A carbon dioxide capture and sequestration process includes a first stage of scrubbing a gas stream containing carbon dioxide with a solution comprising normal ammonium carbonate that is able to absorb the carbon dioxide whereby the carbon dioxide reacts with the ammonium carbonate to produce a solution comprising ammonium bicarbonate. In a second stage, a reactive slurry consisting of a metal silicate rock together with the ammonium bicarbonate solution is passed through a reactor that is controlled so as to promote the reaction between the bicarbonate and the silicate rock to produce metal carbonate and silica.
SYSTEM, APPARATUS AND METHOD FOR CARBON DIOXIDE SEQUESTRATION

Technical Field

This invention relates generally to a system, apparatus and method for carbon dioxide sequestration and more particularly, but not exclusively, to a system and method for the capture and sequestration of carbon dioxide from coal-fired power station flue gases.

Background to the Invention

There is increased focus on reducing carbon dioxide emissions to the atmosphere, to help minimise the effects of global warming. Carbon dioxide sinks exist naturally, with the main naturally occurring sink being the ocean. Plants are also an effective form of carbon dioxide sink and use photosynthesis to remove carbon from the atmosphere by incorporating it into biomass. However, these naturally occurring sinks are not capable of effectively keeping up with the vast quantities of carbon dioxide being produced in today’s power-thirsty climate.

A major source of harmful carbon dioxide gases are large fossil fuel power stations which, when fuelled by black coal, on average typically output around 0.8 to one tonne of the gas for each MegaWatt-hour (MWh) of electricity they generate. For example, a large power station such as the 2,640 MW Bayswater in the Hunter Valley of New South Wales, Australia, in generating 20 million MWh of electricity in a year, would also output 18 million tonnes of carbon dioxide. It would be advantageous if there was a system and method which was capable of capturing and permanently sequestering at least some of the carbon dioxide emitted from such power stations. It would also be advantageous if a system and method were provided for the disposition of the gas to be independently audited in perpetuity.

Summary of the Invention

A first aspect the present invention provides a carbon dioxide sequestration process including the steps of:

(i) scrubbing a gas stream containing carbon dioxide with a solution rich in normal ammonium carbonate that is able to absorb the carbon dioxide, whereby the
carbon dioxide reacts with the ammonium carbonate to produce a solution comprising ammonium bicarbonate;

(ii) passing a reactive slurry consisting of a metal silicate rock together with the ammonium bicarbonate solution through a reactor that is controlled so as to promote the reaction between the bicarbonate and the silicate rock to produce metal carbonate and silica.

In the context of the present specification, the phrase "solution rich in normal ammonium carbonate" will be understood as referring to a solution whereby the main salt present corresponds to the formula for the normal form of ammonium carbonate (N\text{II}O\text{2}CO\text{3}). There solution may, however, consist of other ammonium carbonate salts, and there may also be some molecular ammonia NH\text{3}, and ammonium hydroxide NH\text{4}OH, also present. Further, it should be noted that the terminology "gas stream containing carbon dioxide" does not mean that the stream contains only carbon dioxide, and may contain other off gases.

Hi an embodiment the metal silicate rock is mixed with the normal ammonium carbonate solution prior to absorbing the carbon dioxide in step (i).

Hi an embodiment the reaction causes the bicarbonate in the presence of the metal silicate to partially decompose so as to produce an aqueous phase enriched in molecular ammonia and carbon dioxide.

Hi an embodiment the method comprises the further step of cooling the aqueous phase such that free ammonia and carbon dioxide molecules combine to form ammonium carbonate salts in solution, the ammonium carbonate salts in solution arranged to be recovered for re-use in step (i) of the process.

Hi an embodiment the method comprises the further step of adding an alkali to the recovered ammonium carbonate in solution prior to being re-used in step (i). The alkali may be calcium oxide and/or hydroxide. Hi an embodiment the calcium oxide is extracted from gas stream prior to scrubbing in step (i).
In an embodiment the method comprises the further step of introducing pulverised limestone into a source producing the carbon-dioxide rich gasses. The source may be a coal-fired power station boiler and the pulverised limestone is added upstream of an economiser section of the power station boiler.

In an embodiment a portion of the mixed solution used to scrub the gas stream prior to discharge to the atmosphere is chilled to ensure that a quantity of free ammonia in the gases is below a threshold level. The threshold level may, for example, be set by the relevant government or other regulatory body.

In an embodiment the step of scrubbing the gas stream comprises exposing the carbon dioxide-containing gas stream to the slurry as a spray or deluge operable to maximise the area of exposure between the slurry and the carbon dioxide-containing gas.

In an embodiment the step of controlling the reactor comprises elevating at least one of a pressure and temperature of the reactor so as to enhance the reaction between the carbon dioxide and the metal silicate.

In an embodiment the reactor is a pipeline. The pipeline may comprise multiple flow paths and wherein the reaction takes place along the length of one of the flow paths. Another of the flow paths is utilised to supply the metal silicate slurry to the first stage.

In an embodiment the method comprises the further step of exchanging at least one of pressure and heat between the reactive slurry and the metal silicate slurry before and/or after the pipeline.

In an embodiment the reactor is a chamber located in use underground. The chamber may be located at a depth that provides sufficient pressure by way of static head to enhance the reaction between the carbon dioxide and the metal silicate.
In an embodiment the method comprises the further step of grinding a metal silicate rock to produce the metal silicate slurry. The metal silicate slurry may comprise roughly 25% by weight finely ground metal silicate solids.

In an embodiment the metal silicate is a magnesium-rich silicate. In an embodiment the magnesium rich silicate is a serpentine and/or olivine and/or pyroxene mineral all commonly described as ultrabasic or ultramafic minerals.

In an embodiment the method comprises the further step of cooling the normal ammonium carbonate-metal silicate slurry prior to its use in scrubbing carbon dioxide from flue gases.

In accordance with a second aspect of the present invention there is provided a system for sequestering carbon dioxide from a gas stream, the system comprising:

(a) a first apparatus for removing the carbon dioxide from the gas stream and absorbing it in a normal ammonium carbonate solution whereby the carbon dioxide reacts with the normal ammonium carbonate to produce a solution comprising ammonium bicarbonate; and

(b) a reactor for receiving a reactive slurry consisting of a metal silicate rock together with the ammonium bicarbonate resulting from (a), the reactor being controlled so as to promote the reaction between the bicarbonate and the metal silicate to produce a metal carbonate and silica.

In an embodiment the first apparatus comprises an absorption chamber arranged to circulate the normal ammonium carbonate solution through the carbon dioxide to thereby absorb the carbon dioxide.

In an embodiment the reactor is the pipeline as used in the method according to the first aspect.

In an embodiment the reactor is the chamber used in the method according to the first aspect.
In an embodiment the reaction of the bicarbonate with the metal silicate further produces an aqueous phase containing molecular ammonia, carbon dioxide and water.

In an embodiment the system further comprises a cooling arrangement arranged to cool the aqueous phase such that free ammonia and remaining carbon dioxide molecules combine to form ammonium carbonate salts in solution, the ammonium carbonate salts in solution arranged to be recovered by a recovery arrangement for re-use by the first apparatus.

In an embodiment the system further comprises a separation system arranged to separate the recovered ammonium carbonate in solution from the insoluble metal carbonate-silica phase prior to recovery. The separation arrangement may, for example, be a counter-current decantation (CCD) system comprising one or more stages for separating the solution.

In an embodiment the system further comprises a control arrangement arranged to add an alkali to the recovered ammonium carbonate in solution prior to returning it to the first apparatus for re-use.

In an embodiment the alkali is calcium oxide and/or hydroxide. The calcium oxide is extracted along with other suspended solids (fly ash solids) from the gas stream prior to scrubbing.

In an embodiment the system further comprises a feeder arranged to feed pulverised limestone into a source producing the carbon-dioxide rich flue gases. The point source may, for example, be a coal-fired power station and the pulverised limestone is fed into raw flue gases upstream of the power station boiler’s economiser.

In an embodiment the metal silicate comprises a magnesium rich silicate as used in the method according to the first aspect.
In an embodiment the system further comprises an ammonium carbonate salt recovery arrangement arranged to recover ammonia and ammonium salts accompanying the final product.

In an embodiment, the system comprises a solids-liquids separation system arranged to separate and recover ammonium carbonate salts, from the metal carbonate solid product that is sent for final emplacement.

In accordance with a third aspect of the present invention, in a pipeline, there is provided a first flow path that carries a metal silicate slurry for use by a first apparatus in a carbon sequestration process; and a second flow path that carries a reactive ammonium bicarbonate-metal silicate slurry from the first apparatus, wherein the second flow path is controlled so as to encourage the bicarbonate to react with the metal silicate and produce a metal carbonate and silica.

