Combined Capture of SO_2 and CO_2

Towards validation of lab-based model using CSIRO's PCC pilot plant at Loy Yang

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LOW EMISSION TECHNOLOGY / ENERGY FLAGSHIP
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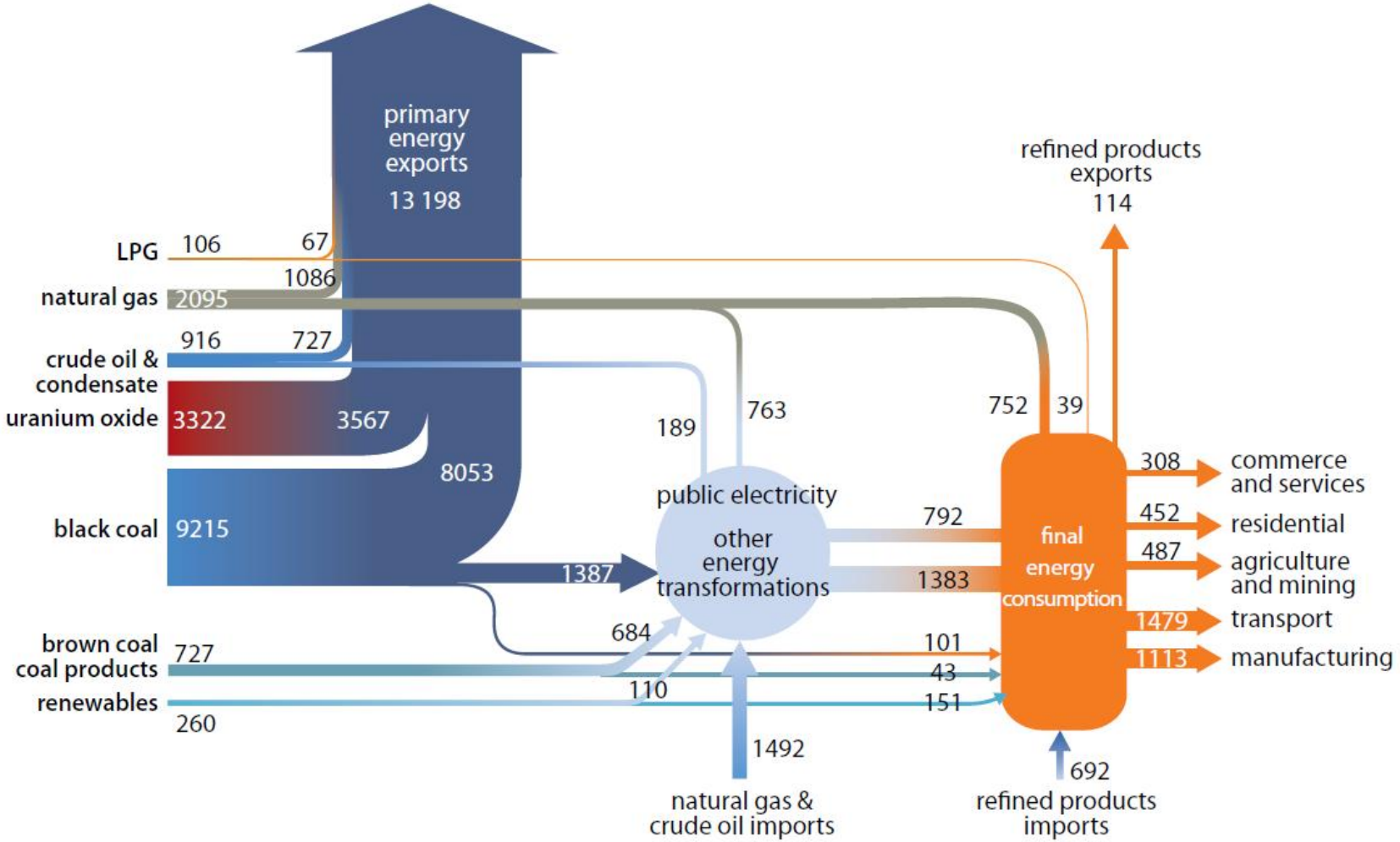
Australia's energy flows: 2010-11 (petajoules)



Source: BREE 2012, Australian Energy Statistics

CSIRO

People	6500
Divisions	12
Locations	58
Flagships	11
Budget	$1B+

Top 1% of global research institutions in 14 of 22 research fields

Top 0.1% in 4 research fields

62% of our people hold university degrees

2000 doctorates

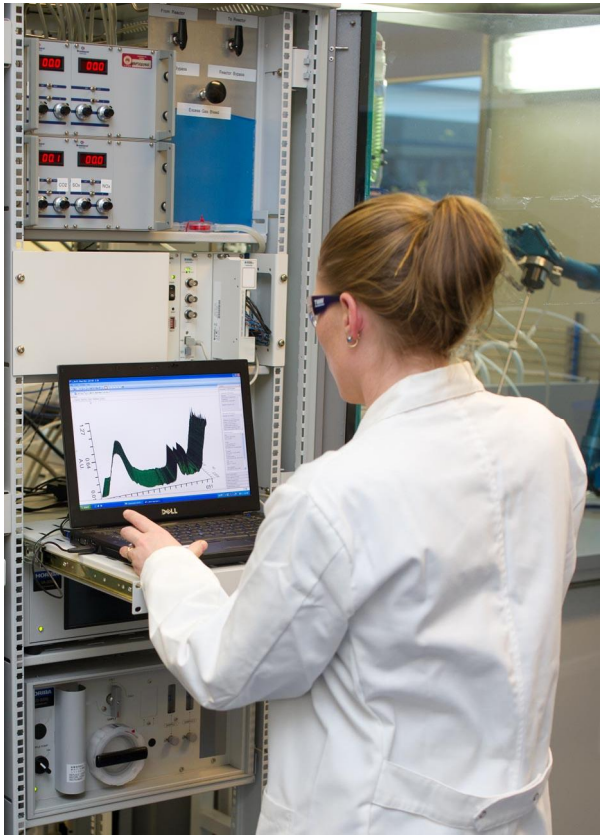
500 masters

With our university partners, we develop **650** postgraduate research students

Our track record:
Top inventions

Carbon capture & storage

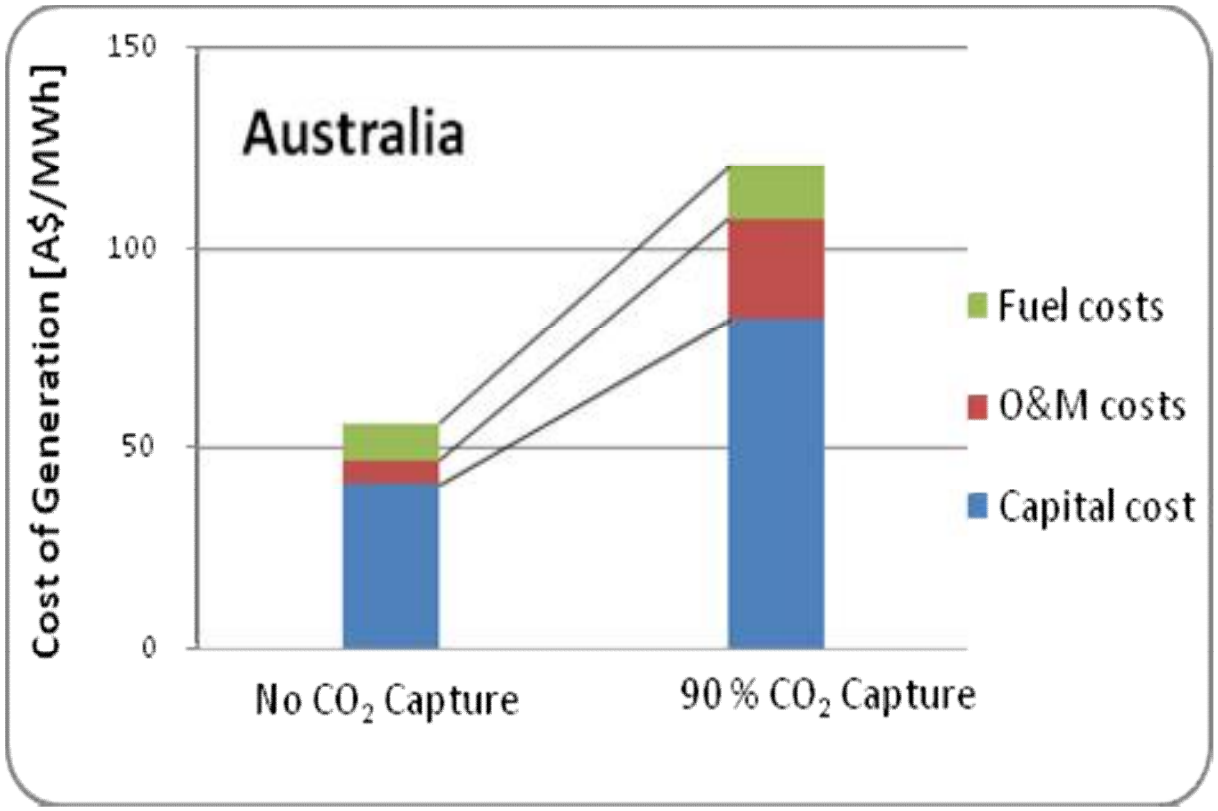
Research focus: post combustion capture, geological carbon dioxide storage



Costs of CO_2 Capture (Paul Feron, GHGT10)

Australia:

