30 January 1936 NRL Report No. P-1234

NAVY DEPARTMENT

BUREAU OF ENGINEERING

FR-1234

First Partial Report

on

Investigation of Dehumidifying Agents for Submarines - Characteristics of Various Drying Agents

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D.C.

Number of Pages: Text - 15 Plates - 2

Authorization: BuEng. ltr. NP14 (5-6-W8) of 12 July 1935.

Date of Test: 5 August to 23 December 1935.

Prepared by:
J.O. Clayton, Contract Employee.

Reviewed by:
P. Borgstrom, Chemist, Superintendent,
Chemistry Division.

Approved by:
H.M. Cooley, Captain, USN, Director.

Distribution:
BuEng. (1)
BuC&R (5)

ejj

APPROVED FOR PUBLIC RELEASE - DISTRIBUTION UNLIMITED

TABLE OF CONTENTS

APPENDIX I

ABSTRACT

In order to ascertain the suitability of various substances for dehumidifying the air of submarines or other closed spaces, measurements will be found in this report on the amount of water absorbed by calcium chloride, lithium chloride, and mixtures of calcium chloride with other chlorides.

Values of the quantities of water absorbed at equilibrium are given for various desiccants.

The rates of absorption of water by calcium chloride and lithium chloride are given.

The data in this report show that both calcium chloride and lithium chloride are effective drying agents, and that there is no advantage to be gained by using mixtures of calcium chloride with other chlorides.

INTRODUCTION

(a) Authorization

1. This problem was authorized by Bureau of Engineering letter NP14 (5-6-W8) of 12 July 1935.

(b) Statement of Problem

2. The purpose of this investigation is to determine the characteristics of chemical drying agents to be used for the dehumidification of air in closed spaces. Only solid drying agents were investigated, although in all cases solutions were formed by absorption of water from the air. The economics, weight, safety, and ease of regeneration will be discussed in the next report. The rates of absorption and final equilibrium values of the ratio of weight of water absorbed to weight of desiccant, were investigated. The experimental work covered in this report deals with calcium chloride, lithium chloride, and mixtures of calcium chloride with other metallic chlorides.

(c) Known Facts Bearing on the Problem

3. It is known that solids or solutions will absorb water from air if the vapor pressure of water above the substance in question is lower than the partial pressure of water vapor in the air.

4. Vapor pressure data of solutions of all of the commoner drying agents exist in the literature.* From these data, the weight of desiccant in forming a solution which will be in equilibrium with the water vapor in the air at a given relative humidity can be calculated. This is done by plotting the change in vapor pressure with the concentration of the solution at a given temperature, and reading the concentration from the curve, which corresponds to the vapor pressure of water in the air. The ratio of weight of water absorbed to weight of drying agent for a given relative humidity is very nearly independent of temperature, as can be seen from the results of Table 1.

---

* International Critical Tables, Vol. III, page 294 et seq.

TABLE 1

RATIO OF WATER TO DESICCANT*

Substance	78% R.H.	°C.	60% R.H.	°C.	40% R.H.	°C.
Aluminum Chloride	4.0	100	2.6	100	2.3**	100
Calcium Chloride	3.4	0	2.2	0	1.6	0
	3.3	40	2.1	40	1.4	40
	3.2	70	2.1	70	1.4	70
Ferrous Chloride	1.7	100	1.2	100		
Lithium Chloride	5.3	0	3.4	0		
	5.2	40	3.2	40	2.1**	
	5.1	60	3.2	60		
Magnesium Chloride	4.1	30	2.5	30		
	4.1	40	2.5	40	1.4**	
	4.2**	50	2.5	50		
Magnesium Nitrate	2.3	100				
Manganous Chloride	2.0	100				
Potassium Carbonate	1.9	30	1.2	30	0.8**	30
	1.9	40	1.2	40	0.9**	40
Potassium Hydroxide	3.9	20	2.4	20	1.6	20
Potassium Nitrite	1.5	100	0.6	100		
Potassium Phosphate (monobasic)	0.5	100				
Potassium Thiocyanate	1.2	40				
Potassium Thiosulphate	0.9	100	0.5**	100		
Sodium Carbonate	1.7**	30				
Sodium Chromate	1.3	100				
Sodium Hydroxide	4.8	20	3.0	20	2.1	20
Sodium Nitrite	2.1	100	1.0	100		
Sodium Thiocyanate	2.3	100	1.3	100	0.8**	100
Zinc Chloride	1.4	100	0.9	100	0.7**	24.6
					0.7**	29.6
					0.6**	100

* International Critical Tables, Vol. III, p. 294 et seq.
** Extrapolated.

5. From Table 1 it is apparent that the only substances which will absorb more water per unit weight than calcium chloride are: aluminum chloride, lithium chloride, magnesium chloride, potassium hydroxide, and sodium hydroxide. Aluminum chloride has properties which render it of little use as a drying agent. In contact with water it hydrolyzes to a great extent liberating **irritating** hydrochloric acid gas according to the following equation:

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl$$

Both sodium and potassium hydroxide present disagreeable features. The concentrated solutions are quite caustic, and can severely burn the skin. The substances also absorb carbon dioxide forming carbonates which are greatly inferior drying agents and which impair the effectiveness of the hydroxide. For these reasons no experimental work was carried out on aluminum chloride, sodium hydroxide, or potassium hydroxide. The experimental work was thus limited to calcium chloride, lithium chloride, magnesium chloride and various mixtures. The results on magnesium chloride will appear in another report.

(d) Original Work at this Laboratory.