In accordance with a fourth aspect the present invention provides a method for causing a slurry consisting of metal silicate rock and an aqueous phase comprising ammonium bicarbonate in solution, to react so as to produce a metal carbonate, the method comprising the steps of:

- positioning a chamber underground at a depth which is sufficient to provide a pressure in the chamber to enhance the reaction between the ammonium bicarbonate and the metal silicate so as to produce the metal carbonate; and providing the slurry to the chamber for a sufficient period to enable it to react.

In an embodiment the slurry provided to the chamber is the reactive slurry produced in the process of the first aspect.

In an embodiment the method comprises the further step of exchanging heat from the product of the chamber with the slurry provided to the chamber.

In an embodiment the heat is exchanged in one or more heat exchanger units arranged in or at adjacent flow paths of the chamber product and the slurry.
In accordance with a fifth aspect there is provided a power station or other point source of carbon dioxide-rich flue gases, such as a blast furnace as used in steel making, or a cement kiln, utilising a carbon sequestration system in accordance with the second aspect, the system arranged to capture and sequester carbon dioxide from flue gas emitted by the power station or other point source.

In accordance with a sixth aspect, in an ammonia absorption process in which a metal silicate rock is mixed with a normal ammonium carbonate salt solution in water so as to produce a normal ammonium carbonate salt solution in water/metal silicate slurry (the ammoniated slurry) for use in a carbon dioxide sequestration process, there is provided the step of chilling the ammoniated slurry to limit losses of ammonia in scrubbed flue gases to the extent necessary to meet emission limits applying at the location in question.

In an embodiment, the process comprises the further step of providing the ammoniated slurry to a scrubbing stage, wherein a gas stream containing carbon dioxide is scrubbed with the chilled ammoniated slurry to thereby absorb the carbon dioxide into a reactive slurry.

In accordance with a seventh aspect of the present invention there is provided a method of extracting a target metal from a metal silicate comprising the step of mixing the metal silicate with an ammonia-rich ammonium carbonate salt solution, and reacting the mixed solution to cause the target metal to dissolve into the solution.

In an embodiment the method comprises the further step of grinding the metal silicate and forming it into a slurry prior to mixing the metal silicate with the solution.

In an embodiment the metal silicate is a magnesium-rich silicate.

In an embodiment the magnesium-rich silicate is a serpentine and/or olivine and/or pyroxene silicate mineral commonly described as an ultrabasic or ultramafic mineral.
In an embodiment the solution comprises normal ammonium carbonate salts dissolved in water (the ammoniated solution).

In an embodiment the target metal dissolves into the solution and then precipitates in the presence of carbon dioxide, as a metal carbonate to be removed for recovery.

In an embodiment the target metal is one or more of magnesium, calcium or iron. The dominant metal within the metal silicate may comprise magnesium.

In an eighth aspect the present invention provides a carbon dioxide sequestration process including the steps of:

(i) in a first stage, mixing a slurry of a metal silicate rock with a normal ammonium carbonate solution so as to produce a normal ammonium carbonate salt/water/metal silicate slurry;

(ii) in a second stage, scrubbing a gas stream containing carbon dioxide with the chilled solution from (i) to thereby absorb the carbon dioxide into a reactive slurry; and

(iii) in a third stage, passing the reactive slurry from (ii) through a reactor that is controlled so as to promote the reaction between the carbon dioxide and the metal silicate and produce a metal carbonate.

Brief Description of the Drawings

An embodiment of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Fig. 1 is a schematic of a carbon dioxide sequestration system according to an embodiment of the present invention;

Fig. 2 is a schematic of a carbon dioxide sequestration system according to an alternative embodiment of the present invention;

Fig. 3 is a process flow diagram showing a method of sequestering carbon
dioxide using the system of either Fig. 1A or IB, in accordance with an embodiment of
the present invention;

Fig. 4 is a schematic of a heat exchange apparatus, in accordance with an
embodiment of the present invention;

Fig. 5 is a schematic of a pressure exchange apparatus in accordance with an
embodiment of the present invention; and

Fig. 6 is a schematic illustrating a metal silicate preparation and grinding
technique, in accordance with an embodiment of the present invention.

Detailed Description of an Embodiment

In the following description, embodiments of the present invention are
described in the context of a system, apparatus and method for the capture and
sequestration of carbon dioxide contained within flue gases emitted by a fossil fuel-fired
power station. However, it is to be understood that the system, apparatus and method
could equally be utilised for the permanent sequestration of carbon dioxide from any
'point' source and is not limited to the particular arrangement described herein.

With reference to Fig. 1 there is shown a flow diagram of a system 10 for
performing a carbon dioxide (CO₂) sequestration process from a gas feed stream
containing carbon dioxide outputted from a power station, in accordance with a first
embodiment of the present invention. With additional reference to Fig. 3, the system 10
is arranged to perform the process 100 of (i) scrubbing a gas stream containing carbon
dioxide with a normal ammonium carbonate solution that is able to absorb the carbon
dioxide, whereby the carbon dioxide reacts with the normal ammonium carbonate to
produce a solution comprising, in the main, ammonium bicarbonate; and (ii) passing a
slurry consisting of a metal silicate rock together with the ammonium bicarbonate
solution through a reactor that is controlled so as to promote the reaction between the
bicarbonate and the silicate rock to produce metal carbonate and silica.

In an embodiment the method may further comprise a stage (iii) of contacting
flue gases with a circulating dilute normal ammonium carbonate solution that may be
chilled to the extent necessary, in a vessel in a counter-current, staged manner so that
residual ammonia in the flue gases is scrubbed from these gases to levels low enough to allow their final discharge in the atmosphere.

In the illustrated embodiment the stages (i) and (iii) are performed within a first apparatus 20 having separate chambers, in the form of an absorption chamber 28 and a scrubbing chamber 30, respectively. Stage (ii) occurs within a reactor either in the form of a pipeline 52 (as shown in Fig. 1) or, as will be described in more detail in subsequent paragraphs with reference to Fig. 2, an underground chamber excavated at a sufficient depth to facilitate conditions for the carbonation reactions to take place. According to Fig. 1, the pipeline 52 may connect the reactor to a mineral quarry site from with metal silicate is sourced.

The carbon dioxide sequestration process utilised in embodiments of the present invention is based on mineral carbonation. Mineral carbonation is a reaction between a metal-oxide-bearing mineral material and carbon dioxide. The metal-oxide bearing material may, for example, be alkaline-earth metals. Advantageously, the process 100 does not require the source of carbon dioxide to be particularly pure. In mineral carbonation, carbon dioxide reacts with the metal oxide bearing material to generate insoluble carbonates, that is to say:

\[ \text{MO} + \text{CO}_2 \rightarrow \text{MCO}_3 + \text{heat} \]  

which is an exothermic reaction, occurring more rapidly at elevated temperature, typically above 150°C. Certain chemicals may serve to increase the rate at which this reaction proceeds without being consumed themselves, i.e. they serve as catalysts. The inventor of the present invention has discovered that using ammonia as a catalyst has the particular advantage of being able to use a single integrated process for both the isolation of carbon dioxide from a mixture of gases, known as carbon capture, and for its permanent sequestration into a stable mineral form (storage). Further, embodiments are inherently operable to make bicarbonate ions as carbon dioxide is absorbed into the ammonia-rich ammonium carbonate solution, without having to handle highly pressurized carbon dioxide.

The exact nature of the insoluble carbonates formed by the reaction depends on the metal-oxide bearing material. Suitable materials may be naturally occurring alkaline-earth metal-rich silicate rocks which contain mineral constituents such as
serpentine (Mg$_3$Si$_2$O$_5$(OH)$_4$), olivine (Mg$_2$SiO$_4$), orthopyroxene (MgSiO$_3$), talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$) and wollastonite (CaSiO$_3$). In practice, the element Iron (Fe) may substitute for some of the Magnesium (Mg) or Calcium (Ca). Other suitable materials include alkaline industry residues such as slag from steel production, the ash (both fly and bottom) from pulverised coal-fired boilers, the ash remaining from the combustion of paper recycling residues (de-inking ash), and cement. The amount of heat generated in the reaction will depend on the specific metal and on the mineral containing the metal oxide as can be seen below in the case of three natural silicates (heat values are given per unit mole of CO$_2$ and at standard conditions (25°C and 0.1 MPa):

10

Olivine

\[ \text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{MgCO}_3 + \text{SiO}_2 + 89 \text{kJ mol}^{-1} \text{CO}_2 \] (2a)

Serpentine

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 \rightarrow 3\text{MgCO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O} + 64 \text{kJ mol}^{-1} \text{CO}_2 \] (2b)

Wollastonite

\[ \text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 + 90 \text{kJ mol}^{-1} \text{CO}_2 \] (2c)

In the illustrated embodiments, the silicate rock comprises the mineral serpentine, Mg$_3$Si$_2$O$_5$(OH)$_4$. AU of the above minerals may be pre-treated to increase the surface area of rock that can subsequently come into direct contact with the carbon dioxide. In an embodiment, the pre-treatment involves crushing, grinding and/or milling of the mineral, as well as some mechanical classification and separation. For example, the minerals could be milled (e.g. wet-milled) in ball mills or equivalent to form a finely ground metal silicate slurry (hereafter 'silicate slurry') wherein 90% of the mineral matter is finer than 40 microns. However, it will be understood that the extent of the pre-treatment is dependent upon the source and type of mineral(s) being used in the process. An example milling and transportation process flow is shown in Fig. 6.

