

# The Addition of Salt to Fluidized Bed Combustors

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## ABSTRACT

Fluidized bed combustion is currently the subject of much research and development on a worldwide basis as a pollution free method of burning low quality fuels. The use of an air fluidized bed of crushed limestone provides the removal of sulfur dioxide from the flue gas. Operating temperatures are low which provides low evolution of nitrogen oxides. Volumetric heat release and heat transfer rates are high yielding a compact boiler size which requires less initial capital to construct. The first 30 MWe Demonstration Unit has come onstream and several large boilers 250 MWe to 800 MWe are in advanced stages of design. Prospects are very good for fluidized bed combustion to be a major factor by the end of the next decade in clean electric power generation. The addition of NaCl salt to fluidized bed combustors has been demonstrated to reduce limestone consumption by up to 50%. The required dosage is about 1% based upon coal. Laboratory and pilot plant scale studies have revealed insights into the mechanism of action of salt on limestones. This has revealed marked changes in the internal limestone microporosity which facilitate diffusion of  $\text{SO}_2$  into the limestone and internal pore utilization.

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## INTRODUCTION

It is of extreme importance to the future of our worldwide standard of living to develop clean, efficient, low cost utilization methods for low value fuels. Of particular importance are high sulfur liquid and solid fuels including coal. One of the most promising methods of achieving this goal is the use of fluidized bed combustion for the generation of steam in a boiler which is used in the generation of electric power. The application of fluidized bed combustion to large scale generation of electric power is currently being evaluated. The first 30 MWe Demonstration Unit has come onstream and several large boilers 250 MWe to 800 MWe are in advanced stages of design. The U.S. Department of Energy is supporting this work in excess of 100 million dollars per year, with additional support being provided by the Electric Power Research Institute, the Tennessee Valley Authority and industrial organizations in the U.S.A. along with the National Coal Board and the British Coal Utilization Research Administration in the U.K. and other significant efforts in Sweden, Japan and other countries.

It has been found that the addition of salt, NaCl, to fluidized bed combustors appreciably enhances the performance and overall economics of the system. Laboratory and pilot plant studies have revealed insights into this mechanism of action and the required engineering considerations important for its application. The current paper summarizes these technical results.

## THE FLUIDIZED BED COMBUSTION PROCESS

In a fluidized bed boiler the combustion of fuel occurs in a turbulent bed of particles fluidized by combustion air. This is schematically represented in Figure 1. The particles may be inert solids such as sand or coal ash or they may be chemically reactive solids such as limestone which, upon reaction with sulfur dioxide, removes  $\text{SO}_2$  from the combustion gases. Theoretically, any combustible solid, liquid, or gaseous fuel can be burned in a fluidized bed combustion system. This sulfur absorbing character of the limestone bed allows the use of high sulfur fuels. The acceptable low  $\text{SO}_2$

