

## **CARBON DIOXIDE ABSORPTION INTO BIPHASIC AMINE SOLVENT WITH SOLVENT LOSS REDUCTION**

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### **Abstract**

The main challenge in the CO<sub>2</sub> capture from flue gases is to reduce the energy consumption required for solvent regeneration. Lipophilic amines exhibit a thermomorphic phase transition upon heating, giving rise to autoextractive behaviour, which enhances desorption at temperatures well below the solvent boiling point. The low regeneration temperature of less than 80°C together with the high cyclic CO<sub>2</sub> loading capacity (c. 0.9 mol<sub>CO2</sub>/mol<sub>absorbent</sub>) of such biphasic amine systems permit the use of low temperature and even waste heat for desorption purposes. In order to improve the capture process and reduce the commensurate energy demand still further, desorption experiments were carried out at 70°C and techniques for enhancing CO<sub>2</sub> release without gas stripping were also studied. The comparison of various amines at a concentration of 3M and for a 15 mol% CO<sub>2</sub> feed gas demonstrates the considerable potential of lipophilic amines for the CO<sub>2</sub> absorption process. Chemical stability is a decisive factor for the industrial application of amine absorbents. Degradation of the novel lipophilic amine absorbents was shown to be minor, while volatility losses represent a major shortcoming of the biphasic solvent systems. Appropriate countermeasures to limit solvent losses were examined experimentally.

**Keywords:** carbon dioxide, amine absorption, desorption, solvent loss

### **1. Introduction**

Chemical absorption using amine-based solvents is the most promising commercial technology for CO<sub>2</sub> capture and sequestration. However, it has been estimated that the absorption step would be responsible for more than half of the overall processing costs, primarily due to the high energy consumption in the solvent regeneration step (for monoethanolamine: 4 GJ/t<sub>CO2</sub>). Various aqueous solvent systems have been proposed by Chowdhury et al.<sup>1</sup> to mitigate the energy requirements, with only modest results. Some undisclosed solvents, which can allegedly cut the regeneration energy by 20-34% compared to MEA were reported by Goto et al.<sup>2</sup> and Mangalapally et al.<sup>3</sup>, but the desorption still needs to be carried out at 120°C. Biphasic amine solvents can reduce the regeneration temperature down to 80°C or even lower, enabling the utilisation of low temperature or even waste heat for regeneration purposes. The regeneration process can be enhanced dramatically<sup>4</sup>, with over 90% of the absorbed CO<sub>2</sub> being released without vapour stripping. Due to the limited aqueous solubility of these "lipophilic" amines, a thermomorphic miscibility gap arises upon modest heating of the loaded solvent in the temperature range of 60-80°C. The organic phase thus formed acts as an autoextractive agent, removing the amine from the aqueous phase and thus favourably displacing the regeneration equilibrium and driving the reaction towards dissociation of the carbamate and bicarbonate species in the loaded aqueous phase according to Le Chatelier's principle.

The lipophilic amine solvents, for example N,N-dimethylcyclohexylamine (DMC) and dipropylamine (DPA) in blends or individually, have been studied extensively in previous work with respect to their CO<sub>2</sub> loading capacities, kinetics, regeneration rates, residual loadings and so forth<sup>5</sup>. The tertiary amine DMC acts as the main absorbent, because of its high CO<sub>2</sub> loading capacity in absorption and low residual loading upon regeneration. DPA may be regarded as an activator, due to its rapid CO<sub>2</sub> absorption kinetics. Blending DMC and DPA in aqueous solution combines the advantages of both. Our screening studies to identify new lipophilic amine solvents were conducted both theoretically and experimentally. A novel absorbent system comprising alkylamines B0 with outstanding regeneration characteristics and A1 exhibiting a significantly faster absorption rate, have been selected from a comparison of over twenty different lipophilic amines. The excellent performance parameters of the new B0+A1 blend make it the most promising candidate for assessing the technical viability in further

development work, since it increases the CO<sub>2</sub> capture efficiency by more than 50% and reduces more the energy consumption by more than 35% in comparison to absorption and regeneration with the benchmark aqueous absorbent MEA, according to the thermodynamic evaluation technique described by Notz et al.<sup>6</sup>

