

The Effect of Water on Low Temperature Heat Transfer Fluid Performance

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Introduction

One of the growth areas in specialty chemical and pharmaceutical intermediate manufacturing is the use of low-temperature processing to improve product yields. Many reactions can achieve higher yields when run at lower temperatures. Processes involving chiral reactions, for example, can increase yields by 1-2% with a 10°C decrease in reaction temperature.

To achieve the -70° to -85°C reactor temperature required is difficult (and very costly) with mechanical refrigeration systems. While cooling with liquefied nitrogen is economically viable at these temperatures, it can be difficult to control the vaporization process within the reactor jackets. Over-feeding the liquid nitrogen (at -167° C) guarantees that product will freeze on the heat exchanger surface.

Temperature control systems that circulate a heat transfer fluid through a separate vaporizer have largely solved the problem of reactor cooling to -85°C or lower. In addition, these systems can be equipped with in-line steam or electric heaters, which significantly increase the process versatility.

However, freeze-ups on the fluid side of the vaporizer still occur when using liquid nitrogen cooling in a single fluid system. These occur at the lower end of the fluid's operating range. High fluid viscosity inhibits heat transfer into the vaporizer, causing liquid nitrogen at -167°C to accumulate inside the vaporizer and freezing a layer of the heat transfer fluid on the outside. Once the entire surface is covered, the system must either be shutdown to defrost the vaporizer or the process itself adjusted to equal the reduced cooling capability.

It is difficult to predict the minimal temperature at which a system can operate without freezing up the coil. Manufacturers' freeze point data is not always reliable since there is no standard method for determining freeze points at low temperatures. Users have experienced some nasty surprises when the heat

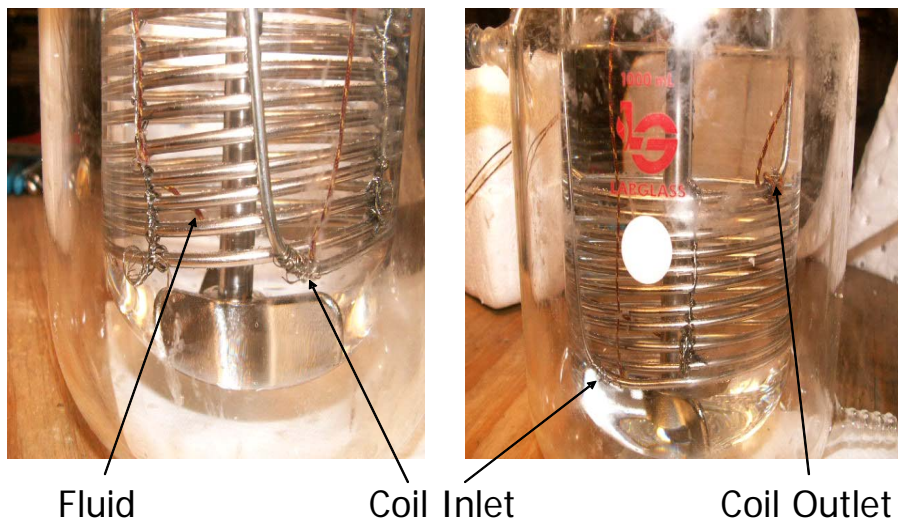
exchanger appears to freeze up suddenly during normal system operation. There have also been reports of erratic phase changes of some types of fluids after contamination by water.

Because these incidents were preventing some pharmaceutical manufacturers from considering alternative heat-transfer fluids, Paratherm Corporation ran a series of tests to determine the behavior of fluids during the coil freeze-up process and to identify whether the minimum operating temperature of some fluid chemistries was more susceptible to water contamination.

Setup

Two available low-temperature heat transfer fluid chemistries—silicone and di-limonene/diethyl benzene blend (d-lim/deb)—were tested alongside Paratherm CR, a synthetic organic/diethyl benzene blend. The test apparatus consisted of a jacketed glass reaction vessel, a stainless steel mixer and a stainless steel vaporizer coil. Thermocouples were installed on coil surface near the nitrogen inlet and outlet and another was suspended in the center near the bottom to measure the fluid temperature.

