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ARTICLE TYPE

New Technology for Post-Combustion Abatement of Carbon Dioxide via in situ Generated Superoxide Anion-Radical

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A novel chemistry for the efficient sequestration of carbon dioxide via swift nucleophilic attack by superoxide anion is disclosed. Relatively stable aqueous solution of the latter is generated in situ by contacting alkali hydroxide solution with hydrogen peroxide at pH 11. Using a simple gas liquid scrubber containing the above blend, carbon dioxide is quantitatively absorbed from a gas stream under ambient conditions and is totally converted to aqueous carbonate. The aqueous solution containing the in situ generated superoxide specie was found to be far more effective for absorbing CO_2 than the standard ethanolamine or soda caustic solutions.

Introduction

Climate change is considered to be one of the greatest environmental threats of our times. [1] The atmospheric concentration of greenhouse gases has increased steadily over the past century and is approaching disturbing levels. [2] Current research shows that there is an excess of approximately 3.9% CO_2 with respect to the natural ‘‘carbon cycle’’. [3] The atmospheric warming is associated with a global climate change and a planetary temperature increase. [4] The growing evidence that links the greenhouse gas, carbon dioxide and global climate change highlights the need to develop cost effective carbon sequestration schemes. [5]

The largest source of CO_2 emission (nearly sixty percent) comes from power generation, public electricity and heat production using fossil fuel combustion. [6] The International Energy Agency (IEA) predicts that fossil fuels will remain the dominant source of energy until 2030. [7] Other pollution sources are combustion systems such as cement kilns, furnaces in industries and iron and steel production plants. In these large-scale processes, the direct firing of fuel with air in a combustion chamber has been (for centuries) the most economic technology to extract and use the energy contained in the fuel. Therefore, the strategic importance of post-combustion capture systems becomes evident when confronted with the reality of today’s sources of CO_2 emissions. [8]

The removal of a gaseous component through contact with a liquid is known as wet scrubbing. Wet scrubbing can be divided into processes where there is a chemical reaction between the sorbate and the sorbent and others where the sorbate is just physically dissolved into the sorbent phase. [9]

A wide range of different methods for carbon dioxide treatment already exists. [10] Adsorption, absorption, ionic liquid technologies were reported and even biological and membrane treatment was suggested. [11] We can characterize these technologies in two main groups of abatement methods, reversible process (absorption/desorption) and mineralization technologies. However, relatively few reversible methods have gained any measure of acceptance from an industrial viewpoint. [12] Currently, CO_2 can be removed from flue gas and waste gas streams by absorption into amine solutions such as mono-ethanolamine (MEA) to form the ammonium carbamate, this is a well understood and widely used reversible technology. [13] MEA has a high CO_2 absorption capacity and it readily reacts with CO_2 under normal conditions. Nevertheless, there are still several serious drawbacks to this methodology: the uptake of water into the gas stream causes serious corrosion in the process infrastructure, the loss of volatile amines and evaporation of water during the driving-off of CO_2 results in an increase in operating costs. [14] In addition, the thermal release of CO_2 from the carbamate solution requires a substantial energy input. The thermal instabilities of both MEA and the carbamate lead to decomposition which can cause environmental problems. [15] Additionally, flue gases coming from coal combustion will contain not only CO_2, N_2, O_2 and H_2O, but also air pollutants such as SOx, NOx, HCl, HF, particulates and other trace organic and inorganic contaminants. [16] Those contaminants can react with MEA to from non sedimentary and heat stable salts such as ammonium nitrate, ammonium sulfate etc. [17] Nonetheless, MEA is currently the industry standard for CO_2 and other acidic gasses reversible absorption technologies, but it is certainly not an optimized reagent, rather one of convenience. [18]

The alternative, irreversible (mineralization) technology for carbon dioxide abatement from flue gas is by aqueous alkaline solutions to generate inorganic carbonates. These processes are known since the 70s of last century. [19] The absorption of CO_2 into strong hydroxide solutions was shown to proceed via an irreversible second order reaction between CO_2 and OH^- ions. [20] Unfortunately, this absorption technology is effective only, under conditions of strong caustic solutions, with low humidity, at high temperature and long liquid/gas contact time. [21] Consequently CO_2 absorption by alkali did not develop into a practical method for carbon dioxide post-combustion capture. [22] In the last decades researches have proposed scores of different interesting technologies for complete mineralization of CO_2. [23] However these technologies have several serious drawbacks. The main drawbacks are slow reaction rates and special reaction conditions. Consequently they cannot be applied as industrial technologies.