Solvent losses in amine based gas treating plants stem from vaporisation, mechanical breakdown, entrainment, foaming and chemical degradation processes<sup>7</sup>. The vaporisation loss is a feature of all amine treatment processes, while the degradation loss can be defined by the deactivated fraction of the amine present which is no longer available for CO<sub>2</sub> capture. The degradation is influenced by temperature, amine concentration, CO<sub>2</sub> loading and the presence of oxygen. So far, only the degradation kinetics of alkanolamines and a few polyamines have been studied in detail<sup>8,9</sup> and with respect to the reaction products<sup>10</sup> and mechanisms<sup>11</sup>. The results suggest that tertiary amines are more stable than primary and secondary amines. Catalysts and inhibitors for MEA oxidation were also investigated by Sexton et al.<sup>12</sup>, but the best inhibitor identified is not effective for all amines. The results obtained in previous work are not transferrable to lipophilic amines, due to the different chemical structures involved. In the present work, thermal, CO<sub>2</sub> induced and oxidative degradation of lipophilic amines were all found to be insignificant, and much lower than with MEA, primarily by virtue of the lower operating temperatures and the less reactive alkyl groups. However, vaporisation losses due to increased amine volatility and foaming were shown to contribute significantly to solvent losses, especially when a separate supernatant organic phase was present in the solution. Stewart and Lanning<sup>13</sup> have described water scrubbers for the recovery of volatile amines, while Thitakamol and Veawab<sup>14</sup> studied the influence of absorption parameters on the foaming coefficient. Although different phenomena and results were found for the lipophilic amine systems, the losses can still be curtailed by modifying reaction conditions and adopting appropriate countermeasures.

## 2. Absorption and Desorption

The absorption experiments were carried out in a 100 mL glass bubble column with 40 mL aqueous amine solution at 40°C. Various amine concentrations from 2.5 to 4 M and gas phase CO<sub>2</sub> partial pressures between 3 and 100 kPa were contacted over periods from 1 to 4 hours, to ensure that equilibrium was achieved. Desorption was initially carried out with N<sub>2</sub> gas stripping at 70°C and 75°C. The feed gas flow rates were regulated by mass flow controllers so as to be constant during the absorption and desorption tests. During the experiments, the outlet gas was monitored on-line by GC (HP6890). After the reaction had taken place, the CO<sub>2</sub> loading was ascertained by the barium chloride method, total amine concentration was determined by acid-base back-titration and the blended amine composition determined by GC analysis.

### 2.1 Screening Tests

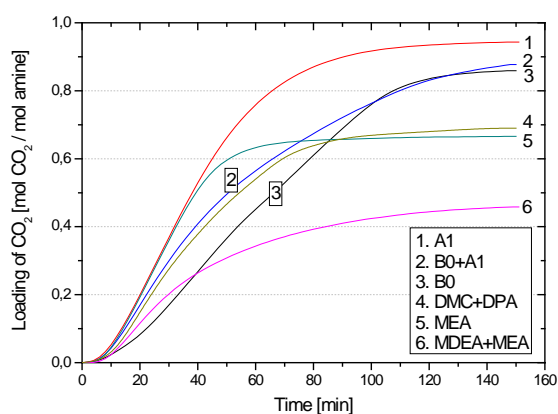
The screening tests focused on the initial reaction rates of the absorbents with CO<sub>2</sub>, together with the cyclic absorption and regeneration capacities. The standard test was carried out at 300 mL/min total gas flow rate, comprising 15 mol% CO<sub>2</sub> with the balance being N<sub>2</sub> and using 3M amine solutions. Over twenty lipophilic amines were examined, but less than ten exhibited an overall performance comparable with, or superior to, commercial alkanolamines. Nevertheless certain lipophilic amines, such as B0 and A1 with their remarkable performance parameters emerged with flying colours from the screening process. The characteristics of selected amines are listed in Table 1, where N-methyldiethanolamine (MDEA) and MEA are used as benchmarks. Compared to MDEA, the absorption rate and cyclic loading capacity of the main solvent B0 is more than twice as high. The absorption rate of activator A1 is comparable to that of MEA, but it offers a 200% higher cyclic loading. The absorption rate and cyclic loading of a blend of B0+A1 are, respectively, up to 100% and 130% higher than for a combined MDEA+MEA solution.

As a consequence of a shuttle Mechanism, A1 - a moderately soluble amine - has a greater opportunity to come into contact with CO<sub>2</sub> and water. It thus reacts with both rapidly at the gas-liquid interface, in the organic phase, at the liquid-liquid interface and in the aqueous phase during absorption. Conversely, the amine B0, which is only partially miscible in the aqueous phase, exhibits an outstanding regenerability, because of the thermomorphic phase transition, i.e., the initially heterogeneous solution becomes homogeneous during absorption and reverts to two phases during desorption.

