

A KINETIC DESCRIPTION OF ALKALI TRANSFORMATIONS
IN COAL COMBUSTION SYSTEMS

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ABSTRACT

A kinetic model was developed to predict concentrations of atomic and molecular sodium species existing in both flame and post-flame zones of pulverized coal combustors. To date, the model has successfully predicted measured literature values of sodium species in the Na/H₂/O₂/N₂ system. At all but the earliest conditions (< 1 ms) sodium hydroxide is predicted to be the dominant species. Atomic sodium levels decay rapidly, representing less than one percent of the total sodium species present at times greater than 5 milliseconds for lean hydrogen flames (H₂/O₂ = 0.6, temperature = 1650°C). Incorporation of sulfur chemistry into the model did not change this conclusion, as sodium hydroxide was still found to dominate. Further development, however, awaits determination as to whether alkali sulfation occurs in the vapor or the condensed phase, as well as the correct corresponding kinetics. Efforts in these areas are discussed.

BACKGROUND

The release of alkali species during the combustion of pulverized coal can seriously affect both deposition and corrosion of boiler components. Deposition can be affected as follows: Subsequent to combustion, vaporized alkali species will condense on, and possibly interact with, the fly ash particles present in the flue gas. Alkali species are known to reduce the viscosity of silica melts. If this interaction generates ash particles with reduced viscosity below the critical point for deformation and adhesion - a likely result - ash particle deposition may substantially increase, as results have shown that reduced particle viscosities generate increased sticking efficiencies (1,2). Direct condensation of alkali species on cooled tube surfaces may also affect deposition by generating a sticky layer on the tube surface, thereby increasing the sticking efficiency of impacting ash particles. Corrosion can also be directly affected by condensation of alkali species on the boiler tube surfaces. Clearly, the extent of influence the alkali species exert on the deposition and corrosion processes will depend upon the particular species present, as the various alkali compounds have different vapor pressures and hence will condense at different temperatures (locations) within a boiler.

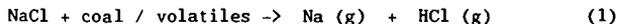
Although it is accepted that the atomic alkali species is the vaporizing species during combustion (except for coals with high sodium chloride

content, in which case it is also as the chloride), it is presently unclear when transformations to molecular oxide species occur, and at what point the assumption of equilibrium is valid. For this reason, a kinetics scheme was developed to follow the transformations of atomic sodium in a combustion environment. The model, which employs the CHEMKIN chemical kinetics code to solve the complex series of reactions, has been used to reproduce species profiles for $H_2/O_2/N_2/Na$ flames appearing in the literature. Modified species profiles resulting from addition of sulfur to the reaction chemistry, utilizing the preliminary sulfation kinetics scheme proposed by Domazetis and Campisi (3), have also been generated, and are discussed herein.

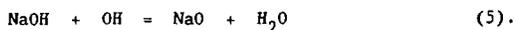
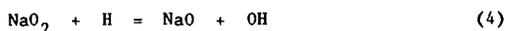
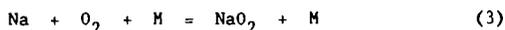
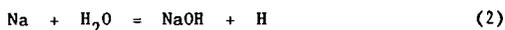
SODIUM VAPORIZATION

Sodium may occur in several forms within a given coal. It may be present as NaCl inclusions, less frequently as small Na_2SO_4 inclusions, or as organically bound material directly attached to the coal structure via carboxylic acid groups. Both of these forms readily vaporize under the high temperature environment of coal combustion, generating atomic sodium and/or NaCl in the vapor phase. Sodium also frequently appears as a component in the clay minerals such as plagioclase, $NaCaAlSi_3O_8$, contained in coals, though thermodynamic calculations have indicated that sodium has low activity in sodium - silica melts (4), thus suggesting that it may be relatively inert to vaporization in this form.

Vaporization of both the chloride and organic forms of sodium occurs rapidly at temperatures well below peak flame temperature, as measured by atomic absorption at SECV and shown in Fig. 1. Sodium carboxylates dissociate in the range 400 to 800°C, forming Na_2CO_3 , which subsequently decomposes further to form atomic Na at temperatures below 900°C. Sodium chloride also vaporizes rapidly under these conditions. Calculations indicate that in the temperature range 1000 - 1100°C, NaCl will completely vaporize in approximately 10 ms, and hence before char oxidation is fully under way. Vaporization of NaCl resulting from reduction to the volatile metallic form may compete with this process, via the reaction (3)



