A Novel Methodology for Online Analysis of Amine Solution Degradation Caused by Fly Ash

Devjyoti Nath, Colin Campbell, Yuewu Feng, Brent Jacobs, Firuz Philip, Amr Henni, Corwyn Bruce, Wayuta Srisang, Stavroula Giannaris, Dominika Janowczyk

Background

- High energy requirement for regeneration, excessive solvent degradation, and high corrosivity are three major drawbacks of the amine scrubbing technology.

- Though 38% of world energy is derived from coal-fired power plants, research work on the investigation of the impact of fly ash on the amine solvent degradation process is still very limited.

- Reliable online monitoring systems and analytical techniques are of great interest to research and industry.

Objective

- Development of a reliable online analytical technique based on Gas Chromatography (GC) to quantify the total amount of amine degradation in the presence of different amounts of fly ash and at different amine concentrations.

- Testing the online sampling system for the analytical GC technique built in the lab and continuous recirculation and analysis of fly ash contaminated amine samples for extended periods of time.

- Observe the influence of fly ash on the degradation of common commercially used amine based solvents such as Monoethanolamine (MEA) and Methyl diethanolamine (MDEA).

- Investigate the effect of metal oxides from the fly ash, such as such as Al_2O_3, TiO_2, Fe_2O_3, CaO, etc., on the solvents.

Characterization of Fly Ash Samples

Fly ash samples (sample A and sample B) collected from a coal burning power plant were analyzed by an third party company, SGS Minerals Services. ASTM D3174, ASTM D7348 and ASTM D6349 were used to measure the Ash content, Loss of Ignition (LOI) and Metal/Inorganic oxides content.

Analysis	Sample A	Sample B
Ash Content (without drying)	87.03%	59.67%
Ash Content (after drying)	88.37 %	84.43 %
Moisture Content	1.52%	29.33%,
Loss on Ignition (LOI, at 750 ^{o}C)	11.63%	15.57%

Oxides	Percentage of oxides (%)	
	Sample A	Sample B
Silicon Dioxide, SiO_2	17.70%	35.98%
Aluminum Oxide, Al_2O_3	9.18%	26.81%
Titanium Dioxide, TiO_2	0.36%	1.29%
Iron Oxide, Fe_2O_3	48.16%	4.56%
Calcium Oxide, CaO	4.84%	5.73%
Magnesium Oxide, MgO	1.41%	3.71%
Potassium Oxide, K_2O	0.59%	0.97%
Sodium Oxide, Na_2O	3.27%	4.52%
Sulfur Trioxide, SO_3	12.42%	2.63%
Phosphorus Pentoxide, P_2O_5	0.41%	2.46%
Strontium Oxide, SrO	0.18%	0.42%
Barium Oxide, BaO	0.47%	2.41%
Manganese Oxide, MnO_2	0.43%	0.09%
Undetermined	0.58%	8.42%
Sum of Oxides	99.42%	91.58%
Base Acid Ratio	2.14	0.3

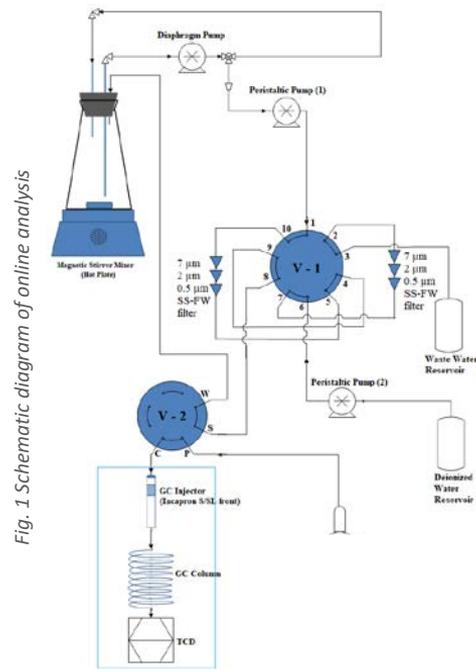## Online Analysis of Amine Solution

Fig. 1 Schematic diagram of online analysis

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## Calibration of the Online Analysis System and Reproducibility

- To calibrate the GC for MEA and water, as well as observe the reproducibility of the online sampling system, 15 wt%, 30 wt% and 45 wt% of aqueous MEA solutions were analyzed with the GC for more than 10 times. Calibration equation for MEA and water are shown in Eqs. (1) and (2), respectively. Regression coefficients (R^2) show that the reproducibility of the analysis (accuracy) is very high.

$$Y_{MEA} = -229.508 + 451.202X \; ; R^2 = 0.9999 \qquad (1)$$

$$Y_{H_2O} = 2761.906 + 559.018X \; ; R^2 = 0.9988 \qquad (2)$$

- Various CO_2 loaded aqueous MDEA and aqueous ammonium bicarbonate (NH_4HCO_3) solutions were used to calibrate the GC for quantification of CO_2. The amount of CO_2 in aqueous MDEA and NH_4HCO_3 solutions was measured by TOC analyzer.

- GC analysis was performed continuously for a week with the clean aqueous MEA solution and aqueous MEA solutions containing fly ash . A total of 522 and 511 sample injections were performed with clean aqueous MEA and aqueous MEA containing fly ash. The major findings of this test were: (1) the filter train can remove the fly ash from the liquid streams, (2) the back flush option successfully prevented clogging of the filter train. However, the reproducibility of analysis (peak areas) changed over time because the solvent was diluted with deionized water from the dead volume inside the filter trains and tubing after the back flush.

Amine degradation due to fly ash

Fig. 2. Experimental setup to observe amine degradation due to fly ash
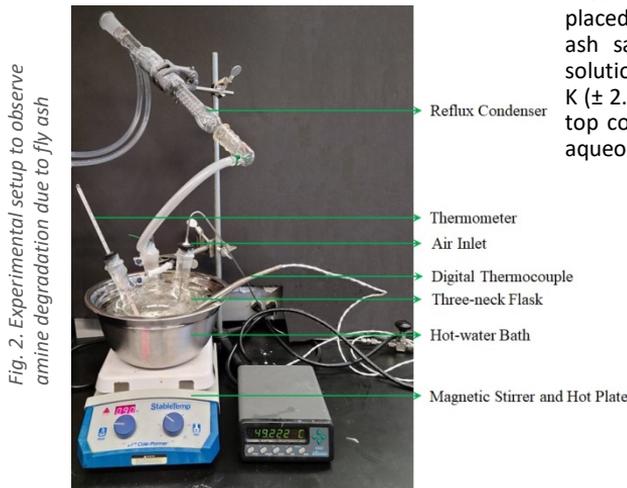
Around 500 ml of aqueous amine solution was placed into the three neck flask. Then 0 to 1 wt% fly ash sample was added into the aqueous amine solution. The temperature was maintained at 323.15 K (± 2.0 K) with a hot water bath. Air from the bench top compress air connection was introduced to the aqueous amine fly ash mixture by bubbling.

Fig. 3. 30 wt.% MEA sample (323.15 K, after 120 hours of air flow) ; (a) 30 wt.% MEA without Fly ash, and (b) 30 wt.% MEA with 0.5 wt% of fly ash

Sample No.	MEA concentration (wt%)	Amount of fly ash (wt%)	Equivalent MEA percentage estimated with TOC analyzer (wt%)	MEA percentage estimated with GC (wt%)	Degradation amount (wt%)
Sample A	30	0	32.4	29.0	10.5
Sample B	30	0.1	36.4	27.9	23.4
Sample C	30	0.5	36.7	30.2	17.5
Sample D	30	1	35.3	22.5	36.2

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