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## The Use of Amine Reclaimer Wastes as a NO<sub>x</sub> Reduction Agent

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### Abstract

Amine reclaimer wastes (ARW) generated in carbon capture and sequestration (CCS) is categorized as a hazardous waste which needs proper disposal. The proposal described in this paper can bring about a multi-effective solution to the problem of CCS waste handling. Both the pilot scale and the full scale experimental trials carried out in this study using ARW and pure monoethanolamine (MEA) confirmed the possibility of utilizing ARW as a potential reagent for the selective non-catalytic reduction (SNCR) of NO<sub>x</sub> in combustion flue gases. Even though the effectiveness of ARW is lower than that of aqueous ammonia, i.e. the most common SNCR chemical reagent used in industry (above 60 % NO<sub>x</sub> reduction efficiency), ARW is nonetheless shown to possess valuable SNCR qualities (at least 20 % NO<sub>x</sub> reduction efficiency) considering its availability as a waste product which has to be safely disposed. A series of thermo-gravimetric analyses provided important information on vaporization characteristics of amine reclaimer bottom wastes. The proposed methodology can lead to simultaneous energy and material resource recovery while primarily solving two environmental pollution problems, i.e. toxic ARW wastes generated in CCS, and emission of NO<sub>x</sub> – a class of highly active greenhouse gases.

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Key words: Amine reclaimer wastes; Carbon capture; Combustion; Monoethanolamine; NO<sub>x</sub> reduction.

### 1. Introduction

As rigorously emphasized in previous GHGT events, carbon capture and sequestration (CCS) is going to be a compulsory and main strategy for achieving global climate control goals. Considering the fact that amine absorption is presently the most matured and ready to use technology available for the immediate deployment in large scale, it is timely to address pollution mitigation steps required to handle amine

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degradation wastes generated in CCS. This study is focused on the safe disposal of monoethanolamine (MEA) reclaimer bottom wastes using industrial combustion processes.

### *1.1. Amine reclaimer wastes (ARW)*

The generation of significant quantities of degraded amine wastes is a key environmental issue related to post combustion CO<sub>2</sub> capture processes [1] used in CCS. Gradual degradation of aqueous amine solutions, which are used as absorbents, occurs due to the presence of heat, oxidizing conditions, and the presence of various impurities such as SO<sub>x</sub>, NO<sub>x</sub>, soot, metallic elements, etc. [2, 3]. An amine reclaimer unit is often installed, connected to CO<sub>2</sub> capture processes, to separate out degraded amine compounds from the usable amine solution. Distillation is a common thermal separation process used for this purpose. The bottom product of distillation amine reclaimer units, termed here as amine reclaimer wastes (ARW), is the subject of this study.

### *1.2. Disposal options*

ARW is categorized as a hazardous liquid waste [1] and is no longer permitted to dispose in landfills [4]. Previous studies [5] carried out on investigating the possibility of biological treatment of these wastes reveal that low C/N (carbon: nitrogen) ratios in these wastes prevent efficient biodegradation. Presence of other toxic contaminants, like heavy metals, is another concern. Accordingly, thermal destruction using a hazardous waste incinerator is the currently acceptable mean for ARW disposal.

### *1.3. Aims of this study*

The overall aim of the study was to investigate the suitability of ARW as a chemical reduction agent for selective non-catalytic reduction (SNCR) of nitrogen oxides (NO<sub>x</sub>) in industrial combustion processes where it would then serve multiple purposes of emission reduction, energy recovery, and waste destruction. Comparison of the NO<sub>x</sub> reduction potential of ARW/MEA against the commonly used industrial SNCR reagent of aqueous ammonia is also included in the scope.

The laboratory pilot scale experiment was aimed at using a simulated flue gas stream to observe the expected SNCR potential of ARW and pure MEA under laboratory controlled steady state operating conditions while making it possible to accurately measure combustion emissions.

The aim of the full scale test trials was to determine the feasibility of using cement kilns as a safe disposal mean for ARW, while utilizing its SNCR potential for emission mitigation in cement industry. It is noted that the substantial calorific value contribution by ARW combustion is also attractive for the kiln operation. The used ARW in this study had a lower heating value (LHV) of 3900 kcal/kg.