In this study we advocate the *in situ* generated superoxide anion radical as a unique reagent for the swift capture, abatement and total mineralization of carbon dioxide. Reactive oxygen species (ROS) such as peroxide and superoxide reagents were tested previously as traps for carbon dioxide. [24] Currently, potassium superoxide is utilized in self-contained breathing equipment for the generation of oxygen gas. [25] The superoxide radical anion is an ROS that possesses both anionic and free-radical properties. The latter is a powerful and effective nucleophile in polar aprotic solvents such as dimethyl sulfoxide. [26] Conversely, in protic solvents, e.g. water, it is presumed inactive, owing to its strong solubility by this medium and its rapid hydrolysis. Aqueous superoxide is therefore not an obvious candidate for practical applications.

We have recently described a novel method for the in-situ generation of a remarkably water stable superoxide anion by reacting sodium or potassium hydroxide with hydrogen peroxide under ambient conditions. [27] This reagent was effectively utilized for the total mineralization of carbon tetrachloride and other polyhalogen compounds. [28] In this manuscript, we demonstrate the unique nucleophilic properties of the as-prepared superoxide anion in water and its instantaneous reaction with carbon dioxide which renders it most likely, the superb reagent for abatement of CO_2 from flue gas.

It should be noted that a technologies for H_2S and CO_2 absorption into alkaline solutions containing an oxidizing agent are already known. [29] However, our new proposed technology has a different reactive species (superoxide) and different final products. The end products of this proposed process are carbonate salt and oxygen that can be used in various processes and products in the chemical and food industry.

Experimental Section

Reagents and Materials

30% aqueous hydrogen peroxide solution was purchased from Bio Lab Ltd. 100 % Air (purity > 99.9%), 30% carbon dioxide in air (gas purity of all components > 99. 5%), 10% nitric oxide dioxide in N_2 (gas purity of all components > 99. 99%), 10% nitrogen dioxide in N_2 (gas purity of all components > 99. 6%), and 10% sulphur dioxide in N_2 (gas purity of all components > 99. 6%), gas cylinders were purchased from Maxima Ltd. Sodium hydroxide, potassium hydroxide, mono ethanol amine were purchased from Sigma-Aldrich Ltd and were used without further purification.

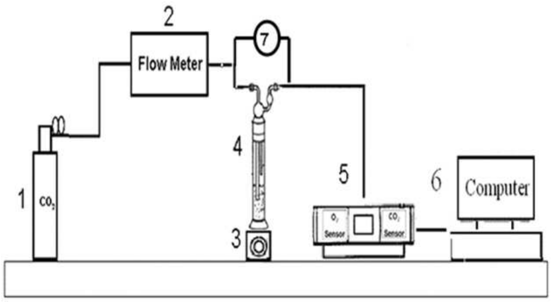

Figure 1: Schematic assembly of the CO_2 absorption system. 1- Carbon dioxide cylinder, 2- flow meter, 3-magnetic stirrer, 4- scrubber, 5- CO_2/O_2 gas analyzer with data logger, 6-computer, 7-bypass.

Physical Measurements

FTIR (Fourier transform infrared spectroscopy) studies were conducted using Peact IR 4000, manufactured by Mettler-Toledo Ltd. XRD (X-ray diffraction) studies were conducted using X-ray diffractometer, Range: 1100 <2θ°> 1680 , D8 advance by Bruker AXS. EPR spectra were recorded using a Bruker EMX-220 X-band (υ = 9.4 GHz) EPR (electron paramagnetic resonance spectroscopy) spectrometer equipped with an Agilent 53150 A frequency counter at room temperature (RT, T = 295 K). To achieve a better signal-to-noise ratio for weak fast decaying signals, each 1024 point EPR spectrum was recorded in over-modulation mode using magnetic field modulation frequency of 100 kHz and modulation amplitude of 0.3 mT, microwave power of 10 mW and 16 fast (10 s) coherent acquisition scans. Processing (base line correction, digital filtering etc.) of EPR spectra was performed by using Bruker WIN-EPR software, simulations of spin adducts were performed using Bruker WINEPR SimFonia and NIEHS/NIH P.E.S.T. WinSim2002 and OriginLab Corp. Origin® software. CO_2 concentration was determined using a gas analyzer with IR detector (the range are 1% - 100%) manufacture by Emproco Ltd.

CO_2 absorption system

Our CO_2 absorption system components: hydroxide base, hydrogen peroxide 30% and experimental post-combustion flue gas (30% of CO_2 gas in 70% of air). Obviously air is a mainly a mix of (oxygen and nitrogen). This system is close enough to natural post-combustion flue gas composition. Post-combustion flue gas contains mainly CO_2, O_2, N_2 and evaporated water. Our experimental post-combustion flue gas excluded water since the absorption scrubber included high water concentration.