Again with specific reference to Fig. 1, the carbon dioxide sequestration system 10 will now be described in detail. The system 10 receives a raw flue gas mixture feed stream 32 that has been generated and subsequently emitted by a power
station or other point source (not shown). In the embodiment described herein, the raw flue gas mixture 32 is passed through a filter 33 to remove most of the particulate matter. Suitable filters may include fabric filters, electrostatic precipitators and the like. Cleaning the raw flue gas mixture 32 may serve to minimise both the maintenance costs in downstream gas-handling equipment and the concentrations of particulates in flue gases ultimately discharged to the atmosphere. It will be understood, however, that while desirable for process reasons, it is not essential that the raw flue gas mixture 32 be cleaned of all particulates before it enters the scrubbing chamber 30. In an embodiment, the filtering process may additionally involve controlling the level of SOx and NOx that is present within the flue gas so as to adjust the pH level of the ammoniated slurry by virtue of the concentration of sulfate and nitrate ions present in it (which in turn affects the reaction rate between the silicate rocks and carbon dioxide by driving magnesium and calcium ions into solution) as will be described in detail below.

To maximise heat recovery in the system 10, the filtered flue gas mixture is then passed through a heat exchange apparatus in the form of a heat exchanger 34 so that the sensible heat of the filtered flue gas mixture (typically at a temperature of around 135°C) is exchanged with the cooler gasses being expelled from the scrubbing chamber 30 of the first apparatus 20 and the filtered flue gas mixture is cooled to its water-vapour saturation temperature (i.e. to about 50°C). Suitable heat exchangers may include, for example, recuperative-type heat exchangers, such as the Ljungstrom rotary design as commonly used for air pre-heating in power stations.

As mentioned in preceding paragraphs, the carbon dioxide sequestration system 10 receives a source of silicate slurry 36. According to the embodiment described herein, the silicate slurry source is located near or at the mine site from which the silicate rocks are sourced. As previously described, the silicate mineral sourced from the mine site is finely ground (e.g. by wet-milling in ball mills or equivalent to form the slurry) wherein roughly 90% of the mineral matter is finer than 40 microns or as determined to be appropriate for the proper operation of the process.

According to Fig. 1, the silicate slurry 36 is first blended with a solution in water of normal ammonium carbonate to create an ammonia rich ammonium carbonate-metal silicate slurry (hereafter "absorbent slurry"). In the illustrated embodiment, the normal ammonium carbonate salts in solution (hereafter "circulating solution") is the solution in water of most of the normal ammonium carbonate salts accompanying the
final metal carbonate/silica product. Specifically, according to the Fig. 1 embodiment, the circulating solution represents the overflow of a first thickener 90a of a counter-current decantation (CCD) thickener separation system 90.

In flowing from the CCD thickener system 90 to the power station site, the absorbent slurry 47 passes through a first pressure-exchange apparatus 38. To minimise power consumption, the pressure of the absorbent slurry 47 may be increased by exchanging pressure with the final metal carbonate/silica product (hereafter 'final product'), typically to a pressure of approximately 100 Bar. In addition, to minimise heat losses from the system 10 (and to ensure that the final product is cooled to a suitable temperature before it is emplaced in its final permanent repository), the absorbent slurry 47 passes counter-currently through a heat exchanger 40 to absorb the surplus sensible heat contained in the final product.

According to Fig. 1, a pipeline 44 connects the first apparatus 20 to the silicate mineral quarry site and is used to transport the absorbent slurry 47 used in the sequestration process 100. As will be described in more detail in subsequent paragraphs, an alternate path 52 in the pipeline 44, in this embodiment, also serves to act as a controlled reactor in which the metal carbonation reaction largely takes place.

At or near to the power station site, the absorbent slurry 47 is passed counter-currently through a second heat exchanger 46 and a second pressure-exchange apparatus 48, where the absorbent slurry 47 is cooled and reduced in pressure by exchange with the reactive slurry discharged from the first apparatus 20, before being fed directly into the scrubbing chamber 30.

After arriving at the power station site, a residual circulating stream passes into a vessel in the form of a residual ammonia scrubber 56, in such a way that flue gases that have been stripped of most of their carbon dioxide content, pass upwards from below. There may be any number of counter-current contacting stages, depending only on the desired implementation. The residual ammonia scrubber 56 is operable such that the cleaned, largely carbon dioxide-free flue gases may leave the system with less than one part per million of ammonia. In order to achieve such low losses of ammonia, the fluid circulating through this vessel may be cooled, even chilled, to an appropriate degree. Specifically, the fluid circulating through this vessel is comprised of the dilute aqueous phase described above (i.e. a clarified, dilute solution in water of normal ammonium carbonate), which enters the vessel and collects in the base of the residual
ammonia scrubber 56 from where it is circulated by pumps to the header sprays to above the uppermost of the contacting stages. It is this circulating flow that is cooled to the requisite extent, by firstly, arranging for it to flow firstly, through one or more first stage heat exchangers that are cooled by circulating water cooled in turn, in a cooling tower, and secondly, through one or more second-stage heat exchangers that are cooled in turn, by a stream of water or other suitable heat-exchange fluid that has been chilled to below ambient temperatures by a chilling plant suitable for the purpose. In an embodiment, the chilling plant is an ammonia absorption chiller 82, the operating principles of which are understood by those skilled in the appropriate art. It is to be understood however, that alternative types of chilling plant provided they have adequate chilling capacity, are equally suitable.

Absorption chillers, including ammonia absorption chillers, require a source of heat for their operation. In an embodiment, some of this heat may be provided by the heat released through carbonation reactions as shown as equations 2a, 2b and 2c, depending on the type of silicate mineral used.

The cooled filtered flue gas mixture passing through the heat exchanger 34 enters the scrubbing chamber 30 where the gas mixture passes upwards through deluging sprays of circulating solution entering from the residual ammonia scrubber 56 from above. When carbon dioxide is absorbed in the circulating solution, a further substantial quantity of heat is liberated, as gaseous carbon dioxide is absorbed into it, and reacts with the normal ammonium carbonate salts in the circulating solution. The reactions include the conversion of the normal ammonium carbonate (NFL₄)₂CO₃ to the bicarbonate NH₄HCO₃, via the reaction:

\[
(NFL₄)₂CO₃ + CO₂ + H₂O \rightarrow 2NH₄HCO₃ \quad \text{(3)}
\]

Normal ammonium Ammonium Carbonate bicarbonate

While this will be the main reaction encountered, other reactions may equally occur in parallel including, when there is free molecular ammonia present in the scrubbing solution:

\[
NH₃ + CO₂ + H₂O \rightarrow NH₄HCO₃ \quad \text{(3a)}
\]
As well, some of the ammonium bicarbonate may lose some combined water to form the carbamate, \( \text{NH}_2\text{COONH}_4 \), hence this compound will likely be present in smaller quantities, perhaps along with some urea, \( \text{CO(NH}_2)_2 \), formed when the carbamate loses additional combined water.

FURTHER DETAIL OF SEQUESTRATION PROCESS

In more detail, the carbon capture process begins with the metal silicate (in this case, ground serpentine) being blended into a circulating solution of serpentine and an aqueous phase containing normal ammonium carbonate in solution to thereby produce the absorbent slurry. The absorbent slurry is then circulated using pumps, through a carbon dioxide absorption chamber 28 which in an embodiment may be the lower half of a tall scrubbing chamber 30 (the upper part being utilised as the residual ammonia desulfurization scrubber 56). The absorption chamber 28 may, for example, take the form of a flue gas desulfurization scrubber, with the absorbent slurry circulated at high flow rates through banks of sprays.

The absorbent slurry is heated by the transfer of latent heat from the flue gases rising from below. Also, as mentioned above, when carbon dioxide gas is absorbed into the absorbent slurry, substantial quantities of heat are liberated, as carbon dioxide reacts with the mainly normal ammonium carbonate \( (\text{NH}_2)_2\text{CO}_3 \), to form the bicarbonate \( \text{NH}_4\text{HCO}_3 \), as per Equation 3 (there may also be some intermediate salts e.g. the sesquicarbonate \( (\text{NFLO}_2\text{CO}_3)_2\text{NH}_4\text{HCO}_3 \), the carbamate \( \text{NH}_4\text{COONH}_2 \), and traces of urea, \( \text{CO(NH}_2)_2 \)). The heat of solution, along with the latent heat released when water vapour in the flue gases condenses, is removed by circulating the absorbent slurry through water-cooled heat exchangers 84.

