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Materials Corrosion in Ammonia/Solid Heat Pump in Working Media

D. F. Wilson
M. Howell
J. H. DeVan

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Metals and Ceramics Division

MATERIALS CORROSION IN AMMONIA/SOLID HEAT PUMP WORKING MEDIA

D. F. Wilson
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MATERIALS CORROSION IN AMMONIA/SOLID HEAT PUMP WORKING MEDIA*

D. F. Wilson, M. Howell, and J. H. DeVan

ABSTRACT

Salt/ammonia complexes will undergo thermal cycles during use as working media for heat pumps. The interaction between container materials and complexes under thermal cyclic conditions was assessed to screen possible containment materials. Aluminum alloys 3003, 1100, and 6063 and carbon steel A214 were tested against possible heat pump working media $SrCl_2/NH_3$, $CaBr_2/NH_3$, and $CaCl_2/NH_3$. None of the containment materials showed susceptibility to stress corrosion cracking. While all the materials demonstrated excellent general corrosion resistance to $SrCl_2/NH_3$, only A214 displayed good general corrosion resistance to $CaCl_2/NH_3$. The complex $CaBr_2/NH_3$ was found to be subject to thermal cyclic instability and should not be used as a heat pump working medium.

INTRODUCTION

Coordination complexes, of use as heat pump working media, are formed from thermochemical reactions between a solid metal inorganic salt (adsorbent) and a refrigerant gas (adsorbate). The overall process can be written as:

$$\text{Salt} + \text{Gas} \leftrightarrow \text{Salt}\cdot\text{Gas}. \quad (1)$$

The adsorption (formation of the complex) process is an exothermic reaction, and the desorption process is an endothermic one. The proper cyclic combination of temperature and pressure differentials, and heat fluxes to drive the complexing reaction reversibly, allows for waste heat recovery or useful refrigeration. The operation of salt/gas systems with vapor pressures,

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independent of the gas concentration over wide ranges of gas concentrations,[1] allows for high temperature lifts and coefficient of performance in heat pumps. The performance of an actual system is dependent not only on the surface sorption reaction, but also on the quantity of the salt that has complexed.

Rocky Research Corporation is in the process of demonstrating the effectiveness of complex salt/ammonia systems for use as industrial heat pumps. In order to better project the cost and lifetime of the heat pump system, the compatibility of the proposed construction materials with the preferred complex salts/ammonia systems must be demonstrated. Rocky Research Corporation has selected three complexes ($SrCl_2/NH_3$, $CaBr_2/NH_3$, and $CaCl_2/NH_3$) and four materials of construction (aluminum alloys 3003, 1100, and 6063 and carbon steel A214). Corrosion and stress corrosion testing were performed at the Oak Ridge National Laboratory to assess materials compatibility.

EXPERIMENT

Equipment

The experimental equipment is shown in Fig. 1. Each cell, consisting of two interconnected steel vessels, allowed for the charging and discharging of the ammonia gas from one vessel into another as the temperatures of the two vessels were cycled out of phase. The cells, as valved, allowed for the addition of ammonia gas and venting for the release of excessive pressure. The steel vessels were surrounded by clam-shell heaters and furnished with fans for forced cooling from below. Associated temperature control, over-temperature, and measuring thermocouples are also displayed in Fig. 1. Metallic shields, which are not shown, enclosed the heaters and fans. The heaters and fans were activated and deactivated via programmable controllers. As instrumented, the system allowed for continuous monitoring and recording of temperatures and pressures of four test cells (Fig. 2).

Specimens

The materials tested were aluminum alloys 3003, 1100, and 6063 and carbon steel A214. Typical compositions of these materials are shown in Table 1. C-ring* test specimens were made by Metal Samples Company Incorporated† from materials they had sourced.

*Specimen design conforms to American Society for Testing Materials (ASTM) standard recommended practices as defined in ASTM G 38-73.

†Metal Samples Company Incorporated, Munford, AL 36368.

