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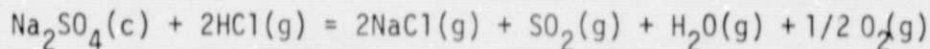
# INTERACTION OF NaCl(g) AND HCl(g) WITH CONDENSED Na<sub>2</sub>SO<sub>4</sub>

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## ABSTRACT

The interaction of Na<sub>2</sub>SO<sub>4</sub>(l) with NaCl(g), HCl(g) and H<sub>2</sub>O(g) was studied in atmospheric pressure flowing air and oxygen at Na<sub>2</sub>SO<sub>4</sub>(l) temperatures of 900 and 1000°C. Thermomicrogravimetric and high pressure mass spectrometric sampling techniques were used. Experimental results establish that previously reported enhanced rates of weight loss of Na<sub>2</sub>SO<sub>4</sub>(l) in the presence of NaCl(g) are due to the reaction



being driven to the right in flowing gas systems. The HCl(g) is the product of hydrolysis of NaCl caused by small but significant amounts of H<sub>2</sub>O(g) present in the system. Thermochemical calculations are used to show that even with sub-ppm levels of H<sub>2</sub>O(g) present, significant quantities of HCl(g) are produced.

## INTRODUCTION

The role that condensed or gas phase sodium chloride plays in the hot corrosion process is not well understood and is the subject of a number of current investigations. When studying the effect of NaCl(c) on Na<sub>2</sub>SO<sub>4</sub>(l)-induced attack of metals, investigators use test methods in which mixtures of the salts are applied as deposits on samples or in which samples are immersed in crucibles containing mixtures of the salts. Maintaining the desired composition of the salt mixture is a problem in long duration, high temperature tests because the NaCl vaporizes preferentially. This is due to the fact that the vapor pressure of sodium chloride is orders of magnitude greater than that of sodium sulfate.

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Pettit and coworkers (refs. 1, 2) attempted to avoid the preferential loss of NaCl from NaCl(c)-Na<sub>2</sub>SO<sub>4</sub>(c) mixtures by adding partial pressures of NaCl(g) to the flowing air used in their tests. They reported that instead of suppressing the loss of NaCl from the mixture, the addition of NaCl(g) resulted in an increased rate of weight loss of the entire deposited mixture. This unexpected behavior prompted them to perform additional experiments with inert metal samples to eliminate any possible corrosion effects. Deposits of Na<sub>2</sub>SO<sub>4</sub>(c) were applied to platinum samples which were then heated to 1650°F in flowing air containing 300 ppm by weight of NaCl(g). Under these conditions, the samples lost weight at a linear rate of 0.4 mg cm<sup>-2</sup> hr<sup>-1</sup>. Furthermore, the same rate of weight loss was observed when the inlet air was bubbled through water. In the absence of the NaCl(g) addition to the air flow, the rate of weight loss was reported to be 0.004 mg cm<sup>-2</sup> hr<sup>-1</sup>. Thus the enhancement in rate of weight loss of Na<sub>2</sub>SO<sub>4</sub>(l), produced by the addition of NaCl(g) ± H<sub>2</sub>O(g) to the air flow, was a factor of 100.

Jones et al. (ref. 3) carried out similar experiments with Na<sub>2</sub>SO<sub>4</sub>(c) deposits on platinum samples. With sample temperature held at 1600°F and 300 ppm NaCl(g) added to flowing air, they reported a weight loss rate of 0.03 to 0.05 mg cm<sup>-2</sup> hr<sup>-1</sup> when the inlet air was passed through Drierite (anhydrous CaSO<sub>4</sub>) and 0.1 mg cm<sup>-2</sup> hr<sup>-1</sup> when the air was bubbled through water.

Smeggil observed thermogravimetric results in his hot corrosion studies (ref. 4) which suggest that NaCl(g) promoted the loss of Na<sub>2</sub>SO<sub>4</sub>(l) from his samples. He performed additional experiments with Na<sub>2</sub>SO<sub>4</sub>(c) deposits on platinum substrates which he heated in flowing air with partial pressures of NaCl(g). Preliminary results indicated anomalously large weight loss rates (ref. 5).

The observations of Pettit et al., Jones et al. and Smeggil appear to be inconsistent with what one would predict on the basis of equilibrium thermodynamics. This fact and our continuing interest in hot corrosion phenomena prompted us to initiate the work reported herein. Our high pressure mass spectrometric sampling facility (ref. 6) is a powerful tool for studying systems at atmospheric pressure. Na<sub>2</sub>SO<sub>4</sub>(l)-NaCl(g) interactions were studied at a total pressure of one atmosphere of air or oxygen for various temperatures of Na<sub>2</sub>SO<sub>4</sub>(l) and for various partial pressures of NaCl(g) and H<sub>2</sub>O(g). Mass spectrometric sampling was used to identify and monitor gas phase species. In addition, continuous recording thermomicrogravimetric

measurements were used to determine condensed phase weight change rates. Experimental measurements were supplemented with thermodynamic calculations. Although this work is still in progress, the results presented here elucidate the interaction of  $\text{NaCl(g)}$  with  $\text{Na}_2\text{SO}_4(l)$ .

## EXPERIMENTAL

Materials.— For all of the experimental results reported here,  $\text{Na}_2\text{SO}_4(c)$  coatings were applied to Pt 20% Rh metal coupon substrates. The coupons were approximately  $2.2 \times 1.3 \times 0.038$  cm in size and had a 0.32 cm diameter hole near one end to facilitate hanging. Coatings of  $\text{Na}_2\text{SO}_4(c)$  were applied by spraying a saturated aqueous sodium sulfate solution onto the faces of the coupon as it was heated on a hot plate to about  $150^\circ\text{C}$ . The quantity of  $\text{Na}_2\text{SO}_4(c)$  applied was determined by weighing and ranged from 2 to  $4 \text{ mg cm}^{-2}$ . Fisher certified grade sodium sulfate was used.