- ~ 60-100 \$/tonne CO_2
- Capital costs dominant
- Equipment cost reductions



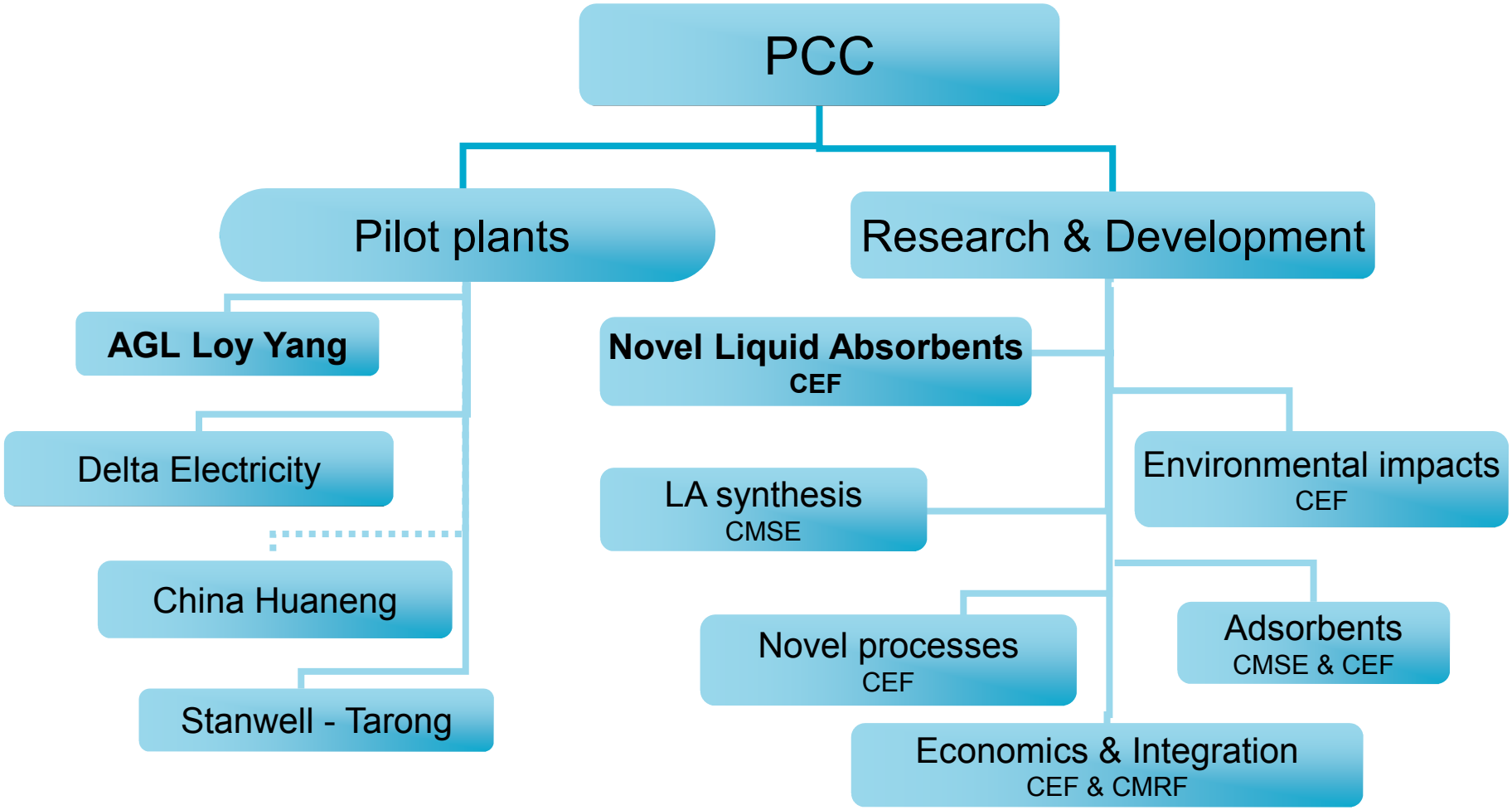
- Focus on kinetics and wear: corrosion and other material interactions

Base figures of Australian coal-fired power stations

	Black Coal	Brown Coal
Total capacity	~ 21 GW	~ 7 GW
Proven resources	106 yrs	570 yrs
Production	180 TWh/a	
Average generation efficiency	35.6 % 0.9 ton CO_2/MWh	25.7% (18-29%) 1.3 ton CO_2/MWh
CO_2-emissions	~ 170 Mton CO_2/a from ~ 60 flue gas streams	
SO_2 levels	200 – 600 ppm	100 – 300 ppm
NO_x levels	300 – 700 ppm	100 – 200 ppm
Flue gas Temperature	120 °C	180 °C
Cooling water	1.5 – 3.0 m^3/MWh	

Data used from CCSD – technology assessment report 62
Demonstrated resources data from ABARE (Jan 2004)

Integrated PCC R&D Programme - overview



CSIRO PCC pilot plant program – Matrix

Plant	Loy Yang	Vales Point	Tarong	Newcastle PDF
Liquid absorbent	Amine	Ammonia/ Amine	Amine	Ammonia/ Amine
Flue gas source	Brown coal	Black coal	Black coal	Synthetic
Scale	50 kg/hr	300 kg/hr	100 kg/hr	20 kg/hr
Focus	Liq. Absorbent benchmarking	Ammonia operation	Process optimisation	Process development
Other activities	Emission study SO_2&CO_2	Pressurised absorption	Concentrated piperazine	Cutting edge processes

Conclusions – IEA CCT 2013, Thessaloniki

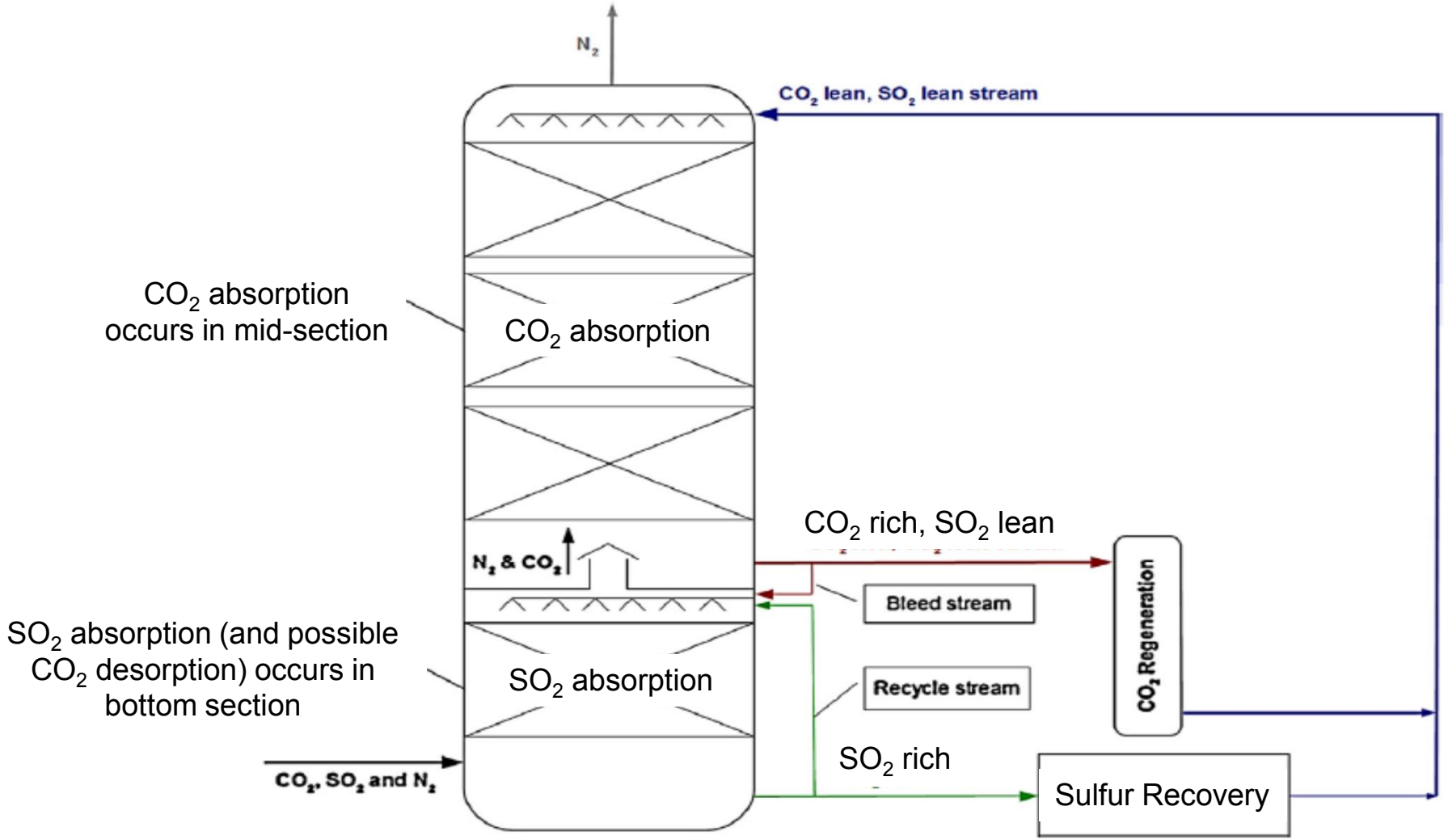
- CASPER (through collaboration with TNO/TUHH/EnBW via *iCap* & *coCAPco*)
  - The **removal-%** of CO_2 by a 3M potassium β-alanate mixture **is 60-85%** in the CSIRO PCC pilot plant at Loy Yang;
  - **SO_2 is completely removed** from a 40-600 ppm SO_2 containing real flue gas, where SO_4^{2-} is formed in the solution;
  - The loaded β-alanate mixture was **successfully regenerated** with regards to CO_2 and SO_2, where $CO_{2\,(g)}$ and $K_2SO_{4\,(s)}$ have been produced;
  - **SO_4^{2-} formation rate** is independent on [SO_2] in flue gas, but **depends on presence of O_2 and seemingly at least one more compound**;
  - (Over-dimensioning) **FGD may be unnecessary** and thereby CAPEX is significantly lower to capture CO_2

- Savings potential has been quantified (Clearwater Clean Coal conference 2014, FL, USA) and scrutinized by independent Engineering firm
  - Confirmed investment savings potential: > $200M per 500 MW power plant

Combined capture of SO_2 and CO_2 with amines - *CS-CAP* -

- AIM:
  - Improve performance:
    - faster kinetics, thereby further lowering CAPEX;
    - Similar or better energy consumption.
  - Challenges:
    - Robust amine system;
    - Corrosion of equipment;
    - Regeneration of sulphur loaded liquid absorbent blend.
- **This study**:
  - Towards validation of chemical, lab-based, model for the system of CO_2 - SO_2 - amine, through **pilot plant operation** with real flue gas.

