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Study of Surface Reaction of Impacted Chlorides on Marine Gas Turbine Hot Corrosion at Low Power Conditions

FINAL REPORT

May 11, 1978 to May 11, 1979

Prepared Under Contract N00173-78-C-0439

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By

E.R. Duffy and A.R. Stetson

for

NAVAL RESEARCH LABORATORY
WASHINGTON, DC

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<p>Because of the importance of Na_2SO_4 and its reaction with the substrate in hot corrosion attack on superalloys, the amount of this compound formed from NaCl and sulfur oxides is extremely important in determining hot corrosion potential.</p> <p>The objective of this program was to determine the influence of surfaces on the kinetics of the conversion of NaCl and MgCl_2 to Na_2SO_4 and MgSO_4, respectively, in a typical combustion environment.</p>		

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In the test program NaCl and $MgCl_2 \cdot 6H_2O$ were deposited in thin layers on various surfaces and the rate of formation of sulfate was measured at temperatures of 650°, 760° and 815°C. The gaseous environment was a synthesized turbine exhaust containing SO_x (0.018 to 0.036 v/o), O_2 (14.5 v/o), CO_2 (4.0 v/o), H_2O (2.4 v/o) and balance N_2 which is equivalent to a turbine combustor effluent burning Diesel No. 2 with 1 to 2 weight percent sulfur. Flow rate of the gas was 1.5 litre/minute or 0.1 meter/second and exposure time was one hour.

The test results at 650°C at 0.036 v/o SO_x on the various surfaces showed a marked effect of the type of surface on the formation of sulfate. For example, the following are the differences noted in sulfate formation from 10 mg/cm² NaCl deposits:

CoCrAlY
MAR-M421 = CaV_2O_7 = Pt > NiAl > SiO_2 = Ni = Al_2O_3
Co

Hot corrosion of the nickel foil indicated that sodium sulfate had been formed and reacted.

At 760° and 815°C in 1-hour exposure with 1- mg/cm² NaCl, no significant differences were detected in sulfate formation due probably to the rapid vaporization of NaCl at these higher temperatures.

Only limited tests were performed on conversion of $MgCl_2$ to $MgSO_4$. The results at 650°C showed:

Pt >> Al_2O_3 = SiO_2

Superalloy pins, pre-oxidized at 925°C to produce a predominantly alumina scale, pre-coated with sodium chloride (1.0 mg/cm²) and exposed for 1 hour to a 0.09 kg/sec combustor exhaust, produced nearly half as much sulfate as detected on unoxidized MAR-M421 pins. Diesel No. 2 fuel which had the fuel sulfur level raised to 1.7 percent was used to provide sufficient SO_2/SO_3 for the conversion reaction. When NaCl or $MgCl_2$ solution was emulsified into the fuel, as much sulfate was detected on test pins exposed to the exhaust as pins pre-coated with NaCl and exposed to exhaust from salt-free fuel. The adherence of a limited quantity of salt deposit to test pins during the high velocity test may explain the similarity of results.

Catalysts that accelerated the $SO_2 \rightarrow SO_3$ equilibrium such as CaV_2O_7 and platinum had the greatest effect on increasing surface formation from NaCl. However, artificially increasing the SO_3 concentration in the test gas upstream of a NaCl coated sample did not increase sulfate formation.

The presence of water vapor appears essential in the conversion of sodium chloride to sodium sulfate in an SO_x environment.

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SUMMARY

Sodium chloride enters the gas turbine in significant quantities, depending upon the fuel and air quality. This compound is a transient phase and is rarely found in deposits on blades and vanes except in engines operating at extremely low temperatures.

Conversion of sodium chloride to the much less volatile sodium sulfate has been the subject of many investigations, most of which have concentrated on gas phase reaction kinetics. Because of the importance of Na_2SO_4 and its reaction with the substrate in hot corrosion attack on superalloys, the amount of this compound formed from NaCl and sulfur oxides is extremely important in determining hot corrosion potential.

The objective of this program was to determine the influence of surfaces on the kinetics of the conversion of NaCl and MgCl_2 to Na_2SO_4 and MgSO_4 , respectively, in a typical combustion environment.

The experimental approach taken pre-supposed that the sodium chloride is delivered to the surface in a solid or liquid form, e.g., from the incomplete vaporization and combustion of fuel droplets under low power conditions or from shedding of salt from the compressor. Delivery of the vapor phase could have an influence on this conversion also, but the experimental approach taken did not isolate NaCl or MgCl_2 vapor as test variables.

In the test program NaCl and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were deposited in thin layers on various surfaces and the rate of formation of sulfate was measured at temperatures of 650°, 760° and 815°C. The gaseous environment was a synthesized turbine exhaust containing SO_x (0.018 to 0.036 v/o), O_2 (14.5 v/o), CO_2 (4.0 v/o), H_2O (2.4 v/o) and balance N_2 which is equivalent to a turbine combustor effluent burning Diesel No. 2 with 1 to 2 weight percent sulfur. Flow rate of the gas was 1.5 litre/minute or 0.2 meter/second and exposure time was one hour.

The test results at 650°C at 0.036 v/o SO_x on the various surfaces showed a marked effect of the type of surface on the formation of sulfate. For example, the following are the differences noted in sulfate formation from 10 mg/cm² NaCl deposits:

CoCrAlY
MAR-M421 = CaV_2O_7 = Pt > NiAl > SiO_2 = Ni = Al_2O_3
Co

At 760° and 815°C in 1-hour exposure with 10 mg/cm² NaCl, no significant differences were detected in sulfate formation due probably to the rapid vaporization of NaCl at these higher temperatures.

