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# Dynamic operation of post-combustion $CO_2$ capture in Australian coal-fired power plants

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**Abstract**

Flexible operation of post-combustion $CO_2$ capture (PCC) plants can improve efficiency through coordinating the balance between consumer demands for electricity and $CO_2$ emission reductions. This strategy however, will impose process disturbances and the immediate and long term impact is unclear. There is a justified need for the development of accurate dynamic PCC models, as well as practical experience in dynamic operation of PCC pilot plants. This paper presents CSIRO PCC pilot plant data from the 2012 and 2013 dynamic campaigns using MEA solvent. The step-change approach to dynamic plant operation was implemented and the use of density meters to instantaneously measure $CO_2$ loading instantaneously was investigated.

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*Keywords:* Dynamic modelling; dynamic operation; flexible operation; post-combustion $CO_2$ capture; model validation; pilot plant operation

## 1. Introduction

The largest contributor to atmospheric greenhouse gases (GHGs) is the combustion of fossil fuels. Fossil fuels remain the primary source of energy for many countries. In 2012-2013, as much as 94.4% of Australian energy consumption was sourced from fossil fuels (coal, oil and natural gas) [1]. Post-combustion $CO_2$ capture (PCC) is one technology that has been commercially available for many years, particularly for purification of natural gas. The

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PCC chemical absorption process is the mass transfer and chemical reaction of $CO_2$ with a chemical substrate. The most commonly used reactive "solvent" in chemical absorption processes is monoethanolamine (MEA). Its reaction forms a carbamate intermediate referred to as rich solvent which is regenerated with heat to produce the original lean solvent and $CO_2$ [2].

Recently, there has been a growing interest in viability of flexible PCC operation [3-10]. Flexible operation coordinates $CO_2$ capture with the trends in electricity demand. This flexible approach to $CO_2$ capture maximises financial performance [11]. As the dependence on fossil fuels for base load energy is expected to continue, flexible operation of PCC plants will be crucial in coordinating the balance between consumer demands for electricity and legislative requirements for $CO_2$ emission reductions. Various studies have proposed operating strategies to address the demand for flexibility, these include:

1) Variable $CO_2$ capture regimes which coordinate capture with electricity demand [11];
2) Venting flue gas to avoid the $CO_2$ capture process completely [12];
3) Bypass system which facilitates partial $CO_2$ capture or zero load operation [5];
4) Solvent storage tank system [13].

The immediate and long term impact of process disturbance resulting from flexible PCC operation is unclear. Thus, dynamic models are important tools to investigate the effects of flexible operation on the PCC process [2]. Although a number of dynamic PCC models have been developed, very few are relevant to flexible operation of PCC. The accuracy of process models depend on validation with reliable experimental data. In the case of dynamic PCC models, there is a lack of reliable dynamic pilot plant data available [14].

This paper presents CSIRO PCC pilot plant data obtained in 2012 and 2013 where 30 wt% MEA solvent was used in dynamic operation campaign. The step-change approach to dynamic plant operation was implemented. Also, the potential for measuring $CO_2$ loading instantaneously with calibrated density meters was investigated. The CSIRO data will be used to validate a dynamic model developed using Aspen Plus® and Aspen Plus Dynamics®.

## 2. Dynamic Pilot Plant Operation

### *2.1. CSIRO PCC Pilot Plant at Loy Yang*

The CSIRO PCC pilot plant captures $CO_2$ from flue gas emitted by the AGL Loy Yang A power station located in the Latrobe Valley of Victoria, Australia. The PCC pilot plant has been designed to process 150 kg/h of flue gas and was first commissioned in March 2008. Figure 1 is a process flow diagram of the pilot plant which consists of a flue gas pre-treatment column, two absorber columns and one stripper column. The pre-treatment scrubber column removes $SO_X$, $NO_X$ and particulates from the flue gas with sodium hydroxide. The pre-treatment process conditions and cools the flue gas before the amine absorption process.

