

Demonstration of CO₂ Capture Process Monitoring and Solvent Degradation Detection by Chemometrics at the Technology Centre Mongstad CO₂ Capture Plant: Part II

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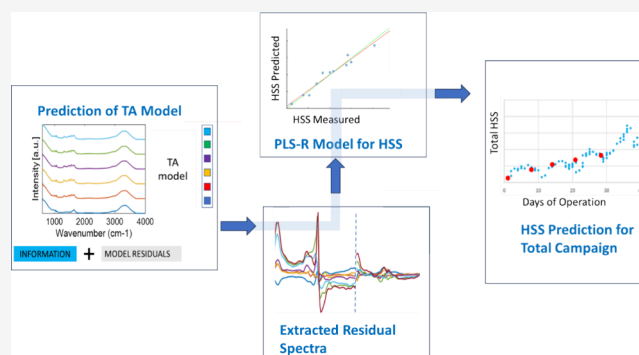
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ABSTRACT: In this work (Part II), we present quantitative monitoring of degradation for 30 wt % aqueous monoethanolamine (MEA) solvent using the residual Fourier transform infrared (FTIR) spectra extracted from the partial least-squares regression (PLS-R) models developed in Part I. The PLS-R models of Part I cover monitoring of TIC (total inorganic carbon, i.e., solvent CO₂ capture capacity) and TA (total alkalinity, i.e., solvent capture “strength”) of continuously degrading MEA solvent; these models incorporate a methodological hierarchy for continuous model update throughout the entire campaign to address the ongoing solvent degradation. Both Parts I and II of our work are based on a 1960-h test campaign conducted at the Technology Centre Mongstad, Norway, in 2015 using 30 wt % aqueous MEA solvent. In Part II, residual spectra were extracted and used to formulate prediction models for in-line followup of degradation species groups: (i) total heat-stable salt (HSS) species and (ii) total amine degradation products. This new tool for continuous solvent degradation quantification can supplement the current practice of indirect estimation of when to start and/or stop solvent reclaiming.



1. INTRODUCTION

The global temperature rise is rapidly approaching the critical Intergovernmental Panel on Climate Change (IPCC) defined threshold of 1.5 °C¹ in just a few years; 2024 could be the first year to experience it.² One mitigating action is the ongoing start-up of postcombustion carbon capture (PCC) gas–liquid absorption units limiting carbon dioxide (CO₂) emissions from fossil fuel burning.

However, one important PCC challenge is still solvent degradation. The composition of a typical solvent system, e.g., aqueous monoethanolamine (MEA), needs to be kept in stable and acceptable technoeconomic condition. For instance, solvent degradation detection and solvent cleaning by, e.g., ion exchange or solvent reclaiming methodology, is critical.³ Solvent reclaimer waste generation is reported to vary in the range of 0.1–14.9 kg reclaimer waste per tonne of CO₂ captured.⁴ Hence, solvent degradation generates both solvent replenishment and waste disposal cost.

Since 2012, our group has been interested in the application of process analytical technology (PAT) for monitoring of PCC gas–liquid absorption technology.^{5–8} The focus of this work is quantitative monitoring of solvent degradation and solvent reclaiming utilizing Test Centre Mongstad demo-scale MEA test campaign data.⁹

Solvent degradation is a continuous process starting slowly but typically following an exponential curve pattern.¹⁰ It is due to, e.g., flue gas impurity absorption as well as thermal and oxidative solvent reactions. In-depth studies are available on degradation mechanisms, the identity of the reaction species as well as the complexity of their chemical identification.^{9,11,12} For instance, heat-stable salts (HSSs) can be produced either by the reaction of amine solvent with CO₂ itself or from amine reaction with flue gas impurities. These early stage degradation species participate subsequently in further solvent degradation reactions¹³ and plant corrosion.^{3,14} Various offline analytics including advanced methods such as triple-quadrupole liquid chromatography–mass spectrometry (LC–MS QQQ) and anion chromatography (IC–ECD) can give detailed molecular information. However, this easily becomes tedious and time-consuming work, possibly requiring specialized subcontractors.^{9,15}

