WORK STATEMENT #1740
SPONSORING TC3.3 Contaminant Control in Refrigerant Systems
CO-SPONSORING TC 3.2

Title: Hydrogen Fluoride Capacity of Desiccants

Executive Summary:

Some desiccants have capacity for removal of acids as well as water, however the type of acid (inorganic vs. organic) makes a difference in this capability. Two previous ASHRAE projects (RP793 and RP1028) developed MOT for desiccant capacity for strong inorganic (HCl) and weak organic acids, respectively, which differ in their adsorption mechanisms. However, hydrogen fluoride (HF) is a special case – a weak inorganic acid. Formed under some conditions by decomposition of fluorine-containing refrigerants, HF may damage system components including the desiccant itself. HF differs sufficiently that a research project is needed to determine adsorption capacities of molecular sieve and activated alumina desiccants. With the results, system designers will be able to judge the degree of protection that the different types of desiccants provide against damage due to hydrogen fluoride. In addition, service engineers will become aware of the potential of the desiccant to mask a breakdown condition indicated by Total Acid Number (TAN) measurements. The project will benefit system and component manufacturers and ultimately consumers as a threat to system reliability and longevity is reduced.

Applicability to the ASHRAE Research Strategic Plan:

Supports Strategic Plan 2010-2015 Goal 9 by establishing techniques and data to improve reliability of the refrigerant system. In particular it addresses removal of a potential system contaminant, as noted in Technical Challenge #9: Potential system contaminants in new refrigerants and their effects on system performance and reliability have not been fully investigated.

Application of Results:

The results will provide information on the management of hydrogen fluoride generated from fluorocarbon refrigerant decomposition. Results and conclusions will be published as an ASHRAE technical paper and in the ASHRAE Refrigeration Handbook Chapter 7 (Control of Moisture and Other Contaminants in Refrigerant Systems). System designers will be able to judge the degree of protection that the different types of desiccants provide against damage due to hydrogen fluoride.

State-of-the-Art (Background):

It has long been known that some desiccants have capacity for acids as well as water. It is also known that the general type of acid (organic or inorganic) makes a difference in the ability of desiccants to remove the acids.

In RP793 (Cavestri 1998) a method of test (MOT) was developed for **inorganic** acid capacity of desiccants in refrigerants. The capacity of silica gel, activated alumina, and molecular sieve for removing hydrogen chloride (HCl) from R22 was measured. In RP1028 (Kauffman 2003) a MOT was developed for **organic** acid capacity of desiccants in refrigerants. The capacity of silica gel, activated alumina, and molecular sieve for removing hexanoic and oleic acids from mixtures of R22/mineral oil, R134a/polyol ester (POE), and R410A/POE was measured.

Advancement to the State-of-the-Art:

Hydrogen fluoride (HF) is a weak inorganic acid. While adsorption of organic acids (weak acids) and strong inorganic acids (HCl) on desiccants has been studied, the adsorption of HF is a special case. Measuring the HF capacity of desiccants advances our knowledge of the ability of desiccants to remove contaminants other than water.

While HF is an inorganic acid like HCl, it may behave differently from HCl. The dissociation constant K, expressed as pKa [where $pKa = -\log(K)$], of HF in water is 3.45, which is similar to an organic acid. For example, the hexanoic acid referred to in RP1028 has pKa of 4.88. (Lower values of pKa indicate stronger acidity.) HCl, on the other hand, is completely dissociated in water ($pKa = -\infty$).

Since we have data on HCl and organic acids, and the acidity of HF is between these two, then we have bracketed the HF. Wouldn't the capacity for HF be somewhere in between? Maybe, but the adsorption mechanisms of HCl and organic acids are different. On molecular sieve, HCl is physically adsorbed and then chemically adsorbed by ion exchange. Organic acids are minimally adsorbed on molecular sieve. On alumina, organic acids are physically adsorbed only, while HCl is physically adsorbed and then chemically adsorbed by reaction with Al_2O_3 to form $AlCl_3$.

Therefore, HF differs sufficiently from HCl that a research project should be run to answer the question of adsorption capacity.

<u>Justification and Value to ASHRAE</u>:

A system can fail or its performance deteriorate due to conditions such as external blockage of condenser coils, under-charging due to system leaks, lack of maintenance, etc. By removing water and acids (organic and/or mineral acids) from the circulating fluids, the desiccant, contained in the filter dryer, helps protect the system from damage due to various causes.

Total Acid Number (TAN) measures the amount of acid found in a compressor lubricant sample. It is a very important indicator of system condition. But the TAN can be misleading if the desiccant is removing some of the acid. More HF may have been formed than is indicated by the TAN, and the capacity of the desiccant for HF has to be considered in interpreting the TAN results. Hence, an important benefit of the project is to determine whether (and to what extent) the desiccant's capacity for HF could mask a breakdown condition of the refrigerant system. We have already studied the effect of desiccant on TAN by removing organic acids. This project will address the hydrofluoric acid effect.