The two absorber columns were operated in series. Each absorber is constructed from 200 DN stainless steel pipe with an inner diameter (ID) of 211 mm. In each absorber, there are two 1.35 m packed bed sections and the total column height is 9.4 m. The stripper column is constructed from 150 DN stainless steel pipe with a diameter of 161 mm ID. The stripper has a packing height of 3.9 m and total column height of 6.9 m. The random metal Pall ring packing used for all of the columns has the following specifications: (i) size of 16 mm, (ii) specific area of 338 $m^2/m^3$, and (iii) packing factor of 306 $m^{-1}$. The reboiler steam is supplied by a 120 kW boiler [15].

### *2.2. Step-Change Approach to Dynamic Operation*

PCC pilot plants undergo dynamic operation on a regular basis, for example start-up and shut down. However, these types of transient behaviour are difficult to reproduce and can be highly variable. The "step-wise" approach to dynamic data collection was developed to improve reliability and reduce variability in the pilot plant results. The idea was inspired by the steady state "snapshots" approach to modelling dynamic behaviour proposed by Gruber (2004). Originally, the technique was developed as a means of modelling dynamic systems using a steady state process simulation program. Incremental changes would be made to the process and the steady state solution simulated. Steady state "snapshots" in time would be plotted together to provide the overall dynamic solution [16].

The step-change approach to pilot plant operation involved successive incremental changes to one flow rate parameter (e.g. flue gas or solvent flows). The successive changes can either increase or decrease the flow parameter gradually. The dynamic behaviour of the pilot plant is demonstrated by plotting variables such as temperature or $CO_2$ loading against the step changes in a flow rate parameter. The advantage of the step-change approach to pilot plant operation is that process disturbances are minimised. Generally, the high impact dynamic scenarios such as start-up, shut-down and trips are difficult to reproduce due to the large disturbances on the system. In contrast, the step-change approach is a series of low magnitude changes that are executed gradually. Furthermore, step-changing a parameter reduces the impact of the disturbances on the process, thus improving data reproducibility.

