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Abstract

Mineral carbonation (MC) using recyclable ammonium salts pH swing processes is considered among the most promising MC techniquees to store CO_2 permanently. However, the main key challenge to use this process at large scale is related to the energy consumption associated to the regeneration of the employed additives and in particular to the separation of the salt to be regenerated from the water solution.

This work investigates the feasibility of a liquid-liquid extraction technique to replace the energy intensive salts/water separation step. Also, the CO_2-balance of a 500 MW coal-fired based power plant with an integrated pH swing MC facility was investigated. Different operating conditions were investigated, including temperature, reaction time, pressure, solid to liquid ratio (S/L), reagents concentration and stirring rate. An ammonium sulphate/water separation higher than 90% was achieved at 25°C, 10 minutes, 1bar, 200g/l S/L ratio, 70% methanol and, 350rpm. The associated energy consumption was calculated, resulting in an energy saving of 35% in comparison to water evaporation.

The process resulted carbon negative when water evaporation was replaced by extraction

technique, with 33% of CO$_2$ sequestered by using a S/L ratios of 300 g/l.

Keywords: Ammonium salt • CO$_2$ fixation • CCS • mineral carbonation • separation

Nomenclature

AMD   -   Acid Mine Drainage

AS   -   Ammonium Sulphate

MC   -   Mineral carbonation

CCS   -   CO$_2$ Capture and Storage

EFC   -   Eutectic Freeze Crystallization

ESDM   -   Experimental Standard Deviation of the Mean

FTIR   -   Fourier Transform InfraRed spectroscopy

GHG   -   GreenHouse Gases

HHV   -   High Heating Value

KNeW   -   Potassium Nitrate Ex Waste

MVR   Mechanical Vapour Recompression

TGA   -   Thermo Gravimetric Analysis

RH   -   Relative Humidity

1. Introduction

The electricity and heat production sectors release around 30 billion of tonnes of CO$_2$ per

year [1, 2]. It is, therefore, essential to find a way to reduce CO$_2$ emissions. A series of

different technologies such as liquid solvents and solid sorbents have been proposed to

capture CO$_2$ for geological storage [3,4,5]. Mineral carbonation (MC) is also becoming

attractive to immobilize CO$_2$ permanently as carbonate rocks. Silicate rocks including

serpentine, olivine and a wide range of inorganic wastes (e.g. steel slags, cement wastes) can

be used in this process. The amount of feedstock minerals would be largely sufficient to store all the CO_2 produced by fossil fuel reserves [2]. In particular, magnesium silicate deposits such as serpentine are known to be available worldwide [6]. MC involves the reaction of CO_2 with metal oxides to form carbonates. Since the carbonates obtained are stable thermodynamically and only a minimal fraction of CO_2 stored could be releases, although on geological timeframes. Mineralization has the advantage to be an overall exothermic reaction and also, it can take place close to CO_2 emitters, where inorganic wastes (e.g. steel slag in a steel work) can be used as in-situ carbonation feedstock. Otherwise, mineralization can be advantageous if mineral deposits are closely located [7].

However, at the current stage of development, MC drawbacks such as its slow kinetics, low efficiency and large energy consumption are limiting its wide deployment. MC can be classified in direct and in-direct processes. In the direct processes, where the dissolution of mineral is the rate-limiting step, Ca/Mg rich solids are carbonated in a single process step. Multiple steps are instead used in the in-direct approach, where the reactive components (Mg^{2+}, Ca^{2+}) are extracted from minerals, using acids or other solvents, followed by the reaction of the extracted components with CO_2 in either the gaseous or aqueous phase [8].

As natural carbonation of silicate rocks is very slow because of low exposed surface and diffusion limitations, ex-situ aqueous in-direct carbonation reactions are being developed to accelerate the process. Indeed, the addition of a mineral dissolution step with the employment of chemicals is able to shorten the reaction times and enhance the reaction extent [8,9]. MC by pH swing using ammonium salts is a promising multistep process, which is extensively described previously [7,10-12]. The process consists of 5 steps: (1) CO_2 capture using ammonia ($NH_3 + CO_2 \leftrightarrow NH_4HCO_3$); (2) the leaching of the Mg/Ca cations from the mineral resource using acid ammonium bisulphate solution (NH_4HSO_4 + Mg/Ca rich silicate $\leftrightarrow$ $MgSO_4 + SiO_2$ + unreacted silicate + $(NH_4)_2SO_4$); (3) pH-regulation (to swing the pH from

pH 1-2 caused by unreacted NH_4HSO_4, to pH 8-9, at which carbonation reaction occurs); (4) the mineral carbonation of CO_2 (bonded as NH_4HCO_3) ($MgSO_4 + NH_4HCO_3 + H_2O \leftrightarrow MgCO_3 \cdot 3H_2O + (NH_4)_2SO_4 + CO_2$); (5) the regeneration of the used chemicals (separation of $(NH_4)_2SO_4$ from the water solution and its decomposition to NH_3 and NH_4HSO_4, which are the re-sued in steps 1 to 3). Overall, this method has the advantage to avoid the compression and the transportation of CO_2, since only an absorption step is used to separate CO_2 from the flue gas and also can be used to co-capture CO_2, SO_2 and NO_x [7, 13]. Aqueous ammonia CO_2 capture has become very attractive compared to the MEA based system, due to its high removal efficiency, low cost, absorption capacity, lower equipment corrosion, low heat energy requirement and low degradation rate [14-15].