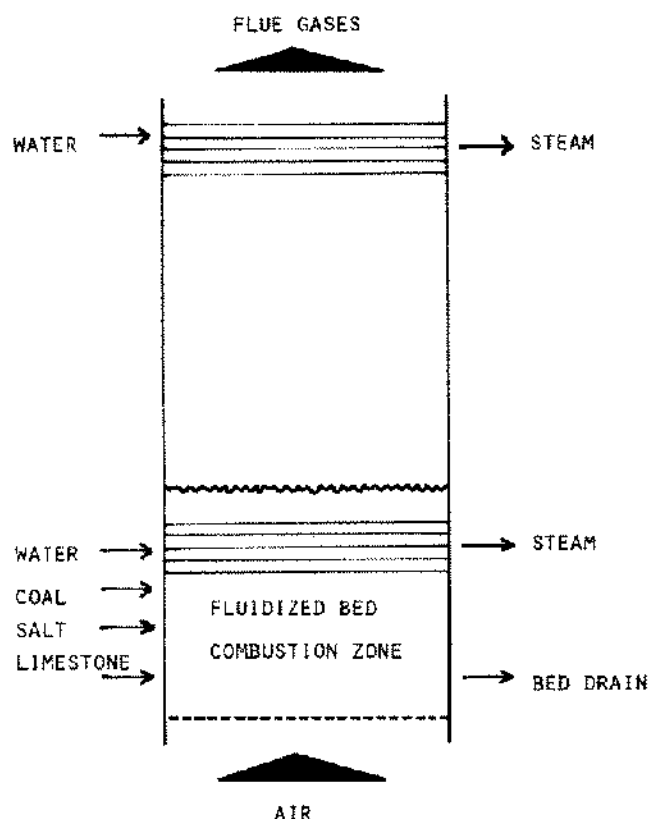


Figure 1. Fluidized bed combustion boiler schematic.

concentration in the flue gases eliminates the need for stack gas scrubbing.

The fluidized bed temperature is maintained at 1500°F–1600°F. This has been determined to be the optimum temperature for sulfur capture by most of the easily available limestones. The advantages of operation at this low temperature include: no coal ash fusion which causes fouling in conventional boilers; nitrogen oxides formation very low; less expensive construction materials in the combustion zone; and lower volatilization of trace elements and other materials which can both cause corrosion in conventional boilers and be emitted as gaseous pollutants.

Fluidized bed combustion of coal is rapid, maintaining a low concentration (less than one percent) of unburned coal in the bed at any time. High volumetric heat release rates are obtained. The combustion gases leave the bed at the operating temperature, containing between 40–50 percent of the heat released, while the balance (50–60%) is transmitted to heat transfer surfaces submerged in the bed.

Heat transfer coefficients to submerged tubes are high due to the turbulent motion of the bed particles. The particle motion decreases the thickness of the cooled boundary layer around the submerged heat transfer surfaces resulting in high heat transfer coefficients over the entire circumference of the embedded tubes. Also, radiative heat transfer occurs around the entire tube circumference in contrast to the con-

ventional boiler where only that portion of the tube directly facing the flame (the projected area of the tube) is effective.

The high combustion rates, heat release rates, and heat transfer rates cause the volume of the fluidized bed boiler to be significantly smaller than that of the combustion chamber of a pulverized coal fired boiler. The reduced volume and reduced heat transfer surface are economic advantages of a fluidized bed boiler. In addition, since scale-up of a fluidized bed is accomplished by adding bed area, it is possible that large fluidized bed boilers can be constructed of cells or modules which are shop-fabricated and transported by rail to the construction site. This reduction in field construction costs may represent a significant economic benefit. Another advantage of fluidized bed combustion technology is its compatibility with existing water wall boiler technology. Since much of the "water side" art is now existing standard practice, this essential compatibility is expected to reduce fluidized bed combustion development time.

The heart of the fluidized bed boiler is the cell, an undivided fluidized bed in which combustion occurs. In this compartment, several phenomena occur simultaneously: a) Coal volatiles are evaporated from coal particles and burn in a homogeneous, diffuse flame. b) Fixed carbon within the coal is combusted heterogeneously. c) Limestone is calcined. d) Calcined limestone is sulfated. e) Generated heat is transferred across submerged heat transfer surfaces.

In order for these phenomena to occur, several input streams are continuously supplied: a) Coal. Large (1/4" top size) coal is used, reducing crushing and pulverizing costs. b) Limestone. Large (1/8" top size) limestone is used. The amount fed is in a fixed molar ratio of calcium in the limestone to sulfur in the coal, determined empirically to yield appropriately low flue gas SO<sub>2</sub> concentrations. c) Air. About 20 percent excess air over stoichiometric combustion air is fed. d) Water. Circulated through heat transfer tubes, the amount of water that is fed is based upon an enthalpy balance where the enthalpy generated by combustion is balanced by the enthalpy increase of the flue gases, the saturated steam, and the superheated steam.

All inputs are fed in ratios determined by the stoichiometry and calorimetry of the systems. Analysis of the possible range of each parameter indicates that all flow rates and performance parameters are dependent upon the fuel and air feed rates.