As mentioned above, the output from the absorption chamber 28 is a reactive solution in the form of a metal silicate slurry in an aqueous phase that is itself a solution of carbonate-rich ammonium carbonates, primarily ammonium bicarbonate. A stream of the reactive ammoniated metal silicate slurry (hereafter ‘reactive slurry’) is drawn from the scrubbing chamber 30 and directed to the mine site via a return pathway 52 of the pipeline 44, which also advantageously acts as a controlled reactor.
On route to the mine site, at or near to the power station, the reactive slurry is pressurised at the second pressure-exchange apparatus 48 to a high pressure of around 120 Bar (above the critical pressures of both carbon dioxide and ammonia) and also heated to at least 100°C and preferably to at least 150°C. Heating is accomplished by transferring heat from the incoming silicate slurry arriving from the mine at the heat exchanger 46, and also, if necessary, by injection of steam 54. The heat contained in the incoming silicate slurry in part originates from reactions 2(a), 2(b), and 2(c), depending on the silicate mineral involved.

The return pipeline 52 of the pipe reactor, at temperatures below 50°C or thereabouts, most if not all of the carbon dioxide present is in the form of ammonium carbonates. When the slurry is heated to at least 100°C under pressures of at least 100 Bar, the tendency is for the various forms of ammonium carbonates in solution to decompose to molecular carbon dioxide CO₂ and ammonia NH₃. These remain substantially in solution in the reactive slurry under these temperature and pressure conditions. A result of this process is the partial pressure of the carbon dioxide will be particularly high, thereby serving to enhance the speed of reaction with the silicate minerals, converting them to insoluble carbonates and silica during the transit. In an embodiment, the pipeline may be 10 kilometres in length to allow adequate time for the reactions to proceed essentially to completion resulting in the metal carbonate product that contained most if not all of the carbon dioxide originally scrubbed from the power station flue gases. It will be understood that the length may vary, however, depending on the actual implementation.

It will be apparent that a high concentration of ammonia is maintained in the slurry throughout its passage from the power station to the silicate rock mine/quarry or other emplacement site.

When the final product in the return pipeline 52 reaches the vicinity of the mine site, as described above, the hot pressurised final product transfers its sensible heat via the heat exchanger 40 to the absorbent slurry being pumped towards the power station, so the process the final product is cooled to a temperature below 50°C. To achieve this temperature in practice, it may be necessary to employ additional cooling to ensure that the temperature of the final product stream is cool enough for the recombination reactions to occur. In an embodiment, the additional cooling is accomplished by means of a heat exchanger cooled by circulating cooling water from
dry (e.g. radiator-type) cooling towers, fin fan coolers, or a natural-draft cooling tower (not shown) such as used for cooling in the power station. A consequence is that free molecular ammonia and carbon dioxide will subsequently re-combine to form ammonium carbonate salts dissolved in the aqueous phase that can be recovered and used in the circulating solution. Since carbon dioxide has been removed from the aqueous phase by reaction with the mineral silicate, the ratio of carbon dioxide to ammonia is lower than it was before the key carbonation reactions occurred. Hence, the predominant form of ammonium carbonate salt formed is normal ammonium carbonate (NKU)\(_2\)CO\(_3\) which, it will be noted, may contain twice as many ammonia units pre carbon dioxide unit as the bicarbonate, NH\(_4\)HCO\(_3\). This is the reason why a solution rich in normal ammonium carbonate may also be referred to as an ammonia-rich ammonium carbonate solution. In any case, it will be understood that other ammonium salts, plus molecular ammonia NH\(_3\) and ammonium hydroxide NH\(_4\)OH, may also be present.

**FURTHER DETAIL OF SEPARATION SYSTEM**

As previously mentioned, the final reacted slurry (i.e. containing mainly normal ammonium carbonate in solution together with the carbonate/silica solids that are the products of carbonation) is passed through a solids-liquids separation process. The separation process generally involves producing a clear overflow solution containing most of the ammonium salts and other soluble chemicals (including any molecular ammonia and ammonium hydroxide NH\(_4\)OH that are dissolved in it) and a dense slurry or even paste-consistency underflow containing all of the solids.

Separation may be accomplished by one or more of several means known to those skilled in the art. In an embodiment, a filtration process may be employed using, for example, rotary vacuum filters. In an alternative embodiment, the filtration process may use plate and frame-type filter presses. In both embodiments, a filter cake is formed on a filtration medium (a filter cloth for example) and wash-water is sprayed onto, or otherwise caused to pass through, the filter cake to wash out residual quantities of soluble materials including ammonium carbonate salts. The filter cake represents the first, solids-rich stream, which may be handled as a cake, or converted to a dense slurry by addition of small quantities of additional water sufficient to allow it to be handled as
a slurry. The aqueous phase, including wash-water passing through the filter cake and filtration medium, represents the second stream. In another embodiment, separation of the solids from the aqueous phase (specifically, the separation of the ammonium carbonate salts and other soluble materials in the aqueous phase) is achieved by a process known as counter-current decantation (CCD), as illustrated in the Fig. 1 and 2 embodiments. This technique involves utilising a number of continuous thickener tanks (in the illustrated embodiment three tanks are used, although it will be understood by persons skilled in the art that more or less thickener tanks may be employed depending on the desired implementation) that are arranged in a series. The CCD thickener system 90 may recover a substantial amount (e.g. around 99 per cent) of all of the dissolved salts and other soluble substances (including ammonia) in the aqueous phase accompanying the final product. The remaining amount of salts will accompany the final product solids as they are pumped to their final permanent repository.

It is noted that in some implementations, only a certain percentage (e.g. 80%) of soluble substances may be recovered by the first thickener 90a of the CCD system 90, with the remainder recovered by subsequent stages. In an embodiment, as shown in Figure 1, the two aqueous-phase streams resulting from the overflows of the first-stage and second-stage thickeners are blended either by arranging for the overflow of the second stage thickener to be blended with the feed stream to the first-stage thickener, or by directly blending the two overflow streams.

In more detail, the final products stream from the reactor, after pressure reduction in the pressure exchangers 38 and cooling in the heat exchangers 40, enters the first thickener 90a of the series. The insoluble solids (the carbonated mineral) suspended in the feed stream settle in the thickener tank 90a to form a dense slurry that is withdrawn as an underflow stream. The balance of the feed entering the thickener tank overflows as a clarified supernatant, which contains most of the soluble ammonium carbonate salts and other soluble materials (i.e. the circulating solution). The underflow may still contain around 10 per cent of the aqueous phase that first entered the thickener, and it is the function of the balance of thickeners in the CCD system to recover these salts to the maximum practicable extent, from the insoluble solids that are to be finally emplaced. In the CCD system 90, the underflow slurry from thickener tank 90a is pumped to the next thickener tank 90b in line. Also fed to tank 90b is the clarified overflow from thickener tank 90c, and so on. Where "N" thickener
tanks are employed, the final thickener tank in the series, tank N, receives a feed stream which is a mixture of the underflow of thickener tank N-I, and fresh water, which may be replaced in part by any surplus aqueous phase recovered from final emplacements of carbonated mineral as this further consolidates and/or drains from the mineral, over time. In an embodiment, a mixture of thickener tanks, one or more stages in series, and filtration units may be used to effect the separation of soluble ammonium carbonate salts from the insoluble carbonated mineral.

The dense slurry stream (in one embodiment a filter cake, in another embodiment the underflow of CCD thickener Unit N) is the final product slurry substantially free of salts, and in a form suitable for permanent emplacement in mine voids or other purpose-built repositories (not shown). In these emplacements the solids can settle and consolidate, releasing additional aqueous phase as a clear supernatant. This supernatant may also be collected and re-used in the process, as described in the paragraph above.

When the CCD system 90 for the recovery of ammonium salts is close to the power station, as may be the case for the underground chamber reactor embodiment (Fig. 2), it may be appropriate to add the remainder of the power station fly ash to the final product slurry from the carbon sequestration process, so the two streams may be handled and co-disposed of as a single stream. An advantage stemming from the presence of fly ash having pozzolanic properties (a tendency to "set" in the presence of alkalis and moisture) in the final product, is that it will assist with the rehabilitation process, by encouraging the final product/fly ash mix to "set", thereby immobilising the contents of the emplacement.

In an embodiment the overflow of the second stage of the CCD thickener system 90, being a relatively dilute, clarified (insoluble solids-free) solution in water of ammonia-rich ammonium carbonate salts may be handled separately (see Fig. 2). In such an embodiment, the stream (hereafter "residual stream") is sent overland from the CCD system 90 (installed near the silicate quarry) to the power station site via a separate, third pipeline 91. Pumps raise the pressure of the contents of the third pipeline 91 to the extent necessary for them to traverse the length of the pipeline 91. However, it will be understood that the third pipeline 91 may be configured to accept some of the heat and some of the pressure energy released when the pressure and temperature of the final products pipeline are reduced via heat- and pressure-exchange equipment.
Whether the third pipeline is configured in this way, or simply used as a conduit for the return of this stream to the power station site, depends on the individual circumstances of the installation.

