

# New Inhibitor System for Lithium Chloride Dehumidification Systems

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## ABSTRACT

Brewery fermenting and aging cellars are typically held at low temperatures. Unfortunately, frost will build up in the internals of the cooling units, reducing their efficiency and necessitating periodic shutdown for defrosting. It has been the practice of most breweries to use a circulated spray of 40% solution of lithium chloride (LiCl) to absorb the moisture inside the cooling units. This practice ensures that the cellars are dry and mold-free. The problem with these systems is that they will corrode, resulting in a high maintenance expense. FMC Lithium, upon request from numerous customers in the brewing industry and their service partner ChemTreat, Inc., has developed an LiCl system with a unique inhibitor and pH-buffering agent for LiCl dehumidification systems. The proprietary treatment program provides greatly improved results compared with any other inhibitor for LiCl brine. This paper summarizes the problems associated with LiCl brine treatment (focusing primarily on systems in breweries). Results of LIMIT<sup>®</sup> 301 product trials are summarized. Conclusions are offered as to the benefits of this new system for wet dehumidifiers.

**Keywords:** corrosion inhibitors, dehumidification, lithium chloride

## SÍNTESIS

Las cavas de fermentación y de maduración cervecera típicamente se mantienen a temperaturas bajas. Desafortunadamente, se tiende a formarse una escarcha en las partes internas de las unidades de enfriamiento, reduciendo su eficacia y necesitando de paradas periódicas para su descongelamiento. Ha sido práctica común en la mayoría de las cervecerías de utilizar una llovizna de una solución al 40% de cloruro de litio (LiCl) para absorber la humedad dentro de las unidades de enfriamiento. Esta práctica garantiza que las cavas se mantienen secas y libres de mohos. El problema con estos sistemas es que se corroen, ocasionando un alto costo de mantenimiento. La empresa FMC Lithium, a solicitud de numerosos clientes en la industria cervecera y de su socio de servicio, ChemTreat, Inc., ha desarrollado un sistema LiCl con un inhibidor novedoso en conjunto con un agente amortiguador de pH para sistemas de deshumidificación con LiCl. Este programa de tratamiento patentado da muy buenos resultados comparado con cualquier otro inhibidor de salmuera de LiCl. Este papel resume los problemas asociados con el tratamiento de salmuera de LiCl, enfocado a los sistemas usados en cervecerías. Se presenta un resumen de resultados de pruebas industriales utilizando LIMIT<sup>®</sup> 301. Se presentan conclusiones en cuanto a los beneficios de este nuevo sistema para sistemas de deshumidificación.

**Palabras claves:** inhibidores de corrosión, deshumidificación, cloruro de litio

## Introduction

Most U.S. breweries and a number of food and chemical plants accomplish air dehumidification in process areas with a lithium chloride (LiCl) salt solution (4). While LiCl offers superior desiccant performance compared with other salt or glycol solutions, numerous problems have occurred in air dehumidification systems during past operation. Corrosion of structural components and heat exchangers has cost some breweries millions of dollars in capital expenditures for equipment replace-

ment. Huge sums of money can be spent annually replacing brine lost because of excessive corrosion.

In addition to equipment corrosion, deposition of a variety of metal salts can occur in heat exchangers, reducing the efficiency of the dehumidification equipment. Some companies have even switched to less-efficient glycol systems in an effort to minimize these problems.

Chemical suppliers have attempted to prevent corrosion and deposition in LiCl brines with minimal success. Molybdate-based corrosion inhibitors have limited effectiveness because of solubility problems in cold LiCl brine. Deposit control agents normally used in closed systems may not prevent deposition in heat exchangers in the hot sections of the brine system.

## Equipment Corrosion

Corrosion of equipment is the biggest single problem facing owners of LiCl brine systems. Most of these systems are designed to operate in the 20-30% LiCl concentration range. While this solution itself is mildly corrosive, lower brine strengths and air stream contaminants can have a devastating effect on the corrosion of mild steel, admiralty, and copper metallurgies.

