

Investigation of 1,4-Cyclohexanebis(Methylamine) as a Regenerative Carbon Dioxide Absorbent

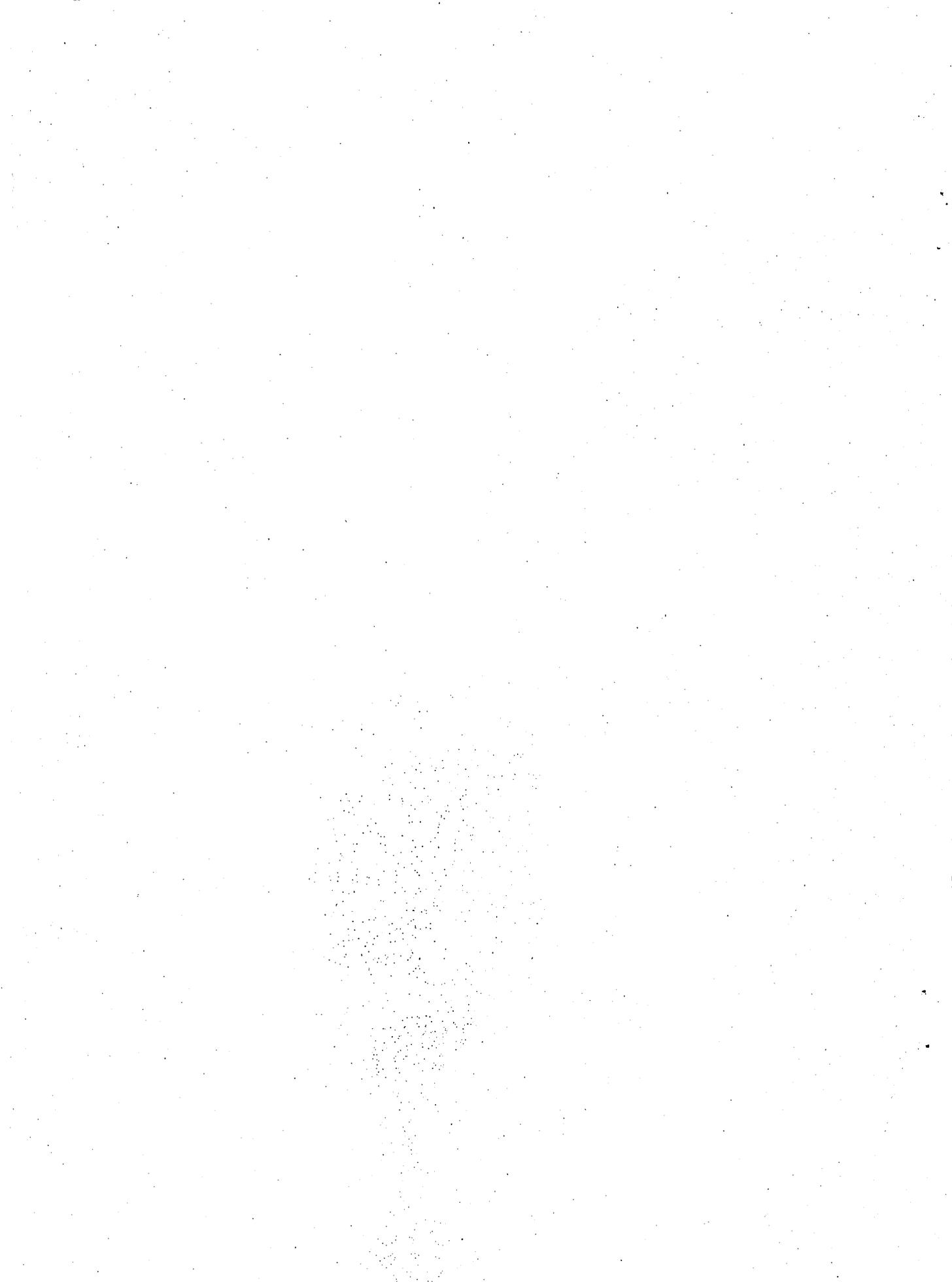
P. R. GUSTAFSON

*Inorganic and Nuclear Chemistry Branch
Chemistry Division*

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NAVAL RESEARCH LABORATORY
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ABSTRACT

The alicyclic diamine, 1,4-cyclohexanebis(methylamine), is an efficient regenerative CO₂ absorbent. Both the CO₂ absorption rate and capacity are equal to that of MEA. The regeneration rate, however, is slightly less. The disadvantages of 1,4-cyclohexanebis(methylamine) as a regenerative CO₂ absorbent are formation of a polymeric-type product when saturated with CO₂ and an inferior oxidation stability. One advantage of the diamine over MEA is its higher boiling point (ca. 240°C compared with 170°C).