6. The rates at which water is absorbed under various conditions were determined for calcium chloride, lithium chloride, and mixtures of calcium chloride with several other chlorides. This was accomplished by placing the drying agent in a closed chamber (desiccator) in which a certain relative humidity was maintained by means of water or saturated salt solutions. Rates were measured at the following relative humidities:

100%	(water)
78%	(saturated ammonium chloride)
60%	(saturated ammonium nitrate)
42%	(saturated potassium carbonate)

The rates of absorption were also determined at various temperatures.

METHODS AND DATA OBTAINED

(a) Preparation of Materials.

7. Lithium Chloride.

L-2. Lithium chloride was partly dehydrated by long continued heating in a porcelain vessel. On analysis for chloride ion, by Mohr's method, this substance was found to contain 97-99% LiCl. The hydrolysis was very slight, the amount of LiOH being less than 0.1%.

L-3. The above lithium chloride was fused by heating it well above its melting point. It was analyzed for LiOH, which was found to be 0.11%.

8. Calcium Chloride.

C-1. This was a commercial product in flake form analyzing 97.3% $CaCl_2$. It was slightly alkaline.

C-2. This was prepared in this Laboratory by evaporating solutions to dryness and breaking the resulting cake into small lumps. The frothy material on the surface was scraped off and discarded. The product analyzed as follows:

$CaCl_2$	96.5%
CaO	0.16%
H_2O (difference)	3%

C-3. The above calcium chloride (C-2) was fused by heating it above its melting point. The substance was not analyzed.

9. Mixtures. The following mixtures were investigated:

Components			
A	B	%B	Remarks
Calcium Chloride	Aluminum Chloride	10	Mixed mechanically in dry state and heated slightly.
" "	Antimony Trichloride	10	ditto
" "	Barium Chloride	10	Fused to clear liquid.
" "	Beryllium Chloride	10	Added solution of B to solid A, heated slightly. Hydrolysis occurred with evolution of some HCl.
" "	Cadmium Chloride	10	Fused to liquid.
" "	Calcium Bromide	10	" " "
" "	Chromic Chloride	10	" " "
" "	Chromous Chloride	10	Mixed in solid state. Heated slightly. Some oxidation occurred.
" "	Cobalt Chloride	10	Fused to liquid.
" "	Cupric Chloride	10	" " "
" "	Ferric Chloride	10	Heated together in solid state. Some oxidation occurred.

(Continued)

Components A	 B	%B	Remarks
Calcium Chloride	Ferrous Chloride	10	Heated together in solid state. Some oxidation occurred.
" "	Lithium Chloride	10	Fused to liquid.
" "	Lithium Chloride	50	" " "
" "	Manganous Chloride	10	" " "
" "	Nickel Chloride	10	" " "
" "	Potassium Chloride	10	" " "
" "	Sodium Chloride	10	" " "
" "	Strontium Chloride	10	" " "
" "	Zinc Chloride	10	Mixed in solid state. Heated slightly. Some hydrolysis occurred.

(b) Description of Experiments.

10. The absorption values given for calcium chloride and lithium chloride were checked experimentally in this Laboratory at a relative humidity of 78%. This was done by placing solutions of different concentrations in a closed vessel over saturated ammonium chloride solution. This latter solution has a vapor pressure equivalent approximately to a 78% relative humidity at room temperature. The solutions of lithium chloride had the following values for the ratio of water to anhydrous salt: 5.30, 5.26, 5.10, and 5.06. For calcium chloride the same ratios were: 3.50, 3.40, 3.29, and 3,20. All of these solutions lost weight and by plotting the loss of weight of water against the ratio, the straight line so obtained intercepted the change of weight axis at 5.02 for lithium chloride and at 3.11 for calcium chloride, thus checking the values in the literature within the limits of experimental error.

11. The same experiment was carried out in the case of a fused mixture consisting of 50% calcium chloride and 50% lithium chloride. In this case the results indicated that at 78% relative humidity the ratio of water absorbed to weight of drying agent was 4.0. The average value for lithium chloride and calcium chloride is 4.07, indicating that in the fused mixture the two salts behave independently of each other.

12. The rate of absorption is dependent on a great many factors, and to eliminate these as much as possible, only comparison values were used. Calcium chloride, in about the same state of subdivision, was always placed in the closed vessel with the other drying agent to be investigated. Even these comparison values could not be reproduced to better than about 10%, so small effects were ignored.

TABLE 2

RATE OF ABSORPTION OF WATER

Substance (X)	Compared with	Temp.	Ratio $H_2O/CaCl_2$ Rel. Humid.	Ratio $\frac{H_2O}{X} / \frac{H_2O}{CaCl_2}$														Final Value (Equilibrium)
				.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	3.8	
LiCl (L-2)	CaCl (gran.)	Room	100	1.35	1.28	1.30	1.71	2.17	2.09	2.00	1.88	1.77	1.68	1.59	1.54	1.51	1.56	1.6
LiCl (L-2)	CaCl (gran.)	Room	42	1.25	1.20	1.57												1.6
LiCl (L-2)	CaCl (gran.)	Room	60	1.10	1.23	1.25	1.86	1.96	1.76	1.60	1.53							1.6
LiCl (L-2)	CaCl (gran.)	Room	78	1.10	1.43	1.41	2.06	2.09	1.90	1.73	1.62	1.53	1.50					1.6
LiCl (L-2)	CaCl (gran.)	4°C.	80	1.52	1.53	1.60	1.61	1.77	1.75									1.6
LiCl (L-2)	CaCl (gran.)	4°C.	80	1.15	1.20	1.18	1.13	1.11	1.12	1.21								1.6
LiCl (L-2)	CaCl (gran.)	38°C.	78	1.17	1.20	1.22	1.20	1.21	1.25	1.26	1.30	1.34	1.36	1.39	1.37	1.36		1.6
LiCl (L-2)	CaCl (gran.)	24°C.	78	1.25	1.25	1.27	1.23	1.21	1.23	1.21	1.22	1.26	1.30	1.33				1.6
LiCl (L-3)	CaCl (fused)	Room	78	2.65	2.85	2.72	2.53	2.28	2.06	1.88	1.71							1.6