A set of thermogravimetric analyses were used to characterize and compare amine wastes with aqueous ammonia and MEA.

## **2. Methodology**

### *2.1. Laboratory pilot scale experiments*

This study, carried out in a laboratory pilot scale test facility (Fig. 1), investigated the possibility of using ARW as a NO<sub>x</sub> reduction agent in an SNCR process. Accordingly, injection of ARW into a simulated flue gas stream was done. The SNCR occurred inside a quartz flow reactor housed inside a

temperature controlled annular furnace. A wide range of temperatures and stoichiometric ratios were tested. A detailed description of this experimental set-up has been reported elsewhere [6].

The ARW used in the pilot study was obtained from a full scale CO<sub>2</sub> capture facility based on a coal fired combustor. The plant uses monoethanolamine (MEA) as the absorbent and has a distillation amine reclaimer unit. Detailed analysis of the waste, reported in a previous publication [5], has revealed that it contains various degradation compounds originating from MEA, including NH<sub>4</sub><sup>+</sup>, and some residual MEA.

In addition to ARW, pure MEA and aqueous ammonia (15 %) were also used in the pilot experiments for the purpose of comparing their SNCR potentials.

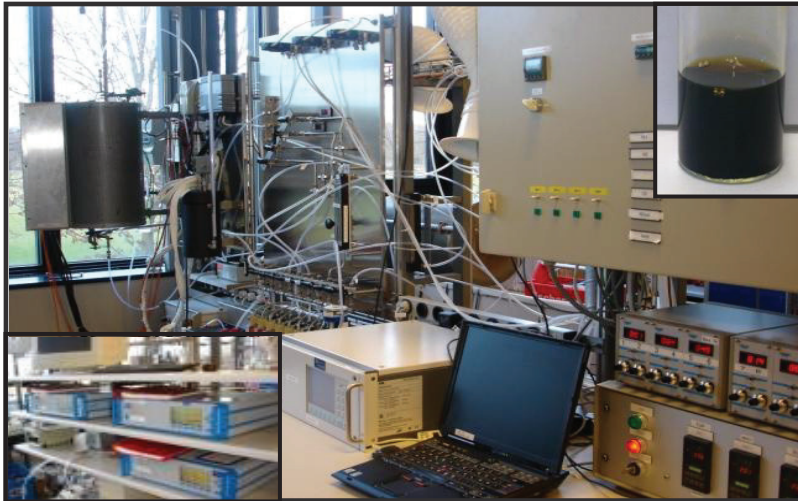


Fig. 1: Pilot scale experimental set-up. (Bottom left dwarf pic: gas analyzers; Top right dwarf pic: an ARW sample).

## 2.2. Full scale demonstration tests

Several demonstration test runs were carried out at a local cement manufacturing plant (Norcem - Brevik, Norway) in order to study the feasibility of the proposed scheme in full scale. Due to the unavailability of large amounts of ARW, pure MEA – one of the main components in ARW, was used in these full scale trials. In addition, aqueous ammonia (15 %) was used as a comparison mean. Each MEA injection run was carried out for approximately 15 min. time duration, which was sufficient to monitor the NO<sub>x</sub> emission response. Fig. 2 shows the schematic of the kiln structure and the MEA injection points. Injections were carried out at several locations along the precalciner (5<sup>th</sup>, 6<sup>th</sup> and 7<sup>th</sup> floor levels) and also at the combustion chamber of the kiln. The combustion chamber temperature was 1100–1150 °C while the approximately uniform temperature along the precalciner was close to 850 °C. Accordingly, chemical injections at different locations along the precalciner experienced approximately the same temperature conditions while the residence times available for the SNCR reaction were different.