Only limited tests were performed on conversion of $MgCl_2$ to $MgSO_4$. The results at 650°C showed:

Pt >> $Al_2O_3 = SiO_2$

Burner rig tests were performed at 650°C to verify these results and to support the hypothesis that surface reactions can take place in a high velocity gas stream. Superalloy pins, pre-oxidized at 925°C to produce a predominantly alumina scale, precoated with sodium chloride (1.0 mg/cm²) and exposed for 1 hour to a 0.09 kg/sec combustor exhaust, produced nearly half as much sulfate as detected on unoxidized MAR-M421 pins. Diesel No. 2 fuel which had the fuel sulfur level raised to 1.7 percent was used to provide sufficient SO_2/SO_3 for the conversion reaction. When NaCl or $MgCl_2$ solution was emulsified into the fuel, as much sulfate was detected on test pins exposed to the exhaust as pins pre-coated with NaCl and exposed to exhaust from salt-free fuel. The adherence of a limited quantity of salt deposit to test pins during the high velocity test may explain the similarity of results.

Within the accuracy of the experimental technique and sulfate analyses, the following conclusions can be drawn from this investigation:

1. At 650°C, surfaces differ markedly in the amount of sulfate ion formed from NaCl and SO_x .
2. At 760 and 815°C no differences were noted in rates of sulfate formed from NaCl due to the high vaporization rate of NaCl.
3. Catalysts that accelerated the $SO_2 \rightarrow SO_3$ equilibrium such as CaV_2O_7 and platinum had the greatest effect on increasing sulfate formation from NaCl. However, artificially increasing the SO_3 concentration in the test gas upstream of a NaCl coated sample did not increase sulfate formation. The high chromium nickel-base alloys, MAR-M421 and IN-738, also appeared to increase sulfate formation at 650°C when compared to cobalt or CoCrAlY or inert oxides such as Al_2O_3 and SiO_2 . Pure nickel was unusual in that sulfate formation was low under all test conditions, but hot corrosion of the nickel foil indicated that sodium sulfate had been formed and reacted.
4. The presence of water vapor appears essential in the conversion of sodium chloride to sodium sulfate in an SO_x environment.

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1

INTRODUCTION

Sodium chloride can enter the gas turbine in significant quantities from the air and/or the fuel. This compound is a transient phase and is rarely found in deposits on blades and vanes except in engines operating at extremely low temperatures.

The impaction of salt containing fuel droplets with turbine blades and vanes can occur during ignition or low power operation when the fuel atomization and combustion processes are less than ideal. Shedding of salt particles from the combustor or compressor could also provide the yield of liquid or solid chloride salts. Burner rig experiments have demonstrated that the surface temperature will influence the amount of conversion of sodium chloride to the much less volatile sodium sulfate (Ref. 1). This investigation examines the hypothesis that the nature of the surface influences the conversion reaction either to accelerate or retard the formation of sodium sulfate. An understanding of the influence of surfaces in the chloride to sulfate conversion reaction may provide additional information for the development of coatings to mitigate hot corrosion attack.

2

EXPERIMENTAL PROCEDURE

An experimental screening apparatus was set up to continually supply sodium or magnesium chloride to a test specimen by periodic dripping of brine on a heated sample. It was hypothesized that by having the brine continually drip on a test surface gas turbine combustor effluent, vaporization of chlorides would be representative of the engine condition in which the chloride salts could impact the vanes and blades. However, this test method had to be abandoned as it was apparent that at the lowest test temperature, 650°C, there was little salt evaporation and even at the higher test temperatures, 760° and 815°C, where rapid vaporization was apparent, the salt did not uniformly wet the surface on impact but the drippings accumulated in mounds of salt on the test sample.

To provide a more realistic evaluation of surfaces on the conversion reaction of chlorides to sulfates, samples were pre-coated with sodium chloride or hydrated magnesium chloride to provide a thin uniform deposit of salt on the test surface. Each specimen was coated with a deposit of 7-16 mg/cm² of chloride salt so as to have enough sulfate present at the end of the test period to facilitate chemical analysis. Similar reasoning was used to limit exposure time to 1 hour.

As with the previously mentioned method for dripping brine onto heated samples, a resistance heated quartz tube was used for the test vessel. Samples were placed on a section of 18 mm I.D. quartz tubing used as a boat to hold the sample pre-coated with sodium or magnesium chloride. The specimen temperature was monitored by placing the test specimens on top of the end of an Inconel sheathed chromel-alumel thermocouple. With the thermocouple and specimen in place, the quartz boat was slid into the 25 mm I.D. test vessel. Gas-tight sealing was provided by ball and socket quartz to pyrex fittings and Swagelok fittings for thermocouple access. A second thermocouple inside the test vessel was used for regulating temperature to $\pm 5^\circ\text{C}$ with an on-off Wheelco temperature controller. Specimen temperature was recorded continuously on a strip chart recorder. As soon as clamps were tightened to provide leak-tight flow of the test atmosphere across the sample, the flow of test gases controlled with rotameters was started. This procedure provided the flow of sulfur-bearing atmosphere at 1.5 litre/minute, which corresponds to an average gas velocity past the heated test sample of 20 cm/second. Figure 1 is a schematic of the furnace screening apparatus showing the method of introducing water content into the test vessel.

The amount of water introduced as part of the test atmosphere was determined gravimetrically by absorption in Drierite or silica gel. Periodic volumetric checks of the drop in water level in the supply column verified that a consistent repeatable amount of water vapor was being supplied. Two different test

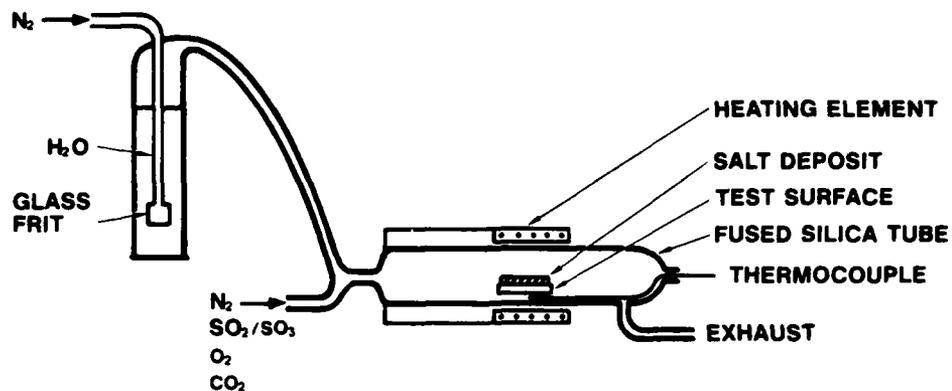


Figure 1. Test Apparatus for Screening Salt (NaCl or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) Coated Surface in Synthesized Combustor Exhaust

atmospheres were used, identical in composition except for sulfur oxide concentrations. The constituents of the test atmospheres are listed in Table 1. The gas compositions are typical of combustor effluent from gas turbines burning liquid fuel containing 1 and 2 percent sulfur with an air:fuel ratio of 50:1. Gas mixtures of N_2 - O_2 - CO_2 and SO_2 were obtained from Matheson gas to a certified accuracy of ± 10 percent of each gas component. Wet chemical analysis of the total sulfur content confirmed this accuracy.