Thermocouple Placement



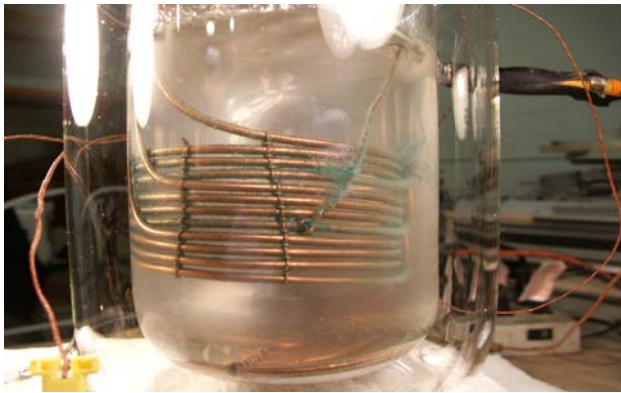
Test

Each of the three heat transfer fluids was tested as is (“From Drum”) and with 1,000 and 4,000 ppm (parts per million) of water dispersed in it. Agitation and nitrogen flow rates were identical for all samples. When ice first appeared on the

coil surface at the nitrogen inlet, the fluid temperature was recorded as the “initial” coil-icing temperature. When the entire coil was covered in frozen fluid, the fluid temperature was recorded as the “final” coil icing temperature.

Some interesting results were obtained during the initial attempt with a copper coil. All three “new” fluid samples tested satisfactorily. When contaminated with water, the silicone and d-lim/deb fluids turned green while the Paratherm CR remained clear. Because of the effect that the dissolved copper oxides might have on the results, the copper was replaced with stainless steel.