Wang and Maroto-Valer have also optimized the MC technique to reduce the water used by increasing the serpentine to water ratio [11]. In order to sequester 1t CO_2, 11.34 t of NH_4HSO_4 were used to dissolve 4.93 t of serpentine at 300 g/l solid to liquid (S/L) ratio, obtaining a dissolution efficiency of 71 % and a carbonation efficiency of 66%. [11] After the carbonation, a water evaporation and a thermal decomposition steps are required to convert aqueous $(NH_4)_2SO_4$ into NH_3 and NH_4HSO_4 [16]. Therefore, to regenerate $(NH_4)_2SO_4$ (after carbonation) a water evaporation step is required involving a large energy penalty. To overcome this, the feasibility of a methanol based liquid-liquid extraction technique modified from existing processes, where sodium ions and sulphates are removed from an acid mine drainage (AMD) [17] and a solution of ammonium sulphate is obtained after the generation of acrylonitrile [18], has been investigated, which successfully removes all the dissolved salts from AMD and converts them into beneficial raw materials for agriculture and industry (gypsum, ammonium nitrate and ammonium sulphate). The latter is extracted from the water solution by adding 30 vol% of methanol in the KNeW (Potassium Nitrate ex Waste) process allowing the crystallization of the ammonium sulphate particles. Bewsey (2014) stated that

the combination of the Ion Exchange and KNeW processes would allow a water recovery superior at 90% and an energy usage very low compared to other techniques. [17].

As shown in Figure 1, in the AMD process, $(NH_4)_2SO_4$ is extracted for the solution by adding methanol (30 vol%) allowing the crystallization of more than 90% $(NH_4)_2SO_4$ with energy usage lower than other techniques [17]. The crystallised ammonium sulphate is then centrifuged, cleaned up and dried. The methanol/water solution is then sent to a distillation column, where the methanol is separated and recirculated in the process. The above process has been modified and applied to the MC by pH swing to evaluate if the large energy penalty related to the separation of the $(NH_4)_2SO_4$ remaining after the MC carbonation step (step 4) by evaporative techniques could be decreased.

Figure 1: Extraction of Ammonium Sulphate [modified from 17]. 1-methanol storage; 2-stirred tank; 3-centrifuge, 4-heat exchanger; 5-pump; 6-distillation column.

2. Material and methods

2.1.1. Material and Apparatus

Ammonium sulphate, methanol, acetone and ethanol were obtained from Sigma Aldrich. A 250mL three necks flask and an oil bath were used to test the liquid-liquid extraction technique at ambient pressure. The bath was filled with silicone oil instead of water to avoid its evaporation during the experiments. A hot stirring plate was used to manage the temperature controller and the magnetic stirrer speed. An open circuit water heat exchanger was connected to the three necks flask to avoid losing liquid from the flask. Finally, a vacuum filter was used to separate the crystals and the salts.

A Parr high pressure reactor was used to run the extraction process at 1 bar. A RTC stirrer motor and a chiller were required for this apparatus. Finally, nitrogen was used to pressurize the vessel to 5 bars.

2.1.2. Experimental method

The experimental conditions were selected modifying those suggested in a recent patent filed for clean up a solution of $(NH_4)_2SO_4$ obtained after the generation of acrylonitrile [18]. According to this patent, the amount of methanol can vary between 1 and 30 times the amount by weight of methanol, relative to the water content of the waste stream; the temperature range can change from 10°C to 60°C; the time of mixing should be at the minimum 0.01 min and at the maximum 50 min as well as the separation technique (filtration, centrifugation or decantation) [18]. Synthetic mother liquors resembling the real dissolution liquors (obtained dissolving 200, 150 and, 100 g serpentine / l solution) were prepared and used for all of the experiments. For that, 800 mL of water were poured in a graduated flask in which the required amount of ammonium sulphate was added (Appendix A). Then, 50 mL of the mother solution and a stirrer bar were placed in the three necks flask. Then, the stirrer motor was turned on and the temperature set to 20°C or 40°C. When the solution reached the required temperature, the required amount of methanol was added to the ammonium sulphate solution. After the required time of reaction (5, 10 or 30 minutes), the temperature and the stirrer were turned off. Finally, the solution containing water, ammonium sulphate and methanol was poured in a vacuum filter and the filter and filtrate were then dried at 60°C for 24 hours.

Acetone tests and high pressure tests were carried out using a 200 ml hermetic stainless steel vessel (Parr) due to its high volatility following the same methanol procedure. 200 mL of the mother solution and the required amount of acetone were transferred in the vessel. The reactor was pressurized with 5 bars of nitrogen where required. At the end of all the

experiment, the solution was vacuum filtered and the filtrate dried in hoven for 24 hours at 60°C.

Different parameters including temperature (25 and 40 °C), stirrer speed (350 and 850rpm), time of reaction (2, 10 and 30 mins), pressure (1bar and 5bars) as well as solid to liquid ratio (200, 150 and 100 g/l S/L ratio), were investigated to establish the feasibility of the liquid-liquid extraction technique when applied to the MC process. Triplicates of tests were run (Appendix B) to obtain the accuracy. The relative uncertainty calculated was 1.53 %. The tests were numbered for convenience (as shown in Tables 1 to 4).

A Thermogravimetric Analyzer (TGA) Q500 was used to determine the ammonium sulphate recovered at the end of the extraction process, after the filtration of test 6 (200 g/L, 70% methanol, 350 rpm, 25°C, 10 min) to evaluate the loss of water and, the decomposition of the ammonium sulphate. The temperature program from 10 to 800°C at 50°C/min under a nitrogen atmosphere was used to evaluate the recovery of ammonium sulphate.