Initially, gold coupons were tested as substrates for  $\text{Na}_2\text{SO}_4(c)$  but recorded weight change curves for various conditions were found to be not reproducible. Visual examination, after interrupting the experiment at various stages, revealed that the  $\text{Na}_2\text{SO}_4(c)$  coating after melting was not uniform over the sample. Distinct droplets of  $\text{Na}_2\text{SO}_4(c)$  were apparent and the size and distribution of the droplets were different for each test. Examination of a gold sample by scanning electron microscopy with energy dispersive X-ray analysis revealed that the  $\text{Na}_2\text{SO}_4(c)$  did not cover the entire surface area with even a thin film. Apparently  $\text{Na}_2\text{SO}_4(l)$  does not wet gold. Such a situation presents an unknown and nonreproducible surface area of  $\text{Na}_2\text{SO}_4(l)$  for vaporization and interaction with  $\text{NaCl(g)}$  during our tests. This then probably accounts for the lack of reproducibility observed in weight change curves for gold substrates.

Visual examination of Pt 20% Rh coupons coated with  $\text{Na}_2\text{SO}_4(c)$  was made at various stages of thermogravimetric tests. It was always noted that  $\text{Na}_2\text{SO}_4(l)$  tended to run down and form a thick section near the bottom of the coupon. Also, some  $\text{Na}_2\text{SO}_4(l)$  usually crept up the hangdown suspension hook. Thus, while the  $\text{Na}_2\text{SO}_4(l)$  appeared to wet the entire coupon surface area, we feel there is still a problem which precludes normalizing weight changes in terms of sample area.

Thermogravimetry.— Weight change experiments were carried out in the apparatus shown schematically in figure 1. A Cain type



RH microbalance, the output of which was continuously measured with a strip chart recorder, was used to follow the coupon weight change. The balance was operated with a sensitivity setting such that 5 micrograms of weight change produced one millimeter of deflection on the recorder chart. Because of noise produced in our flowing gas system, this was the highest practicable sensitivity that could be used.

The sample was hung from the balance with a 0.127 mm diameter hangdown wire with a 0.5 mm diameter wire hook at its lower end. The hangdown wire and hook were Pt 13% Rh alloy. The sample hung in a 2.3 cm inside diameter quartz tube attached to the balance enclosure by a greaseless ball and socket joint. To protect the balance from corrosive vapors, air was passed down through the balance enclosure at a rate of 365 cc/min. An equal flow of air was passed over the sample by flowing air into the inlet at the lower end of the quartz tube. Both gas flows exited from the system through the single gas exhaust shown in figure 1. Exhaust gas was bubbled through a 2.5 cm high column of vacuum pump oil. Air was supplied from the laboratory compressed air service line and each flow was passed through a 6 cm diameter by 20 cm high column of Drierite. When desired, the air flow over the coupon could, by appropriate valving, be bubbled through water before entering the system.

A portion of the quartz tube was located in a 2.86 cm inside diameter by 20 cm high movable furnace. The furnace temperature was controlled by a precision setpoint, proportional controller and silicon controlled rectifier power supply. Sample temperature was measured by a Pt-Pt 13% Rh thermocouple brought in through the bottom of the quartz tube. The thermocouple junction was located adjacent to the center of the sample. Ice-point compensated thermocouple voltage was read with a digital voltmeter.

Partial pressures of NaCl(g) were generated by heating pre-melted sodium chloride contained in a platinum crucible. The crucible was supported on a double bore alumina tube containing a thermocouple whose junction was in contact with the crucible bottom. The alumina tube-crucible assembly could be moved vertically through a slip-seal in the bottom end of the quartz tube. Crucible temperature was varied by vertical positioning of the crucible in the furnace and measured with the ice-point compensated thermocouple and a digital voltmeter. Sample and crucible temperatures were set and controlled to  $\pm 1^\circ\text{C}$ .

The operating procedure was to hang the  $\text{Na}_2\text{SO}_4(\text{c})$ -coated sample from the balance with the furnace cool and lowered below the sample. The salt crucible was lowered below the furnace. Gas flow was initiated and the balance was allowed to settle down to a steady state. The furnace was turned on and once it reached the set-point temperature, it was raised up to the desired position to heat the sample. The sample reached the operating temperature, either 900 or 1000°C, within five minutes after raising the furnace.

Prior to investigating  $\text{Na}_2\text{SO}_4(\text{l})$ - $\text{NaCl}(\text{g})$  interactions, a number of "calibration" experiments were performed. The rate of weight gain due to condensation of  $\text{NaCl}$  on the hangdown wire was measured. This rate,  $R$ , in  $\text{mg hr}^{-1}$  was measured, with an uncoated Pt 20% Rh coupon, as a function of coupon temperature and  $\text{NaCl}(\text{g})$  concentration. The air flow was held constant at  $365 \text{ cc min}^{-1}$  and a fixed position for the furnace was maintained. For coupon temperatures of 900, 950 and 1000°C,  $R$  was found to be linear in time, independent of sample size and dependent on salt crucible temperature,  $T_{\text{NaCl}}$ , according to the Arrhenius relationship:

$$\log R = \frac{-A}{T_{\text{NaCl}}} + B \quad (1)$$

where  $A$  and  $B$  are constants whose value depends on the sample temperature.

The concentration of  $\text{NaCl}(\text{g})$  added to the air flow was measured as a function of temperature of the salt crucible. Concentration,  $C$  in ppm by weight, was determined by measuring the weight loss of salt in the crucible, after fixed increments of time at temperature, and calculating the weight of air that flowed in the time increment. For the flow rate of 365 cc/min,  $C$  was found to vary with crucible temperature according to the relationship:

$$\log C = \frac{-a}{T_{\text{NaCl}}} + b \quad (2)$$

where  $a$  and  $b$  are constants whose value depends on the geometry of the apparatus.