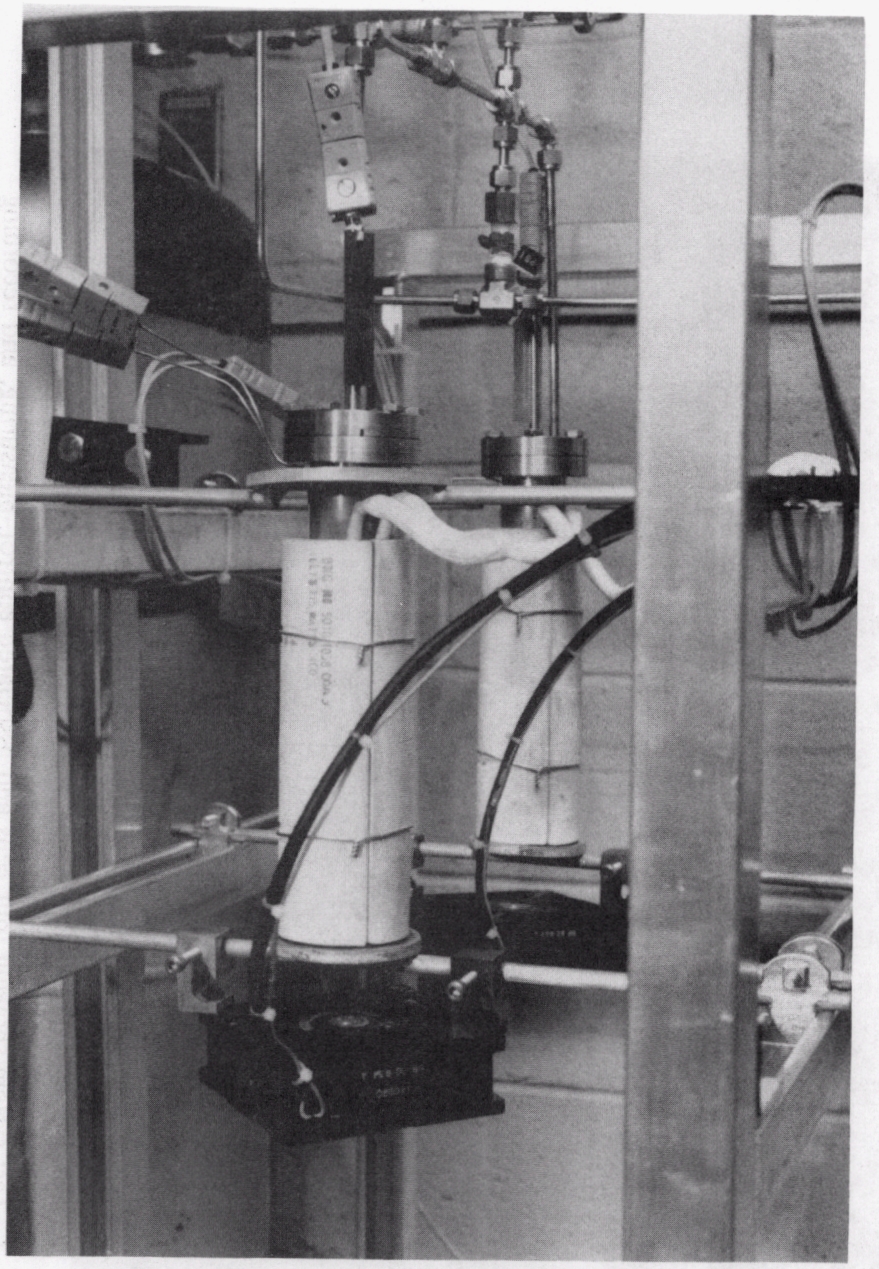

Fig. 1. Test cell showing two reaction vessels and associated heaters, fans, and thermocouples.