The fuel and air are fed in a constant ratio dependent on the stoichiometry of combustion with a small amount of excess air. In order to reduce the area of fluidized bed required per unit of steam generated, it is desirable to feed coal at as high a rate as practical to maximize the heat release per square foot of bed area. The maximum coal feed rate is limited by the amount of heat that can be removed per cubic foot of bed and by the air feed rate which, in turn, is limited by the total pressure drop across the bed and grid plate and by pneumatic elutriation of the bed particles. The

pressure drop represents a system energy cost which affects overall plant efficiency and should be minimized. The elutriation velocity of the bed particles is proportional to the square of the particle diameter which can be selected for as high an air feed rate as desired if using an inert bed. In a sulfur sorbing bed, however, increasing the limestone particle diameter is undesirable. Large limestone particle sizes result in a decreased  $\text{SO}_2$  sorption interfacial area per cubic foot of bed and an increased  $\text{SO}_2$  sorption diffusion path within the particle. Therefore, increasing the particle size of the limestone requires that, to achieve the same sulfur capture, the bed depth be significantly increased with a resulting increase in pressure drop. Therefore, for a sulfur sorbing fluidized bed, economic analysis can be used in the selection of optimum limestone particle size by balancing the operating costs of limestone consumption and pressure drop with the capital cost associated with the heat release rate for a given air flow rate. From this optimum particle size, the maximum airflow rate is specified and is proportional to the coal feed rate, the heat release rate, the steam generation rate and other performance parameters.

The limestone chemical reactions involved are first a calcination reaction:



followed by a sulfation reaction with excess  $\text{O}_2$ :



Due to the large limestone particle size, the limestone reactivity is limited by  $\text{SO}_2$  diffusion. Salt appears to greatly enhance the microporosity of limestone in the appropriate pore size range to enhance both  $\text{SO}_2$  diffusion rates and limestone sulfur capacity. Therefore, the addition of salt to fluidized bed combustors is an important factor in minimizing overall limestone requirements and optimizing the overall economics.

## ADVANTAGES OF FLUIDIZED BED COMBUSTION

A summary of the advantages of fluidized bed combustion boilers is as follows:

1. Combustion is rapid, allowing for high volumetric heat release rates, which result in a small overall combustion zone.
2. Heat transfer to submerged surfaces is rapid, which leads to reduced total heat transfer surface requirements and economical overall capital cost.
3. Shop fabrication can be used extensively, further reducing capital costs.
4. Sulfur is captured within the fluidized bed by limestone, eliminating the need for wet scrubbers to remove sulfur pollutants.
5. The coal ash and sulfated limestone by-products are dry solid materials of potential value in many applications.
6. The solid waste by-products remain in easy to handle dry granular form.
7. The operating temperature is low. Consequently, nitrogen oxide emissions are inherently low.
8. Slagging does not occur at the lower operating temperature and therefore heat transfer surface fouling is low.
9. Trace elements have low volatility at the low operating temperatures. Therefore, corrosion and deposition downstream are less serious and emissions to the environment are reduced.
10. Fluidized bed combustion technology is an extension of existing water wall boiler technology, reducing technology development time.
11. Almost any fuel in the form of solid particles can be burned, including high and low sulfur coal, oil shale, wood and paper wastes, lignite and anthracite culm.

## SALT ADDITION TO FLUIDIZED BED COMBUSTORS

The key feature of minimizing limestone requirements is enhancement of the limestone sulfur capture reactivity. The addition of salt has been found to significantly enhance limestone reactivity and decrease the amount of limestone required. The effect of salt addition was first observed in 1968 by Shelton Ehrlich of Pope, Evans and Robbins, Inc., Alexandria, VA. They found that the level of  $\text{SO}_2$  emissions from fluidized bed combustors with limestone beds could be dramatically reduced if solid salt particles were fed in small amounts to the combustion zone. It became routine until 1975 to add salt to their 9 square foot pilot plant fluidized bed combustion boiler in amounts of about one pound per square foot per hour or about one percent based upon coal. Salt of any convenient size and purity could be used.