5 CHEMICAL REACTIONS

The main chemical processes occurring throughout the process are as follows:

\[ 3\text{CO}_2 + 3(\text{NH}_4)_2\text{CO}_3 + 3\text{H}_2\text{O} \rightarrow 6\text{NH}_4\text{HCO}_3 \]  (4)

\[ 6\text{NH}_4\text{HCO}_3 \rightarrow 6\text{NH}_3 + 6\text{H}_2\text{O} + 6\text{CO}_2 \]  (5)

\[ 6\text{CO}_2 + \text{Mg}_3\text{Si}_2\text{O}_5\text{(OH)}_4 \rightarrow 2\text{SiO}_2 \downarrow + 3\text{MgCO}_3\text{Ψ} + 2\text{H}_2\text{O} + 6\text{NH}_3 + 3\text{CO}_2 \]  (6)

\[ 3\text{CO}_2 + 6\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow 3(\text{NILO}_2\text{CO}_3) \]  (7)

\[ \text{NH}_3 + \text{NH}_4\text{HCO}_3 \rightarrow (\text{NILO}_2\text{CO}_3) \]  (8)

Equation 4 represents the absorption of carbon dioxide into the ammonia-rich ammonium carbonate aqueous phase to produce a solution comprising ammonium bicarbonate. On heating under pressures of at least 100 Bar in the reactor (i.e. pipeline or underground chamber), this ammonium bicarbonate decomposes to molecular ammonia, water and carbon dioxide according to equation 5. As shown in equation 6, under the high pressure and temperature conditions prevailing in the reactor the carbon dioxide reacts with the serpentine (the chemical formula of which is shown in equation 6) or other silicate rock to form insoluble metal carbonates and silica, the final products of the process, which store the carbon dioxide. Equation 7 describes what happens after the reaction products are cooled to below 50°C, i.e. low enough to allow the free molecular ammonia and carbon dioxide to combine to form ammonium carbonate salts in solution. As shown, since much of the carbon dioxide has been absorbed by the metal silicate (here serpentine) the ratio of ammonia to carbon dioxide favour formation of the ammonia-rich normal carbonate. Additional normal ammonium carbonate may form according to equation 8, by reaction between ammonium bicarbonate, and free molecular ammonia.
CONTROLLING ACIDITY IN THE SYSTEM

As mentioned in preceding paragraphs, sulfate ions from SOx, and nitrate ions from NOx respectively, contained in the raw flue gases, may accumulate in the circulating solution of ammonium salts. Oxides of sulfur (SOx) are inevitable byproducts of the combustion of fossil fuels including coal, that incorporate sulfur-containing compounds in reduced form, for example pyrite (iron disulfide FeS2). Oxides of nitrogen (NOx) are also inevitable byproducts of the combustion of fossil fuels including coal, originating from nitrogen-containing compounds in the fuel, and from reactions between oxygen and nitrogen in air induced by the heat of the fuels' combustion, in an Australian context, where coals tend to have low sulfur contents, and assuming use of modern "low-NOx burners", the rates of build-up of nitrate ions will not be high, but their build-up may still need to be limited to maintain the pH range to that most suited for the overall processes. When the SOx and NOx contained in flue gases contact the absorbent slurry as encountered in the scrubbing chamber 30 in the presence of additional oxygen including that contained in flue gases, a series of reactions occur that convert these gases to sulfates and nitrates: SOx to sulfate ions SO4—, and NOx to nitrate ions NO3-. In the normal course of separating out the insoluble solids for example magnesite and silica formed from the reactions between carbon dioxide and the metal silicates, as previously described, the soluble salts dissolved in the aqueous phase from the reactor including sulfates and nitrates are recycled for re-use in the scrubber, apart from the small quantities of such salts that are ultimately emplaced with the final product metal carbonates and silica. A consequence is that while carbon dioxide entering the system forms additional carbonate ions that are ultimately removed at an equal rate as insoluble metal carbonates, the tendency is for both sulfate and nitrate ions to accumulate in the circulating aqueous phase. In an embodiment, the system may implement a process for limiting the build-up of these ions (anions) to avoid an increase in the acidity (reduction in the pH number) of the circulating solution, as the formation of these ions leads to a concomitant formation of hydrogen ions in solution.

It is noted that the system, to some extent, may inherently limit such a build-up by virtue of the fact that, as mentioned in the previous paragraph, not all soluble salts and other dissolved substances will be recovered by way of the solids-liquids separation
process. To further reduce nitrate ion equilibrium concentration, it is necessary to limit correspondingly, the concentrations of NOx gases in the flue gases entering the scrubbing vessel 30. This may be achieved, for example, by using so-called 'low-NOx burners', and by other methods which achieve control of the combustion process to limit NOx formation in the power station's boilers.

To control concentrations of sulfate ions in the circulating aqueous phase, the system 10 may employ an additional control mechanism 96 arranged to add/feed appropriate quantities of calcium oxide or hydroxide (which in water form calcium ions and hydroxyl ions) to a portion of the circulating slurry (a side-stream), wherein the sulfate ions react with it to form calcium sulfate, which mostly precipitates out as the sparingly soluble hydrated salt, gypsum:

\[
\text{SO}_4^{2-} + \text{Ca}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \ \Psi
\]  

Meanwhile, the hydroxyl ions combine with and neutralise a corresponding number of hydrogen ions (to form water molecules), thereby controlling (reducing) the acidity of the circulating solution.

In an embodiment, calcium oxide generally may be naturally present in the power station fly ashes. If present in sufficient concentrations, the appropriate quantities of fly ash may be added by the control mechanism 96 to the circulating solution to control the pH levels to the desired ranges. If the quantities of calcium oxide naturally present in fly ash are inadequate, they may, in an embodiment, be augmented by adding pulverised limestone to raw power station flue gases in the boilers at one or more locations for example immediately upstream of the economiser section of the boilers, where flue gas temperatures are appropriate for the decomposition of limestone to calcium oxide and carbon dioxide (when exposed to furnace temperatures of 1,000°C or more, limestone is calcined to quicklime.

Treatment processes applied to this side stream may also incorporate steps to recover base metals and other valuable components in solution, including nickel, copper and iron, in one form, side-stream treatment may involve adding an inexpensive alkali, e.g. calcined lime, dolomite, limestone or the like. Sulfate ions can be removed via the following equation (shown for normal ammonium sulphate and calcium oxide):
\[
\text{ammonium} \quad \text{quicklime} \quad \text{gypsum} \quad \text{ammonium}
\]
\[
\text{Sulfate} \quad \text{hydroxide}
\]

\[(\text{NIL}_2)_2\text{SO}_4 + \text{CaO} + 3\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NH}_4\text{OH}\] (10)

In an embodiment the control mechanism 96 may be further arranged to add fresh ammonia to the circulating solution, at an appropriate rate, to account for any losses of ammonia.

**FURTHER DETAIL OF ABSORPTION/SCRUBBING CHAMBER OPERATION**

Conditions in the absorption chamber 28 may be strongly oxidising to assist the conversion of the impurity gases dissolving in the aqueous phase of the slurry (i.e. SOx ending up as sulfates rather than sulfites, and NOx ending up as nitrates rather than nitrites). In an embodiment, the cool, saturated condition of the flue gases when in the absorption chamber 28, plus the partial pressure of oxygen in these gases of three per cent or more, may be sufficient to ensure oxidising conditions. As well, the large pool of slurry held in the bottom of the absorption chamber 28 may be aerated using compressed air as is normal practice with flue gas desulfurisation (FGD). However, if additional oxidising is required, the process may further involve irradiation of the flue gases immediately upstream of their entry into the absorption chamber 28 by electron beams or high-voltage brush discharge, to form free radicals from water and oxygen (OH\(^-\) and O\(^\cdot\)). These are powerful oxidising agents, able to convert rapidly, sulfur dioxide SO\(_2\) to the trioxide SO\(_3\), and nitric oxide NO to the dioxide NO\(_2\), the precursors to sulfates and nitrates respectively. Thus, the absorption chamber 28 may serve as a highly efficient scrubber for the removal of SOx and NOx. It may also remove volatile metals that may exist in trace quantities in coal and that end up in flue gases notably mercury (the low operating temperatures and oxidising environment will tend to favour the conversion of any mercury vapour present to non-volatile mercuric oxide, an insoluble solid that will accompany the final product metal carbonate and silica to their permanent emplacement).

**FURTHER DETAIL OF PRESSURE EXCHANGERS**

With reference to Fig. 4, there is shown an arrangement for the pressure-exchange apparatus described above. At the end of the reaction process, the pressure of
the final carbonate-rich product must be reduced from approximately 120 Bar to atmospheric pressure. Instead of merely reducing pressure by throttling valves, thereby losing the energy embodied in this pressure, the energy this pressure represents may be conserved by transferring it to the extent possible, to the silicate slurry. In Fig. 4, slurry A comprises the products of the reactions that occur as the ammoniated, carbonated silicate slurry flow through the pipeline 44 from the power station to the mine site; while slurry B represents silicate slurry from the mine. A consequence of pressure exchange in these two stages is that slurry A's pressure would fall from around 120 Bar to near ambient pressure, while that of slurry B would rise from around atmospheric pressure to perhaps 100 Bar.