High Pressure Mass Spectrometric Sampling.— A high pressure, free jet expansion, modulated molecular beam, mass spectrometric sampler and flow-tube system was used to identify directly gas phase species involved in  $\text{Na}_2\text{SO}_4(\text{c})$ - $\text{NaCl}(\text{g})$  interactions under

various conditions. The apparatus is shown schematically in figure 2. Details of this apparatus have been presented previously (refs. 7, 8). The sample was suspended from a platinum wire in a 2.5 cm diameter quartz tube contained in a tube furnace. A smaller diameter, 1.5 cm, inner quartz tube extended up to within about a centimeter of the sample. Gas (oxygen or air) was fed independently to each tube and the total flow was 365 cc/min. The two-tube arrangement was used to facilitate adding water vapor to the outer tube only so as to protect the salt, contained in the Pt 20% Rh crucible, from hydrolysis. Sample and crucible temperatures were measured as in the thermogravimetric apparatus. All experiments were performed at atmospheric pressure.

The theory and description of the sampler have been presented elsewhere (ref. 6). Briefly, gas enters the sampler through a 0.25 mm diameter Pt 20% Rh sampling orifice located in the apex of a short 106 degree sampling cone. The gas is expanded as a free jet, converted to a molecular beam and passed, via differentially pumped vacuum stages, into a quadrupole mass spectrometer operated at pressures below  $10^{-8}$  torr. The molecular beam is modulated by a rotating segmented disc and synchronous detection is used to measure ion currents resulting from ions produced by electron bombardment of the neutral molecular beam.

When sampling systems containing condensible gas-phase species, it is desirable to have the sampling orifice as hot as practical to minimize clogging of the orifice. In our apparatus, the sampling cone protrudes into the flow tube and furnace as shown in figure 2. The orifice temperature attained in any experiment depends on the selected sample temperature. At sample temperatures below about 1000°C, with NaCl(g) concentrations above about 200 ppm, orifice clogging becomes a problem and limits the duration of experiments. Therefore, most experiments were performed at sample temperatures of 1000°C or higher and with NaCl(g) concentrations below about 150 ppm.

For the majority of the sampling experiments, oxygen was used as the flowing gas because it results in lower "metastable noise" (ref. 9) and produces "quieter" mass spectra than does air. However, even with the high purity tank oxygen used, interference is encountered in certain regions of the mass spectrum. Rare gas impurities contained in the oxygen are the cause of such interference. For example, the  $^{40}\text{Ar}^+$  signal precludes measurement of the  $\text{NaOH}^+$  ionic species.



## RESULTS AND DISCUSSION

Thermogravimetric Experiments.— Figure 3 shows a typical recorded weight change curve for a  $\text{Na}_2\text{SO}_4(\text{c})$ -coated Pt 20% Rh coupon at  $900^\circ\text{C}$ . Also shown in this figure is the linear weight gain curve (obtained for an uncoated coupon at  $900^\circ\text{C}$  when 300 ppm  $\text{NaCl}(\text{g})$  was added to the air flow) that results from  $\text{NaCl}(\text{c})$  pickup by the hangdown wire. Before  $\text{NaCl}(\text{g})$  is added to the flow, the coated coupon is seen to lose weight linearly in time due to vaporization of  $\text{Na}_2\text{SO}_4(\text{l})$ . When a partial pressure of  $\text{NaCl}(\text{g})$  (300 ppm by weight) is added to the "dry" air flow, a rapid weight gain is observed before the curve gradually levels off and transcends to a linear rate of weight loss. Finally, when  $\text{H}_2\text{O}(\text{g})$  is added to the  $\text{NaCl}(\text{g})$ -containing air flow, the rate of weight loss is seen to increase. The perturbation shown when the  $\text{H}_2\text{O}(\text{g})$  was added is due to the disturbance of the balance produced by switching from dry to wet air.

Recorded weight changes for coated coupons must be corrected for (1) the concurrent weight gain due to  $\text{NaCl}$  condensation on the hangdown and (2)  $\text{Na}_2\text{SO}_4(\text{l})$  vaporization weight loss. The first correction is obtained from "calibration" experiments and the second is obtained from the beginning of the curve obtained before the addition of  $\text{NaCl}(\text{g})$ . When such corrections are made, we see that the net weight loss rate resulting from the addition of  $\text{NaCl}(\text{g})$  and  $\text{NaCl}(\text{g}) + \text{H}_2\text{O}(\text{g})$  is appreciable.

The initial weight gain observed upon addition of  $\text{NaCl}(\text{g})$  was presumed to be due to the absorption of  $\text{NaCl}$  by the  $\text{Na}_2\text{SO}_4(\text{l})$ . To verify this presumption, several experiments were interrupted during the initial weight gain by rapidly lowering the furnace and crucible and cooling the sample. The sample was removed from the apparatus and rinsed with water to remove all deposit. The resulting solution was analyzed for chloride. The calculated amount of  $\text{NaCl}$ , corresponding to the quantity of chloride, was found to be in excellent agreement with the respective recorded weight gain. These tests established that indeed the observed initial weight gain upon the addition of  $\text{NaCl}(\text{g})$  is due to the absorption of  $\text{NaCl}$  by the  $\text{Na}_2\text{SO}_4(\text{l})$ . This point will be discussed in more detail later.

Numerous experiments were performed at sample temperatures of 900 and  $1000^\circ\text{C}$  with 300 ppm  $\text{NaCl}(\text{g})$ . In these experiments, the reproducibility of the  $\text{Na}_2\text{SO}_4$  vaporization weight loss rate and initial weight gain upon addition of  $\text{NaCl}(\text{g})$  were found to be

satisfactory. However, the weight loss rates measured after the addition of NaCl(g) and H<sub>2</sub>O(g) showed poor quantitative reproducibility. At the present time, we cannot explain the quantitative variation observed in our experimental results. Nevertheless, we feel the qualitative features observed in the thermogravimetric experiments are significant. Therefore, the results of a typical set of experiments are presented in Table I to serve as a qualitative summary of our observations. These results show that the addition of NaCl(g) to air flowing over Na<sub>2</sub>SO<sub>4</sub>(l) at 900 and 1000°C enhances the rate of weight loss of the Na<sub>2</sub>SO<sub>4</sub>(l). This enhancement increases when H<sub>2</sub>O(g) is also added to the air flow.

