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Recent Developments in the UNO MK 3 Process – A Low Cost, Environmentally Benign Precipitating Process for CO_2 Capture

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Abstract

Substantial progress in the development of the UNO MK 3 process and it's cost reduction capabilities has been made since previously reported [1]. In particular, the recent results of two pilot plant trials of the process continue to demonstrate and confirm the major features of the UNO MK 3 process:

- Low overall cost (up to 50% less than the best amines)
- Multi-impurity capture and production of valuable by-products (no degradation products)
- Low energy of regeneration (less than 2.5 GJ/T CO_2)
- Low volatility and environmental impact (SO_x and NO_x converted to fertilizer products)
- A good fit with existing global potassium markets (no additional potassium required)

These new results are groundbreaking in terms of advancing the process; with no major barriers evident for scaling up the process from the current pilot scale (TRL 5) to larger scale demonstration (TRL 6/7) over the next few years.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: CO_2 capture; Solvent; Post-combustion; Precipitating; Low-energy; Low-cost

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1. Introduction

The UNO MK 3 process is a patented precipitating potassium carbonate (K_2CO_3) process designed to capture 90 % of CO_2 emissions from large scale emission sources such as power stations (pre and post combustion) and other industrial sources. The UNO MK 3 process is suitable for retrofitting to existing emission sources as well as for new builds. The process is applicable to all CO_2 sources and due to its robust nature it is expected to be particularly relevant to high oxygen containing flue gases typical of Natural Gas Combined Cycle (NGCC) generators.

The UNO process was originally developed as a liquid based K_2CO_3 solvent with the original patent covering both pre and post combustion capture [2]. The UNO process was demonstrated in both pre and post combustion capture by pilot plant trials in 2010/11 as part of the Victorian Government's Energy Technology Innovation Strategy (ETIS) [3, 4]. The third phase of the UNO process development (termed UNO MK 3) is based on higher concentrations of the K_2CO_3 solvent solution, which incorporates precipitation of potassium bicarbonate ($KHCO_3$) allowing lower solvent circulation rates and hence lower energy usage and significantly smaller regeneration equipment [5].

In addition to the UNO MK 3 process, the CO2CRC has developed a concentric column design, which replaces the traditional steel absorption and regeneration columns. The new design could result in a significant reduction in cost and the footprint of the capture process [6].

Heat integration strategies, using a method developed by the CO2CRC, are also incorporated into all of the CO2CRC's capture processes, including UNO MK 3, to further reduce the energy requirements [7].

This paper shows how the UNO MK 3 process is delivering the major features by presenting the most recent progress in the development of the UNO MK 3 process in the areas of (i) fundamental research, (ii) pilot plant demonstration and (iii) large scale engineering design and economics.

2. Process Description

The UNO MK 3 process is effectively a typical solvent absorption process comprising CO_2 absorption and regeneration, with a hydrocyclone for rich solvent concentration and an impurities removal process (Figure 1). The reaction of CO_2 in the absorber column with the lean K_2CO_3 solvent to form $KHCO_3$ occurs through Reactions 1 and 2 to give the overall reaction shown as Reaction 3. Both reactions occur in the liquid phase within the absorption column and precipitation will occur once the bicarbonate concentration reaches the solubility limit. Reaction 1 is a fast reaction and can be considered at equilibrium. The main challenge associated with potassium carbonate based separation processes for use with post-combustion flue gases is the rate limiting reaction of CO_2 with hydroxide (Reaction 2). The rate limitations can be overcome by a combination of the introduction of rate promoters, the use of enhanced absorption systems, optimisation of the process conditions and increasing the size of the absorbers.

$H_2O + K_2CO_3 \leftrightarrow KHCO_3 + KOH$	Reaction 1
$CO_2 + KOH \leftrightarrow KHCO_3$	Reaction 2
$CO_2 + K_2CO_3 + H_2O \leftrightarrow 2KHCO_3$	Reaction 3

The concentration of solid $KHCO_3$ in the rich solvent leaving the absorber column can be increased through cooling and separation prior to solvent regeneration. In the regenerator/stripper column, heat is applied to the rich solvent, releasing CO_2 and creating a K_2CO_3 solvent lean in $KHCO_3$, which is recycled back to the absorber column.