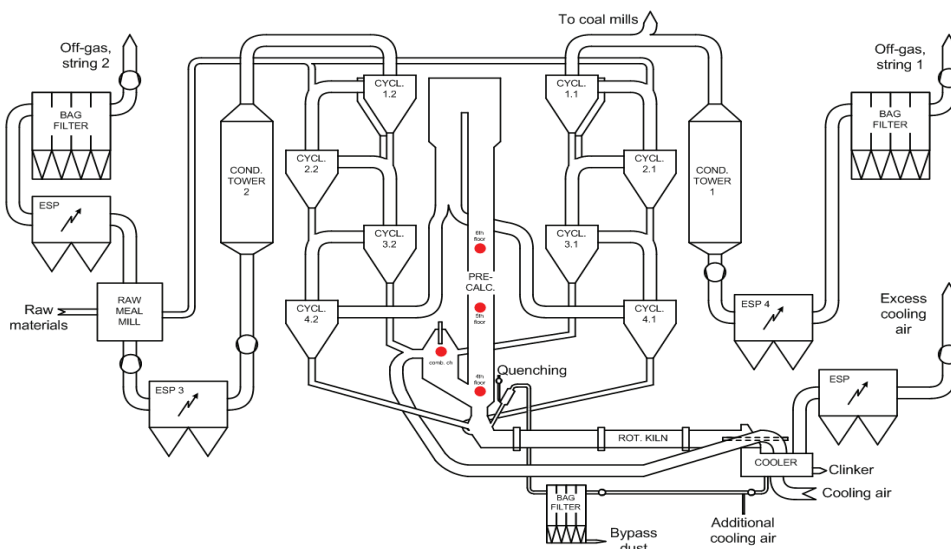


Fig. 2: Schematic representation of the Norcem cement kiln system depicting injection locations (red dots) used during full scale trials.

### 2.3. Waste characterization by thermogravimetric analysis (TGA)

Thermogravimetric analysis was used to identify and compare the mass vaporization characteristics of four different samples, i.e.; aqueous  $\text{NH}_3$  solution (15 %), aqueous MEA solution (54 %), light liquid phase of ARW, heavier ARW sludge deposit (which was not used for any SNCR experiment). The analysis was conducted using a *Perkin Elmer TGA 7* analyzer. Further details on the instrument and the used analytical procedures can be found elsewhere [7]. TGA gives an overview of the mass loss behavior of a substance upon exposing to a thermal reactor environment. These volatility and thermal behavior details, previously unknown for these compounds, are vital for designing SNCR chemical injection systems both in industrial and laboratory experimental scales.

Basically the same temperature program was applied for all four samples, to facilitate comparison, although for the more volatile samples ( $\text{NH}_3$  and MEA solutions) only the first three steps were enough to devolatilize the entire sample. The used general temperature program sequence is;

1. Hold for 30 min. at 25 °C
2. Heat from 25 to 110 °C at 50 °C/min
3. Hold for 30 min. at 110 °C (45 min for the dense ARW phase)
4. Heat from 110 to 850 °C at 20 °C/min
5. Hold at 850 °C for 10 min.
6. Switch from  $\text{N}_2$  to air while holding at 850 °C

### 3. Results and Discussion

#### 3.1. Pilot experiments

ARW is shown to be effective as a reduction agent above  $\sim 750$  °C temperatures. The removal efficiency increases with increasing temperature, reaching the maximum efficiency close to 950 °C (Fig. 3). Further increases in temperature lead to decreasing efficiencies. Quite analogous profiles have been reported for other SNCR reagents such as ammonia ( $\text{NH}_3$ ) and urea [8]. The use of higher than unity stoichiometric ratios (total nitrogen to nitrogen oxides – TN/NO) resulted in a significantly enhanced  $\text{NO}_x$  removal (Fig. 3). Unlike commercial chemical reagents, use of a waste product at higher stoichiometric ratios will not cause an economic burden, as long as the  $\text{NH}_3$  slip is not unacceptably high. This study could not detect such high ammonia emission levels. Emission of carbon monoxide (CO) was also found to be low at higher operating temperatures. At the lower temperature range (400–700 °C), even though the total  $\text{NO}_x$  level was nearly unchanged, conversion of NO to  $\text{NO}_2$  was observed (data shown elsewhere [6]). The above observations can be explained based on the chemistry of combustion products of monoethanolamine (MEA) and its degradation species [6].