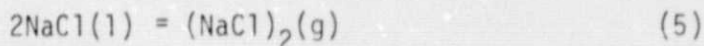
Our results are in qualitative agreement with the results of Jones et al. (ref. 3), but our findings regarding the addition of H<sub>2</sub>O(g) do not agree with the reported observations of Pettit and co-workers (ref. 1). It is also interesting to note that neither of these groups of investigators reported any observations regarding the absorption of NaCl by Na<sub>2</sub>SO<sub>4</sub>(l) exposed to partial pressure of NaCl(g).

The phase diagram for the NaCl-Na<sub>2</sub>SO<sub>4</sub> system has been measured and found to show a single eutectic with no solid solution (ref. 10). Above 900°C, all compositions are completely liquidus. Additionally, Flood et al. (ref. 11) have established that NaCl(l) and Na<sub>2</sub>SO<sub>4</sub>(l) form a practically ideal solution in both branches of the liquidus. Thus the quantity of NaCl(l) absorbed by Na<sub>2</sub>SO<sub>4</sub>(l) in the presence of NaCl(g) can be calculated. Consider Na<sub>2</sub>SO<sub>4</sub>(l) as the solvent, designated by the subscript S, and NaCl(l) as the solute, designated by the subscript s. The weight of solute in the solvent is given by:

$$W_s = \frac{X_s}{1-X_s} M_s \frac{W_s}{M_s} \quad (3)$$

where W is weight, M is molecular weight and X is mole fraction.

Because sodium chloride in the gas phase is made up mainly of monomer and dimer (for all practical purposes, higher order polymers can be ignored), the mole fraction of solute can be determined by considering the equilibria:



If we designate monomer and dimer by the subscripts m and d, respectively, the equilibrium constants for reactions (4) and (5) are:

$$K_4 = \frac{P_m}{X_s} = P_m^\circ \quad (6)$$

$$K_5 = \frac{P_d}{X_s^2} = P_d^\circ \quad (7)$$

where P is pressure and the superscript  $\circ$  refers to the saturated equilibrium vapor pressure of pure NaCl(l). An effective pressure  $P_E$  can be defined as:

$$P_E = P_m + 2P_d \quad (8)$$

so that by substitution we obtain:

$$P_E = X_s P_m^\circ + 2X_s^2 P_d^\circ \quad (9)$$

from which  $X_s$  can be determined by the quadratic formula giving:

$$X_s = \left( \frac{(P_m^\circ)^2}{16(P_d^\circ)^2} + \frac{P_E}{2P_d^\circ} \right)^{1/2} - \frac{P_m^\circ}{4P_d^\circ} \quad (10)$$

Thus we see that the mole fraction of solute is a function of the effective pressure of sodium chloride gas and the equilibrium saturated vapor pressures of the monomer and dimer. Because the equilibrium pressures are a function of temperature, the mole fraction of solute is also a function of the solute-solvent mixture temperature.

For our experiments, the effective pressure is related to the weight concentration, C, of sodium chloride added to the air flow, i.e.:

$$P_E = C \frac{M_{air}}{M_{NaCl}} \quad (11)$$

so that by substitution we obtain:

$$X_s = \left( \frac{(P_m^o)^2}{16(P_d^o)^2} + \frac{C_{M_{air}}}{2P_d^o M_{NaCl}} \right)^{1/2} - \frac{P_m^o}{4P_d^o} \quad (12)$$

From equations (3) and (12), we see that the weight of NaCl(1) absorbed is a function of the weight of Na<sub>2</sub>SO<sub>4</sub>(1) present, the sample temperature and the concentration of NaCl(g) added to the air flow. In figure 4, we have plotted the mole fraction of NaCl(1) in Na<sub>2</sub>SO<sub>4</sub>(1) as a function of NaCl(g) concentration and mixture temperature. Values of the monomer and dimer equilibrium saturated vapor pressures were taken from the JANAF Thermochemical Tables (ref. 12).

For each of our experiments, the measured weight of NaCl(1) absorbed by the Na<sub>2</sub>SO<sub>4</sub>(1) was compared with the corresponding calculated value. As shown for the examples in Table I, the agreement was found to be excellent.

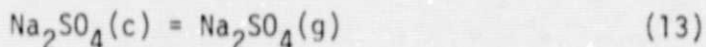
The absorption of NaCl(1) by Na<sub>2</sub>SO<sub>4</sub>(1) deposits exposed to NaCl(g) could have important ramifications for hot corrosion processes. When sodium chloride enters a turbine engine combustor, some will react with sulfur impurities in the fuel to form Na<sub>2</sub>SO<sub>4</sub>(g) (refs. 13, 14) which can, in turn, condense on hot gas path parts to form Na<sub>2</sub>SO<sub>4</sub>(1) (ref. 15). However, thermodynamic considerations predict (ref. 13) that NaCl(g) will also be present because all the sodium chloride is not converted to sulfate. Therefore, NaCl(1) could be absorbed by the Na<sub>2</sub>SO<sub>4</sub>(1) deposit. To assess how important this aspect might be, we have made some calculations for a burner rig test. The test itself is described elsewhere (ref. 15). For a burner rig flame doped with 8 ppm NaCl, 14.8 mg of Na<sub>2</sub>SO<sub>4</sub> were collected on a platinum target at 900°C. Equilibrium calculations for this flame condition (fuel/oxidant ratio = 0.0432, Jet A fuel, 8 ppm NaCl) give 5.62x10<sup>-7</sup> and 6.14x10<sup>-11</sup> atm, respectively, for the pressures of sodium chloride monomer and dimer. For the effective pressure of NaCl resulting from these pressures, we calculate the mole fraction of NaCl(1) absorbed as 2.8x10<sup>-4</sup>. Thus for the 14.8 mg Na<sub>2</sub>SO<sub>4</sub>(1) deposit, the quantity of NaCl(1) absorbed is 1.7 μg. Actual analysis of the collected deposit from this test revealed that the chloride content was not



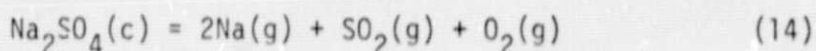
perceptible above the 40  $\mu\text{g}$  chloride background level.

