

SYNERGISTIC CAPTURE MECHANISMS FOR ALKALI AND SULFUR SPECIES FROM COMBUSTION

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Prepared by

T.W. Peterson, F.Shadman, J.O.L. Woadt and P.O. Mwabe.
Department of Chemical Engineering,
University of Arizona,
Tucson, AZ 85721

Submitted to

Felixa Eskey,
Pittsburgh Energy Technology Center,
U.S. Department of Energy,
P.O.Box 10940
Pittsburgh, PA 15236-0940

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SUMMARY

The research described here is directed towards an investigation of mechanisms governing the capture of alkali metals and SO₂ by injection of clay based sorbents into a combustor environment. While the species of interest are products of coal combustion, the earlier parts of these investigations will use a gas flame doped with relevant levels of Potassium, Sodium and Sulphur dioxide typical of a coal flame environment. This ensures that the particles so sampled from the combustor are from the injected sorbents and not mixed with coal ash.

The research is motivated both by results of previous bench scale studies using a simulated flue gas environment and certain 'getter' compounds and by the fact that Sulphur dioxide capture using sorbent injection has been studied extensively.

The approach here is to translate results from bench scale studies into evaluating governing mechanisms at a practical combustor level scale in which there exist both temperature variations and flow mixing characteristics. The research will thus consist of two tasks:

1. Detailed experimental studies for Alkali metals K, Na and toxic metal Cr in the presence of SO₂ in which effect of parameters such as Speciation, Temperature profiles, Injection temperatures, residence time, bulk concentration levels, sorbent particle size and sorbent injection rates will be evaluated.
2. Theoretical modelling: Both equilibrium thermodynamics and reaction kinetic models will be used to correlate the experimental data.

For these experiments the Sorbent type is Kaolinite (Al₂O₃.2SiO₂.3H₂O) which has been identified as most effective in alkali metal capture^[5].

Summary of Work Completed This Quarter:

The following tasks were completed during the period covered by this report:

1. Equilibrium model predictions of Alkali/Sorbent interactions with Temperature as an independent variable.
2. Design, fabrication and testing of sorbent feed system.
3. Four (4) laboratory combustor runs with Potassium Acetate as alkali source.
4. Recruitment and Training of a Research Assistant who will be responsible for sampling and detailed analytical Chemistry work.
5. Training on the Scanning Auger Microscope model Phi-600 which will be used for surface analysis of particles.

DETAILED DESCRIPTION OF WORK PERFORMED

Task 1: Equilibrium Studies of Sorbent/Alkali Metal Interactions:

Software used: Computer program for calculations of complex Chemical Equilibrium compositions by S. Gordon & B. McBride

Parameters: Trace species of Na, K and SO₂ are included in a Methane/Air mixture that simulates flue gas at various Temperatures typical of a combustor environment. Solid Sorbent compositions are also included. Typical input parameters were as follows:

Alkali metal:	approximately 100 ppm of flue gas
SO ₂ :	approximately 80 ppm of flue gas
Temperature:	500 K - 1800 K
Sorbent:	Increased until maximum capture is achieved
Convergence:	0.01 ppmv considered as trace species and is omitted

The above software has been developed by NASA and is suited for equilibrium predictions appropriate for solid-liquid-gas reactions in solid fueled rockets. Chemical equilibrium is formulated in this program using minimisation of Gibbs Free Energy.