TABLE 2 (Continued)

			Ratio $H_2O/CaCl_2$	Ratio $\frac{H_2O}{X}$ / $\frac{H_2O}{CaCl_2}$														
Substance (X)	Compared with	Temp.	Rel. Humid.	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	3.8	Final Value (Equilibrium)
$LiCl-CaCl_2$ 50%	CaCl (fused)	Room	78	2.95	2.88	2.63	2.30	2.00	1.78	1.60	1.46							1.3
$CaCl_2$ - $MnCl_2$ 10%	CaCl (fused)	Room	78	1.61	1.41	1.33	1.28	1.24	1.20	1.16	1.06							1.0*
$CaCl_2$ - $CoCl_2$ 10%	CaCl (fused)	Room	78	1.67	1.50	1.40	1.32	1.28	1.24	1.18	1.07							
$CaCl_2$ - $AlCl_3$ 10%	CaCl (gran.)	Room	78	1.17	1.13	1.10	1.09	1.08	1.06	1.04	1.02	1.01						1.0*
$CaCl_2$ - $SbCl_3$ 10%	CaCl (gran.)	Room	78	1.14	1.19	1.23	1.16	1.11	1.07	1.04	1.00	0.97						
$CaCl_2$ - $BeCl_2$ 10%	CaCl (gran.)	Room	78	0.96	0.99	1.00	1.00	1.00	1.00	1.00	0.98	0.94						
$CaCl_2$ - $CrCl_2$ 10%	CaCl (gran.)	Room	78	0.68	0.62	0.64	0.69	0.75	0.77	0.79	0.84	0.91						
$CaCl_2$ - $FeCl_3$ 10%	CaCl (gran.)	Room	78	1.02	1.04	1.04	1.04	1.04	1.03	1.01	0.99	0.96						
$CaCl_2$ - $FeCl_2$ 10%	CaCl (gran.)	Room	78	1.03	0.99	0.97	0.97	0.98	1.00	1.00	0.98	0.98						0.95*
$CaCl_2$ - $ZnCl_2$ 10%	CaCl (gran.)	Room	78	1.03	1.07	1.13	1.06	1.04	0.98	0.92	0.87	0.82						0.95*

TABLE 2 (Continued)

Substance (X)	Compared with	Temp.	Ratio $H_2O/CaCl_2$ / Rel. Humid.	Ratio $\frac{H_2O}{X}$ / $\frac{H_2O}{CaCl_2}$ .2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	3.8	Final Value (Equilibrium)
$CaCl_2$ - $LiCl$ 10%	$CaCl_2$ (fused)	Room	78	1.23	1.25	1.27	1.27	1.27	1.27	1.26	1.21	1.15						1.1*
$CaCl_2$ - $BaCl_2$ 10%	CaCl (fused)	Room	78	0.90	0.93	0.94	0.94	0.94	0.93	0.93	0.94	0.94						
$CaCl_2$ - $CrCl_3$ 10%	CaCl (fused)	Room	78	1.11	1.11	1.09	1.07	1.04	1.02	1.01	1.00	0.98						
$CaCl_2$ - $CdCl_2$ 10%	CaCl (fused)	Room	78	0.99	1.03	1.01	1.00	1.00	1.01	1.00	0.98	0.96						
$CaCl_2$ - $CuCl_2$ 10%	CaCl (fused)	Room	78	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00							
$CaCl_2$ - $NiCl_2$ 10%	CaCl (fused)	Room	78	0.94	0.96	0.97	0.98	0.98	0.98	0.98	0.97							
$CaCl_2$ KCl 10%	CaCl (fused)	Room	78	1.13	1.13	1.11	1.11	1.11	1.09	1.05	1.00							
$CaCl_2$ - $NaCl$ 10%	CaCl (fused)	Room	78	0.98	1.00	0.98	0.98	0.98	0.97	0.96	0.93							
$CaCl_2$ - $SrCl_2$ 10%	CaCl (fused)	Room	78	0.93	0.92	0.90	0.89	0.89	0.89	0.88	0.88							
$CaCl_2$ - $CaBr_2$ 10%	CaCl (fused)	Room	78	1.14	1.11	1.10	1.10	1.10	1.08	1.06	1.02							

TABLE 2 (Continued)

			Ratio $H_2O/CaCl_2$	Ratio $\frac{H_2O}{X}$ / $\frac{H_2O}{CaCl_2}$														
Substance (X)	Compared with	Temp.	Rel. Humid.	.2	.4	.6	.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	3.8	Final Value (Equilibrium)
$CaCl_2$ - (fused)	CaCl (gran.)	Room	78	0.60	0.59	0.60	0.64	0.70	0.78	0.86								1.0
$CaCl_2$ - LiCl 50%	CaCl (gran.)	Room	78	1.23	1.40	1.48	1.50	1.48	1.45	1.42								1.3
$CaCl_2$ - LiCl 10%	CaCl (gran.)	Room	78	1.12	1.16	1.19	1.22	1.24	1.24	1.24								1.1*
$CaCl_2$ - $CoCl_2$ 10%	CaCl (gran.)	Room	78	0.75	0.80	0.84	0.87	0.90	0.92	0.94								
$CaCl_2$ - $MnCl_2$ 10%	CaCl (gran.)	Room	78	0.73	0.70	0.70	0.73	0.78	0.84	0.91								1.0*

---

* Calculated value.

