# CRYSTAL COMFORT NEWSLETTER December 2010 Prepared by Joseph DeMaio

As part of Crystal Comfort's continued effort to educate owners and operators of Absorption equipment and keep you advised of ways to run your chiller more effectively, we have prepared the enclosed report. This article titled, "Why Absorption Chillers Fail", appeared in <u>Plant Engineering</u>, <u>VOL. 55 NO. 12</u>. It was printed December 1, 2001. Always remember, single-effect, high-pressure and gas-fired Absorbers that are well maintained will run more efficiently and thus save the owner in energy costs. Using service procedures that we have worked diligently to perfect, we can help you save money and avoid downtime!

# Why Absorption Chillers Fail

Lithium bromide based absorption refrigeration is a viable system capable of providing large-tonnage central air conditioning. Water is flash boiled under vacuum at low temperatures. This boiling action cools evaporator or chilled water coils. As the flashed water vapor accumulates inside the chiller, vacuum is lost. Lithium bromide is added to absorb the water vapor, maintaining the vacuum condition.

Diluted lithium bromide cannot continue to absorb water and must be reconstituted to perpetuate the cycle. Reconstituted lithium bromide is returned to absorb water once more, and the boiled-off water is returned to be flashed again. The cycle is then complete.

This thermodynamic cycle would be relatively simple were it not for the fact that lithium bromide, at 50% concentration, is highly corrosive to mild steel. The corrosion process inside absorbers dissolves the chiller from the inside and creates all kinds of maintenance difficulties as the heat exchanger and flash boiling components become fouled with corrosion debris.

The only moving parts in an absorber are the various solution pumps, which circulate the fluids. Even so, it is not uncommon to find, after several years of operation, that many absorbers are performing poorly, cost disproportionate dollars to maintain, and are ready to be scrapped.

#### How Absorbers Deteriorate

Air, or more specifically oxygen, is the culprit. As air leaks into any absorption chiller, it introduces oxygen, which in turn provides the cathodic reaction essential for any metal to corrode in aqueous systems.

As oxygen dissolves in water, it releases free electrons into solution. These free electrons are readily consumed as the ferrous, or iron-containing, metals dissolve, forming first rust and later the magnetic, black iron oxide commonly found abundantly inside all absorption chillers.

An occasional air leak isn't sufficient for dissolving enough iron to plug the fine orifices of spray headers and heat exchangers, causing the chiller to fail. Instead, it is the continuous air leak that causes so much damage in lithium bromide- based systems.

A basic air leak, once stopped, prevents more oxygen from getting into the aqueous system. The corrosion process merely stops by itself.

Since the absorption chiller is very dependent upon its internal vacuum being maintained, loss of vacuum from an air leak will cause system failure. The leak would have to be detected and stopped before a vacuum was restored and the unit placed back on line.

In the real world, absorbers are tricky to maintain. These chillers require specialized service personnel who are not readily found. Absorption maintenance by a qualified mechanic is a type of wizardry unto itself. Listening to the various unique chiller noises, knowing what they mean, touching the external surfaces, sensing internal temperatures and flows, and peering into the chiller's sight glass are highly developed skills essential to understanding the unit's operation.

When a chiller is failing, usually on a 90+ degree day, there just isn't enough time to hunt down troublesome air leaks and fix them properly. An external vacuum pump can be attached to the absorber's purging mechanism. This will augment the vacuum so significantly that, in some cases, the absorber can even operate with a huge hole in its shell.

If air leaks aren't stopped, the system ultimately fails. The unit continues to work because the external pump maintains its vacuum artificially. However, the corrosion becomes intense from the continuous supply of oxygen into the lithium bromide charge. The external vacuum pump, at first the unit's savior, has now turned into its worst nightmare.

### **Chemical Additives**

There is another reason leading to the demise of absorption chillers -- improper solution chemistry. There have been many attempts to deal with this chemical problem by adding various inhibitors to the lithium bromide charge.

All that is needed to produce the refrigeration cycle is lithium bromide and water, but over the years, additional chemicals get added to the brine. These commonly include:

- 48% hydrobromic acid
- lithium hydroxide
- lithium nitrate
- lithium chromate
- lithium arsenate
- lithium molybdate.

Each compound has been introduced in an attempt to control internal corrosion. And while each chemical does have some effect on internal corrosion, without proper and continuous monitoring of the lithium bromide's chemistry, the chemical addition can actually do more harm than good.

There are essentially two metals inside an absorption chiller. These are the iron or ferrous-based metals in the steel shell, etc., and the copper or cuprous-based metals of the heat transfer tubes. Each of these metals reacts with oxygen and corrodes under different conditions, and protecting one metal usually causes the other to suffer.

The ferrous metals are attacked at low pH and solution alkalinity levels while the cuprous components are spared, and vice versa. It becomes a tradeoff trying to protect one metal or the other. A delicate balance needs to be established where both metals can be simultaneously saved. This requires chemical expertise.

Hydrobromic acid and lithium hydroxide modify the solution's pH and alkalinity. The acid lowers these values while the hydroxide increases them. Other chemicals (nitrate, chromate, arsenate, and molybdate) are specific inhibitors mainly designed to protect the ferrous metals.