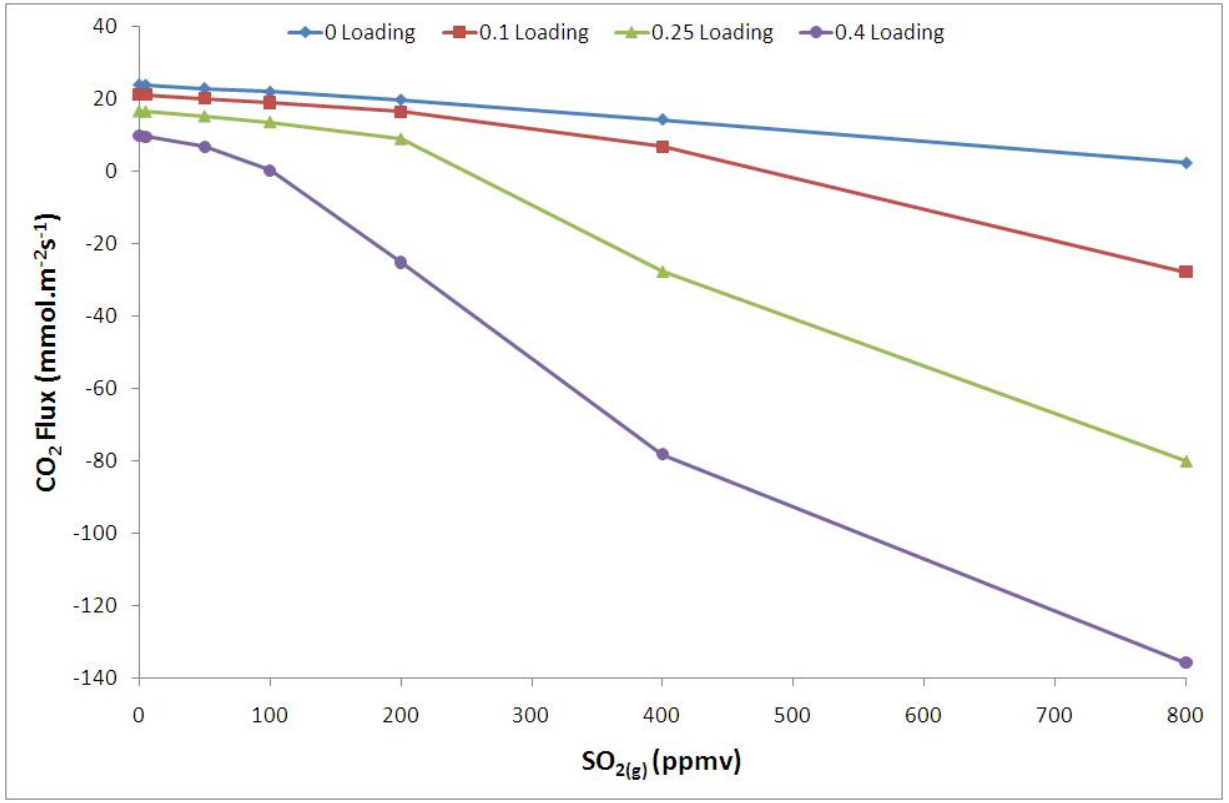
CS-Cap: process scheme



Puxty *et al.*, 2012, WO2012_097406; Beyad *et al*. IJGGC, **31** (2014) 205–213

CO_2 absorption flux vs loading and SO_2-conc

- At lab-scale SO_2 is proven absorbing independent of CO_2 loading in 30 wt-% MEA

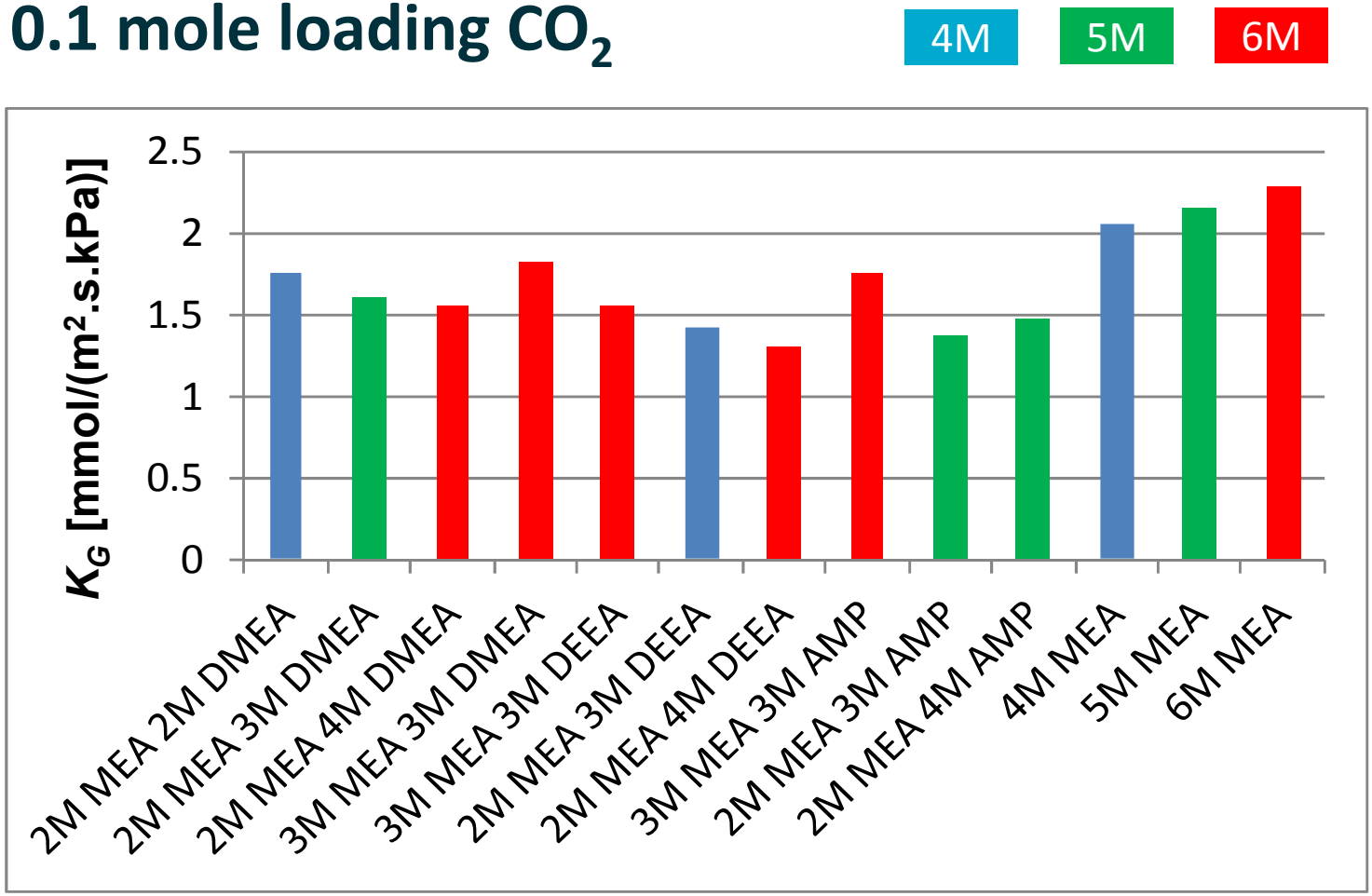


Liquid Absorbent (LA) selection – energy/corrosion

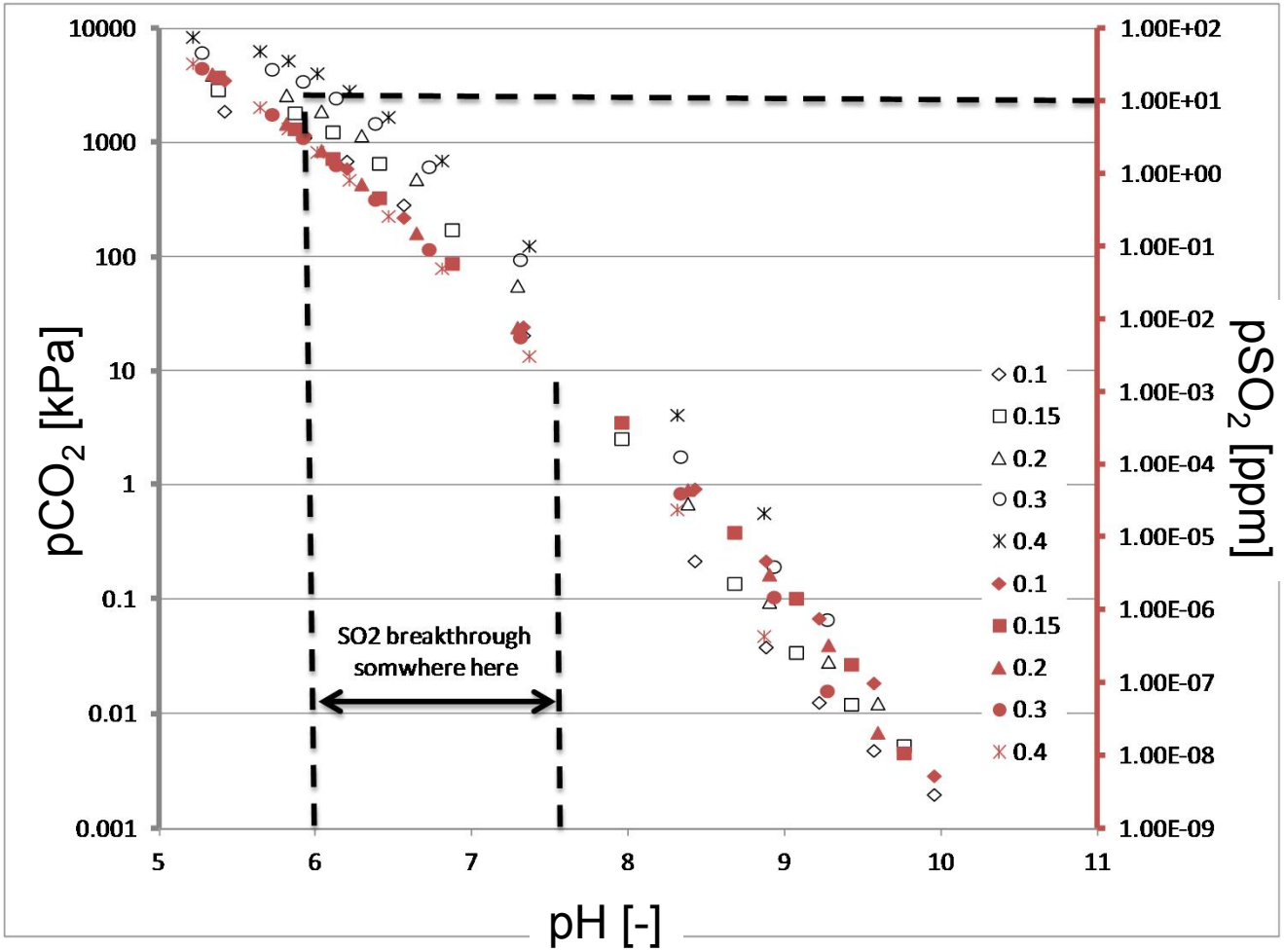
Amine	pK_a at 25°C	ΔH^0 of protonation ($kJ.mol^{-1}$)	Corrosion	Degradation
monoethanolamine (MEA)	9.44	-41	> 300 $\mu m.year^{-1}$	moderate
N,N-dimethylethanolamine (DMEA)	9.23	-34	non-corrosive	low
N,N-diethylethanolamine (DEEA)	9.92	-39	unknown, probably low	unknown, probably low
2-amino-2-methyl-1-propanol (AMP)	9.67	-47	non-corrosive, < 20 $\mu m.year^{-1}$	low