The SO_x and NO_x compounds present in the flue gas react with K_2CO_3 to form potassium sulphate (K_2SO_4) and potassium nitrate (KNO_3). This multi-impurity capture capability leads to cost reduction due to the avoidance of flue

gas treating facilities. The valuable fertilizer by-products (K_2SO_4 and KNO_3) are removed from the UNO MK 3 process using a combination of proven separation techniques.

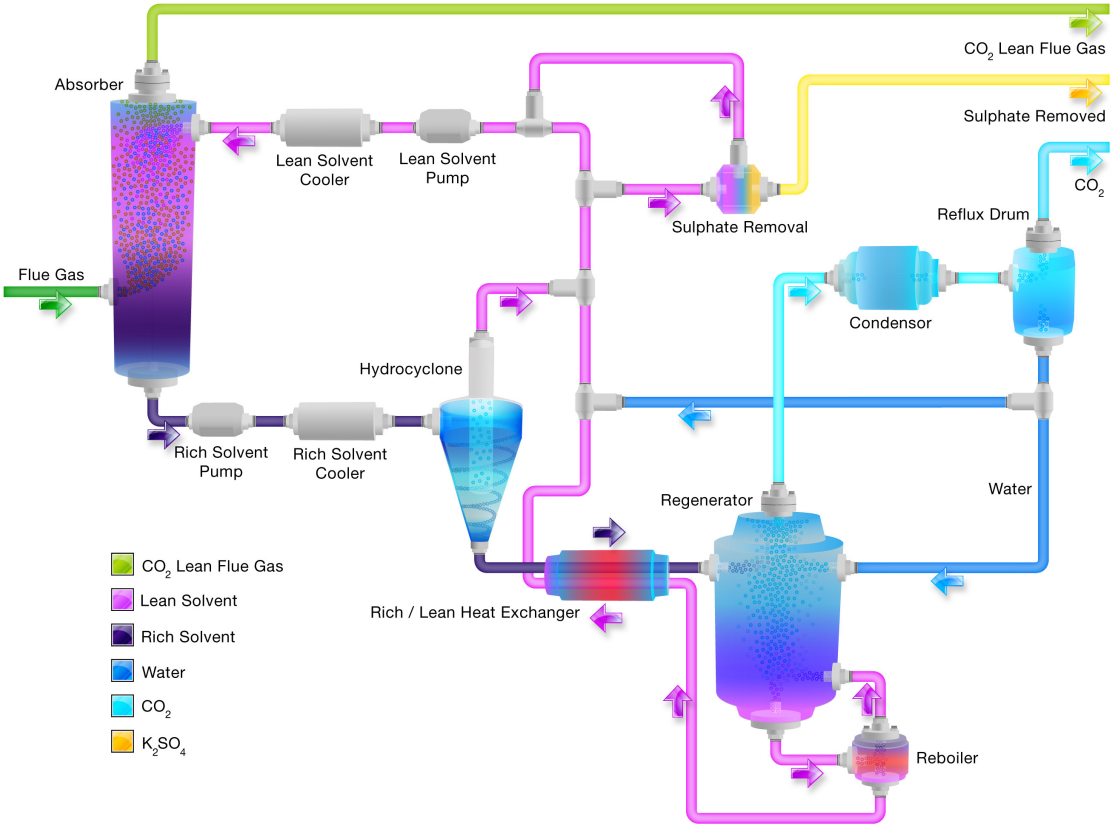

Figure 1: UNO MK 3 simplified process flow diagram

3. Fundamental Research

At the University of Melbourne (UoM), the CO2CRC has continued laboratory research into the potassium carbonate based solvent systems. Work has focused on a rate promoted solvent blend 'P1' which has been trialled in two pilot plants. However, in addition, other promoters with similar low volatility and stability as that used in P1 have been identified and promise to provide at least twice the reaction rate as the promoter in P1.

