Clean Coal by Oxyacidification

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ABSTRACT

Coal has become a controversial fuel due to various pollutants and carbon dioxide generated during combustion. Regulated pollutants include nitrogen oxides and sulfur oxides which react with the water vapor in the atmosphere to form acid rain. Carbon dioxide also reacts with water molecules to form carbonic acid, which gives rise to ocean acidification. This research takes advantage of the acidification tendency of such gaseous pollutants in order to reduce their concentrations. Pollutant molecules in the flue gas are encouraged to combine with water vapor to form droplets of oxyacids which are then separated before the flue gas is discharged into the air.

Keywords: Clean coal, oxyacid, electron affinity

1 PROBLEM

Coal is the most abundant fossil fuel in the world. Coal reserves total about 1 trillion tons which is equivalent to 150 years of production at the current level [1]. Countries with the largest reserves include United States (#1), China (#3) and Germany (#6) which are the major industrialized economies in America, Asia and Europe, respectively [2]. Those countries and many others rely heavily on coal burning power plants for electricity generation. For example in the US, about half of the electricity is generated by using coal due to low cost and plentiful supply.

Unfortunately coal has become a controversial fuel due to various pollutants and carbon dioxide (CO_2) generated during combustion [3]. High ranked coals like anthracite or bituminous coals are reserved for high value applications such as manufacturing of steel. That leaves low ranked coals like sub-bituminous coal or lignite for power generation. Low rank coals contain less carbon and more impurities like sulfur which gives rise to pollution [2]. Regulated pollutants emitted from coal include nitrogen oxides (NOx), sulfur oxides (SOx) and mercury. In the US, about 65% of sulfur dioxide emissions (7 Mtons/year), 20% of nitrogen oxide emissions (3 Mtons/year) and 70% of mercury emissions (45 tons/year) are attributed to coal burning power plants [4]. These percentages could be higher in developing countries where environmental regulations are not as well established as in the US.

Typical stack emissions of a coal based power plant consist of nitrogen gas (N_2) about 70% by volume, water vapor 15%, carbon dioxide 10%, oxygen gas (O_2) 5% [3]. A comparison of the composition of stack emissions with that of air shows that the fraction of (a) oxygen gas decreases significantly (from 20% to 5%), (b) carbon dioxide increases dramatically (from 380 ppm to 10%), and (c) water vapor increases significantly (from several percent to 15%). These changes which are applicable to other hydrocarbon fuels can be attributed to the oxidation of carbon and hydrogen in the fuel during combustion. Stack emissions also include the mentioned pollutants in quantities less than 100 ppm [3]. Low concentration of the pollutants is due to cleaning processes, such as flue gas desulfurization and selective catalytic NOx reduction, installed in power plants. Assuming a reduction of ~90% by such cleaning processes, approximate concentration of the pollutants in the original flue gas is about 1000 ppm (0.1%).

One of the adverse impacts of pollutants like NOx and SOx is that these molecules react with the water vapor in the atmosphere to form aerosols of oxyacids which eventually fall to earth as acid rain. NOx molecules form nitrous acid (HNO_2) and nitric acid (HNO_3). SOx molecules form sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4). Carbon dioxide also reacts with water molecules to form carbonic acid (H_2CO_3). Increasing concentration of carbon dioxide in the atmosphere is believed to be the cause of ocean acidification [5].

$$H_2O + NO + NO_2 \rightarrow 2\mathrm{HNO}_2 \quad (1)$$

$$H_2O + 3\mathrm{NO}_2 \rightarrow NO_2 + 2\mathrm{HNO}_3 \quad (2)$$

$$H_2O + SO_2 \rightarrow H_2SO_3 \quad (3)$$

$$H_2O + SO_3 \rightarrow H_2SO_4 \quad (4)$$

$$H_2O + CO_2 \rightarrow H_2CO_3 \quad (5)$$

2 PROPOSED SOLUTION

One can infer from the past observations that the mentioned gaseous pollutants have a natural tendency to combine with water to form liquid oxyacids. The approach followed in this research to reduce the pollutants in the flue gas is to take advantage of this oxyacidification tendency. Pollutant molecules in the flue gas are encouraged to combine with the water vapor in the flue gas to form droplets of oxyacids which are then separated before the flue gas is discharged into the air. This process can be euphemistically described as creating acid rain inside the power plant.

