A FEASIBILITY STUDY
ON
A TWO STAGE BENEFITS CO2 SEQUESTRATION TECHNOLOGY FOR FOSSIL FUEL POWER GENERATION

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- ## *SUMMARY*

The issue of emission and sequestration of green house gas, especially CO_2, becomes much hot and attracts international society to pay attention. The power generation plants firing fossil fuels, which is the biggest polluter in the world, emit huge amount CO_2 into atmosphere every day and causes a severe environment issue.

A segment of the technical processing of Chinese Fertilizer Industry applies spraying aqueous ammonia into synthesis gas to remove CO_2 from it for purification. Before composition of H_2 and N_2 base fine synthesis gas into ammonia, a part of the final product - aqueous ammonia - is re-circulated and sprayed into raw synthesis gas to remove CO_2 for its purification. The captured CO_2 by ammonia then forms ammonium bicarbonate as byproduct. This processing technology is mature. It has been applied by Chinese Fertilize Industry for more than 40 years. It continues to be used at present.

Initiated by this technology, one processing segment of this technology can be borrowed for a purpose of carbon sequestration. Aqueous ammonia may be sprayed into flue gas, exhausted by fossil fuel firing boilers, for carbon sequestration. At the first stage of

*benefits, the product of ammonium bicarbonate may be utilized as " **CO_2 Carrier**" for further sequestration treatment such as the ocean or geologic storage to instead CO_2 transportation by pipe line or cryogenic. It also can be conventionally used to fertilize plants to absorb more carbon dioxide by photosynthesis. It promotes a positive carbon cycle in the earth.*

*The ammonium bicarbonate is not quite stable when its temperature passes 60 C. During its transportation or being spread into soil, it decomposes into NH_4 and bicarbonate and some part of CO_2 might re-enter into air. In order to asses the value of this method as a direct "**CO_2 Sequester**" for geologic carbon sequestration, it is necessary to conduct a study to make sure how many CO_2 being captured, which will not release and not re-enters to air. It is a critical issue.*

The cost of this type CO_2 sequestration sounds effective, and it is especially suitable to developing countries, and attracts them to join international effort on carbon sequestration.

• *INTRODUCTION*

It is a very clear fact that Carbon Dioxide from energy is the major contributor to green house gas (GHG) emission. It emits almost 82 % of GHG to air comparing to other GHG gaseous. The GHG gas emission to air by human activities induces a great change of global climate in a short-term [1]. Based on a present CO_2 emission rate, the CO_2 concentration in atmosphere is expected to be double in middle of 21 century. Per a prediction by IPCC, it will result into a global warming. The atmosphere temperature might increase about 1.5-4.5 C and the sea level might rise up 0.25-0.5 m [1].

The power generation by fossil fuel firing is a major GHG pollution source regardless in developed or developing nations. In the world, the average fraction of power generation by fossil fuel firing is 51 % (coal 36 % + oil 9 % + gas 16 %). Fossil energy contributes 85 % of total world energy [3]. The fossil energy use will expand over the next several decades.

US is the biggest CO_2 emitter among developed countries and also in the world. The coal firing for power generation in US still exceeds 55 % at present. Gas firing gas is 9 % [3]. The coal fraction might increase due to recent power crisis in California.

China is the secondary largest CO_2 emitter in the world and the largest one among developing countries. China produces and consumes 10 % of the total world fossil fuel production. Therefore the carbon emission by China is also about 10 % of the world total.

Agriculture in most developing countries is a major business. It is easy to suffer a severe impact by climate change because agriculture is considerably sensitive to weather. Chinese agricultural experts indicated that due to the double CO_2 concentration and its related climate change, growth of rice, wheat and cotton will suffer a negative impact since the moisture evaporation from soil becomes fast, severe ocean storm being more often. It could cause, in average, 8% decreasing of agriculture production in China. Other developing counties may suffer a higher loss up to 10-12% [5].

Per estimating, the total carbon emission worldwide by fossil fuel firing is around 6 Giga-tons while 1.8 Giga-tons is contributed from power generation by firing fossil fuels.

In 1999 China produced 1004.7 TWh electricity which was generated by coal firing. The nation-wide average net coal rate of 1999, based on SPC (Chinese State Electric Power Cooperation) statistics, is 396 g/KWh (i.e. grams of standard coal burned to generate one kilowatt-hour electricity) [2]. Chinese power plants in 1999 had burned about 398 million-ton coal. Assuming one kilogram coal contents 70% carbon, a total of 278.5 Mega-tons carbon had been emitted into air in 1999, which was 15.47 % of the world total emitted by fossil fuel firing for power generation. Based on the forecast on the power demand, and 80 % of power by fossil fuel firing, the CO_2 emission in China will pass US in near future.

