How Low Can You Go?

Plants must evaluate a number of design factors when operating heat exchangers at ultra-low temperatures

By Jim Lines

Pharmaceutical, biotechnology and specialty chemical companies are challenging the heat transfer community to provide solutions that enable critical processes to operate at extremely cold temperatures. In the past, it was adequate to operate at temperatures as low as -80˚F (-62.2˚C). Now industry continues to push for colder temperatures. Low-temperature heat transfer fluid manufacturers and heat transfer companies are being asked to provide systems that can run reliably at -148˚F to -184˚F (-100˚C to -120˚C).

Why such low temperatures? For certain chemical reactions the rule of thumb is that the reaction time is increased by a factor of two for each 18˚F (10˚C) reduction in operating temperature. If the temperature is too high, the reaction time is very quick, adversely impacting quality and repeatability of results.

A number of design considerations must be taken into account when operating at these extreme conditions. This article reviews the outcome of recent research of heat exchanger design and heat transfer fluid performance for low-temperature operation. It defines practical low-temperature operation of the various heat transfer fluids for a given type of heat exchanger. The performance characteristics of the different fluids are discussed, as is the performance of heat exchangers as heat transfer fluids begin to freeze within them.

Common low-temperature applications in a pharmaceutical plant are reactor jacket cooling and vacuum freeze drying (lyophilization). A heat transfer system that can provide consistent heat transfer fluid temperature is essential for product quality and repeatable results from batch to batch.

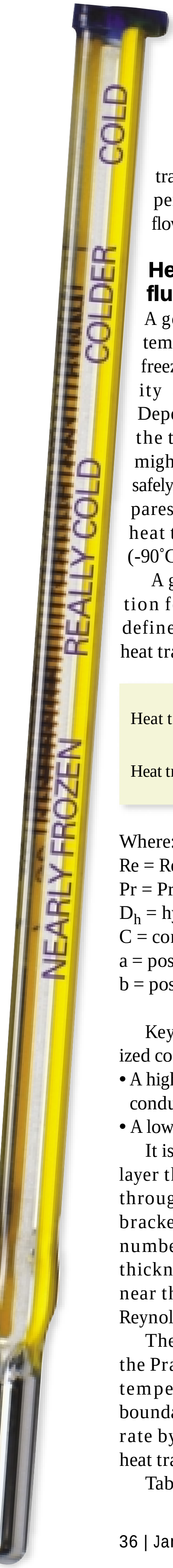
If a heat transfer fluid begins to freeze when exposed to cold operating temperatures, then heat transfer is less efficient. This result leads to temperature increases in the freeze dryer or reactor, compromising product quality.

A heat exchanger performance testing package was constructed to evaluate the operational characteristics of different types of heat exchangers and low-temperature heat transfer fluids. The test setup was fully computerized to capture key operating variables while an exchanger was operating. Each type of exchanger was operated with four different low-temperature heat transfer fluids with identical mass flow rates and temperatures to allow for comparison under identical operating conditions.

During the research, several helically coiled heat exchangers were constructed with thermocouples attached at different locations on the heat transfer surface. The heat transfer surface temperature is markedly different when solid deposits are present. A data acquisition system collected temperature measurements while the exchanger was in operation. These measurements allowed monitoring when heat transfer surfaces developed solid deposits.

The exchangers handled progressively colder heat transfer fluid; liquid nitrogen was used as the coolant in each heat exchanger. This arrangement simulated reactor jacket cooling service, which typically uses liquid nitrogen as the coolant. Variables affecting performance were systematically varied to determine the practical operating ranges for each heat transfer fluid.

Methanol, Syltherm XLT (Dow), Dynalene MV (Dynalene) and HFE 7000 (3M) were the fluids analyzed. Most of the analysis was done with heliflow heat exchangers, although brazed plate heat exchangers were compared as well. The testing involved varying heat



transfer fluid flow rates and inlet temperatures, as well as liquid nitrogen flow rates and operating pressures.

Heat transfer fluid properties

A good heat transfer fluid for low-temperature service must have a low freeze-point temperature, low viscosity and low thermal diffusivity. Depending on the operating range of the temperature control system, it might need to be capable of operating safely at hot temperatures. Table 1 compares the fluid properties of the four heat transfer fluids tested at -130˚F (-90˚C).