Not only was the sulfur capture sorbent more reactive, but also its capacity to contain more sulfur dioxide at saturation was enhanced. The effect seemed to be additive in that sorbent that was apparently saturated with sulfur could be reactivated by the addition of trace quantities of salt to the fluidized bed boiler. Upon cessation of salt feed the sorbent would again become saturated and lose reactivity. It would again regain its reactivity upon resumption of sodium chloride salt feed. The overall effect can be approximated from Figure 2 which is a summary of the Pope, Evans and Robbins data. Figure 2 shows the approximate limestone requirements for two limestones, Greer and Germany Valley, with and without salt addition as demonstrated in the PER

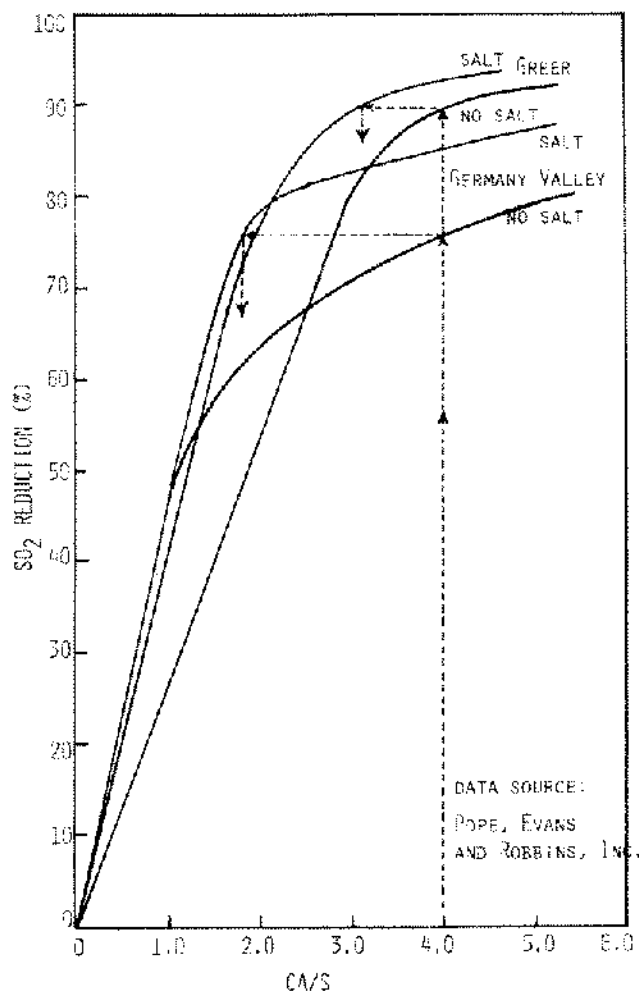


Figure 2. Sulfur capture as a function of limestone feed rate.

pilot plant scale fluidized bed boiler. It can be approximated from these results that for Greer limestone a calcium to sulfur feed ratio of 4.0 will reduce the  $\text{SO}_2$  emissions by about 90% without salt. At this level about a 25% decrease in limestone feed rate is indicated with the addition of salt. Germany Valley limestone is inherently somewhat less reactive. Figure 2 indicates a 76% sulfur capture at  $\text{Ca/S} = 4.0$  without salt which is reduced to  $\text{Ca/S} = 1.9$  with salt addition. The vertical difference between the curves in Figure 2 show enhanced reactivity due to salt addition. For example at a constant feed rate of  $\text{Ca/S} = 2$ , Figure 2 indicates that Greer limestone will remove about 56% of the sulfur without salt or 80% of the sulfur with salt addition.

The major part of the phenomenon is caused by  $\text{NaCl}$  vapor in the internal microcrystalline structures within the limestone particle. Evidence of this is shown in Figure 3. This is part of a run where salt was added to a steady state pilot plant run of Germany Valley limestone and 4.5% sulfur Sewickley coal. What is shown is the mass fraction of particular size cuts of the bed material that is uncalcined

