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### A Novel, V<sup>5</sup>-Stable K<sub>2</sub>CO<sub>3</sub> Promoter for CO<sub>2</sub> Absorption

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## A Novel, $V^{5+}$ -Stable $K_2CO_3$ Promoter for $CO_2$ Absorption\*

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### ABSTRACT

Flexsorb HP is a new, sterically hindered amine-promoted, potassium carbonate-based process for  $CO_2$  absorption from gases. Compared to the conventional diethanolamine (DEA) promoted process, it offers considerable capacity and rate advantages. It has outstanding stability toward the corrosion inhibitor  $V^{5+}$ , which degrades DEA. Its amine promoter aging resistance is much superior to that of DEA. It can serve as a “drop in” technology that can be used in an existing plant, leading to capacity increase without any equipment modification. For grassroots applications it requires lower investments than DEA-promoted units.

\* Presented in part at the AIChE 1994 Spring National Meeting, Atlanta, GA.

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## INTRODUCTION

The use of promoted potassium carbonate in aqueous solution for the removal of carbon dioxide is quite widespread (1-3). Several hundred hydrogen, ammonia, and natural-gas plants worldwide use promoted potassium carbonate. The acid gas cleanup range, i.e., the CO<sub>2</sub> concentration in the treated gas, is generally between 150 ppm and 2%.

Most plants use diethanolamine (DEA) as promoter, sometimes in combination with boric acid. Some plants use As<sub>2</sub>O<sub>3</sub> or glycine. All these promoters are rate enhancers, which increase the rate at which CO<sub>2</sub> is absorbed as compared to unpromoted K<sub>2</sub>CO<sub>3</sub>. However, the equilibrium cyclic capacity, i.e., the amount of CO<sub>2</sub> treated in an absorption-desorption cycle, attainable with DEA, As<sub>2</sub>O<sub>3</sub>, or glycine promoter, is the same as with unpromoted K<sub>2</sub>CO<sub>3</sub>.

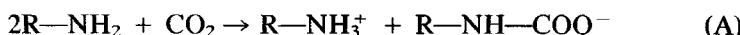
In recent years Exxon Research & Engineering Company has been studying sterically hindered amine promoters. Several new Flexsorb gas treating systems were developed and commercialized in the past (4-9). Most recently, this research has led to the development of a sterically hindered amine-promoted process called Flexsorb HP, which is a capacity improver as well as a rate enhancer for hot potassium carbonate.

## EFFECT OF STERIC HINDRANCE

The increased cyclic capacity observed with Flexsorb HP is due to the lower stability of the hindered amine carbamate as compared to that of DEA. Space-filling molecular models clearly show the dramatic differences in carbamate stability between sterically hindered and conventional amines (Figs. 1 and 2).

In the carbamate of the sterically unhindered *n*-butylamine, rotation around the N—COO<sup>−</sup> bond is unrestricted, whereas in the carbamate of the sterically hindered *tert*-butylamine, rotation around the N—COO<sup>−</sup> bond is only possible if compression of the bulky substituent occurs. Consequently, the carbamate of *tert*-butylamine is much less stable than that of *n*-butylamine (10-12).

Carbamate stability has an important effect on the CO<sub>2</sub>–amine reaction stoichiometry. When CO<sub>2</sub> is absorbed in an amine solution, two reactions can occur:



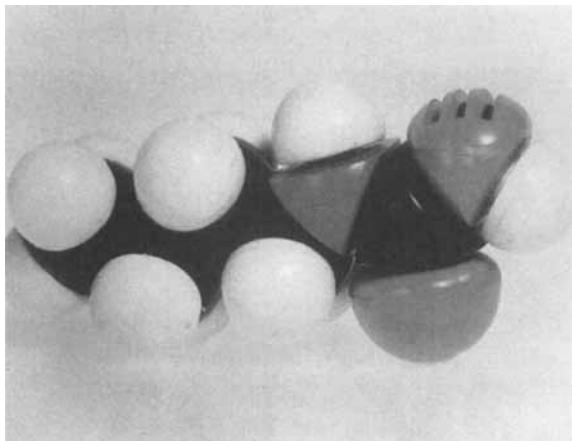
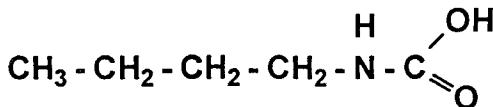


FIG. 1 The sterically unhindered *n*-butylamine forms stable carbamate.