A generalized heat transfer correlation for the heat transfer fluid that defines how fluid properties impact heat transfer is expressed by:

$$\text{Heat transfer coefficient} = C \times Re^{a} Pr^{b} \times \frac{\textit{thermal conductivity}}{D_h}$$

$$\text{Heat transfer coefficient} = C \times \left(\frac{\textit{density x velocity x } D_h}{\textit{viscosity}}\right)^{a} \left(\frac{\textit{specific heat x viscosity}}{\textit{thermal conductivity}}\right)^{b} \left(\frac{\textit{thermal conductivity}}{D_h}\right)$$

Where:
Re = Reynolds number
Pr = Prandtl number
D_h = hydraulic diameter
C = constant
a = positive exponent that is less than 1.0
b = positive exponent that is less than 1.0

Key observations from the generalized correlation include:

- A high density, specific heat and thermal conductivity are good for heat transfer.
- A low viscosity is good for heat transfer.

It is important to keep the boundary layer thin, with efficient heat transfer through the boundary layer. The first bracketed expression is the Reynolds number, which is an indication of the thickness of the fluid boundary layer near the heat transfer surface. A high Reynolds number is important.

The second bracketed expression is the Prandtl number, which affects the temperature gradient through the boundary layer. It is an indication of the rate by which heat is given up by the heat transfer fluid to the coolant.

Table 2 shows just how different the Reynolds and Prandtl numbers can be in the case of 15,000 pounds per hour (lb/hr.) (6,800 kilograms per hour [kg/hr.]) of heat transfer fluid at -130˚F (-90˚C) in a heliflow heat exchanger. The exchanger has 12.3 square feet (sq. ft.) (1.14 square meters [sq. m.]) of heat transfer surface.

Testing showed that an evaluation of the freeze point of a heat transfer fluid is insufficient to determine the suitability of a fluid for a given application. The freeze point, along with the fluid properties, the heat exchanger design and fluid velocity, plays a part in inhibiting the onset of freezing. Just because the temperature of the fluid leaving a heat exchanger is well above the freeze point of that fluid does not necessarily mean the fluid will not freeze inside the heat exchanger. This consideration is key.

How each fluid performed

Freeze-point temperature alone is not an indicator of whether or not a fluid will freeze in a heat exchanger. Fluid properties, velocity and heat exchanger design play important roles as well. Fig. 1 and Fig. 2 compare the four test fluids under identical operating conditions.

Thermocouples attached to the heat transfer surface indicated whether or not the fluid was freezing onto the heat transfer surface. Note how dramatically different the thermocouple-measured temperature was when freezing occured. Once solid deposits are present, they act as an insulator and drive the surface temperature to much colder levels. The difference is more than 100˚F (56˚C) between unfrozen and frozen heat transfer surfaces for the conditions tested.

Even if the outlet temperature from the heat exchanger is well above freezing, deposit buildup can occur inside a heat exchanger. This effect can be insidious, as runaway freeze up can sneak up on the control system if it is not properly configured.

The performance graph for Syltherm XLT shows that one of the thermocouples indicates the presence of frozen deposits even when the outlet fluid temperature is -90˚F (-68˚C). Syltherm XLT freezes well below -90˚F, at -168˚F.

As the Syltherm XLT is progressively cooled to approximately -100˚F inlet and -110˚F outlet, another region in the heat exchanger experiences a condition of freezing and defrosting. When the fluid is cooled further to -110˚F inlet, that region freezes entirely.

The freezing and defrosting condition

Table 1. Heat Transfer Fluid Properties

	Methanol	Syltherm XLT	Dynalene MV	HFE 7000
Conventional units				
Reported freeze point	-143.5˚F	-168˚F	<-200˚F	<-188.5˚F
Specific gravity	0.867	0.97	0.93	1.732
Specific heat, Btu/pounds ˚F	0.515	0.368	0.338	0.224
Thermal conductivity, Btu/hour feet ˚F	0.147	0.0795	0.094	0.0576
Viscosity, cP	6.1	33.7	20	4.9
SI units				
Reported freeze point	-97.5˚C	-111˚C	<-129˚C	<-122.5˚C
Density, kg/cu. m.	867	968.3	930	1732
Specific heat, kilojoules per kilogram ˚Kelvin	2.15	1.541	1.41	0.946
Thermal conductivity, W/meter ˚Kelvin	0.2544	0.1324	0.159	0.0974
Viscosity, milliPascals seconds	6.1	33.7	20	4.9

is imperceptible by a control system monitoring heat transfer fluid outlet temperature. The freezing/defrosting condition occurs because as the ice begins to form, local velocity increases, increasing the local heat transfer coefficient and changing the temperature distribution near the ice surface. A warmer condition is created at the deposit surface, melting the deposit. Not until the fluid temperature is lowered is the temperature differential sufficient to overcome the defrosting condition.

