An Overview of the Use of $Ca(OH)_2$/Fly Ash in Flue Gas Desulphurization

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Most of the SO_2 emission removal techniques have been based on the use of calcium-based materials. For instance, limestone has been used in the wet scrubbing while lime in the dry flue gas desulphurization (FGD) processes. Recent research efforts have prioritized on the semi-dry and dry FGD whose major sorbent, hydrated lime faces the problem of low utilization. Improving sorbent utilization thus posses a challenge in the dry FGD processes. Sorbents obtained by conditioning of lime with different sources of silica lead to a significantly higher calcium conversion compared to those obtained using hydrated lime only. Coal fly ash has a high content of silica and is viable for improving the sorbent utilization. This paper assesses the use of various sorbents and gives an overview of fly ash as one of the conditioners used to improve the sorbent utilization. It further focuses on the hydration process and the conditions that are likely to affect the performance of the resultant conditioned sorbent material during hydration and sulfation processes. The paper further explores the future challenges facing dry and semi-dry FGD processes.

1. Introduction

The use of coal as a major source of power generation is expected to increase due to its abundance, wide distribution worldwide and stability in price. For rapidly developing nations like China, India, South Africa and other developing Asian countries, which heavily rely on coal for energy, pulverized coal combustion (PCC) will for sometime remain the major combustion technology. While China alone will account for some 30 % of increased energy demand by 2030, India's coal usage is expected to grow by 3.3 % per annum to 2030[1]. Consequently, emissions control measures of gas pollutants such as SO_2 (which leads to formation of acid rain, smog and allergies) is of utmost necessity. This means development of an efficient dry FGD technology using ash will be very beneficial to these nations. Although dry and semi-dry FGD processes used for flue gas cleaning have the merit of lower capital cost than the wet process, the conversion of the sorbent is low.

Increasing the utilization of lime in semi-dry/dry FGD systems is one of the current challenges researchers have to deal with. Most of the approaches that have been applied to increase the performance of the sorbent make use of the capacity of the additive to increase the surface area of CaO. The reactivity of hydrated sorbents towards SO_2 is closely related to the sorbent surface area[2, 3, 4].

Inorganic hygroscopic salts such as barium, potassium, sodium and calcium chlorides and nitrates of sodium and calcium have been found to be effective in increasing the performance of hydrated lime. The effectiveness of certain salts also depends on the relative humidity. This is so because when the relative humidity of the gaseous phase is lower than the water activity in a saturated solution of the salt, it would not absorb water and therefore not enhance the $Ca(OH)_2$ (sorbent) reactivity. Ruiz-Alsop and Rochelle[5] observed that chlorides and sodium nitrate modify the properties of the product layer as the reaction takes place, thereby facilitating access of SO_2 to unreacted calcium $Ca(OH)_2$ which remains in the interior of the particle. On the same note, Kind *et al.*[6] found samples of sorbent prepared from chlorides to be highly reactive with SO_2 regardless of slurrying time and sample surface area. Reaction rate was reported to be directly proportional to the concentration and amount of calcium chloride and sodium hydroxide[7]. In their experiment sodium chloride, calcium chloride and sodium hydroxide were used at 71.5 °C temperature, 36.7 % relative humidity and 10-31.2 % by mass. It was reported that despite $CaCl_2$ having poor alkaline and hygroscopic properties, it had the best results among the salts. They, however, observed no significant enhancement on the reaction rate with different amounts of NaCl. This could be attributed to the fact that NaCl's hygroscopic character is not enough to improve the desulphurization power of $Ca(OH)_2$ significantly. Liu *et al.*[8] reported similar results with $CaCl_2$ which they attributed to the ability of inorganic hygroscopic salts to retain a greater amount of water on the sorbent surface and thus increasing the availability of Ca^{2+} ions to SO_2. Recent report by Dahlan *et al.*[9] on the effect NaOH, LiCl, NaHCO, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_2$ and $MgCl_2$ on rice husk activated lime showed that most of these additives increased SO_2 sorption capacity of the sorbent.

2. Siliceous Materials

Some of the siliceous materials which are viable for the conditioning of hydrated lime include fly ash, bottom ash, and incinerator ash. Palm oil ash has also been used recently.

Fly ash is a waste product of coal-fired power plants. This material is solidified while suspended in the exhaust gases and is collected from flue gas by electrostatic precipitators. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape[10]. Fly ash is a pozzolanic material whose main components are usually SiO_2, Al_2O_3, and Fe_2O_3[8]. In the presence of water, the amorphous silica in the fly ash would react with the hydrated lime to form calcium silicate hydrates ($xCaO.SiO_2.yH_2O$), which may lead to sorbents having higher specific surface area. The composition of both the major and minor components in fly ash varies from one report to another. Looking at different literatures it has been noted that ashes collected from different power plants have their chemical composition differing. Table 1 compares

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different results obtained by five research groups[2, 4, 8, 11, 12]. In our research we have analyzed the chemical composition South Africa fly ash and bottom ash supplied[13]. Table 2 shows the chemical analysis of fly ash and bottom ash from South African power plants.

