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# A new method for evaluating heat pipe fluid compatibility

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## HIGHLIGHTS

- A new method for evaluating heat pipe compatibility has been proposed.
- Aluminum/water based fluids are analyzed as a case study using strong oxidizing inhibitors.
- *E*–pH diagrams are generated as a function of temperature creating a "safe-zone".
- Comparison of "safe-zone" to published data shows agreement for two different tests.

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## ABSTRACT

While heat pipes are a widely used and highly efficient means of spreading heat or transferring it from one location to another, there are some fluid-casing combinations which cannot be used due to material incompatibilities. These incompatibilities generally result in the generation of non-condensable gases such as the hydrogen gas produced when water is used with aluminum devices. Some attempts at using inhibitors in aqueous solution are found in literature but a method for screening which inhibitors to use that can also predict and assess the performance of different concentrations is not available. Using a thermodynamic approach, principles of corrosion engineering have been applied to the specific application of phase change heat transfer devices. Experimental data from previous tests has been used to show the *E*–pH diagrams match the reported NCG generation observed experimentally. Using thermodynamic equilibrium diagrams and measurements of heat pipe fluid E and pH can be a valuable tool when investigating passivating fluids for previously incompatible fluid-casing combinations.

## 1. Introduction

Heat pipes are a highly effective means of managing heat generated by electronics and other sources because they are able to transfer heat under near isothermal conditions across the device. Specific applications and implementations are covered extensively in existing literature [1–7]. In a heat pipe, the use of pure water in conjunction with aluminum is an incompatible combination hich will generate hydrogen gas [1]. Hydrogen is a non-condensable gas (NCG) and will build up in the condenser creating a large thermal resistance. This results in catastrophic decreases of the effective thermal performance and often leads quickly to outright failure. Ammonia heat pipes are often used in aluminum casings to avoid NCG generation, however, this has performance drawbacks and care must be taken to ensure only highly anhydrous ammonia is used. Additionally, ammonia heat pipes have a useful range of about −60 to 100 °C while water-based devices typically operate in a range of 30–200 °C [3] and have more favorable thermophysical properties than ammonia. Therefore, the qualification of water-based fluids for use with aluminum would expand the range of operating temperatures for aluminum heat pipes.

Rassamakin et al. [8] looked at aluminum/water thermosiphons and found that a fluid pH of 5–6.5 and select chromate inhibitor concentrations could slow NCG generation. Novotna et al. [9,10] also found success in investigating inhibitors to prevent NCG formation in steel based heat pipes. Other oxidizer-containing aqueous fluids containing chromates and even permanganates have been used with aluminum thermosiphons as well [11–13] with varying success. Terdtoon et al. [14] performed an array of thermosiphon lifetime tests with the goal of studying internal tube corrosion. When disodium hydrogen phosphate was used as an inhibitor it reduced both internal tube corrosion as well as hydrogen generation in iron tubes. However, the researchers found that the aluminum tubes tested with water and any level of additives still produced hydrogen. Terdtoon et al. used tube weight before and after the testing to determine the level of corrosion accumu-

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**Nomenclature**

| Symbol | Quantity (SI unit) |
|---|---|
| $A, B, C, D$ | species placeholders in equilibrium constant equation (dimensionless) |
| $a, b, c, d$ | species coefficients from reaction equation (dimensionless) |
| $a_3$ | species specific constant (J K/mol Pa) |
| $a_4$ | species specific constant (J K/mol) |
| $c_1$ | species specific constant (J/mol K) |
| $c_2$ | species specific constant (J K/mol) |
| $C_p$ | molar specific heat, constant pressure (J/mol K) |
| $E$ | reduction potential (V) |
| $F$ | Faraday's constant (Coulomb/mol) |
| $G$ | molar Gibbs energy (J/mol) |
| $H$ | molar enthalpy (J/mol) |
| $K$ | equilibrium constant (dimensionless) |
| $n$ | number of electrons transferred (dimensionless) |
| $P$ | pressure (Pa) |
| pH | potential of hydrogen (dimensionless) |
| $Q$ | reaction quotient (dimensionless) |
| $R$ | universal gas constant (J/mol K) |
| $S$ | molar entropy (J/mol K) |
| SHE | standard hydrogen reference electrode |
| $T$ | temperature (K) |
| $U$ | molar internal energy (J/mol) |
| $V$ | volume ($m^3$) |
| $X$ | born function ($1/K^2$) |
| $Y$ | born function (1/K) |
| $\Delta$ | change in quantity |
| $\varepsilon$ | dielectric constant, water (dimensionless) |
| $\omega$ | conventional Born coefficient for ionic species (J/mol) |
| $\theta$ | global temperature constant (228 K) |
| $\psi$ | global pressure constant ($2.6 \times 10^7$ Pa) |

