THE FATE OF ALKALIS IN COAL COMBUSTION

G.W. Stewart and C.D. Stinespring
Aerodyne Research, Inc., Bedford, MA 01730

and

P. Davidovits
Aerodyne Research, Inc. and Department of Chemistry, Boston College
Chestnut Hill, MA 02167

INTRODUCTION

In the process of coal combustion, the ash particles deposited on various combustor components can cause serious materials damage. It has been shown that the alkali compounds contained in these particles are among the main causes of corrosion. Such corrosion may be especially damaging in proposed combined cycle power plants where the gas turbine blades are exposed to the combustor and therefore, are in direct contact with particles that escape filtering. To control the corrosive effects of the alkalis, it would be certainly useful to understand the mechanism governing the alkali contents of the particulates.

Over the past few years, a number of measurements have been made to obtain the concentration of trace elements in ash particles. Several of these studies measured the concentrations as a function of particle size.[1-6] In some of the experiments, the surface composition of the larger particulates has also been determined.[7-12] From these data, enrichment factors have been calculated for a large number of elements.[13] A selection from the available data is displayed in Figures 1 and 2 and Table I.

The composition of the smaller particles (a few microns or less) is of special interest since particles in this size range are more likely to escape filtering. It is commonly accepted that enrichment in the submicron particles, as well as on the surfaces of the larger particulates, is due to condensation of volatile species from the vapor phase. This would lead one to expect significant enrichment by elements that are themselves volatile or are found in coal as relatively volatile compounds. By and large, the measurements are consistent with these expectations. Thus, for example, elements such as Pb, Zn, Tℓ, Se, and As which are expected to be volatile, do indeed show significant enrichment in the smaller particles and, where data exist, also on the surfaces of the larger particles. However, an examination of the data shows that the alkalis exhibit a surprising departure from this trend. One would certainly expect the alkalis to be among the more volatile

species. In fact, combustion experiments done under laboratory conditions show significant vaporization of the alkalis.[14] Yet, the data gathered from actual coal combustion plants show that the smaller particles are not enriched by the alkalis. On the other hand, the surfaces of the larger particles do show significant enrichment by them.

The observation that the small ash particles are not enriched by the alkalis suggests that, contrary to expectations, the alkalis are not volatilized under actual case combustion conditions. If this is the case, the observed surface enrichment of the larger particles is not due to condensation, but must be produced by some other process, possibly diffusion from the interior to the surface.

Experiment Results

Evidence for these suggestions is found in the recent work of Stinespring and Stewart[15] and Stewart et al.[16] These experiments studied the behavior of the alkalis in model components under various coal combustion conditions. Since the alkalis are found in the organic as well as the inorganic components of coal, it is important to understand their behavior in both types of sites. Illite, which is a potassium containing aluminosilicate mineral, was chosen as a typical inorganic coal component. Sodium and potassium benzoate were chosen to represent the alkali containing organic fraction. These experiments examined the behavior of several elements; however, we will focus here only on the results relevant to the alkalis. Auger Electron Spectroscopy (AES) was used to determine the surface composition of aluminum silicate minerals which are heated in a well controlled environment. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on the model organic compounds to determine the extent of alkali release from the organic constituent.

The depth profiles for potassium indicate that the surface concentration of potassium begins to increase at temperatures as low as 200°C and it reaches an enrichment of about 13 at 1100°C. The depth of enrichment is about 100A. Order-of-magnitude calculations indicate that diffusion may occur on a time scale compatible with the residence time of ash particles in the combustor. From these results we conclude that alkali enrichment on the larger ash particles may indeed result from segregation rather than adsorption or condensation.

The DTA/TGA studies of sodium and potassium benzoate decomposition show that these model molecules initially decompose to form condensed ring organic molecules, alkali carbonate, and carbon dioxide. This initial decomposition process occurs over the temperature range of 400 to 600°C and is independent of the gas stream composition. Over this temperature range, there is no loss of alkali into the gas phase. Rather, all of the alkali is converted into the corresponding alkali carbonate. At higher temperature, the alkali carbonate decomposes and the course of this decomposition is determined primarily by the composition of the ambient gas. In an inert gas stream, the alkali carbonate decomposes over the temperature range of 700 to 900°C with release of carbon monoxide and atomic alkali. This decomposition has been confirmed by transporation mass spectrometer studies.[17] However, in a stream containing 20% CO_2 between 700 and 900°C, only carbon monoxide is released and the alkali is converted to alkali carbonate. This rection sequence occurs as long as residual carbon and carbon dioxide are present. Once the excess carbon has been converted to carbon monoxide, the alkali carbonate will decompose at temperatures in excess of 1200°C. Experiments were also performed with a combination of SO_2, CO_2, and O_2 in the gas stream. Here, it was found that the alkali carbonate is converted to the alkali sulfate with no indication of alkali loss over the temperature range studied (< 1300°K).