SiO_2 %	CaO %	MgO %	Fe_2O_3 %	Al_2O_3 %	Na_2O %	TiO_2	K_2O %	SO_3 %	I loss	C	Reference
32.83	30.35	4.51	5.61	13.34	2.15	-	1.37	7.36	-	-	2
48.45	16.56	2.95	5.60	17.80	2.57	-	2.90	1.77	-	-	2
21.04	51.02	3.09	3.01	7.31	1.48	-	0.85	9.84	-	-	2
59	1.6	0.9	-	26.7	1.2	1.3	5.5	0.47	2.4	-	8
60	3.0	1.0	4.7	20	-	-	1.1	-	0.3	7.5	11
49.26	1.91	0.85	6.92	30.24	0.64	-	2.44	-	6.31	-	12
30.3	2.5	1.9	9.6	47.2	1.7	2.2	3.0	1.6	-	-	4

Table 1: Composition of fly ash from different studies[2, 4, 8, 11, 12]

Component %	Bottom Ash	Fly Ash
SiO_2	51.28	48.07
TiO_2	1.45	1.53
Al_2O_3	29.55	31.58
Fe_2O_3	5.10	5.99
MnO	0.07	0.05
MgO	1.34	1.37
CaO	8.37	7.36
Na_2O	0.64	0.22
K_2O	0.63	0.88
P_2O_5	0.96	0.54
Cr_2O_3	0.04	0.03
NiO	0.01	0.02
V_2O_5	0.02	0.03
ZrO_2	0.05	0.05
LOI	0.85	1.04

Table 2: The chemical analysis of South African fly ash (FA) and bottom ash[13]

Karatepe *et al.*[2] reported that the relationship between $Ca(OH)_2$/fly ash sorbents and the sorbent surface area changes with respect to the particle size, form of the SiO_2 present in the fly ash (quartz or silicon oxide) and CaO content of the fly ashes. Results by Renedo *et al.*[12], however, showed that the total calcium utilization does not seem to be related to the chemical species in the sorbents. They also indicated that micro-structural properties such as specific surface area and pore volume are not related to the total calcium utilization, as strong differences in the above variables lead to slight differences in calcium utilization.

Bottom ash is also one of the siliceous materials and consists of the accumulated ash particles (normally >100 μm) which are too large to be carried in the flue gases. They are formed in pulverized coal furnaces and stick on the furnace walls or drop through the open gates to an ash hopper at the bottom of the furnace. Its major components are usually SiO_2 and Al_2O_3 with low amounts of Fe_2O_3, SO_3, CaO, P_2O_5, Na_2O, K_2O, MgO and TiO_2 and trace amounts of the elements Pb, Cu, Zn, As, and V[11]. Although the chemical compositions are the same, the mass fraction of these elements in bottom ash is lower than in fly ash[14]. Although chemical components of bottoms show possibility of positive enhancement of Ca – based sorbents, there is not much literature on the activation of lime using bottom ash. Lee *et al.*[11] reported that in spite of both sorbents prepared from bottom ash and incinerator ash having the capacity to absorb SO_2, their absorption capacity is not as high as that of fly ash and oil palm ash. Using X-ray diffraction analysis they detected phases of calcium silicate hydrate, $Ca(OH)_2$ and $CaSO_4$ in the coal bottom ash activated sorbent. It was argued that the presence of $Ca(OH)_2$ showed that some of the CaO was converted to $Ca(OH)_2$ hence limiting the formation of active compounds.

3. Factors Affecting the Performance of Sorbent Materials

3.1 Hydration conditions

Sorbents obtained by hydration of lime or hydrated lime with different sources of silica lead to significantly higher conversion of calcium compared to the conversion obtained using hydrated lime[4, 15]. In the process of conditioning of hydrated lime, in order to increase its SO_2 capture, hydration process has always been used to produce high performance sorbents. The hydration variables however have to be controlled so as to optimize the sorbent chemical and physical properties. Hydration conditions affect the surface area of the resultant sorbents which has influence on the utilization of the sorbent during sulphation. Lee *et al.*[11] reported that the sorbent preparation parameters have a great effect on the sorbent surface area. They found that the hydration process improves the surface area of the resulting absorbent as compared to the raw materials. Diffenbach *et al.*[16] found out that the reactivity of fly ash and its ability to react with $Ca(OH)_2$ to form highly reactive species in the hydrated solids (calcium aluminate silicate hydrates, calcium silicate hydrates, calcium aluminate hydrates, etc) varies depending on the hydration conditions. Additives with silica and alumina contents have proven their importance especially with regard to the pozzolanic reaction between Ca-based sorbents and the additive. Some of the conditions which have been investigated include: hydration temperature, hydration time (slurrying time), $Ca(OH)_2$ /fly ash ratio and additives.