PROBLEM STATUS

This is a final report on 1,4-cyclohexanebis(methylamine); work in other areas is continuing.

AUTHORIZATION

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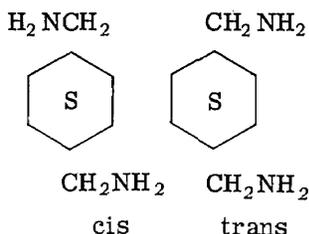
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INVESTIGATION OF 1,4-CYCLOHEXANEBIS(METHYLAMINE)
AS A REGENERATIVE CARBON DIOXIDE ABSORBENT

INTRODUCTION

Monoethanolamine (MEA), the regenerative CO₂ absorbent currently employed, presents problems when scrubbing CO₂ from submarine atmospheres. It is volatile and toxic, has a slow CO₂ stripping rate, tends to foam, resists oxidation poorly, and emits ammonia vapors during oxidative degradation (1).

The Girdler Corporation evaluated amines and other basic compounds (2); following this evaluation various companies have developed new products. One new product is 1,4-cyclohexanebis(methylamine) (CBM). This compound apparently matches MEA's high CO₂ absorption rate and high CO₂ capacity but is less volatile, resists oxidation better, and foams less at the beginning. Its theoretical molecular weight is 142.24, and its stereoisomeric forms are as follows:



For this study we obtained some CBM from Eastman Chemical Products, Inc., with a claimed composition of 40% cis isomer (bp 244 °C) and 60% trans isomer (bp 239 °C) and purity 99% (3). Analysis of this CBM by the Kjeldahl method for total nitrogen and titration of basic nitrogen with HCl on triplicate samples gave an average value of 99.17% amine content.

CHEMICAL AND PHYSICAL PROPERTIES OF CBM
COMPARED WITH MEA

The high pH and high boiling point of CBM compared with MEA (Table 1) are properties that should result in greater CO₂ absorption efficiency and decreased amine volatility.

Table 1
Comparison of Chemical and Physical Properties of CBM and MEA

Absorbent	Theoretical Equivalent Weight	Density (g/cc)		Vol-% Amine in 4.5N Solution	pH of 4.5N Sol.	Boiling Point at 760 mm (°C)
		20/4	4.5N Sol. at 25 °C			
CBM	71.12	0.9419	0.999	34	13.0	239 (trans) 244 (cis)
MEA	61.08	1.018	1.008	27	12.4	170

The viscosities of 4.5N solutions of CBM and MEA (Table 2) were measured by an Ostwald-Fenski viscosity pipette in a constant temperature bath (30°C). The viscosity of CBM is high relative to MEA, particularly the carbonated solutions; the viscosity of a half carbonated CBM solution is already about 1.8 times that of fully carbonated MEA. However, pumping 8-centipoise solutions should not require an intolerable amount of power. On the other hand, precipitation of the carbonated CBM probably will cause difficulties.

Table 2
Comparison of the Viscosities of CBM and MEA

Material	Viscosity of 4.5N Solutions at 30°C	
	Relative	Absolute (centipoises)
Water	1	0.80
CBM	3.67	2.94
MEA	2.35	1.88
CBM carbonated to 50 volumes of CO ₂ absorbed per volume of solution*	10.12	8.10
MEA carbonated to 50 volumes of CO ₂ absorbed per volume of solution	3.08	2.46

*Precipitation started 20 minutes later.

CO₂ ABSORPTION RATE AND CAPACITY

Parallel CO₂ absorption rate studies of 4.5N CBM and MEA solutions were made on 50-ml samples thermostated at 88°F at gas flow rates of 3 liters per minute using air with 3% CO₂ and at 100% R.H. Absorption times were 10, 15, 20, 25, 30, 45, 60, and 90 minutes. The CO₂ contents of the amine solutions at the ends of these periods were analyzed by a gasometric method (2) and checked by integration of the areas under the CO₂ concentration curves recorded by a Liston-Becker CO₂ analyzer.