*Subscript*

| | |
|---|---|
| $(aq)$ | aqueous phase |
| $f$ | formation |
| $(g)$ | gaseous phase |
| $(l)$ | liquid phase |
| $P$ | constant pressure |
| $r$ | reaction |
| $ref$ | reference quantity |
| $(s)$ | solid phase |
| $T$ | constant temperature |

*Superscript*

| | |
|---|---|
| $^\circ$ | standard conditions, 1 molar concentration solution |

lated over different test lengths and fit the results to an Arrhenius model.

Additional data regarding the fluid potential and pH before and after testing would allow for the calculation of how much oxidizers are consumed and the likely products. This would help other researchers to extrapolate the results for different sized thermosiphons and potentially heat pipes with simple wicks. The action of NCG inhibitors for heat pipes is rooted in the chemical reactions at work, therefore their consideration should be addressed in any work attempting to passivate a particular thermosiphon casing material for use with a typically incompatible fluid. $E$–pH, or Pourbaix diagrams, is one way to determine expected thermodynamic products of a particular metal–water system. These diagrams can also be used to judge the effect of adding inhibitors to solution. Using an aluminum thermosiphon with an aqueous fluid as an example case, a more in depth corrosion and chemical reaction analysis has been used to compliment E and pH measurements taken from past experimental compatibility tests to assess the impact of inhibitors in solution.

## 2. Thermodynamic modeling for heat pipe passivation

### 2.1. Process overview

The prevention of hydrogen gas generation using inhibitors in aluminum heat pipes can be investigated by modeling the thermodynamic stability of a multi-component, aqueous solution. Initial screening using thermodynamics can limit the number of chemicals and range of concentrations tested in aqueous solutions tested for compatibility within a sealed phase change heat transfer device such as a heat pipe or thermosiphon. $E$–pH diagrams are used to predict the most thermodynamically stable species at a given fluid pH and potential when equilibrium has been reached. Both pH and potential are dependent upon the specific chemicals and their concentrations existing in solution as well as temperature. An example of an $E$–pH diagram can be found for a simple water system in Fig. 1.

A highly reducing solution will exist below the bottom diagonal line in Fig. 1 where hydrogen gas will be liberated from ionization of water itself. Hydrogen gas can also be generated via chemical reactions with a metal electrode. This hydrogen evolution can be prevented or diminished substantially by establishing a protective oxide barrier on the metal surface. The favorability of an oxide layer can also be determined via thermodynamics, however, more data may be required to evaluate the protectiveness of that oxide. Fig. 2 shows an $E$–pH diagram which considers such a metal–water equilibrium.

Solutions containing strong oxidizers can move the system equilibrium to more oxidizing conditions where both water and a protective oxide coating are thermodynamically stable and gas generation rates are substantially lowered. By overlaying the $E$–pH diagrams of multiple metal–water systems one can get an idea of the stability of each constituent with respect to the $E$–pH conditions created by the concentration of each in solution.

A Matlab code has been written to generate $E$–pH diagrams, such as Fig. 2, as a function of temperature for select species. Fig. 3 shows such a diagram containing information on the stability of chromium, aluminum, and manganese in an aqueous environment. Labels for each region have been left off of this figure to keep the information contained within it manageable, but it should be noted that each enclosed region represents the most thermodynamically stable form of the metal in an aqueous solution. By measuring the E and pH of a system, one can plot the point on the diagram and determine the thermodynamically favored species for each elemental component.

Typically, the resulting reactions from metals in aqueous solution will release either oxygen or hydrogen gas. For metals with a large immunity region encompassing standard pure water conditions, such as copper, this rate is extremely low and often neglected. However, it is important to note that there is no situation in which a metal electrode in aqueous solution will not liberate either oxygen or hydrogen gas. This applies to copper electrodes as well even though it is commonly considered to be "NCG free" when used with water. In copper phase change heat transfer (PCHT) devices, the corrosion and NCG generation rates

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