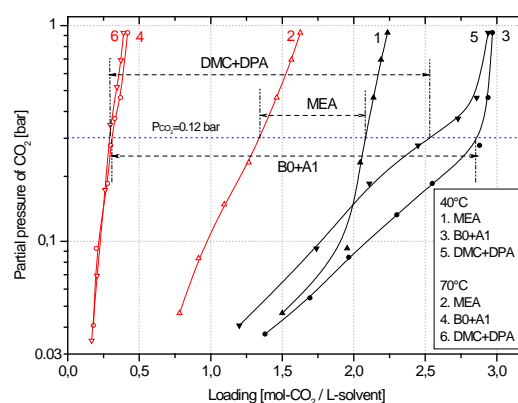
**Table 1.** Characteristics of selected amines in 3M aqueous solutions

Types	Absorbents	Absorption at 40 °C		Absorption at 70 °C		Stripping <sup>b</sup> at 70 °C	
		Absorption rate <sup>a</sup> g/(L·hr)	CO <sub>2</sub> loading g/L	CO <sub>2</sub> loading g/L	Cyclic loading I g/L	Residual loading g/L	Cyclic loading II g/L
Primary solvents	B0	72	101	40	61	13	88
	MDEA	30	59	29	30	16	43
Activators	A1	130	124	94	30	33	91
	MEA	124	72	63	9	42	30
Blends 3:1	DMC+DPA	89	90	36	54	15	75
	B0+A1	94	117	45	72	16	101
	MDEA+MEA	47	62	38	24	18	44

<sup>a</sup> Absorption rate for 0.4 mol/mol CO<sub>2</sub> loading; <sup>b</sup> Stripping with 300 mL/min of N<sub>2</sub>



**Figure 1.** CO<sub>2</sub> absorption into 3M amine solutions with 14 kPa CO<sub>2</sub> at 40°C



**Figure 2.** Vapor-Liquid Equilibrium of 3M amine solutions at various CO<sub>2</sub> partial pressures

### 2.2 Activators in Lipophilic Amine Blends

As a tertiary amine, the CO<sub>2</sub> absorption rate of B0 is rather slow (72 g/L/hr up to a CO<sub>2</sub> loading of 0.4 mol/mol); thus activators have to be introduced to accelerate the reaction. To start with, the secondary amine DPA was employed yielding an initial absorption rate of 125 g/L/hr. However, the limited solubility of carbamate and protonated DPA ions was found to render the system susceptible to precipitation upon scale-up. A new activator A1 (130 g/L/hr) was therefore incorporated in the blend solution. Figure 1 illustrates the remarkable acceleration of the absorption reaction rate, more than 80% faster than that without activator in the initial 30 min, by using A1. In the regeneration step, CO<sub>2</sub> is first liberated from main absorbent B0: due to its limited aqueous solubility, a separate organic phase is formed over the solution. As a result of the similar polarity of amine molecules, A1 is preferentially dissolved in the organic rather than the aqueous phase. B0 adopts the role of an extractive solvent during regeneration, withdrawing the activator from the aqueous phase, and is thus a decisive component for enhancing the solvent regeneration rate.

The absorption in lipophilic amine solutions in the presence of activators takes place up to 50% more rapidly than for the benchmark amine solution MDEA+MEA. The advantage of the lipophilic amine solvent blend lies not only in the high loading capacity but also in the good regenerability in comparison with the benchmark absorbent. Moreover, the cyclic loading capacity of the newly developed solvent B0+A1 is 30% higher than the previous blend DMC+DPA. The most remarkable phenomenon is its rapid reaction rate in both absorption and desorption, since A1 not only serves as a solubiliser for B0 but also leads to a vigorous reaction with CO<sub>2</sub> right from the outset.

### 2.3 Vapour-Liquid Equilibrium (VLE)

Following the screening tests, the blend solutions DMC+DPA and B0+A1 were selected for VLE measurements. Further studies at various blend concentrations and proportions established that a 3M solution containing 25% of activator yields the best performance. The VLE experiments were thus carried out with an aqueous solution comprising 2.25M main absorbent and 0.75M activator at various pressures. N<sub>2</sub> was used as stripping gas in desorption at 70°C. Under these conditions, the superior

performance of the biphasic solvents over conventional solvent MEA is evident (Figure 2). The cyclic  $\text{CO}_2$  loading of the lipophilic amine solutions is more than twice that of MEA.