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The cleaning process is illustrated in Fig. 1. Given a flue gas generated by burning coal or other fuel, a charging device provides electrons to those molecules which have affinity to accept extra electrons. Molecules which acquire electrons and become ions are allowed to float through the flue gas without losing the charged state so that they can electrically attract other pollutants and water molecules to form droplets. Pollutants and water molecules brought into close proximity by the attraction of the ion react to form oxyacids. Charged droplets containing the oxyacids are separated from the rest of the flue gas by manipulating them with electric and/or magnetic forces.

2.1 Electron Affinity of the Pollutants

Ability of a molecule to accept an extra electron can be quantified by calculating its electron affinity (Eea) which is defined as the energy required to detach an electron from its singly charged negative ion [6]. Eea can be calculated from the quantum mechanical energy of the molecule in the neutral state (En) and with an extra electron (Ei).

$$E_{ea} = E_n - E_i \quad (6)$$

Most of the molecules have their lowest energy in the neutral state, therefore Eea is generally negative. For example, energy of CO_2 minus ion is higher than that of neutral CO_2 by about 0.9 eV. If CO2 is bombarded with energetic electrons, an electron with more than 0.9 eV kinetic energy can get temporarily attached to the molecule. A small number of molecules exhibit positive electron affinity. For example energy of O_2 minus ion is about 0.6 eV lower than that of neutral O_2. Such a molecule accepts an extra electron readily and becomes a relatively stable negative ion. An investigation of the electron affinity of molecules typically encountered in the flue gas of a coal plant indicates that many of the pollutants including NO_2, SO, SO_2, SO_3, HgO have Eea>0 {Table 1}. Hence these molecules have the potential to serve as ionic scavengers which can attract and capture other pollutants.

Formula	Molecule	Eea (eV)
NO	Nitrogen monoxide	-0.9
NO_2	Nitrogen dioxide	2.3
SO	Sulfur monoxide	1.3
SO_2	Sulfur dioxide	1.6
SO_3	Sulfur trioxide	1.2
HgO	Mercury oxide	2.4
CO_2	Carbon dioxide	-0.9

Table 1: Electron affinity (Eea) of the pollutants obtained by first principle quantum mechanical calculations [7].

2.2 Interaction Energy

Electron distribution of a molecule provides information about dipole, quadrupole and higher order electronic moments which are important to understand how ions and neutral molecules interact with each other. Flue gas molecules which have dipolar charge distributions include NO, NO_2, SO, SO_2, H_2O, HgO and those with quadrupolar charge distributions include N_2, O_2, CO_2, and SO_3. Generally interaction of an ion with a dipole is stronger than that with a quadrupole. The strength of the interaction between an ion and other molecules in the flue gas can be quantified by calculating the interaction energy. Interaction between pairs of various molecules and ions has been investigated using first principle quantum mechanical calculations [7]. Results indicate that interaction energy ranges from 0.5 eV to 0.9 eV for dipolar molecules like NOx, SOx and H_2O {Table 2}. These interaction energies are large enough for the ion to attract and capture dipolar pollutants and water molecules even at the relatively elevated temperature of the flue gas.

Minus Ion	Molecule	IE (eV)
NO_2	SO	0.6
NO_2	SO_2	0.9
NO_2	H_2O	0.8
SO	H_2O	0.7
SO_2	H_2O	0.8
SO_2	NO	0.5
SO_2	NO_2	0.5

Table 2: Interaction energy (IE) between an ion and dipolar molecules as calculated by first principle methods.

The interaction energy for a quadrupole like N_2 is 0.07 eV which is comparable to the thermal energy of the flue gas. Another quadrupole of interest is CO_2 which has an electron distribution where carbon is slightly positive, 0.74Qe and oxygens are slightly negative, -0.37Qe (Qe: unit charge). When CO_2 is in the vicinity of a negative ion, carbon gets attracted to the ion, whereas oxygens get repelled by the ion which bends the molecule from a linear to an angular shape (Fig. 2). The shape change creates a small dipole which yields an interaction energy of 0.3 eV. Although this energy is smaller than those of the other dipoles mentioned above, it is large enough to enhance the absorption of CO_2 into the droplets {Table 2}.