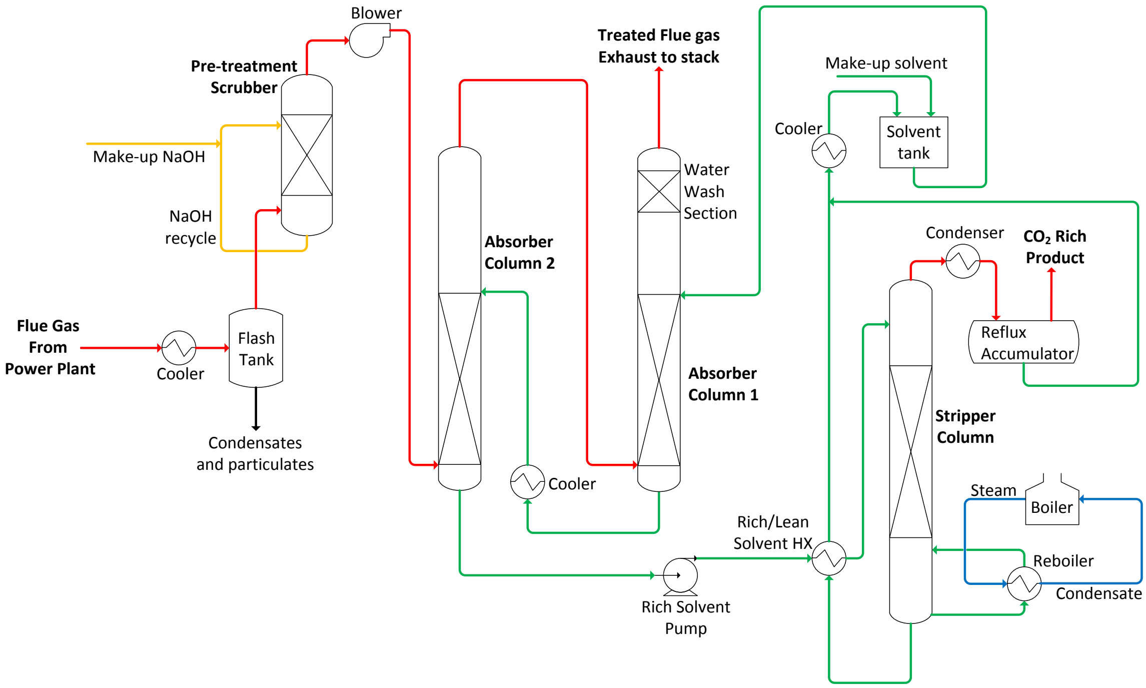


Figure 1 Process flow diagram of the CSIRO PCC pilot plant at Loy Yang Power.

## 3. Dynamic Pilot Plant Results and Discussion

### *3.1. Absorber temperature profiles*

Typically, liquid solvent feeds into the top of the absorber column whereas the flue gas enters from the bottom. The $CO_2$ absorption reaction is exothermic and is enhanced with low temperature conditions in the absorber column [17]. As the solvent flows down through to the bottom of the packed bed, the solvent increases in $CO_2$ loading, thus the bottom of the packed bed is the rich end. There is a point where there is no mass transfer; this is called the pinch point (lowest point on the temperature profile). The region where $CO_2$ absorption rate is the greatest has the highest point on the temperature profile and is referred to as the temperature bulge.

When the solvent is in excess relative to the amount of $CO_2$ in the feed flue gas (i.e. low flue gas flow or high solvent flow), the pinch point tends to be on the lean end and absorption usually occurs at the base of the column. The liquid has greater heat capacity compared to the gas phase. Thus with excess solvent, the heat of reaction is pushed to the bottom and the temperature bulge tends to be at the rich end (bottom) of the packed bed. Conversely, when the amount of solvent is insufficient (i.e. high flue gas flow or low solvent flow), the absorption rate is greatest at the lean end (top) of the packed bed and the pinch point is at the rich end. Thus, the temperature bulge tends to be at the top of the packed bed. It is rare to have the temperature bulge occur at the pinch point, so usually temperature bulge would not impact on mass transfer performance. The only time mass transfer performance is affected is when the pinch point and temperature bulge are both in the middle of the column [18].