#### 2.4 Enhancement of Solvent Regeneration

The objective of regeneration enhancement was to accelerate desorption by physical means. The standard solutions were prepared as a 3M aqueous amine blend (3:1) with a  $\text{CO}_2$  loading of 0.81 in DMC+DPA and 0.95 in B0+A1. The intensified regeneration experiment was carried out without  $\text{N}_2$  stripping. The comparative measurements, for example, were made using a loaded B0+A1 solution at  $75^\circ\text{C}$ . The results demonstrate that the regeneration rate is very slow when no enhancement technique is used, releasing 30 g/L/hr of  $\text{CO}_2$  in the initial 20 min, but that it becomes much faster upon 250 rpm agitation (180 g/L/hr) and even more rapid at 500 rpm agitation (220 g/L/hr). The corresponding desorption rate with 200 mL/min  $\text{N}_2$  stripping is also 220 g/L/hr. This indicates the tremendous potential of exploiting agitation to reduce solvent loss and operating costs in the desorption step still further.

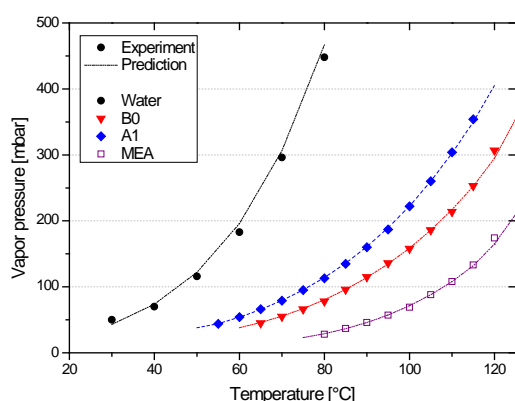
### 3. Solvent Losses & Countermeasures

Solvent losses, including vaporisation and degradation, were observed during the experiments. As a consequence of the more than 90% higher vapour pressures, vaporisation losses with lipophilic amine solvents can be more significant than those for alkanolamines, despite the lower operating temperatures. The optimisation of the operating conditions and the implementation of appropriate countermeasures, such as an additional water scrubber and condenser, were proposed to minimise these losses.

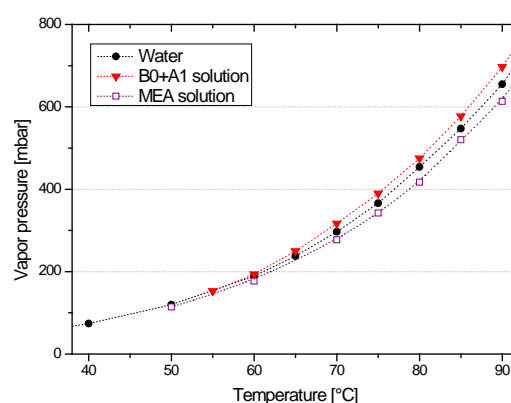
#### 3.1 Vaporisation

The vaporisation of the amine solution is a function of temperature and amine concentration, reflecting volatility and vapour pressure, which must thus be determined for the design of absorption and desorption columns preventing solvent loss. Figure 3 depicts the vapour pressures of the lipophilic amine B0, whose values lie between those of alkanolamines and water. The higher volatility with respect to alkanolamine leads to greater vaporisation losses during operation. The experimental data were fitted using an empirically modified Clausius-Clapeyron equation. The results indicate a good agreement for vapour pressures below 500 mbar. The aqueous lipophilic amine solution, the total vapour pressures of which are a little higher than those of water (Figure 4), may exhibit azeotrope formation. However, this was not observed at atmospheric pressure until  $90^\circ\text{C}$  and thus does not arise for low temperature operation below  $80^\circ\text{C}$ .

Solvent loss through vaporisation is measured by the difference in amine concentrations before and after reaction. The concentration reduction of lipophilic amines is more than three times the value for the alkanolamine MEA (Table 2) and the vaporisation rate approaches 40 mmol/(day) in a 100 mL bubble column with 300 mL/min gas flow rate. Vaporisation thus contributes to 80-90% of the total lipophilic amine losses in the capture process. The vaporised amine should therefore be recovered in subsequent experimentation. According to the GC analysis results, the volatility loss of the activator A1 is minor, even though its vapour pressure is higher, since not only the aqueous solubility of A1 is much higher than for B0, but also the reaction rate of A1 is extremely rapid and the ionised A1 dissolved in aqueous phase hinders its vaporisation.