The importance of carbon sequestration now is gradually addressed by world nations. Various sequestration methods are under development and research. The following summarizes some major methods being undertaken or proposed:

• *MAJOR OPTIONS OF CO_2 SEQUESTRATION FOR FOSSIL FUEL POWER GENERATION*

1. DEEP OCEAN STORAGE

By purifying a mixed gas with CO_2 containing into pure CO_2, then compressed it upto10 MPa. Pressured CO_2 is injected into ocean bed under water for storage over there. The project in Sleiprer North Sea Norway is a sample, where CO_2 is pumped down to 3500 meters deep ocean bed for storage.

2. EOR

By liquefying a high concentration CO_2 gas and then delivery it through pipeline to (several hundred kilometers away) site, CO_2 is then pumped into an almost exhausted oil well to recovery oil and to increase the oil output. This is so-called Enhanced Oil Recovery (EOR) technology.

North Dakota Gasification Company in US & Weyburn Oil Field in Saskatchwen Canada have jointly undertaken an EOR project. In US there are 74 EOR projects being carried out. In China, Only very few preliminary tests of EOR projects had been conducted. The steam and boiler flue gas (approximately 12 % CO_2) was injected into an oil well for enhancing oil recovery. Indicated from their preliminary tests in China, the EOR effect by injection of boiler flue gas was quite successful.

3. ECBM

Purified CO_2 through a pipeline is pumped into coal mining bed to increase the recovery of coal bed methane. It is called as ECBM. The bench scale tests at a coal mine located in Fenn-Big basin in Alberta, Canada were completed. The gas pumped into was CO_2 and CO_2 mixed with N_2.

Chinese Coal Industry is now undertaking a feasibility study on ECBM.

- ***SPRAYING AQUEOUS AMMONIA INTO BOILER FLUE GAS TO CAPTURE CO_2 ---- A NEW METHOD PROPOSED BY THIS PAPER***

1. BRIEF DESCRIPTION OF THIS METHOD

This method proposed here is a technology of two-stage benefits on carbon sequestration technology [4].
The primary purpose of the first stage is to capture CO_2 by spraying aqueous ammonia into boiler flue gas. The product by reaction is the ammonium bicarbonate, which may be utilized as a carrier of CO_2 for further sequestration, such as ocean storage.
Also the ammonium bicarbonate is an ammonia base fertilizer. Chinese agriculture uses it for more than 40 years.
By sell ammonium bicarbonate to further users, including traditional and new applications, it can fully or partially cover the cost of spraying ammonia processing. Therefore the first stage benefit on carbon sequestration is mainly on the " Capture It As CO_2 Carrier" –"CO_2 Carrier".

When the ammonium bicarbonate is spread into field, it decomposes into NH_4 and HCO_3. The NH_4 is nutrition and absorbed by plant. The CO_2 within HCO_3 might more or less still remain under ground. The secondary stage benefit on carbon sequestration is depended on the fate of HCO_3. If a large amount of CO2 in HCO_3 will remain in underground as "geologic sequestration", it is the secondary stage benefit of this method on carbon sequestration.
There are several uncertain factors to be clarified and to realize the secondary stage benefits. The following discusses the key areas, which should be focused.

2. HISTORY BACKGROUND

The proposed method was hinted from a process segment of synthetic ammonia production [6]. It is widely applied by Fertilizer Industry to produce aqueous ammonia as agricultural fertilizer in China for more than 40 years. The raw synthesis gas contains CO_2, which must be removed for further treatments, then to compose into synthesis ammonia. The technology adopts to spay aqueous ammonia for CO_2 removing. The product formed by the purification processing is ammonium bicarbonate.
At ambient temperature ammonium bicarbonate is a white powder and stable. If the temperature exceeds above 60 C, the ammonium bicarbonate becomes unstable and, it starts gradually to decompose and to release NH_3 and CO_2.
Chinese agriculture uses it to fertilize rice growth for long time. The attached picture 1 is a photo of the ammonium bicarbonate fertilizer bag for retail sell.
The product of ammonium bicarbonate must be stored after produced and through transportation and distribution system to reach hands of final users. There is no report to declare a big loss during distribution in China. At present there are considerable amount of such fertilizer plants under operation in China.

The NH_4 is a nitrogen base fertilizer, and absorbed by plants. It promotes plant growth and increases the photosynthesis to further absorb more CO_2 from air. The bicarbonate, which remains in soil, might react with the alkaline oxides or alkaline hydro-oxides to form stable carbonates - $CaCO_3$ and $MgCO_3$ - for permanent capture of the carbon within soil.

