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# Statistical Modeling of Constituents in Ash Evolved From Pulverized Coal Combustion

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***Abstract*—**Industries using conventional fossil fuels have an interest in better understanding the mechanism of particulate formation during combustion since such is responsible for emission of undesired inorganic elements that directly impact the atmospheric pollution level. Fine and ultrafine particulates have tendency to escape the flue gas cleaning devices to the atmosphere. They also preferentially collect on surfaces in power systems resulting in ascending in corrosion inclination, descending in the heat transfer thermal unit, and severe impact on human health. This adverseness manifests particularly in the regions of world where coal is the dominated source of energy for consumption.

This study highlights the behavior of calcium transformation as mineral grains verses organically associated inorganic components during pulverized coal combustion. The influence of existing type of calcium on the coarse, fine and ultrafine mode formation mechanisms is also presented. The impact of two sub-bituminous coals on particle size and calcium composition evolution during combustion is to be assessed. Three mixed blends named Blends 1, 2, and 3 are selected according to the ration of coal A to coal B by weight. Calcium percentage in original coal increases as going from Blend 1 to 3.

A mathematical model and a new approach of describing constituent distribution are proposed. Analysis of experiments of calcium distribution in ash is also modeled using Poisson distribution. A novel parameter, called elemental index λ, is introduced as a measuring factor of element distribution.

Results show that calcium in ash that originally in coal as mineral grains has index of 17, whereas organically associated calcium transformed to fly ash shown to be best described when elemental index λ is 7.

As an alkaline-earth element, calcium is considered the fundamental element responsible for boiler deficiency since it is the major player in the mechanism of ash slagging process. The mechanism of particle size distribution and mineral species of ash particles are presented using CCSEM and size-segregated ash characteristics. Conclusions are drawn from the analysis of pulverized coal ash generated from a utility-scale boiler.

***Keywords*—**Calcium transformation, Coal Combustion, Inorganic Element, Poisson distribution.

## I. Introduction

IN general, fine and ultrafine particulates may escape the flue gas cleaning devices (or particle control devices) to the atmosphere as emissions and also preferentially collect on surfaces in power systems reducing the efficiency of the heat transfer thermal unit and causing corrosion. These emissions are severely detrimental to health due to breathing emissions due to the concern in countries where coal is the dominant source of energy.

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Particulates in the submicron range remain in the atmosphere for a long time. Particulate properties and formation mechanisms are so complicated [1] that many research projects are directed towards understanding the process of ash formation and mineral transformation and distribution as well as its constituents in the post-combustion zone. Moreover developing a proper model that has the capability to accurately interpret the mechanism of formation is of concern. Existence of some elements in association form to the actual coal material not to the minerals is making the mechanism even more complication. This is particularly true for calcium and sodium in low rank coals [2].

Studies have shown that submicron particulates contain a wide range of elements depending on the type of coal and process of chemical reaction [1]. Reference [3] reported that the constituents of fine ash particles are limited by not only coal blend but also particle size. Their study concluded that submicron particulates are abundant in Fe and Ca whereas relatively larger sizes are rich in Si and Al in addition to Fe and Ca. Reference [4] identified numerous ash particles of low rank coal as Ca-rich which are primarily CaO derived from the carboxylic-bound calcium present in the coal.

Calcium can act as a flux to decrease viscosity and increase degree of coalescence of particles causing formation of coarse particles. Previous studies have shown calcium is associated with the organic matrix in sub-bituminous coal and its mode of occurrence in the coal has a significant impact on the ash formation and size distribution.

The most significant problem that limits the successful application of SCR catalysts to sub-bituminous coal is the formation of low-temperature calcium sulfates on the surfaces of catalysts and the carryover of deposits that assist in plugging the catalyst openings resulting in ascending pressure drop and descending device efficiency. The degree of the ash-related impacts on SCR catalyst performance depends upon the composition of the coal, the type of firing systems, flue gas temperature, and catalyst design [4].

The fate of calcium during combustion is determined by the mode of occurrence in the parent coal as discrete minerals or organically bound. In both modes, calcium reacts with clay minerals to form a molten glassy phase [5]. However, Ca-rich particles accumulated within the pores and on the surface of the catalyst can react with $SO_2$ and $SO_3$ to form calcium sulfate which causes catalyst pore blinding in the SCR.