Carbon dioxide source is a gas cylinder containing 30% CO_2 mixed with air (in Figure 1). The gas flows through the FM (flow meter) (2) in a flow rate of 1 lit/min and then into the scrubber (4), the scrubber contains 0.25 mol hydroxide base in 30 ml distilled water and 0.375 mol of aqueous hydrogen peroxide 30%. The scrubber solution is mixed with a magnetic stirrer (3). The initial CO_2 concentration was measured by using a bypass, through which the flue gases flow directly into the analyzer, thus determining the CO_2 concentration at time zero.

Subsequently the absorber trap was connected and the CO_2 gas concentration in the outlet of the trap was measured by an infrared (IR) CO_2/O_2 analyzer (Emproco Ltd) with a range of 0-100% (5). Gas analyzer connected directly to computer (6). All experiments were conducted at an average temperature of 25^oC with atmospheric pressure. Gas/Liquid contact time was adjusted to be 0.01 sec. The scrubber has a total volume of 100 cm^3 and total diameter of 3 cm, the distance between the bottom of the gas bubbling tube and bottom of the scrubber is 2 cm and bubbling tube inner radius/bubble diameter is 0.5 cm. The end product of CO_2 absorption process detected by means of analytic equipment such as FTIR, XRD, CO_2/O_2 analyzer, EPR and pH-meter.

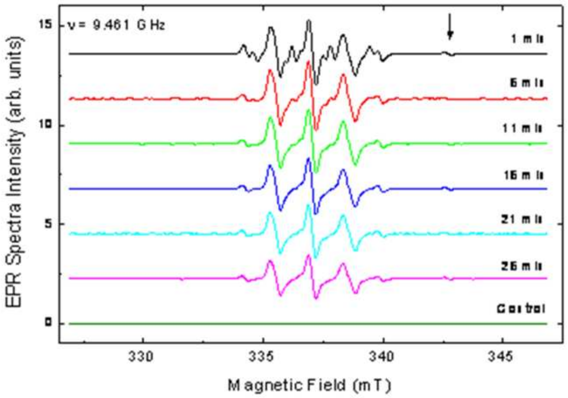

Figure 2: Detection and time evaluation of superoxide EPR spectra. Reaction conditions: 200 mmol sodium hydroxide, 300 mmol Hydrogen peroxide and 200 mmol DMPO. Arrow points out artifact signal with g = 1.973 appearing in all EPR spectra of superoxide-DMPO samples.

Absorbed amount calculated according to mmol of sorbate(CO_2) / g of sorbent (superoxide). E - is the efficacy of CO_2 removal (conversion) [30] calculated as shown in Equation 1. The E values were measured under different reaction conditions, including stirring speed, gas flow rate, hydroxide and hydrogen peroxide concentration. E and conversion is a percentage of utilized sorbate, according to monitoring of sorbate (CO_2) decreases and carbonate salt increase. This definition is universal and matches variety of treatment process in variable conditions.

$$E = \frac{C_i - C_o}{C_i} \cdot 100$$

Equation 1: The definition of E - CO_2 Efficiency of removing. C_i and C_o are the concentrations of CO_2 in the inlet and outlet gas streams, respectively.

Results and Discussion

Absorption of carbon dioxide by sodium or potassium superoxide

Carbon dioxide is thermodynamically and kinetically stable. However, it is acidic in nature and the carbon atom is electrophilic and can be swiftly attacked by bases and by nucleophiles. [31] Superoxide is known as a powerful, stable and effective nucleophile in polar aprotic solvents, such as DMSO (dimethyl sulfoxide). [32] Conversely in protic solvents, it suffers from rapid hydrolysis and disproportionation, (Equation 2). [33]

$$2KO_2 + H_2O \rightarrow 2KOH + 1.5O_2$$

Equation 2: Spontaneous hydrolysis of superoxide in aqueous media.

At a first glance aqueous superoxide is not appropriate for CO_2 absorption. Nonetheless, we proposed herewith a new in situ technology for alkali superoxide generation by blending sodium or potassium hydroxide and hydrogen peroxide in aqueous solution at ambient temperature and pressure. We have shown that the formation of superoxide proceeds in two steps: first formation of alkali peroxide that is then oxidized by hydrogen peroxide to superoxide. [27]

$$2MOH + H_2O_2 \rightarrow M_2O_2 + 2H_2O$$
$$M_2O_2 + 2H_2O_2 \rightarrow 2MO_2 + 2H_2O$$

Equation 3: Spontaneous formation of supreroxide anion by interaction of hydroxide and hydrogen peroxide in solution (M = Na or K).