The published papers from agriculture users in China have reported that by a long-term application of ammonium bicarbonate might cause soil hardening depending on the soil properties. It verified that the CO_2 in bicarbonate could be permanently remained underground. The problem of soil hardening concern might be improved by cultivation and by fertilizing method. It could allow the bicarbonate deeply penetration into earth crust.

3. FUNDAMENTALS

Spraying aqueous ammonia into synthesis gas to capture CO_2 and to form ammonium bicarbonate, is a serial complex gas-liquid chemical reaction. It could be in general expressed by the following chemical reaction [5]:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$

The actual reaction steps are complex, and through several intermediate reaction steps:

$$NH_3 + CO_2 = NH_2COONH_4$$

The formed NH_2COONH_4 further hydrolysis:

$$NH_2COOH_4 + H_2O = NH_4HCO_3 + NH_3$$

Then the NH_3 reacts with H_2O to form NH_4OH:

$$NH_3 + H_2O = NH_4OH$$

The hydrolyzed products NH_4HCO_3 reacts with NH_4OH to form $(NH_3)_2CO_3$

$$NH_4HCO_3 + NH_4OH = (NH_4)_2CO_3 + H_2O$$

The $(NH_4)_2CO_3$ then absorbs CO_2 to form ammonium bicarbonate:

$$(NH_4)CO_3 + CO_2 + H_2O = 2NH_4HCO_3.$$

4. IMPROVING STABILITY BY ADDITIVES

The Institute of Applied Ecology, Chinese Academy of Science has developed a method to stabilize the ammonium bicarbonate by adding very few amounts of additives [5,7]. It has patented (Chinese Patent NO. ZL90105012.1). The few amount stabilizing additive (Dicyandiamide, i.e. DCD) helps to co-crystallize the ammonium bicarbonate. The ammonium bicarbonate made by adding additives is named as long-term effect ammonium bicarbonate.

5. TECHNICAL DETAILS ON CO_2 REMOVING BY SPRAYING AMMONIA

From the period of 60's, Chinese chemical industry utilizes coal's shift reaction to produce synthesis H_2 and N_2, then further to compose synthesis gas into aqueous ammonia as primary product. The raw synthesis gas contents certain amounts of CO_2, CO and others as impurities. These impurities must be removed before composing process. Chinese technology applies to spray aqueous ammonia, which is a part of the primary product, into raw synthesis gas for CO_2 removing and raw gas purifying. CO_2 reacts with the aqueous ammonia and to form ammonium bicarbonate as secondary product, which is a nitrogen base fertilizer. Chinese Chemical Industry names this process by a term - "Carbonization" [6].

Within recent several years, the annual production of the ammonium bicarbonate varies around 8 million tons (accounted by pure ammonia weight), which is almost a half of the total production of nitrogen base fertilizer in China.

The attached Fig. 2 shows the overall processing flow chart. The Fig. 3 shows the details of "Carbonization Process". The Table 1 shows the components of synthesis gas at various locations.

The overall processing technology may be understood through the flow chart. A certain size coal or coke is fed into a fixed-bed gasifier. Air and steam are alternatively supplied into the bed to produce synthesis gas by shift reaction. After cooling down, raw gas enters to a storage tank. By removing dust, raw gas flows into a de-SOx system after being pressured. The sulfur-free synthesis gas is further compressed and sent into a scrubber system to remove most of CO by shift reaction. The gas then enters the carbonization reactor to remove CO_2. The semi-clean and CO_2-free synthesis gas is pressured again and enters the $CuSO_4$ washing tower to remove the residue of CO. After the above treatments, the synthesis gas becomes quite pure. The amount of CO+CO_2 is lower below 20 ppm. The clean synthesis gas then is pressured to 32 MPa for NH_3 composition. The primary product – aqueous - ammonia is produced by composition. A part of primary product NH_3 is re-fed into the loop for CO_2 removing. The reaction forms the secondary product-ammonium bicarbonate.

Note, after the aqueous ammonia being sprayed in carbonization tower, the concentration of CO2 sharply dropped from 29.6% down to 0.30%. It demonstrates that the spraying ammonia captures CO_2. It clearly indicates that the CO_2 removed by aqueous ammonia is quite efficient.

Note only the processing of carbonization is "borrowed" from the mature Chinese technology for CO_2 sequestration in this paper.