Experiments studies also found that alkaline-earth elements such as calcium react with $SO_3$ on the catalyst resulting in plugging of pores. Calcium also plays a role in mitigating other toxic volatiles such as arsenic and selenium [6].

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Although intensive research has been focused on the behavior of calcium during combustion, it is noticed that most of the studies have presented the calcium as associated with included and/or excluded minerals ignoring the influence of organically associated calcium. This study can be considered among the first works that attempt to illustrate the impact of Ca as an organically- associated element versus mineral inclusion/exclusion on the ash formation and size distribution. This study seeks also to understand the influence of blending coals on the Ca distribution and assess the effectiveness of organically bounded mode on particle control equipment that captures Ca.

Particulates in the submicron range remain in the atmosphere for long time [1], [4]. Its properties and formation mechanism are so complicated that it gives understanding the process of ash formation and mineral transformation and distribution as well as its constituents in the post combustion zone serious attention. What is making this complication worse is that some elements may be associated to the actual coal material and are not in a mineral form. This is particularly true for calcium and sodium in low rank coals, making developing a proper model that has capability to accurately interpret the mechanism of formation is necessary.

Although intensive research has been focused on the behavior of calcium during combustion, it is noticed that most of the studies have presented the calcium as included and/or excluded minerals and ignored the influence of organically associated mode particularly on the PSD. The present work can be considered among the first efforts that attempt to illustrate the impact of Ca as organically associated element versus mineral inclusion on the ash formation and size distribution.

## II. Inorganic Impurities

Impurities from inorganic constituents can be alkali and alkaline-earth elements that are organically associated in the coal matrix. Fine particles that penetrate into pores can come from alkali and alkaline-earth elements. These particles can be enriched in elements such as sodium, potassium, phosphorus, known as catalyst poisons, and calcium. Na, K, and Ca-rich particles accumulated within the pores and on the surface of the catalyst may react with $SO_2$ and $SO_3$ to cause catalyst pore blinding [4]. Sodium and calcium are associated with the organic matrix in sub-bituminous coal. Aerosols from sodium-rich coals produce ash deposits and very small particles that are less than 1 micrometer (μm) in size. These small particles can come from a char surface shedding calcium-rich particles. Sodium and calcium can act as a flux to decrease viscosity and increase degree of coalescence of particles thereby forming larger particles [7].

Calcium can come from calcite. Calcite loses carbon dioxide to form calcium oxide. Organically associated calcium diffuses from the carbon matrix to the reducing environment of the boundary layer of a burning char particle from where it encounters oxygen to form calcium oxide.

## III. Transformation of Calcium During Combustion

The key factor of the deposits ash on the boiler water jacket and superheaters is the conversion of calcium during combustion to calcium sulfate [1]. Partitioning of calcium during coal combustion depends upon mode of occurrence (association and chemical characteristics), distribution in minerals, and combustion conditions. Calcium in fly ash may be derived from one of the following paths:

- Agglomeration and/or oxidation of organically associated calcium to form CaO.
- Sulfation of CaO to form $CaSO_4$.
- Reaction of CaO with amorphous alumina and silica that derived from the original. Kaolinite to form Ca-Al-Si compounds.

Another alternative path is the coalescence of minerals. Reference [8] has identified anthracite and brown millerite during low rank coal combustion, which may consider as proof for Ca, Fa, and aluminosilicate coalescence.

## IV. Modeling of Calcium Size Distribution

Distribution of calcium in ash particulates may be described by Poisson distribution formula [9]:

$$P(k;\lambda) = \frac{e^{-\lambda} \times \lambda^k}{k!} \ (k = 0, 1, 2, 3,..) \tag{1}$$

where $P(k; \lambda)$ stands for Poisson distribution; $\lambda$ is the constituent element index; $k$ is the number of occurrence in certain time. Small value of $\lambda$ means that certain element is abundant in small sizes whereas large $\lambda$ can be understood as the constituent is concentrated in large particle sizes.

$\lambda$ can be determined from experimental data using the cumulative weight percent of calcium in ash as CaO or calcite-aluminum-silicate minerals.