This calculation and comparison with a burner rig experiment indicate that, for the concentrations of  $\text{NaCl(g)}$  expected in turbine engines and the quantities of  $\text{Na}_2\text{SO}_4$  deposits typically measured in practice, the amount of  $\text{NaCl(l)}$  absorbed is low.

Mass Spectrometric Sampling Experiments. - A typical set of experimental results obtained with  $\text{Na}_2\text{SO}_4(\text{c})$  on a Pt 20% Rh sample are shown in figure 5. The measured ion intensities are relative to the one atmosphere oxygen signal and no corrections (cross section, Mach-number focusing and mass discrimination) were applied to measured values. In the first experiment with just oxygen flowing over the  $\text{Na}_2\text{SO}_4(\text{c})$ , the only pertinent species detected were  $\text{O}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{Na}_2\text{SO}_4(\text{g})$ . The  $\text{H}_2\text{O}(\text{g})$  is derived from the 600 ppm by volume of water vapor contained in the tank oxygen used. The  $\text{Na}_2\text{SO}_4(\text{g})$  results from the vaporization reaction:



The saturated vapor pressure of  $\text{Na}_2\text{SO}_4(\text{g})$  at  $1000^\circ\text{C}$  is  $4.23 \times 10^{-7}$  atm (ref. 13). No dissociation products of  $\text{Na}_2\text{SO}_4$  were detected; this is as expected because for the reaction:

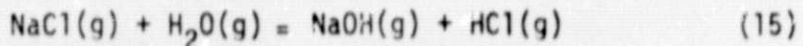


at one atmosphere oxygen pressure and  $1000^\circ\text{C}$  the partial pressures of  $\text{Na}(\text{g})$  and  $\text{SO}_2(\text{g})$  are calculated to be  $1.3 \times 10^{-8}$  and  $6.7 \times 10^{-9}$  atm respectively and these levels are below the detection limit of our sampler.

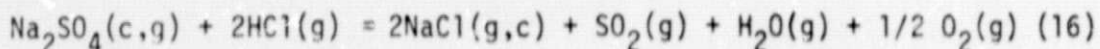
When about 100 ppm by weight of  $\text{NaCl(g)}$  was added to the oxygen flow, numerous pertinent vapor species were identified. In addition to the  $\text{H}_2\text{O}(\text{g})$  and various sodium chloride species, the mass spectrum was found to be relatively rich in  $\text{Na}^+$ ,  $\text{SO}_2^+$  and  $\text{HCl}^+$  ions.  $\text{Na}_2\text{SO}_4^+$  and  $\text{Na}_3\text{SO}_4^+$  ions were also measured. The  $\text{Na}^+$  ion probably all derives from fragmentation of  $\text{NaCl(g)}$  in the electron bombardment (30 ev electron energy) ion source. The  $\text{Na}_2\text{SO}_4^+$  ion results from ionization of the  $\text{Na}_2\text{SO}_4(\text{g})$  vaporization product. The precursor of the  $\text{Na}_3\text{SO}_4^+$  ion is presumed to be  $\text{NaClNa}_2\text{SO}_4(\text{g})$  which loses a chlorine by fragmentation upon ionization. At the present time, we have not established whether the molecule  $\text{NaClNa}_2\text{SO}_4(\text{g})$  is the product of a gas-solid interaction or gas-phase reaction.

For our considerations here the important ions observed are

HCl<sup>+</sup> and SO<sub>2</sub><sup>+</sup>. Because some H<sub>2</sub>O(g) is present in the flowing gas system, we attribute the HCl<sup>+</sup> ion to the small amount of HCl(g) produced in the reaction:



even though interference prevented us from measuring NaOH(g). The SO<sub>2</sub><sup>+</sup> ion is produced by ionization of SO<sub>2</sub>(g) resulting from the reaction:



When additional H<sub>2</sub>O(g) was added to the NaCl(g)-O<sub>2</sub>(g)-Na<sub>2</sub>SO<sub>4</sub>(c) system, the hydrolysis product HCl(g) and reaction product SO<sub>2</sub>(g) each increased markedly.

Experiments were performed where only 0.2% HCl(g) was added to the oxygen flow. In these experiments, NaCl(g) and SO<sub>2</sub>(g) were detected as products. At temperatures below about 1100°C, orifice clogging was a problem. This was due to the relatively high concentration of NaCl(g) produced from reaction (16).

Results qualitatively similar to those discussed above were obtained when air was substituted for oxygen as the flowing gas. With air the amount of reaction of Na<sub>2</sub>SO<sub>4</sub>(c) was increased. This was ascertained by measuring the SO<sub>2</sub><sup>+</sup> signals with air and oxygen under the various conditions. For example, with NaCl(g) and H<sub>2</sub>O(g) added to the gas flow, the SO<sub>2</sub><sup>+</sup> intensity with air was about two times greater than with oxygen. The increased reaction in the presence of air is due to the lower oxygen pressure associated with the air system.

The mass spectrometric results allow us to now qualitatively interpret the thermogravimetric experiments observations. Na<sub>2</sub>SO<sub>4</sub>(c) in flowing oxygen alone vaporizes and the Na<sub>2</sub>SO<sub>4</sub>(c)-coated sample loses weight at a low rate in proportion to the sample temperature and flow conditions. When NaCl(g) is added to the gas flow, some of it is hydrolyzed by water contained in the gas and the HCl(g) produced reacts with Na<sub>2</sub>SO<sub>4</sub>(c) according to reaction (16). Under this condition, the sample loses weight by both vaporization and reaction of Na<sub>2</sub>SO<sub>4</sub>(c) and the rate of weight loss is greater than before the NaCl(g) was added. When more H<sub>2</sub>O(g) is added to the gas flow, more HCl(g) is produced and more reaction of Na<sub>2</sub>SO<sub>4</sub>(c) takes place. Thus the addition of more H<sub>2</sub>O(g) results in a greater rate of weight loss of Na<sub>2</sub>SO<sub>4</sub>(c). Weight losses are observed in these experiments because the products of the Na<sub>2</sub>SO<sub>4</sub>(c) reaction are continually

being swept away from the sample by the flowing gas.