Upon vaporization, the atomic Na quickly encounters the complex chemical environment surrounding the reacting particle. Many species, including H, OH, CO, O, and H_2O are present in this environment, and may potentially affect the conversion of sodium to bound molecular states. Work in laboratory hydrogen flat flames has indicated this to be true, as experimental measurements of Na and OH coupled with kinetic modeling in lean flames demonstrated that Na profiles roughly track the decay of H atoms (5). In that study, the authors demonstrated that despite the existence of some twenty forward/reverse reactions affecting sodium species in their hydrogen flame, the complex sodium chemistry was dominated by just four reactions:

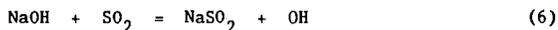


MODEL DEVELOPMENT AND RESULTS

By utilizing these four reactions in conjunction with a detailed hydrogen oxidation reaction sequence (6), CHEMKIN was used to determine species concentration levels for comparison to the data of reference (5). Note that the authors of reference (5) successfully modeled the kinetics in their study using measured OH as an input; in the model described and tested herein, OH is a predicted quantity. For typical lean flame data of $\text{H}_2/\text{O}_2/\text{N}_2$ equal to 0.6/1/1, corresponding to an average measured temperature of 1917 K (6), sodium levels are predicted to decay rapidly. As the curves in Figure 2 demonstrate, this decay parallels the rapid decrease in atomic hydrogen concentration. Sodium hydroxide is seen to be the dominant sodium compound at all times greater than 0.5 ms, as predicted by the measurements and calculations in reference 5.

Calculations were repeated under higher temperature conditions, where $\text{H}_2/\text{O}_2/\text{N}_2$ ratios of 1.8/1/3 yielded flame temperature of 2350 K. Under these conditions (results not shown), atomic sodium persisted for longer periods of time, and was present in levels comparable to NaOH. Again, the concentration profiles predicted here agree closely with those measured (OH and Na) and predicted by the investigators of the aforementioned study.

Calculations were also carried out subsequent to the incorporation of sulfur into the reaction matrix. Sodium-sulfur species are of prime interest in this study, as they are thought to play a major role in initiating deposition in the cooler regions of utility boilers. Although several studies have indicated the major sodium - sulfur reaction to be (7)



the entire sulfur reaction sequence, including all anticipated reactions with H, OH, and O was incorporated into the kinetic model discussed herein. Values for the reaction rate coefficients for this set of reactions were obtained from Domazetis and Campisi (3).

The effect of low levels of sulfur (0.4% by volume) on the sodium reaction chemistry can be seen by comparing species concentrations in Figure 2 with those presented in Figure 3, which includes sulfur. Temperature was assumed equal in both calculations, as the small amount of sulfur added will have a negligible effect. At 1917 K for the $\text{H}_2/\text{O}_2/\text{N}_2$ levels considered previously,

NaOH is still seen to be the dominant sodium species. Both NaSO_2 and NaO_2 are also predicted to occur, but at only 1% of the level of NaOH.

Although vapor phase Na_2SO_4 was considered in the reaction sequence, the calculations performed to date suggest that it will not form under these flame conditions. The possibility has not been excluded, however, as we have not yet identified a fundamental kinetic mechanism which permits the formation of Na_2SO_4 based upon collisions of gas phase species. This raises an interesting point as to the exact origin of sodium sulfate, as sodium sulfate is often identified in boiler deposits, and is frequently assumed to be the cause of initiation of convective pass fouling. The limited experimental data available to date indicate that vapor phase sodium sulfate may indeed form at flame conditions (not specified) (8), as determined by molecular beam mass spectrometry, though further evidence including a plausible kinetics scheme has not been presented. An independent set of calculations (3) suggest another mechanism for formation of Na_2SO_4 in the "vapor," as a result of complexing of species such as NaOH and NaSO_2 during condensation. This proposed non-elementary formation process has not been verified experimentally.

Efforts are currently under way on several fronts in the coal combustion community in an effort to conclusively determine the point (and phase) of alkali sulfation. Atomic sodium release and oxidation in coal systems is being studied through atomic laser-induced fluorescence (9), while at PSIT, techniques which permit direct measurement of alkali chloride and hydroxide in the vapor phase (10) are being employed in a combustion experiment to determine the location of sulfation. Traditional combustion experiments geared toward inducing preferential condensation of the sulfate are also under way at PSIT.