XRD analysis were carried out using a Bruker Nonius X8-Apex2 CCD diffractometer equipped with an Oxford Cryosystems Cryostream, typically operating at 100 K, was used for the XRD analysis.

3. Results and Discussion

3.1.1. Extraction process results

For each S/L ratio, a first experiment called 'test 0' was run to determine the minimum amount of methanol required for the solution to react. Then, the amount of methanol was increased in order to improve the ammonium sulphate recovery efficiency. Tables 1, 2 and 3 report the extraction process results for 200, 150 and 100g/l S/L ratio, respectively. The yellow colour highlights the optimum parameters (defined as highest % AS recovered) evaluated while the red colour shows the efficiency (in terms of percentage of ammonium

sulphate recovered at the end of the process) obtained experimentally using these optimum parameters.

These optimum parameters were determined by comparing the efficiency of two tests, with only one variable differing. For example, comparing tests 1 and 2, the percentage of recovered ammonium sulphate at 40°C was 67.11% (test 1, Table 1) while it was 70.17% at 25°C (test 2, Table 1). Since the method was more effective at 25°C, it was then considered as the optimal temperature parameter. The other optimum conditions were determined in the same manner.

Tests 1 and 2 clearly indicate that there is not gain in terms of AS recovered, when the temperature was increased from 25 to 40°C or the stirring rate increased from 350 to 850 rpm (tests 2 and 3). Similarly, the AS recovered slightly decreased when the pressure was rose from 1 to 5 bar (tests 2 and 5). The amount of solvent used in the extraction process resulted the most important parameter in terms of recovered AS. The optimal percentage of methanol used differed depending on the S/L ratio (200 g/l ≡ 70% of methanol, 150 g/l ≡ 80% of methanol and, 100 g/l ≡ 115% of methanol). It is important to note that the amount of methanol required to run the extraction process with a suitable efficiency, is the key parameter (in terms of energy efficiency), since the methanol will need to be recovered from the water after the separation of the $(NH_4)_2SO_4$. Therefore, the tests in presence of 100 g/l and 150 g/l were run to evaluate the optimal amount of methanol to be used. Overall, the solution having a ratio of 200 g/l was considered to be the most advantageous, since it used the lowest amount of methanol (70%). The optimum conditions within the range of value investigated to run the extraction process were obtained at S/L ratio of 200 g/l, using 70% of methanol, 25°C, 350 rpm for 2 minutes. It should be noted that the reaction time had little influence on the process efficiency, but the shorter the better to decrease the energy consumption. The

presence of a more concentrated solution (200 g/l) involves the use of less methanol in the

extraction process as can be seen in the tables below.

Table 1: Extraction process results for the 200 g/l S/L ratio solution.

	Test 0	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Amount of methanol (%)	25%	50%	50%	50%	50%	50%	70%
Amount of methanol (ml)	12.50	25.00	25.00	25.00	25.00	25.00	35.00
Temperature (°C)	40	40	25	25	25	25	25
Time (min)	10	10	10	10	2	10	10
Pressure (bar)	1	1	1	1	1	5	1
Stirrer speed (rpm)	350	350	350	850	350	350	350
	Result 0	Result 1	Result 2	Result 3	Result 4	Result 5	Result 6
% of AS recovered	7.28	67.11	70.17	66.89	70.20	65.44	90.58

Table 2: Extraction process results for the 150 g/l S/L ratio solution.

	Test 0	Test 6	Test 7	Test 8	Test 9
Amount of methanol (%)	40%	50%	60%	80%	90%

Amount of methanol (ml)	20.00	25.00	30.00	40.00	45.00
Temperature (°C)	25	25	25	25	25
Time (min)	10	10	10	10	10
Stirrer speed (rpm)	350	350	350	350	350
	Result 0	**Result 6**	**Result 7**	**Result 8**	**Result 9**
AS recovered (%)	2.35	34.09	45.70	84.80	95.89

Table 3: Extraction process results for the 100 g/l S/L ratio solution.

	Test 0	**Test 10**	**Test 11**	**Test 12**	**Test 13**
Amount of methanol (%)	58%	80%	90%	100%	115%
Amount of methanol (ml)	29.00	40.00	45.00	50.00	57.50
Temperature (°C)	25	25	25	25	25
Time (min)	10	10	10	10	10
Stirrer speed (rpm)	350	350	350	350	350
	Result 0	**Result 10**	**Result 11**	**Result 12**	**Result 13**
AS recovered (%)	10.64	57.43	67.69	74.60	93.15

As seen in Table 4, an additional set of tests using the 200 g/l solution was carried out at the optimum conditions within the values evaluated (25°C, 350 rpm, 1 bar, 70% of solvent, 10 min), to evaluate the possibility of using alternative solvents as acetone and ethanol.

Ethanol was selected for being no toxic and acetone because of its lower boiling point (56°C). However, the use of ethanol and acetone did not achieved good AS recovery efficiency under the studied conditions. The reason could be that the selected conditions are not ideal for ethanol and acetone. Also, the set-up used was not ideal for using acetone due to its high volatility.

Table 4: Extraction process results for the 200 g/l S/L ratio with other solvents.