VLSE data, liquid phase speciation using ^{1}H and ^{13}C NMR spectroscopy and physical property data has been generated for P1. This data has been used to develop Aspen Plus® models using the Electrolyte Non-Random Two-Liquid activity coefficient model with the Redlich-Kwong equation of state (ENRTL-RK).

Laboratory scale experiments were conducted to identify the best combination of separation processes for recovering the sulphates and nitrates from the solvent for use in the fertiliser chain. Characterisation of the operating window for crystallisation of the impurities and for ion-exchange resins for impurity removal has been completed. Designs have been completed incorporating ion-exchange resins for Australian conditions, where due to low sulphur coal there is currently no requirement for flue gas desulphurisation. Promising improvements have also been made in identifying more selective resins, especially for the nitrates.

4. Pilot Plant Demonstration

The UNO MK 3 process has been operated on two pilot scale plants since 2012 [8]. The first, co-funded by the Australian National Low Emissions Coal Research and Development (ANLEC R&D) is located at the UoM. It used a synthetic flue gas mixture of 10 to 25 vol% of carbon dioxide in nitrogen, contacting the solvent in 3 x 0.8 m sections of 10 mm, 304SS pall rings in a 100 mm diameter borosilicate glass absorber. The second plant, co-funded by the Brown Coal Innovation Australia Ltd (BCIA), operated for over a 1000 hours at a Victorian brown coal-fired power station, processing a slipstream of 70 to 350 kg/hr of flue gas directly from the power station. The absorber is a 200 mm diameter column with 2 x 2.9 m sections of Sulzer M350X packing. Both pilot plants were designed to handle various levels of solids in the rich solvent streams and trialled a mixture of plate and spiral heat exchangers and slurry pumps. A hydrocyclone and impurities removal process was added to the power station pilot plant. The regenerators for both used random packing and the solvent reboiling was supplied via electric element heaters.

4.1. Absorption Performance

The two pilot plants operated with un-promoted potassium carbonate systems with and without precipitation and using the P1 promoted solvent blend with various levels of precipitation inside and outside of the absorber. The UoM pilot plant absorbed up to 32 % of the incoming CO_2 with the limited packing height available in the absorber column, whilst the power station pilot plant was able to demonstrate an absorption rate up to 50 % of the CO_2 in the flue gas with the increased, but still limited, packing height. Laboratory bench experiments promised up to 3 times more absorption due to the addition of the rate promoter. On the UoM pilot plant, P1 increased the CO_2 absorption up to 6 times, whilst at power station pilot plant the absorption rate was between 2.2 and 2.9 times the un-promoted solvent rates. The observed increases in reaction rate from the bench scale have largely been confirmed as the differences in the improvement can be explained by variation in the operating conditions of each trial in each of those plants.

The power station pilot plant was also operated with a pure amino acid solvent as a commercial solvent analogue and the CO_2 capture rate was between 40 and 50 % with higher capture rates occurring with increasing liquid to gas ratios. In addition two novel gas-liquid contacting systems were trialled with the UNO MK 3 solvent, both proved to have good solids handling capabilities that are required for a precipitating system.

4.2. Solvent Stability

The solvent on the power station pilot plant operated for over 44 days with the P1 solvent with no observable loss in absorption performance. The colour of the solvent in both pilot plants changed from clear to brown over the course of the trials with the change occurring more rapidly at the power station pilot plant. The foaming tendency of the solvent increased during the trials and the surface tension of the solvent also decreased. The chemical/physical change that resulted in the variation to colour, surface tension and foaming tendency has not been fully identified. However given that the changes were observed on the UoM plant which contained no impurities, the thermal cycling, in particular the high skin temperature of the electric reboiler elements is one area of focus. The addition of an antifoam to the solvent later in the trials helped in reducing the foaming tendency of the solvent.