Figure 1 (2) shows the effect of brine strength on mild steel corrosion rates for uninhibited brine in a laboratory environ-

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ment and for brine in an actual system from a U.S. brewery. This indicates that lower brine strengths are not only less effective as dehumidification agents but are also more corrosive to equipment, both in laboratory and actual system brines.

Many breweries are constantly scrubbing carbon dioxide from the air in brewing areas, with LiCl brine as the desiccant. Sulfur and nitrogen compounds present in chemical plants are also removed via air scrubbing. All of the above contaminants serve to lower the pH of the LiCl brine, further increasing corrosion rates. Figure 1 shows the effect of these contaminants in an actual system at a major U.S. brewery, in which low pH causes iron oxides to quickly accumulate in these solutions as a result of excessive corrosion. Turbidity drastically increases, and physical corrosion (erosion) of system metallurgy may result.

A variety of measures have been employed in an attempt to reduce this corrosive tendency. One of the most popular measures has been to avoid using metallic components.

Newer desiccant systems use chlorinated polyvinyl chloride (CPVC) and fiber-reinforced polymer (FRP) components to replace carbon steel, galvanized, or copper-alloyed metallurgy where possible. However, nonmetallic components cannot be used in high-temperature areas, so there will always be metallurgy that must be protected from corrosion.

Exotic alloys such as copper nickel blends and even titanium have been used in heat exchangers and other high-temperature areas where plastics cannot be used. These components are cost prohibitive to most customers. Many breweries have mistakenly accepted the fact that heat-exchanger replacement is inevitable on a routine basis.

Another way to reduce corrosion is to maintain high brine strength, since more-concentrated (30%) LiCl brine is less corrosive than weaker concentrations (Fig. 1). Customers were encouraged to simply maintain higher brine strengths as a solution to corrosion problems. This actually does reduce corrosion to the 6-12 mm per year range in most systems; however, in breweries, this tactic can prove to cause another problem in the hot areas of the system, namely the deposition of metallic salts.

## Use of Corrosion Inhibitors

Molybdates, silicates, borates, and various organic phosphorus compounds have been used in a variety of combinations in an attempt to lower corrosion rates in LiCl systems. These attempts have met with limited success, especially in lower-strength brines (less than 25%), which are commonly present in most breweries. Corrosion rates can be lowered by using these techniques, but not lowered sufficiently to handle periodic upsets (contaminants) or to guarantee long-term equipment life. In addition, solubility problems and foaming tendencies in LiCl prevents the use of products such as nitrite, borate, azoles, and silicates at sufficient concentrations to remedy corrosion.

## Deposition

The formation of tenacious deposits in dehumidification systems can reduce heat transfer to the point that the systems must frequently be taken off line and acid-cleaned, further reducing equipment life with each cleaning.

While pH depression in the LiCl desiccant solution will cause corrosion, pH elevation from certain contaminants will lead to the deposition of metal salts such as lithium or zinc carbonate.

Iron oxide, or silicate, deposits may also occur when pH excursions occur and when certain contaminants are present in the recirculating air being dehumidified by the LiCl solution. Where do these contaminants come from? Ammonia refrigeration is commonly used in breweries, food plants, chemical plants, and other facilities in which a large square footage of refrigeration is required. Ammonia gas from this equipment may be scrubbed from air by LiCl solutions. Ammonia contamination of LiCl will cause pH elevation commensurate with the degree of ammonia present.

Carbon dioxide gas evolution is an inherent part of the brewing process, and CO<sub>2</sub> is one of the natural components of the air we breathe. CO<sub>2</sub> is scrubbed from plant air and can form acidic solutions or alkaline salts based on the presence of other contaminants. When ammonia and CO<sub>2</sub> are present in the air being dehumidified, the localized brine pH may be elevated and various carbonate salt deposits may occur, especially on heat-exchanger surfaces.

Lithium, zinc, and ammonium carbonate are all very insoluble, tenacious deposits that drastically impede heat transfer, reducing the operational capability and efficiency of the system.

The primary problem in attempting to use chemicals to prevent this type of deposition is that very few polymeric dispersants are soluble in these brine solutions to the degree needed. LiCl solution temperatures can range from 30°F in the dehumidifying areas to more than 150°F when the brine moisture is being evaporated to reconstitute the solution strength.