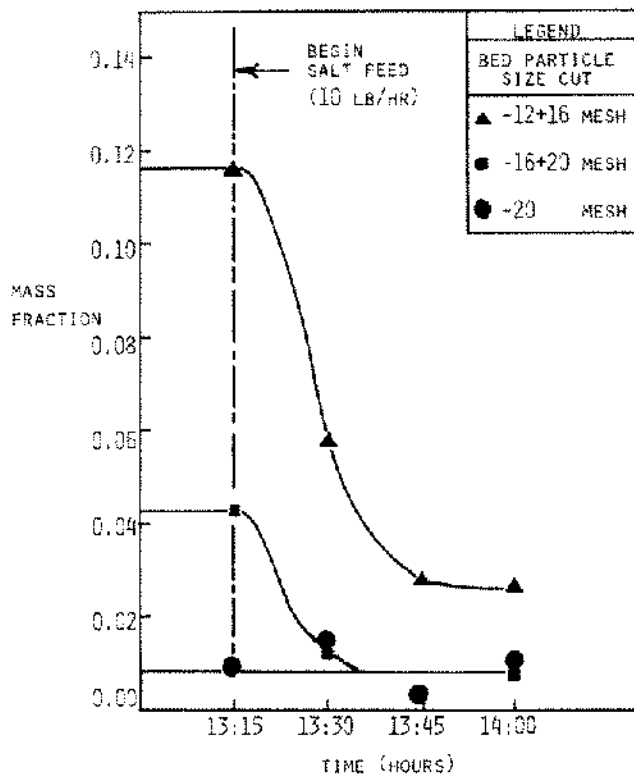


Figure 3. Uncalcined limestone after salt feed initiation.

limestone. It can be seen that the level of uncalcined limestone is greater in the larger particles which is in accordance with the concept that an uncalcined core exists in large particles due to diffusion resistance. The result of the salt addition is a dramatic decrease in uncalcined limestone content of the bed upon the addition of only a trace of salt. After only 15 minutes of salt feeding (2.5 lb.  $\text{NaCl}$ ) to the 800 lb. steady state partially calcined bed, half of the uncalcined limestone in the bed has disappeared. This level of salt addition precludes the possibility of liquid salt wetting all of the internal surface of the limestone. This effect on the internal microstructure can be explained if  $\text{NaCl}$  vapor diffuses into the limestone internal volume acting at internal crystal sites to open up new pores or widen existing pores, thus causing a dramatic change in the resistance to gas diffusion through the sulfated shell of the limestone particle.

Another observation is that this level of sodium addition corresponds to the highest natural levels of sodium content in limestones. The internal natural sodium content of limestones is known to have a beneficial effect on both limestone calcination and sulfation. Perhaps, natural sodium has the same effect as added sodium on the internal limestone microstructure.

One observation that enhances our understanding of this subject concerns the molar volumes of reactants and products of reaction which are as follows:  $\text{CaCO}_3$ , 36.93;  $\text{CaO}$ , 16.59;  $\text{CaSO}_4$ , 45.99  $\text{cm}^3/\text{mole}$ . It can be seen that upon

calcination  $36.93 \text{ cm}^3$  of  $\text{CaCO}_3$  should at equilibrium go to  $16.59 \text{ cm}^3$  of  $\text{CaO}$ , a volume shrinkage of 65%. Available evidence indicates that at these temperatures a constant volume upon calcination is a better approximation. This indicates that the calcined limestone crystal structure is under extreme stress to recrystallize in its equilibrium structure. This shrinkage of the internal microcrystals in a constant volume limestone particle would leave open microvoids which would open up pores and reduce diffusion resistance. It is suggested that the major mechanism of action of salt consists of promoting this shrinkage of internal microcrystals. This occurs due to the transitory presence of a reactive monovalent species in a microvoid causing a disruption in the metastable divalent divalent crystal structure of the calcined limestone allowing localized recrystallization to form the equilibrium  $\text{CaO}$  crystal structure. Both sodium and chloride are appropriate reactive monovalent species. Evidence in the literature suggest that all halogens and all monovalent alkali species would be expected to have some reactivity. Certain other factors could also contribute to the same phenomenon, these are high temperature, hydration and  $\text{CO}_2$  reassociation.

