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Combined Physical Property and Corrosion Assessment of Advanced Solvents for CO₂ Capture Systems

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Abstract

Detailed knowledge and understanding of a solvent's degradation and corrosion behavior under the effect of flue gas pollutants absorbing in solution is invaluable before moving to upscaling. In this work we are researching the effect of long-term exposure at elevated temperature and oxidative conditions, to identify and quantify the effect of degradation on the physical properties and corrosion behavior of four solvents, including monoethanolamine (MEA), diethanolamine (DEA), the phase-change solvent (PCS) S₁N (N1-Cyclohexylpropane-1,3-diamine) / DMCA (N,N – Dimethylcyclohexylamine) [1], and the commercial APBS-CDRMax[®] solvent, developed by Carbon Clean. We cover pure, contaminated (with sulfur and nitrogen dioxides), CO₂-loaded and unloaded forms. We then investigate the variation of physical properties of the liquid samples over time and evaluate their corrosion behavior with electrochemical techniques.

Keywords: CO₂ utilization; Rotating Packed Beds; reactive precipitation; CaCO₃; rate-based model

1. Introduction

Solvent degradation is an important issue in amine-based CO₂ capture systems contributing significantly to a plant's operating cost [2]. Three main co-existing routes to solvent degradation have been described in published literature, i.e., thermal, oxidative and the one that results from the reaction of amine molecules with flue gas contaminants, like SO_x, NO_x and fly ash. Following dissolution of contaminants in the liquid phase and reaction, heat stable salts and other unwanted byproducts accumulate in the solvent with adverse effects on solvent reactivity and absorption capacity, and on the quality of the capture plant's emissions [3]. Other issues include solvent foaming, equipment fouling and elevated corrosion rates [4]–[6]. Regardless of the degradation route, the result is a solvent with varying physical and chemical properties on a time – dependent manner. Given that these properties are important to the systems' design and operation and even co-determine the capture process' efficiency, their behavior under aging conditions is crucial to monitor.

Lab-scale studies assessing thermal and/or oxidative degradation are performed in autoclaves or other custom-made setups [2], [7], where the solvent is sampled intermittently and analyzed offline. These studies emphasize mainly on the “chemistry”

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of degradation and target the identification of degradation products and their possible formation mechanisms. Thus, they often overlook how other physical properties of the solvent are affected, that play an important role in the capture process, like viscosity, density and equilibrium capacity. On the other hand, degradation studies performed in pilot plants present a more complete picture, as they employ online monitoring of such properties during pilot plant campaigns [8], [9]. Nonetheless, they are highly plant-specific and such data are inevitably restricted to solvents that have been tested at pilot scale for quite some time, thus exposing a relative gap in the available datasets for other solvents.

Interestingly, the degradation routes may be catalyzed by metal cations that are introduced in the circulating solvent through the fly ash carried by the flue gas and via leaching due to corrosion of the equipment [10]. Fly ash, though, is not typical for every flue gas type, thus we focus on the corrosion aspect that is omnipresent. Locations prone to corrosion in pilot plants are those that face high acid gas loadings and temperature, such as the bottom of the absorber, stripper, condenser etc. [11], [12]. The charged products that form after the reactions of amine with CO₂ provide the conditions for corrosion. In turn, the type, abundance and ratio of metal cations is strongly dependent upon the interplay of the amine type with the selected construction materials. The metal ion leaching phenomenon is quite complex and includes several codependent steps itself [11], in the sense that equipment corrosion and solvent degradation are linked to each other possibly through a “closed loop” process where the initial leaching of metal ions is the input, causing potentially increased degradation rates, increased formation of (corrosive) degradation products and resulting in potentially increased corrosion rates. This corrosion – degradation link has been the subject of some experimental [8], [12], [13] and model-based [14], [15] studies that mostly deal with aqueous MEA. Such results once again underline the need to enrich our understanding of the degradation – corrosion interplay and to expand the existing dataset to other solvents, beyond MEA, before moving to large-scale facilities. Thus, the combined assessment of solvent corrosivity and induced degradation as expressed by varying physical properties is an important step that must precede the design of the CO₂-capture facility and the decision-making process.