Flooding of the absorber as a result of foaming and/or precipitation was an issue that occurred more on the power station pilot plant than the UoM plant. The power station pilot plant generally operated with a higher lean loading, had a higher absorption rate and therefore contained more solids than the rich solvent at the UoM. Also, it used structured packing rather than the random packing used on the pilot plant at the UoM.

4.3. Solids Characterisation

One unknown, when designing the pilot plants, was the crystal size that would be generated within the absorber and the rich solvent cooler. This limited the ability to design appropriate solids handling equipment, however broad

assumptions delivered workable designs. The two pilot plants yielded invaluable data on the particle size distribution of the bicarbonate as shown in Figure 2. The mean particle diameter obtained from the outlet of the absorber is between 150 and 250 μm depending on the operating conditions of the absorber and, as expected, the mean diameter is smaller when the rich solvent cooler is in operation which will lead to more rapid cooling of the solvent. The operation of the hydrocyclone was tested at the power station pilot plant and concentration of the bicarbonate in the underflow was demonstrated.

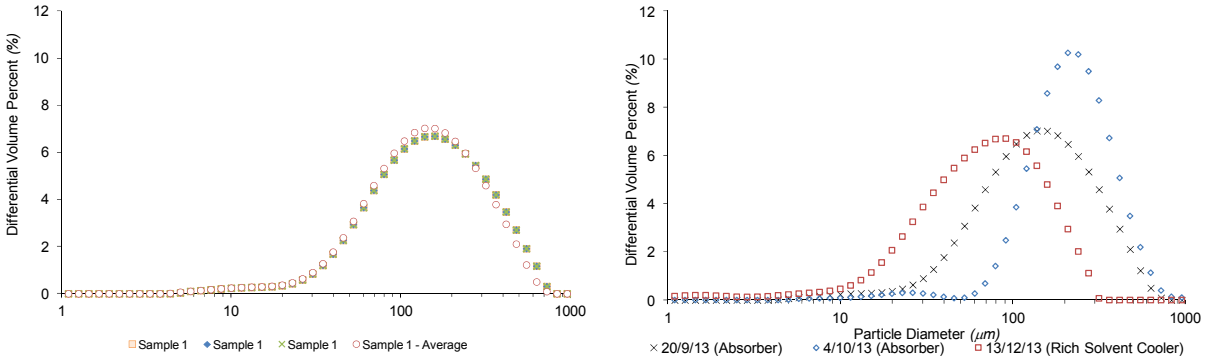

Figure 2: (A) Particle size distribution in the rich solvent leaving the absorber at the UoM pilot plant, and (B) Particle size distribution in the rich solvent leaving the absorber and exiting the rich solvent cooler at the power station pilot plant.

5. Large Scale Engineering Design and Economics

Large scale (300 to 550 MW) engineering designs and cost estimates of the UNO MK 3 process in post-combustion applications have been extended from previous brown coal retrofit work [1] (Figure 3) to include black coal [9] and natural gas [10] in new build and retrofit applications (Figure 4). The results continue to demonstrate the cost reduction trends of UNO MK 3 over other solvent technologies.