The cumulative percent of the Poisson distribution, $F(k;\lambda)$, is written as:

$$F(k;\lambda) = \sum_{i=0}^{k} \frac{e^{-\lambda} \lambda^i}{i!} \tag{2}$$

Calcium in coal as inorganic included mineral occurs as calcite or aluminum silicate. During combustion, minerals could be decomposed and some calcium released as calcium oxide in fly ash. However, little of included calcium release and oxidize [10]. Rather, included calcium may react with other elements to form a more sophisticated morphology such as Al-Si-Ca. Hence, it is reasonable to assume that calcium oxide in fly ash is mainly formed from organically associated and part of inorganic inclusion minerals.

To illustrate the influence of organically associated calcium on Particle Size Distribution PSD, the cumulative percent of calcium in ash resulted from transformation of included minerals, depicted in Fig. 1 (a), is evaluated. Comparing with experimental data, (Fig. 1 (b)), done by UND using 400 MW pulverized coal fired power plant, it is clearly shown that

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calcium is existed in large particulates and just less than 2% of included calcium are oxidized to form CaO. The modeling method shows that the experiment data can be best presented when $\lambda$ is 17.

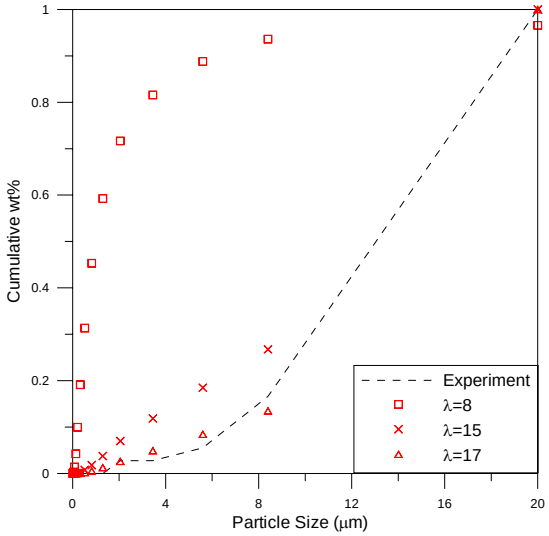



Fig. 1 (a) Cumulative wt% of Included Calcium

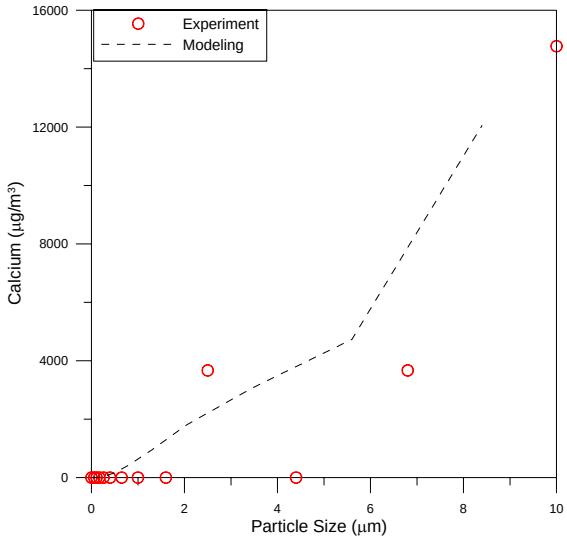



Fig. 1 (b) PSD of included Calcium

In case of organically associated calcium, which after burns completely converts to calcium oxide, experimental data is best represented by $\lambda$ =7 as shown in Figs. (2 (a) & (b)). Such index impresses that organically associated element dramatically impacts the PSD.