Liquid Absorbent selection – kinetics

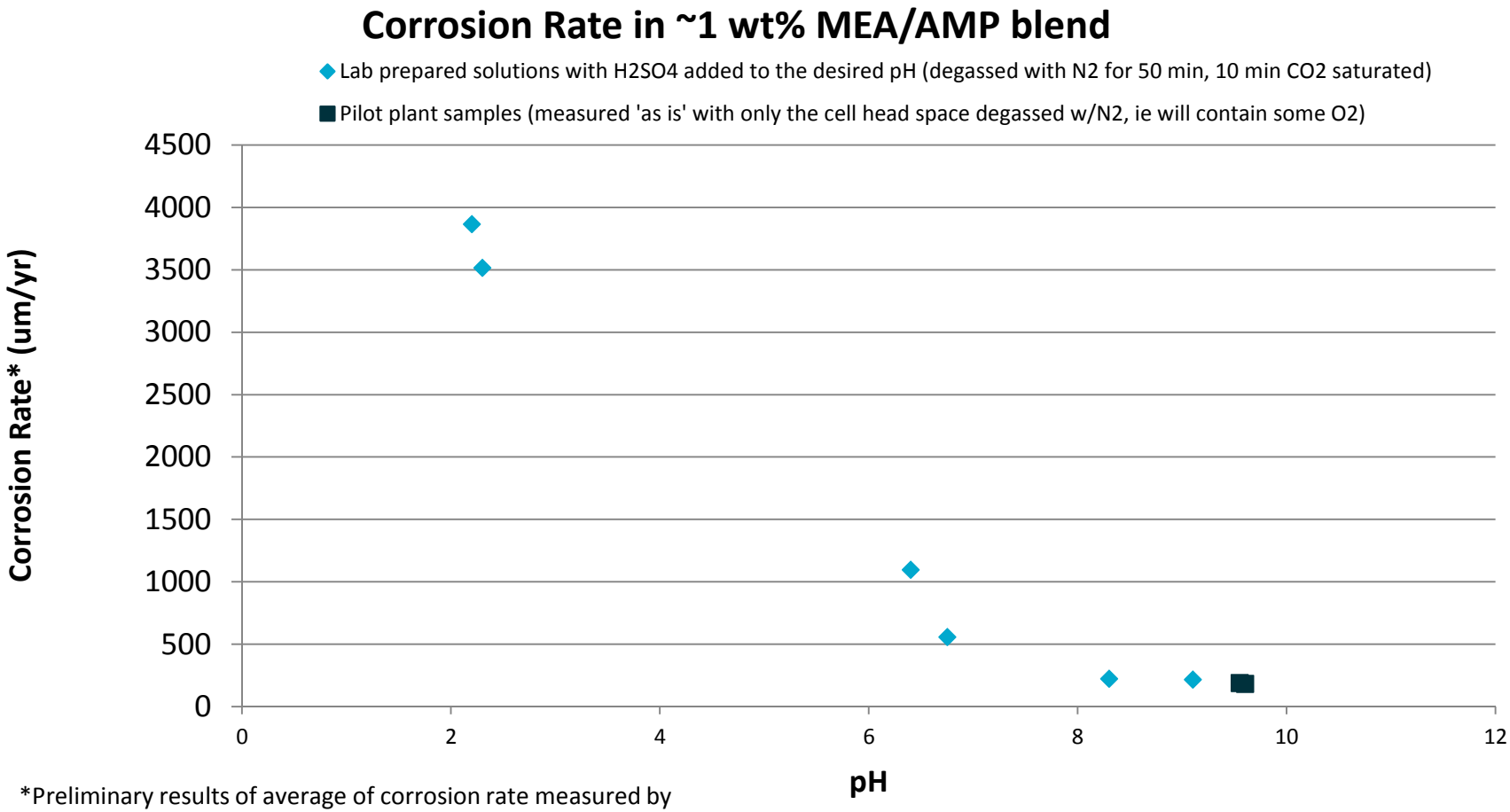
K_G at 0.1 mole loading CO_2



Lab-based forecast of SO_2 breakthrough



Forecast corrosion with EIS (protect equipment)



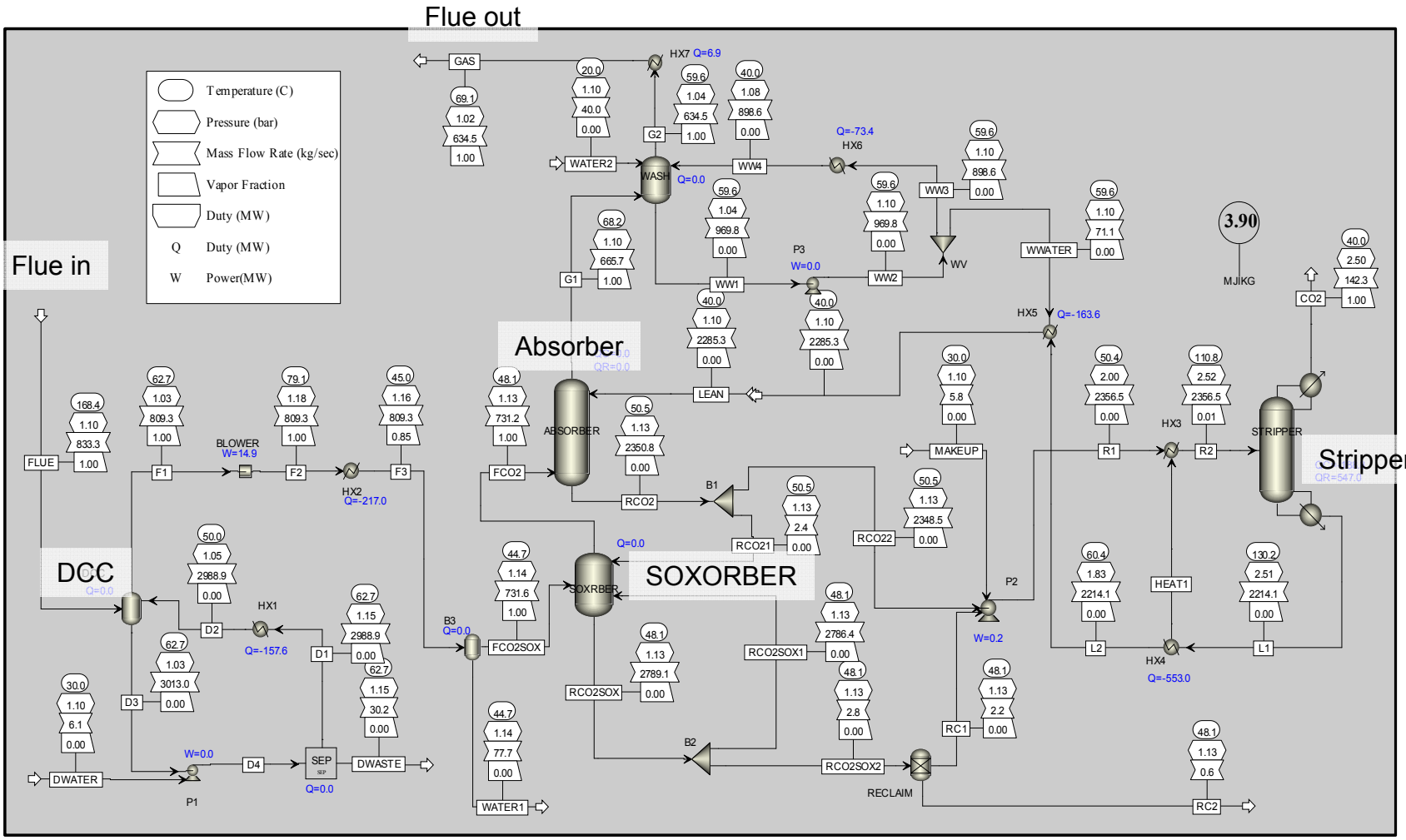
*Preliminary results of average of corrosion rate measured by Linear Polarization Resistance, Electrochemical Impedance Spectroscopy

Pearson *et al*., ELECTROCHIMICA ACTA 2013 (Description of Analytical Technique)

Process modelling - Aspen

- Aspen-Plus process simulator, Version 7.3 was used
- Flue gas assumed in modelling:
  - 168 ^{o}C
  - water ≈ 25.5% v/v,
  - CO_2 ≈ 11.8% v/v,
  - O_2 ≈ 3 .2% v/v,
  - N_2 ≈ 58.8% v/v,
  - SO_2 ≈ 240 ppmv, SO_3 ≈ 0.03 ppmv,
  - NO ≈ 190 ppmv and NO_2 ≈ 10 ppmv,
- Note - Flue gas at Loy Yang:
  - O_2 5-6% at LY
  - SO_2 140 ppm on average at LY
  - NO_2 at Loy Yang is 1-2 ppmv.

Process modelling – Process Flow Diagram



Reactions

DCC

2 H2O <–> H3O+ + OH-
CO2 + 2 H2O <–> HCO3- + H3O+
HCO3- + H2O <–> CO3-2 + H3O+
2 H2O + SO2 <–> H3O+ + HSO3-
H2O + HSO3- <–> H3O+ + SO3-2
2 NO2 + 3 H2O <–> NO2- + NO3- + 2 H3O+
2 NO2 + HSO3- + 4 H2O <–> 2 NO2- + SO4-2 + 3 H3O+
2 OH- + 2 NO2 <–> NO2- + NO3- + H2O
SO3 + 2 H2O <–> HSO4- + H3O+
HSO4- + H2O <–> SO4-2 + H3O+

CO_2 Absorber

2.0 H2O <–> H3O+ + OH-
CO2 + 2.0 H2O <–> HCO3- + H3O+
HCO3- + H2O <–> CO3-2 + H3O+
MEAH+ + H2O <–> MEA + H3O+
MEACOO- + H2O <–> MEA + HCO3-

SOXORBER

2 H2O <–> H3O+ + OH-
CO2 + 2 H2O <–> HCO3- + H3O+
HCO3- + H2O <–> CO3-2 + H3O+
MEAH+ + H2O <–> MEA + H3O+
MEACOO- + H2O <–> MEA + HCO3-
2 H2O + SO2 <–> H3O+ + HSO3-
H2O + HSO3- <–> H3O+ + SO3-2
2 NO2 + 3 H2O <–> NO2- + NO3- + 2 H3O+
2 NO2 + HSO3- + 4 H2O <–> 2 NO2- + SO4-2 + 3 H3O+
2 OH- + 2 NO2 <–> NO2- + NO3- + H2O
SO3 + 2 H2O <–> HSO4- + H3O+
HSO4- + H2O <–> SO4-2 + H3O+
2 MEA + SO3 + H2O <–> 2 MEAH+ + SO4-2
2 MEA + SO2 + 0.5 O2 + H2O <–> 2 MEAH+ + SO4-2

Process modelling – conclusions

- Conclusions
  - Addition of 1 kg/s of CO_2 rich aqueous MEA re-circulating within the SOXORBER at 1.1 t/s results in SO_2 concentration at exit of about 1.7ppm;
  - Roughly 1‰ of flow rate of CO_2 rich MEA is required to be added to SOXORBER;
    The same flow rate must be taken from the SOXORBER and regenerated in the SO_x-regenerator.
  - The liquid to gas mass ratio within the SOXORBER will be 3.8 and the total sulfate ion mass concentration could reach up to as much as 21 .4% w/w in the liquid stream leaving the SO_X absorber;

Process modelling - Challenges

- Challenges
  - High recirculation rate of liquid to provide the required surface area for G/L mass exchange in SOXORBER costs (too) much energy.

- Opportunity/Challenge
  - High SO_2 loading possible.

- Recommendations
  - L/G contactor with high gas side mass transfer characteristics, low gas side pressure drop and low liquid flow rate is required;
  - Validate Aspen results with Pilot Plant campaign.