Table 1

Test Atmospheres

	A Volume Percent (1)(3)	A Volume Percent (2)(3)
N_2	77.0 (Bal)	77.0 (Bal)
CO_2	4.0- 4.1	4.0- 4.1
O_2	14.5-15.0	14.5-15.0
SO_2	0.018	0.036

- (1) Equivalent to the combustion product of Diesel No. 2 fuel with a 50:1 air:fuel ratio and a sulfur content of 1%.
- (2) Same as (1) except fuel sulfur would be equivalent to 2%.
- (3) Does not include water vapor content (2.4-3.0 v/o)

The test procedure consisted of a of 1-hour exposure at temperature after which the test gases were turned off, and the specimen quickly removed from the hot zone of the quartz tube furnace. After re-weighing the sample, any residual salt deposit and spalled oxide, in the case of some elemental and alloy samples, were rinsed off with deionized water. Rinsing of the sample also included ultrasonic agitation to assure that all of the salt deposit had been removed. For samples which were pressed and sintered powder pellets, the entire pellet was crushed into a powder using a high density alumina mortar and pestle. The powder was then washed into a volumetric flask to assure that all of the salt in the sample had been dissolved. The amount of total soluble sulfate was determined by barium atomic absorption techniques. Chloride ion analysis was performed with a specific ion electrode.

Since a variety of metal, ceramic and powdered oxide materials was used as test samples, two different test specimen sizes were required. When only a powder was available, a cylindrical plug, 12.5 mm in diameter and 6.3 mm thick, was molded using flaked Carbowax (3-5%) in a hardened steel die. After removing the pellet from the die the carbowax was removed by slowly heating to approximately 300°C. The powder plug was subsequently sintered at 1370°C for 16 hours in air. The remaining test surfaces were cut into rectangular samples 18 mm by 12.5 mm. The sources of the various test materials are listed in Table 2.

Each specimen was abraded on 400 grit silicon carbide paper to minimize the effect of surface finish on the conversion reaction. After measuring the overall dimensions with a micrometer, each specimen was rinsed in acetone and weighed to the nearest tenth of a milligram. Reagent grade sodium chloride was applied by spraying a salt-alcohol slurry using a DeVilbiss spray gun. Reagent grade magnesium chloride ($MgCl_2 \cdot 6H_2O$) was applied by placing several drops of an alcohol-chloride solution on one side of each sample. Only one surface of each sample was pre-coated with salt. The gross overall dimensions of this surface was used in estimating surface area of the sample and for computing the weight of salt to be applied for a 7-16 mg/cm² coverage.

Confirmation of the ratings of surfaces and their effects on conversion of chloride salts to sulfate salts was made on selected surfaces in a ducted burner rig in which the exhaust products of Diesel No. 2 fuel at 0.8 Mach were directed at rotating pin samples. Chloride salts were introduced by pre-coating the 6.3 mm diameter pins with sodium chloride (0.95-1.2 mg/cm²) or by emulsifying an H₂O-4.5%NaCl solution or H₂O-3.0%NaCl-0.2%MgCl₂ into the fuel using a gear pump. The method of introducing the salt solution into the fuel is schematically illustrated in Figure 2. The details of the burner rig operating parameters are listed in Table 3. The sulfur level of the fuel was artificially increased by adding carbon disulfide. Figure 3 maps areas of constant temperature in the combustor flame encountered by the rotating pin samples. These temperatures were measured by an aspirated chromel-alumel thermocouple with an exposed junction bead. Rotating samples were placed into the flame after the desired air-to-fuel ratio was reached. The maximum sample temperature was monitored with a chromel-alumel thermocouple inside a hollow Hastelloy X drone sample. Optical pyrometry indicated that this temperature measurement technique resulted in temperatures 25°C lower than actual surface temperatures.

Table 2

Surfaces Evaluated in Furnace Screening Tests of Sodium Chloride Conversion to Sodium Sulfate

<u>Material</u>	<u>Description</u>
Platinum	Rod rolled into thin sheet.
Calcium vanadate	Reagent grade powder obtained from Pfaltz and Bauer induction melted in flowing argon in an alumina crucible. Slices of fused melt abrasive cut for samples.
SiO ₂	Section of fused silica tubing.
Al ₂ O ₃	Section of high purity (99.8%) fused alumina crucible.
FSX-414	Slices from cast bar.
NiAl	Pack aluminized (Solar coating designation S1-120-7) coupons from cast MAR-M421
MAR-M421	Sections of cast turbine blade.
IN-792	Section of cast turbine blade.
IN-738	Section of cast turbine blade.
CoCrAlY	Physical vapor deposited by Airco Temescal (Coating ATD-2B, Co-26Cr-9.5Al-0.23Y) on Hastelloy X coupons. Coupons peened and heat treated after coating application.
Cobalt	Commercially pure 99.5+% (0.14%Ni) cobalt sheet.
Nickel	High purity nickel foil (99.8%).
1010 Steel	Mild steel sheet.
NiO	Reagent grade powder from J.T. Baker Chemical Co., pressed and sintered.
Cr ₂ O ₃	Reagent grade powder from Allied Chemical, pressed and sintered.
NiO·Cr ₂ O ₃	Mixture of NiO and Cr ₂ O ₃ powders, pressed and sintered.
TiO ₂	Chemical grade powder from Ferro Corp.
ZrO ₂	Calcia stabilized powder from Norton Co.
CoO	Reagent grade Co ₃ O ₄ powder from J.T. Baker Chemical. Conversion to CoO by heating 1 hour in argon at 950°C, pressed and sintered into pellets.