Take note of how different the thermocouple-measured temperature is between an unfrozen and frozen condition. The thermocouple measures a temperature at the heat transfer surface of approximately -150˚F when deposits are not present.

When a deposit is formed, it represents a step change in temperature. The temperature drops very quickly to approximately -275˚F. The solid is an insulator. Warm heat transfer fluid cannot readily conduct heat through the deposit. Therefore, the surface temperature under the deposit approaches the liquid nitrogen coolant temperature.

Dynalene MV, a fluid that has a reported freeze point of less than -200˚F, actually froze at a temperature comparable to Syltherm XLT's freeze point of -168˚F. It is not clear why this occurred; therefore, further testing/analysis is needed. Nevertheless, Dynalene MV is comparable to Syltherm XLT in terms of a practical operating temperature without freezing, even though it is reported to have a lower freeze point.

HFE 7000 was the best fluid tested for the purposes of the test. It could reach the coldest temperature without loss of performance as a result of freezing. Furthermore, HFE 7000 has a very low viscosity, even at cold temperatures, which keeps pressure drop across the heat exchanger low. For the conditions of the test represented in the graph, HFE 7000 could run at an inlet of approximately -140˚F. The fluid underwent freezing and defrosting; however, the unit performed well.

Methanol worked well for temperatures above -130˚F. Because it is a single component, it had the most stable thermocouple-measured temperatures. Dynalene MV, Syltherm XLT and HFE 7000 are mixtures. They are composed of a number of different fluids, with each having varied freeze points. Methanol cannot reach the cold temperatures that HFE 7000 can; however, it does perform well at temperatures above -130˚F.

Figure 1. 15,000-pph Syltherm XLT/300 pph LN2 (59 psia)
96C6C-16S Heliflow - Heat rejection 36,000 to 40,000 Btu/hr.

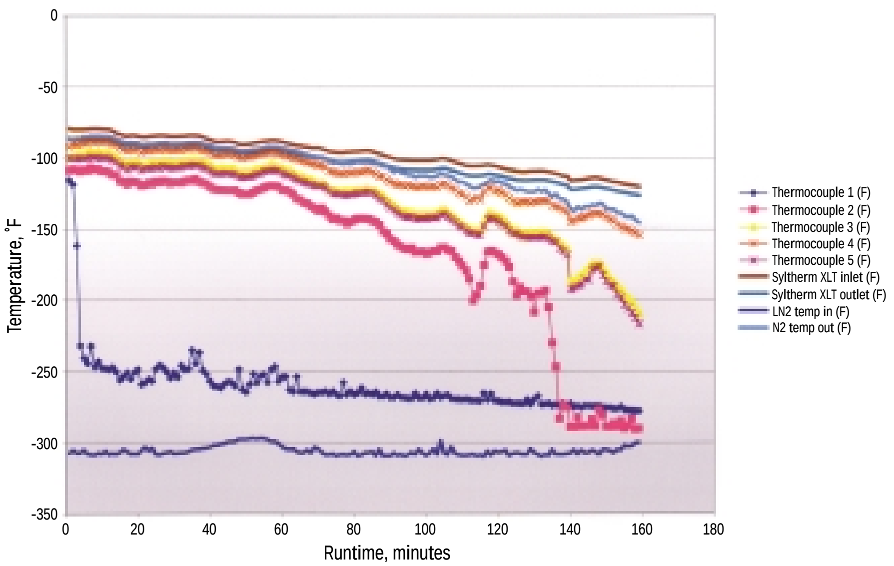
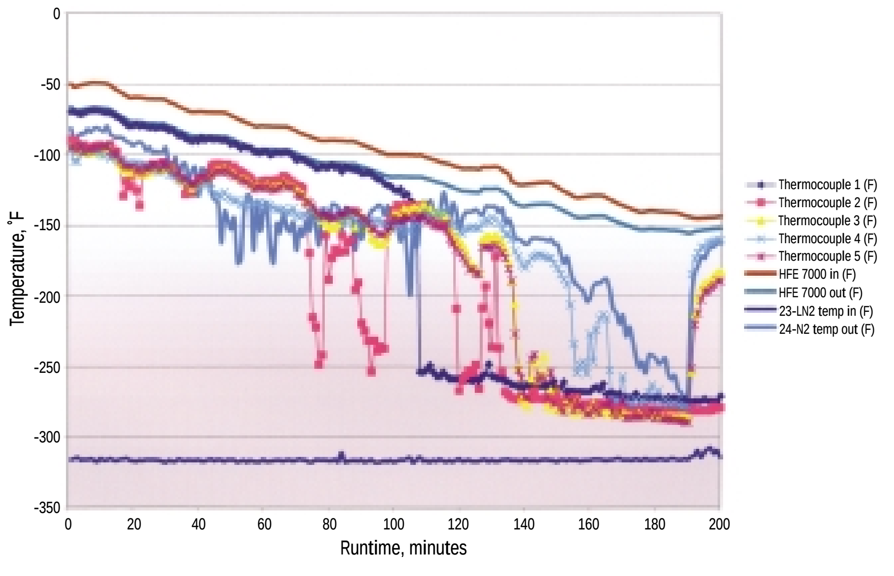