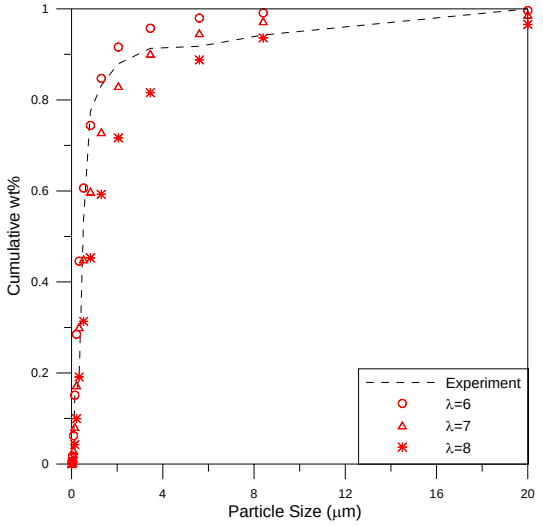



Fig. 2 (a) Cumulative wt% of organically bounded Calcium

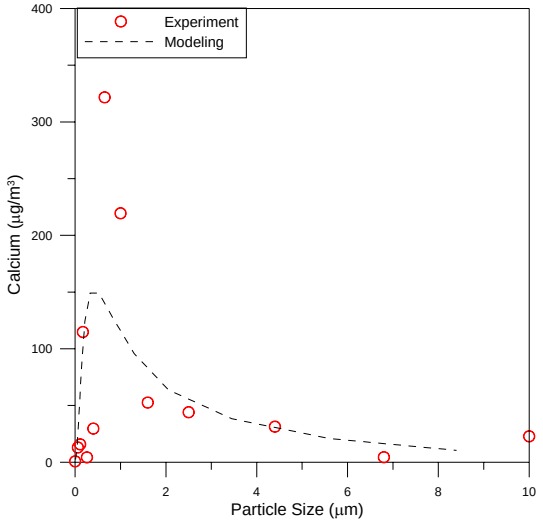



Fig. 2 (b) PSD of organically bounded Calcium

## V. Inlet/Outlet PSD for Calcium as Organically Associated

Measurements of Ca concentration before and after the scrubber have confirmed that there is slight discrepancy in the concentration between scrubber inlet and outlet for Blend 1 as shown in Fig. 3 (a).

As the coal becomes abundant in calcium, the decrement becomes more obvious particularly for large size particulates, as seen in Fig. 2 (b). Fig. 3 (c), which illustrates the calcium distribution at inlet and outlet to the scrubber for Blend 3, is clearly manifested the reduction of constituent across the scrubber. The differences could be returned to the fact that coalescence of small particles that abundant in calcium will form large particles. Such new particles are easy to capture in the scrubber causing remarkable reduction in calcium.

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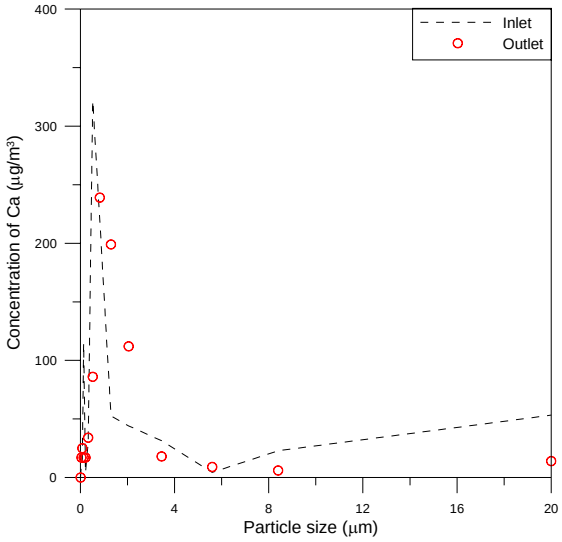



Fig. 3 (a) Calcium Size Distribution for coal (A/B = 75/25)

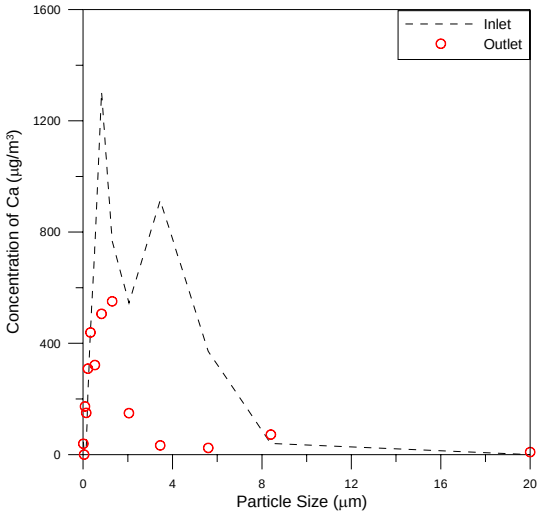



Fig. 3 (b) Calcium Size Distribution for coal (A/B = 50/50)