In addition to deposition on heat exchangers, hard scale deposits form on equipment internals, periodically sloughing off as "chip scale," which can accumulate to an extent that brine supply lines become blocked with this debris.

From a summary of the above problems, one can easily understand why a new approach to LiCl brine corrosion and deposit prevention is needed. It is also easy to see why some corporations were switching to less-efficient glycol systems for dehumidification. While glycol can accomplish dehumidification, LiCl performs the equally important function of cleaning the plant air via its strong desiccant properties. This is especially important in low-temperature areas such as brewing storage and aging cellars.

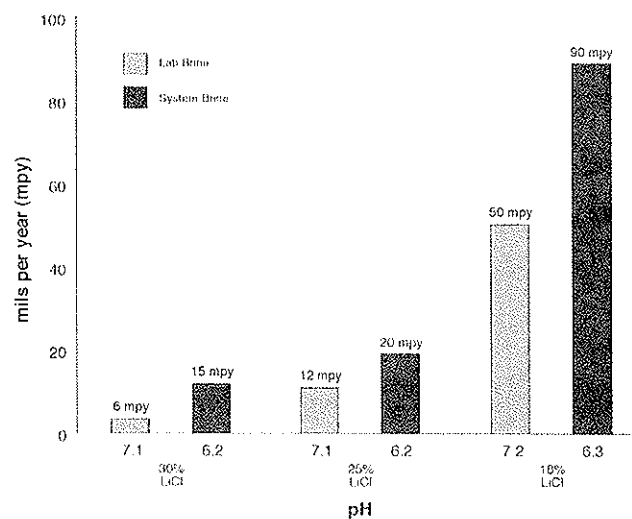


Figure 1. Effect of brine strength on mild steel corrosion rates in millimeters per year (mpy).

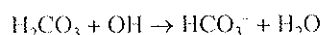
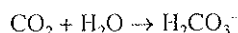
## Brine Corrosion, Deposit Control, and What Works

FMC Lithium developed a system for all strengths of LiCl desiccant solutions. Working in conjunction with ChemTreat, Inc., and a major U.S. brewery for product testing, a field test on a large, wet LiCl air dehumidification system took place for the last two plus years, with exceptional results.

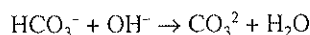
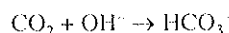
The proprietary formulation incorporates a corrosion inhibitor coupled with a pH-buffering agent. The active ingredients remain soluble throughout the LiCl concentration ranges.

### Inhibitor-Buffer System (LIMIT® 301)

The FMC approach to solving the corrosion problem in LiCl brines involves dual mechanisms of pH stabilization plus corrosion inhibition. Carbon dioxide is a common contaminant that reacts rapidly with alkalinity in the brine solution. This reaction may dramatically reduce brine pH via the formation of carbonic acid or bicarbonate (at pH <8.0).



Under alkaline conditions ( $\text{NH}_3$  contamination) with pH >10,  $\text{CO}_2$  reacts to form a bicarbonate and a carbonate as follows:



The effect of  $\text{CO}_2$  on pH becomes more predominant and pH depression occurs more rapidly as the LiCl brine strength is lowered to 25%. Buffering additives can provide significant capacity to resist pH reduction in these solutions (5).

Actual field test results of the addition of pH-buffering agents are illustrated in Figure 2, in which pH stabilization (6.8–7.0) was achieved upon additive addition on day 44.

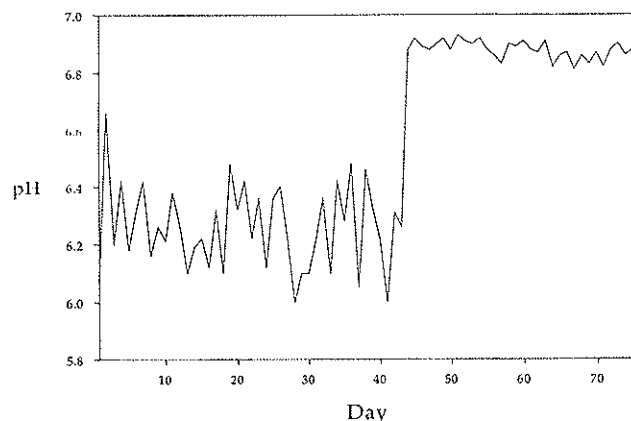


Figure 2. pH of lithium chloride solution versus days.