**Figure 3.** Vapor pressure of various amines with fitting by Clausius-Clapeyron equation



**Figure 4.** Vapor pressure of 3M aqueous amine solutions

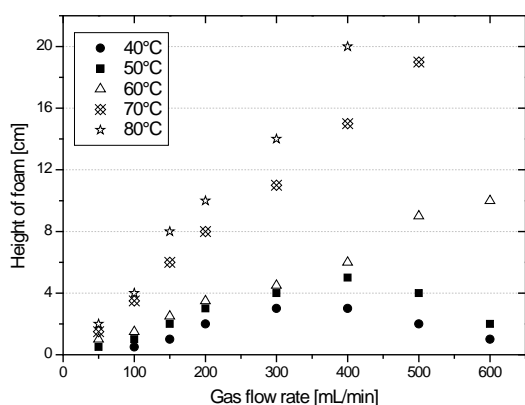
**Table 2.** Vaporisation loss and solvent reactivity

Solution (initial $c_{\text{amine}}=3M$ )	$t = 2.5 \text{ hr}^a$ at $40^\circ\text{C}$		$t = 1 \text{ day}^b$ at $40\text{-}75^\circ\text{C}$		$t = 1 \text{ week}^c$ at $50^\circ\text{C}$	
	$C_{\text{amine}}$	Loading	$C_{\text{amine}}$	Loading	$C_{\text{amine}}$	Loading
	$M$	$\text{mol/mol}$	$M$	$\text{mol/mol}$	$M$	$\text{mol/mol}$
B0+A1	2.95	0.96	2.79	0.93	1.80	0.78
MDEA+A1	2.99	0.71	2.95	0.68	2.85	0.31
MEA+A1	2.99	0.67	2.82	0.58	2.63	0.13
MEA	3.00	0.68	2.88	0.51	2.74	0.11

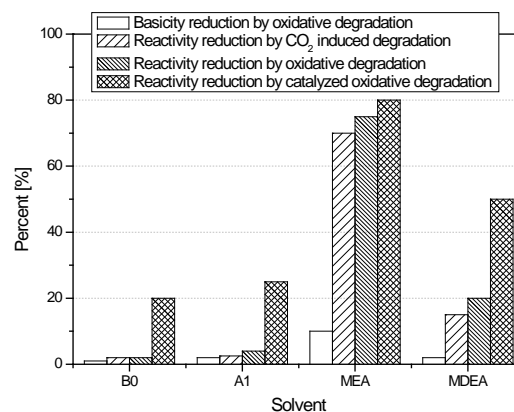
<sup>a</sup> absorption at  $40^\circ\text{C}$  with  $100 \text{ mL/min}$  CO<sub>2</sub> &  $100 \text{ mL/min}$  N<sub>2</sub>;

<sup>b</sup> 4 absorption cycles as <sup>a</sup> & 3 desorption cycles at  $75^\circ\text{C}$  with N<sub>2</sub> stripping  $200 \text{ mL/min}$ ;

<sup>c</sup> absorption at  $50^\circ\text{C}$  with  $2 \text{ mL/min}$  CO<sub>2</sub> &  $98 \text{ mL/min}$  N<sub>2</sub>



**Figure 5.** Influence of gas flow rate and temperature on foaming in 3M B0+A1 solution



**Figure 6.** Solvent loss via degradation during a one week experiment at  $50^\circ\text{C}$

### 3.2 Foaming

Solvent foaming was found to be important in the biphasic system. It is mainly influenced by gas flow rate, amine concentration, CO<sub>2</sub> loading, temperature and contaminants. Due to the surface tension of the lipophilic amine phase which forms a supernatant phase on top of the aqueous solvent, foaming becomes significant with accumulation of organic phase. Low CO<sub>2</sub> loading, high amine concentration, solvent volume and temperature, promoting the formation of two liquid phases, will thus enhance foaming. Figure 5 indicates that foaming can be initially enhanced by increasing gas flow rate and temperature, but suppressed afterwards with higher gas flow rates under low temperature operating conditions due to turbulence. Foaming was not found with the solution of the activator A1 but was intensified by increasing concentrations of B0.