Another pressure-exchange apparatus is also utilised at the power station site. Here, using the terminology of Fig. 4, slurry A represents the hot silicate slurry arriving via the pipeline from the mine; while slurry B comprises slurry exiting the scrubbing chamber 30 (i.e. silicate slurry now charged with ammonia and carbon dioxide, but at close to ambient pressures). A consequence of pressure exchange in this stage is that slurry A's pressure would fall from its arrival pressure (this may be 120 Bar, a pressure that would be maintained by booster pumping stations at strategic locations along the pipeline 44 to overcome friction losses), to near ambient pressure. This pressure may be transferred (exchanged) to the extent possible to slurry B, thereby minimising the amount of pumping energy required to raise the pressure of this slurry to the levels required, here assumed to be 120 Bar. Since slurry A at this point will be at well below 120 Bar, pressure-exchange between slurries A and B alone may not be capable of raising the pressure of slurry B to 120 Bar. Also, the volume of slurry B may exceed that of slurry A. This is because of the much higher contents of carbon dioxide and ammonia, and of water condensed out of the power station flue gases. In an embodiment, additional pumping capacity may be installed to boost slurry B pressures to those required for the pipeline 44, and to pressurise those (relatively small) quantities of slurry B that cannot be pressurised by pressure-exchange with slurry A. For this function, conventional high-pressure diaphragm pumps, such as the Geho pump manufactured by Weir Netherlands b.v., may be implemented. This pumping, together with the pumping energy required to maintain pressures along the length of the pipelines, account for a substantial proportion of the total mechanical energy input to the total process. Other suitable pressure exchange/pump-turbine sets may comprise...
centrifugal pumps and radial-type hydraulic turbines. As the pressures are relatively high, the type of centrifugal pump may be a multi-stage barrel-type pump.

With reference to Fig. 5 there is shown a configuration for the heat exchanger arrangements 40 & 46, according to an embodiment of the present invention. As previously discussed, high temperatures are required to initiate and accelerate the carbon sequestration reactions: the conversion of metal silicates to carbonates. These reactions, being exothermic, yield additional heat that can and should be applied to assist with creating the conditions needed for these reactions to proceed most efficiently. As shown, the heat-exchanger arrangement is in the form of a simple shell-and-tube heat exchanger, consisting of two concentric pipes: the inner forms the "tube", the outer, the "shell". An advantage with this arrangement is that the heat exchanger can be made as long as is required to affect the desired transfer of heat: if necessary, many hundreds of metres long. For heat exchanger 40 (i.e. the heat exchanger on the silicate rock quarry site side), heat energy is transferred between the final carbonate/silica product (i.e. slurry A), which is hot, and the silicate slurry (slurry B), which is cool. For heat exchanger 46 (i.e. the heat exchanger on the power station side), slurry A would be hot silicate slurry from the quarry, while slurry B would be slurry exiting the scrubbing chamber 30 (i.e. now charged with ammonia and carbon dioxide, but at close to ambient temperatures).

UNDERGROUND REACTOR

Turning now to Fig. 2, there is shown an alternative system 200 for performing carbon dioxide sequestration which utilises (where geological conditions permit) an underground chamber as the reactor, as opposed to a pipeline reactor as illustrated in Fig. 1. In this embodiment, the reactor is in the form of a chamber 70 excavated from bedrock at a depth sufficient to allow the conditions for the core carbonation reactions to be generated entirely or partly by static head alone (e.g. 100 Bar). A chamber 70 excavated at a depth of approximately 800 meters and having a volume of 300,000 cubic meters, sufficient to allow for a 24 hours' detention time for the contents, may be envisaged for holding the reactive slurry output from a system 200 fitted to an efficient 1,000MWe coal-fired power station. In practice a smaller chamber may suffice, should it arise that the reactions are essentially completed in less time.

The silicate slurry 36 may be prepared either at the serpentine quarry site and
pumped overland to the power station site, or, the mineral could be railed, trucked or otherwise suitably transported to the power station site, and prepared there. Were the former implementation adopted, pipeline arrangements 44 would be considerably simpler than for the pipeline reactor embodiment described above with reference to Fig. 1. Specifically, the silicate slurry 36 would not be required to collect and transport heat and pressure energy from the quarry site to the power station site, nor to host any residual ammonium salts. The pipeline 44 would simply be utilised for mineral transport; whether it was transported as a lump product by rail or as slurry by pipeline would be determined by economic and environmental considerations. It will be appreciated that in this embodiment, silicate slurry density may be substantially higher (e.g. 60 per cent solids by weight), thereby reducing the volumes of silicate slurry required to be pumped, and allowing a lower pipeline velocity because of the reduced tendency for the solids in denser slurries to segregate and silt up the pipeline 44. Also, arrangements for conserving heat and pressure are much simpler than they would need to be for the pipeline reactor alternative.

In Fig. 2, an injection pump 72 is utilised to drive the circulation of the reactive slurry from the scrubbing chamber 40, through a plurality of counter-current heat exchangers 74, 76, underground reactor 70 and counter-current decantation system for the separation of normal ammonium carbonate and other salts in the aqueous phase of the products of the underground reactor, and the insoluble carbonated mineral solids that are to be emplaced permanently.

Heat exchangers 74, 76 are shown in schematic form at two locations on Fig. 2. The heat exchangers 74, 76 may be long, shell-and-tube designs, as shown in Fig. 4: they may span most of the vertical distance from the scrubbing chamber 40 down to the underground chamber 70. This is to say, whereas two separate pipelines are implied in Fig. 2, in practice, for most of their length they may be concentric: the annulus formed between the outer and concentric inner pipe transporting the hot reaction products, while the inner pipe transports the products heading downward to the Reaction chamber. It will be understood by persons skilled in the art that this selection may be reversed.

In contrast to the pipeline reactor configuration shown in Fig. 2, heating of the reactive slurry may be accomplished by exchanging heat from the hot reaction products
rising first from the ammonia gas recovery vessel 78, and as the raw slurry descends further, from hot slurry rising from the underground chamber 70. While some supplementary heat may be required, the heat generated by Equation 2(b) would be conserved, and available to heat raw reactive slurry.

The design of the underground chamber 70 may be optimised to achieve some plug-flow characteristics. In an embodiment, the chamber 70 may have a high length-to-diameter ratio of 10:1 and be vertically aligned. Utilising a vertically aligned chamber provides that the incoming reactive slurry, being cooler hence slightly denser than the average contents of the reactive chamber 70, will tend to stratify at lower levels, displacing hotter slurry upwards. In an embodiment, the underground chamber 70 may be subdivided into two or more vertically stacked sub-chambers.

In an embodiment, the reactive chamber 70 may employ an agitator (not shown) to maintain the solids in suspension. This may be advantageous where large residence times are required, implying in turn large reactor volumes.

As will readily be appreciated, heat losses from the underground chamber 70 and pipelines may be much smaller than they would be even from a lagged above-ground pipeline and may be further reduced by insulation surrounding the reactor, pipelines and any other underground process vessels. Whereas an overland pipeline represents a plug-flow reactor, ideal conditions for a relatively slow series of reactions as are involved in carbon sequestration are also obtained in the embodiment illustrated in Fig. 2.

It is noted that in the Fig 2 embodiment, the two overflow streams from the CCD system are handled separately. The overflow of the first thickener tank 90a is blended with the silicate slurry 36, incoming from the quarry site to form the circulating solution to be sent to the absorption chamber 28.

The balance of the process in relation to sequestration, separation and emplacement is as for the overland pipeline reactor case.
Example

Again with specific reference to Fig. 3, a non-limiting example process flow for carbon sequestration for the first system configuration 10 described herein (i.e. the system depicted in Fig. 1) will now be given, wherein for convenience, like parts to those shown in the foregoing embodiment have been numbered with like numerals.

Example 1

Table 1: Indicative mass balance figures from 1.000 MWe of black coal-fired electricity generation plant.