Minus Ion	Molecule	IE (eV)
NO_2	N_2	<0.1
NO_2	CO_2	0.4
SO	N_2	<0.1
SO	CO_2	0.3
SO_2	N_2	<0.1
SO_2	CO_2	0.3

Table 3: Interaction energy (IE) between an ion & quadrupolar molecules as calculated by first principle methods.

One can conclude from this analysis that the ions created within the flue gas would attract dipolar pollutants

and water molecules to form droplets. CO_2 which exists in large quantities within the flue gas will also be absorbed into these droplets. Chemical reactions between the pollutants, CO_2 and water molecules brought into close proximity within the droplets would create oxyacids. Relatively high temperature of the flue gas can be also expected to facilitate the oxyacidification reactions. Since the droplets are charged and they are in motion towards the exit, they can be manipulated with electric and/or magnetic forces to separate them from the rest of the flue gas. For example a wet electrostatic precipitator can be used to collect and condense the charged droplets. One can neutralize the oxyacids by treating them with a suitable base like $Ca(OH)_2$.

2.3 Charging Method

Electrons which contribute to charging of pollutants can be created using a number of different approaches including electrical breakdown of a neutral molecule, thermionic emission from a metal, optical excitation of a photocathode, triboelectrical charging, and the like. An important consideration is to minimize electrical power necessary for the charging in order not to reduce the efficiency of the power plant. In this application thermionic emission is the preferred method, since combustion of coal creates thermal energy at very high temperatures (~1500 degree C) and a thermionic emitter can take advantage of that heat. Basic principle of thermionic emission is the escape of electrons from a metal surface heated to a high enough temperature that energy of some of the electrons exceeds the work function of the metal. Typical operating temperatures are about 600-1000 degree C which is within the range of temperatures obtained during the combustion of coal. Emitted electrons do not have to be energetic, since pollutants which have positive electron affinity acquire them without effort. Thermionic emission is a mature technology widely used, for example, in cathode ray tubes or fluorescent lamps.

3 CONCLUSIONS

A multi-pollutant reduction method for coal burning power plants is proposed. This method involves:

1) Providing electrons to those pollutant molecules which can accept extra electrons by virtue of having a positive electron affinity, and
2) Allowing the charged pollutants to float through the flue gas without losing the charged state.
3) The charged pollutants electrically attract other pollutants and water vapor in the flue gas to form droplets;
4) Pollutants and water molecules brought in close proximity react to form oxyacids;
5) These droplets are separated from the rest of the flue gas by manipulating them with electric and/or magnetic forces.

Advantages of the proposed method can be listed as follows:

Removing multiple pollutants with one ion: The proposed method is self amplifying where one ionized pollutant can attract and capture many other pollutants in the flue gas. Each pollutant does not have to have a positive electron affinity and does not have to be individually charged.

Creating stable scavengers which have long lifetimes: A molecule which has positive electron affinity becomes energetically more stable when it acquires an extra electron. It can maintain the charged state for an extended period of time which is advantageous to scavenge more of the pollutants in the flue gas.

Energy efficient charging: Electrons needed to create the ions are generated by thermionic emission which takes advantage of the high temperatures generated during combustion of coal.

Gas to liquid transformation: The proposed method converts gaseous pollutants to liquid oxyacids, which can be neutralized to benign and beneficial by-products.