Evidence of this effect is shown in Figures 4 and 5. Figure 4 is a scanning electron microscope view of about  $25 \times 20 \mu\text{m}$  of the surface of a pellet of reagent grade  $\text{CaCO}_3$  which was calcined at  $915^\circ\text{C}$  for 1 hour. Reagent grade was used to isolate the effects of any impurities. It can be seen that the typical grain has straight edges of 1–5 microns in length. This dimension was observed to not significantly change due to calcination alone. It can be hypothesized that the 65% of the internal volume previously occupied by  $\text{CO}_2$  consists of microvoids with approximately the same dimension of a  $\text{CO}_2$  molecule, about  $1.4 \text{ \AA}$ .

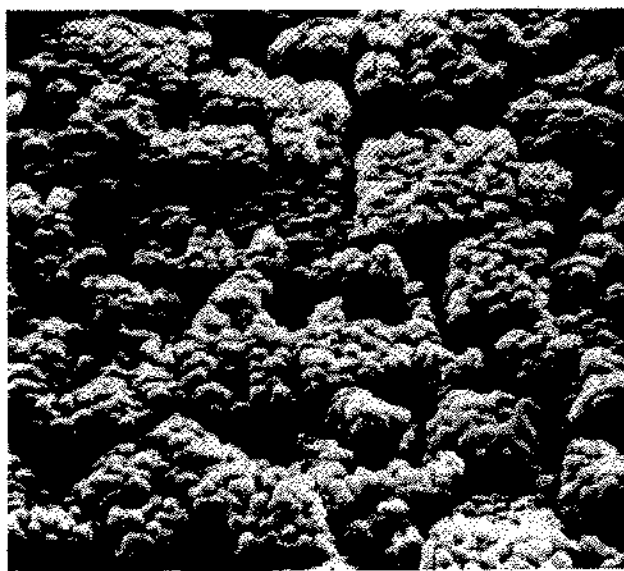


Figure 4. Calcined  $\text{CaCO}_3$  ( $20 \times 25$  micrometers).

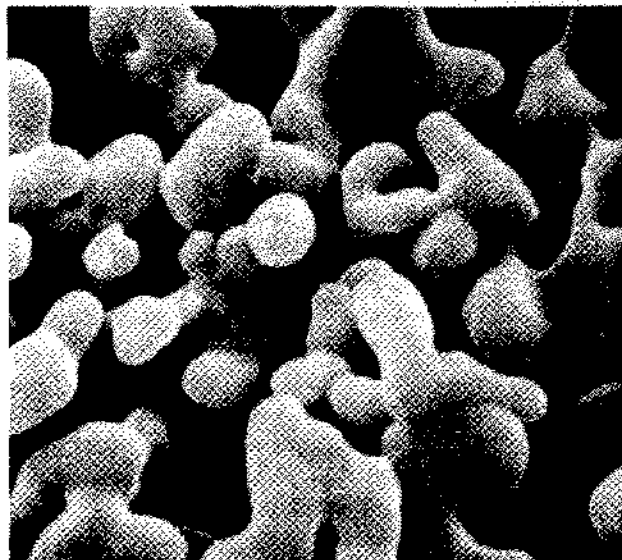


Figure 5. Calcined  $\text{CaCO}_3 + 1\% \text{ NaCl}$  ( $20 \times 25$ ).

Figure 5 shows at the same magnification the surface of a pellet which was identical to the above except that 1% salt was added prior to calcination. It is obvious that significant shrinkage of the microcrystals has occurred, that micropore volume has been exchanged for macropore volume and that the diffusion resistance for gases through the resulting macropores should be significantly less.