<table>
<thead>
<tr>
<th>Material</th>
<th>Per year</th>
<th>Per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CO₂ generated:</td>
<td>6.4 m. tonnes</td>
<td>800 t</td>
</tr>
<tr>
<td>(NKU)₂CO₃ to absorb 90% of this CO₂</td>
<td>1,600 t</td>
<td></td>
</tr>
<tr>
<td>Resulting quantity of NH₄HCO₃ formed</td>
<td>2,400 l</td>
<td></td>
</tr>
<tr>
<td>Water to make up 25% solution of NH₄HCO₃</td>
<td>7,200 t</td>
<td></td>
</tr>
<tr>
<td>Serpentine to absorb 90% of this CO₂, 80% eff.</td>
<td>17.2 m tonnes</td>
<td>2,150 t</td>
</tr>
<tr>
<td>Total slurry with NH₄HCO₃</td>
<td>9,350 t</td>
<td></td>
</tr>
<tr>
<td>Slurry density:</td>
<td>1.2 t/m³</td>
<td>1.2 t/m³</td>
</tr>
<tr>
<td>Slurry volume, m³</td>
<td>8,000 m³</td>
<td></td>
</tr>
<tr>
<td>Product (carbonate plus silica) solids:</td>
<td>20.6 m. tonnes</td>
<td>2,600 l</td>
</tr>
<tr>
<td>Slurry pipe dia. with 3 m/s velocity:</td>
<td>1.0 metres</td>
<td>1.0 metres</td>
</tr>
<tr>
<td>Ammonia lost due to SOx (90% recovery via Eq. 10)</td>
<td>4,660 t</td>
<td>0.2 t</td>
</tr>
<tr>
<td>Ammonia lost due to NOx</td>
<td>3,000 l</td>
<td>0.37 t</td>
</tr>
<tr>
<td>Total losses of ammonia:</td>
<td>4,600 l</td>
<td>0.57 t</td>
</tr>
</tbody>
</table>

Table 1 provides an indicative detailed mass balance for a carbon dioxide sequestration process, assuming:

- 90 per cent carbon dioxide capture and sequestration from 1,000 MWe of black coal-fired electricity generation plant, which when operating in base-load mode might expect to generate annually 8,000 GWh of electricity;
- where on a dry ash-free basis, the coal is 81.3% by weight carbon and 0.65% sulphur (as S) and the flue gases contain 400 ppm NOx.
An advantage of the carbon dioxide sequestration process 100 and systems 10, 20 according to embodiments of the present invention is that by selecting ammonia as a catalyst/promoter, a single integrated process can be provided for both capture and sequestration of carbon dioxide. In an embodiment, sequestration of the carbon dioxide takes place in a reactor, in the form of a return pathway 52 of a pipeline 44, which advantageously connects the power station (i.e. the source of carbon dioxide) to the source/destination of the absorbent material being used in the process. In an alternative embodiment, where geological conditions permit, the reactor may take the form of an underground chamber which advantageously facilitates the reaction without requiring pressure-exchange and head-recovery equipment required for the pipeline embodiment.

Another advantage of the carbon dioxide sequestration process and systems is that the reaction kinetics may be improved by using ammonia. Therefore, by using ammonia and exploiting the heat generated by the exothermic reaction, the energy consumption of the process 100 can be kept to a minimum. As the reaction products are thermodynamically stable, carbon dioxide can be stored in a permanent stable solid form. Following from this, further advantages include lower operating and capital costs.

Persons skilled in the art will appreciate that further advantages may arise from carrying out certain steps of the aforementioned embodiments in isolation. For example, the catalytic effect of a solution of ammonia with an ammonium salt (that may be ammonium carbonate formed by exposing an ammonia-rich solution to a gas stream containing carbon dioxide) in the carbon dioxide sequestration process can also be utilised for extracting metals (e.g. magnesium, iron, nickel, copper and other metals present in the silicate rock) from metal silicates, such as magnesium-rich metal silicates.

In such an embodiment a solution of ammonia-rich ammonium carbonates in water may be mixed with a metal silicate (typically in slurry form) to allow the dissolution of magnesium ions by ammonia to recover the metal, in this embodiment a metal compound in the form of magnesium carbonate. The mixing may occur in an ammonia absorption chamber such as that previously described in connection with the preceding embodiments. Preferably the solution contains molecular ammonia in the presence of ammonium salts in solution, such as ammonium carbonate, to prevent the precipitation of magnesium hydroxide, hence allowing the dissolution of magnesium ions by ammonia to continue, substantially free of concerns over tendencies for otherwise...
insoluble magnesium hydroxide to coat, and restrict access to the silicate mineral by carbon dioxide and ammonia. A further advantage arising from this process is that after extraction of magnesium carbonate, other minerals (metals) present within the silicate rock are also amenable to recovery. The silicate rock may comprise mafic or ultramafic rocks (i.e. rocks with respectively a high or very high ratio of magnesium to silicon content).

Expressed another way, the catalytic effect of the ammonia follows from its tendency to form complexes (ammines) with certain metal ions including magnesium (Mg²⁺), divalent iron (Fe²⁺), copper (Cu²⁺) and nickel (Ni²⁺). The presence of ammonium salts notably the various carbonates formed from the reaction between ammonia and carbon dioxide prevents precipitation of the otherwise insoluble magnesium hydroxide. Magnesium carbonate is however insoluble in such an environment, so a precipitate of this compound will form from the reaction between magnesium hydroxide and ammonium carbonate, to yield ammonium hydroxide and free molecular ammonia in solution, the latter continuing to extract additional magnesium and other metals from the silicate rock through formation of ammine complexes until all such susceptible metals have been extracted.

Finally, it is to be appreciated that various alterations or additions may be made to the parts previously described without departing from the spirit or ambit of the present invention. The process is not limited to having a single two-stage continuous reactor, or a single tube-like reactor, as the process may be arranged to utilise alternatively configured items of equipment as necessary to accommodate process variables, arising from different source materials, capital and operating costs. For example, in the exemplary embodiment previously described the plant design is based on the emission of 800 tonnes CO₂/GWh generated from a state-of-the-art black coal-fired electricity generation plant. By comparison, the Bayswater Power Station and the Liddell Power Station, both in the Hunter Valley of New South Wales, Australia, able to generate 2,640 MWe and 2,040 MWe respectively, being older hence less efficient can be expected to emit between 850 and 900 tonnes CO₂/GWh.

Thus the concentration and rate of carbon dioxide emissions in the flue gas emitted by the power plant may vary such that the plant equipment design may be re-configured to accommodate these variables. For example, alternative equipment can be configured for the various heat and pressure exchange stations. The carbon dioxide
absorption zone and the scrubbing zone may be arranged in series in two separate vessels (rather than the nested configuration shown in Fig. 1). The conversion of carbon dioxide to insoluble carbonates may be limited to a lower value, such as 70% whilst still obtaining a good overall conversion from the reactor(s). As well, the corresponding solids concentration in the slurry feed may be higher or lower than 25% solids by weight. It is possible that the metal silicate solution may comprise a blend of metal silicates, e.g. mixture of serpentines and olivines, even pyroxenes. The reaction kinetics may require heat to be removed from the reactive solution (rather than heat addition as described above). These factors will impact and alter the system pressures.

There might be two or more pipelines for transporting the metal silicate solution and the reactive solution; because there are more pipelines, additional heat exchangers and pressure-exchange apparatus may be used. The power station flue gas may include additional pre-processing steps including flue gas desulphurisation (FGD) and selective catalytic reduction (SCR) to reduce concentrations of SOx and NOx respectively hence losses of ammonia from the system. Furthermore, the availability of services, such as steam and cooling water may require different equipment arrangements.

Any reference to prior art contained herein is not to be taken as an admission that the information is common general knowledge, unless otherwise indicated.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.
Claims:

1. A carbon dioxide sequestration process including the steps of:
   (i) scrubbing a gas stream containing carbon dioxide with a solution rich in normal ammonium carbonate that is able to absorb the carbon dioxide, whereby the carbon dioxide reacts with the ammonium carbonate to produce a solution comprising ammonium bicarbonate;
   (ii) passing a reactive slurry consisting of a metal silicate rock together with the ammonium bicarbonate solution through a reactor that is controlled so as to promote the reaction between the bicarbonate and the silicate rock to produce metal carbonate and silica.

2. A process in accordance with claim 1, wherein the metal silicate rock is mixed the normal ammonium carbonate solution prior to absorbing the carbon dioxide in step (i).

3. A process in accordance with claim 1 or claim 2, wherein the reaction causes the bicarbonate in the presence of the metal silicate to partially decompose so as to produce an aqueous phase enriched in molecular ammonia and carbon dioxide.

4. A process in accordance with claim 3, comprising the further step of cooling the aqueous phase such that free ammonia and carbon dioxide molecules combine to form ammonium carbonate salts in solution, the ammonium carbonate salts in solution arranged to be recovered for re-use in step (i) of the process.

5. A process in accordance with claim 4, comprising the further step of adding an alkali to the recovered ammonium carbonate in solution prior to being re-used in step (i).

6. A process in accordance with claim 5, wherein the alkali is calcium oxide and/or hydroxide.
7. A process in accordance with claim 6, wherein the calcium oxide is extracted from a flue gas stream prior to scrubbing in step (i).

8. A process in accordance with any one of the preceding claims, comprising the further step of introducing pulverised limestone into a source producing the carbon-dioxide rich flue gasses.

9. A process in accordance with claim 8, wherein the source is a coal-fired power station boiler and wherein the pulverised limestone is added upstream of an economiser section of the power station boiler.