Table 1. Corrosion rates of mild steel in lithium chloride-aerated solution<sup>a</sup>

| Additive          | Corrosion rate (millimeters per year) |
|-------------------|---------------------------------------|
| None              | 10.6                                  |
| Lithium molybdate | 5.3                                   |
| LIMIT® 301        | 0.6                                   |

<sup>a</sup> In lithium chloride-aerated solution (25 wt. %, pH ~8.5) at 37.8°C for 4 weeks.

## Corrosion Inhibition

In addition to pH neutralization, which lowers acidic corrosiveness, additional protection is needed because of the aggressive nature of LiCl toward metals. Another component, an inhibitor, was added to the LiCl solution to provide protection for metal components. Test results for mild steel and copper are shown in Tables 1 and 2 (1,3,5).

Carbon steel coupons were placed in an actual system and showed significantly decreased corrosion in comparison to uninhibited LiCl and molybdate-inhibited LiCl. Field observation of heat-exchanger surfaces after extended LIMIT® 301 service showed little visible corrosion and no buildup of carbonates on the tube surfaces.

### Turbidity

Solution turbidity is a result of carbonate and bicarbonate formations in the LiCl and of metal corrosion. Neutralizing the pH greatly reduces the formation of carbonates and bicarbonates, thereby reducing acidic metal attack. LiCl metal corrosion attack is controlled through the addition of a combination of a pH buffer and a corrosion inhibitor. Figure 3 highlights the reduced average turbidity upon the addition of the additive in May.

### Conversion of Existing Systems

Existing LiCl systems that have been treated with other products are easily converted to the LIMIT® 301 program via a two-step process.

- The pH buffer and inhibitor are added as separate products to initially charge the system. Both products are compatible with all lithium and molybdate treatments.
- Subsequent treatment simply involves ordering additional replacement LIMIT® 301 LiCl brine.

There is a simple test kit and a more-detailed laboratory test for verification of the proper concentrations of pH buffer and corrosion inhibitor in treated systems.

Table 2. Corrosion rate of copper in lithium chloride-aerated solution<sup>a</sup>

| Additive          | Corrosion rate (millimeters per year) |
|-------------------|---------------------------------------|
| Lithium molybdate | 5.0                                   |
| LIMIT® 301        | 2.0                                   |

<sup>a</sup> In lithium chloride-aerated solution (25 wt. %, pH ~8.5) at 37.8°C for 4 weeks.

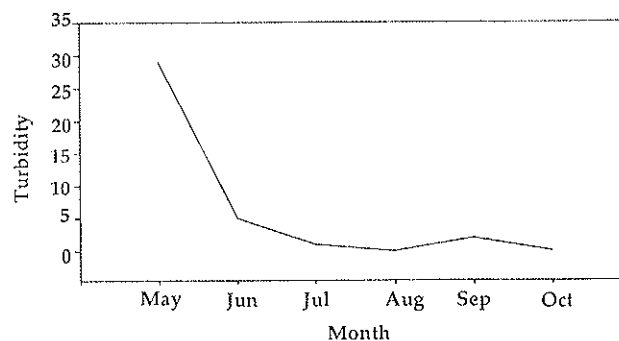


Figure 3. Average turbidity versus month.

## Conclusion

An extensive field test demonstrated the superior performance of FMC Lithium's LIMIT® 301 LiCl solution. Improved asset life and machine life cycle cost are realized through:

- Reduced replacement component cost as a result of reduced corrosion;
- Reduced formation of unwanted contaminants that build up on heat-transfer surfaces and reduce efficiency;
- Reduced filtration cost as a result of reduced solids;
- Eliminated leaks, previously a result of corrosion;
- Reduced LiCl solution cost through reduced leaks; and
- Lower cost of materials of construction (carbon steel versus high alloy metals and plastic resins).

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