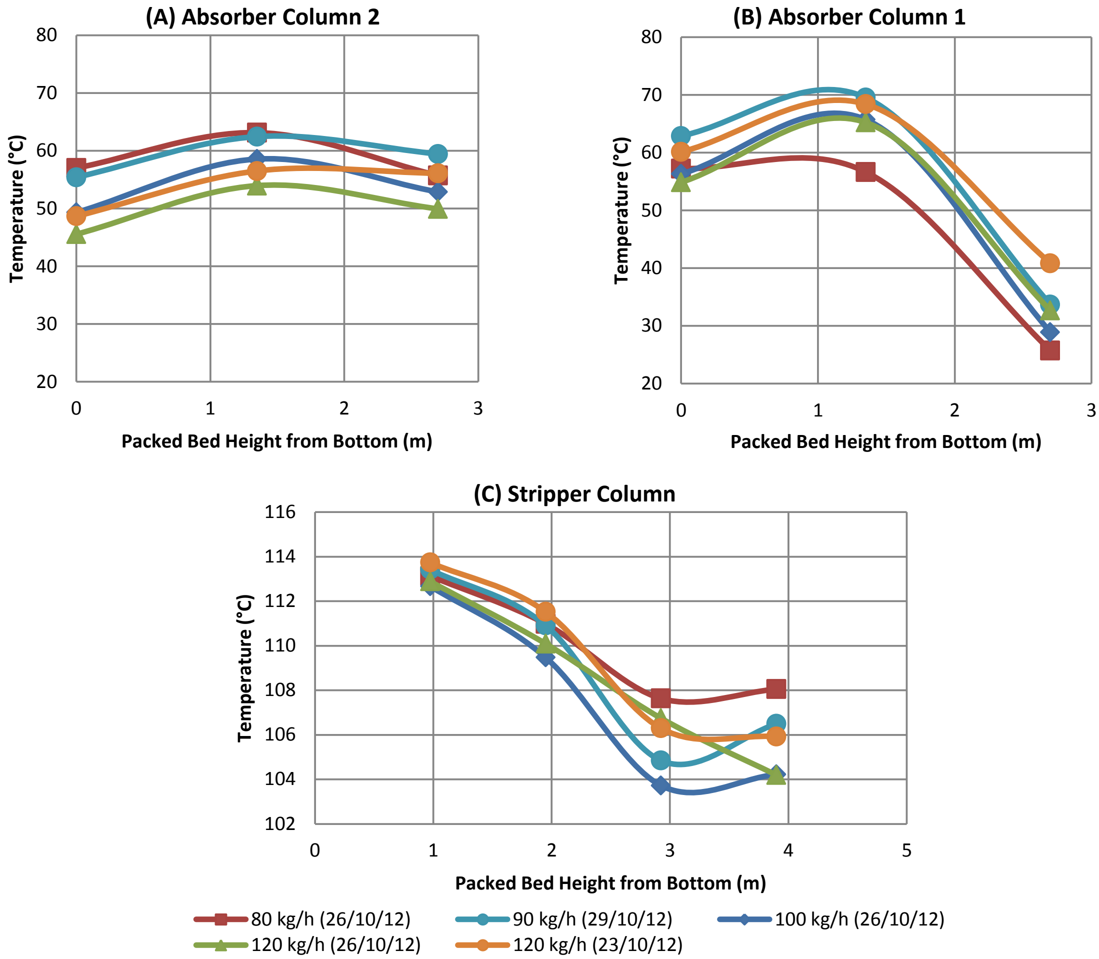


Figure 2 Column temperature profiles for (A) absorber column 2, (B) absorber column 1, and (C) the stripper column showing step-change in flue gas flow. At the CSIRO PCC pilot plant in Loy Yang, the operating set point conditions are solvent flow rate of 5.5 L/min and reboiler steam pressure 140 kPag.

### *3.2. Step-change in flue gas flow*

The column temperature profiles for step-changes in flue gas flow are shown in Figure 2. Generally with the absorbers in the series configuration, the ABS2 temperature profile shifts down to lower temperatures as the flue gas flow increases. In contrast, the column temperature profile for ABS1 shifts to higher temperatures as flue gas flow increases. The ABS2 flue gas feed is at a lower temperature than the input MEA solvent. Conversely, ABS1 flue gas input is higher temperature compared to the MEA solvent feed. The rich solvent exiting ABS2 enters the cross-heat exchanger (seen in Figure 1) where it is counter-currently heated by the lean solvent stream from the stripper. The temperature of this lean solvent is directly dependent on the reboiler temperature. An increase in flue gas flow has a: (i) heating effect in ABS1, (ii) cooling effect in ABS2, which in turn (iii) cools the stripper.

The pilot plant results showed that increasing flue gas flow reduces the $CO_2$ recovery %. Increased flue gas flow results in excess $CO_2$ relative to the solvent flow and the greatest absorption at the top of the column. Theoretically, the increase in flue gas flow should shift the temperature bulge to the top of the packed bed in both absorber columns. However with only three points, the shifting of the temperature bulge is difficult to identify in Figure 2.

### 3.3. Step-change in solvent flow

Figure 3 shows the temperature profiles for each column during step-changes in solvent flow when the absorbers were operating in series. The step-wise increase of solvent flow rate has the opposite effect on the pilot plant performance compared to increased flue gas flow. As MEA solvent flow is increased, the temperature profile of ABS2 shifts to higher temperatures whilst ABS1 shifts lower. Due to the unique configuration of the CSIRO pilot plant, increased solvent flow heats up ABS2 whereas ABS1 is cooled. The higher temperature in ABS2 from increased solvent flow will shift the stripper temperature profile to higher temperatures.