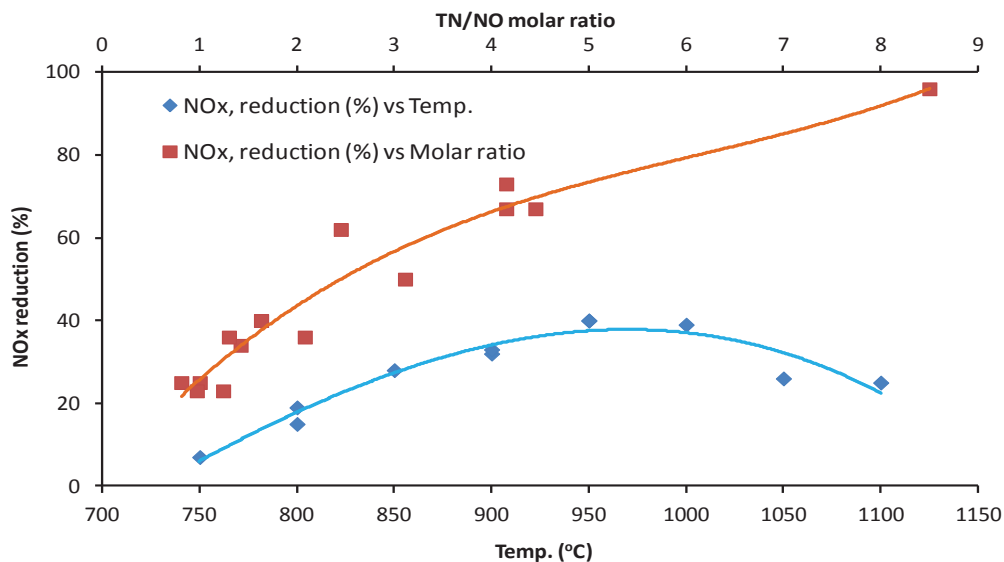


Fig. 3. Average  $\text{NO}_x$  reduction by ARW injection at different temperatures (at the TN/NO ratio of 1.63) and at different TN/NO ratios (at 950 °C).

The tests conducted with aqueous ammonia (15 %) and pure MEA showed that their SNCR potentials are about 2.14 and 1.71 times (respectively) superior to ARW at the interpolated TN/NO ratio of 1 (data shown elsewhere [6]).

#### 3.2. Full scale tests

The full scale demonstration tests conducted using aqueous  $\text{NH}_3$  and MEA corroborated the observations made in pilot scale experiments. Fig. 4 illustrates  $\text{NO}_x$  reduction vs. time evolution data from one experimental run conducted with MEA injection at a rate of 550 l/hr corresponding to a TN/NO ratio of 1.

NO<sub>x</sub> reduction up to about 30% is observed at this condition. It took a certain time before the NO<sub>x</sub> level reached its minimum level, apparently due to the time lapse needed for the system to reach uniform mixing of chemical throughout the reaction volume. Once the chemical injection had stopped, the NO<sub>x</sub> level gradually rose to its pre-injection level. Fig. 4 also indicates CO emission during the injection period. Corresponding to the maximum NO<sub>x</sub> reduction, the CO level shows a peak increase. This behavior can mainly be due to the fast consumption of OH radicals by amine compounds as shown in Eq. 1.



When the OH radical concentration drops, the burn out reaction of CO (Eq. 2) becomes less favorable and that leads to the accumulation of CO. Generation of CO as a product of an SNCR reaction of MEA itself is also a possibility. Kelly et al. (2006) [9] suggested an SNCR pathway involving methylamine (CH<sub>3</sub>NH<sub>2</sub>) which emits CO as a by-product (Eq. 5).



CO accumulation is, however, not observed during the pilot scale tests involving real amine waste (ARW) apart from the tests conducted at lower temperatures (< 800 °C). Hence, CO emission is not considered to be an issue of ARW combustion when proper temperature windows are selected. Javed et al. (2009) [10] have reported that at lower temperature operations, a significant CO emission is observed when urea is used as the main reductant together with several liquid additives (H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub>, and C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>). At higher temperatures (approx. > 950 °C), however, the CO concentration rapidly dropped despite of the use of high amounts of liquid additives. This is very consistent with the observations made in our pilot experiments (data shown elsewhere [6]) which are conducted with ARW and MEA.

Fig. 5 summarizes the results of several full scale injection runs carried out with aqueous ammonia and MEA. The NO<sub>x</sub> reduction potential of MEA (average 28 % reduction) is clearly not as superior as aqueous NH<sub>3</sub> (average 63 % reduction) under these conditions, as can be understood based on the relatively straight forward SNCR chemistry of NH<sub>3</sub> (overall reactions given in Eqs. 3 and 4). SNCR reaction mechanisms directly involving MEA have not yet been clearly identified. However, NH<sub>3</sub> has been recognized as a major end product of thermal decomposition and oxidative degradation of MEA [2, 3, 11].