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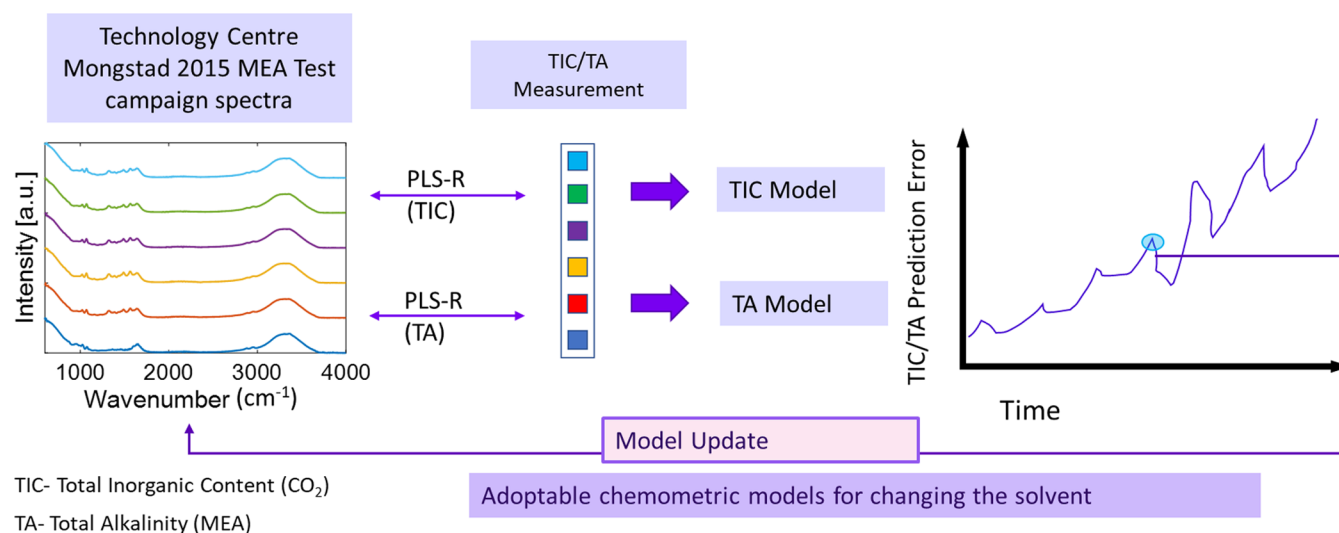
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Table 1. Abbreviations/Statistical Parameters

abbreviations/ statistical parameter	stand for	note
PLS-R models	partial least-squares regression models	NIPALS algorithm used; input variable is raw FTIR or residual spectra; output variables are TIC, TA, HSSs, and ADPs
TIC model	PLS-R model of total inorganic content	sum of all species containing CO ₂ ; for more details, see Wagaarachchige et al. ⁸
TA model	PLS-R model of total alkalinity	sum of all solvent species reacting with protons, which is equivalent to “solvent strength”; for more details, see Wagaarachchige et al. ⁸
RMSECV	average model error of cross validation	selects optimum LVs and compares the model performance
RMSEP	average model error of prediction	selects optimum LVs and compares the model performance
LVs	latent variables	no. of components of a PLS-R model
Q-residuals	quantification of the spectral part that is not used in the PLS-R model (the summation of squares of the residuals) ²⁰	unusual spectral changes are evident, and an increase in Q-residuals indicates a more altered solvent condition compared to the fresh solvent state

**Figure 1.** PLS-R model (TIC and TA) calibration and model updating.

In 2015, the Technology Centre Mongstad (TCM), Norway, conducted a 1960-h 30 wt % aqueous MEA solvent test campaign. For this campaign, we reported in Part I of this work Fourier transform infrared (FTIR) spectroscopic partial least-squares regression (PLS-R) models for monitoring of TIC (total inorganic carbon, i.e., solvent CO₂ capture capacity) and TA (total alkalinity, i.e., solvent capture “strength”) of continuously degrading MEA solvent. Furthermore, the study included a methodologic hierarchy for continuous model updating throughout the entire campaign period to cope with ongoing solvent composition change (degradation), thus extending the application of the PLS-R method to commercial aqueous alkanolamine CO₂ capture campaigns.

In this Part II of our work, we report quantitative monitoring of solvent degradation using the extracted residual FTIR spectra from the PLS-R models developed in Part I⁸ of our work.

As demonstrated in other industries, e.g., chemical and pharmaceutical, in-line FTIR real-time monitoring provides a more complete time-based database for PLS-R modeling compared to manual sample acquisition.¹⁶ For instance, the TCM database of the 1960-h MEA test campaign utilized for Parts I and II of this work contains 17 offline-analyzed manual samples.⁹ For this work, one in-line FTIR spectrometer could have provided complete time-based monitoring information substituting a manual sample campaign connected to

respective offline analyses requiring specialized instruments and handling of analytical logistics. Furthermore, the 1960-h TCM 30 wt % aqueous MEA test campaign also included a 92-h thermal reclaiming part. For optimal thermal solvent, reclaiming online analysis or frequent manual solvent sample/analysis was proposed.¹¹

Previously, Grimstvedt et al. proposed PLS-R and FTIR online techniques to be an attractive option for PCC solvent monitoring by observing a correlation between the PLS-R residuals and the level of HSS species present in a degraded aqueous MEA solution. Furthermore, detection of a residual threshold could be used to trigger detailed offline solvent analysis.¹⁷ In our contribution, for the first time, we demonstrate that this suggestion is generally applicable for followup of PCC solvent degradation at the demo test scale using real flue gas. Hence, we report quantitative monitoring of solvent degradation and solvent reclaiming. Furthermore, we also show that solvent degradation can be handled as one group of molecules and not as individual molecules, making the followup of individual degradation molecules less critical.