3.2 Temperature

Temperature has been one of the investigated hydration conditions on most of the hydration experiments. This can be attributed to the fact that most reactions involving and forming chemical compounds are affected by temperature changes. Fernandez *et al.*[17] indicated that temperature, pressure and water/solids ratio are not individually significant, but their crossed influences are. They observed that at 170 °C, the results show that the highest value of the specific surface area corresponds to the solids prepared at the highest fly ash/hydrated lime ratio (3/1) and hydration time (4 h) with the lowest water/ solids ratio. Solids prepared at 110 °C had lower specific surface areas and a different relationship between the independent variables and the specific surface area. It was reported that high temperature in conjunction with the other variables combined were responsible for the increase in the surface area of the solids formed. Investigating of hydration variables on $Ca(OH)_2$ /fly ash sorbent con version Davini[18] reported that higher temperatures and longer mixing time favour sorbent conversion.

3.3 Slurrying time

Just as the hydration process has been found by most researchers to have positive influence on improving utilization of $Ca(OH)_2$, so is the hydration time for the hydration process. Most authors concur that an increase in hydration time results in the increased specific surface area hence improved sorbent performance. For instance, the results of Liu *et al.*[8] showed an increase in specific surface of the sorbent with increase in slurrying time. Peterson and Rochelle[19] pointed out that high surface area solids are less reactive when they are formed in slurries containing low concentrations of dissolved calcium. They showed that longest hours of hydration time used resulted in the possibility of a better sorbent performance. Dissolved calcium content in the slurry filtrate after hydration varied inversely with hydration time and fly ash/$Ca(OH)_2$ weight ratio. Investigating mainly the influence of $CaSO_3$/$CaSO_4$ in a solution of fly ash/$Ca(OH)_2$/$CaSO_3$/$CaSO_4$, Kind *et al.*[6] reported that hydration time has positive input. This was in agreement with Fernandez *et al.*[20] who reported a higher value of specific surface area at the highest hydration time and calcium ratio. The specific surface area of sorbents prepared at different slurrying times were found to increase with the slurrying time.

Recently Lee *et al.*[21] reported that the hydration conditions which positively affect the surface area of the resultant sorbent from hydration process were hydration time, amount of fly ash and amount of $CaSO_4$.The values of these variables obtained in their experiments were 32 h, 10.6 g and 5.7 g respectively. In their view, even though the sorbents at these three conditions produced maximum surface areas and would therefore result in higher desulphurization activity, there was limitation of a long hydration period of 32 h was required. They suggested that such a long period of hydration time is not likely to be used in practice due to practical constraints and economic considerations. This calls for optimization of the other variables with a practical hydration time.

3.4 CaO/Fly ash ratio

The reactivity of $Ca(OH)_2$/fly ash with SO_2 increases with decreasing $Ca(OH)_2$/fly ash weight ratio[14]. It has been reported that the ratio 10/90 had the highest specific surface area and sorbent conversion. In an attempt to optimize the specific surface area of the sorbent, Lee *et al.*[21] found 5g CaO, 13.1 g fly ash and 5.5 g $CaSO_4$ to produce a maximum surface area of 62.2 m^2/g. Lin *et al.*[22], however, reported that the ratio of 3/7 had the highest local maximum specific surface area of 257.6 m^2/g. Down playing the effect of slurrying time, it was reported that the effect of slurrying time on the specific surface area was small. Thus indicating that the amount of calcium silicate hydrates and the microstructure of the sorbents remained almost the same during the period of the slurrying time of between 25 min to 16 h. This showed that the effect of hydration time on the hydration process was somehow not positive on the specific surface area of the solids. Various reports however show different ratios prompting the need to find a range in which the sorbent would be most effective.

3.5 Additives

In the presence of water, amorphous silica in fly ash reacts with hydrated lime to form calcium silicate hydrates which may lead to sorbents having higher reactivities towards SO_2 than the hydrated lime. The controlling step of this reaction, if enough $Ca(OH)_2$ is present seems to be the dissolution rate of alumina and /or silica from the vitreous phase into the aqueous phase. The dissolution rate can be enhanced by increasing the temperature, the reaction time and/or by adding $(NH_4)_2HPO_4$ or NaOH[17, 18].