10. A process in accordance with claim 2, wherein a portion of the mixed solution used to scrub the gas stream prior to discharge to the atmosphere is chilled to ensure that a quantity of free ammonia in the gases is below a threshold level.

11. A process in accordance with any one of the preceding claims, wherein the step of scrubbing the gas stream comprises exposing the carbon dioxide-containing gas stream to the solution as a spray.

12. A process in accordance with any one of the preceding claims, wherein the step of controlling the reactor comprises elevating at least one of a pressure and temperature of the reactor so as to enhance the reaction between the carbon dioxide and the metal silicate.

13. A process in accordance with any one of the preceding claims, wherein the reactor is a pipeline.

14. A process in accordance with claim 13, wherein the pipeline comprises multiple flow paths and wherein the reaction takes place along the length of one of the flow paths.

15. A process in accordance with claim 14, wherein another of the flow paths is utilised to supply the metal silicate slurry to the first stage.
16. A process in accordance with claim 15, comprising the further step of exchanging at least one of pressure and heat between the reactive slurry and the metal silicate slurry before and/or after the pipeline.

17. A process in accordance with any one of claims 1 to 12, wherein the reactor is a chamber located in use underground.

18. A process in accordance with claim 17, wherein the chamber is located at a depth that provides sufficient pressure by way of static head to enhance the reaction between the carbon dioxide and the metal silicate.

19. A process in accordance with any one of the preceding claims, comprising the further step of grinding a metal silicate rock to produce the metal silicate slurry.

20. A process in accordance with claim 19, wherein the metal silicate slurry comprises approximately 25% by weight finely ground metal silicate solids.

21. A process in accordance with any one of the preceding claims, wherein the metal silicate is a magnesium-rich silicate.

22. A process in accordance with claim 21, wherein the magnesium rich silicate is a serpentine and/or olivine and/or pyroxene.

23. A process in accordance with any of the preceding claims, comprising the further step of cooling the normal ammonium carbonate-metal silicate slurry prior to scrubbing.

24. A system for sequestering carbon dioxide from a gas stream, the system comprising:

(a) a first apparatus for removing the carbon dioxide from the gas stream and absorbing it in a normal ammonium carbonate solution whereby the carbon dioxide
reacts with the normal ammonium carbonate to produce a solution comprising ammonium bicarbonate; and

(b) a reactor for receiving a reactive slurry consisting of a metal silicate rock together with the ammonium bicarbonate resulting from (a), the reactor being controlled so as to promote the reaction between the bicarbonate and the metal silicate to produce a metal carbonate and silica.

25. A system in accordance with claim 23, wherein the reactor is the pipeline as defined in any one of claims 13 to 16.

26. A system in accordance with claim 23, wherein the reactor is the chamber as defined in any one of claims 17 or 18.

27. A system in accordance with any one of claims 24 to 26, wherein the first apparatus comprises an absorption chamber arranged to circulate the normal ammonium carbonate solution through the carbon dioxide to thereby absorb the carbon dioxide.

28. A system in accordance with any one of claims 24 to 27, wherein the reaction of the bicarbonate with the metal silicate further produces an aqueous phase containing molecular ammonia, carbon dioxide and water.

29. A system in accordance with claim 28, further comprising a cooling arrangement arranged to cool the aqueous phase such that free ammonia and remaining carbon dioxide molecules combine to form ammonium carbonate salts in solution, the ammonium carbonate salts in solution arranged to be recovered by a recovery arrangement of the system for re-use by the first apparatus.

30. A system in accordance with claim 29, further comprising a control arrangement arranged to add a controlled amount of alkali to the recovered ammonium carbonate in solution prior to returning it to the first apparatus for re-use.
31. A system in accordance with claim 29 or 30, further comprising a separation arrangement arranged to separate the recovered ammonium carbonate in solution from the insoluble metal carbonate-silica phase prior to recovery.

32. A system in accordance with claim 31, wherein the separation arrangement comprises a counter-current decantation (CCD) system.

33. A system in accordance with any one of claims 30 to 32, wherein the alkali is calcium oxide and/or hydroxide.

34. A system in accordance with claim 33, wherein the calcium oxide is extracted from the raw flue gas stream prior to scrubbing.

35. A system in accordance with any one of the preceding claims 24 to 34, comprising a feeder arranged to feed pulverised limestone at a source producing the carbon-dioxide rich flue gasses.

36. A system in accordance with claim 35, wherein the point source is a coal-fired power station boiler and wherein the pulverised limestone is fed into raw flue gasses upstream of an economiser section of the power station boiler.

37. A system in accordance with any one of claims 24 to 36, wherein the metal silicate comprises a magnesium rich silicate as defined in any one of claims 21 or 22.

38. In a pipeline, the provision of a first flow path that carries a metal silicate slurry for use by a first apparatus in a carbon sequestration process; and a second flow path that carries a reactive ammonium bicarbonate-metal silicate slurry from the first apparatus, wherein the second flow path is controlled so as to encourage the bicarbonate to react with the metal silicate and produce a metal carbonate and silica.

39. A method for causing a slurry consisting of metal silicate rock and an aqueous phase comprising ammonium bicarbonate in solution, to react so as to produce a metal carbonate, the method comprising the steps of:
positioning a chamber underground at a depth which is sufficient to provide a pressure in the chamber to enhance the reaction between the ammonium bicarbonate and the metal silicate so as to produce the metal carbonate; and providing the slurry to the chamber for a sufficient period to enable it to react.

40. A method in accordance with claim 39, wherein the slurry provided to the chamber is the reactive slurry produced in the process of any one of claims 1 to 12, or 19 to 22, when dependent on any one of claims 1 to 4.

41. A method in accordance with claims 39 or 40, comprising the further step of exchanging heat from the product of the chamber with the slurry provided to the chamber.

42. A method in accordance with claim 41, wherein the heat is exchanged in one or more heat exchanger units arranged in or at adjacent flow paths of the chamber product and the slurry.

43. A power station utilising a carbon sequestration system in accordance with any one of claims 24 to 37, the system arranged to sequester carbon dioxide from flue gas emitted by the power station.

44. A method substantially as hereinbefore described with reference to the accompanying drawings.

45. A system substantially as hereinbefore described with reference to the accompanying drawings.
Scrub gas stream containing carbon dioxide with a solution rich in ammonium carbonate that is able to absorb the carbon dioxide, whereby the carbon dioxide reacts with the ammonium carbonate to produce a solution comprising ammonium bicarbonate.

Pass slurry consisting of metal silicate rock together with ammonium bicarbonate solution through a reactor that is controlled so as to promote the reaction between the bicarbonate and metal silicate to thereby produce a metal carbonate and silica.
Pumping stroke
Pump cylinder under high pressure
(Pressure in high-pressure B main > pressure in high-pressure A main)

Return stroke
Pump cylinder under low pressure
(Pressure in low-pressure A main > pressure in low-pressure B main)

Figure 5
Figure 6

Serpentine from quarry

Grizzly

Primary crusher

-150mm

Grizzly

Secondary crusher

-20mm

Train loading

Live stockpile

Mine water

Slurry storage

Ground silicate mineral slurry, to process, -70 microns

Wet milling option shown, using ball and/or semi-autogenous grinding mills. Other options include dry grinding. It is assumed here, that rail transport is used; however pipeline transport such as illustrated in Fig 1 may be preferred depending on desired implementation.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.
BO1D 53/62 (2006.0 1) CO1B 31/20 (2006.0 1)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI and EPODOC: IPC marks BO1D/-, C01B3 1/20- and keywords such as carbon dioxide,- CO\textsubscript{2}, Sequest\textsuperscript{+}, Captur\textsuperscript{+}, Separat\textsuperscript{+}, Deposit\textsuperscript{+}, +Carbonat\textsuperscript{+}, Silica\textsuperscript{+} and similar keywords in Google patents and Esp@cenet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>X</td>
<td>AU 20082 17572 B2 (RICHARD HUNWICK) 28 August 2008 See claims 1, 3, 6-10, page 1 lines 30-34, page 2 lines 1-5, page 6 line 21, page 13 lines 25-27, page 16 lines 30-33, page 17 lines 1-5, page 3 lines 4-12 and lines 20-25, page 5 lines 14-21, claim 30, figures 1, 5, page 24 lines 8-12</td>
<td>1-43</td>
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</table>

* Further documents are listed in the continuation of Box C

X See patent family annex

* Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier applications patent but published on or after the international filing date

'L' document which may throw doubts on prior art claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'R' document member of the same patent family

Date of the actual completion of the international search
16 April 2010

Date of mailing of the international application
19 May 2010

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. +61 2 6283 7999

Authorized officer

HERAMB M BAL

AUSTRALIAN PATENT OFFICE
(ISO 9001 Quality Certified Service)
Telephone No: +61 2 6283 7966

Form PCT/ISA/2 10 (second sheet) (July 2009)
### Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:  
   because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 44, 45  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
   The claims do not comply with Rule 6.2(a) because they rely on references to the description and/or drawings.

3. Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.