Understanding the desiccant capacity for HF will benefit system manufacturers, component manufacturers and ultimately consumers. It will help improve reliability and longevity of systems equipped with hermetic compressors by providing the knowledge to design filter-dryers to remove hydrogen fluoride, a corrosive contaminant. Knowing the HF capacity along with the water capacity of the different desiccant materials helps system designers determine the type and quantity of system-protecting desiccant needed as insurance against potential system damage.

It should be emphasized that the objective to understand the HF capacity of the desiccant is in no way a reflection on the stability of well-designed/engineered HFC/HFO systems, but rather a need to understand the fundamental properties of the desiccant itself.

In addition to developing the MOT, the project will determine HF capacity of relevant desiccant materials. Hence the benefits will begin to accrue as soon as the data are obtained and published by ASHRAE. There is minimal opportunity for intellectual property rights from the project.

<u>Objectives</u>:

- Develop and report a method of testing desiccants for their equilibrium hydrogen fluoride adsorption capacity.
- Determine the equilibrium hydrogen fluoride capacity of samples of molecular sieve.
- Determine the equilibrium hydrogen fluoride capacity of samples of activated alumina.
- Determine the equilibrium capacities of each desiccant at two levels of temperature (room temperature and 52°C) and two levels of water loading with one aprotic solvent, such as R-218, and six levels of HF addition to the solvent. The Project Monitoring Subcommittee (PMS) shall have the authority to change the temperatures and to specify the water loadings, solvent, and HF addition values.
- Determine the effect of HF adsorption on the equilibrium water adsorption capacity of each desiccant.

<u>Scope/Technical Approach</u>:

The overall task is to develop a method of testing the equilibrium hydrogen fluoride capacity of desiccants and use the method to determine the equilibrium hydrogen fluoride capacity of molecular sieve and activated alumina desiccants at the conditions specified in the scope section of this WS.

Since hydrogen fluoride is a potentially dangerous chemical, it is paramount that the contractor fully understand the hazards involved in working with it. The contractor shall, in the proposal, identify in detail the measures to be taken to reduce hazards through use of proper Personal Protective Equipment, laboratory facilities, and procedures. In the selection process weight will be given based on the quality of safety measures.

The method of introducing and contacting the solvent containing dissolved HF shall be specified.

The project shall determine whether the HF removal mode is by reversible physical adsorption or irreversible chemical adsorption or a combination of the two.

TASKS: Note: ** denotes a Task Deliverable (see Deliverables/Where results will be published)

1. Submit detailed test procedure (including safety measures) to the PMS for review and approval**.
2. Obtain required equipment and materials and set up test apparatus**
3. Determine the equilibrium hydrogen fluoride capacity of samples of molecular sieve (types 3A and 4A beads) and activated alumina beads.
    a. The equilibrium HF capacities shall be determined**
        i. For three desiccants (molecular sieve type 3A, molecular sieve type 4A, and activated alumina)
        ii. At two levels of temperature (room temperature and 52°C)
        iii. At two levels of water loading on the desiccants to be specified by the PMS. For each water loading on molecular sieve and alumina, determine the water concentration in the solvent in equilibrium with the desiccant at room temperature. (Total of 6 determinations.)
        iv. At six levels of mass of HF added to system (grams of HF added per gram of desiccant in the system), as specified by the PMS.
        v. With one aprotic solvent, such as R-218.
        vi. The above constitutes 72 experimental runs (3x2x2x6x1)
        vii. Each experimental run shall produce the following measured data
            1. mass of HF added
            2. fluoride content of desiccant,
            3. fluoride content of solvent, and
            4. acidity of solvent (total acid number).
        viii. Report preliminary results to PMS after the 6^{th}, 12^{th}, 24^{th}, 48^{th}, and 72^{nd} run.**
        ix. Additional measurements of TAN or F in solvent shall be done to determine when equilibrium has been reached.**
    b. Determine the reactivity versus time of the system by making blank runs with no desiccant at the two temperatures given above and two water concentrations to be specified by the PMS. Be aware of potential passivating effect of HF on the system materials**.
    c. The HF capacity data shall be reported in three ways:
        i. In tabular form (in Excel spreadsheet)
        ii. Plotted as isotherms of Hydrogen Fluoride Content (g HF per 100 g of desiccant) vs. Residual HF Content of Solvent (ppm/wt)
        iii. Plotted as Hydrogen Fluoride Content of desiccant vs. Total Acid Number of solvent.
    d. HF capacity data evaluation
        i. Reproducibility of the method shall be established using at least six duplicate runs
        ii. For each run, the Material Balance on fluoride shall be calculated from amounts of fluoride added to the system (A), removed from the system (R), accumulated (adsorbed) on the desiccant (D), and accumulated in the solvent (S):