Whether reaction A or B predominates depends on the stability of the carbamate. If R is not bulky, i.e., if the amine is unhindered, the carbamate will be stable and reaction A will occur, which means a half mole of CO<sub>2</sub> is absorbed per mole of amine. If R is bulky, i.e., if the amine is hindered, the carbamate will be unstable and reaction B will occur, which means 1 mole of CO<sub>2</sub> is absorbed per mole of amine. The bulkiness of R has an important effect on the stability of the carbamate, and consequently on the stoichiometry of the reaction with CO<sub>2</sub>. The formation of a stable carbamate is the thermodynamic limitation to the capacity of conventional amines for CO<sub>2</sub> removal. Attaching a bulky substituent to the amino group overcomes the thermodynamic limitation and leads to the theoretical capacity of 1 mole of CO<sub>2</sub> per mole of amine.

When desorption is carried out, i.e., reactions A and B go from right to left, reaction A will be incomplete owing to the stability of the carbamate, whereas reaction B will be complete. Therefore, both the amount of CO<sub>2</sub> absorbed and the amount of CO<sub>2</sub> desorbed are higher in the case of the

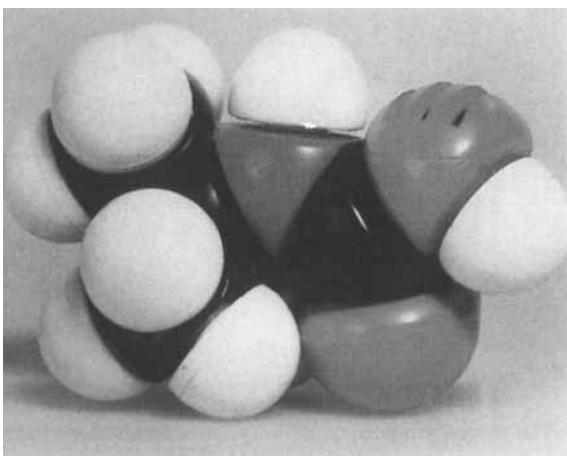
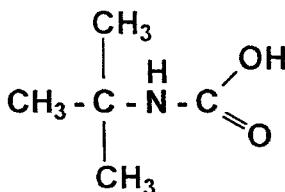


FIG. 2 The sterically hindered *tert*-butylamine forms unstable carbamate.

hindered than of the unhindered amine. In other words, the capacity of the hindered amine is higher than that of the unhindered amine.

### AMINE STABILITY TO V<sup>5+</sup>

The desire to use a V corrosion inhibitor maintained in the 5+ state by air injection places significant constraints since most amines are oxidized by this severe environment.

It is well known that the oxidizing power of multivalent metal ions, e.g., Cr<sup>6+</sup>, Mo<sup>6+</sup>, V<sup>5+</sup>, and Mn<sup>7+</sup>, is stronger under acidic than under basic conditions. This means that V<sup>5+</sup> is a more powerful oxidizing agent under CO<sub>2</sub>-rich than under CO<sub>2</sub>-lean conditions. We have confirmed this while studying the oxidation of *N*-*sec*-butyl glycine and pipecolinic acid by V<sup>5+</sup>. Under rich conditions at 100°C, they reduce V<sup>5+</sup> within a few hours, whereas under lean conditions no reduction is observed for several

days. As a consequence, we have carried out our subsequent stability experiments under rich conditions.

Table 1 shows the results of experiments on amino acid stability to V<sup>5+</sup>. Primary amino acids are stable if they are sterically hindered. Alpha secondary amino acids are stable if they are alanines carrying a bulky alkyl group attached to the nitrogen. Beta and gamma cyclic secondary amino acids are also stable. Furthermore, tertiary amino acids are stable.

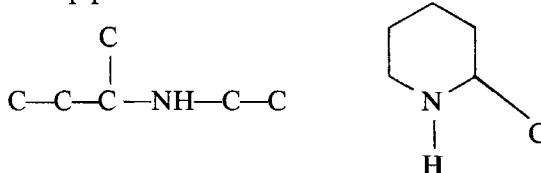
We believe that V<sup>5+</sup> attacks amino acids at the carboxyl. If the amino group is nearby, i.e., alpha, and unhindered, it will be attacked and degradation will occur. That is the case with *N*-sec-butyl glycine, pipercolinic acid, and *N*-cyclohexyl glycine. If the amino group is alpha but sterically hindered, e.g., *N*-isopropyl alanine, no attack is observed. It should be noted that *N*-*tert*-butyl glycine is less stable than *N*-isopropyl alanine, although more hindered based on Taft's parameters (13). The reason is that the alpha methyl in *N*-isopropyl alanine, being located between the amino group and the carboxyl, hinders the attack of the amino group by