In this work, we look into solvent degradation and corrosion in a combined framework. Our study expands to four solvents; MEA, diethanolamine (DEA), the novel phase-change solvent (PCS) S₁N (N1-Cyclohexylpropane-1,3-diamine) / DMCA (N,N –Dimethylcyclohexylamine) [1], as well as the commercial APBS-CDRMax[®] solvent, developed by Carbon Clean. The investigations pertaining to the use of APBS-CDRMax[®] are in the context of the EU-funded HiRECORD project [ref] [16] that intends to test this solvent in a 10 t/d carbon capture plant which employs rotating packed bed technology. We cover pure, contaminated (with sulfur and nitrogen dioxides), CO₂-loaded and unloaded forms of solvent, and their combinations. We subject them to an ageing – degradation protocol in contact with metal alloys relevant to pilot plant’s construction materials. We then evaluate the liquid samples for metal ion accumulation with inductively coupled plasma spectroscopy (ICP), viscosity, density, amine concentration and CO₂ loading. We also separately observe the metal specimens under electron microscopy and energy dispersive X-ray spectroscopy (SEM – EDS) for evidence of corrosion and depositions of degradation products. Our study also employs a range of electrochemical techniques, including Open Circuit Potential measurements (OCP), Potentiodynamic and Cyclic Polarization curves, and Electrochemical Impedance Spectroscopy (EIS), to provide insights into the corrosion behavior.

Nomenclature

MEA	monoethanolamine
DEA	diethanolamine
S ₁ N	N1-Cyclohexylpropane-1,3-diamine
DMCA	dimethylcyclohexylamine
PCS	phase-change solvent
SCE	saturated calomel electrode
OCP	open circuit potential

2. Experimental section

2.1. Materials and Solvent preparation

The materials used in the preparation of the aqueous solutions of solvents and for the analyses that followed are listed in Table 1. The chemicals were used as received, without further purification. Depending on the experiment, the solvent was prepared either in the pure form (free of pollutants and CO₂), or with the addition of flue gas SO_x, NO_x pollutants and CO₂. Pollutants were added in the liquid phase in the form of sulfuric acid (H₂SO₄) and nitric acid

(HNO₃). Their concentration was selected to represent an extreme case of contamination at 1.9 wt.% H₂SO₄ and 1.2 wt.% HNO₃ (total concentration of acid 3.1 wt.%) and the respective solutions were prepared by weighing. After the addition of pollutants, CO₂-loaded solvents were prepared in an experimental apparatus [17], where pure CO₂ was bubbled for a pre-estimated time interval targeting a specific CO₂ content for each solvent. Before proceeding with the ageing protocols, the starting total amine content was quantified via NaOH – HCl titrations and the CO₂ loading was determined via the BaCl₂ method [17].

Table 1. Chemicals used in this work

Chemical	CAS No.	Procurement
MEA 99 %	141-43-5	Merck
DEA ≥ 98 %	11-42-2	Merck
S ₁ N ≥ 95 %	3312-60-5	TCI Chemicals
DMCA ≥ 98 %	98-94-2	Acros Organics
APBS-CDRMax®	-	Carbon Clean
H ₂ SO ₄ ≥ 95 %	7664-93-9	Fischer Chemicals
HNO ₃ 70 %	7697-37-2	Thermo Scientific
CO ₂ 99.995 %	124-38-9	Buse gas
NaOH ≥ 98 %	1310-73-2	Merck
BaCl ₂ ≥ 99 %	10326-27-9	Merck
HCl 1M	7647-01-0	Merck
H ₂ O deionized	7732-18-5	-

2.2. Methodology of solvent ageing and corrosion measurements

Solutions of S₁N/DMCA 1:3 3M, MEA 30 wt.% and APBS-CDRMax® were examined in their CO₂-unloaded and CO₂-loaded form. Glass containers were filled with 200 g of solution and an SS 316L corrosion coupon was immersed. The containers were sealed and placed in a heating furnace at 90 °C for 30 days. Every 10 days containers were retrieved. Liquid samples and corrosion coupons were analysed separately to determine the effect of ageing on physical properties, corrosivity and the extent of corrosion, as shown in Figure 1.