$$\text{Material balance} = (D+S) / (A-R)$$

   e. The method of test for fluoride content of desiccant shall be pyrohydrolysis and ion selective electrode (UOP 2006), or another proven method (to be approved by the PMS). NIST reference material SRM-120c (NIST) shall be used to standardize the fluoride method.
   f. If a fluorinated solvent, such as R-218, is used, proof must be provided that the fluoride content of the desiccant that is reported represents inorganic fluoride (from HF that has adsorbed on or reacted with the desiccant) rather than organic fluoride from adsorbed solvent.
4. Determine reversibility of the HF adsorption on 12 samples to be selected by the PMS**.
5. Determine the effect of HF adsorption on the equilibrium water capacity of the desiccants**.
   a. The equilibrium water capacity of all desiccant samples already exposed to HF in Task 3 above shall be measured in air. This constitutes 72 experimental runs. Additionally, for comparison the water capacity shall be determined on desiccants not exposed to HF. Report preliminary results to PMS after the 6^{th}, 12^{th}, 24^{th}, 48^{th}, and 72^{nd} run.**
   b. For molecular sieves, the equilibrium water capacity shall be measured with the desiccant at room temperature and a relative humidity in the range of 10% to 30%. Contractor will choose the relative humidity within the specified range and reproduce it to ±2% relative humidity.
   c. For activated alumina, the equilibrium water capacity shall be measured with the desiccant at room temperature and a relative humidity in the range of 60% to 80%. Contractor will choose the relative humidity within the specified range and reproduce it to ±2% relative humidity.
   d. Water capacity data shall be reported in two ways:
      i. In tabular form (in Excel spreadsheet)
      ii. Plotted as water capacity (g H2O per 100 g of dry desiccant) vs. HF content of the desiccant (g HF per 100 g of desiccant)
   e. Equilibrium water capacity data shall be evaluated for repeatability with at least six duplicate analyses.
6. Determine the crush strength of all desiccant samples exposed to HF in Task 3 above as well as the activated starting desiccants, using the method of ASTM standard 4179. The PMS shall have the authority to modify the procedure of ASTM 4179 to accommodate the materials of this project.**
7. Produce reports in accord with ASHRAE deliverables. The Final Report shall include a detailed Method of Test as well as the experimental data.

<u>Deliverables/Where Results Will Be Published</u>:

Progress, Financial and Final Reports, Technical Paper(s), and Data shall constitute required deliverables (“Deliverables”) under this Agreement and shall be provided as follows:

**Task Deliverables: Report results to PMS for review and approval prior to proceeding to next task.

a. Progress and Financial Reports

   Progress and Financial Reports, in a form approved by the Society, shall be made to the Society through its Manager of Research and Technical Services at quarterly intervals; specifically on or before each January 1, April 1, June 1, and October 1 of the contract period.

   Furthermore, the Institution’s Principal Investigator, subject to the Society’s approval, shall, during the period of performance and after the Final Report has been submitted, report in person to the sponsoring Technical Committee/Task Group (TC/TG) at the annual and winter meetings, and be available to answer such questions regarding the research as may arise.

b. Final Report

   A written report, design guide, or manual, (collectively, “Final Report”), in a form approved by the Society, shall be prepared by the Institution and submitted to the Society’s Manager of Research and Technical Services by the end of the Agreement term, containing complete details of all research carried out under this Agreement. Unless otherwise specified, six copies of the final report shall be furnished for review by the

Society's Project Monitoring Subcommittee (PMS).

Following approval by the PMS and the TC/TG, in their sole discretion, final copies of the Final Report will be furnished by the Institution as follows:

- An executive summary in a form suitable for wide distribution to the industry and to the public.
- Two bound copies
- One unbound copy, printed on one side only, suitable for reproduction.
- Two copies on CD-ROM; one in PDF format and one in Microsoft Word.

c. HVAC&R Research or ASHRAE Transactions Technical Paper

One or more papers shall be submitted first to the ASHRAE Manager of Research and Technical Services (MORTS) and then to the "ASHRAE Manuscript Central" website-based manuscript review system in a form and containing such information as designated by the Society suitable for publication. Papers specified as deliverables should be submitted as either Research Papers for HVAC&R Research or Technical Paper(s) for ASHRAE Transactions. Research papers contain generalized results of long-term archival value, whereas technical papers are appropriate for applied research of shorter-term value, ASHRAE Conference papers are not acceptable as deliverables from ASHRAE research projects. The paper(s) shall conform to the instructions posted in "Manuscript Central" for an ASHRAE Transactions Technical or HVAC&R Research paper. The paper title shall contain the research project number (XXXX-RP) at the end of the title in parentheses, e.g., (XXXX-RP).