TABLE 1  
Stability to V<sup>5+</sup> Controlled by Amino Acid Molecular Structure

Aminoacid Type	Stable to V <sup>5+</sup>	Moderately Stable to V <sup>5+</sup>	Unstable to V <sup>5+</sup>
Primary	$\begin{array}{c} \text{C} \\   \\ \text{H}_2\text{N}-\text{C}-\text{C}-\text{C}-\text{COOH} \\   \\ \text{C} \\ \text{NH}_2 \\ \text{COOH} \end{array}$	$\text{H}_2\text{N}-\text{C}-\text{COOH}$	$\begin{array}{c} \text{C} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \end{array}$
Secondary	$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \\   \\ \text{C} \\ \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \\ \text{HN} \quad \text{COOH} \\ \text{HN} \quad \text{COOH} \end{array}$	$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \\   \\ \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \\   \\ \text{C}-\text{C}-\text{C}-\text{NH}-\text{C}-\text{COOH} \\ \text{HN} \quad \text{COOH} \\ \text{HN} \quad \text{COOH} \end{array}$
Tertiary	$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \\   \\ \text{C}-\text{C}-\text{C}-\text{N}-\text{C}-\text{COOH} \end{array}$		

the  $V^{5+}$  attached to the carboxyl. This, combined with the bulkiness of the isopropyl attached to the amino groups, prevents an attack by  $V^{5+}$ . In *N*-*tert*-butyl glycine no obstacle is present between the amino group and the carboxyl, therefore the  $V^{5+}$  attached to the carboxyl can approach the amino group despite the presence of the bulky *tert*-butyl. When the amino group is in a ring and removed from the carboxyl, i.e., beta or gamma, the  $V^{5+}$  attached to the carboxyl cannot approach the amino group. This explains why nipecotic and isonipecotic acids are stable, whereas their isomer pipecolinic acid is unstable.

The fact that  $V^{5+}$  attacks an amino acid at the carboxyl is demonstrated by the observation that amines obtained by replacing the carboxyls in *N*-*sec*-butyl glycine or pipecolinic acid with a methyl group, i.e., ethyl *sec*-butyl amine and 2-pipecoline



are stable to  $V^{5+}$ .

An alternative explanation for the oxidation susceptibility of amino acids invokes a mechanism described as the Strecker degradation mechanism (14). Strecker studied the oxidation of amino acids by hydrogen-accepting organic molecules as well as inorganic oxidizing agents. Extensive studies by Strecker and subsequent investigations concluded that dehydrogenation involves the loss of hydrogen from the alpha carbon to produce an imino group which readily hydrolyzes to the unstable keto acid.

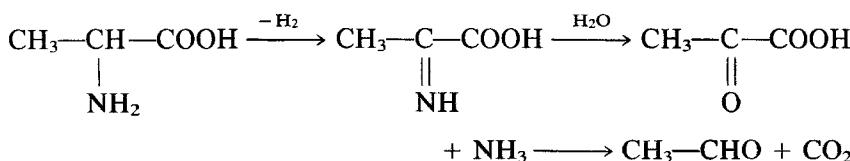


TABLE 2  
Amine Behavior toward  $V^{5+}$ : 25 wt%  $\text{K}_2\text{CO}_3$  (100% converted to  $\text{KHCO}_3$ ), 165°C

Promoter	Color		
	Initial	After 1 day	After 30 days
DEA + $\text{H}_3\text{BO}_3$	Yellow	Dark	Dark
Flexsorb HP amine	Yellow	Yellow	Yellow

TABLE 3  
Flexsorb HP Stability to V<sup>5+</sup>: 18.5 wt% K<sub>2</sub>CO<sub>3</sub>  
(100% converted to KHCO<sub>3</sub>), 0.5 wt% V<sup>5+</sup>

Days at 100°C	% V <sup>5+</sup> remaining (by <sup>51</sup> V NMR)
0	100
6	101
15	106
35	99

Our observations are consistent with this mechanism. Although the vanadium oxidation is probably assisted by the formation of vanadium salts of the carboxylic acid, the variation in stability among the different  $\alpha$ -amino acid structures tested demonstrates that the hydrogens on the alpha carbon attached to an amino group play a significant role. Hindering this position, substantially reducing the number of hydrogens on the alpha carbon, or still better eliminating them altogether, greatly improves stability or eliminates the oxidation problem.