	Test 6	Test 7	Test 8
Solvent	Methanol	Acetone	Ethanol
% of AS recovered	90.58	0.00	48.14

3.1.2. FTIR, XRD and TGA analyses

Figure 2 shows the FTIR of the extraction liquid sample of the solution recovered after the filtration of test 6 (200g/L, 70% CH_3OH, 350rpm, 25°C, 10min) (●) together to H_2O (♦), $(NH_4)_2SO_4$ (■) and CH_3OH (▲) standards . As it can be seen, the liquid sample contains only H_2O and CH_3OH. Therefore, after filtration the solution does not contain any $(NH_4)_2SO_4$, which indicates complete separation of the salt. This may also indicate that the AS recovery efficiencies shown in Tables 1-3 are probably higher than those reported in the tables and that a recovery efficiency close to 100 % is actually achieved, but some AS is lost in the process operations (e.g. remains in the filter paper). The composition of the solid sample recovered at the end of the extraction process (Test 6) was evaluated by FTIR and was represented by the pink curve in Figure 2. Again, the solid product is compared to ammonium sulphate, methanol and water standards, to evaluate its purity. The peaks of the solid product

correspond very well to those of the ammonium sulphate standard. Also, it is clear the presence of peaks (1650 cm^{-1} and 3400 cm^{-1}) related to water in the dry sample.

Figure 2: FTIR profile of (a) the liquid ammonium sulphate solution obtained after the filtration of the test 6; (b) the solid ammonium sulphate sample obtained after extraction process of test 6. Sample after extraction (test 6: 200g/L, 70% CH_3OH, 350rpm, 25°C, 10min) (●) together to H_2O (♦), $(NH_4)_2SO_4$ (■) and CH_3OH (▲) standards.

TGA analyses were used to confirm the composition of the separated salt. Figure 3 (test 6) shows a first peak at 100°C with about 9 wt % of the weight lost, which is due to loss of water whereas the second peak located between 280 and 460°C (about 91 wt %) corresponds to the decomposition of the ammonium sulphate. The comparison of the thermo-gravimetric profile of the standard ammonium sulphate with that of the solid salt produced in the test 6 indicated that the mineral phase of the salt was likely $(NH_4)_2SO_4$.

XRD analysis of materials remaning after tests 6 and 8 were carried out to establish if the separated ammonium sulphate was in anydrous of hydrated mineral phase, since it was not possible to define this by the TG plots.

Figure 4 shows the XRD patterns of the materials recovered in tests 6 and 8. The diffraction patterns of both materials corresponds very well with those of standard $(NH_4)_2SO_4$ indicating that the liquid-liquid extration precipitates out anydrous ammonium sulphate and the water present (see Figure 3) is absorbed moisture.

Figure 3: TGA profile of (a) the ammonium sulphate recovered after the test 6 of the extraction process; (b) Standard Ammonium sulphate.

Figure 4: XRD patterns of the material recovered after tests 6 and 8 and correspondence with $(NH_4)_2SO_4$ standard (diamond).

3.1.3. Energy consumption

The energy consumed by the water evaporation step required prior to the $(NH_4)_2SO_4$ regeneration was calculated, in order to be compared to the energy required for the alternative extraction process proposed here. HSC Chemistry 5.1 software was used to calculate the amount of energy consumed by each step of the MC process considering the mass balance reported previously [11]. Table 5 shows the mass balance and heat balance of the CO_2 capture step. The reaction is exothermic with a total heat of 527.9 Mcal (or 612.83 kWh) released during the CO_2 capture. Appendix C shows the energy balance calculations for each step of the process. The calculations are made for a 200, 150 and, 100 g/l S/L ratio solution. Knowing the amount of serpentine (1049.424 kg of $Mg_3Si_2O_5(OH)_4$) required to sequester 1t of CO_2, the amount of water used can be calculated.

Table 6 sums up the final energy balance for sequestering 1t of CO_2 by the MC ammonium salts technique. Three different S/L ratios were investigated. As it can be seen in this table, the energy used for the water evaporation step is different according to the S/L ratio. Therefore, the higher is the S/L ratio, the lower is the amount of water to evaporate and energy can then be saved. Table 6 also shows that the water evaporation step requires 3411.7 kWh for a 200g/l S/L ratio which is energy intensive. To make the pH swing MC process feasible at large scale it is necessary to improve this regeneration step.

Table 5: Energy balance for the CO_2 capture.

	Temp °C	Amount kmol	Amount kg	Amount Nm³	Latent H (Mcal)	Total H (Mcal)
IN						
NH₃(g)	10	22.722	386.968	518.03	-2.9	-252.39
CO₂(g)	10	22.722	1000	517.866	-3	-2140.02
H₂O	10	22.722	409.345	0.446	-6.12	-1558.39
OUT						
NH₄HCO₃(ia)	10	22.722	1796.313	0	0	-4478.09

BALANCE	Amount kmol	Amount kg	Amount Nm³	Latent H (Mcal)	Total H (Mcal)	Total H (kWh)
IN1	68.167	1796.314	1036.343	-12.02	-3950.8	
OUT1	22.722	1796.313	0	0	-4478.09	
BALANCE	-45.444	0	-1036.343	12.02	-527.29	-612.83

The energy calculations made for the CO_2 capture, mineral dissolution, pH adjustment, removal of impurities, carbonation, regeneration of additives and, ammonia adsorption were considered equal for the two techniques: thermal evaporation and liquid liquid extraction. Also, the energy required for the extraction of ammonium sulphate was very low (stirrer speed and vacuum filter) so it was disregarded. Nevertheless, the evaporation of methanol was taken into account (methanol's boiling point which is at 64.8°C) and the energy calculation can be found in Appendix D [19].