Pilot plant CS-Cap campaigns

- Benchmark
  - 30 wt-% MEA for benchmark

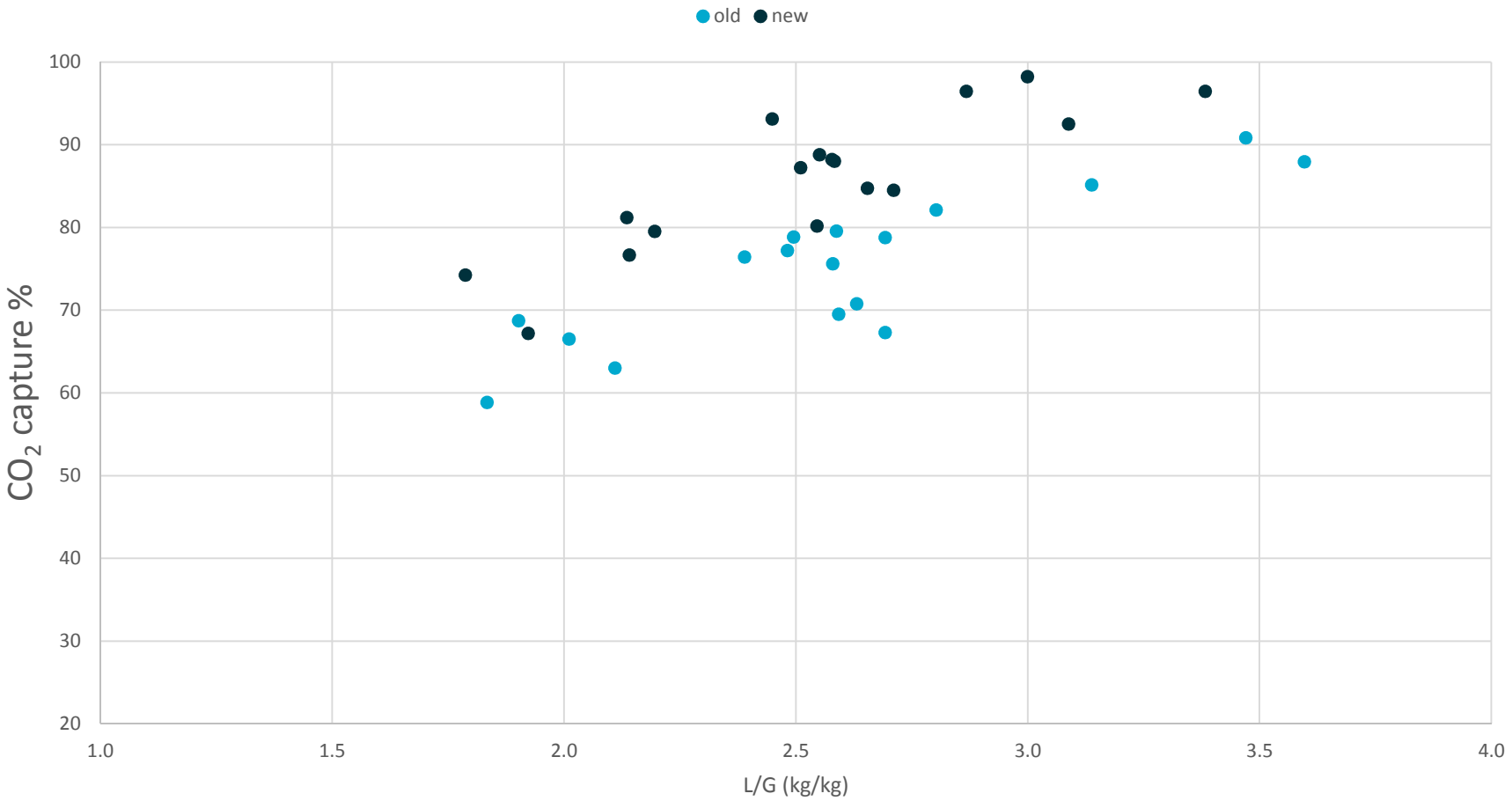
- Campaign:
  - 20% MEA
  - 0.5 % MEA
  - 2% MEA + AMP
  - 5% MEA + AMP
  - 20% MEA (as we speak pH 6.6)

Validation in PCC pilot plant at Loy Yang

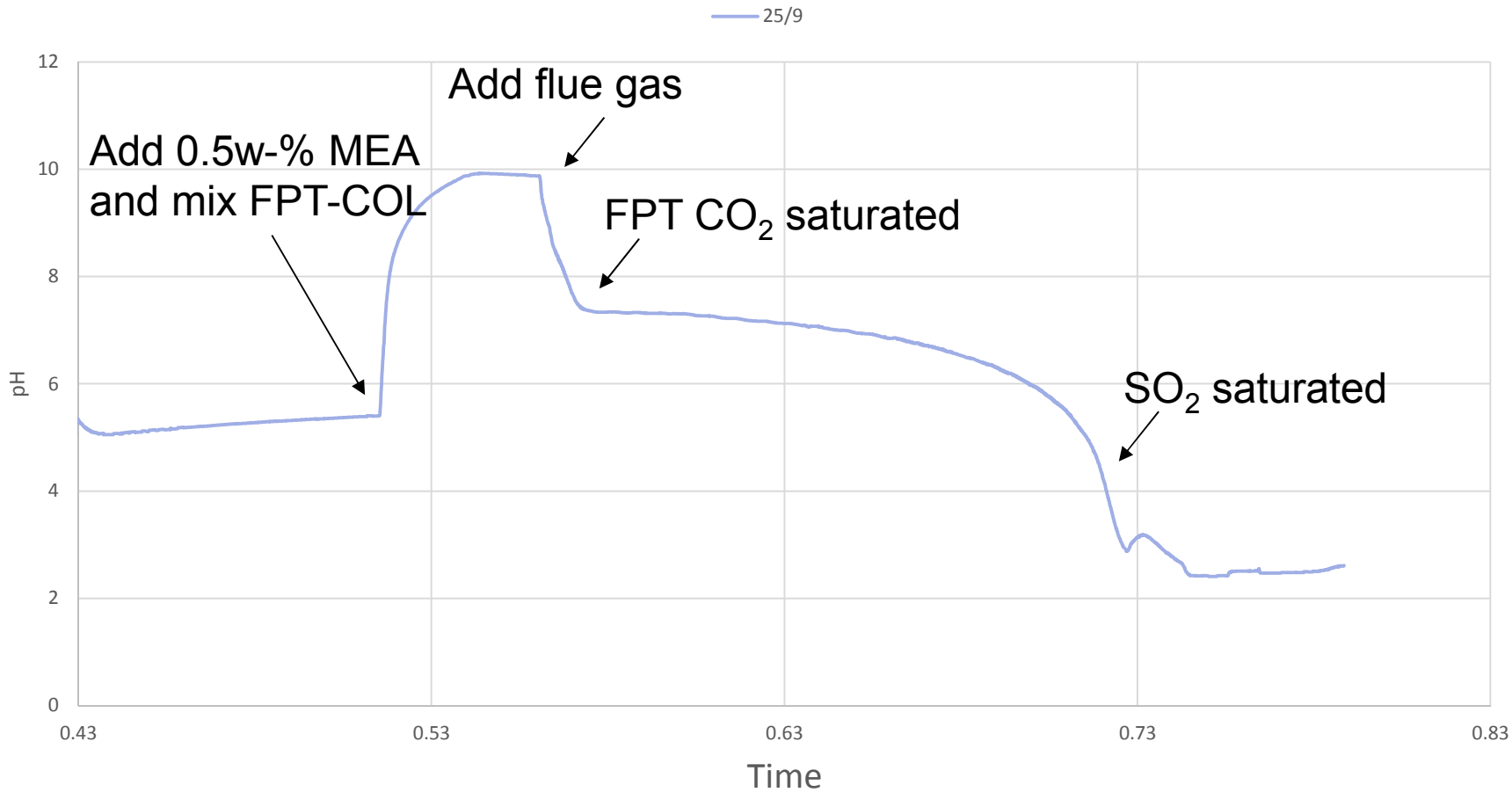
- Modification to improve performance:
  - Structured packing (RhineRuhr and Sulzer) in Column 1
  - Extra bed with Pall rings in COL 2
  - Liquid distributors (gravity fed)
  - Demister before water wash.

- Modified process flow for *CS-Cap*.