The blocking of a sterically unhindered amino group by forming carbamate also reduces oxidation susceptibility. The relatively high stability of glycine is due to the fact that under rich conditions a considerable fraction of the amino acid is in the form of carbamate. The electron-donating ability of the amino group is reduced if an electron-attracting —COO<sup>-</sup> is attached to it.

Flexsorb HP is much more stable than DEA-promoted carbonate, and it withstands V<sup>5+</sup> even under very severe conditions, e.g., 165°C (Table 2).

A quantitative test can be carried out in the following way. The Flexsorb HP amine promoter, V<sub>2</sub>O<sub>5</sub>, KHCO<sub>3</sub>, and water are put into an NMR tube, which is then sealed and brought to 100°C. Periodically, the tube is removed and V<sup>5+</sup> concentration determined by <sup>51</sup>V NMR. No change in V<sup>5+</sup> concentration occurs in the course of a month (Table 3).

TABLE 4  
DEA, Flexsorb HP Amine Aging Experiments: 28 wt% K<sub>2</sub>CO<sub>3</sub>, 120°C for 1000 Hours

Promoter	CO <sub>2</sub> /K <sub>2</sub> CO <sub>3</sub> mole ratio during aging	% of initial amine left in aged solution
DEA	0	100
Flexsorb HP amine	0	97.5
DEA	1	26 (two liquid phases)
Flexsorb HP amine	1	95

TABLE 5  
DEA, Flexsorb HP Amine Aging Experiments: 25 wt%  $K_2CO_3$ , 165°C for 1000 Hours

Promoter	$CO_2/K_2CO_3$ mole ratio during aging	% of initial amine left in aged solution
DEA	0	54
Flexsorb HP amine	0	97
DEA	0.6	5
Flexsorb HP amine	0.6	92

### THERMAL STABILITY OF FLEXSORB HP

Flexsorb HP has great thermal stability and is definitely superior to DEA-promoted carbonate. We have carried out two series of aging experiments on promoted  $K_2CO_3$ . In a first series, aging was at 120°C for 1000 hours. The Flexsorb HP amine promoter does not degrade under either lean or rich conditions; DEA is stable under lean conditions but undergoes substantial degradation under rich conditions. Furthermore, phase separation occurs in the case of DEA (Table 4).

In another series of experiments, we aged DEA-promoted  $K_2CO_3$  and Flexsorb HP at 165°C for 1000 hours (Table 5).

DEA degrades under lean conditions and more extensively under rich conditions. The Flexsorb HP amine promoter is quite stable, even under rich conditions.

We carried out standard  $CO_2$  absorption tests with the plant solution, fresh Flexsorb HP amine promoter + the plant solution, and the two aged solutions. Addition of Flexsorb HP amine promoter to the plant solution leads to a definite increase in capacity and rate; the advantages persist even if the solution is aged under lean or rich conditions (Table 6).

TABLE 6  
Performance of Fresh and Aged Solutions

Solution	Liters of $CO_2$ absorbed	
	Total	First minute
Plant solution	22.5	6.7
Flexsorb HP amine + plant solution, fresh	30.7	10.5
Flexsorb HP amine + plant solution, aged under lean conditions	27.9	10.5
Flexsorb HP amine + plant solution, aged under rich conditions	28.2	10.2

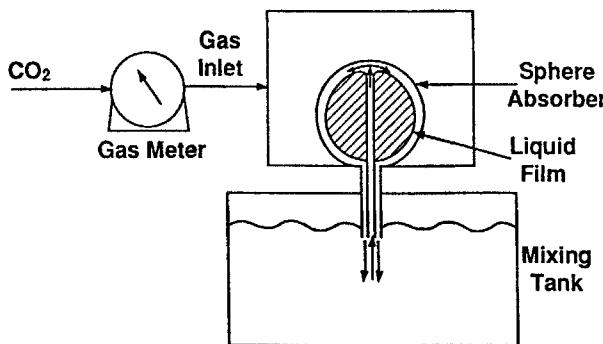


FIG. 3 Schematic of sphere absorber for rate measurement.