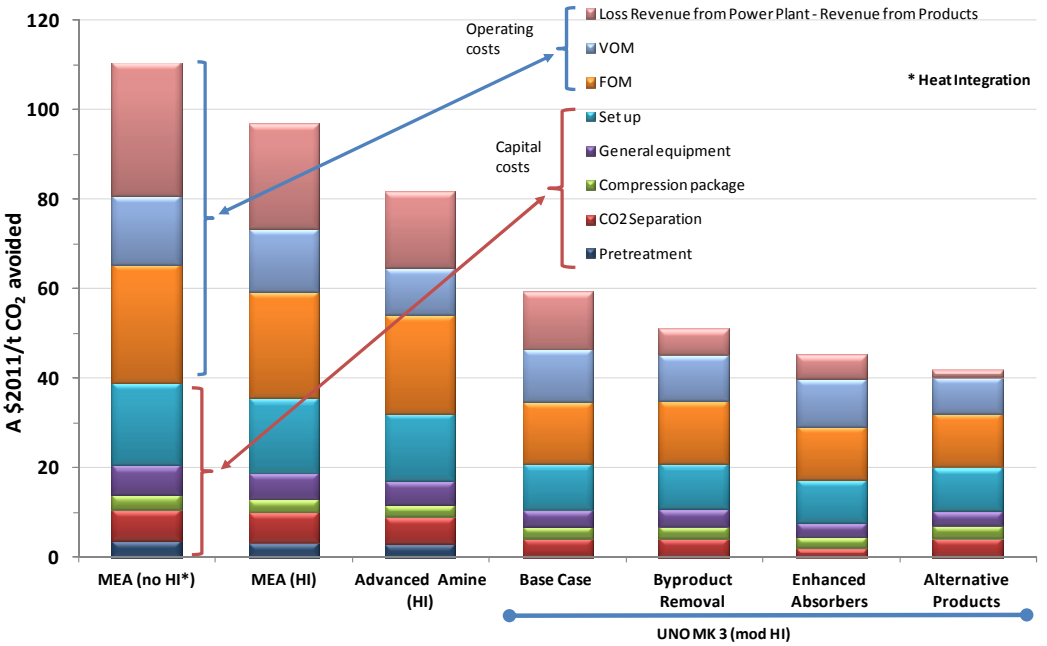

Figure 3: Cost of capture (A$2011/t CO_2 avoided) for the UNO MK 3 case studies based on retrofit to a 500 MW Victorian brown coal fired power station [1]