The qualitative description and reactions presented here to explain observed high temperature interactions of  $\text{NaCl(g)}$  with  $\text{Na}_2\text{SO}_4(\text{c})$  under oxidizing conditions depend on the presence of  $\text{H}_2\text{O(g)}$ . It is therefore of interest to calculate the dependence of such interactions on pressure of  $\text{H}_2\text{O(g)}$ . The equilibrium chemical composition of the Na-O-S-H-Cl system over liquid 0.954 (mole fraction)  $\text{Na}_2\text{SO}_4$ -0.046  $\text{NaCl}$  at 1200K was calculated as a function of pressure of  $\text{H}_2\text{O(g)}$ . This  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  solution composition is that which is in equilibrium with 300 ppm by weight of  $\text{NaCl(g)}$  at this temperature. Calculations were performed with a modified version of the NASA Chemical Equilibrium Composition computer program (ref. 16) for an air atmosphere of 0.21 atm  $\text{O}_2$ -0.79 atm  $\text{N}_2$ . The results of these calculations are presented in figure 6 and show that even in air at equilibrium with Drierite some  $\text{HCl(g)}$  and  $\text{NaOH(g)}$  are present.

We feel that it is extremely difficult to remove low levels of water from flowing air or oxygen. While we had previously shown that the level of water vapor in ambient laboratory air ( $\sim 10^{-2}$  atm) is reduced by passage through Drierite (ref. 6), we have measured the level of water vapor in the tank oxygen used here and shown that it is unaffected by passage through a Drierite column. Thus we contend that without very special precautions, any study of the  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  system should include considerations of the interactions of water vapor.

Although the equilibrium constant for reaction (16) is much less than one for the conditions of our experiments, it is not surprising that the addition of  $\text{HCl(g)}$  leads to the removal of  $\text{Na}_2\text{SO}_4$ . This is due to LeChatelier's principle; continuous removal of the gaseous products of a reaction will cause the equilibrium to shift to the right. However, the same principle would imply that the addition of  $\text{NaCl(g)}$  should suppress the formation of gaseous products. This apparent paradox shows that thermodynamic considerations alone cannot explain the behavior observed here for the  $\text{Na}_2\text{SO}_4$ - $\text{NaCl}$  system. Kinetically, for our experimental conditions, small amounts of  $\text{HCl(g)}$  are obviously more effective than large amounts of  $\text{NaCl(g)}$ .

One additional mass spectrometric experiment was carried out to determine the effect of the addition of excess  $\text{SO}_2$  to the  $\text{NaCl(l)}$ - $\text{Na}_2\text{SO}_4(\text{l})$ - $\text{H}_2\text{O(g)}$ - $\text{O}_2(\text{g})$ - $\text{SO}_2(\text{g})$  system. Gaseous  $\text{NaCl}$ , 54 ppm by weight, was added to the oxygen flowing over a  $\text{Na}_2\text{SO}_4(\text{l})$ -coated coupon. The coupon temperature was held at 1273K and a sufficient time was allowed to elapse to assure that  $\text{NaCl(l)}$  dissolved in



the  $\text{Na}_2\text{SO}_4(l)$ . For these conditions, the mole fraction of  $\text{NaCl}(l)$  was calculated to be  $3.4 \times 10^{-3}$ . Finally, the flow of  $\text{NaCl}(g)$  was stopped and  $\text{SO}_2(g)$  was added to the  $\text{O}_2(g)$  flow. The  $\text{SO}_2(g)$  was about 0.2% by volume. The mass spectral measurements revealed that both  $\text{HCl}(g)$  and  $\text{Cl}_2(g)$  were present. The measured partial pressure of  $\text{HCl}(g)$  was about two orders of magnitude greater than the partial pressure of  $\text{Cl}_2(g)$ . McKee et al. (ref. 17) reported for a similar experiment only the detection of  $\text{Cl}_2(g)$ .

To supplement our experiment, equilibrium calculations of the type used to produce figure 6 were made. The results of these calculations, given in figure 7, show that  $\text{HCl}(g)$  is indeed predicted to be a more abundant species than  $\text{Cl}_2(g)$  for the level of water vapor found in the tank oxygen we used in the experiments. Furthermore, the results of the calculations indicate that the species  $\text{HCl}$ ,  $\text{Cl}$  and  $\text{ClO}$  should be more abundant than  $\text{Cl}_2$  even for levels of water vapor below the theoretical value for  $\text{H}_2\text{O}$  in equilibrium with Drierite.

#### CONCLUDING REMARKS

The removal of  $\text{Na}_2\text{SO}_4(l)$  by  $\text{NaCl}(g)$ , observed in our experiments and those of Pettit et al., Jones et al. and Smeggil, results from reaction (16) being driven to the right in a flowing gas system. The  $\text{HCl}(g)$  originates from the hydrolysis of  $\text{NaCl}$  by small amounts of water vapor present in the system. The only new gas phase species identified in  $\text{Na}_2\text{SO}_4(l)$ - $\text{NaCl}(g)$  gas interactions is  $\text{NaClNa}_2\text{SO}_4(g)$  and experimental evidence suggests that it plays only a minor role in this interaction. Quantitative differences reported in measured thermogravimetric results are probably due to variability of  $\text{H}_2\text{O}(g)$  content and  $\text{Na}_2\text{SO}_4(l)$  surface coverage.

The results reported here have implications for hot corrosion processes and establish the importance of even trace amounts of water in the systems considered. Additional experiments and analysis are needed to further elucidate the role of  $\text{NaCl}(g)$  and  $\text{NaCl}(c)$ .