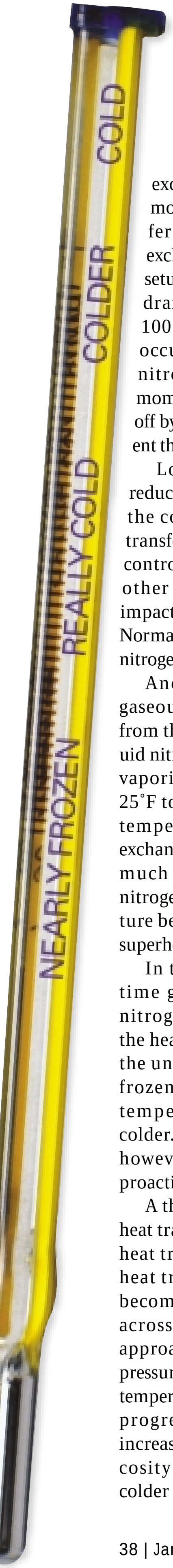
Figure 2. 15,000-pph HFE7000/500 pph LN2 (59 psia)
96C6C-16S Heliflow - Heat rejection 60,000 to 70,000 Btu/hr.



Monitoring heat exchanger performance

Freezing can occur inside a heat exchanger even if the heat transfer fluid temperature out of the exchanger indicates the temperature is well above freezing. A control system that measures heat transfer fluid outlet temperature is unreliable. It is not a good way to avoid freezing. Runaway freezeup is likely to occur when this type of control is used.

The ideal way to monitor heat



exchanger performance is via thermocouples attached to the heat transfer surface; however, not all heat exchangers lend themselves to such a setup. When a thermocouple senses a dramatic drop in temperature, say 100˚F or more, freezing already is occurring at that location. Liquid nitrogen flow rate can be lowered momentarily until the deposit is driven off by the change in temperature gradient that will result.

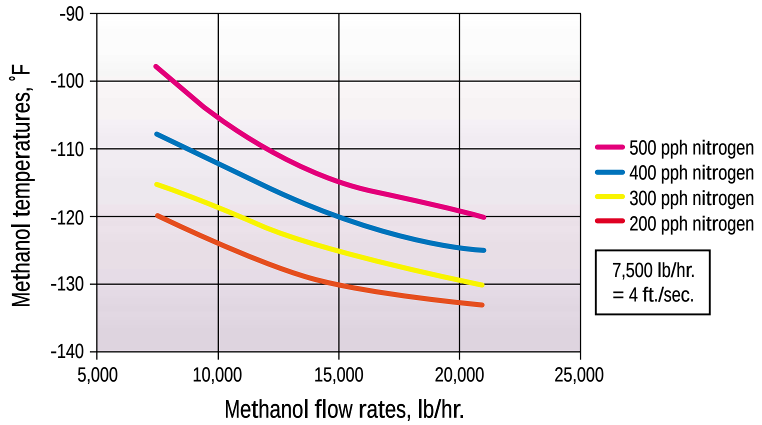
Lower liquid nitrogen flow rate reduces the heat transfer coefficient on the coolant side, warming the heat transfer surface. This type of proactive control is excellent and far better than other reactive methods. It does not impact heat rejection by the exchanger. Normally, one or two minutes of reduced nitrogen flow are all that is needed.