Table 6: Final balance for sequestering 1t of CO_2 by MC technique using evaporation.

Heat released	kWh
CO2 Capture	-612.83
Mineral dissolution	-148.57
pH adjustment	-292.96
Removal of impurities	-36.17
Carbonation	-20.71
TOT HEAT RELEASED	-1111,25
Heat required	kWh
Water evaporation 200g/l	3411.68
Water evaporation 150g/l	4548.90
Water evaporation 100g/l	6823.35
Regeneration of additives	1004.49
Ammonia adsorption	48.79
TOT HEAT REQUIRED 200g/l	4464.96
TOT HEAT REQUIRED 150g/l	5602.19
TOT HEAT REQUIRED 100g/l	7876.64

For 5247.12 kg of water, 2702.267 kg of $(NH_4)_2SO_4$ needed to be added which represents a total amount of 7949.42 kg of ammonium solution. Thus the total amount of methanol (70% of the solution by volume) was equal to 5564.57 kg. To evaporate this methanol, the total energy required was the sum of the energy to heat the methanol from 25°C to 64.8°C and the methanol latent heat. Table 7 sums up the final energy balance for sequestering 1t of CO_2 by MC technique including the methanol extraction step.

Table 7: Final balance for sequestering 1t of CO_2 by MC technique using liquid-liquid extraction.

Capture of 1t of CO_2	
Heat released	kWh
CO2 Capture	-612.83
Mineral dissolution	-148.57
pH adjustment	-292.96
Removal of impurities	-36.17
Carbonation	-20.71
TOT heat released	-1111.25
Heat required	kWh
water extraction 200g/l	1854.70
water extraction 150g/l	2587.11
water extraction 100g/l	5060.35
Regeneration of additives	1004.49
Ammonia absorption	48.79
TOT heat required 200g/l	2907.98
TOT heat required 150g/l	3640.39
TOT heat required 100g/l	6113.63

Figure 5 shows the energy consumption (kWh) according to the technique and the S/L ratio used. For each ratio the extraction process allows to save energy, but the energy consumption is lower at 200 and 150 g/l S/L ratio. Liquid-Liquid extraction process using methanol is then very promising because 35% of energy can be saved compared to the water

evaporation step with a similar efficiency in terms of ammonium sulphate recovery (90-95%).

Figure 5: Energy use for the ammonium sulphate-water separation.

3.2 MC scale-up

In the previous sections, it has been shown that the liquid-liquid extraction process (90% efficiency and, 35% energy saved compared to water evaporation step) can reduce the energy consumption compared to evaporative techniques for the separation of the AS from the carbonation solution. This section investigates the feasibility of a 500 MW coal-fired based power plant with an integrated pH swing mineralization facility. A comparison is conducted between water evaporation step and extraction technique at industrial scale. Coal-fired power plants represent ~40% of the worldwide global electricity production. A 500MW coal-fired power plant emits about 3.3 million tonnes of CO_2 annually or 377 tCO_2/h (assuming 365 working days per year). However, previous studies show that pH swing MC process would work better for plant emitting < 0.5 Mt CO_2/y, which is why this assessment is focussed on storing 55 tCO_2/h.

3.2.1. Heat released and required

CO_2 emissions balance was evaluated to investigate the feasibility of a mineralization facility for a coal-fired power plant to sequester 55 tCO_2/h. The mass and the energy balances performed previously to store 1t of CO_2 (Table 3) was used in this assessment. Table 8 compares the heat required or release in the overall process when water evaporation or methanol liquid-liquid extraction are used to recover ammonium sulphate. As can be seen in the table, the use of the methanol-based water extraction requires 102,000 kWh/55tCO_2, while the water evaporation method consumes 187,642 kWh/55tCO_2, resulting in a heat requirement reduction of 45%.

Table 8: Heat balance to sequester 55t of CO_2 using the different water/salts separation methods.

Water evaporation			Methanol extraction		
Heat released	kWh		Heat released	kWh	
CO_2 Capture	-33705.65		CO_2 Capture	-33705.65	
Mineral dissolution	-8171.53		Mineral dissolution	-8171.53	
pH adjustment	-16112.78		pH adjustment	-16112.78	
Removal of impurities	-1989.31		Removal of impurities	-1989.31	
Carbonation	-1139.22		Carbonation	-1139.22	
TOT heat released	-61118.49		TOT heat released	-61118.49	
Heat required	kWh		Heat required	kWh	
Water evaporation 200g/l	187642.26		water extraction 200g/l	102008.46	
Regeneration of additives	55247.21		Regeneration of additives	55247.21	
Ammonia absorption	2683.33		Ammonia absorption	2683.33	
TOT heat required 200g/l	245572.80		TOT heat required 200g/l	159939.00	

3.2.2. Energy requirement and CO_2 emissions

To evaporate the water from ammonium sulphate solution and to regenerate ammonium bisulphate salts from ammonium sulphate crystals, a Mechanical Vapour Recompression (MVR) evaporator and a melting vessel were considered. Assuming that the heat required for these two stages was provided by natural gas, the relative CO_2-emissions were calculated. CO_2 emission from generating heat from natural gas was considered to be 0.20 kgCO_2/kWh [20]. CO_2 emissions could be minimised assuming the use of renewable energy instead of

natural gas. Based on the emissions factors from the 2012 Guidelines to DEFRA/ DECC's GHG Conversion Factors for Company Reporting [20], a 'carbon neutral' emissions factor for biodiesel of 0.12 kgCO_2e/kWh (net CO_2e emissions assuming carbon sequestration) can be considered for the calculations.