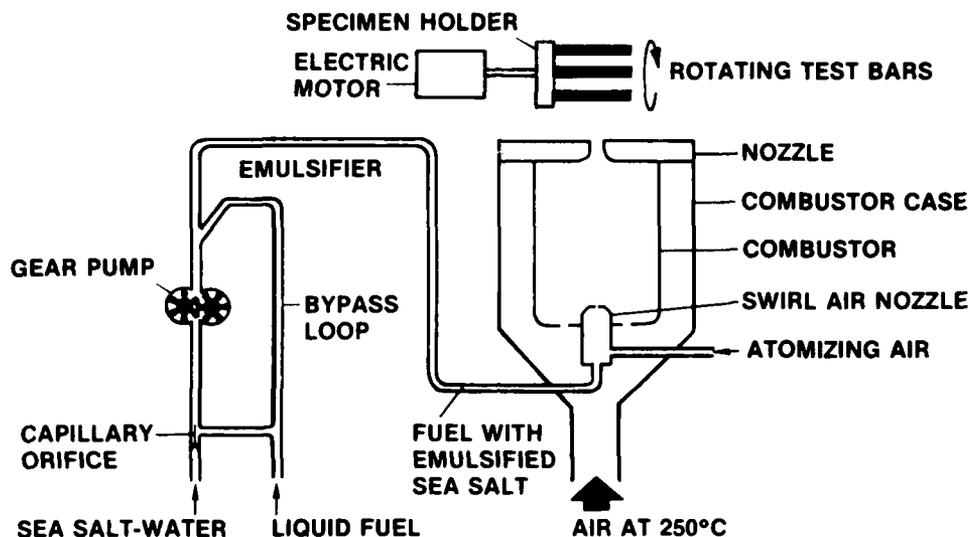


Figure 2. Schematic of Burner Rig for Salt Solution Injection in the Diesel Fuel

Table 3

Burner Rig Test Conditions

Fuel	Diesel No. 2 - 1.8% S
Flame temperature	640-1060°C
Air/fuel	30/1
Jet velocity	Mach 0.8
Salt dopant levels	520-760 ppm salt in fuel
Fuel/Salt Water emulsion	10-15 μ m salt solution droplets in fuel
Exposure time	1 hour
Deposition rate	1.15-1.15 mg/cm ² /hr
Maximum sample surface temperature	650-665°C

A calibration with an optical pyrometer was made at temperatures providing sufficient thermal emissivity for measurement. This calibration was extrapolated for surface temperatures below which optical pyrometry is not practical. Fuel flow was controlled throughout the test so that the maximum surface temperature did not exceed 665°C. The salt deposit was confined to the outer tip of the test sample, approximately 2.5 cm of the end pins were typically salt covered. The deposit was removed and analyzed in the same manner as the screening test samples.

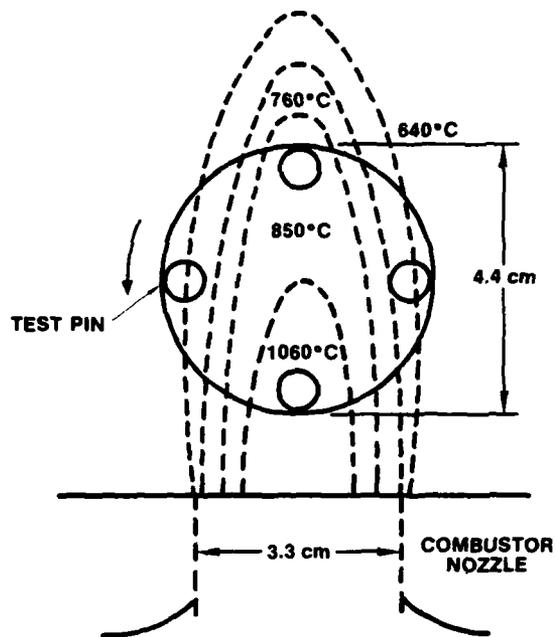


Figure 3. Burner Rig Flame Temperature Distribution Which Maintained a Maximum Sample Temperature of 665°C

3

EXPERIMENTAL RESULTS

Although most of the samples were tested with uniform deposits of NaCl (7-12 mg/cm²) several samples had thicker deposits. In verifying the precision of the screening test on calcium vanadate samples it was determined that there is a dependence of the amount of soluble sulfate detected with the amount of sodium chloride applied to the surface. A linear regression of the analysis of the data for exposure of NaCl coated calcium vanadate at 650°C for 1 hour to the simulated turbine exhaust containing 0.036% SO₂/SO₃ is shown in Figure 4. An analysis of the variance of the regression, as described by Laitinen (Ref. 2) indicated that there was a dependence of soluble sulfate on the amount of sodium chloride applied.

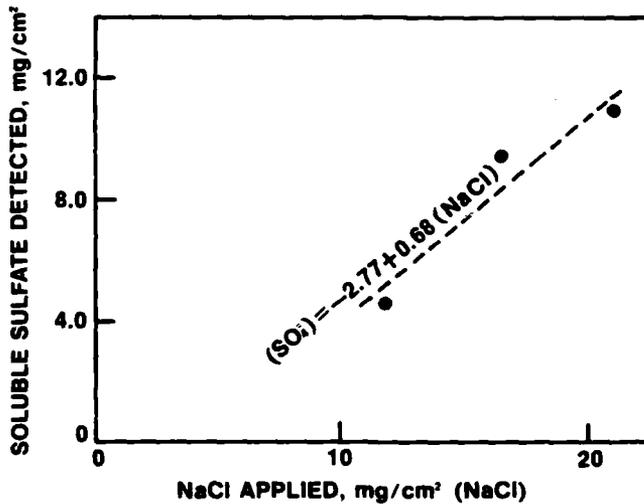


Figure 4. Effect of Weight of NaCl Deposit on Amount of Sulfate Detected on Calcium Vanadate Exposed at 650°C for One Hour to a Synthesized Combustor Effluent With 0.036% Sulfur Oxides

Data on the conversion of NaCl to Na₂SO₄ on different surfaces is presented in Figure 5 as the amount of soluble sulfate per exposed area for a given amount of NaCl applied to the surface. Each point represents one test result. Results on samples prepared from powders were purposely omitted from this figure as the added surface area from a porous sample presents an unknown variable to the test results.