2. MATERIALS AND METHODS

2.1. Materials. This work (Part II) employs the same real plant data gathered during the TCM MEA2 campaign (30 wt % aqueous MEA) as that in Part I.⁸

MEA2 campaign, a 1960-h operation, commenced on July 6, 2015, and concluded on October 17, 2015.⁹ The base case

Table 2. Data Used for Modeling of Solvent Degradation Groups

degradation groups (model output)	assigned species to the molecular group	spectral input data	input data analysis method ⁹	input data unit	number of utilized samples
total heat-stable salts (HSSs)	formate	TIC model prediction residuals	ion exchange and following titration	mol/kg	11
	acetate				
	glycolate				
	oxalate				
	sulfate				
total amine degradation products (ADPs)	HEPO	TA model prediction residuals	LC–MS QQQ	mg/L	10
	HEGly				
	HEI				
	HEF				
	OZD				
	HEA				
	<i>N,N'</i> -bis(2-hydroxyethyl)oxamide (BHEOX)				

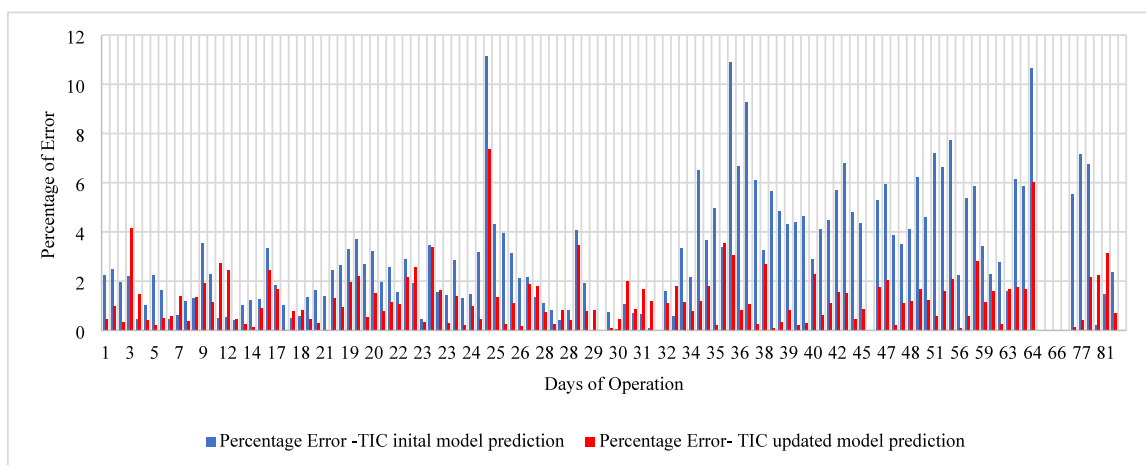


Figure 2. Percentage of errors of the TIC model: blue, initial model; red, updated model.

testing took place on September 7, 2015, under steady-state conditions, around 8 weeks after the startup.¹⁸ Morken et al. illustrated the overall campaign operational hours,⁹ wherein Gjernes et al. tabulated the overall test activities¹⁹ of the MEA2 campaign. The MEA2 campaign is mainly composed of the primary stages of an amine-based CO₂ capture plant operation. Statistical parameters and abbreviations of this work are given in Table 1.

2.2. Methods. In Part I of this work,⁸ two PLS-R models were calibrated and validated for predicting CO₂ (TIC model) and MEA (TA model) species of the TCM MEA2 campaign. We used one-third of the campaign data for model preparation and reserved the remaining two-thirds for model updating and validation.

These models were used to demonstrate model updating during operation, resulting in improved predictions of the entire campaign with reduced uncertainty.⁸ Figure 1 illustrates how the models were prepared and updated using the TCM data.

For the current work (Part II), a set of residual spectra (the portions of the FTIR spectra not used for the models' predictions) was extracted during the TIC and TA modeling process that was reported in Part I.⁸ Gathered residual spectra were used to prepare PLS-R models for degradation product groups, i.e., total HSS and total amine degradation species. Section 3.1 presents the key findings of Part I to establish a

good foundation for understanding the results presented in the current work (Part II).

Table 2 indicates the details of the data used for these degradation species models. Two degradation species group models were prepared to predict the total HSS and total amine degradation species of the degrading solvent. Reference values for these models were obtained from offline measurements of the MEA2 campaign, corresponding to specific species groups. Variable selection was done using an approximate estimation of common anion IR vibrational bands of degradation products. These models were prepared using only 10–11 samples and validated by using the full cross-validation method due the absence of sufficient reference data.²¹ Finally, the use of residual spectra-based models for the degradation product speciation of the total MEA2 campaign was tested. Section 3.2 provides the results of this work.

All data analysis were performed on the MATLAB platform using *PLS Toolbox* 8.6.2 software.

3. RESULTS AND DISCUSSION

Section 3.1 outlines the results of Part I⁸ to provide a distinct understanding of the complete study. In section 3.2, the discussion focuses on the results of this work (Part II).