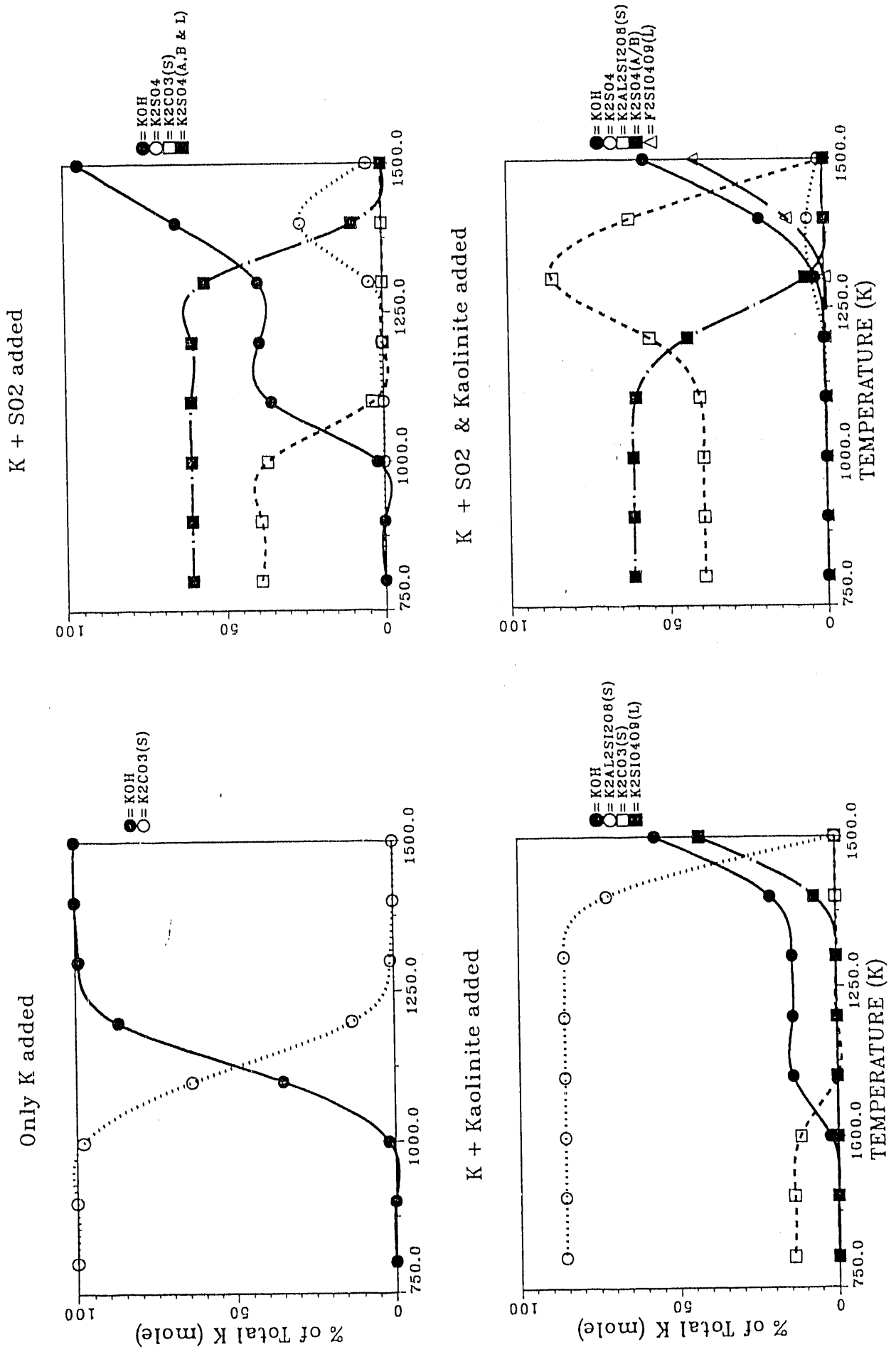
It is worth pointing out at this stage that the predicted stable species from complex reactions depend on the available species in the program data bank. The data on alkali aluminosilicates has been found to be limited. Results presented should be treated with caution. They are, nevertheless, useful in order to give a qualitative picture of possible species formed.

The capture of alkali metals using activated Kaolinite represents a combination of solid/gas reactions together with solid/condensed phase reactions of the alkali metal compounds. In an *in-situ* application, both the residence time and the temperature profiles become critical factors. It is further postulated that at higher temperatures, the reaction rates may be fast enough to achieve equilibrium, thus maximising the alkali metal capture. At lower temperatures, the solid phase transformations that would lead to lower captured alkali metals are slow, so that the alkali metal is 'frozen' in a non equilibrium concentration in the sorbent matrix.