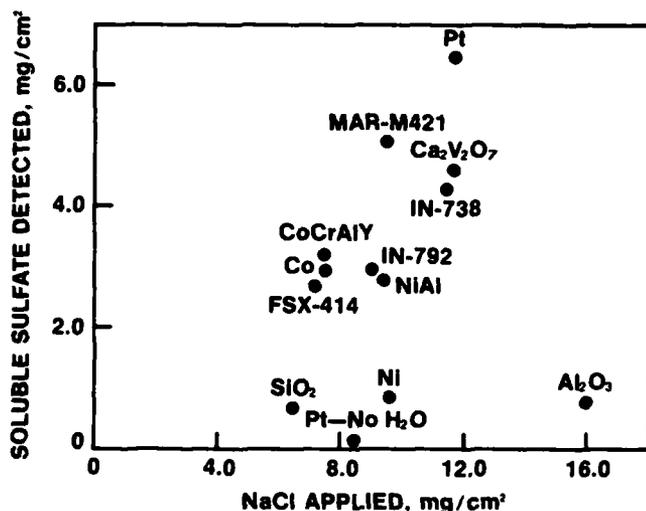


Figure 5. Soluble Sulfates Detected on Various Surfaces Pre-Coated With NaCl (6.5-16 mg/cm²) After Exposure to a Flowing Synthesized Combustor Effluent Containing 0.036 Percent Sulfur Oxides at 650°C for One Hour

The surfaces appear to be separated into three groups in their effect on the amount of sulfate produced at 650°C. Group 1 - Pt, MAR-M421, Ca₂V₂O₇, IN-738; Group 2 - CoCrAlY, IN-792, Co, Ni, Al, FSX-414; and Group 3 - SiO₂, Al₂O₃, Ni. The two nickel-base alloys with high chromium contents (15.5-16.0% Cr as compared to 12.2-12.5% Cr for IN-792) along with two materials known for their ability to catalyze the reaction $\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3$ produce the highest amount of sulfate (Group 1). The cobalt-base alloys, a nickel-aluminide coating and IN-792, form an intermediate group of surfaces which produce a lower amount of sulfate (Group 2). Finally, nickel, silica and alumina were the Group 3 which yielded the least amount of sulfate under the same test conditions.

The nickel foil samples were found to contain a significant amount of sulfur, 0.09%, after exposure to the environment described in Figure 5, as compared to the as-received sulfur content of the foil, 0.004%. Both metallographic and chemical analysis indicates that not all of the sulfate produced by nickel foil is being detected by washing off the surface deposit. Rather, a portion of the sulfate produced is reacting with the substrate in a hot corrosion reaction. Nickel may not, therefore, belong in Group 3.

The water content of the test atmosphere appears to be critical to the conversion reaction, as indicated by the data (representing results of two tests) point in Figure 5 labeled "platinum no H₂O". In this test a gas mixture of N₂-14.5%O₂-4.0%CO₂-0.036% SO₂ was flowed through a drying column of silica gel to remove the moisture content in the gas. The amount of sulfate produced has been reduced by more than an order of magnitude.

Figure 6 presents the sulfate detected on solid surfaces (as opposed to the sintered powder compacts) at 650°C but at half the sulfur oxide content of the gas environment used in Figure 5. Exposure time was 1 hour. There appears to be little effect of surfaces on the amount of sulfate produced aside from the inert nature of a fused silica sample on which no sulfate was detected. Even platinum appears to behave as an inert surface in the lower sulfur oxide atmosphere.

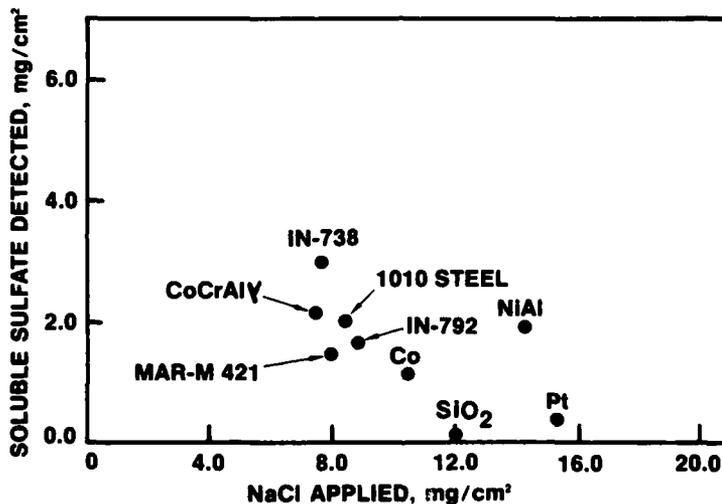


Figure 6. Amount of Sulfate Detected on Surface Exposed at 650°C to a Synthesized Combustor Effluent Containing 0.018 Percent Sulfur Oxides

In presentation of all screening test data at 650°C, each data point was normalized by assuming a ratio of sulfate produced at 15 mg/cm² with the actual amount of sulfate detected for the amount of NaCl applied to the surface. This normalization was done to minimize the effects of thicker salt deposits, as shown in Figure 4. The results are presented in this form in Figure 7. The standard deviation of these results was computed from the linear regression analysis performed on the calcium vanadate samples and indicated in Figure 4. Two standard deviations representing a 95% confidence limit would be a spread of ± 1.7 mg/cm² of soluble sulfate detected. This two standard deviation spread is indicated in Figure 7.