The cuprous metals are naturally protected at low pH and low solution alkalinities. It is the ferrous metals that suffer under these conditions. If low pH and alkalinity are maintained in the lithium bromide brine, all that is needed is an inhibitor to protect the steel.

Nitrate works by increasing the formation of iron oxide commonly found in all absorbers. The idea is that this oxide will coat the steel surface and prevent additional corrosive attack. It is a good concept, except that the oxide layer becomes too thick, ultimately falling off the steel into the solution.

This debris then fouls all of the internal orifices, causing significant problems. There is no way to control the amount of iron oxide produced when lithium nitrate is added. The oxide layer continues to accumulate.

As the nitrate is consumed, it forms ammonia. Corroding steel generates hydrogen gas. Hydrogen reacts directly with nitrate, reducing it to ammonia. Ammonia is very harmful to cuprous materials. It increases the overall corrosion rate of copper-based metals and can be a component of more exotic corrosion failures, such as stress corrosion cracking.

Because nitrate has the ability to "calm" an absorption chiller by scavenging the corrosion-generated hydrogen gas, service personnel, attempting to keep chillers operating, have overused it. A casual addition of a pound or two of extra nitrate into a chiller, while it may initially help to restore lost vacuum, ultimately speeds up the chiller's demise.

Similar to lithium nitrate is lithium arsenate. Used only in early two-stage chillers, the arsenic didn't really solve any corrosion problems. Since it did not produce ammonia in the system, the copper tubes were spared from stress corrosion failures. But the arsenic equivalent to ammonia is arsine gas, and this causes stress-related failures in some stainless steel tubing. Also, since arsine is toxic, its application was very short lived in absorption chemistry.

Lithium chromate and lithium molybdate protect steel without the formation of ammonia or iron oxide. They don't scavenge hydrogen gas formed when the iron corrodes. They stop iron from corroding in the first place. These are effective corrosion inhibitors in brine systems such as lithium bromide.

Since chromates are pollutants, their usage has been highly reduced over the years. However, it is still quite reasonable to apply chromates in closed systems such as absorption chillers, since nothing is being discharged into the environment. The trend has been toward using molybdate instead. But molybdate isn't as effective a corrosion inhibitor as chromate, and it is a mistake not to utilize chromates where they can be correctly applied.

Lithium bromide corrosion control in absorption refrigeration is a very complex scheme of proper mechanical operation and the balance of added chemicals. What complicates the situation still further is that there aren't a large number of highly skilled personnel available to service absorption systems.

These conditions lead to many absorption machines suffering from severe corrosion. They are performing very poorly at best and many are ready to be scrapped prematurely. But, these machines can be saved.

## Saving An Absorption Chiller

Once an absorption chiller starts to corrode, it can degenerate quickly. Fine particulates of rust, magnetic iron oxide, copper, and copper oxide can easily plug spray header nozzles and heat exchangers, reducing efficiency. A large amount of debris can foul pumps and reduce heat transfer.

When an absorption chiller no longer meets the needs of the facility, owners must consider replacing the unit or continuing to maintain a marginal piece of equipment.

It is not a simple process to remove and replace a chiller. These systems are often very large, requiring that portions of the building housing the chiller be demolished to get the old unit out and the replacement installed.

Often today's replacement may not be available in a size equivalent to the tonnage of the older unit, necessitating additional equipment. There is also the piping retrofit to consider and disposal of the waste lithium bromide.

Faced with such overwhelming considerations, it becomes feasible to look closely into restoration of the old chiller. In order to accomplish this, qualified absorption service personnel capable of dealing with lithium bromide-based refrigeration systems and their chemistries are required.

At an expense of 40-60% of new equipment cost, a deteriorated chiller can be restored. That means it would not be necessary to tear apart a building or refit piping and avoid additional construction costs. With proper mechanical and chemical maintenance, a chiller should last a long time and perform well.

Controlling the lithium bromide corrosion, cleaning up debris, and repairing any mechanical damage is the recipe for saving any absorption machine.

#### Analytical Chemical Analysis For Absorption Chillers

<u>Test</u> <u>Significance</u>

Specific gravity / Lithium bromide Measure of strength of lithium bromide charge. Indicates

operational status of absorber.

Alkalinity / pH Indicator of possible air leakage into chiller. Affects metal

corrosion.

Dissolved copper Measure of corrosion of tubing and / or pump windings.

Dissolved iron / suspended solids Measure of corrosion of steel interior.

Indicates degree of internal fouling.

Lithium nitrate Measure of nitrate inhibitor strength.

Ammonia Indicates amount of nitrate inhibitor reduced to ammonia.

Can indicate the degree of corrosion of copper portions. Indicates potential for stress corrosion cracking of copper

tubing.

Lithium arsenite Measure of arsenite inhibitor strength.

Lithium chromate Measure of chromate inhibitor strength.

Lithium molybdate Measure of molybdate inhibitor strength.

Non-Destructive Testing For Absorption Chillers

<u>Test</u> <u>Significance</u>

Eddy Current Testing Test the integrity & wear of copper tubes

Ultrasonic Thickness Gauge Test the integrity and wear of steel shells & piping