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Do we underestimate the impact of particles in coal-derived flue gas on amine-based CO₂ capture processes?

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Abstract

The effect of particulate matter on the amine-based capture process has, up till now, not been considered in much detail due to the relatively low concentration of particulate entering the capture plant. In this study we present results of leaching tests with 30 wt% MEA utilising real fly ash samples from a range of European coal-fired power plants. The effect of a number of parameters including CO₂ loading, temperature, pH, leaching time, solid/liquid ratio & organic heat stable salts have been investigated. These experiments show that the behaviour of the various compounds and elements is not uniform with different conditions. A strong correlation between reducing pH/increasing CO₂ loading and Fe, Cr & V levels is observed, but is not seen for other heavy metals. This impact of pH on metal solubility is striking and suggests that Fe, in particular, may be transported by the liquid system and stored as deposits in the stripper where increased pH reduces the solubility of Fe compounds. The presence of oxalate as a heat stable salt leads to the precipitation of calcium oxalate when calcium phosphate is leached out of the ash. This could result in deposits in areas such as the reboiler that may lead to plugging, reduced heat transfer efficiency and even corrosion issues. Solid/liquid ratio was also found to have some effect with lower solid/liquid ratios showing higher relative solubility for heavy metals. Temperature and leaching time were also investigated but only minor increases in metals content were observed by increasing either of these parameters. The results observed strongly suggest that the effects of particulate matter on the post-combustion capture process should not be ignored, particularly if levels are sufficient to lead to significant build up of ash in the solvent. Ash captured in the liquid has the potential to release significant amounts of Fe, Mg, Ca and PO₄³⁻ into the solvent with Fe levels, in particular, being a concern for the enhancement of solvent degradation processes.

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1. Introduction

Amine-based post-combustion CO₂ capture on coal-fired power plant is an end of pipe technology and can be affected by any upstream processes that alter the quality of the incoming flue gas. Flue gas being emitted from coal fired power stations fulfils the requirements of relevant emission permits. Compliance with these permits is achieved by the use of a range of emissions control technologies that reduce levels of certain species in the flue gas, but generally do not eliminate them entirely and may add low levels of other components to the flue gas. Coal-derived flue gas typically contains a CO₂ concentration of approx. 13 vol% dry at 6 vol% dry O₂ as well as other gaseous compounds such as SO₂ & NO_x, which may chemically react with the capture solvent. Typically in German coal-fired power plant approx. 65 ppmv dry SO₂ and 100 ppmv dry NO_x remain in the treated off gas and therefore need to be considered at the inlet of a CO₂ capture plant. Additionally, there are also low concentrations of particulate matter in the flue gas, levels of which are highly site dependant due to coal ash concentration/composition and the installed flue gas treatment equipment. The emission of particulate matter usually does not exceed a level of 20 mg/m³ (STP, dry, 6 % O₂), for German coal-fired power plants. Particulate matter in the flue gas derives from:

- Fly ash which has not been removed by the electrostatic precipitator (ESP) and the wet flue gas desulphurisation plant (FGD) which is usually positioned behind the ESP.
- Small droplets of the FGD absorber liquor that are not captured by the demister installed on top of the FGD absorber.

The effect of particulate matter on the amine-based capture process has, up till now, not been considered in much detail and is poorly understood due to the relatively low concentration of particulate entering the capture plant. However, due to the continual recirculation of the solvent in the process, low levels of particulate matter may build up in the solvent over time. Even if only a part of the total flue gas particulate is captured in the in the plant this may lead to the build-up of ash-derived metals in the solvent that could lead to enhanced solvent degradation, corrosion and potential plugging effects. Therefore, it is important that the effect of particulate matter on the design of demonstration-scale plants is assessed.

2. Materials and Methods

Due to the low concentration of fly ash particulate matter in the flue gas behind the FGD (typically 1-2 mg/m³) obtaining reliable samples of sufficient material for characterisation is highly problematic. Therefore, ash captured in the ESP is used in these studies as a proxy for the particulate matter found after the FGD due to its ready availability and ease of sampling. Fly ash behind FGD compared to ESP ash has a smaller size distribution and, due to the higher specific surface area, generally a higher concentrations of heavy metals and compounds from condensation processes that occur during the flue gas path between the boiler and the air preheater of coal-fired power stations [1], [2]. However, the general composition of fly ash and ESP ash do not differ significantly if the ashes are considered without considering the levels of carbon residue. This can be implied from studies that show that when integral ESP ash (all stages) is compared to ESP ash from the final stage of the ESP alone, the differences in composition are small [3]. On this basis it is assumed that ESP ash is an acceptable proxy for studying the effects of particulate matter on the capture solvent.

Spot samples of the ESP ash at a range of European power stations (PP1 – 5) have been taken from the total flow of captured ESP ash to the storage silo using standard internal methods. The average particle size of the samples was much lower than 10 mm, the maximum size for leaching tests. The composition of ash was characterised by X-ray Fluorescence (XRF). To ensure good quality spectra a

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