3.1. TIC and TA Models and Solvent Reclaiming Followup. This section provides details about the initial TIC

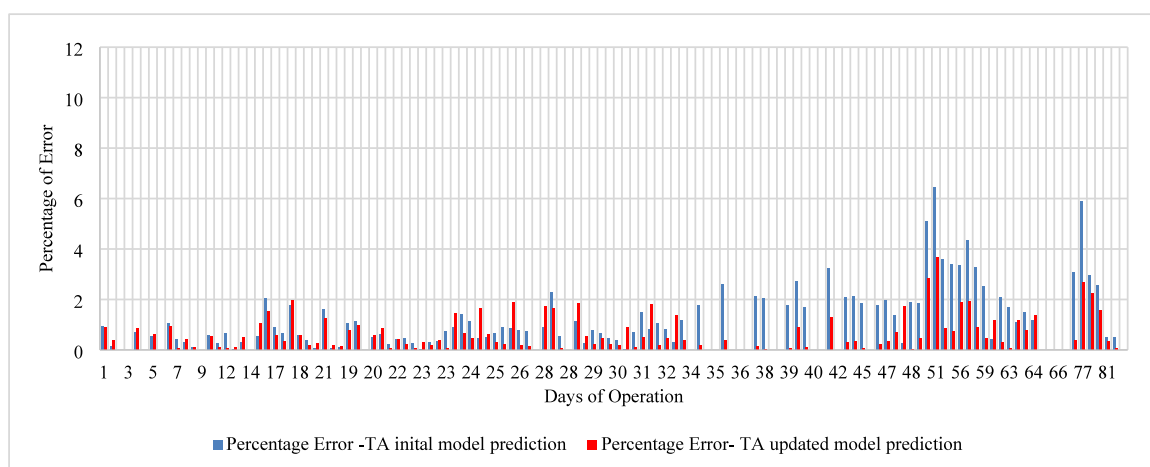


Figure 3. Percentage of errors of the TA model: blue, initial model; red, updated model.

and TA models, the process of model updating, and the subsequent followup on solvent reclaiming.

The TIC and TA models were prepared to predict the concentration of CO₂ and amine species during the total MEA2 campaign. Variable windows of the TIC model—[1590–1467] and [1407–1301]—were selected to cover the FTIR vibrational bands (1562, 1486, 1320, 1387, and 1362 cm⁻¹) of MEACOO⁻, CO₃²⁻, and HCO₃⁻ species.⁸ Similarly, the vibrational bands at 1020, 1638, and 1067 cm⁻¹ were accounted for the selection of variable windows of the TA model—[1670–1590] and [1113–944]—to cover MEA and protonated MEA species.⁸ These two PLS-R models were calibrated using the nonlinear iterative partial least-squares (NIPALS) algorithm and validated using an independent data set of the same campaign.²² All spectra were baseline-corrected using the Whittaker filter²³ to remove baseline noise. The prediction errors of these models for the total campaign predictions were discussed and proposed as a method to update the models accordingly to avoid increasing prediction errors.⁸

Figures 2 and 3 indicate the prediction errors of the TIC and TA models, respectively. The blue columns represent the initial model's prediction errors, showing an increasing trend, whereas the red columns correspond to the predictions of the updated TIC model. As a result of these updates, both models demonstrated an average reduction of approximately 50% in their prediction errors.⁸

Spectroscopic measurement provides a chemical fingerprint of the measured solvent sample, indicating the vibrational bands of all chemical species. When model predictions are obtained using FTIR spectra, these models extract useful information from the spectra, while the unused parts are filtered out as spectral residuals. Figure 4 depicts the schematic representation of the model residual extraction.

These spectral residuals were used to calculate the average residuals of the spectra, which are known as Q-residuals (Q_s).²² In long-term monitoring of the solvent system, these residuals indicate changes in the solvent over time such as solvent degradation. Figure 5 shows Q_s versus days of operation of the MEA2 campaign. In Figure 5, blue dots indicate Q_s calculated before the reclaiming starts, and the red dashed line represents the time when the reclaiming started. These blue dots demonstrate that the TIC model's Q_s increase with the time of the campaign operations. However, from day

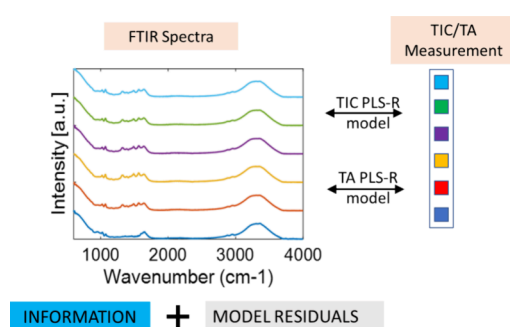


Figure 4. Schematic representation of the model residual extraction.