This unique condition evidently renders the anion-radical to be a stable and effective nucleophile in aqueous environment. The stability of superoxide radical in water is already confirmed. [34] This stable and effective nucleophile can promptly attack and totally mineralize carbon dioxide, as shown in Equation 4.

$$CO_2 + 2MO_2 \rightarrow M_2CO_3 + 1.5O_2$$

Equation 4: Absorption of carbon dioxide by superoxide (M = Na or K).

Commercial superoxide radicals are very unstable with very short lifetimes. Therefore, they can often be detected only indirectly by capturing them with spin trappers. [35] Nitrone spin traps are widely used for monitoring free - radicals in numerous biological and chemical reactions. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) is recognized as the most efficient nitrone spin trap for detecting superoxide radical. [36] Generation of our superoxide radical in aqueous solution was detected by EPR spectroscopy, as shown in Figure 2.
Comparison of the efficacy of CO_2 removal (E) by caustic base (sodium hydroxide) versus its capture by superoxide mixture ($NaOH/H_2O_2$) is shown in Figure 3 and Figure S1 in the supporting information. Superoxide generation involves the mixture of H_2O_2 and NaOH as initial reagents and Na_2O_2 as an intermediate by product. Clearly, hydrogen peroxide is not an effective CO_2 absorbent. Thus, hydrogen peroxide alone is inert to CO_2 (absorbed amount of 0 mmol/g). Similarly, sodium peroxide alone cannot ensure CO_2 absorption at aqueous environment, due to fast decomposition (absorbed amount of 0 mmol/g).

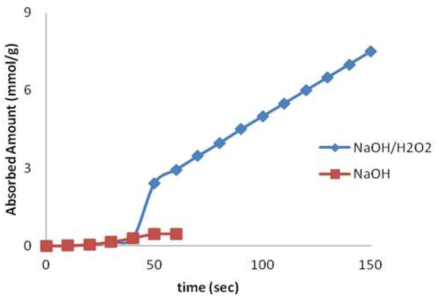

Figure 3: Hydroxide vs. superoxide as CO_2 absorber under identical conditions. Reaction conditions: 0.25 mol sodium hydroxide, 0.375 mol hydrogen peroxide vs. 0.25 mol sodium hydroxide at room temperature and with CO_2 flow rate of 1 lit/min, the scrubber contains 30 ml distilled water.

Alkali Base	CO_2 efficacy of removal (%)	Absorbed amount (mmol/g)
Sodium hydroxide	100	12.5
Potassium hydroxide	98	12.25
Calcium hydroxide	25	3.12

Table 1: Abatement of CO_2 by different alkali bases combined with hydrogen peroxide. Reaction conditions: 0.25 mol of hydroxide base, 0.375 mol hydrogen peroxide at CO_2 flow rate of 1 lit/min, the scrubber contains 30 ml distilled water, reaction time 250sec.

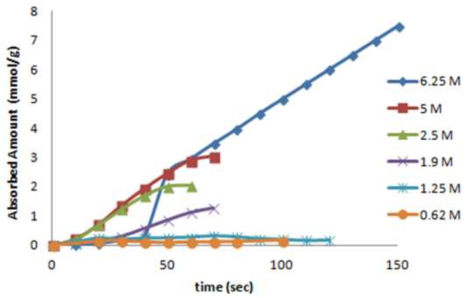

Figure 4: CO_2 absorption as function of sodium hydroxide concentration. Reaction conditions: 0.625-6.25 M of sodium hydroxide, 0.375 mol of hydrogen peroxide at 30 ml of distilled water and CO_2 flow rate of 1 lit/min, at room temperature and standard pressure.

Alkali absorbents have high absorption capacity for carbon dioxide at very specific conditions of temperature, pressure, humidity and exposure time.[37] However, at ambient temperature and pressure and short exposure time the CO_2 removal efficacy is less than 20% (absorbed amount of only 2.2 mmol/g) and the kinetics of the process is extremely slow.[38] On the other hand, reaction rate with peroxides is much faster, five orders of magnitude larger than hydroxides.[39] As expected, in the absence of hydrogen peroxide the absorption reaction performed poorly, less than 20% absorption, compared with 100% of CO_2 removal efficacy (absorbed amount of 5 mmol/g in 100 seconds) by the combined system of hydrogen peroxide and sodium hydroxide. Further, the absorption kinetics also improved for combined system, absorbed amount of 12.5 mmol/g in 250 seconds with the same quantity of alkali base (0.25 mol). We may safely conclude that sodium superoxide is a superior nucleophile and CO_2 absorber than sodium hydroxide.