Results:

Typical results from these studies are summarised in Tables 1 and 2 and Fig. 1 for the potassium/kaolinite system. When kaolinite is added to the potassium system in the absence of SO₂, the predicted (equilibrium) captured species is K₂O.Al₂O₃.2SiO₂(s) (Kaliophilite). The proportion of Kaliophilite remains constant up to a temperature of approximately 1450°K. Above this temperature, the fraction of kaliophilite drops rapidly and the major

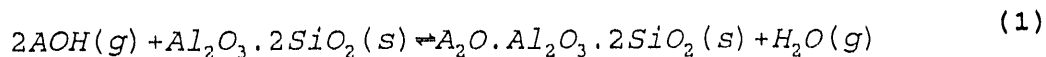
FIG 1. EQUILIBRIUM DISTRIBUTION OF MAJOR POTASSIUM SPECIES
 K, SO₂, Kaolinite in Nat. gas/Air combustion



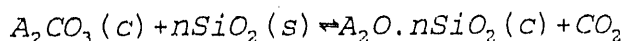
kaolinite/potassium species that increasingly becomes stable, is the condensed glassy form $K_2O \cdot 4SiO_2(c)$. When SO_2 is added, the formation of condensed sulphates reduces the total kaliophilites formed by approximately 40%, up to a temperature of $1100^\circ K$. Above this temperature, the proportion of kaliophilites increases and reaches a maximum at $1300^\circ K$, a temperature at which the effect of SO_2 addition is negligible. Above $1300^\circ K$ the fraction of kaliophilite drops linearly with temperature, to reach zero at $1500^\circ K$.

Similar trends were observed for Sodium but in the absence of data for Nephelite etc only the glassy reactions forming $Na_2O \cdot SiO_2(s/c)$ between kaolinite and Sodium is presented as the stable species. This result is possibly suspect.

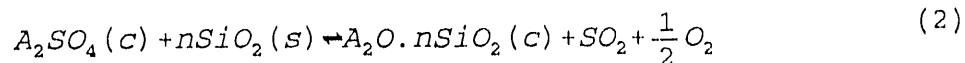
The program, CET86, does not contain data on nephelite and it is conceivable that the glassy reactions presented is the second best reactions available for sodium. The stable species for potassium, predicted by CET86, agrees with the results of earlier work by Punjak & Shadman and the proposed reaction (1) will be considered as the major capture reaction. This reaction is given as¹:



At temperatures above $1300^\circ K$, both sodium and potassium appear in glassy condensed species possibly given by reactions such as:



or



with $n = 4$ for the case of CET86 model results.

It may be concluded that reaction (1) above is the major reaction of alkali metal capture while the glass reactions (2) are the minor capture reactions above $1300^\circ K$. In the presence of SO_2 both reactions (1) and (2) will be inhibited, with Reaction 1 inhibited by the reduced gas phase concentration of AOH as a result of formation of condensed sulphates. Reaction (2) is inhibited by an equilibrium shift to the left in the presence of SO_2 .

In summary, it can be seen that the presence of trace SO_2 may result in reduction of Alkali metal capture by as much as 50%. This will obviously be of interest in the in situ application of sorbents to capture alkali metals.

¹

A denotes Alkali metal species and is used throughout the report.

Task 2: Design Fabrication and Testing of Sorbent feeder.

An ideal feeder would probably consist of a hopper mounted on set of load cells in which feed rates are monitored continuously via a chart recorder. For reasons of cost and time this will not be used at the moment instead a simple design consisting of an Auger bit screw feeder in a low pressure dilute phase (4 psi/ 1 cfm) pneumatic conveying system was designed. A 4" X 12" cyclone separator was also designed and used for measuring an average feed rate of sorbent. The results were found to give reasonably acceptable sorbent feed rate data.

The problem with this system is it depends on ability of the sorbent to flow freely and is prone to leaks at the seals. In all experiments, the sorbent is baked overnight to reduce its moisture content and increase its flowability. Leaks can be minimised by running the system at lower pressures (~2 psi to be tried) and use of a full sorbent hopper.

TASK 3.

Combustor Studies.

A downfired 17kW industrial type combustor was used for the experiments (Fig. 2). Design and features of this combustor are contained in previous works of Bassham^[8]. Of interest is the fact that the residence time in the combustor is order of 2-3 seconds and the the Temperature range is between 400°C to 1400°C.