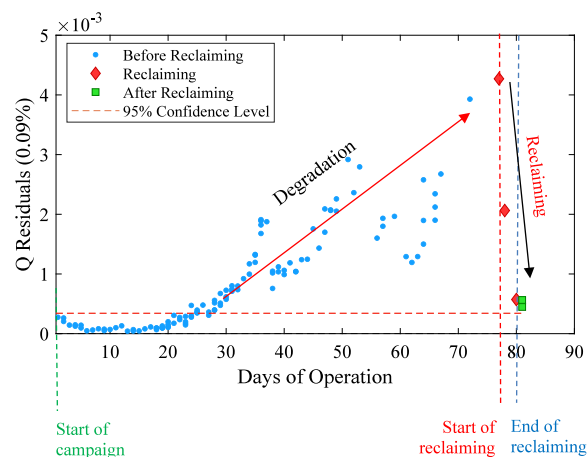


Figure 5. TIC model Q_s versus days of the MEA2 campaign operation.

77 onward (when the reclaiming started on day 77), the Q values of predictions decrease, eventually closely resembling the fresh solvent state (at the 95% confidence level). This observation can also be seen in the variation of the TA model's Q_s over time, as shown in Figure S1. The possibility of applying multivariate statistical process control (MSPC) for the followup and control of solvent reclaiming is discussed in Part I.⁸

3.2. Thermal Solvent Reclaiming at Technology Centre Mongstad (TCM-DA). Thermal reclaiming of degraded aqueous MEA solvent has been practiced in gas-treating plants²⁴ and PCC plants^{25,26} for quite some time.

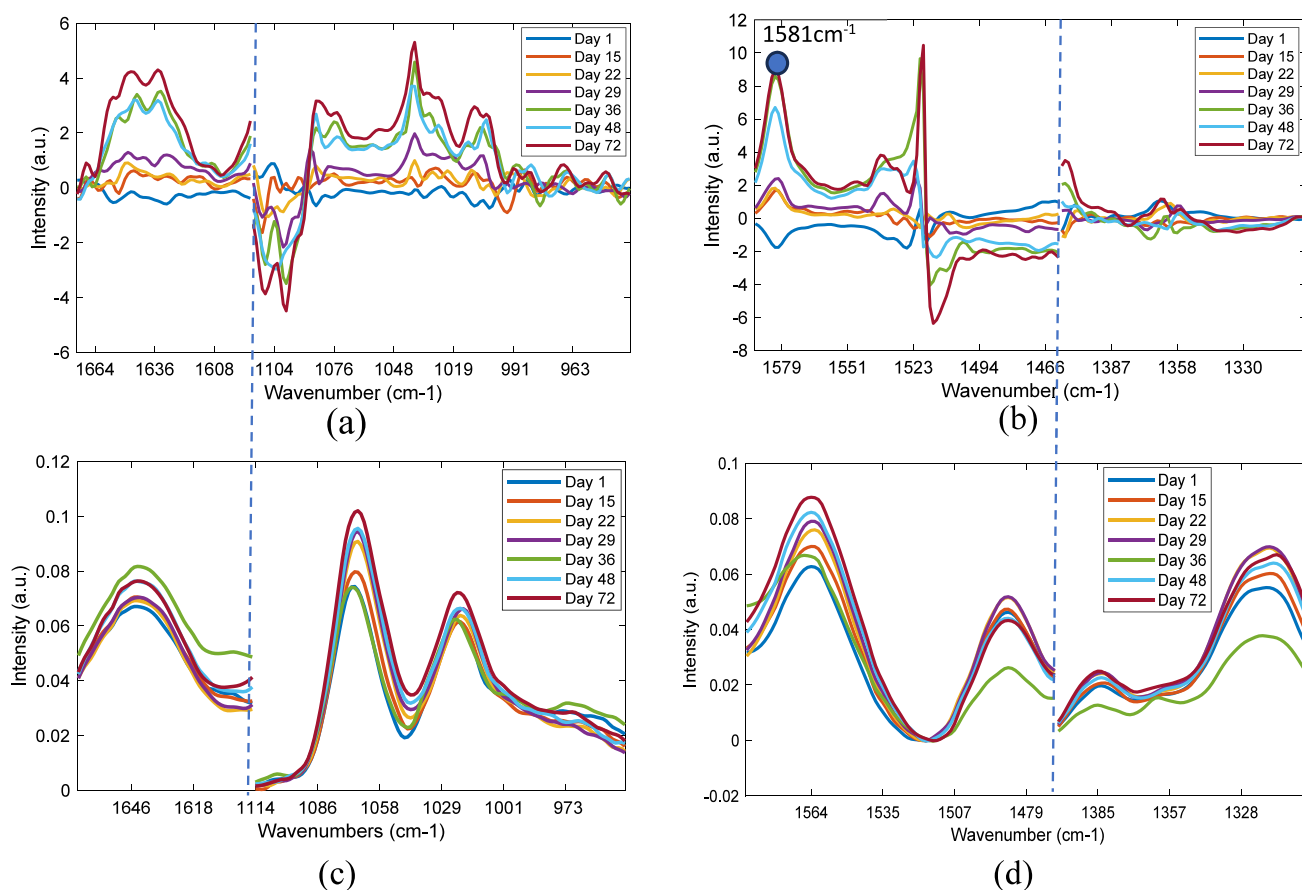


Figure 6. Residual spectra from the (a) TA and (b) TIC models and the corresponding FTIR spectra from the (c) TA and (d) TIC models.