CONCLUSIONS

Thus, the results of the measurements and experiments discussed above do provide a plausible way to begin an explanation for the distribution of alkali in the ash particulates. To summarize:

1. Under typical coal combustion conditions in an atmosphere rich in CO_2 and/or SO_2, the alkalis in the organic fraction do not vaporize but remain bound in the ash as stable carbonates or sulfates.

2. The alkalis in the inorganic fraction diffuse to the surface producing enrichment by a factor of about 13 to a depth of about 100A.

The results, however, do not provide conclusive evidence about the fate of the alkalis. The effect of water vapor in the combustion stream has not yet been studied. Clearly, water could have an important effect on the vaporization process. Furthermore, the reasoning we have followed to explain the absence of alkali enrichment in the submicron particles requires that the volatilization of the alkalis in both the organic and inorganic fraction not be significant (say less than 20%).

It is possible to make a reasonably clear statement about the alkalis in the organic fraction under various combustion conditions. Here, the volatilization of the alkalis is primarily determined by the heterogeneous chemical reaction of the alkalis with the gas stream. Such detailed information, however, is not available for the alkalis in the inorganic fraction. Here, experimental data were not obtained under appropriate conditions. Thus, the combustion experiments of Mims et al., which do show significant alkali vaporization, were performed in an O_2 atmosphere without CO_2 or SO_2 enrichment. The experiments of Stinespring and Stewart, with the inorganically bound alkalis, measured only enrichment and did not study vaporization. The results of recent vaporization studies of Hastie et al.[18] were also not performed under conditions directly applicable to coal combustion. Clearly, a wider range of experimental data will have to be obtained. Specifically, the effects of surface chemistry on the alkali in the inorganic fraction will have to be studied before a more conclusive statement can be made about the fate of the alkali in coal combustion.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy/Morgantown Energy Technology Center under Contract No. DE-AC21-81MC16244.

REFERENCES

1. D.F.S. Natusch and J.R. Wallace, Science 186, 695 (1974).

2. R.L. Davison, D.F.S. Natusch, J.R. Wallace, and C.A. Evans, Jr., Environ. Sci. & Technol. 8, 1107 (1974).

3. J.M. Ondov, R.C. Ragaini, and A.H. Biermann, Environ. Sci. & Technol. 13, 947 (1979).

4. D.G. Coles, R.C. Ragaini, J.M. Ondov, G.L. Fisher, D. Silberman, and B.A. Prentice, Environ. Sci. & Technol. 13, 455 (1979).

5. L.E. Wangen, Environ. Sci. & Technol. 15, 1081 (1981).

6. R.D. Smith, Prog. In Energy & Comb. Sci. 6, 53 (1980).

7. R.W. Linton, A. Loh, and D.S.F. Natusch, Science 191, 852 (1976).

8. J.A. Campbell, R.D. Smith, and L.E. Davis, Appl. Spectrosc. 32, 316 (1978).

9. S.J. Rothenberg, P. Denee, and P. Holloway, Appl. Spectrosc. 34, 549 (1980).

10. R.W. Linton, P. Williams, C.A. Evans, Jr., and D.S.F. Natusch, Anal. Chem. 49, 965 (1977).

11. L.D. Hulett and A.J. Weinberger, Environ. Sci. & Technol. 14, 965 (1980).

12. L.D. Hansen, D. Silberman, and G.L. Fisher, Environ. Sci. & Technol. 15, 1057 (1981).

13. Enrichment factors are obtained by normalizing to the bulk composition of the large particles (say > 30 μm).

14. C.A. Mims, N. Neville, R.J. Quann, and A.F. Sarofim, "Laboratory Studies of Trace Element Transformation During Coal Combustion," Presented at the 87th AIChE Meeting, August 1979, Boston, Mass.