During the dynamic pilot plant campaign, the impact of significantly aged and degraded MEA solvent was also investigated. The viscosity increased as the solvent aged, subsequently leading to challenging operating conditions. The pilot plant became prone to unstable behaviour and required constant supervision and monitoring. Also at high flow rates for flue gas (≥120 kg/h) and solvent flow (≥7 L/min), the stripper level fluctuated significantly. The fluctuating liquid level in the stripper resulted in temperature profile inconsistencies at these high flow rates.

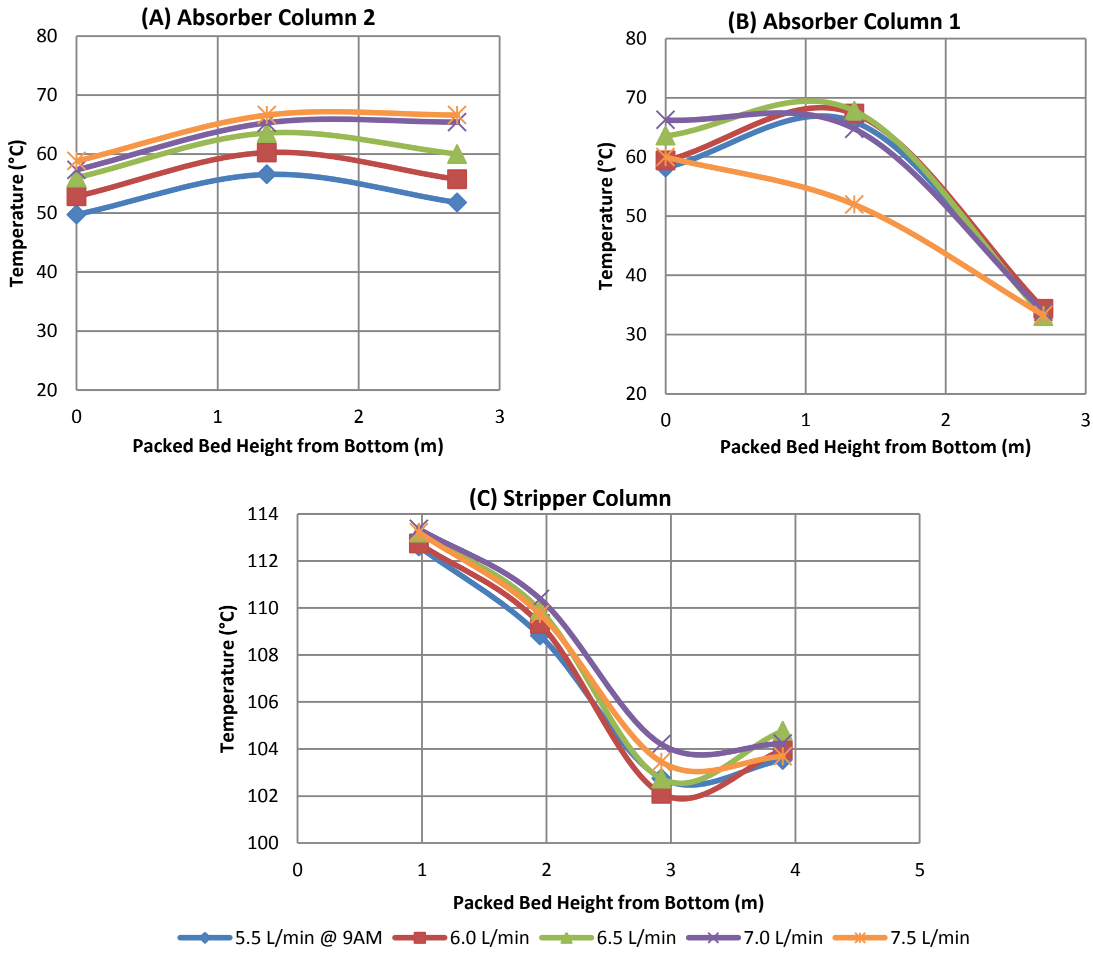


Figure 3 Column temperature profiles for (A) absorber column 2, (B) absorber column 1, and (C) stripper column showing step change in solvent flow on 12 November 2012. At the CSIRO PCC pilot plant in Loy Yang, the operating set point conditions are flue gas flow rate of 100 kg/h and reboiler steam pressure 140 kPag.