Previous studies carried out on the SNCR potential of other amines have also shown somewhat similar results. According to Kelly et al. (2006) [9] methylamine (CH<sub>3</sub>NH<sub>2</sub>), dimethylamine ((CH<sub>3</sub>)<sub>2</sub>NH) and trimethylamine ((CH<sub>3</sub>)<sub>3</sub>N) showed a considerable SNCR performance above 400 °C. They have further observed that even though the NO conversion is quite high, effective NO<sub>x</sub> reduction potentials of these amines are quite low compared to NH<sub>3</sub> due to the formation of NO<sub>2</sub> in the presence of amines. Methylamine showed the highest, about 30 %, NO<sub>x</sub> reduction of all three tested amines. Kelly et al. (2006) [9] suggested a reaction pathway (Eq. 5- overall reaction) for the SNCR behavior of methylamine. This is an oxidative-reduction mechanism with nitroso-methylamine as an intermediate. Even though the NO<sub>2</sub> generation observed in our full scale tests (conducted above 850 °C) was not significant (about 1 %

of the total NO<sub>x</sub> level), the laboratory pilot experiments clearly indicated the NO<sub>2</sub> generation potential of ARW and MEA under low temperature operating conditions. These results have been published elsewhere [6].

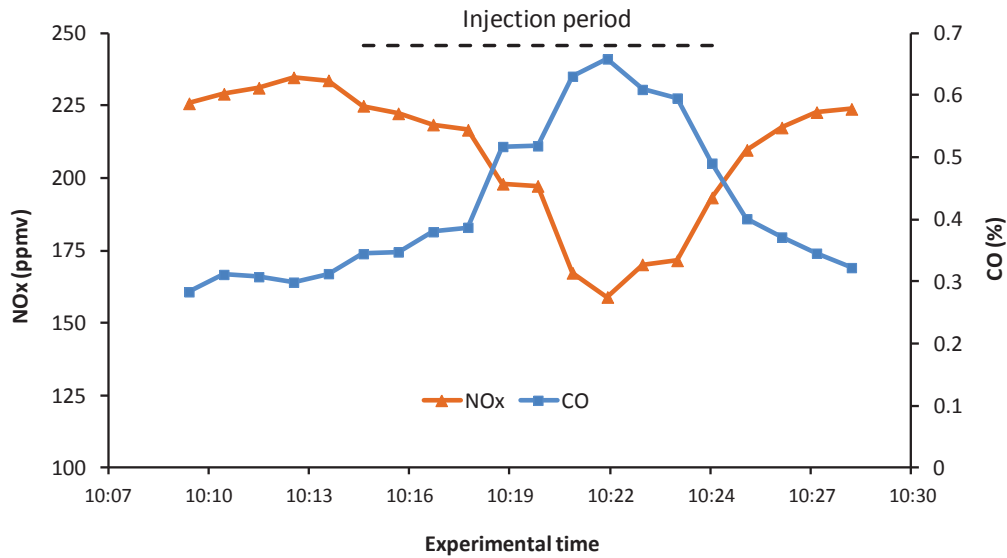
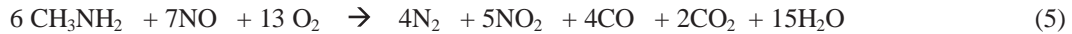


Fig. 4: NO<sub>x</sub> and CO concentration variation during one full scale trial conducted with MEA injection at a rate of 550 l/hr (Injection position: 5th floor level of the precalciner).