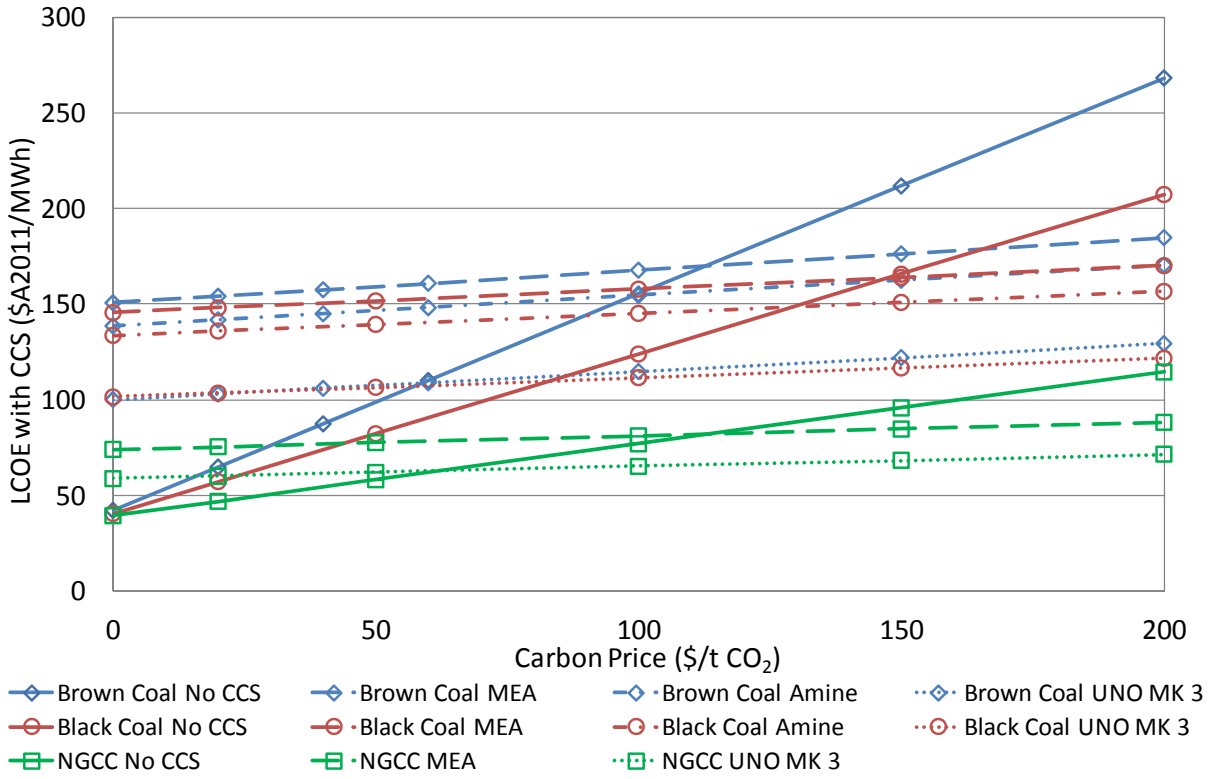

Figure 4: Levelised Cost of Electricity (LCOE) (Brown coal [1], Black coal [9], and NGCC [10]) with CCS using MEA, a state of the art amine and the UNO MK 3 process. Costs are for 90 % capture of CO_2 emissions retrofitted to an existing Australian power station using moderate heat integration, and enhanced absorbers.

5.1. Coal Fired Power Stations

Cost estimates for partial capture cases for brown [11] and black coal [9] fired power stations have also been developed where the CO_2 emissions are reduced to levels equivalent to open cycle and combined cycle gas turbines. As the energy penalty is lower than for full capture the resultant LCOE is lower, however as economies of scale in the capture plant are not fully realised, the cost of CO_2 avoided is marginally higher. These strategies have been used to inform potential CCS introduction pathways.

Furthermore estimates of the impact of converting the capture plant to operate with air cooling rather than cooling water from cooling towers have been made for Victorian conditions. The addition of any solvent capture process will increase the water requirements of the power station considerably, with UNO MK 3 the increase is approximately 60 %. However, with dry cooling applied, even only to the retrofitted capture plant, the power station total water requirement will actually reduce by more than 35 %. The large water savings are offset by a modest increase in the LCOE of between 1 and 2 $/MWh.

5.2. Natural Gas Turbines

At gas prices of 4 $/GJ the LCOE of NGCC power stations is the same (± 3 $/MWh) as the coal fired power stations but with a lower emissions intensity, therefore it is likely that the production of power from gas turbines will increase in the short term. However, when considering the addition of CO_2 capture to NGCC plants, the low content of CO_2 in the gas turbine exhaust results in larger absorption equipment for the same amount of CO_2 captured, when

compared to studies completed with coal fired power stations. Furthermore the high oxygen content in the exhaust gas can adversely affect the solvent stability for traditional amine based solvents, whereas the UNO MK 3 solvent is oxygen tolerant and therefore is particularly applicable for CO_2 capture from gas turbines.

Unlike amine solvents the UNO MK 3 solvent system is improved significantly with the addition of exhaust gas recycle (EGR) to increase the CO_2 content of the gas; the use of EGR with UNO MK 3 can reduce the total energy penalty of CO_2 capture by 15 %. The regeneration energy with 35 % EGR is estimated to be between 2.7 and 3.2 GJ/t of CO_2 depending on the assumptions made. The optimal operating point will depend on the particular capital versus operating cost profiles for each project. The reported energy requirements are similar to those for advanced amines such as 3.2 – 3.6 GJ/t for the Econamine FG Plus^{SM} [12] and potentially as low as 2.7 GJ/t for MHI KM-CDR^{TM} process using KS-1 or the Siemens PostCap^{TM} process [13].

Additionally converting an open cycle gas turbine to a combined cycle power station with CO_2 capture can lead to greater power output, lower emissions intensity and reduced LCOE by increasing the power station load factor and incorporating a purpose built steam generation cycle. The optimum steam cycle for a new build NGCC or repowered open cycle with CO_2 capture is different to a conventional NGCC. The heat recovery steam generator (HRSG) would be used for a portion of the solvent regeneration and a dual rather than triple pressure steam cycle is the preferred design.