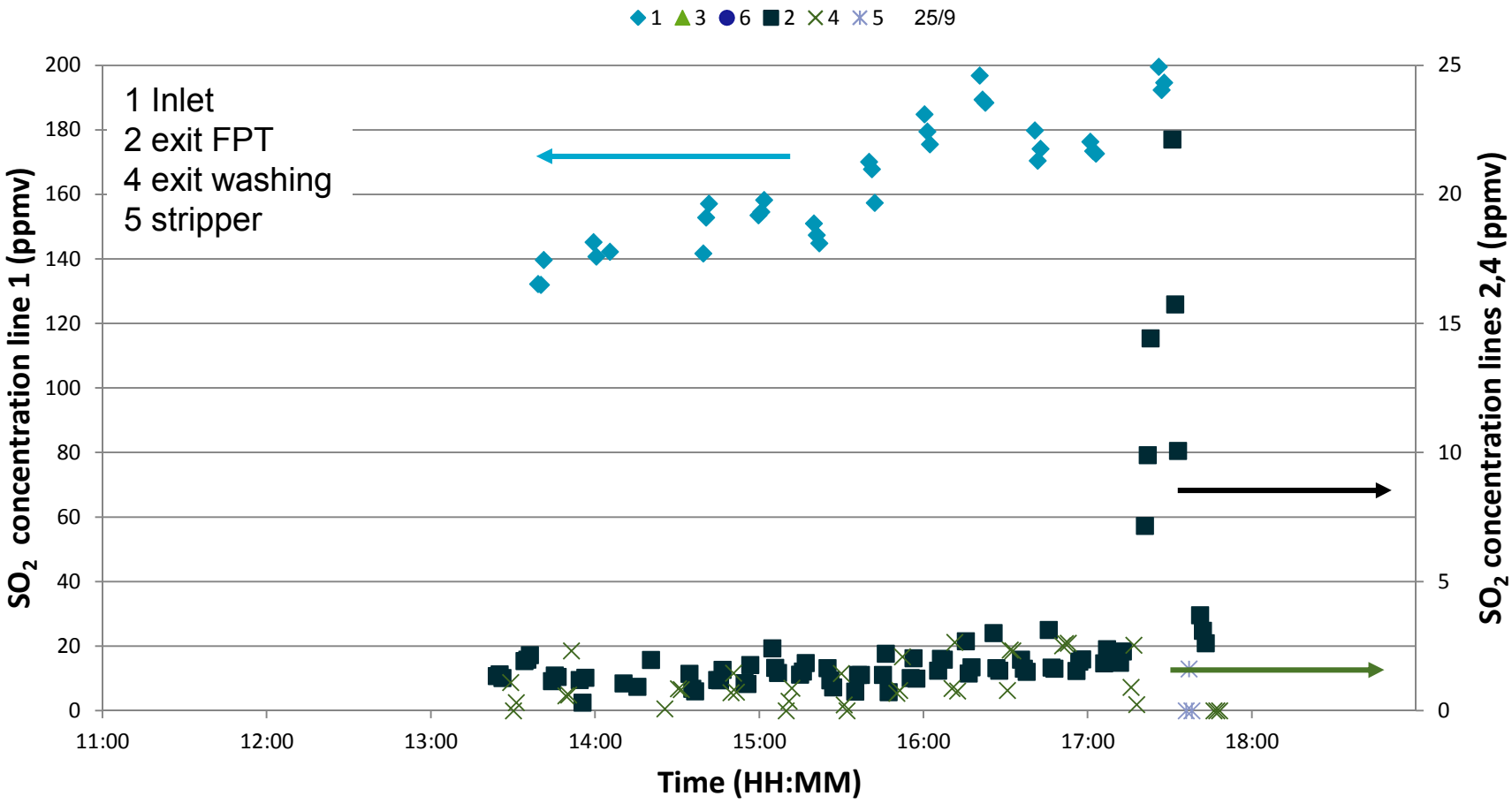
Comparing MEA baseline graphs



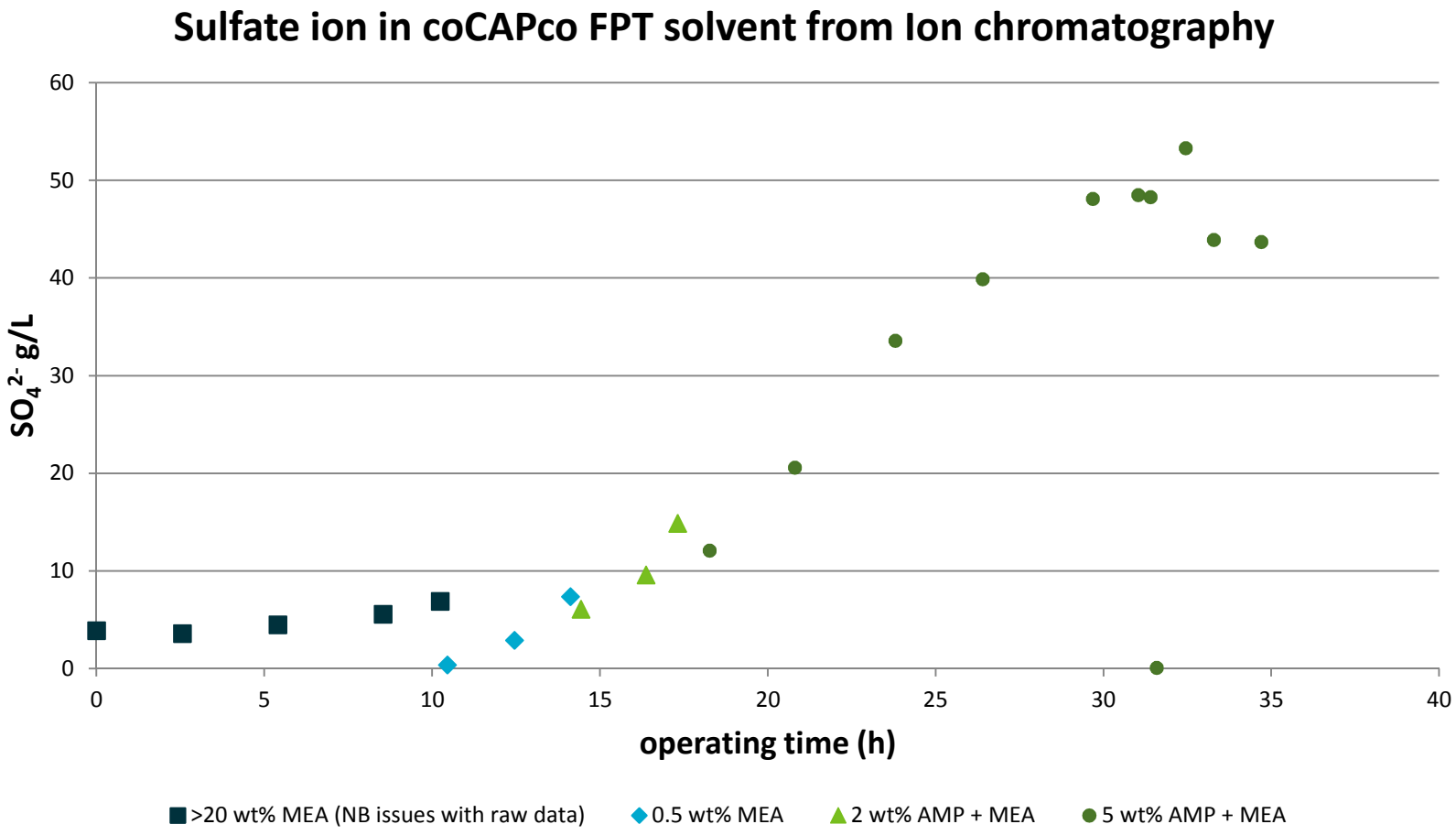
Typical run (rerun - 0.5 w-% MEA)



SO_2 concentration towards breakthrough



Sulphate build-up during campaign



Organic degradation products by cation exchange and GC/MS (Fed Uni)

		Blank	Sample #937	14.43h			Sample # 956	33.28 h		
Compound	CAS	Concentration (g/kg)	*PQL (g/kg)*	*Recovery (%)*	Concentration* (g/kg)		*PQL (g/kg)*	*Recovery (%)*	Concentration* (g/kg)	
					Replicate 1	Replicate 2			Replicate 1	Replicate 2
ORGANIC ACIDS										
Formic acid	64-18-6	0.05	*0.39*	*189*	<0.08	<0.08	*0.59*	*351*	0.34^	0.30^
Acetic acid	64-19-7	0.09	*0.12*	*256*	0.10^	0.12	*0.18*	*265*	3.7	0.19
Oxalic acid	144-62-7		*0.15*	*118*	<0.03	<0.03	*0.22*	*465*	<0.04	<0.04
VOCs										
2-oxazolidione	497-25-6	0.54	*0.73*	*177*	<0.15	0.20^	*1.1*	*21*	0.44^	3.6
N-(2-hydroxyethyl)imidazole	1615-14-1	<0.05	*0.24*	*NR*	*NR*	*NR*	*0.37*	*NR*	<0.07	<0.07
N-(2-hydroxyethyl)succinimide	18190-44-8	<0.05	*0.23*	*151*	<0.05	<0.05	*0.35*	*147*	<0.07	<0.07
Bicine	150-25-4	<0.02	*0.1*	*85*	<0.02	<0.02	*0.15*	*33*	<0.03	<0.03
N-(2-hydroxyethyl)imidazolidione	3699-54-5	0.15	*0.31*	*164*	0.07^	0.11^	*0.46*	*116*	0.16^	0.17^
Diethanolamine	111-42-2	<0.24	*1.2*	*249*	<0.24	<0.24	*1.8*	*188*	<0.3	<0.3
N-(2-hydroxyethyl)ethylenediamine	111-41-1	<0.07	*0.34*	*104*	<0.07	<0.07	*0.52*	*51*	<0.1	<0.1
N,N'-bis(2-hydroxyethyl)oxalamide	1871-89-2	<0.02	*0.09*	*159*	0.04^	<0.02	*0.14*	*175*	<0.03	<0.03

- Compounds identified
- No proof for accelerated ageing

PQL, practical quantitation limit
NR, not reported
*Reported concentrations are corrected for the blank response but have not been corrected for recoveries
^Concentration is below the PQL

Analytical techniques by Alicia Reynolds, submitted to Energy and Fuels

Overall Conclusions

- SO_2-CO_2-amine(s) chemical model developed;
- CSIRO's PCC Pilot plant at Loy Yang was modified to allow for CS-Cap operation;
- Pilot plant was operated to validate model;
- Forecasting SO_2 breakthrough concentration as a function of pH in absorber was validated and also used to decide on operation times;
- Forecasting corrosion was used to support the above decision;
- Regeneration will be focal point (PhD position available at Fed Uni).
- Process equipment requires further improvement (Aspen).

Moverover:

- Modification on internals allows for higher capture efficiency.

Acknowledgement

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Furthermore, AGL Loy Yang and Federation University are kindly acknowledged for their involvement.

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Thank you

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Back up slides

SO_2-water chemistry

Equilibrium constants and rate constants for the reactions of SO_2 in aqueous solutions. Unless otherwise indicated the values are for 20 °C. H_2O in parenthesis indicates the reaction is pseudo-first-order in this species.

Reaction	$\log_{10}K_i$	k_i	k_{-i}	ΔH (kJ mol^{-1})
$SO_{2(aq)}(+H_2O) \overset{k_1, k_{-1}, K_1}{\longleftrightarrow} H_2SO_3$	−1.3[a]	3.4×10^6 (s^{-1})[a]	6.3×10^7 (s^{-1})[a]	
$SO_{2(aq)} + OH^- \overset{k_2, k_{-2}, K_2}{\longleftrightarrow} HSO_3^-$	14.7[b]	3.64×10^8 ($M^{-1}\,s^{-1}$)[b]	7.7×10^{-7} (s^{-1})[b]	
$SO_3^{2-} + H^+ \overset{K_3}{\leftrightarrow} HSO_3^-$	7.16[c]	Instantaneous	Instantaneous	3.65[c]
$HSO_3^- + H^+ \overset{K_4}{\leftrightarrow} H_2SO_3$	0.501[a]	Instantaneous	Instantaneous	
$SO_{2(aq)} \overset{K_H}{\longleftrightarrow} SO_{2(g)}$	−0.17[c]	Not applicable	Not applicable	−26.97[c]
$2HSO_3^- \overset{k_5, k_{-5}, K_5}{\longleftrightarrow} S_2O_5^{2-}(+H_2O)$	−1.3[d]	7.00×10^2 (M^{-1}) at 24.7 °C[e]	10^4 (s^{-1}) at 24.7 °C[f]	−17.7[d]

[a] Eigen et al. (1961).
[b] Wang and Himmelblau (1964).
[c] Goldberg and Parker (1985).
[d] Ermatchkov et al. (2005).
[e] Betts and Voss (1970).
[f] k_{-5} calculated from the relationship $K_5 = k_5/k_{-5}$.

CO_2-water chemistry

Equilibrium constants and rate constants for the reactions of CO_2 in aqueous solutions. Unless otherwise indicated the values are for 20 °C. H_2O in parenthesis indicates the reaction is pseudo-first-order in this species.