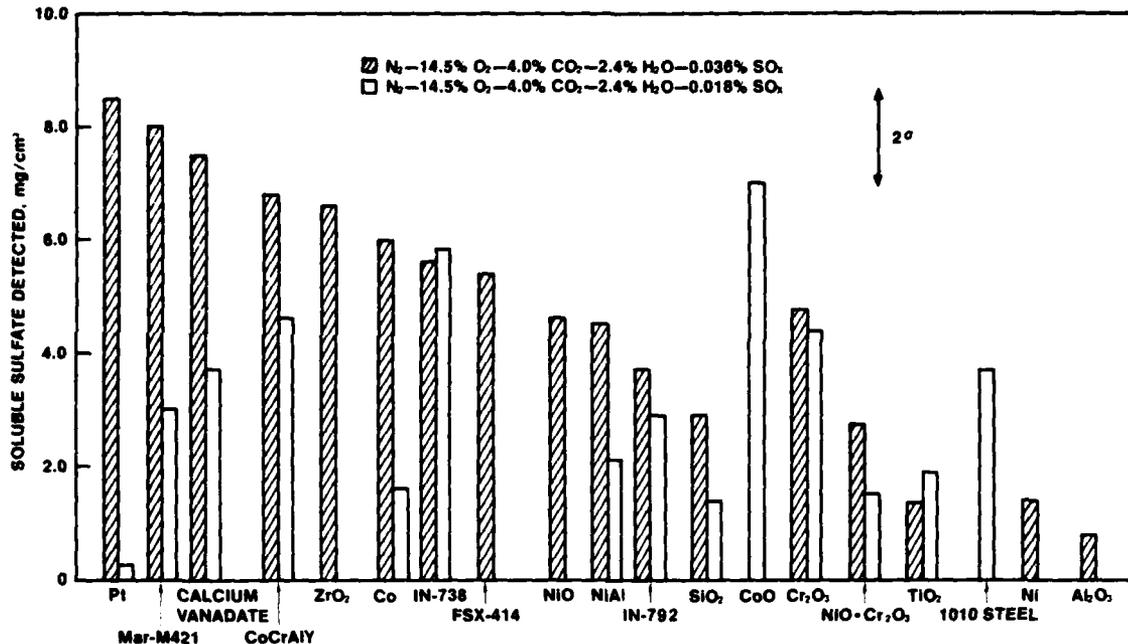


Figure 7. Normalized Sulfate on Surfaces Pre-Coated With NaCl (7-16 mg/cm²) and Then Exposed to Synthesized Combustor Exhausts at 650°C for One Hour

The results of sulfate analysis from NaCl deposits on powders sintered into pellets are also included in Figure 7. Surfaces tested in this manner and included in Figure 7 were: NiO, CoO, Cr₂O₃, NiO·Cr₂O₃, ZrO₂ and TiO₂. This group of surfaces provide a larger surface area because of their porosity and therefore, any comparison with the data on the denser, solid surfaces is difficult to make.

Interference tests with the sulfate detection method were made with all of the surfaces from sintered powder and with calcium vanadate which was received as a powder but subsequently induction melted in a dense solid. No interference was found except with titania powder. For the amount of titania (TiO₂) used in one test pellet, 0.6 mg of sulfate was detected using the barium atomic absorption technique. This represents a positive systematic source of error of 0.8 mg/cm² sulfate with tests performed with TiO₂ pellet samples.

The effects of several selected surfaces on the conversion of magnesium chloride (~12 mg/cm²) to magnesium sulfate at 650°C is presented in Figure 8. The same surface which produced a higher amount of sulfate from sodium chloride at 650°C behaved similarly in their effects on magnesium chloride. The same is true of magnesium chloride coated silica and alumina which produced little or no sulfate after 1 hour of exposure at 650°C in a simulated turbine exhaust.

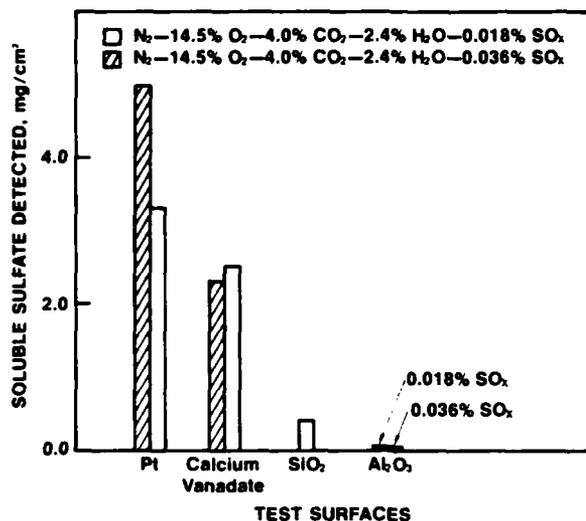


Figure 8. Amount of Soluble Sulfate Detected on Surfaces Pre-Coated With $MgCl_2 \cdot 6H_2O$ and Exposed to a Simulated Combustor Exhaust for One Hour at $650^\circ C$

Figures 9 and 10 are plots of soluble sulfate detected on surfaces after one hour exposure at $760^\circ C$. The sulfur oxide content of the test gas used for the results in Figure 10 are half of the SO_2/SO_3 content used in Figure 9 (i.e., 0.018% versus 0.036%). Each data point represents the results of one test. Figures 11 and 12 are plots of sulfate versus amount of sodium chloride sprayed on the surface after exposure at $815^\circ C$. Again, each data point represents one test result. The results plotted in Figure 12 are for the low sulfur oxide environment. No trend is apparent in the effect of surfaces on the conversion of sodium chloride to sodium sulfate at higher temperatures.

Based on the results of Figure 7, two materials were chosen to represent a high and low sulfate former from the conversion of sodium chloride to sodium sulfate at $650^\circ C$ for burner rig tests. MAR-M421 was chosen for the high amount of sulfate detected and IN-713 was chosen because of its higher aluminum content which, with a proper pre-oxidation treatment, should produce an alumina scale (Ref. 3) on its surface. A low amount of sulfate was detected on NiAl and alumina surfaces.

As indicated in the experimental procedure, two different methods of chloride introduction were used. In the first, the pins were pre-coated with NaCl ($0.95-1.22 \text{ mg/cm}^2$) and then exposed to the combustor effluent. In the second method, chloride solutions were emulsified into the fuel.