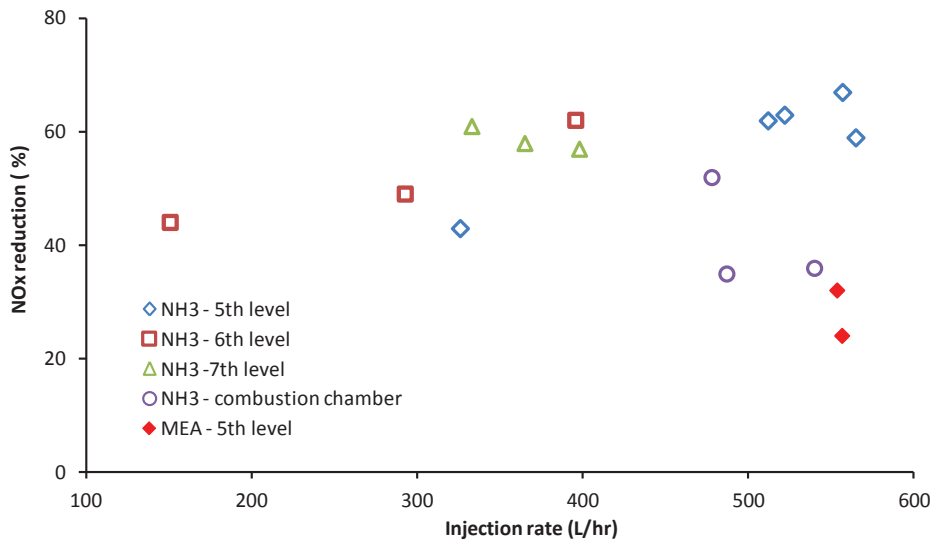
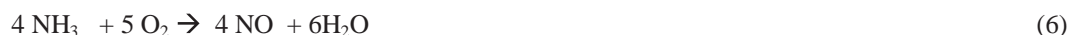


Fig. 5: A summary of different full scale injection trials.



For the aqueous ammonia (15 %) injections carried out at the combustion chamber (temperature 1050–1200 °C), the observed NO<sub>x</sub> reduction (on average 41 %) is lower than for the injections carried out at precalciner locations (temperatures 850–900 °C). This is due to the fact that at higher temperatures, oxidation of ammonia into NO becomes increasingly competitive, (Eq. 6), leading to decreased NO<sub>x</sub> reduction efficiency. This behavior was also observed in the pilot scale experiments (Fig. 3).



### 3.3. Thermogravimetric (TGA) analysis

Fig. 6; curves (a)-(d) illustrates the TGA behaviors observed for the four tested samples. The common temperature program used is also shown in the same figure. Curve (a) shows the TGA analysis results for an aqueous ammonia (15 %) sample. The whole analysis was run in an inert atmosphere of N<sub>2</sub> flow. The solution was quite volatile, so the bulk of the solution evaporated in half an hour at room temperature. Increasing the program temperature to 110 °C (ramp 50 °C/min) increased the evaporation rate, and the sample ended up being completely evaporated, as expected. (The program temperature was 110 °C, but because of the water boiling point, the sample reached a temperature of only 100 °C in the second/third step.)

Curve (b) is for an MEA sample (54 % aqueous solution). The whole analysis run was once again carried out in an inert atmosphere of N<sub>2</sub>, using the same temperature program as used for aqueous ammonia. It is apparent that MEA behaves fairly similar to ammonia water, but the weight loss is happening slower. This can be explained by considering the heavier molecular mass of MEA compared to ammonia.

Curve (c) is for an ARW sample (the light liquid phase which was used for all SNCR experiments). The first period of the experiment was run in an inert N<sub>2</sub> atmosphere. After reaching the maximum temperature of 850 °C air was supplied to the system. It can be seen that evaporation takes place much slower than for ammonia water and MEA solution, suggesting that the waste contains components that are less volatile than ammonia and MEA. Distinctive breakpoints in the mass loss curve are observed at a temperature of about 350 °C and also at about 500 °C. These are indications that the waste material contains different components having vastly different volatilities. A sharp mass loss occurred when the temperature was being increased from 110 to 850 °C. When the atmosphere was changed from N<sub>2</sub> to a mixture of N<sub>2</sub> and air at 850 °C, a slight drop in the mass loss curve was noted indicating that mostly low volatile organic compounds were remaining at this stage which would then burn up with oxygen to cause a further slight mass loss. Finally, the sample was left with a material residue of about 10 % of the original sample. This is presumably the inorganic, non-volatile part of ARW.

