

THE RELATIONSHIP BETWEEN  
CATION MOBILITY AND ACID-BASE BEHAVIOR  
IN COAL ASH AND SIMILAR OXIDE SYSTEMS

Karl S. Vorres

Chemistry Division  
Argonne National Laboratory  
Argonne, IL 60439

ABSTRACT

Acids and bases were defined earlier in terms of the ionic potential or cationic charge/radius ratio. Values range from about 10 for acids to about 1 for bases when crystallographic radii in Angstrom units are used. The ionic potential reflects the relative attraction of a cation for charges on a uniform anionic surface. Surface cations have different mobilities on a common anion surface. The most basic ions have the greatest mobility due to the relatively weak attraction for surface anions, which minimizes the energy requirement for surface diffusion and leads to an enhancement of sintering.

INTRODUCTION

The physical properties of mixtures depend on the chemical composition of the constituents. In coal, the mineral matter is a mixture of mineral species. These minerals have been formed from cationic and anionic constituents of widely differing charge and radius. The different charges and sizes lead to different acid-base behavior for the mineral matter. Earlier the ionic charge and radius was used to develop a scale of ionic potential (ionic charge/crystallographic radius of the cation) values for comparing behavior and properties (1,2) of coal ash and similar oxide systems. This scale has been used to interpret the viscosity behavior of molten coal ash (3), and can be used as a guide to selection of additives for modifying the melting behavior of ash.

MINERAL MATTER SOFTENING AND MELTING

The mineral matter in coal is usually a mixture of relatively high-melting species. On heating the interactions between these species takes place slowly and sometimes produces glassy phases. As a result, coal ash and mineral matter samples do not exhibit sharp melting points. The ASTM procedures for reporting ash soft-

tening and melting behavior reflect this behavior (4).

The relatively slow reactions are attributed to the time requirements to bring the reactants together and for the reaction to form new phases. For the relatively silica-rich phases there is relatively little of the mobile species to diffuse rapidly.

#### ACID AND BASE BEHAVIOR

The thermal behavior of coal ash has been described in terms of the melting, viscosity, fouling and slagging. The latter two terms refer to the accumulation of ash material on tubes or wall of boilers. Correlations have been made of ash melting behavior with compositional parameters including silica ratio, dolomite percentage, ferric percentage, sodium content, base content and base-to-acid ratio (5,6,7,8).

In earlier correlations, acids were defined as oxides of Al, Si, and Ti, while bases were defined as oxides of Na, K, Ca, Mg and Fe (6). Other species were not defined, and oxidation states were not involved in the definition, other than to refer to the form of the oxide commonly reported in the analysis. The behavior as an acid or base is related to the structural inorganic characteristics of the ions involved. The inorganic cations may be ranked according to their size or ionic radii for their common valences. In general, ionic radii decrease with increasing cationic charge and also decrease with increasing atomic weight for a given valence.

Values for the cation radii selected from a set given by Ahrens (9) for the metals indicated above are listed below in Angstrom units:

ion	radius	ion	radius
Si <sup>+4</sup>	0.42	Fe <sup>+2</sup>	0.74
Al <sup>+3</sup>	0.51	Na <sup>+1</sup>	0.94
Fe <sup>+3</sup>	0.64	Ca <sup>+2</sup>	0.99
Mg <sup>+2</sup>	0.67	K <sup>+1</sup>	1.33
Ti <sup>+4</sup>	0.68		

The two values for iron are given to indicate that each is important and that the behavior of iron compounds is affected by the oxidation state, which is in turn governed by the gaseous environment and temperature.

#### IONIC POTENTIALS

Another structural concept is that of ionic potential. The ionic

potential is defined as the quotient of the valence or cationic charge and the cationic radius for a given cation. This parameter is a measure of the electrostatic attraction or ability of a given cation to compete with other cations around it for coordinating a common anion, such as the oxide ion. A high value of the ionic potential indicates a strong ability to compete effectively with other cations to form some coordinated complex. Conversely a low value indicates a weak electrostatic attraction or poor ability to compete to form a complex. Therefore a relatively small amount of energy would be required to dislodge the cation from a given complex or site on a surface. The values of the ionic potentials from the cation radii, in Angstrom units, indicated earlier and the oxidation states of the the species of interest are indicated below:

ion	ionic potential	ion	ionic potential
Si <sup>+4</sup>	9.5	Fe <sup>+2</sup>	2.7
Al <sup>+3</sup>	5.9	Ca <sup>+2</sup>	2.0
Ti <sup>+4</sup>	5.9	Na <sup>+1</sup>	1.1
Fe <sup>+3</sup>	4.7	K <sup>+1</sup>	0.75
Mg <sup>+2</sup>			

The highest values belong to the acid group of Si, Al and Ti while the lowest values are associated with the bases K, Na, Ca and also ferrous iron. This scale is useful in understanding and quantifying acid and base behavior.

#### SURFACE DIFFUSION

Other properties also depend on the ionic potential parameters. One of them is surface diffusion. The structure of an idealized solid oxide surface is an ordered array of sites occupied by anions (oxide ions) and a variety of cations. Diffusion across the surface depends on the availability of enough energy to move a surface species from one site to an adjacent site. The energy requirements for a system which can be considered primarily in terms of ionic bonding are a function of the electrostatic forces between the surface substrate and the mobile surface species. In coal ash or mineral species the predominant anion is the oxide ion. To a first approximation, the surface can be considered as a set of oxide anions arranged at sites whose locations and distances apart are a function of the associated cations. Surface cations will be attracted to anionic sites by electrostatic forces, particularly so for the more ionic species characterized by low charge and large radii. These properties are also used to characterize bases on the the ionic potential scale. The energy required to move an ion from one site to an adjacent similar site is largely determined by the magnitude of the ionic potential of

the ion. Therefore those ions with the lower ionic potential will move more easily, or for a given amount of thermal energy, a larger fraction of the ions with the lower ionic potential will migrate from the original sites to adjacent and other ones in a given amount of time.

For two adjacent particles with somewhat different chemical compositions, such as coal mineral matter or ash particles, the ions with the higher mobility or lower ionic potential will preferentially migrate to other particles with the smaller concentration of these ions. As a result the surface of the other particles will be coated with a lower melting phase than would have been possible from the interaction of the species within the higher melting particle. This process will continue at a rate dependent on the supply of low ionic potential ions from the original particle, bulk diffusion of the ions and thermodynamic equilibria.

The diffusion of low ionic potential particles is likely to be much more rapid across surface (by an order of magnitude) than bulk diffusion due to the relative ease when attracted on only one side, and the lack of need to tunnel into the relatively solid oxide structure or to find pores within it. The relatively larger size of these ions also limits the bulk diffusion rate. The result of rapid surface diffusion is "fluxing" or formation of lower melting phases which contribute to the sintering of two or more adjacent particles.

#### ACKNOWLEDGMENTS

The author expresses appreciation to the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, whose support made this work possible.

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