### 3.4. Density meter calibration

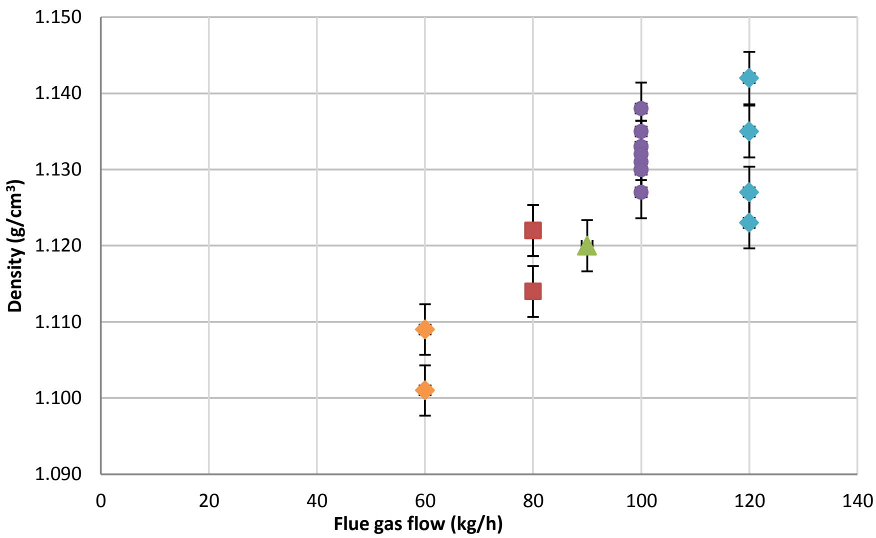


Figure 4 The influence of flue gas flow rate on the solvent density at the base of absorber column 2 (measured by density meterABS-DE03). The error bars for density meter measurements are adjusted in accordance to the manufacturer calibration error.

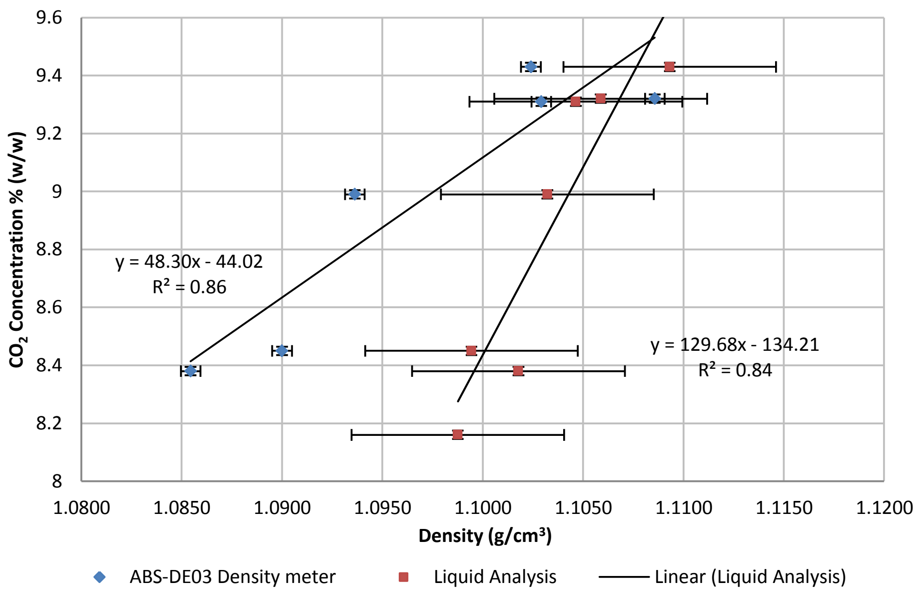


Figure 5 Comparison of steady state density measurements from the density meter ABS-DE03 (blue ♦) and liquid analysis (red ■) plotted with $CO_2$ concentration % (w/w). Note liquid analysis measurements are conducted as duplicates and the error bars shown are standard errors for the measurements