Figure 1 shows the absorption of CO₂ by CBM and MEA. The amounts of CO₂ absorbed by CBM and MEA per unit time and their total CO₂ capacity under the flow conditions mentioned earlier are summarized in Table 3. Both Fig. 1 and Table 3 show that CBM absorbs CO₂ more effectively than MEA during the first 20 minutes (up to a V_g/V_s of about 33). However, MEA's rate beyond this point becomes slightly superior. One reason may be that a sharp increase in viscosity of the diamine compound occurs during carbonation (Table 2). In one respect, however, the absorption of CO₂ by CBM differs significantly from absorption by MEA—precipitation of CBM carbonate occurs; the precipitate forms readily near the saturation point ($V_g/V_s = 50$), and the quantity of precipitate increases with time until the entire solution is transformed into a solid mass. This solid mass appears to be a sort of condensation product between the CO₂ and diamine. The entire solution however, will not be transformed into a solid cake unless carbonated near its CO₂ capacity. Below this level, a lesser amount of precipitation will occur. The solid product will liquefy if warmed to around 90°C and not reappear on cooling if the solution is stripped of CO₂. This precipitate will also form at V_g/V_s levels as low as 25 on standing undisturbed for several days.

It was found that the precipitation of CBM carbonate could be inhibited by addition of a highly basic amine. MEA gave the best results of several amines tested. With MEA the initial precipitation did not begin until several hours elapsed, whereas normally

Table 3
Carbon Dioxide Absorption Rates and Capacity of 50-ml Samples of CBM and MEA
for a Gas Flow Rate of 3 Liters/Minute (STP), a Contact Temperature of 88°F, and 100% R.H.

Sample	Volume of CO ₂ Gas at STP Absorbed Per Volume of Solution (V _g / V _s) at 5-Minute Intervals													
	5	10	15	20	25	30	35	40	45	50	55	60	90	
CBM 1	8.64	16.89	—	—	—	—	—	—	—	—	—	—	—	
CBM 2	8.73	17.25	25.41	32.94	—	—	—	—	—	—	—	—	—	
CBM 3	8.67	17.07	25.08	32.58	—	—	—	—	—	—	—	—	—	
CBM 4	8.76	17.43	25.86	33.24	39.78	—	—	—	—	—	—	—	—	
CBM 5	8.79	17.34	25.44	32.85	39.18	43.80	46.70	48.36	51.04	—	—	—	—	
CBM 6	8.30	17.28	25.47	33.03	39.63	44.73	47.94	49.79	51.07	52.06	—	—	—	
CBM 7	8.82	17.49	25.80	33.54	40.32	45.57	48.84	50.76	52.14	53.28	—	—	—	
CBM 8	8.76	17.39	25.47	33.18	40.29	46.48	—	—	—	—	—	—	—	
CBM 9	8.79	17.46	25.86	33.72	40.83	46.38	49.92	51.84	53.10	54.06	54.84	55.44	56.34	
Average	8.70	17.29	25.55	33.14	40.00	45.43	48.35	50.19	51.83	53.13	—	—	—	
Av Gasometric	—	16.64	24.61	32.00	40.30	42.87	48.36	49.70	—	52.10	—	—	—	
MEA 1	8.13	16.14	23.94	31.38	38.16	44.04	48.30	50.49	51.57	52.20	52.39	52.70	—	
MEA 2	8.25	16.26	24.27	32.07	39.27	45.51	50.25	52.86	54.00	54.75	55.38	55.95	56.91	
MEA 3	8.40	16.44	24.42	32.13	39.32	45.86	—	—	—	—	—	—	—	
MEA 4	8.22	16.17	24.03	31.61	38.57	44.75	49.73	52.76	54.29	—	—	—	—	
Average	8.25	16.25	24.16	31.80	38.83	45.04	49.43	52.04	53.29	53.48	53.88	54.33	—	
Av Gasometric	—	15.48	—	30.94	—	41.29	—	—	50.30	—	—	—	—	