SUMMARY

In summary, a kinetic model utilizing sodium reaction sequences and rate coefficients from the literature has been incorporated into CHEMKIN. The model was able to successfully predict literature values of species concentrations in lean $\text{H}_2/\text{O}_2/\text{N}_2$ flames doped with sodium. Extension of the model to incorporate gas phase sulfur chemistry suggested that NaOH will still dominate under oxygen rich atmospheres, though NaO_2 and NaSO_2 will also form. The absence of vapor phase Na_2SO_4 suggests that Na_2SO_4 formation is a condensed phase reaction, though further mechanistic information is required before this can be conclusively determined. The possible existence of this species under other conditions is currently under investigation experimentally, as conclusive determination of the phase in which reaction to form alkali sulfate occurs remains to be accomplished.

ACKNOWLEDGMENTS

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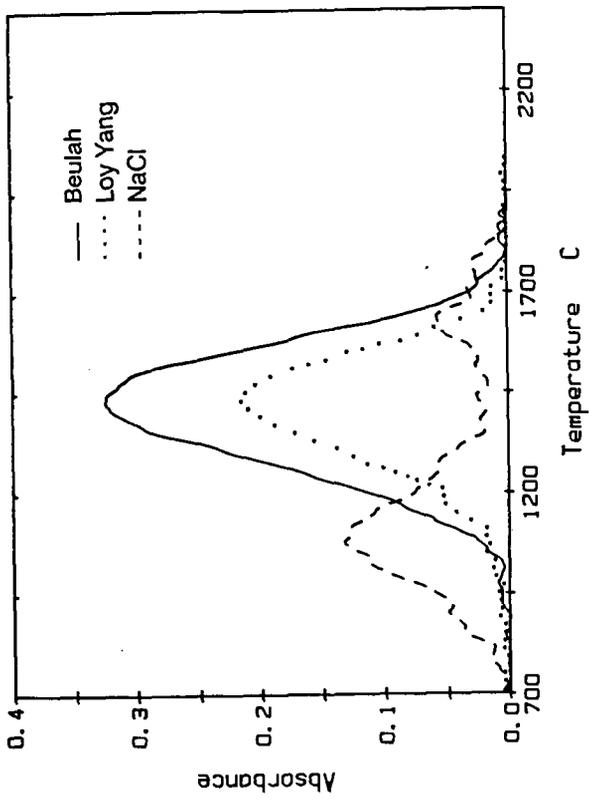
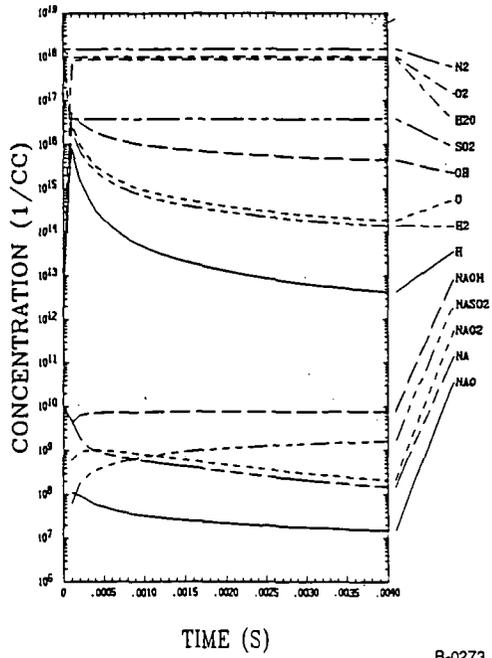


Figure 1 - Atomic Na formation profiles from Beulah and Loy Yang coals by AA

H₂ / O₂ / N₂ / S
0.6 / 1.0 / 1.0 / 0.01



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Figure 2 Model Predictions Without Sulfur

H₂ / O₂ / N₂ / S
0.6 / 1.0 / 1.0 / 0.00

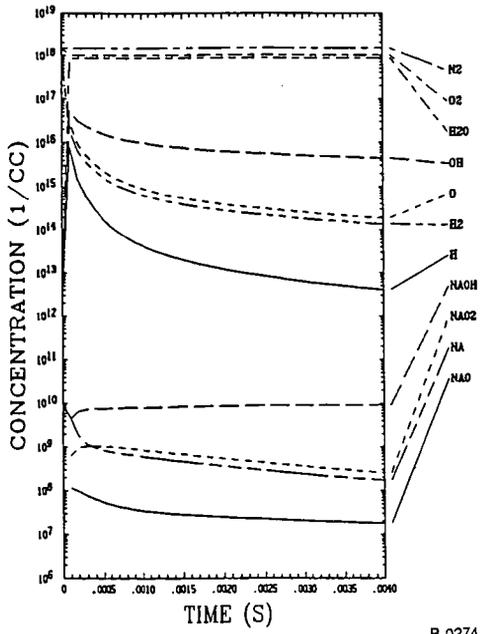


Figure 3: Model Predictions Incorporating Sulfur