Effect of the nature and concentration of the base

We propose a technology for the *in situ* formation of superoxide anion based on blending an alkali base and hydrogen peroxide. The nature and concentration of alkali base is one of the significant parameters in CO_2 absorption reaction. We examined the CO_2 absorption efficiency with different bases namely sodium, calcium and potassium hydroxide under otherwise identical conditions. The results are shown in Table 1 and in Figure S2 in supporting information. In the superoxide generation reaction, the alkali base is an essential bi-functional reagent. The main role of the alkali base is to control the total reaction pH. Under conditions of pH less than 11, super oxide generation is insignificant.[40] The second role of the alkali base is to balance and stabilize the superoxide reagent. However, superoxide which is too stable can decrease the nucleophilic activity and reduce the CO_2 removal efficacy (absorption). Since the atomic radius increases in the order of $Na^+ < K^+ < Ca^{2+}$. Sodium superoxide is expected to be more aggressive reagent and consequently it was selected as the reagent for the CO_2 sequestration. We measured the absorption of CO_2 at different concentrations of sodium hydroxide while maintaining the hydrogen peroxide concentration constant at 12M. Results are shown in Figure 4 and Figure S3 in supporting information. Sodium hydroxide concentration is an important parameter for effective superoxide radical generation. At concentration of less than 2.5M, superoxide production is very insignificant. However, at concentration of 6.25M superoxide radical formation is optimal. Therefore, the optimal sodium hydroxide concentration that allows the most favourable carbon dioxide absorption rate was 6.25M. It should be noted, that working at hydroxide concentration higher than 6.25M resulted in inferior absorption rate.

Effect of hydrogen peroxide concentration

We tested the role of hydrogen peroxide concentration in the absorption process. Results are exhibited in Figure 5 and Figure S4 in supporting information. It is apparent that a concentration of at least 9.25M is essential to attain effective absorption of CO_2. This is the optimal concentration for full stoichiometric reaction of alkali base with H_2O_2. Under conditions of concentration less than 5 M, the superoxide creation is very insignificant.

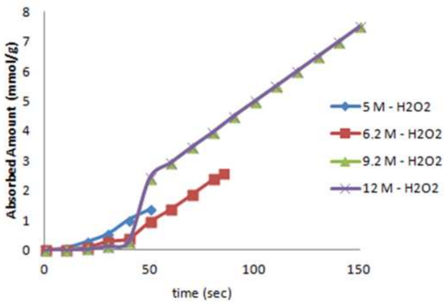

Figure 5: Carbon dioxide absorption as function of initial H_2O_2 concentration. Reaction conditions: 0.25 mol of alkaline in 30 ml distilled water and CO_2 flow rate of 1 lit/min, at room temperature and standard pressure.

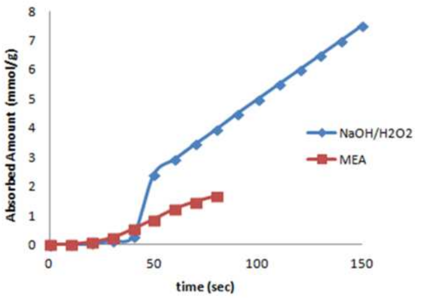

Figure 6: Superoxide vs. MEA absorption of CO_2. Reaction conditions: 0.25 mol sodium hydroxide in 30 ml distilled water, 0.375 mol of 30% hydrogen peroxide, total volume of 42 ml and CO_2 flow rate 1 lit/min. MEA: 0.5 mol in water, total volume of 42 ml, CO_2 flow rate 1 lit/min.

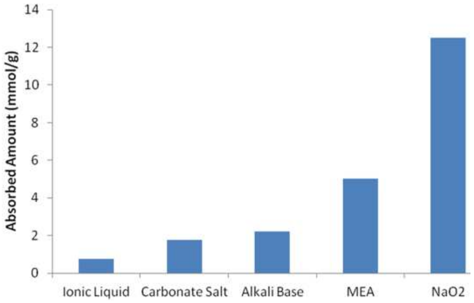

Figure 7: Total absorbed amount in different CO_2 absorption scrubbers. Reaction conditions: 0.25 mol of sodium hydroxide or sodium carbonate, 0.5 mol of MEA or ionic liquid (BMIMF) and 0.25 mol of superoxide at CO_2 flow rate of 1 lit/min, reaction time 250 sec.