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TABLE I

THERMOGRAVIMETRIC RESULTS FOR PLATINUM SAMPLE  
 (AREA - 5.5 cm<sup>2</sup>) COATED WITH 13 mg OF Na<sub>2</sub>SO<sub>4</sub> AND  
 HEATED IN FLOWING AIR\* (FLOW VELOCITY - 1.6 cm/sec)

System	Steady State Rate of Sample Weight Change, mg/hr		Weight of NaCl Absorbed Initially, mg	
	Temp, °C		Temp, °C	
	900	1000	900	1000
Na <sub>2</sub> SO <sub>4</sub> + Dry Air	-0.01	-0.18		
Na <sub>2</sub> SO <sub>4</sub> + Dry Air + NaCl(g)**	-.08	-.32		
Experimental			0.38	0.09
Calculated			.39	.09
Na <sub>2</sub> SO <sub>4</sub> + Wet Air + NaCl(g)**	-.14	-.87		

\*Dry Air - Air Flowed Through Column of Drierite.

Wet Air - Air Bubbled Through Column of Water at 25°C.

\*\*300 ppm (by Weight) of NaCl(g).

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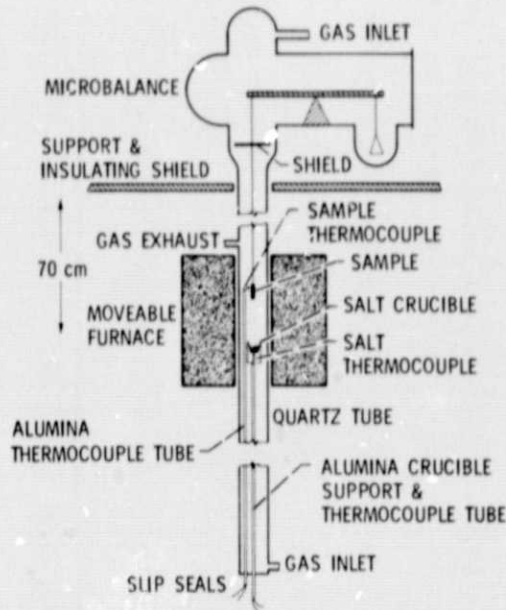


Figure 1. - Schematic of thermogravimetric apparatus.

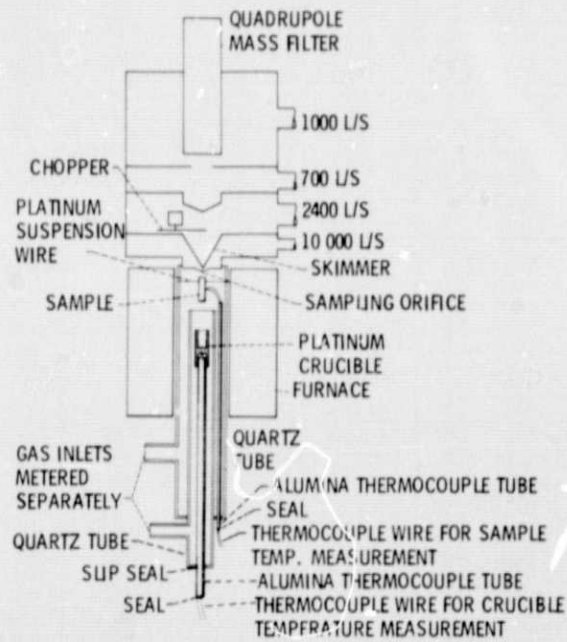


Figure 2. - Schematic of high pressure mass spectrometric sampling apparatus.

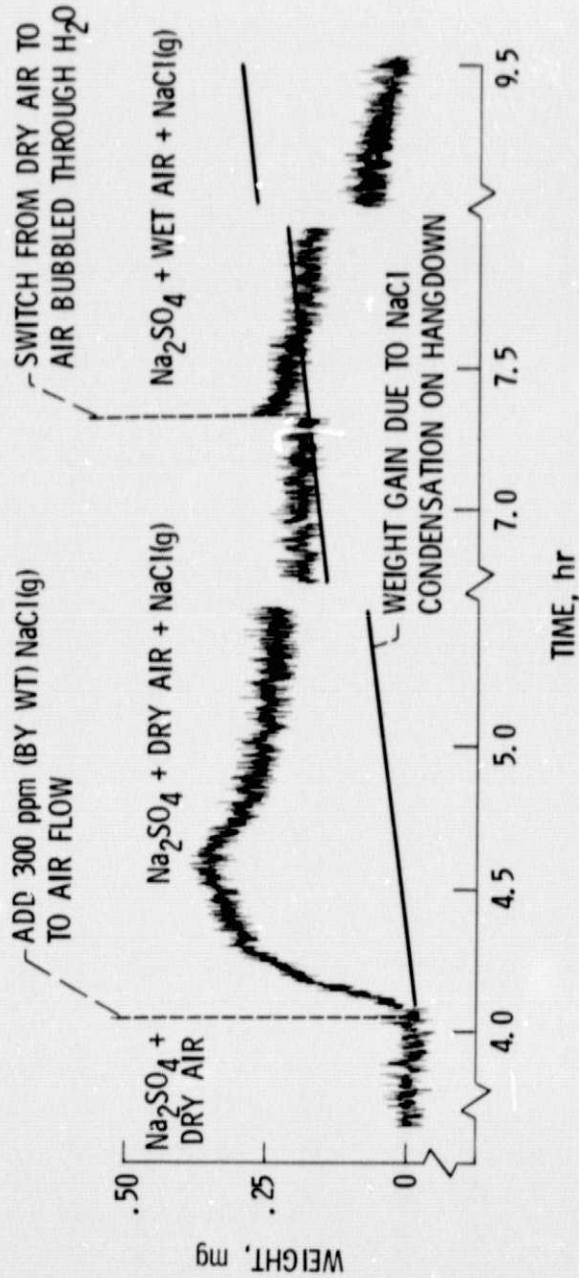


Figure 3. - Thermogravimetric recording of weight change of platinum sample (area = 5.5 cm<sup>2</sup>) coated with 13 mg Na<sub>2</sub>SO<sub>4</sub> and heated at 900° C in flowing gas (flow velocity = 1.6 cm sec<sup>-1</sup>).