Calcium sulphate ($CaSO_4$) is one of the products formed during the desulphurization process. Recent studies have shown that addition of $CaSO_4$ has an effect on the fly ash/CaO sorbents. In 2005 Lee *et al.*[11] indicated that $CaSO_4$ promotes the formation of calcium silicate by suppressing the crystal growth of $Ca(OH)_2$ hence forcing the reactivity of $Ca(OH)_2$ to produce hydrated products. The purpose of $CaSO_4$ in the $Ca(OH)_2$/fly ash sorbent hydration process helps to buffer the solution by maintaining a high level of calcium in the solution for longer hydration time[6]. This would result in the increased formation of calcium silicate hydrates by exposing calcium to react with dissolved silica. On the contrary Fernandez *et al.*[19] reported that the sorbents with $CaSO_4$ showed low performance as regards to the degree of SO_2 capture. They noted a general improvement of the desulphurization activity higher than $Ca(OH)_2$ but lower than the sorbents prepared from fly ash/$Ca(OH)_2$ without $CaSO_4$.

3.6 Future challenges of dry FGD technologies

Research and development in dry FGD systems face challenges of increase of desulfurization efficiencies and improvement of its reliability: A dry FGD system is usually installed between the air heater outlet and particulate collector. The short ductwork between the air heater and electrostatic precipitator (ESP) inlet makes it difficult to take the gas from the air heater outlet to the dry FGD equipment and return it to the ESP inlet. Modifications are required on the ESP to accommodate this process. Besides, compared to wet FGD which is well established technology with proven reliability, plentiful reagents and ready reliability, dry FGD technology does not have many facilities in operation especially in larger power plants. Lime sprayer-dryer FGD systems are in operation but ranging in sizes less than 10 MW to 600 MW power plants[23].

Although integrated gasification combined cycle (IGCC) and fluidized bed combustion can substantially reduce CO_2, SO_2 and NO simultaneously, their implementation in the developing countries like China, India and South Africa will take longer. Intensive research is therefore needed to come up with technologies which will simultaneously remove SO_2 and NO. This will reduce the cost of flue gas technology installations. The use of transitional metals such as V, Fe, Cu, and Mn with the dry FGD sorbents has been reported to have positive effect. Further research in this area is required.

Despite ongoing extensive research, more knowledge of the inherent kinetics, the controlling processes and/or reactions in the solid-gas SO_2 capture mechanism is needed. For instance, there is need to understand the chemical mechanisms that make the sorbents additives to be effective. There is the challenge of making the additives to be commercially available as well as the developed sorbents.

The problem of low sorbent utilization in the dry and semi-dry FGD processes limits their economic feasibility. Preparation techniques need to focus on the optimization of the preparation variables such as hydration time, ratio of the parent sorbent to the additives. For example amount of fly ash to $Ca(OH)_2$ that would give maximum SO_2 capture.

In spite of these challenges of dry FGD technologies it is still the technology of the future owing to its environmental friendliness and lower cost of installation. Unlike wet FGD facilities whose construction require expensive corrosion-resistant materials like stainless steels, dry FGD absorbers can be constructed using less expensive carbon steel due to the absence of water saturated gas and waste. The waste product contains $CaSO_3$, $CaSO_4$, $CaCO_3$ and unreacted sorbent which can be in the form of $Ca(OH)_2$ and fly ash are easy to handle and can be cheaply disposed of in the landfill without environmental and health threat. There is also potential of this waste being used as agricultural soil conditioning and brick preparation.

4. Conclusions

Low calcium utilization in the dry and semi-dry FGD processes has driven research in ways of increasing the utilization and thus reducing sorbent costs. The use of inorganic hygroscopic salts such as barium, potassium, sodium and calcium chlorides and nitrates of sodium and calcium have been found to be effective in increasing the sorbent utilization. Fly ash, a by-product of coal combustion, has found increasing attention over the last decade. Hydration of either $Ca(OH)_2$ or CaO with fly ash produces a porous sorbent with a high specific surface area. This provides more area for the reaction between the SO_2 and the calcium ions in the sorbent. Various hydration parameters, however, influence the structure of the resulting CaO/Fly ash sorbent. Increasing the hydration temperature and time increases the specific surface area of the resulting sorbent. However, due to cost constraints, there is a limit to how long the hydration process can be carried out. The CaO/Fly ash ratio also has an influence on the structure of the produced sorbent and an optimum ratio of 7:3 has been suggested. Various additives, specifically $CaSO_4$, and $(NH_4)_2HPO_4$ or NaOH, have also been shown to improve the hydration process when added in small amounts. The development of these sorbents still faces challenges as researchers try to understand the kinetic mechanism of the desulphurisation process at low temperatures.

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