Table 1 The Component of the Synthesis Gas @ Different Processing Stages

Components %	Raw Synthesis % @point 1	Shifting Gas % @ point 2	Carbonization Gas % @ point 3	Finest Gas % @point 4

H2	**38.50**	**50.11**	**70.99**	**73.98**
N2	**21.19**	**16.61**	**23.53**	**24.60**
CO	**28.54**	**2.60**	**3.69**	**-**
CO_2	**10.16**	**29.60**	**0.30**	**-**
CH_4	**1.21**	**0.96**	**1.35**	**1.42**

* The locations of the points are marked @ Fig.2 the flow chart.

6. ECONOMICS

The cost of spraying aqueous ammonia for CO_2 sequestration is another key point for wide practical applications. The production cost of ammonium bicarbonate includes two parts: the cost for purchasing ammonia and the cost for daily operation etc. Here authors take Chinese marketing prices as an example for analysis.

- To produce one ton ammonium bicarbonate needs 0.25 tone ammonia;
- One ton ammonia costs 1500 RMB ($ 182 US)—price in NE-China region;
- To produce one ton ammonium needs 375 RMB ($ 46 US) ammonia;
- The marketing price of one ton ammonium bicarbonate is 600 RMB in China ($ 73 US);
- Without accounting operation cost, and based on the present market prices, there is 225 RMB ($27 US) ***gain*** for selling ammonium bicarbonate (carbon sequestration byproduct) to next users.

Therefore the economic of this method is attractive. The above estimation of economic effect is only accounted by sell ammonium bicarbonate to agriculture as traditional user. If its application extends to areas of EOR/ECBM or ocean sequestration, the profits will greatly increase.

• *KEY POINTS OF THE FIRST STAGE BENEFITS ON CARBON SEQUESTRATION*

1. REACTION CONDITION DIFFERENCE

The working principle of spraying aqueous ammonia into boiler flue gas for CO_2 sequestration, as authors proposed, is basically same procedure comparing to the carbonization segment of processing loop applied by Chinese mature synthesis NH_3 production. The differences are the chemical reaction conditions – CO_2 concentration - within reactors:

	Synthesis NH_3	***Capture CO_2 from Flue Gas***
CO_2 concentration %	***30***	***10-14***
Reaction Pressure	***ambient***	***ambient***
Temperature C	***150***	***slightly above ambient***

2. NETL TESTS

Someone may concern the differences on the reaction conditions, which might become a problem to apply the spraying ammonia for CO_2 sequestration of boiler flue gas. Dr. Yeh, NETL/DOE/USA has carried out tests of spraying aqueous ammonia to a 15% CO_2 + 85% N_2 blended gas for CO_2 sequestration [8]. NETL tests verified that under the ambient conditions, 97% CO_2 of blended gas was removed by 28% aqueous ammonia solution. If the aqueous ammonia solution concentration reduced to 10%, the 70% CO_2 from blended gas was removed.

Therefore there should be no problems by introducing flue gas from a fossil fuel fired boiler directly into CO_2 scrubber tower for CO_2 sequestration.

NETL test results strongly support authors proposal. It will greatly attract fossil fuel fired power plants to adopt it for CO_2 sequestration. The first stage benefit **–** "***CO2 Carrier***"-- is technically ready at present for application.

3. FIRST STAGE BENEFITS

- ***CO_2 CARRIER*** **FOR OTHER SEQUESTRATION OPTIONS**

The first stage benefits on carbon sequestration is its unique feature of " ***CO_2 Carrier***". The captured CO_2 contains within ammonium bicarbonate, which is a white crystal. It likes other powder goods, which can be easily distributed to anywhere for applications by ordinary existing transportation systems without any extra investment. It can be shipped to site for deep ocean or geologic storage. It can be sold for EOR and ECBM applications. It also can be sold to agriculture for conventional fertilizing.

Deep ocean has a huge capacity for carbon sequestration, but normally its dumping site is far from CO_2 sources. There are few options being considered to ship CO_2 to site for injection, such as via pipe line or by cryogenic to get solid state carbon dioxide then shipping to site with refrigerator transportation way. Comparing to other CO_2 shipping options, it is the most valuable and cost-effective way.

- **AGRICULTURE**

As the benefits on agriculture, comparing to ordinary ammonium bicarbonate, the long-term effective ammonium bicarbonate increases the fertilizer utilization about 10 %. It promotes the development of plant roots, and in turn to help plant growth well. The plant photosynthesis therefore is enhanced to absorb more CO_2 from atmosphere. It reduces 75 % of N_2O releasing from soil, comparing to use of ordinary ammonium bicarbonate [7].

- **AMMONIA SUPLING**

The countries with natural gas resource might sell their ammonia to users. They can manufacture ammonia by natural gas with lower cost than other suppliers.