To evaporate the methanol from ammonium sulphate solution an evaporator also was required. The heat required was about 157 MWh (566GJ). Different equipment that releases CO_2, such as conveyors belt, axial pumps, agitators and compressor were considered for the MC process. The electric consumption required for these devices was then calculated and was included in the CO_2-balance calculations. The energy requirement calculations are shown in Appendix E. Table 9 reports the electric consumption of mineralization facility using water evaporation step or extraction process. The total electric consumption of a mineralization facility was then about 10 MW/h. based on natural gas fuel, the MC CO_2-emissions from equipment using water evaporation step would be 1.93 tCO_2/h and 2.19 tCO_2/h using the extraction process [21].

Table 9: Electric consumption of mineralization facility.

Equipment	Water evaporation	Extraction process
Conveyor	44.52 kW	44.52 kW
Pumps	5.7 MW	5.7 MW
Agitators	3.9 MW	5.2 MW
TOTAL	9.64 MW	10.94 MW

3.3. CO_2 balance

Tables 10 shows the CO_2 experimental capacity based on CO_2 fixation obtained in previous work at different S/L ratios (100, 200 and 300 g/l) [7,11]. According to Wang and Maroto-Valer, the CO_2 fixation efficiency are 67%, 44% and 47% respectively for a 100 g/l,

200g/l and 300 g/l S/L ratio, respectively, as reported in Table 10 [7,11]. The decrease of dissolution efficiencies at high S/L ratio was associated to precipitated magnesium sulphate (MgSO$_4$) [11]. Since the solubility of MgSO$_4$ is 52.9 g/100 g water at 90°C, MgSO$_4$ would precipitate during the dissolution stage using NH$_4$HSO$_4$ when the S/L ratio is above 280 g/l if 100% dissolution efficiency is achieved [11]. It was also found that the dissolution efficiencies increase slightly when the S/L ratio increases from 200 g/l to 300 g/l. This may be due to inter-collisions at high S/L ratio, that may break down particles or remove the product layer, and thus increasing the diffusion of NH$_4$HSO$_4$ into the pore space of the mineral particles [11,22]. Therefore, the mineralisation facility design to store 55 tCO$_2$/hr could then in practice sequester between 26 tCO$_2$ and 37 tCO$_2$ depending on the S/L ratio used as shown in Table 10.

Table 10: CO$_2$ experimental capacity according to S/L ratio [9,11] .

Ratio (g/l S/L)	Dissolution efficiency (%)	Carbonation efficiency (%)	Fixation efficiency (%)	Experimental CO$_2$ capacity (tCO$_2$/h)
300 [11]	71.3	65	47	25.85
200 [11]	65.6	67	44	24.2
100 [7]	70.7	95.9	67.8	37.29

Table 11 shows the CO$_2$ emissions related to the regeneration of additives according to technique employed, fuel used (natural gas and bio-diesel) and S/L ratio. The extrapolation considered to measure the energy balance of a 300g/l S/L ratio in reported in Appendix F. The heat requirement for both techniques increases inversely proportionally to the S/L ratio due to large volumes of water to separate. Heat requirement is higher for the evaporative

technique using 100 and 200 g/l, while become comparable using 300 g/l. This is related to the increased amount of methanol that is required using 300 g/l solution and in the same time, to the similar experimental CO_2 capture capacity at 200 and 300 g/l [11]. Also, CO_2 emissions change depending on the fuel used in the assessment, with bio-diesel emitting considerably less amount of CO_2 compared to natural gas. Therefore, the use of bio-fuels would increase the sequestration capacity of the system, independently to the technology employed.

Considering natural gas as source of energy, the total CO_2 emitted using the thermal water evaporation process results larger than the capture capacity at 100 and 200 g/l solid/liquid ratios (as can be seen comparing the data in Table 10). The CO_2 sequestration technique (using natural gas as source of heat) becomes carbon negative at S/L ratios approaching 300 g/l, where about 22% of the starting 55 tCO_2 are sequestered. The carbon balance is more favourable when the extraction technique is employed as shown in Table 12.

MC using the extraction process performed better in terms of energy consumption than using evaporative technique, but was still carbon positive at 100 g/l S/L ratio (+7% CO_2 emissions). Increasing the S/L ratio to 200 and 300 g/l decreased the heat required to run the MC process. Less water was present in the solution, and therefore, less water was required to be evaporated and in the same way, less methanol was required to precipitate the salts. Indeed, the process was able to sequester 7.5% (4.1 t/h) and 33% (17.81 t/h) of the CO_2 treated (55t/h) at 200 and 300 g/l, respectively. To conclude, the ammonium salts pH swing MC process designed for a coal-fired power plant would be carbon negative only if the S/L ratio used get close to 300 g/l, which could results in salts being lost by precipitation due to its solubility limits.

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Table 11: CO_2 emissions related to regeneration of additives according to technique and S/L ratio.

S/L ratio (g/l)	Water evaporation & decomposition			Extraction & methanol evaporation & decomposition		
	Heat required, MW	CO_2 emissions [Nat. Gas] (t/h)	CO_2 emissions [biodiesel] (t/h)	Heat required, MW	CO_2 emissions [Nat. Gas] (t/h)	CO_2 emissions [biodiesel] (t/h)
300	57.5	11.5	6.9	56.18	11.2	6.7
200	243	48.6	29.2	157	31.4	18.8
100	430.5	86.1	51.7	333.4	66.7	40

Table 12: Summary of CO_2 emissions related to regeneration of additives according applying the extraction technique and using biodiesel fuel.