Benchmarking of the proposed new system with the leading market technology for CO_2 abatement

Absorption of carbon dioxide by mono ethanolamine (MEA) is the standard industrial (reversible) carbon dioxide capture technology. [41] The MEA absorption process consumes substantial amount of thermal energy particularly for the recovery of CO_2 and regeneration of the sorbent. The total energy demand for both steps are is estimated at 330-340 kWh per ton of CO_2 recovered. [42] Generally, MEA absorption process consumes around 20- 30% of the total power generated, not including transportation and storage cost. [43] Transportation and storage are the most expensive ingredients of this technology. Moreover, carbon dioxide storage is a major environmental problem. [44]

Our proposed technology advises two different approaches, reversible and irreversible processes. The first is via production of alkali carbonate without CO_2 recovery (irreversible with total mineralization of CO_2). The energy penalty in this alternative is almost negligible (few percent of power loss). [45] The economic estimation of reagents cost and availability is compatible with Euro 2020 regulations. This type of final product (solid useful and environmental friendly product without CO_2 recovery) can solve a major problem of carbon dioxide storage in CCS (carbon capture and storage) technologies. The other option is (reversible cyclic absorption/desorption) process. The sorbent regeneration and CO_2 recovery by using an improved causticization cycle. [46] The heat requirement in this route is similar to the heat demand for the sorbent regeneration in theMEA - based CO_2 capture systems. However, in this study we do not attempt to present a cheaper system for CO_2 absorption. This study presents new, effective and environmentally friendly approach for the treatment of gases emission during fossil fuel combustion process.

We experimentally compared the absorption rate and the overall capacity of the proposed sodium superoxide technology with that of MEA based systems under identical (ambient) reaction conditions. The results are shown in Figure 6 and Figure S5 in supporting information. Similarly, we evaluated the absorption capacity of superoxide technology versus other leading reversible and irreversible (mineralization) technologies such as alkali bases (irreversible), carbonate salts (irreversible and reversible) and ionic liquid (reversible) absorption systems under identical reaction conditions. Results are shown in Figure 7 and Figure S6 in supporting information. As shown below the superoxide methodology has a clear kinetic and conversion advantage over the contending methods MEA (~40% CO_2 absorption, 5 mmol/g), sodium hydroxide (~18% CO_2 absorption, 2.2 mmol/g), sodium bicarbonate (~14% CO_2 absorption, 1.75 mmol/g) and ionic liquid (~5% CO_2 absorption, 0.75 mmol/g) carbon dioxide absorption technologies. Conversely, our new scrubbing system allows for abatement of 100% of carbon dioxide emissions (12.5 mmol/g) in aqueous solvent at room temperature and atmospheric pressure.

Flue gas from coal combustion process

The flue gases emitted from coal combustion will naturally contain not only CO_2 but also N_2, O_2 and H_2O and hazardous air pollutants such as SOx, NOx, fly ash and other traces of organic and inorganic contaminants. Our new technology allows the simultaneous absorption of CO_2 and oxidation and mineralization of SO_x and NO_x to sodium sulphate and nitrate respectively. More than 90% removal of these contaminants, both with initial concentration of 1000 ppm, was realized using the above experimental system, as shown in Figure 8. The real gas stream from coal post combustion process contains 12% of CO_2 and thousands of ppm of NO_X and SO_X. This disproportion creates a strong preference for carbon dioxide abatement. Therefore, the end products in the case of flue gas from coal post combustion process were a mix of sodium carbonate (main product) and a small amount of sodium sulphate and sodium nitrate.

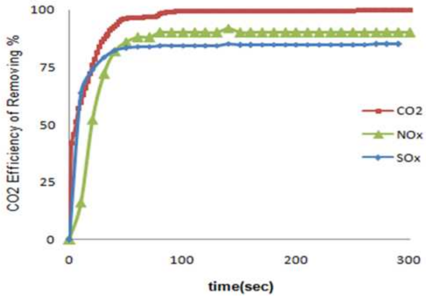

Figure 8: Abatement of mixed CO_2, NO_2, NO (NO_X) and SO_2 (SO_X) gases by superoxide reagent. Reaction conditions: 0.25 mol alkaline in 30 ml distilled water, 0.375 mol of hydrogen peroxide at room temperature and standard pressure, CO_2 flow rate of 1 lit/min, NOx and SOx initial concentration 1000ppm each.

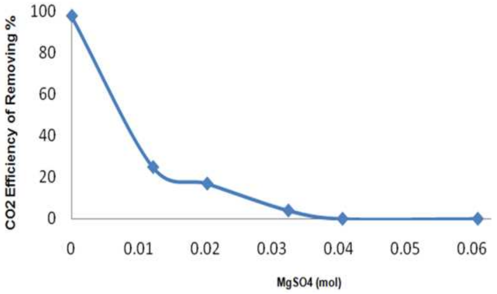

Figure 9: Carbon dioxide absorption as function of $MgSO_4$ addition. Reaction conditions: 0.25 mol alkaline in 30 ml distilled water, 0.375 mol of hydrogen peroxide with magnesium sulphate quantity gradient and CO_2 flow rate of 1 lit/min, at room temperature and standard pressure.