The main thrust of these initial runs were to test the following system parameters:

- Sampling system
- Effect of various filters on particle collection data.
- Alkali metal bulk concentration and Atomic Absorption results.
- Sorbent feeder performance.

In all the runs (Run No 1 - Run No 4). The fuel was Natural gas at approximately 1 cfm. Air as oxidant was added at a rate to give a stoichiometric ratio of 1.2; Sorbent was fed at top port no. 3 and all particle samples taken at bottom port no 13. A temperature profile was taken after warming the furnace for approximately 8 hours. Particle sampling was carried using Anderson 1 ACFM impactor.

It was found that the furnace exhaust temperature did fluctuate by about 10⁰ C during the next 8 hrs of sampling which is acceptable and may be considered as steady state conditions. A total run time for this kind of experiments is approximately 16-20 hours i.e 8 hrs warming up and further 8 hrs for 6 impactor samples. The results of these runs are still awaiting Atomic Absorption analysis and will be used for design of all next quarter experiments.

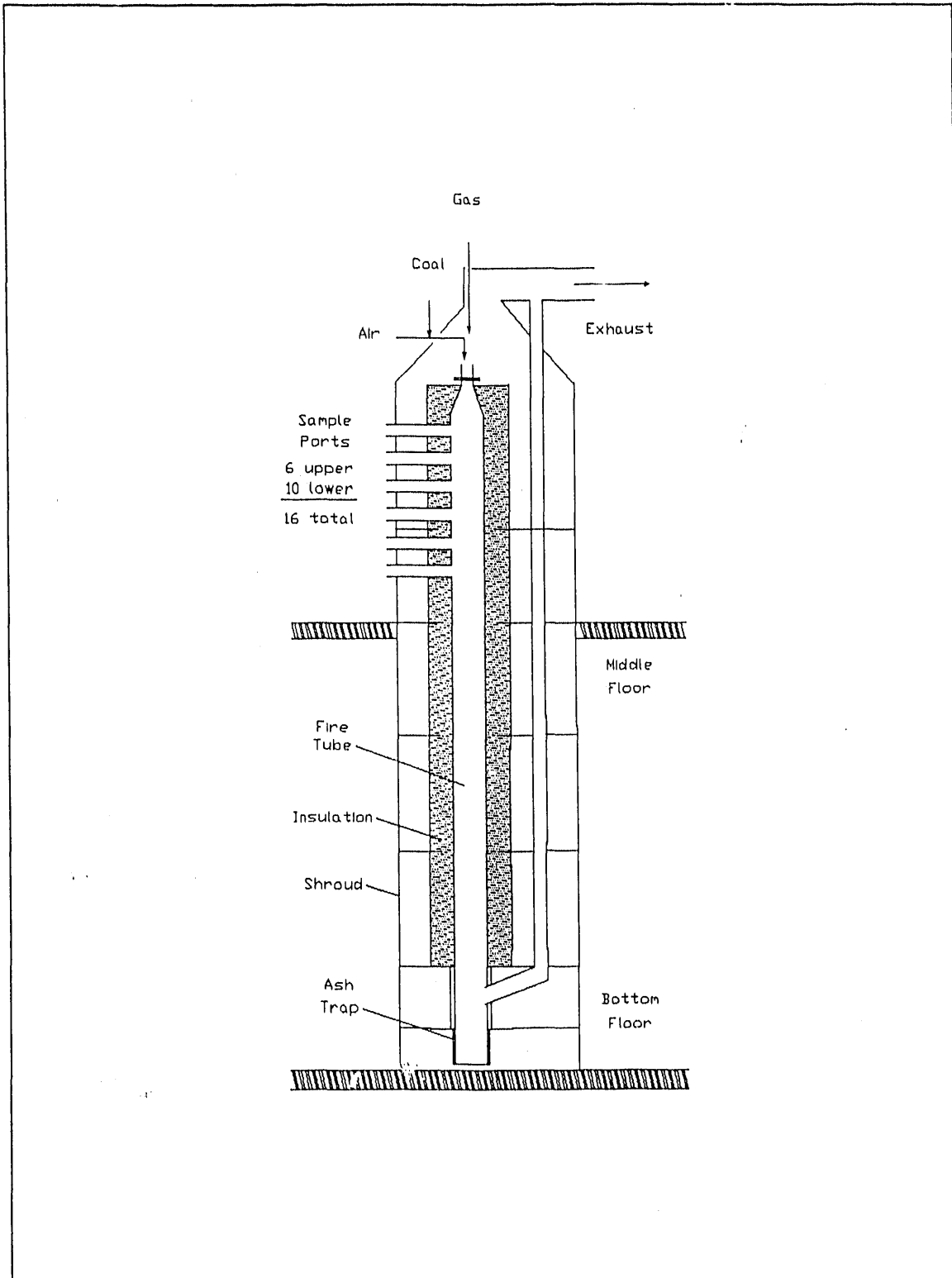


Figure 2: Downflow Laboratory Combustor

POT1; DISTRIBUTION OF POTASSIUM IN COMBUSTOR (No SO ₂ added)													
Burn conditions:													
Fuel: Nat. gas; Oxidant: Air ; SR: 1.2 ; Sorbent: Kaolinite Al ₂ O ₃ ·2SiO ₂ (S) 0.06% of fuel (mole)													
T, DEG K	1800	1700	1600	1500	1400	1300	1200	1100	1000	900	800	700	600
SPECIES	% DISTRIBUTION OF TOTAL POTASSIUM												
K	2.1	1.0	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KO	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KOH	97.6	98.7	71.3	69.2	53.7	7.7	7.7	7.7	6.1	0.2	0.0	0.0	0.0