Reaction	$\log_{10}K_1$	k_1	k_{-1}	ΔH (kJ mol^{-1})
$CO_{2(aq)}(+H_2O) \overset{k_1, k_{-1}, K_1}{\longleftrightarrow} H_2CO_3$	$K_1 = \exp\left(\frac{-10.000}{8.314T} - \frac{55}{8.314}\right)$[a] −2.93	$k_1 = \exp\left(22.66 - \frac{7799}{T}\right)$[b] 0.0194 (s^{-1})	$k_1 = \exp\left(31.15 - \frac{8019}{T}\right)$[b] 16.4 (s^{-1})	10[a]
$CO_{2(aq)} + OH^- \overset{k_2, k_{-2}, K_2}{\longleftrightarrow} HCO_3^-$	$K_1 = \exp\left(\frac{5000}{8.314T} - \frac{23}{8.314}\right)$ (M^{-1})[a] 7.71	$k_2 = 2 \times 10^{14} \exp\left(-\frac{64.000}{T}\right)$[a] 5253 (M^{-1} s^{-1})	$k_2 = 3 \times 10^{16} \exp\left(-\frac{114.000}{T}\right)$[a] 6.90×10^{-5} (s^{-1})	−50[a]
$CO_3^{2-} + H^+ \overset{K_3}{\longleftrightarrow} HCO_3^-$	$K_3 = 10^{\frac{-2902.39}{T} - 0.02379T + 6.4980}$ (M^{-1})[c] 10.37	Instantaneous	Instantaneous	−11[d]
$HCO_3^- + H^+ \overset{K_4}{\longleftrightarrow} H_2CO_3$	$K_4 = 10^{\log_{10}K_1 - \left(\frac{-5251.43}{T} - 36.7816T + 46.6685\right)}$ (M^{-1})[e] 3.33	Instantaneous	Instantaneous	1.9[f]
$CO_{2(aq)} \overset{K_H}{\longleftrightarrow} CO_{2(g)}$	$K_H = \exp\left(0.16916 + \frac{70.763}{T} - \frac{16929.7}{T^2}\right)$ (kPa M^{-1})[g] 1.48	Not applicable	Not applicable	13.3[h]

[a] Wang et al. (2010)
[b] Soli and Byrne (2002)
[c] Harned et al. (1941).
[e] Calculated according to micro reversibility from K_1 and the correlation for the reaction $CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$ in Edwards et al. (1978).
[f] Calculated from the temperature dependence of K_4 over the range 20–120 °C.
[g] Converted from mole fraction to M and taken from Crovetto (1991).
[h] Calculated from the temperature dependence of K_H over the range 20–120 °C.

CO_2-amine chemistry

Equilibrium constants and rate constants for the reactions of CO_2 with MEA in aqueous solutions. Unless otherwise indicated the values are for 20 °C. H_2O in parenthesis indicates the reaction is pseudo-first-order in this species.

Reaction	$\log_{10}K_l$		k_l	k_{-l}	ΔH (kJ mol^{-1})
$CO_2 + MEA \overset{k_6, k_{-6}, K_6}{\longleftrightarrow} MEACOOH$	$K_6 = \exp\left(\frac{23{,}000}{8.314T} - \frac{43}{8.314}\right)$[a]	1.59	$k_6 = 5.8 \times 10^{10} \exp\left(-\frac{41{,}000}{8.314T}\right)$[a]	2868 ($M^{-1}\,s^{-1}$)	40.3 (s^{-1})[b]	−23[a]
$H^+ + MEACOO^- \overset{K_7}{\longleftrightarrow} MEACOOH$	$K_7 = \exp\left(\frac{53{,}000}{8.314T} - \frac{41}{8.314}\right)$ (M^{-1})[c]	7.30	Instantaneous		Instantaneous	−53[a]
$H^+ + MEA \overset{K_8}{\longleftrightarrow} MEAH^+$	$K_8 = \exp\left(\frac{41{,}000}{8.314T} + \frac{42}{8.314}\right)$ (M^{-1})[d]	9.50	Instantaneous		Instantaneous	−41[d]

[a] Conway et al. (2011).
[b] k_{-6} calculated from the relationship $K_6 = k_6/k_{-6}$.
[c] Fernandes et al. (2012a).
[d] Fernandes et al. (2012b).

SO2-amine chemistry

- Aqueous MEA and SO2 monitored by 1H-NMR for 1 year at 40 and 100°C showed no reaction

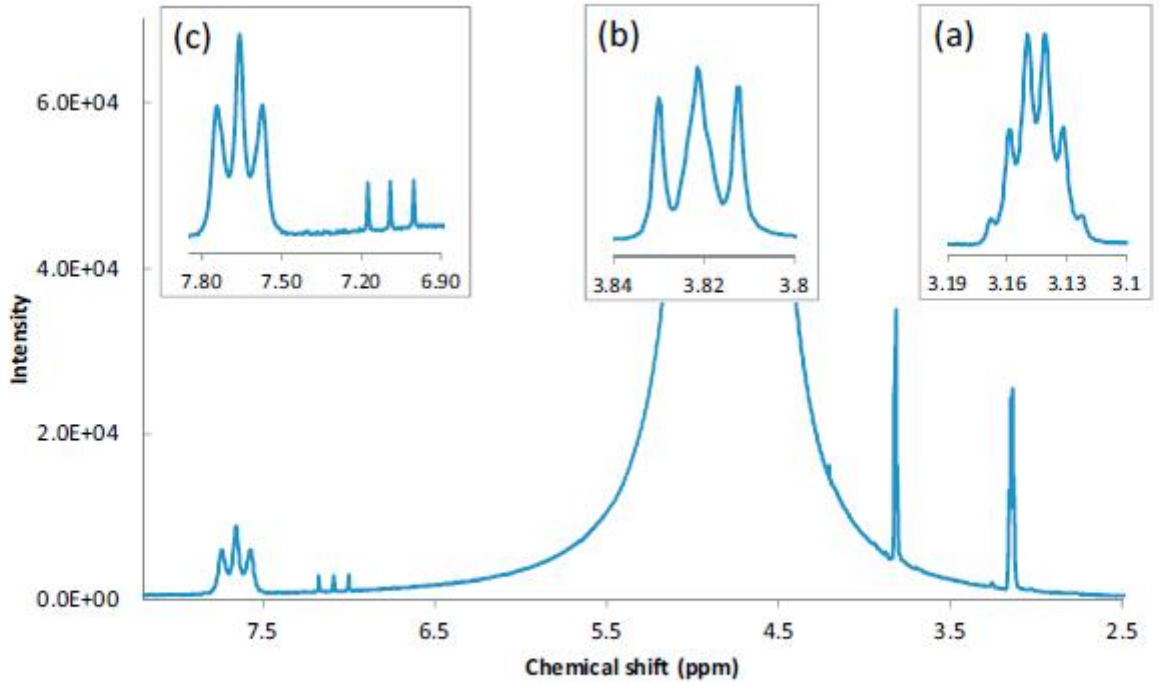
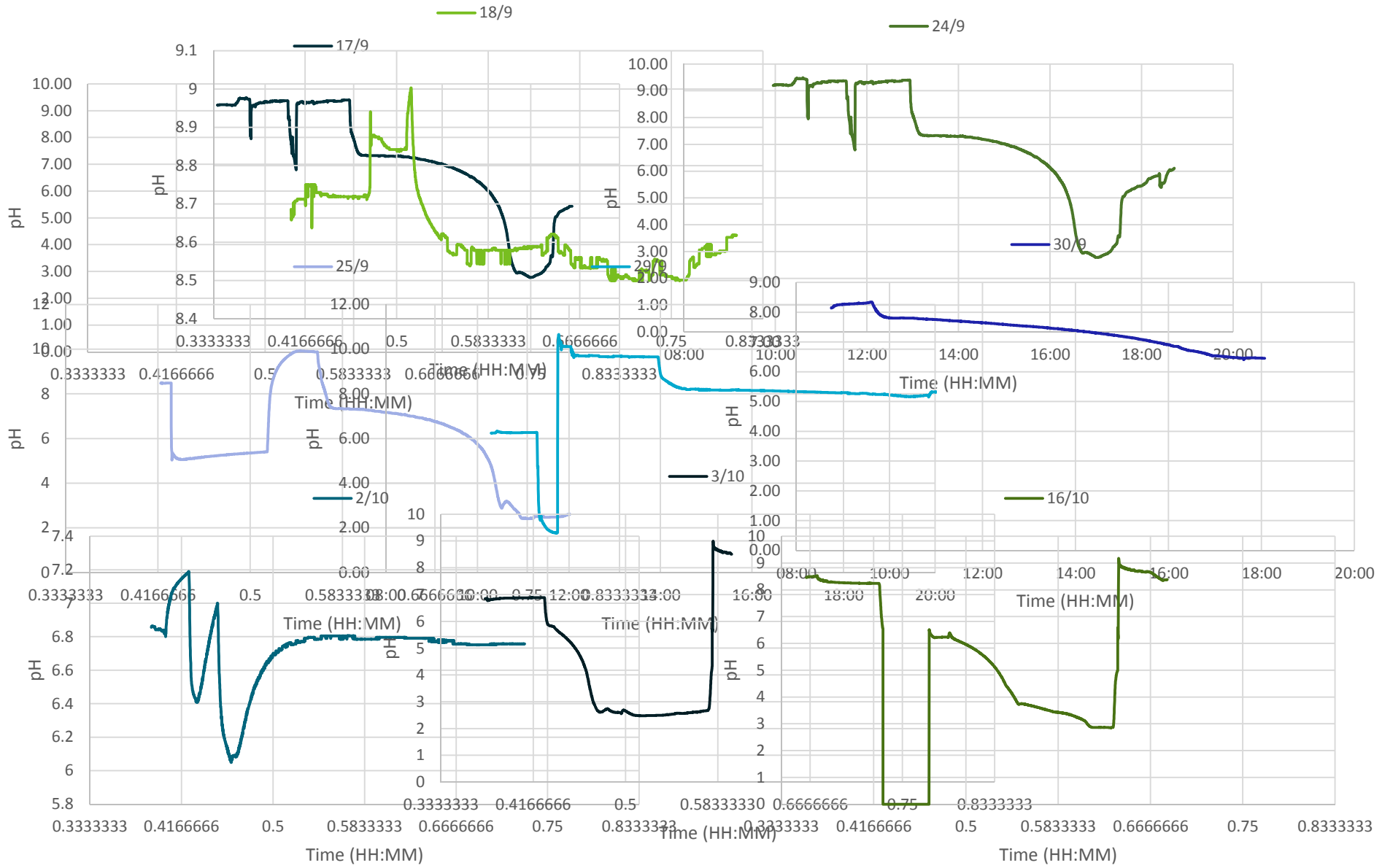
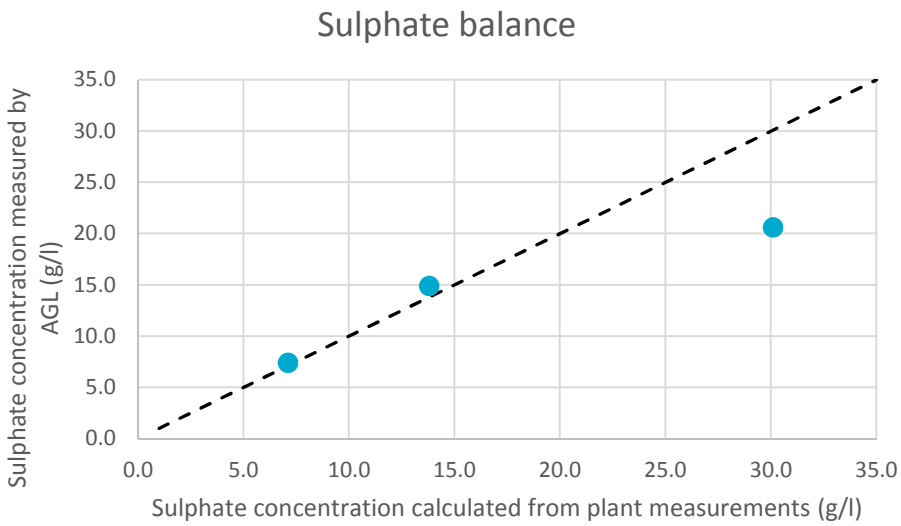