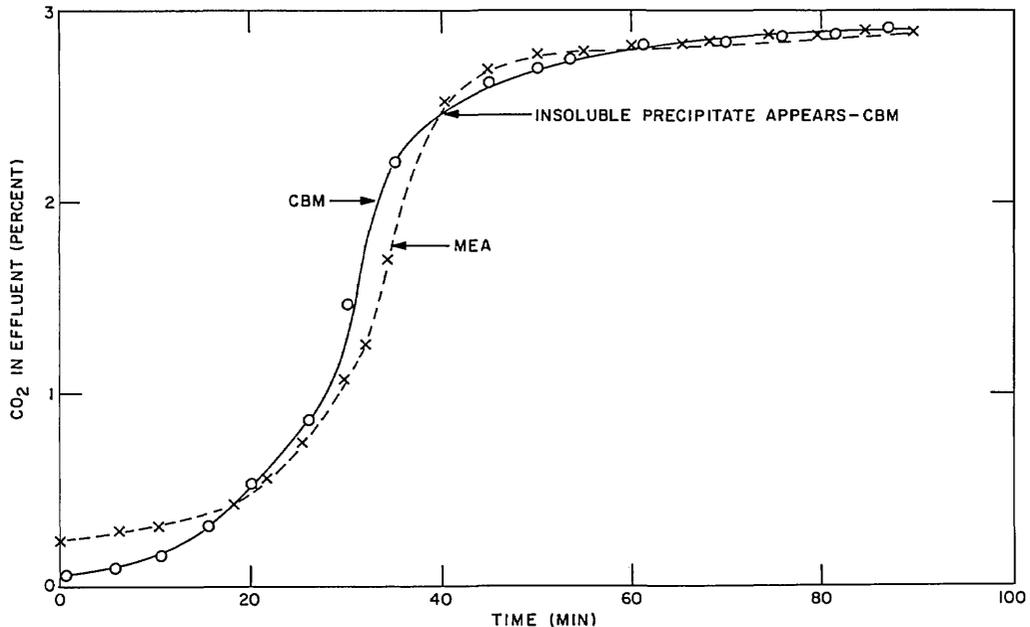


Fig. 1 - Comparison of the absorption of CO₂ by CBM and MEA from air containing 3% CO₂ and at 100% R.H. The gas flow rate was 3 liters/minute (STP) through 50-ml samples at 88° F.

precipitation would occur within 20 minutes. At an equivalence concentration of MEA one-sixth that of CBM (keeping the combined normality of the solution at 4.5N), MEA reduced the viscosity of a CBM precipitation slurry to such an extent that the material could be poured from one vessel to another. This fluid condition persisted beyond a month.

Figure 2 shows the apparatus employed in these CO₂ absorption studies. Air, reduced to a pressure of 3 psi, mixed with CO₂ in the tube of a precision bore flowrater. The CO₂-air mixture then passed through two 125-ml gas washing bottles thermostated at 88° F. The first, contained distilled water and saturated the gas stream, and the second contained 50 ml of the amine being investigated (sample depth was 6 cm). The gaseous effluent then passed through a small condenser and through a 250-ml round bottom flask (A) which divided the gas stream into two fractions. The main stream passed through a wet test meter, while the smaller fraction (ca. 600 ml per minute) passed through a needle valve at (B) and on to a Liston-Becker CO₂ analyzer. The gas pressure drop through the Liston-Becker analyzer was maintained at 2 cm of water maximum by a water-filled pressure relief. After passing through the CO₂ analyzer, the gas joined the main effluent stream at (C). The wet test meter, therefore, measured the entire gas flow. The CO₂ concentration of the influent gas stream was periodically checked by diverting the gas momentarily through the sample bypass to the CO₂ analyzer. Dilute HClO₄ placed in the round bottom flask (D) was back-titrated with standard NaOH solution to determine the amine carryover. Loss of amine from the sample vessel was essentially zero.