In short, the thermal reclaimer setup at the TCM-DA demo unit¹¹ consists of passing a lean solvent stripper slipstream to the reclaiming vessel where extra steam is added to separate useful solvent components, which are returned to the process. The remaining waste is discharged from time to time. The operating pressure corresponded to the stripper pressure.

In the case of the 2015 30 wt % aqueous MEA test campaign, reclaiming was performed for 92 h after 1838 operation hours. The plant was run for an additional 28 h before the final test conclusion.

The main finding was that reclaiming treatment is harsh ($T = 160\text{ }^{\circ}\text{C}$) to the solvent (degradation); hence, the solvent residence time in the reclaimer vessel should be minimized. Hence, solvent reclaimer runs should be shorter but more frequent. Furthermore, online monitoring or frequent manual solvent sampling is recommended for solvent followup.

3.3. PLS-R Models for Degradation Species Groups: Total HSSs and ADPs. In an amine-based CO₂ capture plant, the solvent is changing for several reasons, e.g., amine degradation, flue gas impurity accumulation, piping corrosion products accumulation, solvent emissions, etc. Additionally, it is obvious that the concentrations of these degradation species tend to increase in the solvent during long-term operation.

This group of degradation species is a heavy mix of different types of chemical compounds, e.g., HSSs, ADPs, corrosion products, etc. In 2016, Morken et al. discussed such identified and unidentified degradation products of the MEA2 operation.⁹ If these species can quantitatively be identified by using inline monitoring with a spectroscopic method, it will

minimize the use of specific offline sample analysis methods like titration, IC, LC–MS, etc.

In the following sections, the PLS-R model preparations based on residual spectra for two main degradation species groups are discussed.

Residual spectra from TA and TIC model development are shown in parts a and b of Figure 6, respectively. Nonetheless, these spectra are a valuable source for monitoring low concentration species. Although the spectra look different from the normal FTIR spectra, these figures show something important about the solvent changes. The most distinct observable is the increase in the intensity of residual spectra with the operation time, as shown in Figure 5. The anion analysis of this campaign shows that the formate anion has the highest concentration, with the acetate anion in the second position among all HSS species.⁹ Ito et al. published the IR vibrational band for C–O stretching of formate and anions at 1585 and 1555 cm⁻¹, respectively.²⁷ As shown in Figure S2, the attenuated-total-reflectance (ATR)-FTIR analysis results of specific species indicate distinctive peaks for formate and acetate at 1581 and 1550 cm⁻¹, respectively. Interestingly, Figure 6b depicts a distinctive residual peak variation at 1581 cm⁻¹, which might indicate formate or the presence of a formate–glycolate–oxalate mixture (Table 3). This identification supports that the residual spectra show the vibrational bands of HSS species, which are not clearly visible (Figure 6d). Consequently, the identification of degradation species by FTIR analysis can be a suitable preprocessing approach.

Among the identified degradation species of the MEA2 campaign, the HSS is a major group. At the starting point of

Table 3. HSS Species, Identified IR Bands, and Corresponding Literature IR Bands

HSS species	identified IR bands	IR bands in the literature/observed lab testing
formate	1581	C–O stretching: 1585, ²⁷ 1581 ^a , 1411,
acetate		C–O stretching: 1555, ²⁷ 1550 ^a
glycolate	1581	1581 ^a , 1411 ^a , 1320 ^a , 1072 ^a
oxalate	1581	1581 ^a , 1303 ^a
nitrate		1350 ^a , 1411 ^a
nitrite		1334 ^a , 1226 ^a

^aConfirmed by lab testing in USN lab.

solvent reclaiming, the HSS concentration is recorded as 1 wt % MEA.⁹ HSSs represent salts formed by the reaction of acid with amine base, forming anionic species like formate, acetate, oxalate, glycolate, nitrate, sulfate, etc. Consequently, the HSS species group is very complex in assigning exact IR band assignments. In Figure 6b, the TIC model's residual spectra may indicate the presence of formate/glycolate/oxalate anions or a mixture of all anions by the peak at 1581 cm⁻¹. Additionally, based on the chemical structures of all identified anionic species,⁹ the HSS group might be presented in the TIC variable range due to their vibrational bands, i.e., C–O_{str}, –CO₂⁽⁻⁾_{asy}, –CH₃_{asy}, –SO₂_{asy}, and C–H_{asy}.²⁸ Therefore, the

total variable range of the TIC model's residual spectra was selected for the PLS-R model calibration of the HSS group.