The corrosion measurements that we present here were performed on fresh solvents with the addition of pollutants, that were either loaded with CO₂ or remained unloaded. All electrochemical tests were conducted using a three-electrode setup, with a saturated calomel electrode (SCE) as the reference electrode and a platinum rod as the counter electrode. Before each electrochemical experiment, the open circuit potential (OCP) of the specimens was recorded until a steady-state value was reached. A scanning rate of 2 mV/s was applied for all polarization measurements, with the cathodic-to-anodic scan range set from –800 mV to +900 mV (versus SCE) relative to the OCP. After the experiments, the Tafel extrapolation method was used to determine the corrosion rate. Each electrochemical experiment was repeated at least three times to ensure the consistency of the results. Electrochemical impedance spectroscopy (EIS) was performed at the OCP across a frequency range of 10 kHz to 0.1 Hz, using a 10 mV peak-to-peak voltage excitation. To verify reproducibility, all electrochemical tests were conducted three times. In the following section we are presenting results acquired so far from our ongoing study.

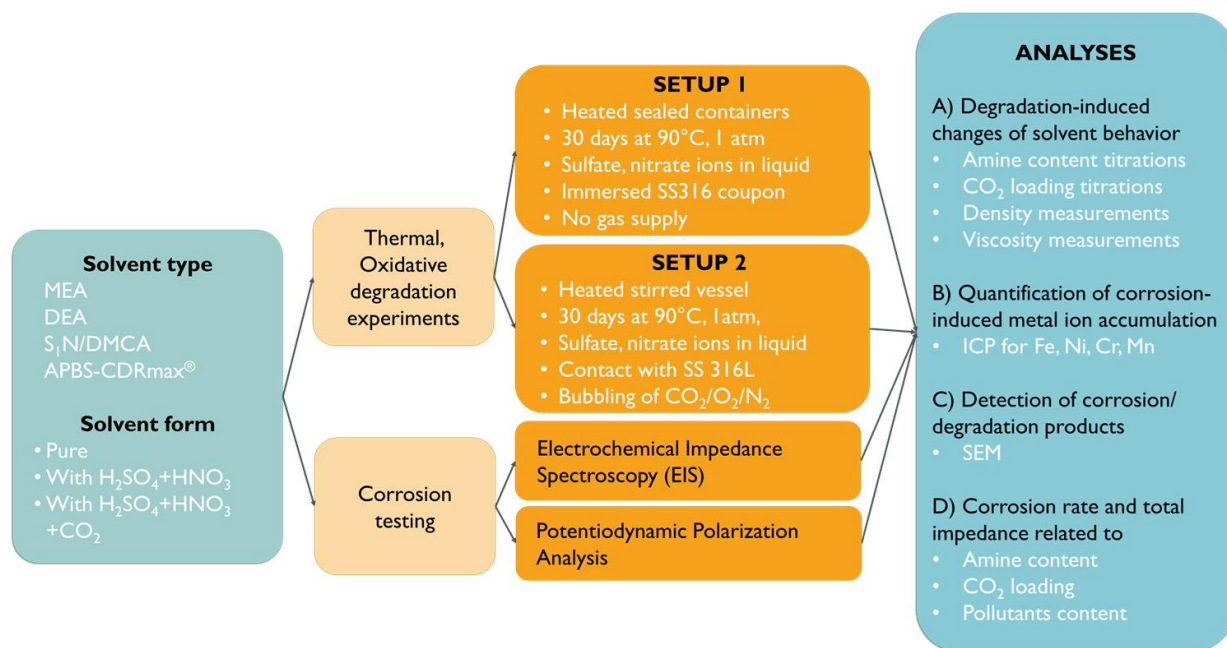


Figure 1. Experimental methodology and analyses designed for studying the effect of degradation on solvent properties and corrosion behavior