STRIPPING PROPERTIES

Important properties that must be considered when evaluating a regenerative absorbent are the time and energy required for stripping the solution of CO₂. Figure 3 shows that at 98° C and 1 atmosphere pressure, the regeneration rate of a carbonated CBM solution corresponds closely to that of MEA. However, at elevated temperatures

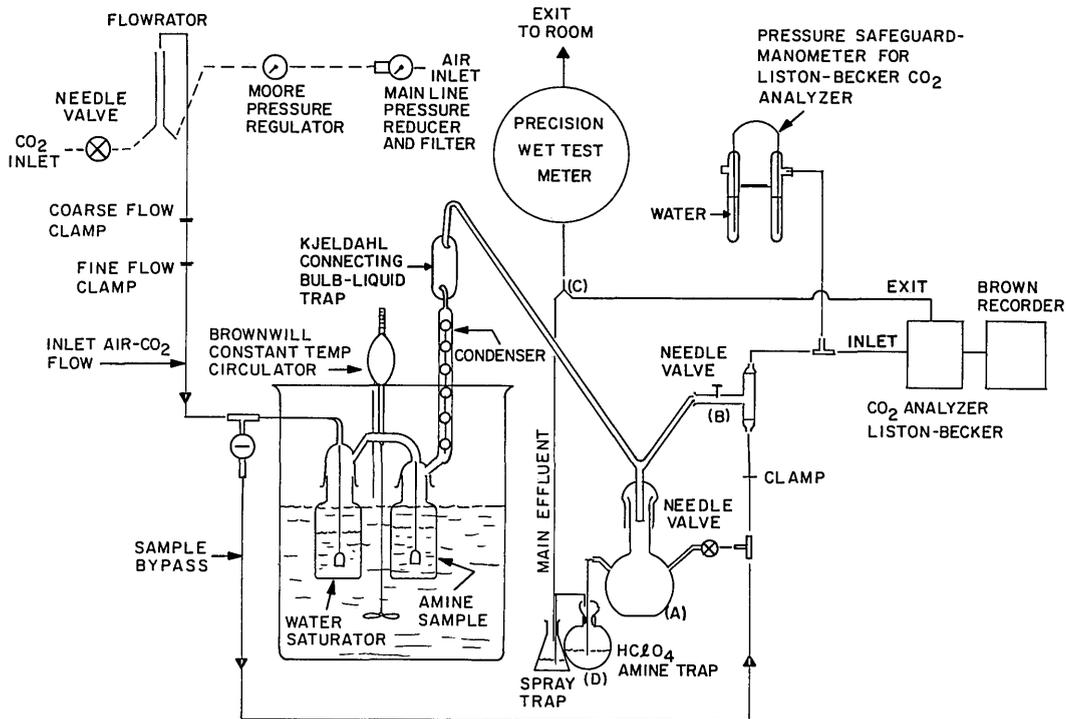


Fig. 2 - The apparatus

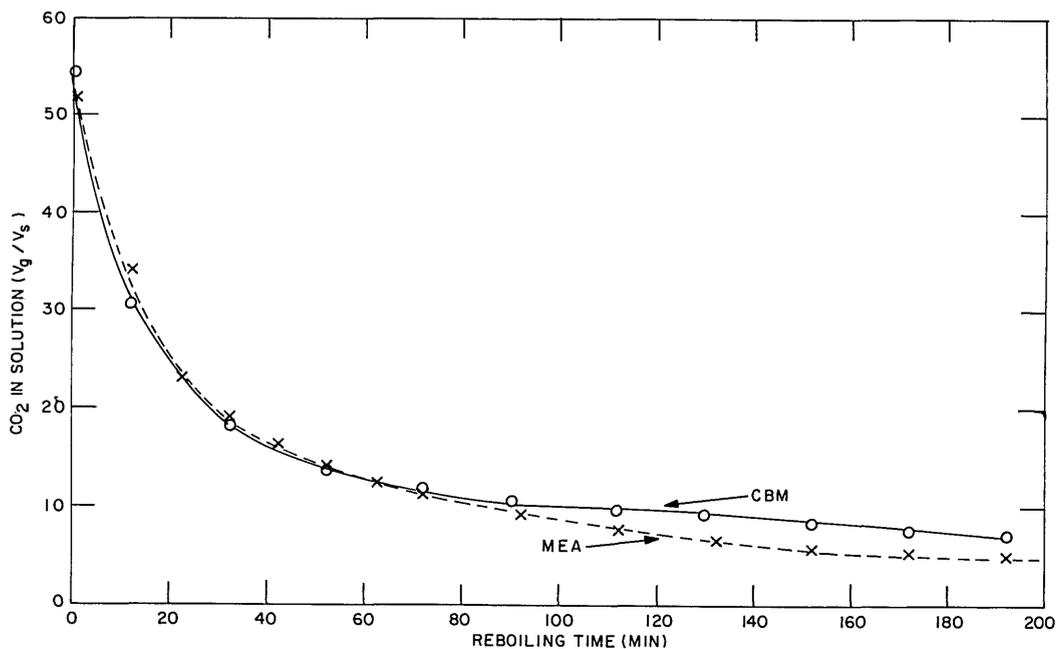


Fig. 3 - Comparison of the regeneration rates of CBM and MEA (4.5N solutions at 98°C and atmospheric pressure)

and pressures, the relative stripping rates could differ significantly. The data of Fig. 3 were obtained by refluxing a single 50-ml sample of carbonated amine solution at 1 atmosphere for the entire regeneration period of 200 minutes. During the run nitrogen was passed over the surface of the amine to insure transport of the evolved CO_2 away from the gas/liquid interface. The CO_2 was absorbed by 100 ml of 2.5N sodium hydroxide solution which was renewed periodically. CO_2 not absorbed by the caustic was trapped by tared ascarite tubes and weighed.

The CO_2 absorbed by the sodium hydroxide was determined by titration with HCl to phenolphthalein and methyl orange end points (4). BaCl_2 was added to the caustic before the titration to precipitate the carbonate. The precipitate, however, was not removed from the solution. Titration to the phenolphthalein end point measured the amount of excess sodium hydroxide; titration to the methyl orange end point (after blank corrections) measured the absorbed CO_2 . Therefore, the CO_2 evolved from the amine during the time interval under consideration was the sum of the CO_2 titrated in the sodium hydroxide solution and the CO_2 weighed in the ascarite tube associated with that interval.

The energy required for regeneration was evaluated by measuring the inlet and outlet water temperatures of the reflux condenser. The difference between them was consistently 6°C for a water flow rate of 70 cc per minute. This amounts to a heat input of approximately 420 cal per minute for both amines. To minimize heat losses, the condenser was insulated by wrapping the jacket with three layers of asbestos tape.