6. Environmental Impacts

The environmental benefits of the UNO MK 3 process were confirmed by an independently audited life cycle assessment (LCA) [14] following the ISO 14040 and ISO 14044 framework. The LCA was modelled using SimaPro software using data libraries from ecoinvent and the Australasian LCA database. The goal of the LCA was to assess the environmental impacts of CO_2 separation using a traditional MEA solvent process compared with the UNO MK 3 process. The application of CO_2 separation used in this study was the removal of CO_2 from post combustion flue gases from a brown coal fired power station, typical of those in the Latrobe Valley, Victoria. The overall results of the LCA for the MEA, UNO MK 3 SS (stainless steel absorber) and UNO MK 3 C (concrete absorber) are shown in Figure 5. As seen from this figure, the UNO MK 3 process has a lower environmental impact for all indicators.

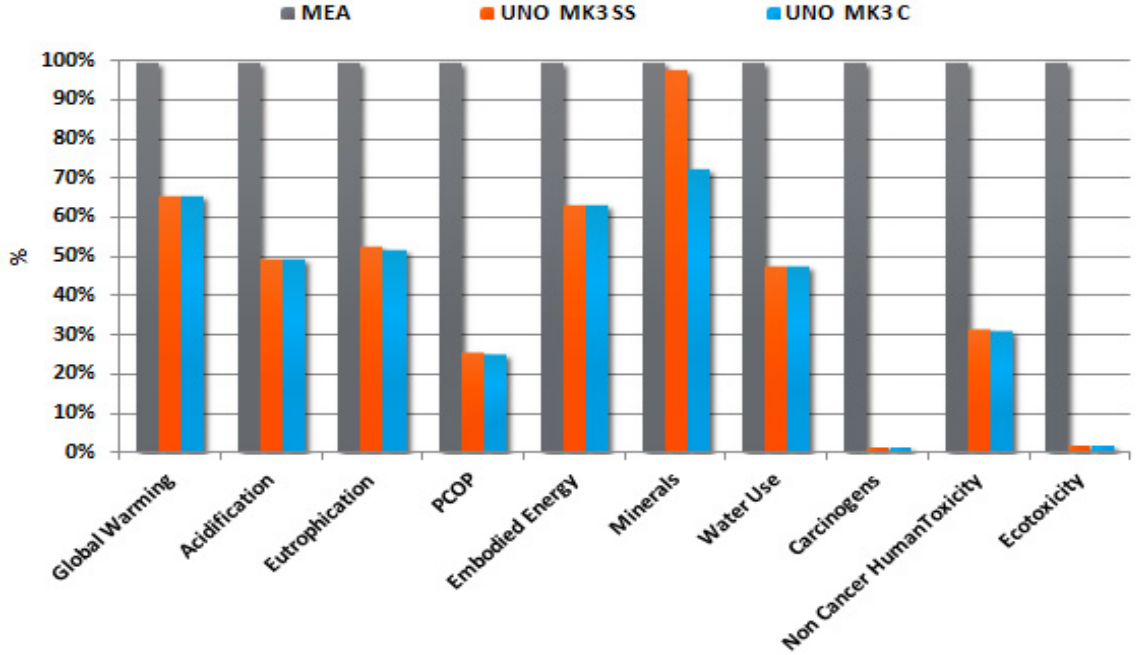

Figure 5: Comparison of Environmental Impact Results for MEA, UNO MK 3 SS and UNO MK 3 C Relative to MEA

7. Conclusions

The UNO MK 3 solvent system has continued to progress from laboratory scale to pilot scale without any major impediments to the continued development to demonstration scale in the next few years. The results from the pilot plants confirmed that the results from the bench scale can be confidently used in larger plants and the large amount of data obtained from the pilot plants will continue to provide an invaluable source of information for improving confidence in the models and the process.

The next phase of the UNO MK 3 development to commercialisation will be trials with a full height absorber to increase the capture rate to 90 %, the trialling of the targeted high rate promoter and continue to validate, improve and optimise the simulation models for the full UNO MK 3 process as it is scaled up through the larger TRL's.

Acknowledgements

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