### RATE ADVANTAGES OF FLEXSORB HP

In addition to capacity and stability advantages over DEA-promoted K<sub>2</sub>CO<sub>3</sub>, Flexsorb HP has considerable rate advantages. That was shown by carrying out single-sphere experiments in which we measured gas-liquid mass-transfer rates at increasing loading while maintaining a constant gas-liquid contact surface area (Fig. 3). By plotting the overall gas-phase mass transfer coefficient,  $K_g$ , as a function of CO<sub>2</sub> loading for DEA-pro-

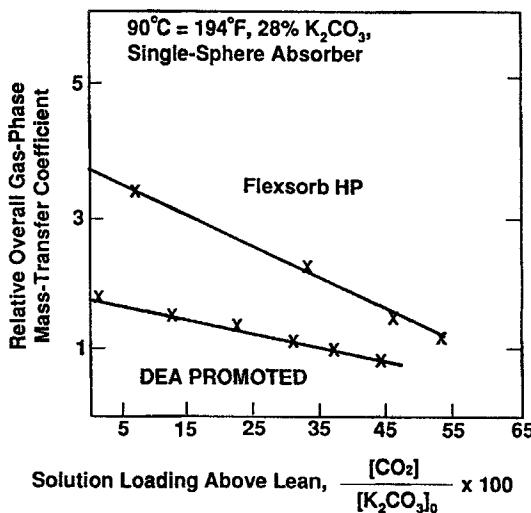


FIG. 4 Flexsorb HP solutions have much higher absorption rates than DEA-promoted solutions.

moted  $K_2CO_3$  and Flexsorb HP, we saw a dramatic difference in favor of the latter (Fig. 4).

Other advantages of Flexsorb HP are no volatility of the amine promoter and negligible foaminess.

### COMMERCIALIZATION OF FLEXSORB HP

Flexsorb HP solvent has been used since November 1987 in a grass roots  $H_2$  plant. This is an Exxon plant with an  $H_2$  capacity of 21 MSCFD at design. The  $CO_2$  removal system uses a promoted hot carbonate solution with a vanadium corrosion inhibitor. This unit achieved 70% of design capacity with a DEA-promoted solution. Upon the direct addition of 5.5 wt% of the Flexsorb HP amine promoter, the  $CO_2$  leak dropped and the unit achieved 105% of the capacity originally designed for the Flexsorb HP solvent. The absorber operates at greater than 80% flood. The annual make-up of amine has been about 30 to 50% of the initial charge. Since the hindered amine has a low vapor pressure, the amine losses are due primarily to physical losses.

In 1991 Flexsorb HP solvent was commercialized in two ammonia plants where it gave the expected process credits. These included steam savings and stability advantages at one plant and increased production capacity at the other plant.

In January 1992 a hydrogen plant located in an Imperial Oil Limited refinery switched from a DEA to the Flexsorb HP promoter, using the add-on procedure previously described for the European plant. The  $CO_2$  content of the process gas exiting the top of the adsorber dropped from

TABLE 7  
Flexsorb HP vs DEA-Promoted  $K_2CO_3$ <sup>a</sup>

	DEA-Promoted $K_2CO_3$	Flexsorb HP
Relative capacity	Base	125%
Commercial experience	Extensive	Two $H_2$ plants, two $NH_3$ plants
Corrosivity at design conditions	Base	Base
Promoter volatility	Base	<Base
Promoter stability	Base	>Base
Amine degradation product removal	Required	Not required
Materials of construction	Base	Base
Reboiler duty	Base	80%

<sup>a</sup> Same diameters and solution circulation rates.

1.5 to 0.3% at constant solution circulation rate. As a consequence, less hydrogen is consumed by the methanation of the residual CO<sub>2</sub>, resulting in incremental hydrogen production at an increased purity. Subsequent operation with 4.5% of Flexsorb HP amine permitted operation at 105% of design plant capacity as limited by tray hydraulics. This operation has been smooth so far, i.e., there is no corrosion, foaming, or solvent carryover. Table 7 compares commercial experience with DEA and the Flexsorb HP promoter.

## CONCLUSIONS

Flexsorb HP has significant capacity and rate advantages over DEA-promoted carbonate. It has good thermal stability and is not attacked by V<sup>5+</sup> corrosion inhibitor. It has negligible volatility and low foaminess. It is a "drop in" technology that can be easily utilized in an existing plant, providing capacity increase with no modification of the equipment. Grass-roots facilities will have lower investments compared to DEA-promoted systems.

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