Copper Coil In Silicone Fluid With 1000 ppm Water

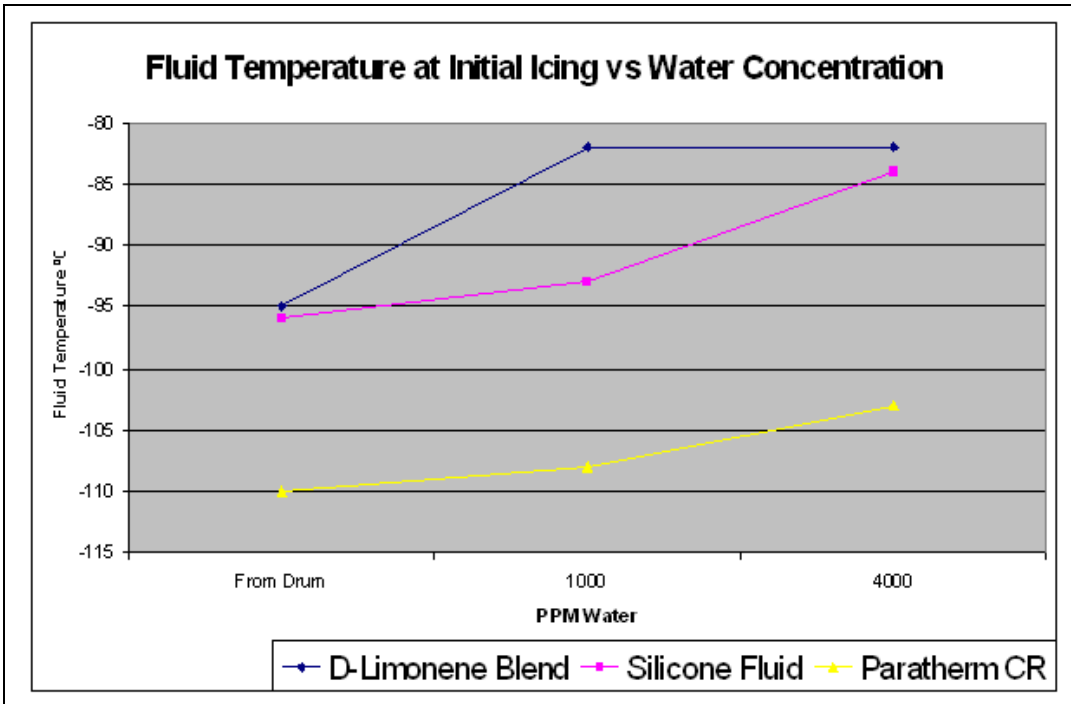


Copper Coil in Paratherm CR with 1000 ppm Water



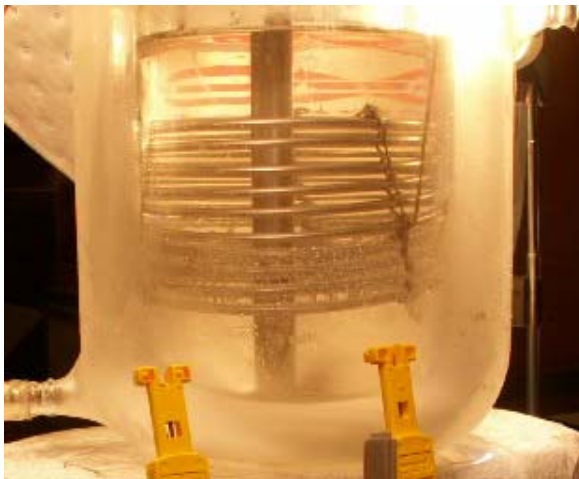
Results

None of the samples became a solid or exhibited any unusual changes during the tests. The only solids observed were the solid “ice” coating on the coil. This coating first formed at the nitrogen inlet and advanced up the coil from inlet to outlet covering 1 to 2 loops in single jumps. The fluid temperature continued to decrease as the ice covered the coil although at different rates. Once the coil was completely covered, the test was terminated. No abrupt coil freeze-ups or phase changes were observed in any of the fluids during the tests. However, there were differences in the lowest temperature that the fluids reached before the ice began to form. The di-lim/deb showed a 13°C increase in the lowest fluid temperature at 1000 ppm water with no further increase noted as the water concentration was increased to 4000 ppm. The Paratherm CR and the silicone both showed an almost linear increase in fluid temperature as the water concentration increased.