To test the suitability of using raw FTIR spectra for degradation product speciation, the raw FTIR spectra were subjected to the PLS-R algorithm, and the model plots generated for one and two latent variables (LVs) are shown in parts a and c of Figure 7, respectively. The plot depicts the raw FTIR spectral correlation with the HSS concentrations using two LVs: $R^2(\text{CV}) = 0.952$ and $\text{RMSECV} = 0.0117$ mol/kg. The calibrated PLS-R model using the TIC model's residual spectra in Figure 7b has a clear correlation with $R^2(\text{CV}) = 0.933$ and $\text{RMSECV} = 0.0144$ mol/kg only using one LV. Hence, HSS species concentration calibration is possible either using raw FTIR spectra or residual spectra from the TIC modeling. However, for the identification of degradation species, the residual extraction approach is superior to the approach of models based on raw FTIR spectra. Furthermore, models based on residual spectra are less complex than those based on the raw FTIR spectra. Figure 8 shows the total HSS concentration mapping of measured and residual spectra (TIC)-based model-predicted values of the MEA2 campaign.

HSS species (e.g., organic acids) react with MEA and CO₂ to generate new amine degradation compounds. A simplified scheme for this was given by Morken et al.⁹ In the present

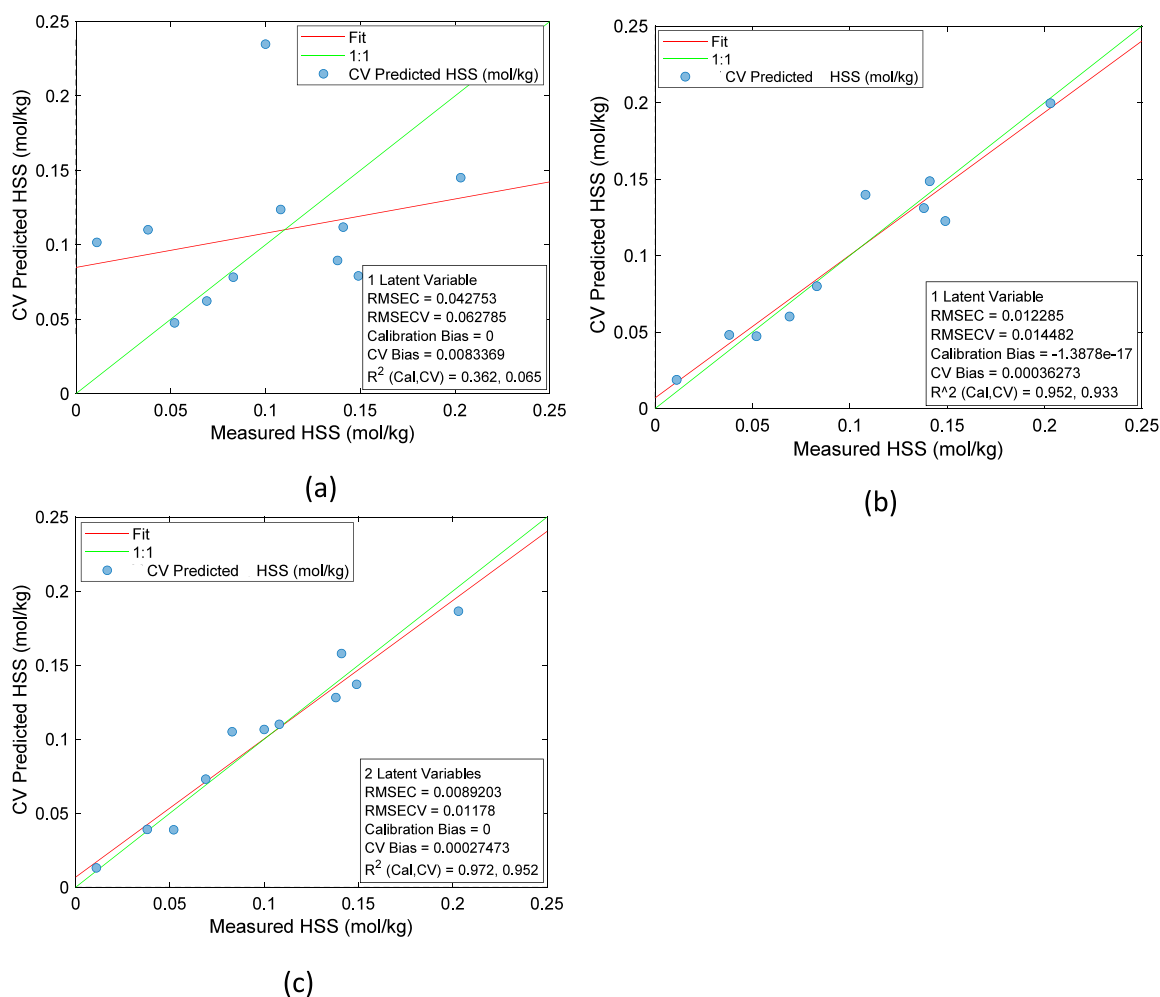


Figure 7. PLS-R model for HSS using (a) raw FTIR spectra with one LV, (b) residual spectra of the TIC model, and (c) raw FTIR spectra with two LVs (a variable range of the TIC model is used).