Another option is to measure gaseous nitrogen outlet temperature from the heat exchanger. Normally, liquid nitrogen enters the exchanger and is vaporized and superheated to within 25˚F to 40˚F of the heat transfer fluid temperature. As deposits form, the exchanger becomes less efficient. Not as much heat is given up to the liquid nitrogen. The nitrogen outlet temperature becomes colder as the amount of superheating is reduced.

In the HFE 7000 temperature vs. time graph, note how the gaseous nitrogen temperature diverges from the heat transfer fluid temperature. As the unit develops progressively more frozen deposits, the nitrogen outlet temperature becomes colder and colder. This type of control will work; however, it is a reactive rather than a proactive control.

A third control option is to measure heat transfer fluid pressure drop. As the heat transfer fluid solidifies onto the heat transfer surfaces, flow passages become restricted and pressure drop across the exchanger increases. This approach is harder to control because pressure drop does increase as operating temperature becomes colder. As a fluid is progressively cooled, its viscosity increases. Certain fluids have steep viscosity vs. temperature curves in the colder operating range. The increase in pressure drop could be the result of increased viscosity, not freezing.

Figure 3. Methanol Practical Operating Range – Heliflow Heat Exchanger Nitrogen Pressure at 60 psia



Practical operating ranges

Each fluid has a particular practical operating limit in coiled tube heat exchangers. A coiled tube exchanger offers the lowest practical operating temperature. Shell-and-tube exchangers have warmer practical limits as a result of maldistribution of flow on the shell-side and localized areas of low velocity. Freeze occurring in these regions will compromise exchanger performance.

Brazed plate heat exchangers also will have warmer limits because the thermal efficiency of a plate heat exchanger maximizes the heat transfer fluid and liquid nitrogen heat transfer coefficient — which normally is what is desired — however, here it causes premature freezing. Also, the narrow passages in a plate heat exchanger make it extremely susceptible to runaway freezeup. Under this condition, performance is lost very quickly, and the unit freezes solid. No heat transfer occurs, and a reaction or freeze-drying batch must be discarded.

What influences performance

Once a fluid is selected, steps can be taken to maximize performance and improve cold temperature operation. For example, heat transfer fluid velocity is extremely important. A higher velocity is better than a lower one. Fig. 3 shows when liquid nitrogen flow is 300

Table 2. Heat Transfer Fluid Comparison

	Methanol	Syltherm XLT	Dynalene MV	HFE 7000
Fluid velocity ft./sec. (m./sec.)	8.4 (2.6)	7.5 (2.3)	7.8 (2.4)	4.2 (1.3)
Reynolds number	3,160	571	960	3,900
Prandtl number	52	377	174	46

Table 3. Practical Operating Limits in Coiled Heat Exchangers

Fluid	Practical temperature limit,˚F (˚C)
Methanol	-110 to -130˚F (-79 to -90˚C)
Syltherm XLT	-115 to -125˚F (-82 to -87˚C)
Dynalene MV	-115 to -130˚F (-82 to -90˚C)
HFE 7000	-145 to -165˚F (-98 to - 109˚C)

pounds per hour (pph) for a heliflow heat exchanger, at 4 feet per second (ft./sec.) (7,500 pph) methanol could be cooled to -115˚F without freezing occurring. At 6 ft./sec. (11,000 pph). methanol at -121˚F was acceptable. For 8 ft./sec. (15,000 pph) and 12 ft./sec. (21,000 pph), methanol temperatures of -126˚F and -130˚F, respectively, are achievable.

Another possibility is to increase the nitrogen supply pressure. The vaporization temperature of nitrogen varies greatly with pressure.

As operating pressure increases, the boiling temperature increases. A higher boiling temperature will help to keep the heat transfer surface warmer and, consequently, reduce the possibility of freezing the heat transfer fluid. Nitrogen pressure of 150 psia vs. 50 psia can lower the practical operating temperature of a heat transfer fluid by 10˚F to 15˚F.

A third possibility is try to minimize liquid nitrogen usage by maximizing the amount of superheat. Once liquid nitrogen is vaporized, the gas is heated (superheated) in the exchanger. The closer the nitrogen gas outlet temperature is to the heat transfer fluid temperature, typically, the colder the heat exchanger is able to operate. A lower nitrogen flow will reduce the nitrogen heat transfer coefficient and cause the heat transfer surface to be warmer. This approach helps to avoid freezing.