Curve (d) is the TGA analysis results for the sticky semi-solid part of the MEA reclaim bottom waste (ARW liquid phase exists at the top of this sticky semi-solid sludge). This phase was, as can be expected, even less volatile than liquid ARW so that the mass loss was only about 10 % after 30 minutes at room temperature and another 30 minutes of gradually increasing program temperature up to 110 °C. Even though the general appearance of the mass loss curve is quite similar to liquid ARW phase, significantly lower volatility of this semi-solid sludge is clearly apparent. Several break points are once again observed, confirming the complex composition of this substance. Provision of air at 850 °C gave a small mass increase possibly due to the oxidation of some compounds present in the sample. Note that even



after a long rest time at 850 °C, the sample still retains more than 50 % of its original mass, confirming the presence of large amounts of inorganic residues in this semi-solid fraction of reclaimer bottom waste.

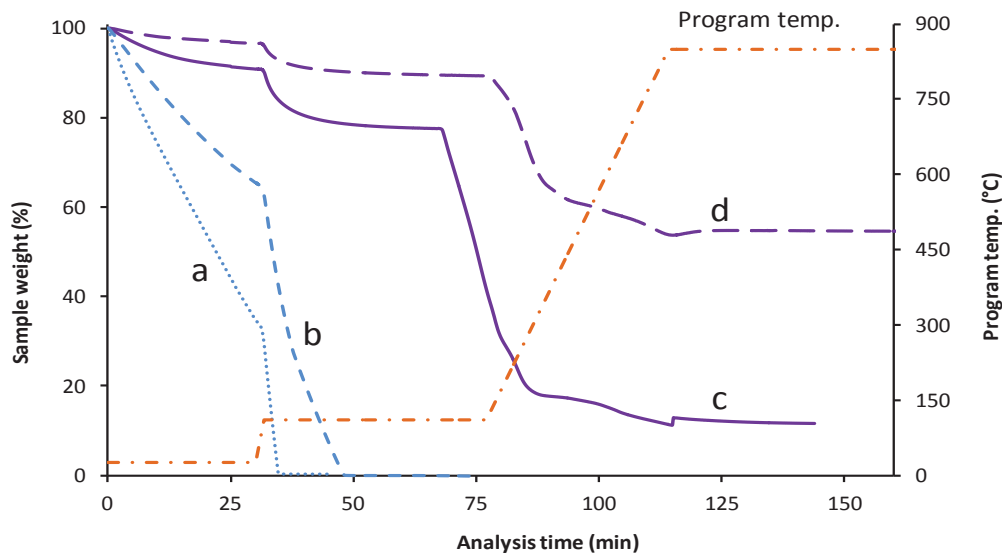


Fig. 6: Thermogravimetric analysis of aqueous ammonia (curve *a*), aqueous MEA (curve *b*), liquid ARW (curve *c*), and ARW sludge deposit (curve *d*).

#### 4. Conclusions

This study proposes an innovative mean for the disposal of hazardous amine wastes generated in CCS. The pilot scale experiments confirmed the effectiveness of ARW as an SNCR agent for NO<sub>x</sub> removal in combustion flue gas streams. Temperatures close to 950 °C and higher than unity stoichiometric ratios are recognized to be effective under laboratory conditions. The full scale experimental trials conducted in a cement plant have also confirmed the applicability of this methodology in industrial combustion facilities.

NO<sub>x</sub> reduction efficiencies of the three reagents tested in laboratory pilot scale at the TN/NO ratio of unity were found to be about 60, 35 and 28 % for NH<sub>3</sub>, MEA and ARW, respectively. According to the full scale tests, NH<sub>3</sub> and MEA gave about 63 % and 28 % NO<sub>x</sub> reduction, respectively. Based on these results, even according to a rather conservative estimate, ARW should at least give about 20 % NO<sub>x</sub> reduction efficiency in industrial scale applications. That is a significant SNCR potential for a waste by-product which needs safe disposal through combustion.

Thermogravimetric analysis revealed vaporization and composition characteristics of amine reclaimer wastes in comparison with aqueous ammonia and pure MEA. These details are important for designing injection systems and also deciding injection locations for industrial SNCR systems.

The use of process industry combustion devices, such as cement kilns, can lead to multiple benefits of resource recovery (material and energy) and pollution mitigation while providing a convenient disposal option for toxic CCS wastes. When adopted, based on further verification trials, the proposed

methodology can cover a total solution for the sustainable use of amines in CCS while aiding to mitigate an additional emission issue related to NO<sub>x</sub>.

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