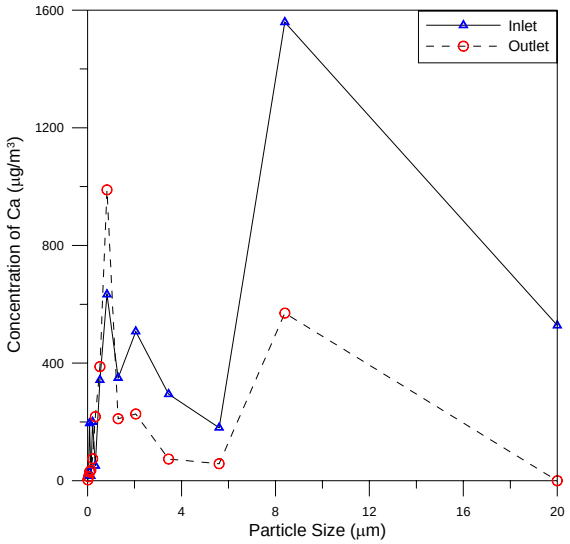



Fig. 3 (c) Calcium Size Distribution for coal (A/B = 25/75)

To demonstrate the impact of calcium concentration in original coal on the ash size distribution, three blends of the two sub-bituminous coals (A/B) are compared. Fig. 4 depicts the impact of calcium as organically associated in the coal on the particle size distribution. It is readily concluded that associated Ca in coals is normally founded in fine and ultrafine ash particulates. However, Ca may be existing with significant amount in large particles when blends with higher Ca constituents burn. This is return to the fact that particulates involved Ca has attitude to coalesce with others to form large particles. Hence, the more associated Ca exists in the coal, the more probability the full coalescence process observed.

In term of ash constituent distribution model, index $\lambda$ will be directly changed with the coal blend. For our situation, $\lambda$ is equivalent to 6, 7, and 10 respectively.

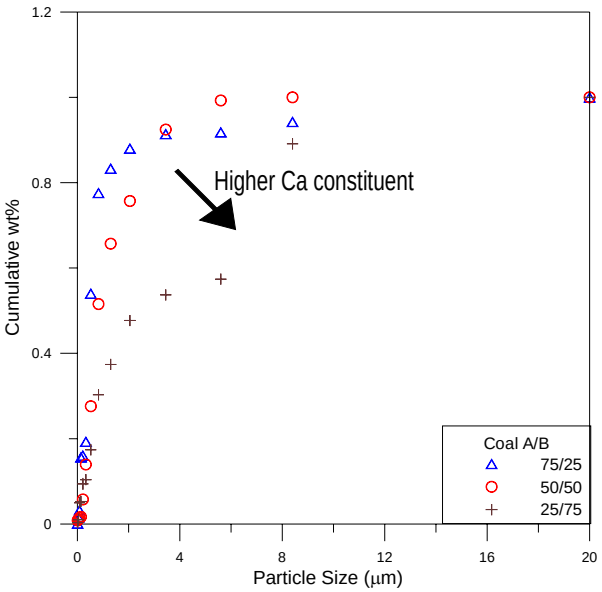



Fig. 4 Comparison between the three blends

## VI. Conclusion

The mechanism of particle size distribution and mineral species of ash particles for three blends of two sub-bituminous coals is analyzed using CCSEM and size-segregated ash characteristics. The impact of calcium mode in parent coal and its transformation during combustion on PSD are also presented by modeling the distribution of calcium in ash before and after scrubber.

Fourteen runs in a 400 MW pulverized coal fired power plant have been statistically modeled for the three blends. The constituent index that describes calcium distribution in ash is shown to be higher for included minerals than organically associated. This could be returned to the fact that carboxyl-bound calcium in the coal transforms to fine and ultrafine particulates during combustion, shifting the peak of PSD profile toward the small size region.

Calcium distribution in ash is modeled using Poisson distribution by proposing a parameter named *elemental index* $\lambda$. Modeling of calcium in ash that originally in coal as mineral grains has index of 17 whereas organically associated calcium

transformed to fly ash shown to be best described when elemental index λ is 7.

Analysis of the experiments revealed that Ca exists more in the intermediate size (fine to coarse) range than ultrafine for Blend 1. Other coal blends had more Ca existing in the ultrafine size range. Ash exhibited mass distributions with the lowest mass in the ultrafine and fine fraction for Blend 1. Mass increases for the submicron size fraction when burning Blend 2. The highest submicron size fraction for ash is shown in Blend 3.

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