- **INTERNATIONAL EFFORTS**

The green house gas effect is a global concern. It is no boundary. The carbon sequestration needs more countries to join the international efforts. The most developing countries are depended on firing fossil fuel to generate power. The China is the second largest GHG emitter in the world next of US, but it will excess US in near future based China economic development.

This ammonia spay method is a low investment and cost-effective way. The product by ammonia spray is a fertilizer, which is high demand in developing countries. With this method for carbon sequestration, as expected many developing countries would like to join the international carbon sequestration activities.

- ***THE TARGET OF THE SECONDARY STAGE BENIFTS & KEY TECHNICAL POINTS***

The target of the secondary stage benefits on CO_2 sequestration is no longer to be limited within the "***CO_2 Carrier***". It should be extended into the area of geologic sequestration as "***CO_2 Sequester***". When the ammonium bicarbonate is spread into field for agricultural fertilizing, the most of captured carbon in bicarbonate should remain under ground for a permanent sequestration. This is the concept of "***CO_2 Sequester***". To achieve this final target, there are several technical points must be addressed.

1. KEY TECKNICAL POINTS

There are few points of this method needed to be further investigated.
The critical one is the fate of the bicarbonate after the ammonium bicarbonate is spread into soil. The fraction of the CO_2 released from bicarbonate and re-entering into air is a criterion to evaluate the value of this method for "***CO_2 Sequester***". After the ammonium bicarbonate being spread into soil, it decomposes into NH_4 and HCO_3. The NH_4 is plant nutrition. However the fate of bicarbonate is still not clear.

There are probably three ways for bicarbonate:

It might be absorbed by plants and becomes a biomass. However by traditional agricultural theory, plant does not directly absorb the bicarbonate from soil. Due to the CO_2 releasing from soil, the CO_2 concentration within in the plant surrounding area above the ground is much higher than other locations. It certainly promotes plant photosynthesis to absorb more CO_2 and plants growth quickly to make more biomass. Scientists of Chinese SIAE have conducted preliminary tests to verify the promotion by a higher CO_2 concentration. They plan to conduct more tests soon. The more CO_2 absorbed by plant photosynthesis helps a good carbon circle in the Earth. Only very few believes that the plant roots can directly absorb bicarbonate. However so far there is no evidence to support. Only C_{14} isotopic bicarbonate tests can verify it.

The earth crust contents alkaline oxides such as CaO and MgO. The amount varies from area to area. The bicarbonate existing in soil might penetrate to deep and react with these alkaline oxides to form $CaCO_3$ and $MgCO_3$ for permanently geologic carbon sequestration.

The last way, which creates a negative impact to this method. That is the bicarbonate decomposes and releases CO_2 and the CO_2 re-enters into air.

2. R&D FOR THE SECONDARY STAGE BENEFITS

There are two R&D steps might be taken to learn which way is dominate & what is their contribution:

- Carbon 14 isotope tracing. It is accuracy but cost is high.
- Lump sum measurement. Within an enclosure system, where have plants and fertilizing by ammonium bicarbonate, the way of carbon dioxide can be

determined. It is a cheap way. NPCC and SIAE in China have an intention to conduct it.

- ***CONCLUSIONS***

1. The GHG emission by fossil fuel firing for power generation is the biggest GHG source in the world. To effectively control the GHG by firing fossil fuels, The GHG gaseous from boiler flue gas should be sequestrated before it exhausted in to environment.
2. Chinese fertilizer industry produces the synthesis ammonia and ordinary/long-term effect ammonium bicarbonate for many years. To remove CO_2 from the raw synthesis gas, aqueous ammonia spraying is adopted for purification. The annual production fraction of ordinary and long-term effect ammonium bicarbonate is still greater than 50% of total nation-wide fertilizer production at present. The technology is mature.
3. By hint from the above Chinese technology, spraying aqueous ammonia into boiler flue gas for carbon sequestration is technically ready. The first stage benefits as "***CO_2 Carrier***" on carbon sequestration highlights many advantages.
4. The fate of bicarbonate after ammonium bicarbonate being spread into soil is a key issue. It relates whether the method can be extended the benefits of ammonium bicarbonate from a "***CO2 Carrier***" into a "***CO2 Sequester***" for geologic carbon sequestration.
5. R&D on the issue of the second stage benefits should be conducted ASAP.

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- ***ATTACHMENTS***

Fig. 1 The photo of a commercial fertilizer bag
Fig. 2 Overall Flow Chart of Synthesis Ammonia
Fig. 3 Flow Chart of Carbonization Process