3. Results and discussion

3.1. Physical properties and degradation products following the ageing experiments

The physical properties of APBS-CDRMax® exhibited remarkable resilience to degradation during the 30 day ageing process, compared to MEA and S₁N/DMCA. Starting with titration measurements of CO₂-preloaded samples, on the 30th day of ageing, APBS-APBS-CDRMax® exhibited insignificant loading capacity reduction (-0.07%) compared to the other solvents, followed by S₁N/DMCA (-16.5 %), MEA (-19.2%) and DEA (-51.9%). During the same ageing period, the density of APBS-CDRMax® was practically unaltered (-0.03%), MEA showed a similar behavior, while S₁N/DMCA showed a small variation (-4.1%) that could possibly indicate some sensitivity towards the thermal treatment. The viscosity measured at absorption-relevant temperature (40 °C) showed the greatest variation among other properties. Especially DEA and MEA exhibited significantly increasing trends, while S₁N/DMCA presented a moderate increase (Figure 2a). APBS-CDRMax® presented the smallest variation of viscosity (+4.9%).

The ICP measurements (Figure 1b) for accumulated metals in solution leaching from the immersed SS 316L coupon revealed overall low concentrations, below 1 ppm, after 30 days of ageing for all tested metals (Fe, Ni, Cr, Mn). Fe was found with the highest concentration for all solvents, followed by Ni and Cr. The mixture S₁N/DMCA presented the lowest Fe concentration, compared to MEA and DEA (Figure 2b). APBS-CDRMax® showed slightly lower Fe compared to S₁N/DMCA.

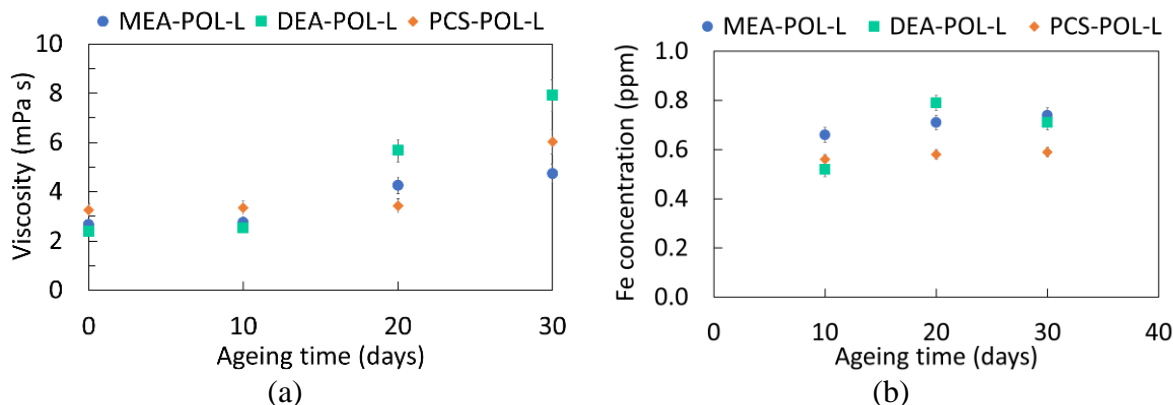


Figure 2. a) Variation of viscosity and b) Accumulation of metals in solution during a 30-day ageing period at 90 °C. Solvents MEA, DEA and S₁N/DMCA pre-loaded with CO₂ and contaminated with 3.1 wt.% total acids concentration and with absorbed CO₂

SEM-EDS assisted observation of SS316L coupons that were immersed in APBS-CDRMax® revealed 3 types of degradation products depositing on its surface. Namely, type 1 products predominantly contained Cl, K, Na atoms; type 2 darker spots predominantly contained carbon, nitrogen and oxygen; type 3 depositions contained iron, chromium, nickel silicon and may exhibit a dark grey layer on top (all depicted in Figure 3).