13. The results show that in the solid state the rate of water absorption is approximately constant, and in the case of the solutions the rate falls off, such that the ratio of weight of water absorbed to weight of desiccant approaches the equilibrium value asymtotically. Table 2 gives values of the comparison of the various desiccants with calcium chloride. The figures give the ratios of the water absorbed per unit weight of calcium chloride at various intervals. Due to the many uncontrolled factors influencing the time-rate of absorption values, these values are given at various increments in the quantity of the amount of water absorbed by the calcium chloride used as a comparison standard, rather than at various time intervals. The last column gives the value of the ratios after equilibrium has been reached. This table shows that the rate of absorption of water by lithium chloride is considerably faster than the rate of absorption by calcium chloride, especially in the preliminary stages of absorption. Comparing the two substances in the fused state, the rate of absorption by lithium chloride is two to three times that of calcium chloride.

14. In the case of the mixtures of calcium chloride and other chlorides, the initial rate is sometimes raised somewhat, but after the solid has dissolved in the absorbed water the rate drops off rapidly, approaching the equilibrium value. A few of the substances investigated lowered the rate of absorption appreciably. This was especially true in the case of barium chloride, strontium chloride, and chromous chloride. The chromous chloride used had oxidized somewhat and the chromic oxide or oxychloride may have formed a film on the surface of the calcium chloride, decreasing the rate of absorption. None of the mixtures investigated warranted further study except those containing lithium chloride.

15. The mixture of calcium chloride with lithium chloride containing 50% by weight of each constituent, proved to have an initial rate about as great as that of pure lithium chloride. (In the one experiment tried the initial rate was considerably greater.) However, this rate soon fell off and approached a value about equidistant between that of calcium chloride and lithium chloride. Solutions containing varying concentrations of this equiweight mixture were placed in a closed vessel above saturated ammonium chloride solution, and the final equilibrium value was obtained as previously mentioned. This value was 4.0, the same as the average of the values for calcium chloride and lithium chloride. The saturated solution of the mixture was also investigated. It was analyzed by evaporating a known weight to dryness, fusing, weighing the residue, and determining the chloride ion by Mohr's method. The following results were obtained:

$LiCl$ 0.65 moles)
$CaCl_2$ 0.36 moles) per 100 grams of water

The solubility of each of the pure salts in water is:

$LiCl$ 1.85 moles per 100 grams of water
$CaCl_2$ 0.65 moles per 100 grams of water

The common ion effect in the mixture thus lowers the solubility of lithium chloride considerably. The vapor pressure of the saturated solution of the mixture was then compared with that of a saturated solution of lithium chloride, by placing the two solutions in small crucibles in an empty, dry, closed vessel. Water distilled from the solution of the mixture to the solution of lithium chloride, indicating that the latter had the lower vapor pressure. In 49 hours there had been a transfer of about .15 gram of water, and as the weighings were made to an accuracy of .001 gram, the effect was much larger than the probable error. The only possible advantage to be gained in using an equiweight mixture of calcium chloride and lithium chloride is a high initial rate of absorption which, however, rapidly falls below that of pure lithium chloride. Aside from this very slight effect the mixture behaves as though the two components were independent.

16. This latter effect holds true in the case of all of the mixtures investigated, as is apparent from the change in rate as the absorption progresses. In every case the rate of absorption approaches a value which would be predicted by a consideration of the equilibrium values of the two components, considering that no inter-action takes place on mixing them. Usually there is a slight increase in the initial rate of absorption, but this effect is relatively small. In view of these facts, there is no advantage in the use of mixtures of calcium chloride with other chlorides, over the use of pure calcium chloride or pure lithium chloride.

(b)(1) Effect of Varying Humidity on Absorbing Power of Desiccants.

17. Weighed samples of calcium chloride and lithium chloride were placed in containers, above solutions of ammonium chloride, ammonium nitrate, and potassium carbonate, and were weighed at time intervals to study the rate of absorption of water. As long as solid desiccant was present, the rate of absorption should be proportional to the vapor pressure of water because the concentration of calcium chloride would remain constant. This proved to be the case as the following results indicate. The weight of water absorbed per gram of drying agent was plotted against the time, and the slope of the resulting straight line was measured for each humidity. The rate of absorption was assumed to be given by equations of the type $\frac{\Delta R}{\Delta t} = Kp$, where $\frac{\Delta R}{\Delta t}$ is the rate, K is a constant, and p is the pressure. The constant was determined by substituting the rate of absorption at 78% relative humidity in the equation, assuming a vapor pressure of 20 cms. for saturated air. The calculated rates at the other humidities were then compared with the measured rates. The equation for lithium chloride is:

$$\frac{\Delta R}{\Delta t} = 0.000596\ p$$

and for calcium chloride is:

$$\frac{\Delta R}{\Delta t} = 0.000391\ p$$

Table 3 gives the comparisons.

TABLE 3

Lithium Chloride ($\Delta R/\Delta t = 0.000596\,p$)

Relative humidity	78	60	42
Saturated salt solution used	Ammonium Chloride	Ammonium Nitrate	Potassium Carbonate
Vapor pressure of water	15.6 cms.	12.0 cms.	8.4 cms.
$\Delta R/\Delta t$(observed)	0.0093	0.0070	0.0050
$\Delta R/\Delta t$(calculated)	0.0093	0.0071	0.0050

Calcium Chloride ($\Delta R/\Delta t = 0.000391\,p$)

Relative humidity	78	60	42
Saturated salt solution used	Ammonium Chloride	Ammonium Nitrate	Potassium Carbonate
Vapor pressure of water	15.6 cms.	12.0 cms.	8.4 cms.
$\Delta R/\Delta t$(observed)	0.0061	0.0054	0.0031
$\Delta R/\Delta t$(calculated)	0.0061	0.0047	0.0033

The values of the constants in the above equations have no physical significance and would vary from one determination to another because the rate of absorption is dependent on many factors besides the vapor pressure of water. However, the results conclusively show that the speed of drying would decrease proportionately with the relative humidity in the case of the solids.