### 3.3 Degradation

Due to the limitation of operating temperatures to below  $80^\circ\text{C}$ , no significant solvent basicity reduction was observed as a result of thermal degradation. Subsequent studies thus focused on CO<sub>2</sub> induced and oxidative degradation. The absorption was carried out at  $50^\circ\text{C}$  with  $2 \text{ mL/min}$  CO<sub>2</sub> and  $98 \text{ mL/min}$  N<sub>2</sub> or O<sub>2</sub>. Before analysis, the solution was treated with 15% CO<sub>2</sub>, so that the results can be compared with those in the VLE test. The amount of residual amine was determined by basicity measurements and the reactivity of the absorbent. In order to minimise the influence of solvent vaporisation, chilled water at  $5^\circ\text{C}$  was used in the condenser and a control experiment without O<sub>2</sub> was also carried out for the purposes of comparison and to distinguish oxidative degradation from other losses.

In the control experiment, the amine concentrations remained at a high level even after one week of operation, but the CO<sub>2</sub> loadings were reduced significantly, 70%, 15% and 2% reductions were observed in solutions of MEA, MDEA and B0, respectively (Figure 6). This implies that up to 70% of remaining bases in MEA were no longer reactive. The residual inactive bases are the products of CO<sub>2</sub> induced degradation via alkylation, dealkylation or oligomerisation and they are apparently too weak to react with CO<sub>2</sub> since their amino groups have been deactivated by additional alkyl chains or steric

hindrance. Nevertheless, the reactivity reduction in lipophilic amine solution B0 is much lower than for alkanolamines, which exhibits a good chemical stability during long term operation. After one week of oxidation, the solvent basicity reductions in solutions of B0, MEA and MDEA are only 3%, 10% and 2% respectively, but for the more significant reactivity, the reduction approaches 75% in MEA but only 2% for B0, a value quite comparable to that of MDEA. The GC-MS analysis results confirmed that only traces of degradation products were to be found in B0. In a further experiment 0.2 mM iron ions  $Fe^{2+}/Fe^{3+}$  were added as an oxidation catalyst. A 20% reduction of reactivity was observed in the B0 solution while reactivity diminished by 50% and 80% in MDEA and MDA solutions after one week of catalysed oxidative degradation. To summarise, the tertiary amine B0 proved to be remarkably chemically resilient during the experiment.

### 3.4 Countermeasures

A water scrubber has been successfully employed for solvent recovery and to cut vaporisation losses in alkanolamine systems. Due to lower aqueous solubility of lipophilic amines, the efficacy of such a water scrubber is much lower than that in alkanolamine system. Only 15-20% of the vaporised amines from solution B0+A1 were captured in a single water absorption stage at room temperature, but the process is still technically feasible when multistage counter-current operation is considered. Condensation with chilled water at 5°C rather than 20°C was also evaluated and a vaporisation loss reduction of over 60% was achieved. In addition, foaming was observed to be a serious problem during absorption when contaminants were present in the solution. However, after removal of the contaminants, the formation of foam was clearly reduced. A water scrubber was able to achieve efficient defoaming and recover 80% of the foaming losses.

## 4. Conclusions

Thermomorphic lipophilic amine blends potentially permit extensive regenerability - 70% without gas stripping at the low regeneration temperature of 80°C rising to 85% when other measures are adopted, thus permitting a more flexible and expedient thermal integration of the CO<sub>2</sub> capture process. The performance observed is comparable, if not superior, to that of commercial alkanolamines. The cyclic loading capacity (40-70°C: 100 g-CO<sub>2</sub>/L<sub>3M-B0+A1</sub>) is also much better than for the standard aqueous amine system (40-120°C: 60 g-CO<sub>2</sub>/L<sub>5M-MEA</sub>).

The activating component of lipophilic amine blends exhibits a vaporisation loss which is significantly higher than that for MEA. This loss, however, can be substantially reduced by 60% or even more using a chilled water scrubber. Foaming is a further disadvantage of biphasic amine systems, but it can be well controlled or eliminated by means of a liquid spray, foam breakers and water scrubbing. Irreversible chemical degradation of lipophilic amine blends is 75%-95% less than for MEA. It is conjectured that both the aqueous chemistry of the oxidative reaction and the lower operating temperature contribute to the improved chemical stability, one of the major unresolved weaknesses of conventional amines in the CO<sub>2</sub> separation from flue gases.

## Acknowledgement

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