The conventional technique to determine $CO_2$ loading, density and concentration of MEA of solvent during pilot plant studies is off-line liquid analysis [15, 19-21]. Density meters were installed at the CSIRO PCC pilot plant as a continuous alternative to classic liquid analysis techniques. Studies demonstrate that solvent density strongly correlate with $CO_2$ loading, MEA concentration and temperature [19, 22-24]. Thus, online measurements of density could illustrate the dynamic changes in solvent composition and temperature. Solvent density measurements from the pilot plant were calibrated against $CO_2$ loading and will be used to validate the dynamic model.

There are three density meters in the pilot plant: (i) ABS-DE01 on the feed lean solvent stream into ABS1, (ii) ABS-DE03 at the base of ABS2, and (iii) STR-DE01 on the lean solvent stream after the cross heat exchanger. In 2012, the density meters had recently been installed and it was unclear whether density readings would be sensitive to flow changes. Figure 4 demonstrates that the density meters have sufficient sensitivity to solvent composition changes. Also, step-changes in flow clearly have a significant influence on solvent density. Thus, calibrated density meters can be a convenient alternative to the standard liquid analysis technique, especially in cases when solvent sampling is not possible.

A second campaign using 30 wt% MEA solvent was conducted in 2013 to collect some data to calibrate the density meters against liquid analysis measurements. Figure 5 is a calibration example of the ABS-DE03 density meter and liquid analysis density measurements against $CO_2$ concentration % (w/w). The density measurements from both techniques demonstrate a strong correlation with $CO_2$ concentration. The variance in density meter and liquid analysis measurements may be attributed to the different conditions during density measurement. The dynamic solvent environment inside the absorber is significantly different to those ambient lab conditions used for liquid analysis.

### *3.5. Experience with Dynamic Pilot Plant Operation*

In the case of outdoor pilot plants that treat real flue gas, measurements are influenced by external factors such as (i) weather or ambient temperature, (ii) temperature change of flue gas from the power station, (iii) change in flue gas composition, and (iv) change in cooling water temperature. The effect of MEA solvent degradation on the operability of the pilot plant was also studied. The 2012 campaign demonstrated that solvent degradation has a significant impact on pilot plant behaviour (e.g. unstable behaviour and stripper level fluctuations). As the solvent aged, the property changes that occur in the amine solution included higher viscosity, lower $CO_2$ absorption capacity and darker colouration. To accommodate such changes, operators are required to modify standard pilot plant operating procedures and set-point conditions.

## 4. Conclusion and Further Work

The step-change approach to pilot plant operation is a promising technique to improve reproducibility and reduce variability in dynamic data. There is strong potential in utilising calibrated density meters to measure solvent density instantaneously and monitor the dynamic changes in the solvent. The practical experience of operating the pilot plant with aged solvent has improved understanding about the dynamics of the PCC process. Further work with an existing dynamic model in Aspen Plus Dynamics® will include validation with the available dynamic step-change results from the CSIRO pilot plant. Additionally, the technical feasibility of flexible operation in PCC plants will be investigated. By incorporating pilot plant work with process modelling, this research has taken a practical and theoretical approach to studying dynamic behaviour. However, to improve the understanding of dynamic PCC processes and flexible operation strategies, further research required includes: (i) similar dynamic operation studies in different pilot plants; (ii) investigate the impact of variable configurations on $CO_2$ capture efficiency; (iii) validate dynamic models with dynamic pilot plant data to improve accuracy of predictions; and (iv) identify key process parameters that have a significant impact on dynamic and flexible operation.

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