The formation of type 1 degradation products is attributed to impurities inherently present in the water used during solvent preparation. Type 2 products must be an organic chemical compound, most probably a by-product of amine degradation. Fe atoms were fourth in abundance, after C, N, O as suggested by the atomic analysis, which could indicate a type of bonding/complexing between the amine degradation product and the metal substrate. Type 3 products are characterized by a strong presence of elements also found in SS316L. This product could be interpreted as: a) a mass of corroded metal that stayed near the surface and formed a new compound or b) a deposited crystal that is too thin to be analysed and is penetrated by the x-ray beam “seeing” the metal substrate.



Figure 3. Degradation products forming during the 30-day ageing period and depositing on the surface of the SS316L corrosion coupon

3.2. Corrosion testing results

Figure 4 provides insight into the corrosion behavior of 316L stainless steel in different amine-based solutions, evaluated through corrosion rate calculations. The amine systems in this corrosion study are either lean (unloaded) or loaded with CO₂, with pollutants present in all cases.

Figure 4a depicts the calculated corrosion rates for the tested amine systems. Without the presence of CO₂, APBS-CDRMax® has the lowest corrosion rate, indicating it offers better protection when not loaded with CO₂. MEA exhibits higher corrosion rate, but it remains relatively low. On the other hand, the corrosion rate for the PCS increases dramatically, with PCS exhibiting the highest corrosion rate, orders of magnitude higher compared to the other two solvents. When the solvents are loaded with CO₂, MEA experiences an increase in corrosion rate, though it maintains better performance compared to PCS. APBS-CDRMax® shows the smallest increase in corrosion rate, confirming its superior resistance to corrosion even when loaded with CO₂. Interestingly, the PCS exhibits a lower corrosion rate compared to when it is not loaded. This is likely due to the presence of pollutants, which appear to affect the PCS

more when it is unloaded. The increased corrosion rate of the PCS in when it is not loaded with CO₂ may be attributed to the degradation of the amine caused by the introduction of pollutants [18].

The Bode plot in Figure 4b is derived from Electrochemical Impedance Spectroscopy (EIS) measurements for 316L stainless steel in various amine systems with pollutants, comparing unloaded and CO₂-loaded conditions. In the lowest frequency region, APBS-CDRMax® shows the highest impedance, particularly when it is not loaded, with a clear separation between the loaded and unloaded states. Higher impedance in this region indicates better corrosion resistance, likely due to more effective protective layers or passive films. MEA and the PCS have lower overall impedance, with relatively small differences between their loaded and unloaded states. However, the PCS shows slightly lower impedance than MEA in both conditions, suggesting slightly inferior corrosion protection.

As expected, the impedance for all systems decreases as the frequency increases. The solution resistance is clearly observable in the cases of MEA and the PCS, as indicated by the plateau in the high-frequency region. On the other hand, for APBS-CDRMax®, the solution impedance is less discernible, which suggests enhanced impedance of the amine system. However, the separation between the loaded and unloaded states diminishes at higher frequencies. APBS-CDRMax® again shows higher overall impedance compared to the other systems, indicating better protection across the frequency range.

In all amine systems, lower impedance is observed when CO₂ is present, suggesting that CO₂ loading negatively impacts corrosion resistance, likely by weakening the passive film on the 316L stainless steel surface or increasing electrochemical activity [19], [20]. The APBS-CDRMax® system experiences reduction in impedance in the presence of CO₂ but remains superior to MEA and PCS in both conditions. The significant separation between the loaded and unloaded states in APBS-CDRMax® further highlights the impact of CO₂ loading on resistance, though it still outperforms the other systems. MEA and the PCS exhibit similar trends but show lower impedance than APBS-CDRMax®, indicating weaker corrosion resistance. The fact that MEA and the PCS are not as significantly impacted by CO₂ loading suggests that the prior introduction of pollutants may have led to the degradation of these amines, making them less susceptible to further degradation upon CO₂ loading [21].