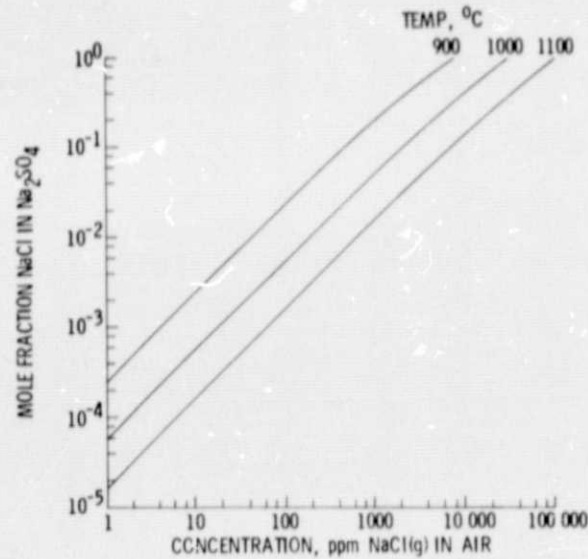


Figure 4. - Variation of mole fraction of NaCl in  $\text{Na}_2\text{SO}_4$  with concentration of NaCl in air at three mixture temperatures.

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SYSTEM	ION	RELATIVE INTENSITY <sup>oo</sup>	MOLECULE
$\text{Na}_2\text{SO}_4(\text{c}) + \text{O}_2(\text{g})$ 1000° C	$\text{H}_2\text{O}^+$ $\text{Na}_2\text{SO}_4^+$		$\text{H}_2\text{O}$ $\text{Na}_2\text{SO}_4$
$\text{Na}_2\text{SO}_4(\text{c}) + \text{O}_2(\text{g})$ + $\text{NaCl}(\text{g})$ 1000° C	$\text{H}_2\text{O}^+$ $\text{Na}^+$ $\text{NaCl}^+$ $\text{Na}_2\text{Cl}^+$ $\text{Na}_3\text{Cl}_2^+$ $\text{SO}_2^+$ $\text{HCl}^+$ $\text{Na}_2\text{SO}_4^+$ $\text{Na}_3\text{SO}_4^+$		$\text{H}_2\text{O}$ $\text{NaCl}$ $\text{NaCl}$ $(\text{NaCl})_2$ $(\text{NaCl})_3$ $\text{SO}_2$ $\text{HCl}$ $\text{Na}_2\text{SO}_4$ $\text{NaClNa}_2\text{SO}_4$
$\text{Na}_2\text{SO}_4(\text{c}) + \text{O}_2(\text{g})$ + $\text{NaCl}(\text{g}) + \text{H}_2\text{O}(\text{g})$ 1000° C	$\text{H}_2\text{O}^+$ $\text{NaCl}^+$ $\text{SO}_2^+$ $\text{HCl}^+$ $\text{NaOH}^+$	 NOT MEASURED DUE TO INTERFERENCE	$\text{H}_2\text{O}$ $\text{NaCl}$ $\text{SO}_2$ $\text{HCl}$ $\text{NaOH}$
$\text{Na}_2\text{SO}_4(\text{c}) + \text{O}_2(\text{g})$ + $\text{HCl}(\text{g})$ 1100° C	$\text{HCl}^+$ $\text{NaCl}^+$ $\text{SO}_2^+$		$\text{HCl}$ $\text{NaCl}$ $\text{SO}_2$

<sup>o</sup>TANK OXYGEN  $\text{H}_2\text{O}$  CONTENT INDEPENDENTLY ANALYZED AS 600 ppm BY VOL.

<sup>oo</sup>MEASURED ION INTENSITIES (UNCORRECTED) RELATIVE TO 1 atm  $\text{O}_2(\text{g}) = 1$ .

Figure 5. - Mass spectral analysis of major vapor species emanating from a  $\text{Na}_2\text{SO}_4$ -coated platinum sample heated in flowing oxygen with and without impurity additions.

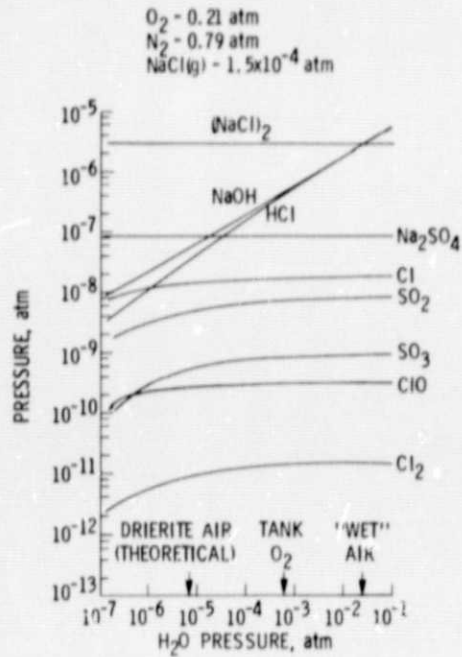


Figure 6. - Equilibrium composition of Na-O-S-H-Cl system over liquid 0.954 Na<sub>2</sub>SO<sub>4</sub>-0.046 NaCl at 1200 K.

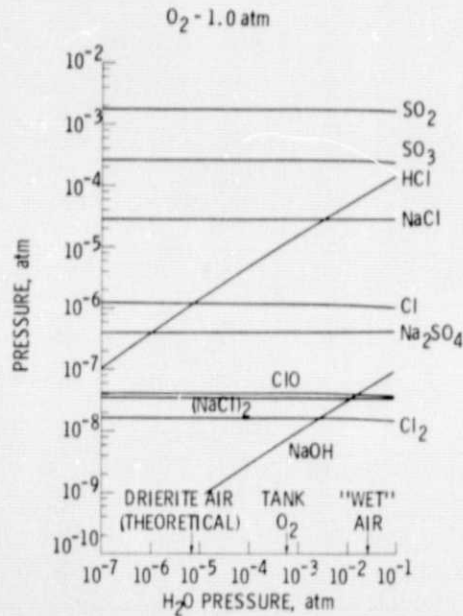


Figure 7. - Equilibrium composition of Na-O-S-H-Cl system over liquid 0.9966 Na<sub>2</sub>SO<sub>4</sub>-0.0034 NaCl at 1273 K.