K2AL2SI2O8(S)	0.0	0.0	0.0	0.0	0.0	92.3	92.3	92.3	92.3	92.3	92.3	92.3	92.3
K2CO3(S)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	7.5	7.7	7.7	7.7
K2SI4O9(L)	0.0	0.0	28.1	30.5	46.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
% gas phase	99.7	99.7	71.6	69.3	53.7	7.7	7.7	7.7	6.1	0.2	0.0	0.0	0.0
% S/L phase	0.0	0.0	28.1	30.5	46.1	92.3	92.3	92.3	93.9	99.8	100.	100.	100.
% Capture	0.0	0.0	28.1	30.5	46.1	92.3	92.3	92.3	92.3	92.3	92.3	92.3	92.3

POT2; DISTRIBUTION OF POTASSIUM IN COMBUSTOR FLUE GAS WITH SO₂ ADDED

Burn conditions:

Fuel: Nat. gas; Oxidant: Air ; SR: 1.2 ; Sorbent: Kaolinite Al₂O₃-2SiO₂(s) 0.06 mole % of fuel
 SO₂ added : 0.035 mole % of fuel approximately 28 ppm

T, DEG K	1800	1700	1600	1500	1400	1300	1200	1100	1000	900	800	700	600
% DISTRIBUTION OF TOTAL POTASSIUM IN PRESENCE OF SO ₂													
K	2.1	1.0	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KO	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KOH	97.9	99.0	71.6	69.1	49.9	6.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ SO ₄	0.0	0.0	0.0	0.3	4.0	2.5	1.2	0.1	0.0	0.0	0.0	0.0	0.0
K ₂ Al ₂ Si ₂ O ₈ (S)	0.0	0.0	0.0	0.0	0.0	91.6	90.0	48.7	46.3	46.2	46.2	46.2	46.2
K ₂ SO ₄ (A)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	53.9	53.9	53.9
K ₂ SO ₄ (B)	0.0	0.0	0.0	0.0	0.0	0.0	8.4	51.2	53.8	53.9	0.0	0.0	0.0
K ₂ Si ₄ O ₉ (L)	0.0	0.0	28.1	30.5	46.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
% gas phase	100	100.	71.9	69.5	53.9	8.5	1.7	0.1	0.0	0.0	0.0	0.0	0.0
% S/L phase	0.0	0.0	28.1	30.5	46.2	91.6	98.4	100.	100.	100.	100.	100.	100.
% Captured	0.0	0.0	28.1	30.5	46.2	91.6	90.0	48.7	46.3	46.2	46.2	46.2	46.2
% reduction in capture due SO ₂ addition	0.0	0.0	0.0	0.0	0.0	0.7	2.3	43.6	46.0	46.1	46.1	46.1	46.1

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