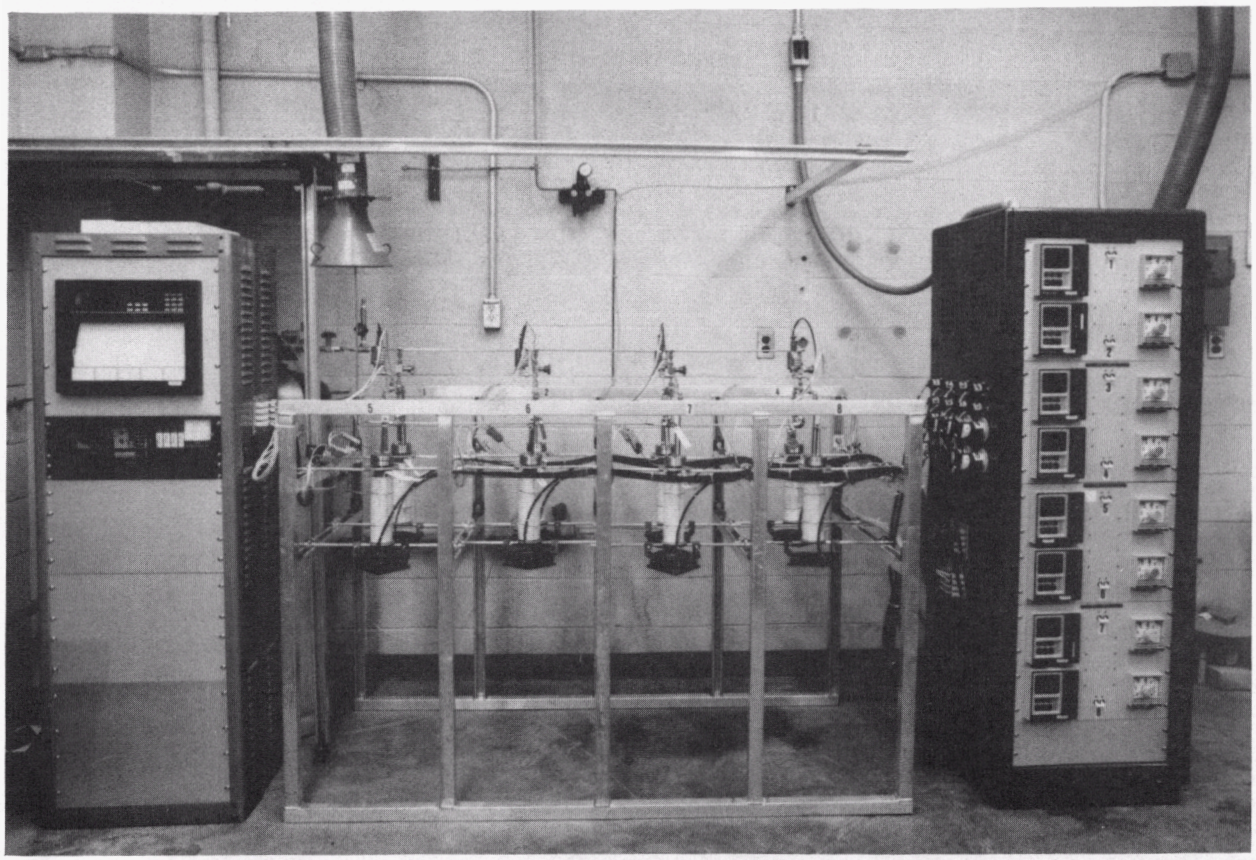

Fig. 2. Test system showing four cells and associated control, measuring, and recording devices.

Table 1. Nominal chemical composition (wt %) of the materials tested

	Materials[a]			
Element	Al 3003	Al 1100	Al 6063	Steel A214
Si	0.6 max	0.95 max	0.60 to 0.20	
Fe	0.7 max		0.35 max	Remainder
Cu	0.20 to 0.05	0.20 to 0.05	0.10 max	
Mn	1.5 to 1.0	0.05	0.10 max	0.420
Zn	0.10	0.10	0.10 max	
Mg			0.9 to 0.45	
Cr			0.10 max	
Ti			0.10 max	
C				0.090
P				0.005
S				0.006
Al	Remainder	Remainder	Remainder	
Others	0.15 max	0.15 max	0.15 max	

[a] *Source*: Metals Samples Company Incorporated.

Procedures

A stainless steel bolt fitted with ceramic insulators was inserted through the holes of the C-ring and tightened such that the outer diameter of the ring was reduced by 1.3 mm (0.050 in.). This procedure ensured that the material opposite the opening was stressed to its yield point, thus providing the necessary stress for stress corrosion cracking if such was inherent to the material/complex salt/ammonia systems. One C-ring of each material was stressed and archived in a desiccator as a control.