15. C.D. Stinespring and G.W. Stewart, Atmos. Environ. 15, 307 (1981).

16. G.W. Stewart and A. Chakrabarti, High Temperature-High Pressure (In press) (1982).

17. A. Chakrabarti, D.W. Bonnell, G.W. Stewart, and J.W. Hastie, To be published (1981).

18. J.W. Hastie, E.R. Plante, and D.W. Bonnell, Interim Report No. NBSIR 81-2279, U.S. Department of Commerce, National Bureau of Standards, Washington, DC 20234 (1981).

SURFACE AND BULK ENRICHMENT OF COAL COMBUSTION ASH FOR SELECTED ELEMENTS

ELEMENT	ENRICHMENT		
	BULK*	BULK**	SURFACE***
As	9.4	13.4	---
Cd	11.5	---	---
Cr	2.4	6.2	3.3
Pb	3.8	8.4	11.0
Sb	7.9	---	---
Se	10.4	5.4	---
Tℓ	---	4.9	10.0
W	7.1	---	---
Zn	7.8	6.2	7.2
Aℓ	1.0	1.6	1.1
Ca	1.1	1.0	1.6
Cℓ	1.1	1.0	---
Cs	1.2	---	---
Fe	1.3	1.3	0.8
K	1.1	1.3	7.6
Mg	1.3	---	0.9
Mn	1.5	1.7	6.4
Na	1.5	---	15.2
Rb	1.1	1.7	---
Ti	1.2	1.2	0.9
Be	1.6	---	6.0
Cu	2.3	2.2	
V	3.8	2.7	2.0

*Bulk enrichment defined as the ratio of the concentration in a 1μ particles to that in an 18.5μ particle, from D.G. Coles, R.C. Ragaini, J.M. Ondov, G.L. Fisher, D. Silberman, B.A. Prentice, Environ. Sci. & Tech., 13, 455 (1979).

**Bulk enrichment defined as the ratio of the concentration in a 0.15μ particle to that in a 20μ particle, from R.D. Smith, Prog. in Energy & Comb. Sci., 6, 53 (1980).

***Surface enrichment defined as the ratio of the surface composition divided by the composition at 500 Å, from R.W. Linton, P. Williams, C.A. Evans, Jr., and D.S.F. Natusch, Anal. Chem., 49, 1514 (1977).

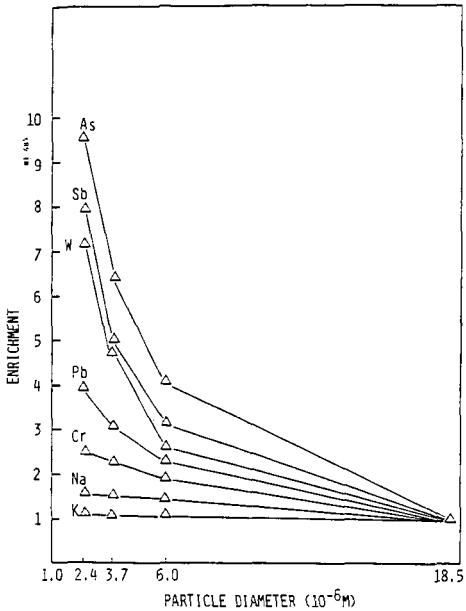

Figure 1, Enrichment vs. Particle Size, Based on Data from Coles et al., Environ. Sci. and Tech., 13, 455 (1979).

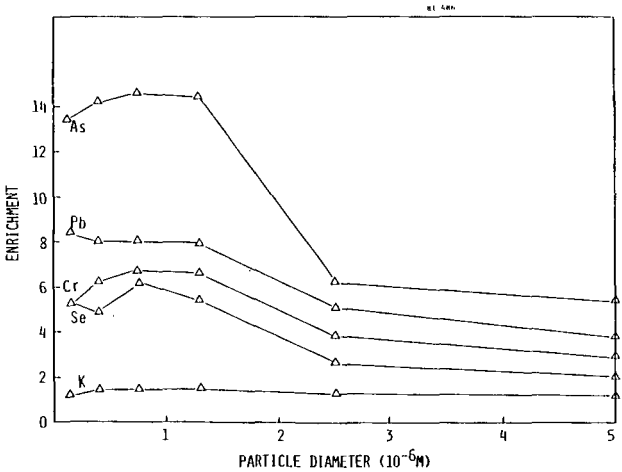

Figure 2. Enrichment vs. Particle Size, Based on Data by Smith, Prog. Energy and Comb. Sci., 6, 53 (1980).