#### SUMMARY OF "SALT EFFECT" MECHANISM

1. Upon calcination of limestone or dolomite sorbents, pores are formed by the release of  $\text{CO}_2$ . These pores occupy about 65% of the calcite internal structure.
2. These pores are too small,  $\sim 10 \text{ \AA}$ , to be effectively utilized by the larger sulfate molecules. Sulfate occupies about 50% more volume than does carbonate.
3. Even those pores that are available for utilization tend to become blocked at their mouth by large sulfates. This blockage prevents utilization of the available pores that are more internal to the microcrystal.
4. The limestone internal structure consists of very small microcrystals of calcite embedded in an inert matrix. This matrix effectively fills the volume between microcrystals such that bulk diffusion of  $\text{SO}_2$  gas to the center of the particle is hindered.
5. Salt acts as a sintering agent on the calcite microcrystals. This has two effects:
  - A. The individual calcite microcrystals shrink slightly. This opens up cracks and crevices between the microcrystals and their surrounding inert matrix. A much greater fraction of the microcrystal surface area is exposed for reaction. Also bulk diffusion of  $\text{SO}_2$

gas towards the center of the limestone particle is enhanced as passageways open.

- B. The sintering promotes crystalline rearrangements internal to the calcite microcrystals. These rearrangements increase the size of the individual micropores. The larger size of these micropores facilitates diffusion of  $\text{SO}_2$  to the center of the microcrystal, provides more pores that are large enough to contain the sulfate and makes pore plugging more difficult.
6. The active species is sodium chloride vapor. This dissociates within the calcite structure. Both sodium and chloride diffuse independently through the crystal forming transitory complexes with the calcium oxide structure. The calcium oxide in the metastable calcite lattice is stretched such that the calcium-oxygen-calcium distance is about 1.5 times that of the equilibrium calcium oxide crystal distance. A sodium or a chloride forming a complex with the oxygen or the calcium atom, respectively, causes a local electronic imbalance such that the closest bond disrupts and the neighboring calcium-oxygen bond length decreases to the equilibrium level.
7. Sodium chloride liquid tends to lead to massive recrystallization such that the entire crystal reverts back to the nonporous calcium oxide equilibrium structure. This yields an inactive, deadburned limestone. The liquid state should, therefore, be avoided.
8. Some evidence indicates that the natural sodium and chloride normally contained in limestone and coal leads to the identical effect as added salt.
9. Some of the major evidences of the above interpretation are as follows:
  - A. Pure calcite exhibits a salt effect as does limestone.
  - B. A detailed analysis of the thermodynamics of the possible chemical reactions involved indicates that salt in the vapor phase is greatly more favored.
  - C. Salt when added as a vapor shows the effect.
  - D. Trace amounts of salt, as low as 1 ppm of the weight of the limestone, enhance the sulfation reaction.
  - E. Neither sodium nor chloride residual concentrations can be found in calcite pellets after demonstration of the salt effect.
  - F. Sintering, the salt effect, and sulfation pore plugging have been visually confirmed by scanning electron microscopy.

## ENGINEERING CONSIDERATIONS

We have also concluded as a result of our research that salt should preferably be added as a vapor to a concentration just below its equilibrium saturation vapor pressure. The salt effect is rapid with times of the order of five minutes yielding the full effect. Repeated (for example: 5 minutes out of every 30) or continuous exposure to salt vapor improves performance over a single one-time treatment.

Salt leaves the bed as vaporized  $\text{NaCl}$ ,  $\text{Na}_2\text{O}$  or  $\text{HCl}$ . A chloride balance has found that the chloride that left the bed condensed on the particulates with a trace escaping, presumably on the submicron particulates. The presence of salt on these micron and submicron particulates should enhance the performance of electrostatic precipitators. Other materials containing monovalent alkali metals or halogens such as sodium carbonate or calcium chloride may be substituted for salt. In general, however, their cost is prohibitive.

In order to implement the addition of salt to fluidized bed boilers, a method must be devised and corrosion must be considered. The simplest method of adding salt is to simply add solid salt to the combustor as shown in Figure 6a. After seven years of the addition of solid salt to hundreds of test runs no evidence of salt induced corrosion was found in the PER test boiler. It would be expected that special alloys would be required for surfaces that could not be water cooled. Chemical additives could possibly be used to control corrosive volatiles in the flue gases if downstream corrosion were a consideration. An alternate method of salt treatment could be external to the combustor such as an  $\text{NaCl}$  pretreatment combined with high  $\text{CO}_2$  precalcination as depicted in Figure 6b or by means of a side stream reactivation system such as shown in Figure 6c.  $\text{NaCl}$  vapors would be stripped from the solids by hot entering flue gas and condensed out in a condenser-preheater. This condenser may contain cooled spent bed and operate countercurrent as part of the final bed drain system. This method of operation would isolate possible corrosion outside of the boiler itself. Also, salt treatment corrosion problems may not be severe since no liquid phase ever exists and since sodium or chloride concentrations may never be greater than those associated with burning certain coals or using certain limestones. In addition, since sodium and calcium chlorides have been used for decades as deicing additives in the winter rail shipment of coal, considerable experience may already exist with respect to adding salt to coal fired utility boilers.