18. In the case of the solutions formed, the rate of **absorption** should be proportional to the product of the vapor pressure of water and the concentration of calcium chloride or lithium chloride in solution, that is -

$$\Delta R/\Delta t = K_1\,(H_2O)\,(LiCl) + K_2$$

The results obtained here show the proportionality of the rate of absorption with the concentration of the desiccant, but sufficient measurements were not made to **accurat**ely determine the relationship in the case of water vapor pressure for the solutions. If the vapor pressure of water is constant, we can write -

$$\Delta R/\Delta t = K_1\,(LiCl) + K_2, \text{ or } \quad \Delta R/\Delta t = K_1\,(CaCl_2) + K_2, \text{ where}$$

$\Delta R/\Delta t$ is the rate of absorption of water, (LiCl) is the concentration of lithium chloride, ($CaCl_2$) is the concentration of calcium chloride and K_1 and K_2 are constants. K_2 will not have the value zero in this case because the rate of absorption approaches zero at some finite concentration of dissolved salt; that is where the vapor pressure of water in the air is in equilibrium with the salt solution. The constants in the above equations were determined from the experimental data, and are as follows:

For lithium chloride $\Delta R/\Delta t = 0.1043\ (LiCl) - 0.0246$

For calcium chloride $\Delta R/\Delta t = 0.04245\ (CaCl_2) - 0.0107$

In both cases the water vapor pressure was constant and had a value of about 15.6 cms.

19. Table 4 shows the agreement between the measured values and the values calculated from the above equations.

TABLE 4

Lithium Chloride			Calcium Chloride		
(LiCl)	$\Delta R/\Delta t$ (observed)	$\Delta R/\Delta t$ (calculated)	($CaCl_2$)	$\Delta R/\Delta t$ (observed)	$\Delta R/\Delta t$ (calculated)
0.476	0.025	0.025*	0.476	0.0091	0.0095
0.435	0.025	0.021	0.435	0.0080	0.0078
0.400	0.018	0.017	0.400	0.0071	0.0063
0.370	0.015	0.014	0.370	0.0044	0.0050
0.333	0.011	0.010			
0.313	0.008	0.008*			

---

* Points used in determining the constants of the equation.

While in the case of the solid the rate of absorption was constant for a given relative humidity, in the case of the liquid the rate fell off as water was absorbed due to the dilution of the desiccant in the resulting solution. This is shown in Plates 1 and 2.

(b)(2) Effect of Varying Temperature on Rate of Absorption.

20. Experiments were carried out at three different temperatures to determine the variation in the rate of absorption with temperature. The anhydrous calcium chloride and lithium chloride were placed in closed vessels above saturated ammonium chloride solutions, and the vessels were then put in a refrigerator or thermostated bath. The temperatures used were approximately $3^{\circ}C.$, $25^{\circ}C.$, and $38^{\circ}C.$ At the low temperature the water absorbed by calcium chloride forms the hexahydrate which freezes solid, and no solution is formed until the desiccant has picked up a weight of water about equal to itself. At these temperatures the rates of absorption had a negligible temperature coefficient, and the rate of absorption for the solid calcium chloride hexahydrate at $3^{\circ}C.$ was the same as would be predicted for the saturated solution. Table 5 shows

the variation of the rate of absorption with temperature. The calculated values were determined by assuming that the temperature coefficient was zero and that the change in rate was proportional to the change in vapor pressure of the water.

TABLE 5

Lithium Chloride - Rate $\Delta H_2O/\Delta t$

$H_2O/LiCl$	3°C.	25°C. (observed)	25°C. (calculated)	37.8°C. (observed)	37.8°C. (calculated)
0.1	0.0077	0.029	0.031	0.07	0.06
0.2	0.0074	0.029	0.031	0.07	0.06
0.4	0.0071	0.029	0.029	0.07	0.06
0.6	0.0069	0.029	0.028	0.07	0.06
0.8	0.0056	0.025	0.023	0.05	0.05
1.0	0.0059	0.022	0.024	0.05	0.05
1.2	0.0063	0.022	0.025	0.05	0.05
1.4	0.0063	0.022	0.025	0.05	0.05
1.6	0.0063	0.018	0.025	0.05	0.05
1.8	0.0063	0.018	0.025	0.05	0.05
2.0	0.0061	0.018	0.025	0.04	0.05
2.5		0.013		0.03	0.03*
3.0		0.008		0.02	0.02*

Calcium Chloride - Rate $\Delta H_2O/\Delta t$

$H_2O/CaCl_2$	3°C.	25°C. (observed)	25°C. (calculated)	37.8°C. (observed)	37.8°C. (calculated)
0.1	0.0057	0.025	0.023	0.050	0.045
0.2	0.0057	0.022	0.023	0.044	0.045
0.4	0.0061	0.025	0.025	0.044	0.048
0.6	0.0059	0.020	0.024	0.044	0.047
0.8	0.0056	0.018	0.023	0.044	0.045
1.0	0.0051	0.018	0.021	0.040	0.041
1.2	0.0042	0.017	0.017	0.033	0.033
1.4	0.0030	0.014	0.012	0.033	0.024
1.6		0.011		0.025	0.022*
1.8		0.010		0.020	0.020*
2.0		0.008		0.018	0.016*
2.2		0.005		0.013	0.010*

In determining the calculated values, the following pressures were used for water vapor:

Temperature °C.	Pressure (mm.)
3.0	4.6
25.0	18.6
37.8	36.6

The figures marked with an asterisk were determined by multiplying the observed results at 25°C. by the ratio 36.6/18.6, and all others by multiplying the observed results at 3°C. by the ratio 36.6/4.6.