	Extraction & methanol evaporation & decomposition		

S/L ratio (g/l)	Extraction, CO_2 emissions [biodiesel] (t/h)	Equipment, CO_2 emissions [biodiesel] (t/h)	Total CO_2 emissions [biodiesel] (t/h)	Experimental CO_2 capture capacity (tCO_2/h)	NET CO_2 sequestration (t/h)
300	6.7	1.3	8.04	- 25.85	- 17.81
200	18.8	1.3	20.1	- 24.2	- 4.1
100	40	1.3	41.3	37.29	+ 4.01

4. Conclusions

This work investigated the feasibility of a liquid-liquid extraction technique as alternative method for the separation of AS salts from the water solution remaining after the CO_2 sequestration using an ammonium-salts based process in order to reduce the energy consumption of the overall process.

An ammonium sulphate/water separation higher than 90% was achieved at 25°C, 10 minutes, 1bar, 200g/l S/L ratio using 70% methanol as solvent. In order to achieve the optimum efficiency, it was necessary to lower the temperature and notably to reduce the stirrer speed to increase the interactions between methanol and ammonium sulphate and render the extraction more effective. However, these parameters had a marginal effect on the extraction efficiency in comparison to the S/L and the % methanol added to the solution during this process. Regarding the time of reaction, it did not affect the efficiency. At a large scale for industrial applications, the extraction process presents the advantage of requiring only 2 minutes to achieve the maximum efficiency. The FTIR results show that there was no ammonium sulphate in the filtered solution. The TGA results showed that water was still present in the ammonium sulphate solids in a small quantity, about 9 % wt.

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The extraction process would require 2908 kWh of heating energy while water evaporation step would require 4465 kWh to sequester 1t of CO_2. Therefore, by replacing the water evaporation step by the extraction process, the energy consumption decreased by 35%. Finally, a CO_2-balance study of a 500 MW coal-fired based power plant with integrated pH swing MC facility was investigated based on the heat needed and electric consumption required for the mineralization process. The CO_2-balance evaluation indicated that the process is carbon negative if the water evaporation is replaced by methanol extraction technique using S/L ratios of 200 and 300 g/l, with 7% and 33% CO_2 sequestered, respectively. This suggests that the efficiency of the dissolution and carbonation steps must be increased to enhance the CO_2 sequestration capacity of the process.

Acknowledgements

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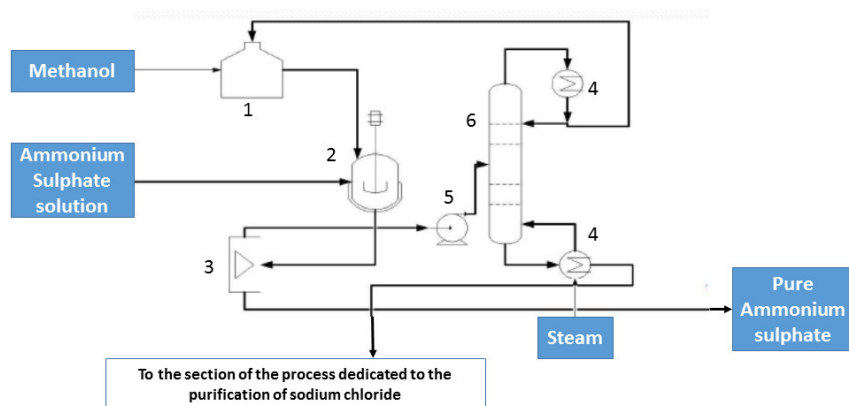
Figure Captions

Figure 1: Extraction of Ammonium Sulphate [modified from 17].