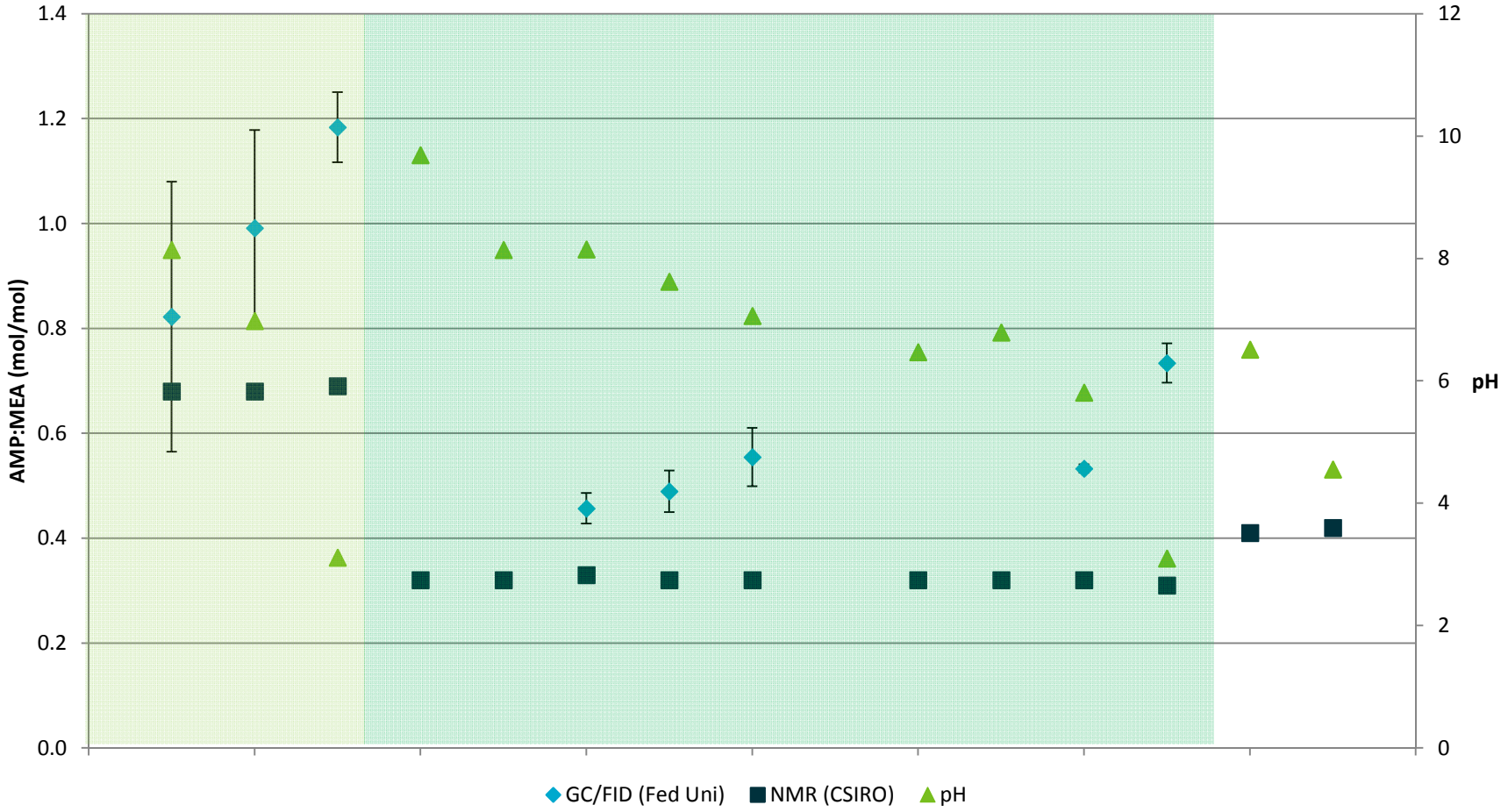
Fig. 2. ^{1}H NMR spectra of 0.05 M MEA solution with 0.1 M sulphite at pH 7.2 (adjusted with HCl) after equilibrating for five months at 100 °C. Insets are enlargement of (a) the peak from hydrogens on carbon CH_2—NH_2, (b) the peak on hydrogens on carbon CH_2—OH, and (c) the peaks from ammonium ions, NH_4^+, and the protonated nitrogen of MEA, CH_2—NH_3^+.

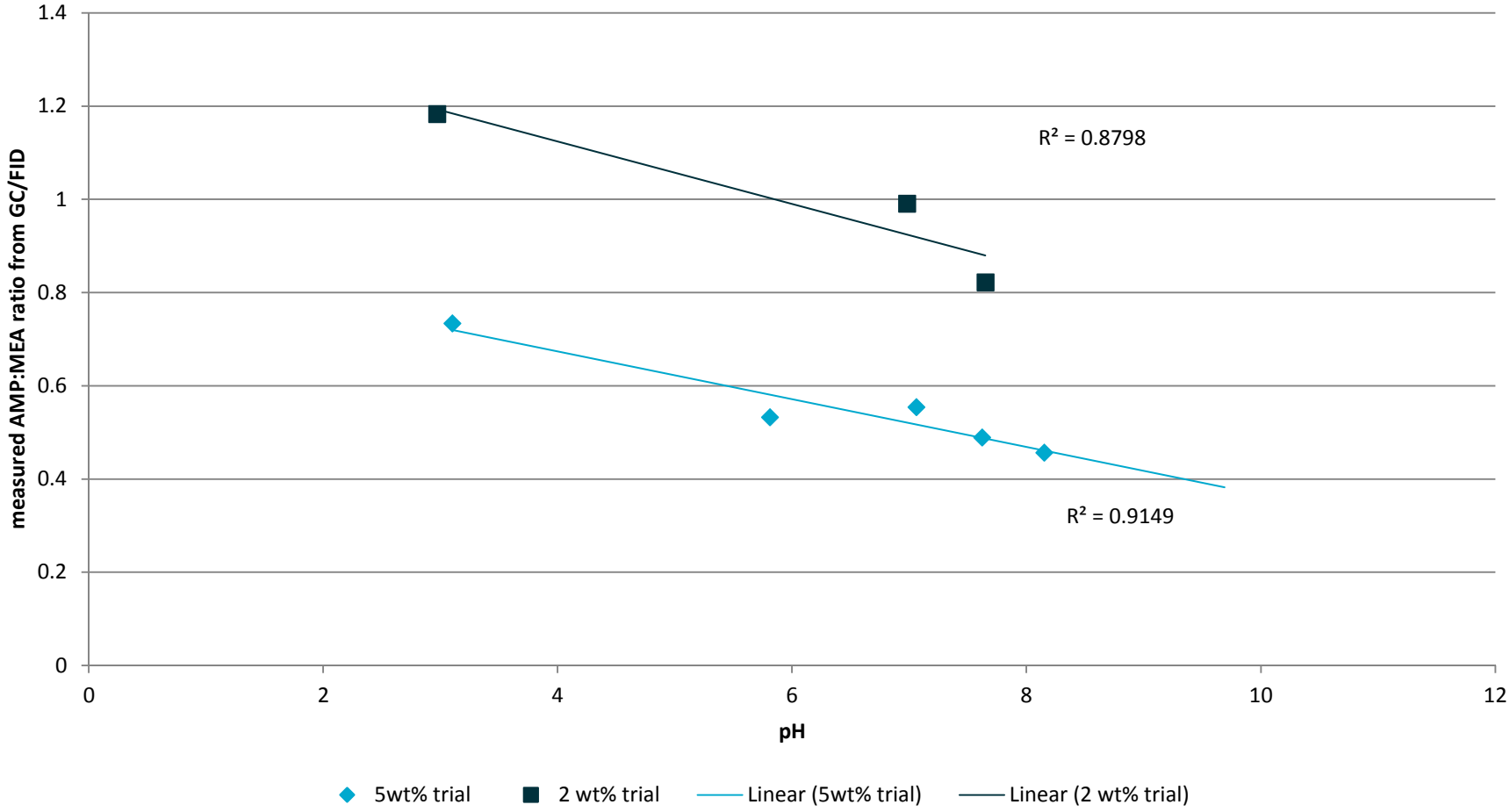

18/9
17/9
24/9
25/9
30/9
3/10
2/10
16/10
pH
Time (HH:MM)

Sulphur mass balance.

Copy of 141205 Process B v4 - summary pH amineCONC ratio operating hours SO4 Analysis total S




AMP:MEA (mol/mol)
pH
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
12
10
8
6
4
2
0
GC/FID (Fed Uni)
NMR (CSIRO)
pH


1.4
1.2
1
0.8
0.6
0.4
0.2
0
measured AMP:MEA ratio from GC/FID
0
2
4
6
8
10
12
pH
R² = 0.8798
R² = 0.9149
5wt% trial
2 wt% trial
Linear (5wt% trial)
Linear (2 wt% trial)

Analysis

- Liquid samples from FPT COL loop
- Amine and CO_2 concentration – by pH titration. Addition of SO_x results in a drop of pH in amine solution and the standard titration method is affected. (CSIRO) Concentration calculated from tank level and measured by GC/MS.
- SO_4^{2-} by ion chromatography (AGL)
- Total sulfur – samples were oxidised to convert any SO_3^{2-} to SO_4^{2-} (Fed Uni) then SO_4^{2-} quantified by ion chromatography (AGL)
- Degradation products – samples pretreated by cation exchange, and organic compounds identified by GC/MS (Fed Uni)

Corrosion

- The presence of SO2 will increase the corrosion rate, however in the CCL loop, the SO2 concentration is not likely to be higher in coCAPco than under the standard PCC conditions, where it has been found to have less effect on corrosion than CO2 concentration. Under coCAPco, the concentration of amine in the FPT column is low, so the effect of SO2 will be more significant. Choice of materials to construct the FPT will be crucial. At a minimum, grade 316 stainless steel will be required.