OXIDATION RESISTANCE

Evaluation of the oxidation resistance of CBM compared with MEA (both used as received, with no further purification) was made by contacting 50-ml samples (in glass cells) of 2.25N amine at 205°F with an oxygen- CO_2 mixture (95.5% O_2 and 4.5% CO_2) at a flow rate of 200 cc per minute. The evolution of ammonia was monitored by passing the effluent gas through 2% boric acid solutions which were titrated afterward with HCl.

Figure 4 shows a comparison of the oxidation resistance of CBM with MEA, both with and without additives. The stabilizers, added in combination of 1.5% each, were the tetrasodium salt of ethylene diamine tetraacetic acid (EDTA) and the monosodium salt of N,N-diethanolglycine (VFS).

According to Fig. 4, the oxidation rate of CBM (additives not present) was approximately that of unstabilized MEA during the first 60 hours. Beyond this period, however, the degradation of CBM was greater than MEA. A brown condensation product that increased with time occurred during the CBM oxidation experiment. The addition of both VFS and EDTA not only reduced the rate of ammonia evolution but also lowered the amount of CBM condensation product formed over a given time interval. After 35 hours, the evolution of ammonia exceeded that of the unstabilized CBM solution. This effect was probably due to the destruction of the additives by this time and the accumulation of oxidation intermediates. The combined stabilizers (VFS and EDTA) were considerably more effective with MEA than with CBM.

Oxidation tests of 6-1/2 hours duration were also conducted on unstabilized 4.5N CBM and MEA amines under the same experimental conditions as the 2.25N solutions. In this interval the ammonia evolution of CBM was approximately that of MEA. The nonbasic nitrogen loss of CBM (3 meq per 100 ml of amine) was less than half that of MEA (6.8 meq.).