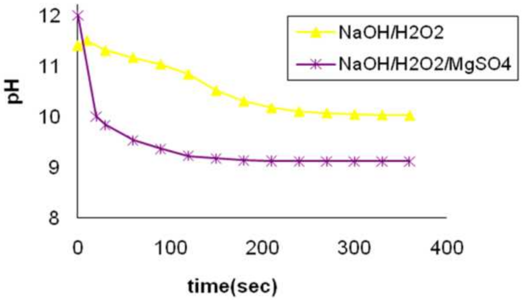

Figure 10: CO_2 Effectiveness of absorption as function of $MgSO_4$ addition. Reaction conditions: 0.25 mol alkaline in 30 ml distilled water, 0.375 mol of hydrogen peroxide, 0.01mol of magnesium sulfate, CO_2 flow rate of 1 lit/min, at room temperature and standard pressure.

Hydrogen peroxide stabilizers

A crucial limitation of the above procedure is the fast and spontaneous decomposition of hydrogen peroxide, particularly under strong basic conditions. The reaction of hydrogen peroxide with alkali hydroxide is strongly exothermic under ambient pressure and temperatures and is accompanied by decomposition of the peroxide and evolution of molecular oxygen, Equation 5.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Equation 5: Spontaneous decomposition of hydrogen peroxide.

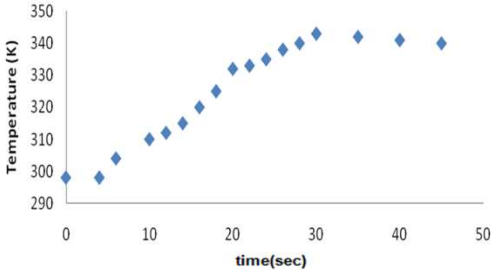

Figure 11: Temperature profile of CO_2 mineralization reaction. Reaction conditions: 0.25 mol sodium hydroxide in 30 ml of water, 0.375 mol of hydrogen peroxide and CO_2 flow rate of 1 lit/min.

Currently, to carry out the process, stabilizers adding or cooling of the reaction area is required. By the stability of various solutions of peroxide compounds is meant the capability to preserve their available oxygen for a long time. The best stabilizers for concentrated alkaline solutions with hydrogen peroxide are $Na_4P_2O_7$ and $MgSO_4$ with a clear preference to magnesium sulphate.We have examined the potential of additives to stabilize the peroxide. The proven stabilizer magnesium sulfate was added to the absorption mixture and the CO_2 abatement was monitored. Results are presented in Figure 9. Surprisingly magnesium sulfate had a harmful effect on the CO_2 absorption process in our reaction conditions. We attribute this decrease in activity with reaction pH reduce. Sulfuric acid is a main product at hydrogen peroxide and magnesium sulfate stabilizing reaction. Sulfuric acids formation reduces the total reaction pH, to pH less than 11, as shown in Figure 10. It is already known, that under conditions of pH less than 11, super oxide creations is very insignificant.[47] Yet, in our moderate reaction conditions, pH 11 and higher during the CO_2 absorption reaction, hydrogen peroxide decomposition to oxygen is insignificant (less than 1% in 3 min).

Temperature Effect

Carbon dioxide absorption reaction is an exothermic process. We may safely assume that our reaction system is adiabatic in nature. Typical experiment was started at 298K and reached maximum temperature of 343K after 30 second. The temperature profile is shown in Figure 11. We found that the initial temperature is a crucial parameter [27] the reaction does not set off at all with initial temperature below 298K. However, raising the initial temperature did not affect at all the behaviour of the reaction. That is shown in Figure S7 in supporting information. The lack of temperature effect may indicate that the absorption process is not chemically controlled but rather diffusion controlled.

Decomposition of superoxide by SOD

In order to positively confirm the presence and the role of superoxide anion in the absorption process we have carried out the process in the presence of the enzyme superoxide dismutase (SOD).

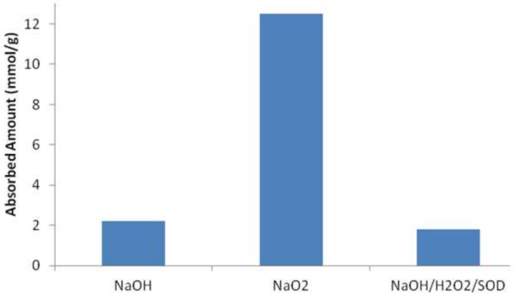

Figure 12: CO_2 absorption as function of SOD enzyme addition. Two minutes test. Reaction conditions: 0.25 mol alkaline in 30 ml distilled water, 0.375 mol of hydrogen peroxide, 6U of SOD and CO_2 flow rate of 1 lit/min.