Figure 2: FTIR profile of (a) the liquid ammonium sulphate solution obtained after the filtration of the test 6; (b) the solid ammonium sulphate sample obtained after extraction process of test 6. Sample after extraction (test 6: 200g/L, 70% CH_3OH, 350rpm, 25°C, 10min) ($\bullet$) together to H_2O ($\blacklozenge$), $(NH_4)_2SO_4$ ($\blacksquare$) and CH_3OH ($\blacktriangle$) standards.
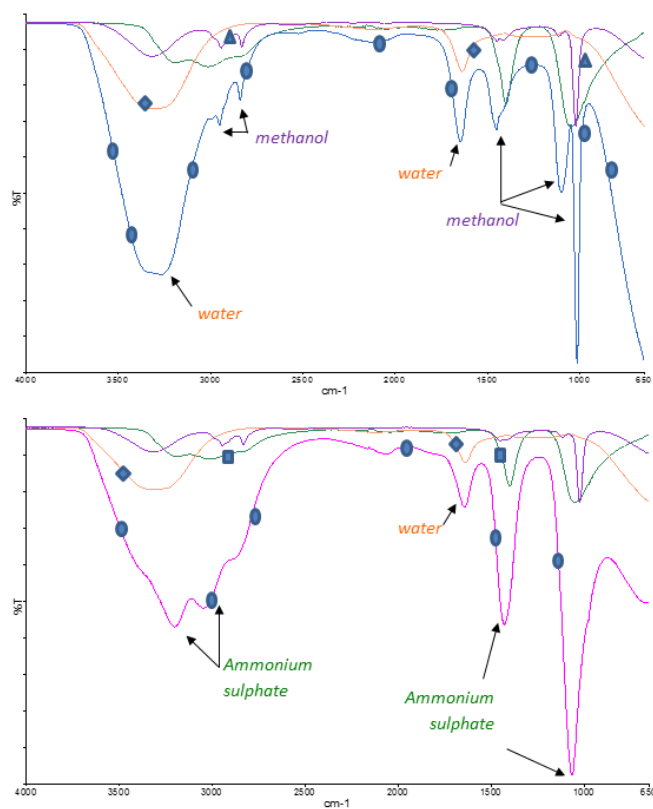
Figure 3: TGA profile of (a) the ammonium sulphate recovered after the test 6 of the extraction process; (b) Standard Ammonium sulphate.
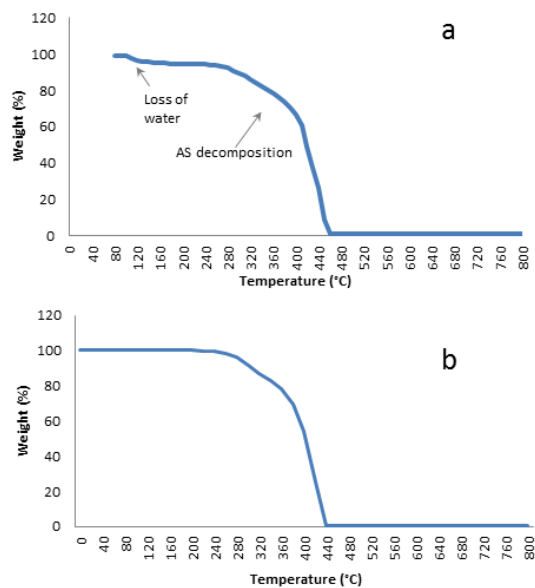
Figure 4: XRD patterns of the material recovered after tests 6 and 8 and correspondence with $(NH_4)_2SO_4$ standard (diamond).

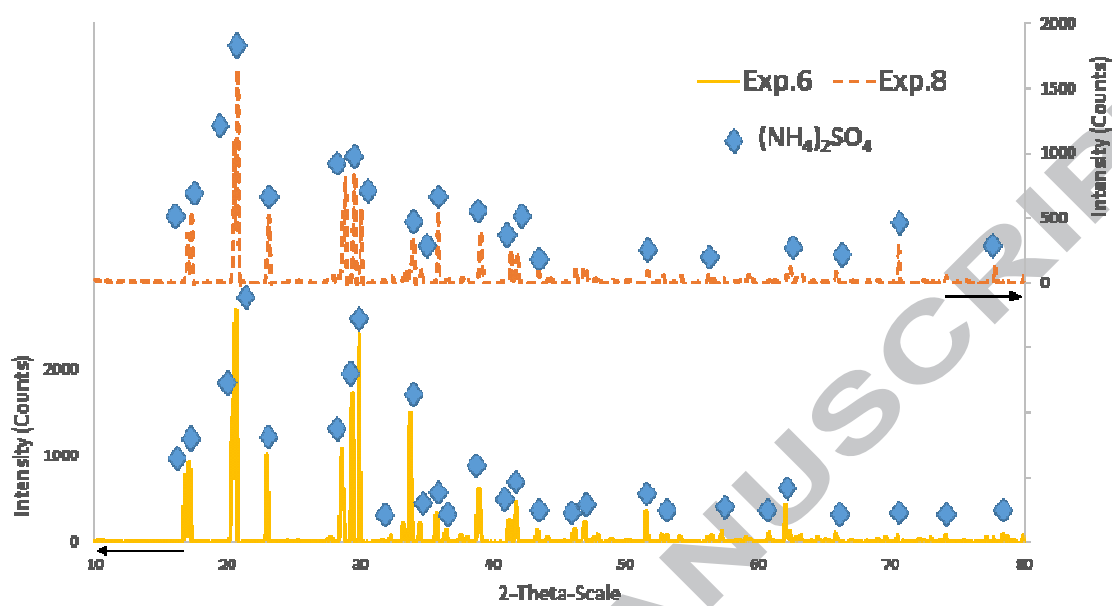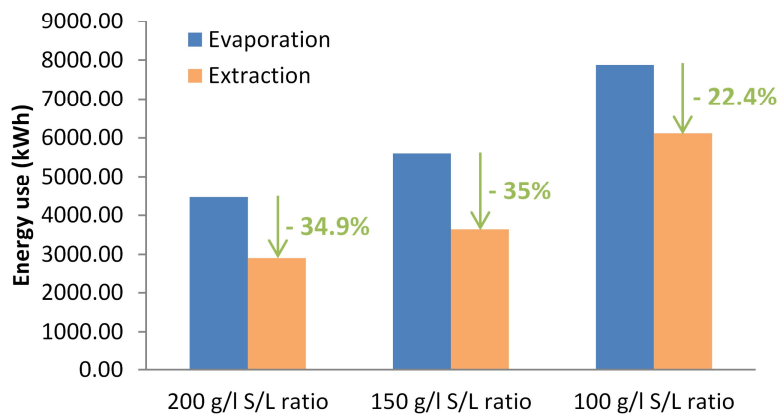**Figure 5:** Energy use for the ammonium sulphate-water separation.

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Highlights

➢ The feasibility of a liquid-liquid extraction applied to pH swing mineral carbonation was studied

➢ An ammonium sulphate/water separation higher than 90% was achieved

➢ The process resulted in an energy saving of 35% in comparison to water evaporation

➢ The CO$_2$ sequestration process was able to sequester 33% of the treated CO$_2$