From the Methanol Practical Operating Range graph, at 15,000 pph of methanol (8 ft./sec.), 200 pph of nitrogen allowed the temperature of the heat transfer fluid to reach -130˚F without freezing. For 300 pph nitrogen, it is -125°F. At 400 pph and 500 pph nitrogen flow, -120°F and -115°F, respectively, were the coldest temperatures without incurring freezing.

Figure 4. 15,000-pph Dynelene MV/300 LN2 (59 psia)
96C6C-16S Heliflow - Heat rejection 36,000 to 40,000 Btu/hr.

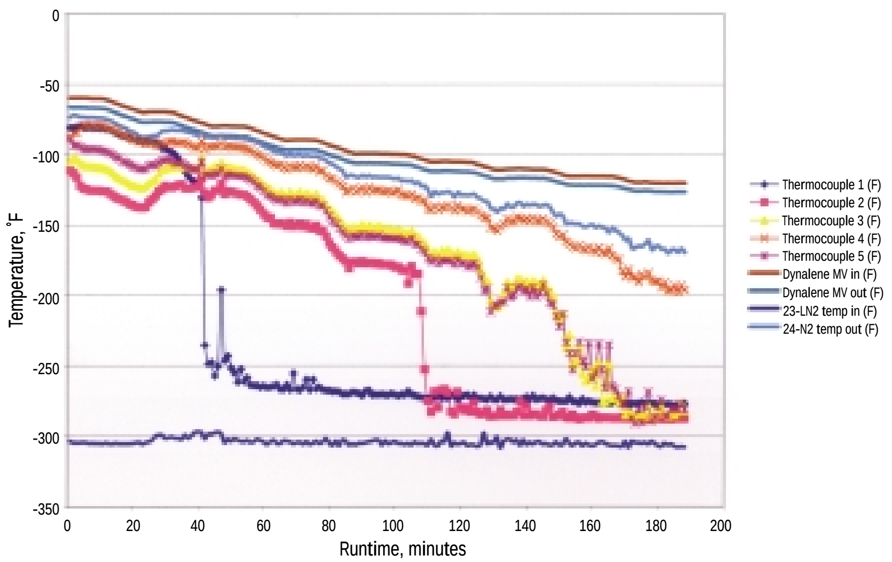
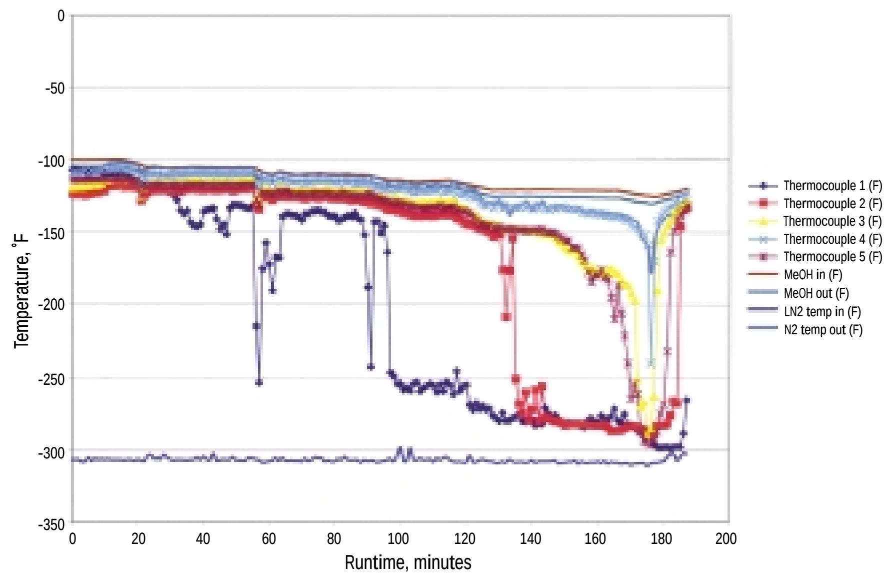


Figure 5. 15,000-pph MeOH/300 LN2 (59 psia)
96C6C-16S Heliflow - Heat rejection 38,000 Btu/hr.



Conclusion

Low-temperature applications in which heat transfer fluid temperatures are below -100˚F (-73˚C), are challenging. Plants must consider more than the heat transfer fluid freeze point. The physical properties of the fluid, the type of heat exchanger and nitrogen supply conditions play key roles in satisfactory performance. Cold operation is possible; however, special care with heat transfer fluid selection, the control system to monitor freezing and heat exchange design are important. **CP**

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