The amount of sulfate detected on MAR-M421 pins was nearly 80% higher than that detected on the IN-713 pins for the pre-coated chloride burner rig tests. This difference is negated somewhat by the fact that MAR-M421 test pins had a slightly heavier NaCl coating ($0.95 \text{ vs. } 1.22 \text{ mg/cm}^2$). This result strengthens the conclusions from Figure 1 that surfaces do affect the conversion reaction.

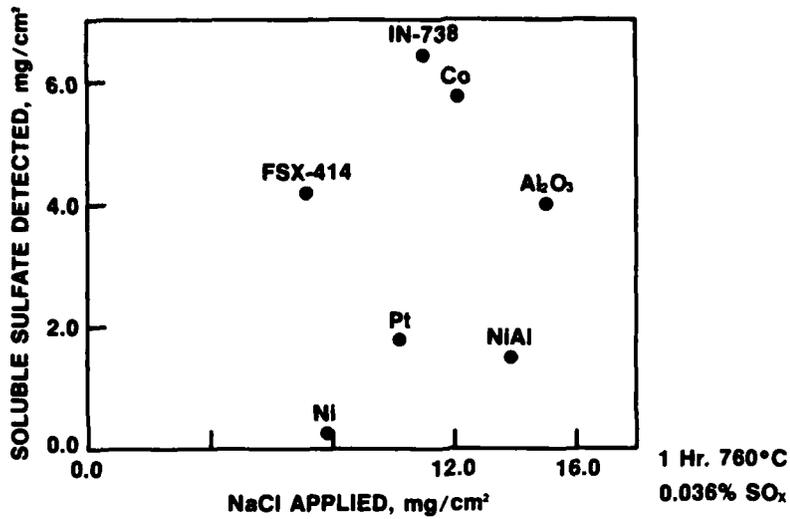


Figure 9. Sulfate Detected on Various Surfaces Pre-Coated With NaCl and Then Exposed to a Simulated Combustor Exhaust Containing 0.036 Percent SO_x for One Hour at 760°C

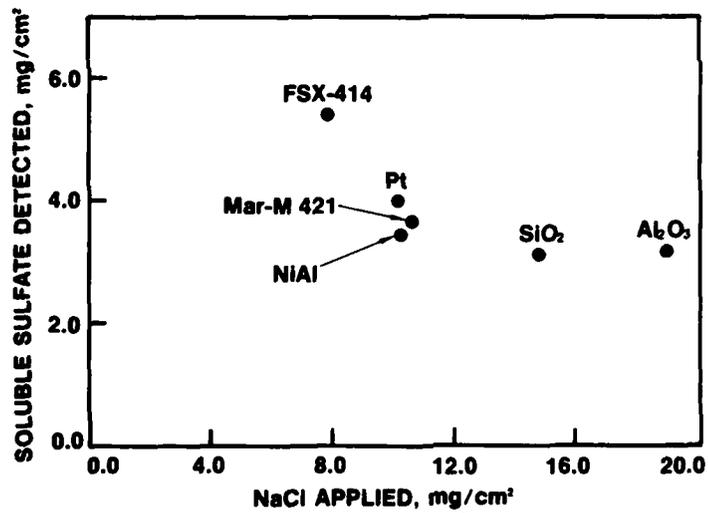


Figure 10. Sulfate Detected on Various Surfaces Pre-Coated With NaCl and Then Exposed to a Simulated Combustor Exhaust Containing 0.018 Percent SO_x for One Hour at 760°C

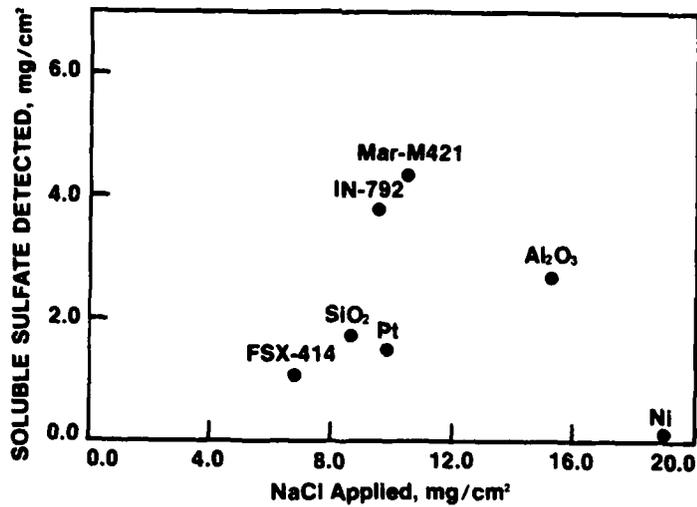


Figure 11. Sulfate Detected on Various Surfaces Pre-Coated With NaCl and Then Exposed to a simulated Combustor Exhaust Containing 0.036 Percent SO_x for One Hour at 815°C

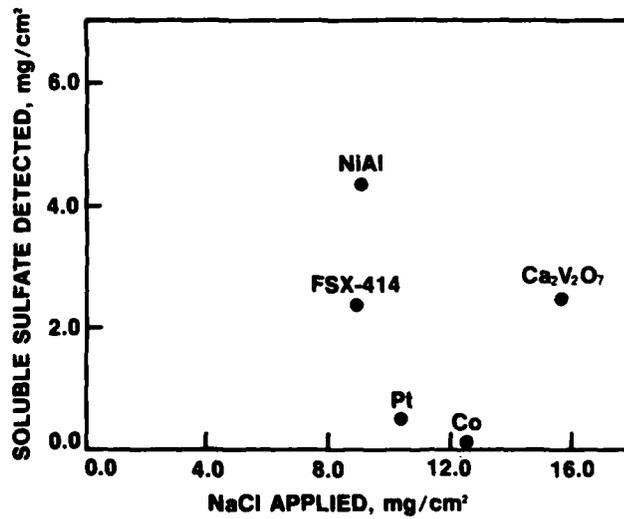


Figure 12. Sulfate Detected on Various Surfaces Pre-Coated With NaCl and Then Exposed to a Simulated Combustor Exhaust Containing 0.018 Percent SO_x for One Hour at 815°C

The results from chloride solutions emulsified into the fuel, along with sulfate from chloride deposits converted in situ are shown in Figure 13. All of the above-mentioned burner rig tests were for 1 hour. The deposits from the NaCl-MgCl₂ emulsion appeared to be glassy as if melting had occurred. This may be explained by the low melting eutectic between NaCl and MgCl₂ at 450°C (Ref. 4). No chloride deposits were detected in any of the salt deposits.