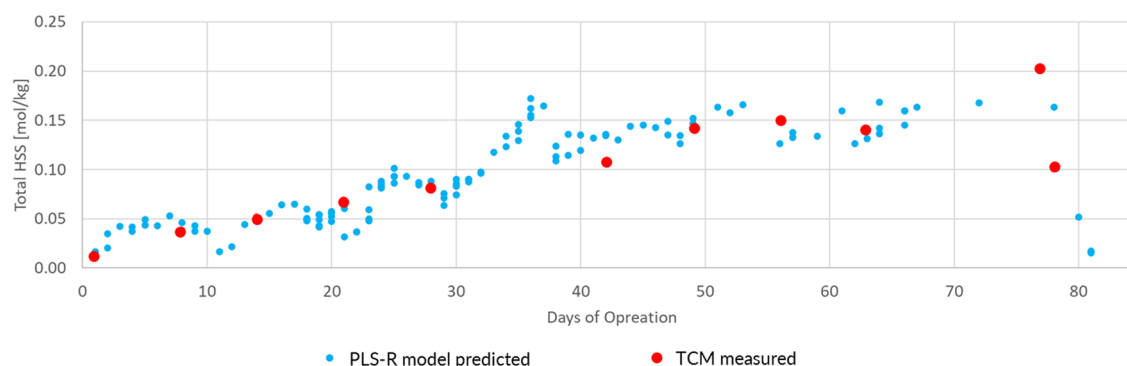


Figure 8. HSS quantification of the MEA2 campaign: red, TCM measured; blue, residual-based model prediction.

work, we attempt to calibrate a speciation model for the sum of ADPs that were identified during the MEA2 campaign. Hence, HEPO (CAS No. 23936-04-1), HEGly (CAS No. 5835-28-9), HEF (CAS No. 693-06-1), HEA (CAS No. 142-26-7), HEI (CAS No. 1615-14-1), and OZD (CAS No. 497-25-6) were used in the PLS-R calibration. Because these species show up in the same spectral range as that used in the TA model, the model was calibrated using the residual spectra of the TA model. The prediction plot of the total ADP model is shown in Figure S3. The R^2 (CV) and RMSECV of the model are 0.916 and 4621 mg/L, respectively.

However, these HSS and ADP models are prepared by using a very limited number of samples and validated with cross-validation only. Therefore, before being used in a PAT application, proper validation by the use of more and independent data is required.

4. CONCLUSION

Following the approach suggested by Grimstvedt et al., we have demonstrated a tool for degradation monitoring and solvent management followup based on the residuals of solvent speciation models (TIC and TA) of the 2015 TCM MEA2 test campaign.

This contribution (Part II) presents the continued work of the endeavor by Wagaarachchige et al. (Part I) demonstrating the application of process analytical spectroscopy and chemometric modeling as a tool for the real-time followup of solvent change in a CO₂ capture unit.⁸ Our new tool for continuous solvent degradation quantification can supplement the current practice¹⁹ of indirect estimation of when to start and/or stop solvent reclaiming.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.4c00019>.

Initial TA model's prediction Qs with days of operation of the MEA2 campaign (Figure S1), ATR-FTIR lab analysis spectra of formate and acetate anions (Figure S2), and PLS-R model calibration for ADPs using residual spectra of the TA model (Figure S3) (PDF)

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Author Contributions

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The authors declare no competing financial interest.

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■ ABBREVIATIONS

ADPs = amine degradation products

CO₂ = carbon dioxide

FTIR = Fourier transform infrared

HEA = *N*-(2-hydroxyethyl)acetamide (CAS No. 142-26-7)
HEF = *N*-(2-hydroxyethyl)formamide (CAS No. 693-06-1)
HEGly = *N*-(2-hydroxyethyl)glycine (CAS No. 5835-28-9)
HEI = *N*-(2-hydroxyethyl)imidazole (CAS No. 1615-14-1)
HEPO = 4-(2-hydroxyethyl)piperazin-2-one (CAS No. 23936-04-1)

HSS = heat-stable salts, i.e., compounds not regenerable by heat for new CO₂ absorption reaction (Table 3)

IC = ion chromatography

IR = infrared

LC–MS QQQ = triple-quad liquid chromatography–mass spectrometry

LVs = latent variables

MEA = monoethanolamine

MEA2 = TCM 2015 MEA campaign

MSPC = multivariate statistical process control

OZD = 2-oxazolidone (CAS No. 497-25-6)

PAT = process analytical technology

PLS-R = partial least-squares regression

Q = Q-residual

RMSECV = root-mean-square error of cross validation

RMSEP = root-mean-square error of prediction

TA = total alkalinity, i.e., the sum of all solvent species reacting with protons, which is equivalent to “solvent strength” (see ref 8)

TCM-DA = CO₂ Technology Center Mongstad

TIC = total inorganic content, i.e., the sum of all species containing CO₂ (see ref 8)

USN = University of South-Eastern Norway

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