CONCLUSIONS AND RECOMMENDATIONS

21. The data included in this report indicate that lithium chloride is superior to calcium chloride as a dehumidifying agent, both from the point of view of rapidity of absorption of water and weight efficiency. However, due to the high price of lithium chloride, the cost of removing water is many times greater in the case of lithium chloride than in the case of calcium chloride. These two substances will be compared with magnesium chloride in a later report and definite recommendations will be made at that time.

SUMMARY

22. This investigation shows that lithium chloride is a better dehumidifying agent than calcium chloride when considering either the rate of absorption of water or the amount of water absorbed at equilibrium. The rate of absorption of water by the former is approximately twice that of calcium chloride under similar conditions, and the final equilibrium value is 1.6 times as great for lithium chloride as for calcium chloride. There is no advantage to be gained by using mixture of calcium chloride with other chlorides.

APPENDIX I

The following tables give all the measurements made in this Laboratory on calcium chloride, lithium chloride, and mixtures. The letter (S) following a figure indicates that the desiccant was in the solid state, and while it may have been moist, no solution had yet run off of the particles. When no letter follows the figure the desiccant was in the form of a solid and solution. The letter (L) following a figure indicates that the drying agent was completely in solution.

		$CaCl_2$-$MnCl_2$ 10%	78	"	.138	.233	1.194			
					45	73	94	188	332.5	502 hrs.
M	11/18	$CaCl_2$(fused)	78	Room	.206	.362	.477	.745	1.22	1.91L

Series	Date of Start*	Substance	Relative Humidity	Temperature	Ratio H_2O/Desiccant								
A	8/23				4	69	93	117	141	165	261	285 hrs.	
		LiCl(L-2)	100%	Room	.0605S	.795	1.118	1.45L	1.74L	1.98L	2.69L	2.84L	
B	8/27				24	48	72	168	193.5	511 hrs.			
		LiCl(L-2)	100	Room	.53S	1.05	2.13L	3.64L	3.89L	6.14L			
		$CaCl_2$(gran.)	100	Room	.42S	.70S	.99	2.36L	2.56L	3.94L			
C	9/5				23	95	119	143	167	191	263	335 hrs.	
		LiCl(L-2)	42	Room	.09S	.31S	.41S	.53S	.65	.79	1.31	1.64L	
		$CaCl_2$(gran.)	42	Room	.08S	.30S	.37S	.45S	.52S	.58S	.64S	.72S	
D	9/5				22.5	94.5	118	142	166	190	262	334 hrs.	
		LiCl(L-2)	60	Room	.15S	.67S	.85	1.32	1.70L	1.91L	2.24L	2.46L	
		$CaCl_2$(gran.)	60	Room	.15S	.56S	.66S	.77S	.88S	1.03S	1.37L	1.64L	
E	9/5				21.5	94	117.5	141.5	165.5	189.5	261.5	333.5 hrs.	
		LiCl(L-2)	78	Room	.19S	.86	1.37	1.77	2.04L	2.28L	2.64L	2.92L	
		$CaCl_2$(gran.)	78	Room	.17S	.61S	.70S	.84S	.99S	1.20	1.70L	1.94L	
F	9/12				25	96	120.5	147	167.5	196.5	268.5	290	460 hrs.
		LiCl(L-2)	80	4°C.	.142S	.48S	.60	.72	.82	.96	1.41L	1.53L	2.22L
		$CaCl_2$(gran.)	80	4°C.	.097S	.32S	.39S	.46S	.52S	.60S	.86S	.91S	1.24
G	9/24				4.5	21	44.5	72	145.5	311 hrs.			
		LiCl(L-2)	80	3°C.	.050S	.174S	.35	.53	.98	1.96L			
		$CaCl_2$(gran.)	80	3°C.	.044S	.150S	.29S	.46S	.88S	1.51			
H	9/24			(100°F.)	4.5	20.5	44.5	72	145.5 hrs.				
		LiCl(L-2)	78	37.8°C.	.270	1.19	2.30L	3.05L	3.71L				
		$CaCl_2$(gran.)	78	"	.230	.98	1.71L	2.20L	2.74L				
I	10/1			(75°F.)	19	49	141	169 hrs.					
		LiCl(L-2)	78	23.9°C.	.60	1.27L	2.77L	3.02L					
		$CaCl_2$(gran.)	78	"	.48	1.05	2.10L	2.25L					

(Continued)