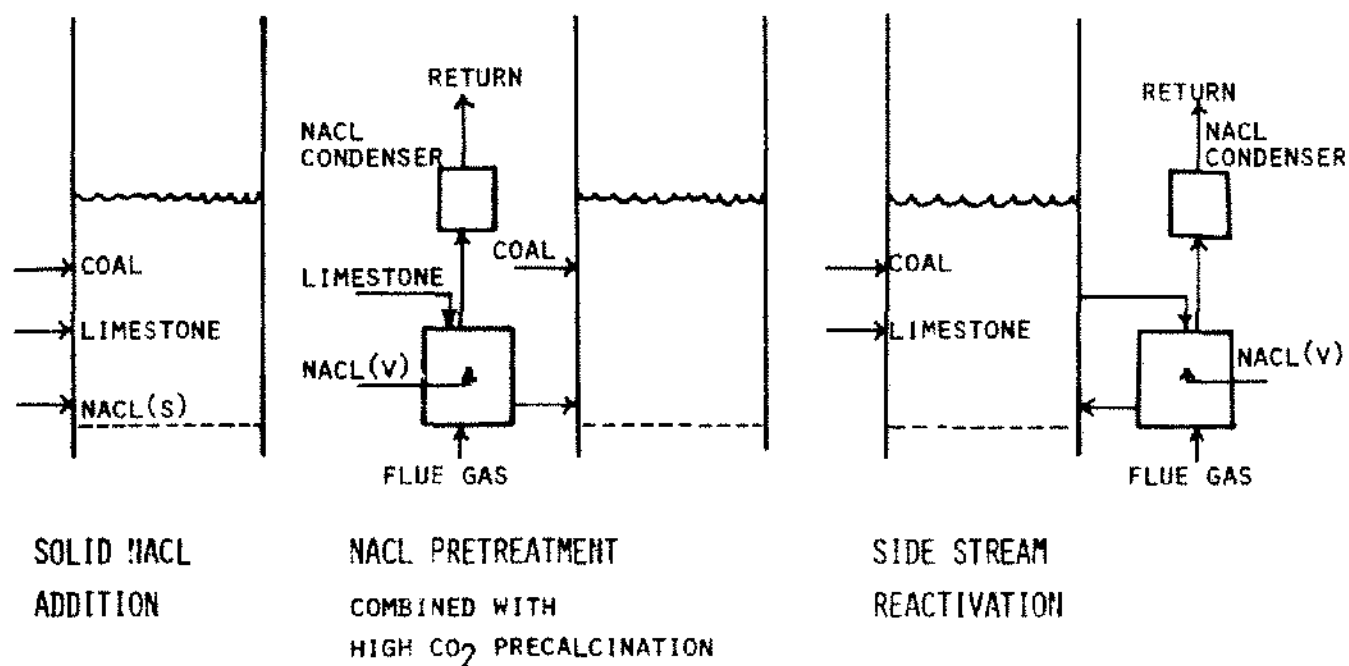


Figure 6. Alternative methods of salt addition.

### CONCLUSIONS

Fluidized bed combustion is a very promising clean air method for utilization of low value solid fuels such as high sulfur coal. Salt addition at a rate of about 1% based upon coal dramatically improves the limestone reactivity and overall economics. Significant advances in the understanding of the "salt effect" mechanism and in the engineering application of salt addition technology have recently been

made. The extent, if any, that corrosion would be changed by salt addition is not currently understood.

### ACKNOWLEDGEMENT

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