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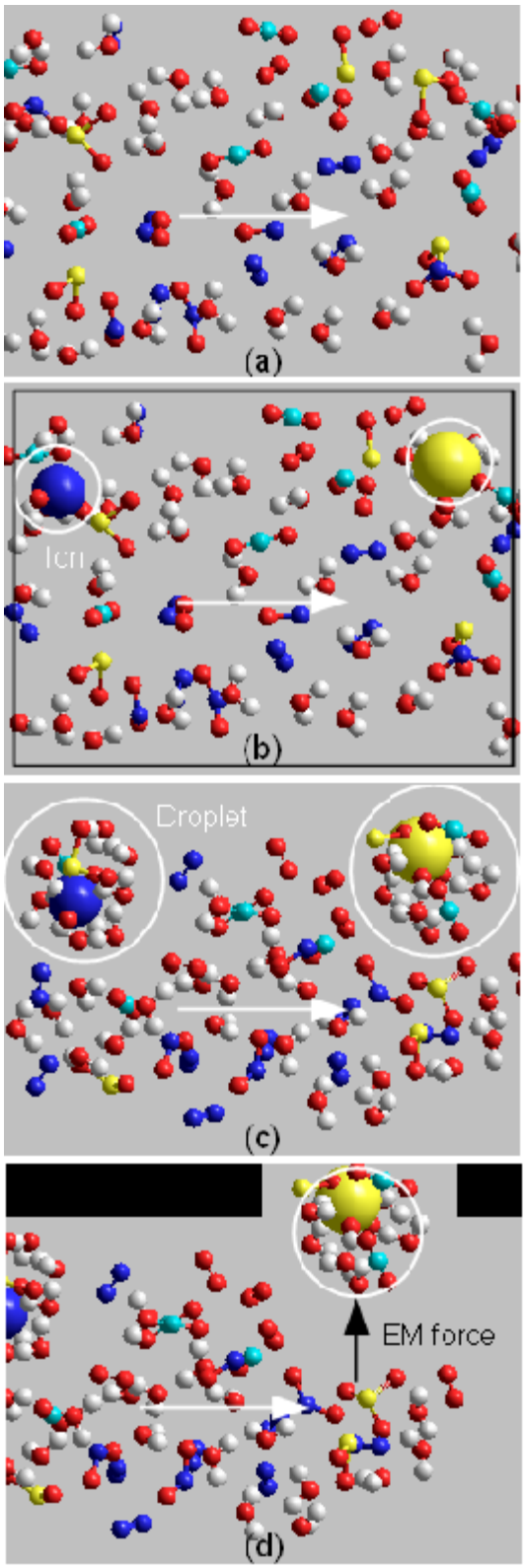

Figure 1: The proposed cleaning process: (a) Given a flue gas generated by burning coal, (b) provide electrons to molecules which have positive electron affinity; (c) allow the ions to attract other pollutants and water molecules to form droplets; (d) separate charged droplets with electric and/or magnetic forces.

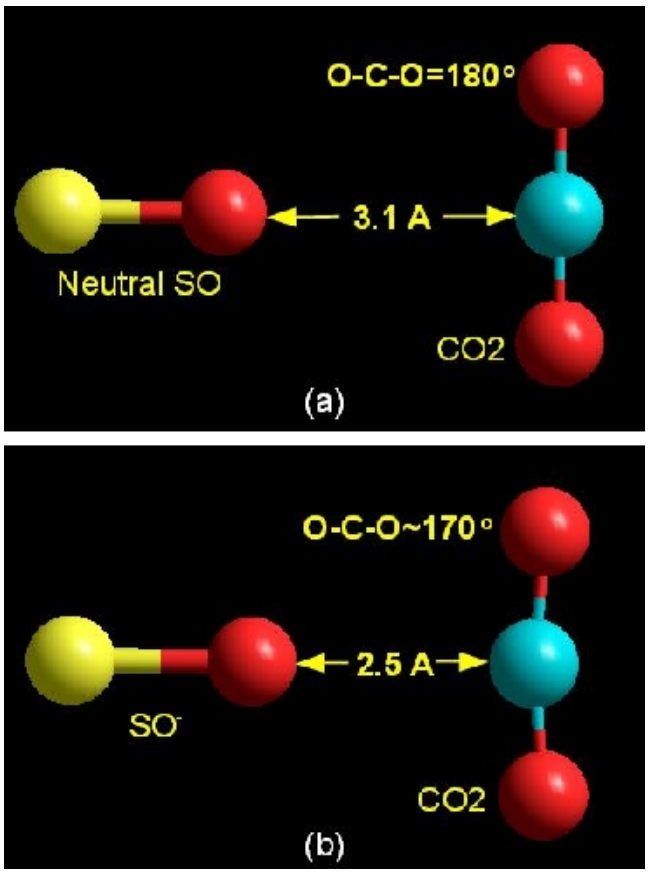

Figure 2: The interaction between (a) neutral SO and CO_2, (b) SO minus (SO-) ion and CO_2; under the influence of the ion, CO_2 changes from a linear molecule to a slightly angular one creating a small dipole.