Series	Date of Start*	Substance	Rel. Humid.	Temp.	Ratio H_2O/Desiccant								
					17.5	41.5	113.5	163	191	212	283	**450**	619 hrs
J	11/13	LiCl(L-3)	78	Room	.125S	.290	.642	.955	1.185	1.37L	1.69L	**2.**32L	2.77L
		$CaCl_2$(fused)	78	"	.067S	.127S	.232S	.331	.422	.50	.625	1.03	1.62L
		LiCl-$CaCl_2$ 50%	78	"	.137S	.342S	.700	.987	1.193	1.35L	1.61L	2.04L	2.36L
		$CaCl_2$-$MnCl_2$ 10%	78	"	.088S	.190	.367	.481	.591	.68	.83	1.27L	1.72L
		$CaCl_2$-$CaCl_2$ 10%	78	"	.084S	.188	.385	.511	.629	.72	.87	1.32L	1.73L
K	11/13	$CaCl_2$(gran.)	78	Room	.084	.191S	.401S	.572S	.700S	.80S	.94S	1.34L	1.74L
		$CaCl_2$-$AlCl_3$ 10%	78	"	.099S	.224S	.450S	.627S	.766S	.87S	1.02S	1.41	1.76L
		$CaCl_2$-$SbCl_3$ 10%	78	"	.089S	.217S	.479S	.705S	.835	.93	1.05	1.41L	1.69L
		$CaCl_2$-$BeCl_2$ 10%	78	"	.079S	.185S	.398S	.579S	.704	.81	.94	1.35	1.64L
		$CaCl_2$-$CrCl_2$ 10%	78	"	.059S	.129S	.249S	.366S	.469	.55	.69	1.09	1.59L
		$CaCl_2$-$FeCl_3$ 10%	78	"	.086S	.195S	.416S	.602S	.730S	.83S	.97S	1.37	1.69L
		$CaCl_2$-$FeCl_2$ 10%	**78**	"	**.087**S	.193S	.392S	.551S	.674S	.78S	.91S	1.34	1.73L
		$CaCl_2$-$ZnCl_2$ 10%	**78**	"	**.082**S	.196S	.426S	.638S	.757	.85	.985	1.26L	1.47L
					24.5	48	307.5 hrs.						
L	12/10	$CaCl_2$(fused)	78	Room	.112	.196	1.109						
		$CaCl_2$(gran.)	78	"	.189	.332	1.340						
		$CaCl_2$-LiCl 50%	78	"	.230	.449	1.911						
		$CaCl_2$-LiCl 10%	78	"	.212	.381	1.664						
		$CaCl_2$-$CaCl_2$ 10%	78	"	.141	.259	1.251						
		$CaCl_2$-$MnCl_2$ 10%	78	"	.138	.233	1.194						
					45	73	94	188	332.5	502 hrs.			
M	11/18	$CaCl_2$(fused)	78	Room	.206	.362	.477	.745	1.22	1.91L			
		$CaCl_2$-LiCl 10%	78	"	.253L	.451	.605	.945	1.55L	2.11L			
		$CaCl_2$-$BaCl_2$ 10%	78	"	.185	.335	.450	.699	1.14L	1.79L			
		$CaCl_2$-$CrCl_3$ 10%	78	"	.228S	.406	.529	.796	1.25	1.83L			
		$CaCl_2$-$CdCl_2$ 10%	78	"	.204	.372	.486	.755	1.23	1.82L			
N	11/18	$CaCl_2$(fused)	78	"	.258	.466	.629	1.018	1.69	2.23L			
		$CaCl_2$-$CuCl_2$ 10%	78	"	.258	.472	.630	1.030	1.67L	2.14L			

(Continued)

Series	Date of Start*	Substance	Rel. Humid.	Temp.	Ratio H_2O/Desiccant 45	73	94	188	332.5	502 hrs.
O	11/18	$CaCl_2$(fused)	78	Room	.153	.282	.378	.614	1.00	1.55L
		$CaCl_2$-$NiCl_2$ 10%	78	"	.143	.268	.364	.594	.98L	1.51L
		$CaCl_2$-KCl 10%	78	"	.169	.321	.433	.684	1.12	1.56L
		$CaCl_2$-NaCl 10%	78	"	.149	.281	.376	.601	.98	1.46L
		$CaCl_2$-$SrCl_2$ 10%	78	"	.141S	.262S	.347	.553	.89	1.36L
		$CaCl_2$-$CaBr_2$ 10%	78	"	.176S	.318	.421	.672	1.10	1.59L

* 1935

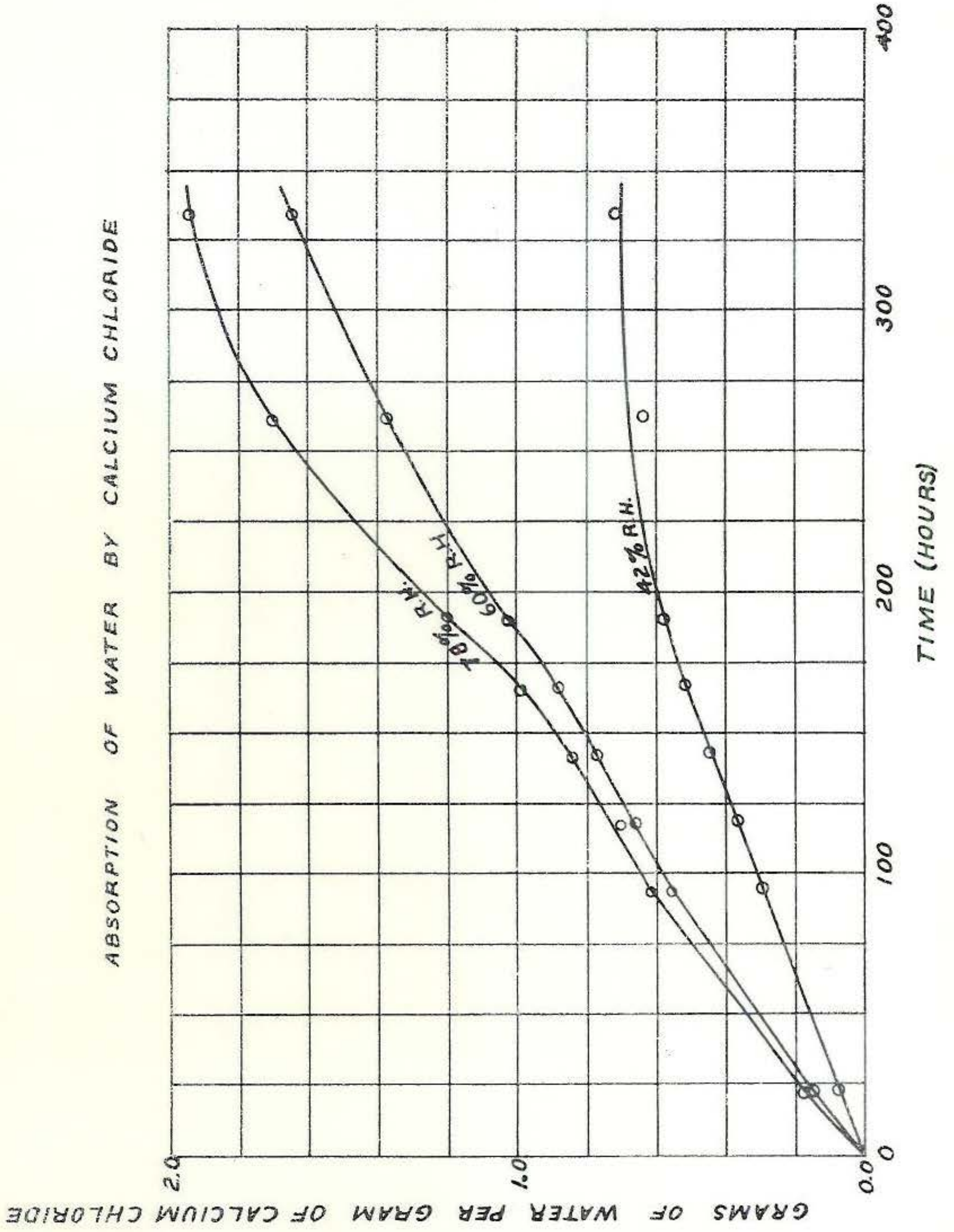
ABSORPTION OF WATER BY CALCIUM CHLORIDE
GRAMS OF WATER PER GRAM OF CALCIUM CHLORIDE
0.0
1.0
2.0
TIME (HOURS)
0
100
200
300
400
78% R.H.
60% R.H.
42% R.H.