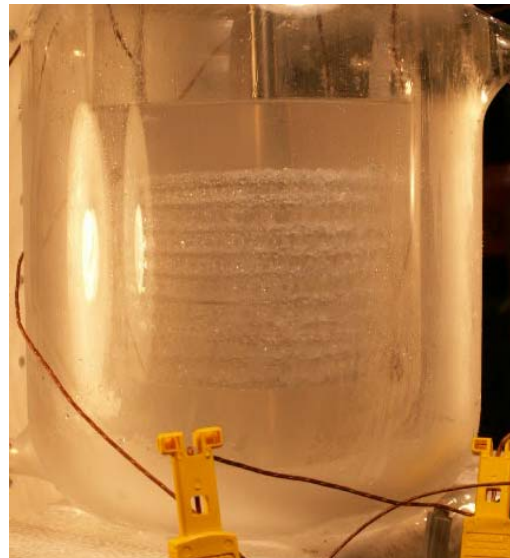


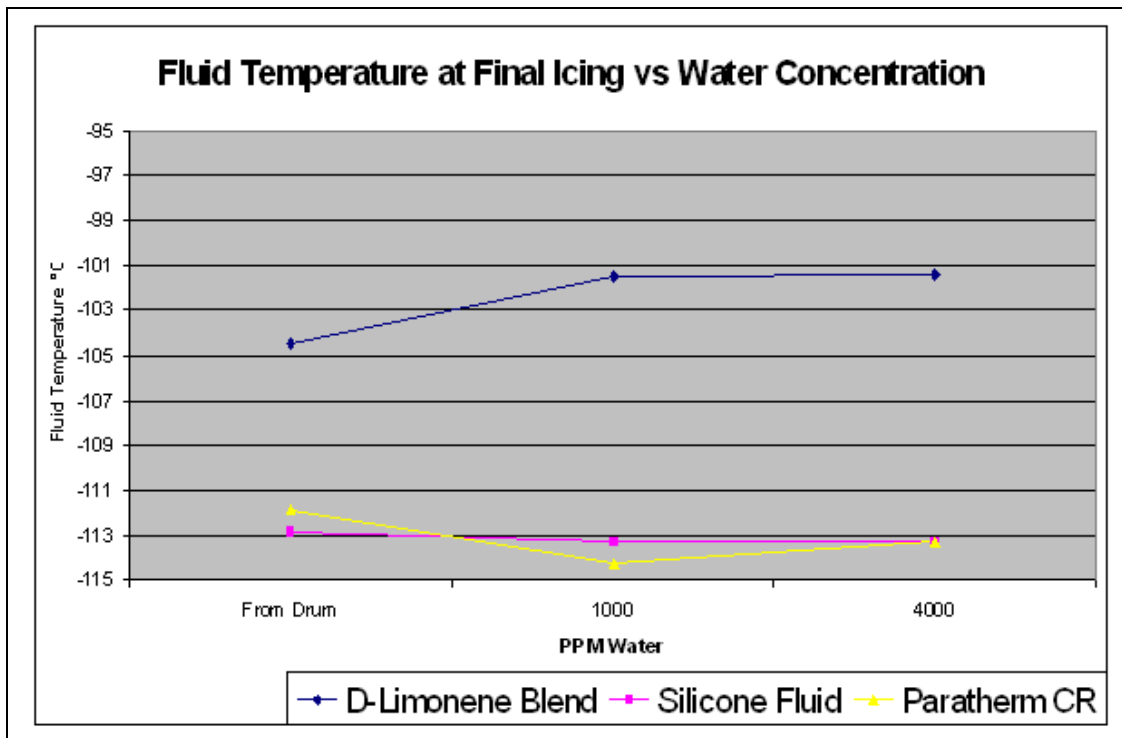
There were also differences in the time required to completely ice the coil and the change in fluid temperature from initial to final. The silicone fluid required the longest time and had the largest fluid temperature drop (15-20°C). The CR took roughly 60% as long for the coil to completely freeze and had the smallest temperature decrease (6-10°C).

Initial Coil Freeze-Up



Complete Coil Icing





Test Conclusions

1. Fluid chemistry does effect how the fluid icing temperature changes due to water contamination. The di-lim/deb chemistry shows more change at low amounts of water contamination while silicone and Paratherm CR showed lesser change.
2. All three fluids behaved the same at the fluid “freeze-up“temperature. This suggests that any abnormal or abrupt heat exchanger freeze-ups that occur in operating systems most likely were due to other causes.

Founded in 1988, Paratherm Corporation has become a leading U.S. manufacturer of specialized heat transfer fluids and system cleaners. The firm offers a wide range of heat transfer fluids (currently 7 fluids and 2 cleaners) covering temperatures from -148°F to +650°F. Paratherm serves a diverse number of industries including the chemical industry, food processing, and plastics manufacturing to name a few of the more prominent ones. The company has a network of distributors and warehousing locations throughout North America to offer regional service and quick delivery.

For information on Paratherm fluids for hot and cold process applications – contact Jim Oetinger (joetinger@paratherm.com) at Paratherm Corporation, 4 Portland Road, West Conshohocken, PA 19428. 800-222-3611 or 610-941-4900, (Fax 610-941-9191), info@paratherm.com – www.paratherm.com. Jim Oetinger, and Paratherm Corporation will be exhibiting at the CPhI Exposition in Frankfurt, Germany , September 30 to October 2, 2008.