Each vessel of a cell was loaded with two degreased, C-ring, stressed specimens and a predetermined weight of the same salt. The weight was chosen so as to completely cover the specimens and minimize the post ammoniation dead space in the vessels. The cells were evacuated [~ 17.33 Pa (0.0025 psi)] and the vessels heated to the salt-ammoniating temperature. The vessels were maintained at temperature under dynamic vacuum overnight. The following day, the system was pressurized with ammonia to a pressure slightly above the calculated equilibrium pressure for at least 4 h. Monitoring of the temperature changes (increasing and then decreasing) as complexing occurred provided a very good indication of the end of reaction. At the end of complexing, the cells were checked for leaks (wet pH paper) and thermal cycling begun.

Each 9-h cycle consisted of: (a) heating to operating temperature, (b) holding at operating temperature, (c) cooling to room temperature, and (d) holding at room temperature. Since the vessels were cycled out of phase, during the cool-down phase of one vessel, there is a secondary temperature spike due to ammonia charging from the other vessel, which is in its heat-up phase. The ammoniating temperatures and pressures and the operating temperatures of the salt complexes are presented in Table 2.

Table 2. Test parameters used in this corrosion study

	Salt complexes		
Parameter	$SrCl_2$	$CaCl_2$	$CaBr_2$
Ammoniating temperature	333 K (60° C)	323 K (50° C)	398 K (125° C)
Ammoniating pressure	0.34 MPa (49 psi)	0.26 MPa (38 psi)	0.37 MPa (54 psi)
Operating temperature (max)	389 K (116° C)	380 K (107° C)	462 K (189° C)
Length of test	2352 h	2496 h	2496 h

Evaluation

At the conclusion of testing, the specimens were cleaned and subjected to optical microscopic examination.

RESULTS AND DISCUSSION

There was corrosion failure of a silver-plated copper gasket in one of the reactors holding the $CaCl_2$ complex, resulting in loss of ammonia. The greenish corrosion product observed was indicative of an ammonia/copper reaction and was the result of a pin hole in or damage to the silver plate. After replacement of this gasket, the system was re-ammoniated and returned to the test mode.

Examination of the recorded temperature and pressure profiles revealed no change in these profiles with time except for the $CaBr_2$ complex, indicating that the reaction vessels were properly sealed and that two of the salt complexes behaved in a reproducible manner. In the case of the $CaBr_2$ complex, a trend of increasing pressure with number of test cycles, as presented in Fig. 3, was observed. This increasing pressure, indicative of an unstable salt/ammonia complex, may preclude the use of this complex in heat pump applications. Instability may be due to deactivation of surface sorption sites or compaction of the salt (decrease in the quantity of salt complexed). The differences in percentage change in pressure shown in Fig. 3 are most likely due to slight differences in the amount of salt initially added to the vessels.