PLATE I

ABSORPTION OF WATER BY LITHIUM CHLORIDE

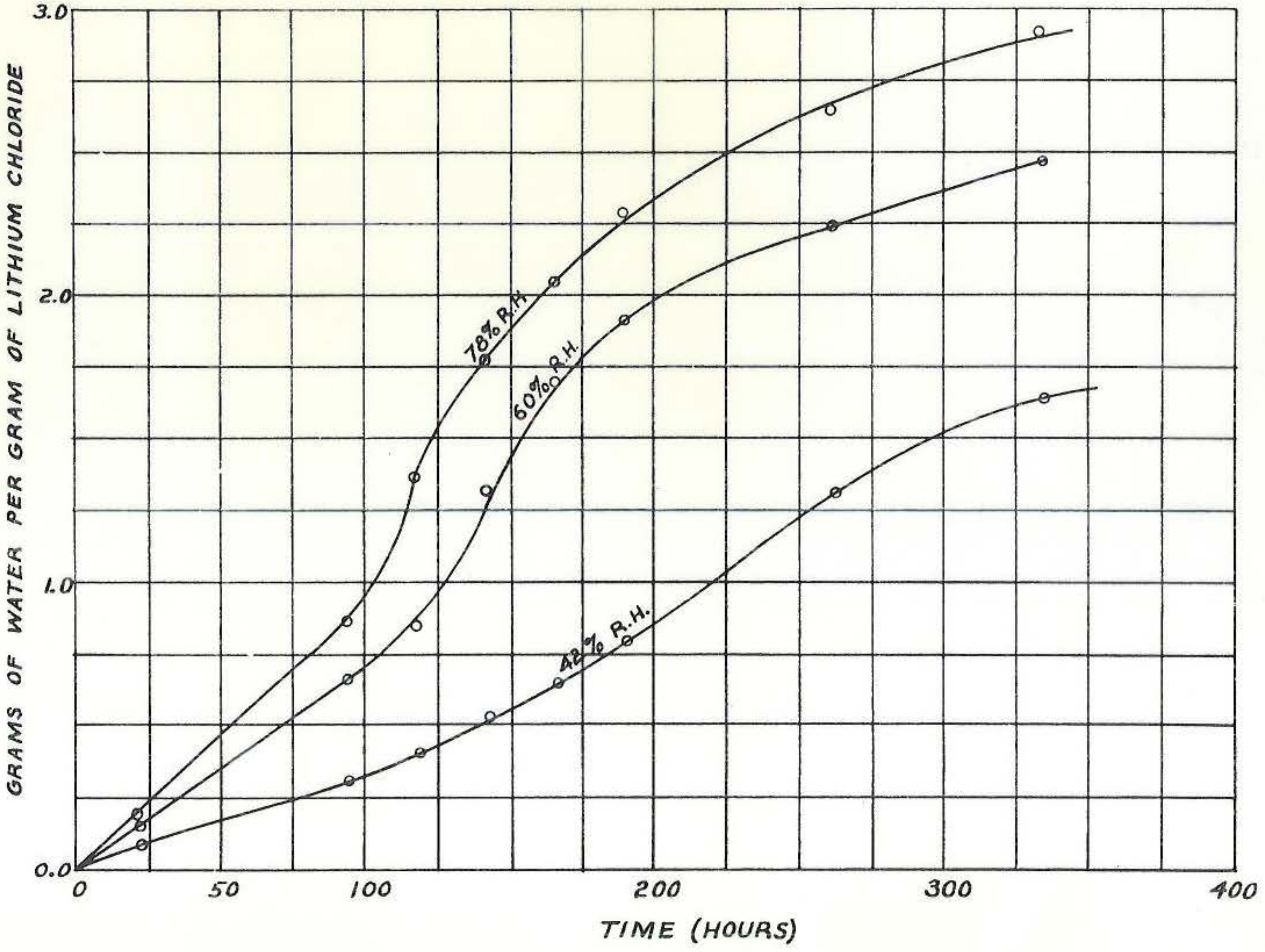

PLATE 2