to substitute their default values in the process simulator. We then present the first test of the Reverse Osmosis technique for the separation of the hydroxyl ion from the mixture to reduce its presence in the absorber as much as possible. This information is then used in the following section to model and analyse a proposed configuration for the absorption refrigeration cycle. In the final section we