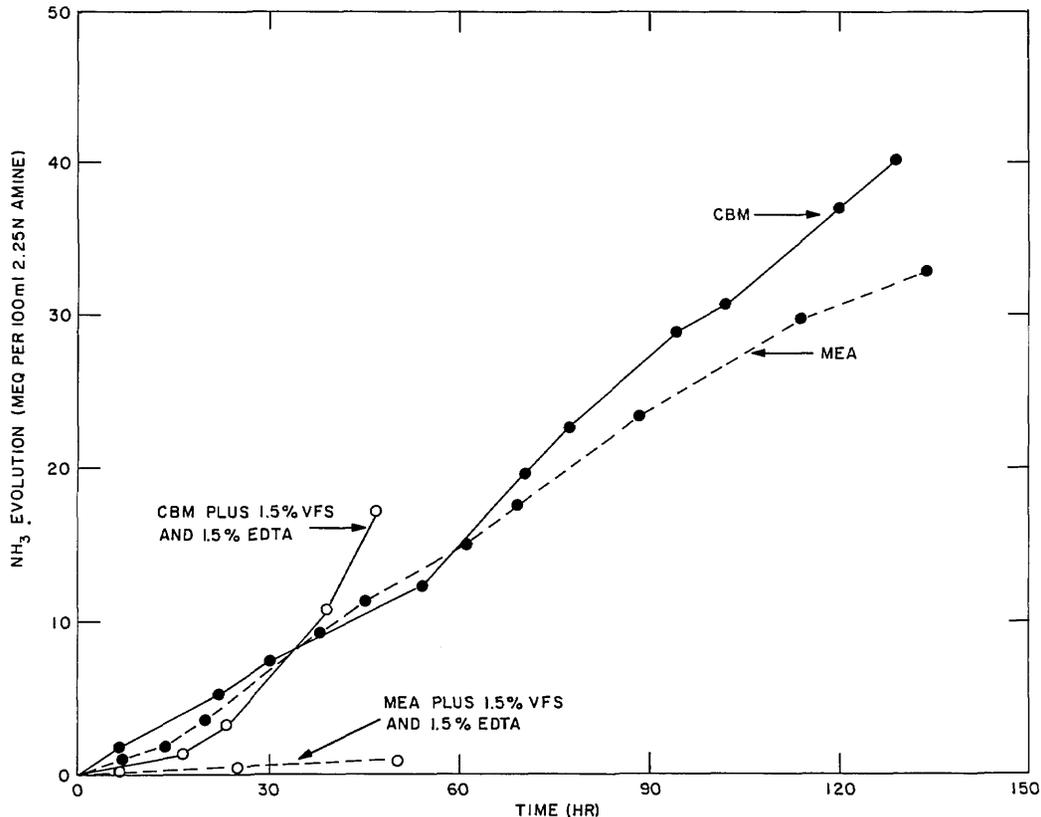


Fig. 4 - Comparison of the oxidation resistances of CBM and MEA with and without additives (50-ml samples at 205°F contacted with 95.5% oxygen and 4.5% CO₂ at a flow rate of 200 cc/min)

SUMMARY AND CONCLUSIONS

1. Both the CO₂ absorption rate and CO₂ capacity of CBM equal that of MEA.
2. The stripping rate of CBM equals that of MEA initially but the overall CO₂ removal rate is slightly less than for MEA. The difference, however, is probably insignificant.
3. The formation of a polymeric mass in CBM solutions near the V_g/V_s value of 50 can be retarded by the incorporation of 15 to 30 mole-percent MEA. The condensation product, if it occurs, will then be in the form of a fluid gel rather than a cake.
4. The oxidation resistance of CBM, on the basis of accelerated tests, was inferior to that of MEA. Addition of VFS and EDTA combined did reduce the degradation of CBM but much less efficiently than with MEA. However, other types of stabilizers may improve the stability to a greater extent than the VFS and EDTA combination.

REFERENCES

1. Blachly, C.H., and Ravner, H., "The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers," NRL Rpt 6189, Dec. 4, 1964
2. Reitmeier, R.E., Atwood, K., et al., "Carbon Dioxide Absorbents," The Girdler Corporation, Report on Contract No. Nobs-50023, June 1, 1950
3. Eastman Technical Data Sheet X-116, 1,4-cyclohexanebis(methylamine); Eastman Chemical Products, Inc., Kingsport, Tennessee
4. Kolthoff, I.M., and Sandell, E.B., "Textbook of Quantitative Inorganic Analysis," revised edition, New York: MacMillan, pp. 556-558, 1964

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