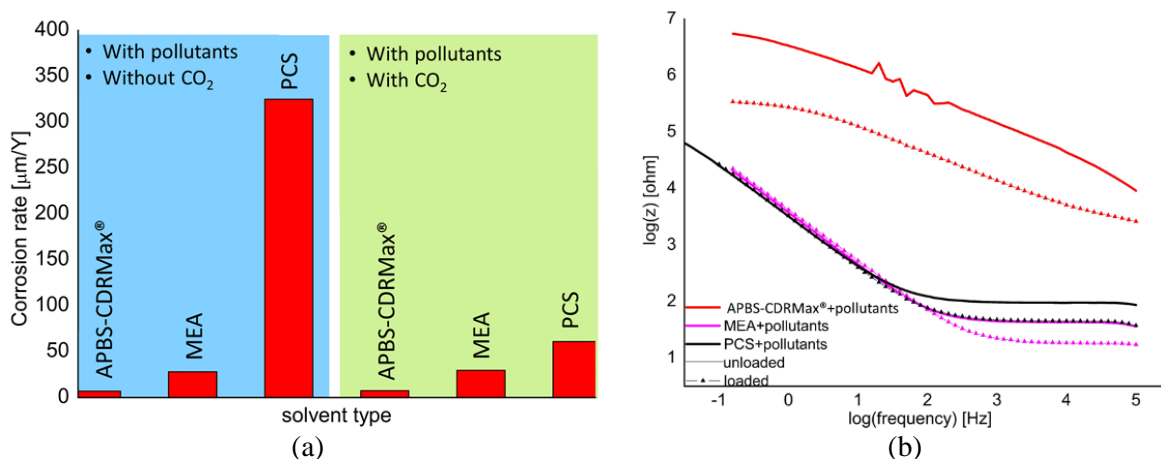


Figure 4. a) Corrosion rates extracted from Tafel extrapolation for all amine systems tested. (b) Bode plots for in various amine systems with pollutants, comparing unloaded and CO₂-loaded conditions.

4. Conclusions

This study evaluates the stability of APBS-CDRMax® compared to other solvents over a 30-day ageing period at 90 °C. APBS-CDRMax® demonstrated exceptional stability, with negligible changes in CO₂ loading capacity (-0.07%) and density (-0.03%). In contrast, solvents like S₁N/DMCA (PCS), MEA, and DEA showed reduction in loading capacity (up to -51.9%) and varying density changes. Viscosity variations were most pronounced, with APBS-CDRMax® exhibiting only a slight increase (+4.9%), while MEA and DEA showed substantial increases. ICP analysis indicated low metal concentrations from SS 316L coupons, with iron (Fe) being the most prevalent.

SEM-EDS analysis identified three types of degradation products on the coupons, suggesting interactions between corrosion products and the substrate. The Bode plot confirms that APBS-CDRMax® provides superior corrosion protection for 316L stainless steel, showing a noticeable reduction in impedance when loaded with CO₂ but still maintaining higher impedance than MEA and PCS. MEA and PCS demonstrate comparable performance, though both experience a significant reduction in corrosion resistance relative to APBS-CDRMax®, as reflected by their lower impedance values. Regarding the corrosion rates, APBS-CDRMax® continues to exhibit the best corrosion resistance in both unloaded and CO₂-loaded conditions. The corrosion rate increases slightly when CO₂ is present, but APBS-CDRMax® remains the most resistant system overall. MEA shows moderate corrosion resistance, with only a relatively small increase in corrosion rate when CO₂ is present. The PCS is the most susceptible to corrosion, especially when there is no CO₂, where its corrosion rate rises significantly. These findings overall highlight APBS-CDRMax®'s robustness, stability and potential for applications requiring long-term and reliable performance with reduced risk of equipment corrosion.

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