Note: A research or technical paper describing the research project must be submitted after the TC has approved the Final Report. Research or technical papers may also be prepared before the project's completion, if it is desired to disseminate interim results of the project. Contractor shall submit any interim papers to MORTS and the PMS for review and approval before the papers are submitted to ASHRAE Manuscript Central for review.

d. Data

The Institution agrees to maintain true and complete books and records, including but not limited to notebooks, reports, charts, graphs, analyses, computer programs, visual representations etc., (collectively, the "Data"), generated in connection with the Services. Society representatives shall have access to all such Data for examination and review at reasonable times. The Data shall be held in strict confidence by the Institution and shall not be released to third parties without prior authorization from the Society, except as provided by GENERAL CONDITION VII, PUBLICATION. The original Data shall be kept on file by the Institution for a period of two years after receipt of the final payment and upon request the Institution will make a copy available to the Society upon the Society's request.

e. Project Synopsis

A written synopsis totaling approximately 100 words in length and written for a broad technical audience, which documents 1. Main findings of research project, 2. Why findings are significant, and 3. How the findings benefit ASHRAE membership and/or society in general shall be submitted to the Manager of Research and Technical Services by the end of the Agreement term for publication in ASHRAE Insights

The Society may request the Institution submit a technical article suitable for publication in the Society's *ASHRAE JOURNAL*. This is considered a voluntary submission and not a Deliverable.

All Deliverables under this Agreement and voluntary technical articles shall be prepared using dual units; e.g., rational inch-pound with equivalent SI units shown parenthetically. SI usage shall be in accordance with IEEE/ASTM Standard SI-10.

Level of Effort:

The project anticipates 2.0 professional-months for the principal investigator and 4.5 professional-months for a research technician. The estimated cost is $120,000 and the project is expected to take 12 months.

Other Information for Bidders (Optional):

A flowing system is not required. A static/mixed system may be proposed for simplicity.
Equilibration time should be considered when estimating elapsed time and resources. See RP793 (Cavestri 1998) and RP1028 (Kauffman 2003).

Proposal Evaluation Criteria:

1. Contractor's understanding of Work Statement as revealed in proposal. 15%
   a) Logistical problems associated
   b) Technical problems associated
2. Quality of methodology proposed for conducting research. 25%
   a) Organization of project
   b) Management plan
3. Contractor's capability in terms of facilities. 15%
   a) Managerial support
   b) Data collection
   c) Technical expertise
4. Qualifications of personnel for this project. 20%
   a) Project team 'well rounded' in terms of qualifications and experience in related work
   b) Project manager person directly responsible; experience and corporate position
   c) Team members' qualifications and experience
   d) Time commitment of Principal Investigator
5. Student involvement 5%
   a) Extent of student participation on contractor's team
   b) Likelihood that involvement in project will encourage entry into HVAC&R industry
6. Probability of contractor's research plan meeting the objectives of the Work Statement. 15%
   a) Detailed and logical work plan with major tasks and key milestones
   b) All technical and logistic factors considered
   c) Reasonableness of project schedule
7. Performance of contractor on prior ASHRAE or other projects. 5%
   (No penalty for new contractors.)
8. Other Safety Measures included in items 1, 2, 3, 4, 5, and 6 above.

References:

ASHRAE Handbook Refrigeration, Chapter 6, 2002.

ASTM Standard 4179. “Standard Test Method for Single Pellet Crush Strength of Formed Catalyst Shapes.” American Society for Testing and Materials. West Conshohocken, PA, USA www.astm.org

Cavestri & Schooley, “Test Method for Inorganic Acid Removal Capacity of Desiccants Used in Liquid Line Filter Driers” RP793, ASHRAE Transactions 1998.

Kauffman & Gunderson, “Test Method for Organic Acid Removal by Adsorbents Used in Liquid Line Filter Driers” RP1028, ASHRAE Transactions, Vol 109, Part 2, 2003

NIST Standard Reference Material SRM 120c, National Institute of Standards and Technology, Gaithersburg, Maryland, USA. http://srdata.nist.gov/gateway/gateway

UOP912-06 “Fluoride in Catalysts, Molecular Sieves, and Aqueous Solutions by Ion Selective Electrode,” ASTM International, West Conshohocken, PA, USA. 2006. www.astm.org

Further Reading:

Cohen & Blackwell, “Inorganic Fluoride Uptake as a Measure of Relative Compatibility of Molecular Sieve Desiccants with Fluorocarbon Refrigerants.” ASHRAE Transactions V 101, Pt 2. 1995

Cohen & Tucker, “Drying R-407C and R-410A Refrigerant Blends with Molecular Sieve Desiccants.” ASHRAE Transactions V104, Pt 1. 1998.

Mays, R.L. “Molecular Sieve and Gel-Type Desiccants for Refrigerants 12 and 22.” ASHRAE Journal, August 1962.

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