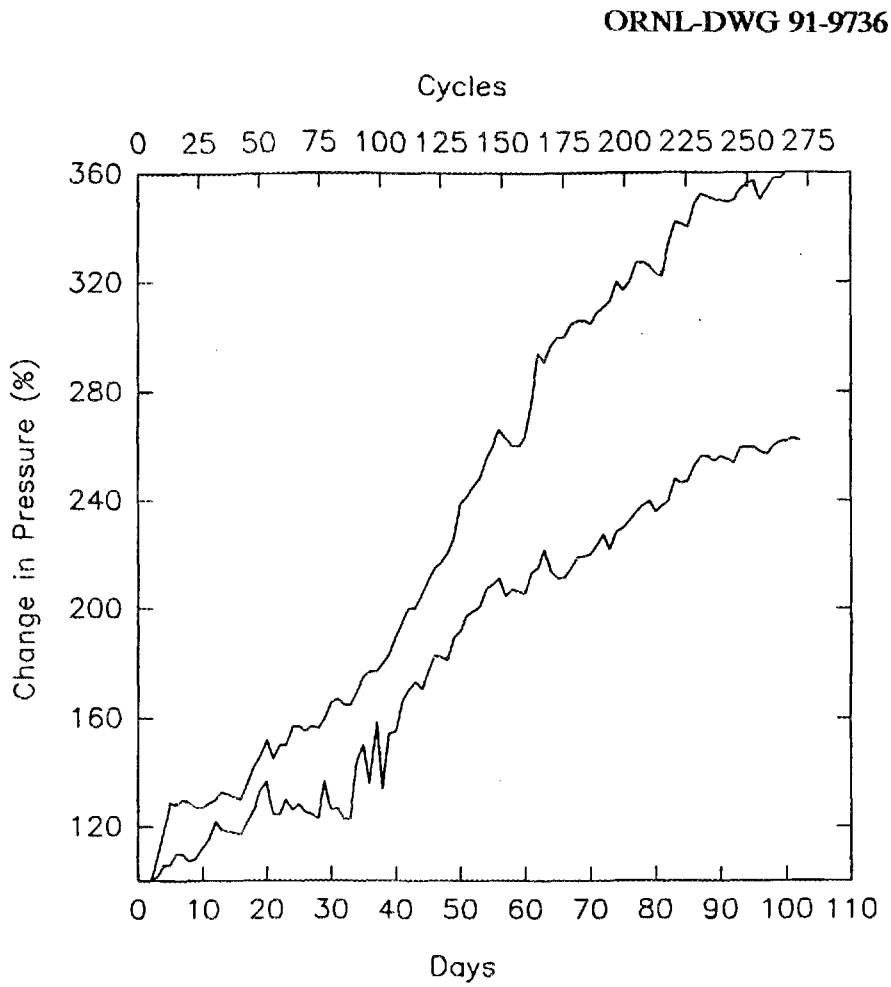

Fig. 3. Change in pressure for an ammonia/$CaBr_2$ complex for two connected reactors that were sequentially heated to 189°C and cooled to room temperature out of phase with each other.

Prior to post-test optical examination, all specimens were inspected to ensure that relaxation of tension by, for example, failure of the stressing bolt or crevice corrosion under the bolt or insulator, had not invalidated the test. No relaxation of tension was found.

Optical microscopic examination was performed on every specimen. None of the specimens showed any indication of localized corrosion and/or cracking. Therefore, the lifetimes of these materials should depend upon their general corrosion rates. While a rate was not specifically obtained in these tests, inferences about rates can be obtained from observations of the corrosion product. Differences in the appearance of the materials exposed to various salt complexes resulted in a corrosivity ranking (least to most) as follows: $SrCl_2/NH_3$, $CaBr_2/NH_3$, and $CaCl_2/NH_3$. The materials' ranking and appearance are presented in Table 3. All the tested materials had excellent corrosion resistance to $SrCl_2/NH_3$ with A214 and Al 6063 showing slightly greater resistance than Al 3003 and Al 1100. While Al 3003, Al 1100, and A214 demonstrated

Table 3. Appearance of materials after exposure to salt complexes. Materials and salt complexes are listed in order of their corrosion resistance and corrosivity, respectively.

Complex	Material[a]	Comment
$SrCl_2$	A214	Bright
	Al 6063	Bright
	Al 3033	Slight staining
	Al 1100	Slight staining
$CaBr_2$	Al 3003	Dull in appearance
	Al 1100	Dull in appearance
	A214	Black tarnish
	Al 6063	White, powdery, thick film; etched appearance beneath film
$CaCl_2$	A214	Scattered red-brown stain
	Al 3003	Finely spalled, thick film
	Al 6063	Finely spalled, thick film
	Al 1100	Coarsely spalled, thick film

[a]Materials that are not separated by a horizontal line are of equal corrosion resistance.

good corrosion resistance to $CaBr_2/NH_3$, Al 6063 developed a thick, powdery film indicating poor resistance. All the tested materials demonstrated the lowest corrosion resistance to $CaCl_2/NH_3$ with A214 performing best. The finely spalled, thick films on Al 3003 and Al 6063 may be precursors to a more coarsely spalled, thick film as observed on Al 1100. Thus, without the benefit of longer term testing and identification of corrosion products, the aluminum alloys are not recommended for use with $CaCl_2/NH_3$ complex.

CONCLUSIONS

Based on the results of these 2000-h thermal cyclic tests in salt/ammonia heat pump working media, the following can be concluded.

- A214, Al 6063, Al 3003, and Al 1100 showed excellent corrosion resistance to $SrCl_2/NH_3$ complex.
- Al 3003, Al 1100, and A214 demonstrated good corrosion resistance to $CaBr_2/NH_3$ complex.
- A214 displayed good corrosion resistance to $CaCl_2/NH_3$.
- The $CaBr_2/NH_3$ complex, which demonstrated thermal cyclic instability, is not recommended for use as a heat pump working medium.

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