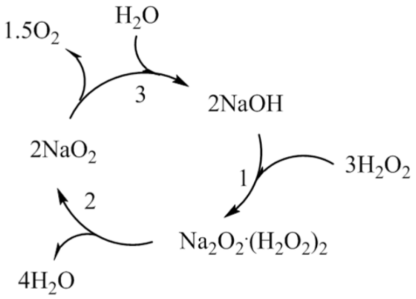

Figure 13: The recycled and in situ super oxide production.

This enzyme, which is stable under high pH conditions, [48] rapidly oxidizes superoxide anions into oxygen molecules. [49]

Indeed in the presence of SOD the CO_2 abatement process was almost completely inhibited, less than 20% of CO_2 absorption, 2 mmol/g), as shown in Figure 12 and Figure S8 in supporting information.

Proposed mechanism for carbon dioxide absorption

The CO_2 abatement process is composed of two consecutive steps. The first stage is in situ super oxide generation, Equation 3 which we described in our previous study. [27] The second stage is a rapid nucleophilic attack of the superoxide anion on carbon dioxide to generate alkali carbonate production. This stage itself consists of two critical steps. First, superoxide (nucleophile) rapidly reacts with carbon dioxide (electrophile) to generate mono sodium carbonate. Then, in the presence of excess of superoxide anion, this intermediate is converted to sodium carbonate and oxygen, as shown in Equation 4. The end product of CO_2 absorption reaction is white sediment. The latter was filtered and dried and tested by means of FTIR and XRD analysis. FTIR proved that our product has the same spectrum as sodium carbonate (peak at 1400cm^{-1}). The XRD results clearly showed that the end product of CO_2 absorption reaction is a mixture of 73% sodium carbonate and 27% of trona (hydrated sodium carbonate). It should be noted that in extended exposure of sodium carbonate to excess carbon dioxide, sodium bicarbonate is obtained. [50] The post combustion gas stream of coal based furnaces contains at least 12% of carbon dioxide. [51] It is creates a distinct partiality to reaction with CO_2 than reaction with water or steam. However, even if super oxide reacts with water or steam it is immediately recycled, as shown in Figure 13. This effective *in situ* recycling allows working at high superoxide concentration (at least 8M) in aqueous solution. This critical concentration of superoxide, required for maximum CO_2 absorption capacity, is thus maintained.

Potential corrosiveness of the reagent

One of the main reasons of corrosion appearance is oxidation environment. The use of strong oxidizing agent in industrial process requires considering potential corrosiveness of the equipment. Therefore we examined the corrosion of metals in the presence of the superoxide reagent.

Corrosion gravimetric test done with standard carbon steel (CS) 1010 slice with affixing analytical mass purchased from Holland-Moran Ltd. The CS slice inserted to the scrubber contains 1 mol hydroxide base in 150 ml distilled water, 2 mol of aqueous hydrogen peroxide 30% and CO_2 with a flow rate of 1 lit/min for 100 hours. At the end of the process the CS slice was dried and gravimetrically tested. The corrosion (mass increased of CS 1010) in presence of sodium hydroxide and hydrogen peroxide mixture have shown that even with very high concentration of both reagents ($NaOH/H_2O_2$), up to four times higher than the standard reaction conditions and with longer exposure time, the corrosion is negligible. See Figure S9 in supporting information. The corrosion caused by our reagent was 0.012% after 100 hours.

Conclusions

Absorption capacity and rate of carbon dioxide strongly depends on the nucleophilicity of the absorbent material. We created a unique CO_2 absorbent material which is superior over the standard methods for CO_2 abatement. The new formulation is a simple mixture of sodium hydroxide and hydrogen peroxide which evidently generates stable aqueous sodium superoxide under ambient conditions. A 100% of CO_2 efficiency of removing in gas stream to carbonate is demonstrated. A conceptual design for a CO_2 absorption unit based on the proposed technology is shown in Figure S10 in the supporting information.

Abbreviations

IEA- International Energy Agency
MEA - Mono-ethanolamine
ROS - Reactive oxygen species
FTIR- Fourier transform infrared spectroscopy
XRD - X-ray diffraction
EPR - Electron paramagnetic resonance spectroscopy
DMSO - Dimethyl sulfoxide
DMPO - 5,5-dimethyl-1-pyrroline N-oxide
CCS - Carbon capture and storage
SOD - Superoxide dismutase

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