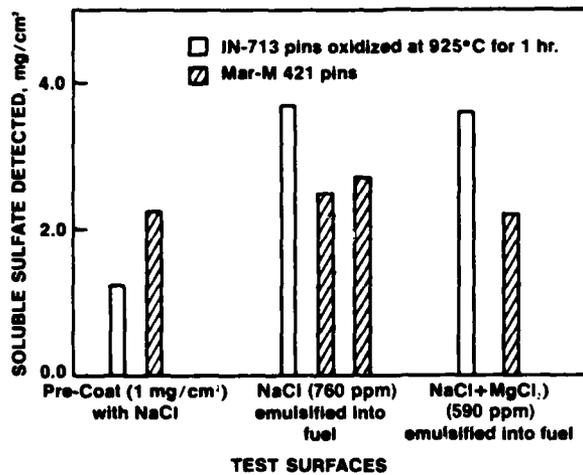


Figure 13. Sulfate Analysis of Deposits From Burner Rig Tests at 650°C for One Hour

4

DISCUSSION OF RESULTS

The results presented in Figures 5 to 7 indicate that not only does conversion of sodium chloride to sodium sulfate occur at 650°C, but it occurs quite rapidly. Although the gas compositions are representative of gas turbine effluent from burning diesel fuel with one and two percent sulfur, the furnace screening tests and the burner rig tests were both performed at one atmosphere. The amount of sulfur oxides therefore available per unit volume in a 10 atmosphere environment at equivalent sulfur concentration would be ten times as great as present in these experiments. Conversely the highest level of sulfur oxide concentration in our one atmosphere furnace and burner rig tests would be equivalent to the concentration of sulfur oxide per unit volume in a 10 atmosphere gas turbine burning diesel fuel with 0.1 and 0.2 percent sulfur. Sulfur levels of 1.0 percent are typical (Ref. 5) for fuel for marine gas turbines especially for refueling in Europe.

Figure 4 indicates that the amount of sulfate detected is dependent on the amount of sodium chloride initially applied. Each point in Figure 4 represents only one test. As indicated in Figure 7, a range of sulfate per area would be a more accurate representation, as indicated by the "2 σ " arrow in Figure 7. Figure 4 is meant to show only that there is a dependence of the amount of sulfate detected by the amount of sodium chloride initially applied. The equation representing a linear regression analysis of the data in Figure 4 merely indicates a linear dependence of sulfate detected on the amount of salt (NaCl) applied. The data presented in Figure 4 should not be used as a basis for indicating a greater percentage of sulfidation with a thicker NaCl deposit. There is insufficient data, as indicated by the 2 σ spread in Figure 7, for reaching this conclusion.

One measure of the amount of conversion that does occur would be to attribute all of the sulfate that was detected to formation of Na₂SO₄. This assumption is valid when considering such surfaces as Al₂O₃, SiO₂, platinum and the relatively unreactive inert metal oxides. However, when considering metal substrates, complex reaction can occur that yield sulfur in forms other than Na₂SO₄. For example, analyses show some formation of soluble nickel and cobalt sulfates on alloys containing these elements. Also, movement of elemental sulfur into the substrate as a result of reduction of the SO_x or SO₄⁻ ion is a possibility. To test this hypothesis nickel foil was exposed to the standard 0.036% SO_x atmosphere for one hour at 815°C. The soluble sulfate obtained was 0.6 mg/cm² but the sulfur in the nickel foil had increased from 0.004% to 0.09%. The low sulfate content found on nickel may be in part due to the reduction of sulfate ion rather than low reaction rate of SO_x with NaCl.

A cobalt and sodium ion analysis of the wash water from sodium chloride (12.1 mg/cm^2) applied to cobalt foil and exposed to a one hour furnace tests at 760°C with the high sulfur oxide level (0.036%) indicated only six percent of the total sulfate detected was from cobalt sulfate. This is assuming that all of the soluble cobalt detected was present as CoSO_4 . Shores (Ref. 6) found that all of the NaCl in a $\text{Na}_2\text{-SO}_4\text{-}25\%\text{NaCl}$ deposit (5mg/cm^2) on a $\text{Co-}22\text{Cr-}12\text{Al}$ surface was converted to sulfate within a few hours after exposure to a $\text{O}_2\text{-}0.1\%\text{SO}_2$ atmosphere at 750°C . A platinum catalyst was used upstream of the sample to equilibrate SO_2/SO_3 concentrations in the gas stream.

The amount of conversion of sodium chloride to sodium sulfate as a function of temperature on three different surfaces is shown in Figure 14. Only fully dense surface were chosen to assess accuracy of sulfur reaction area. The three surfaces chosen, platinum, alumina and silica were chosen for their chemical reactivity in forming a sulfate. By confining an examination to just these surfaces, one may be more confident that all of the sulfate detected is from sodium sulfate and not a transition metal sulfate.

The distinction between surfaces, Figure 14, becomes difficult to make at the higher test temperatures. As temperature is increased there are several competing reactions which can affect the amount of available chloride for conversion. One consideration is the loss of sodium chloride due to vaporization and a second is the change in the partial pressures of sulfur trioxide to sulfur dioxide in the test environments. The large amount of sodium chloride lost due to evaporation at the higher test temperatures obscures the effect of surface on the conversion of chlorides to sulfates. The same conditions would be true for magnesium chloride which has an even higher vapor pressure than sodium chloride. If sulfur trioxide is critical for the conversion reaction to occur, as suggested by the high catalytic activity of platinum metal and calcium vanadate, temperature change would be critical. Figure 15 illustrates the change of the equilibrium partial pressures by the SO_2/SO_3 ratio along with experimentally determined vaporization rates of sodium chloride and sodium sulfate. Note that under equilibrium conditions more sulfur trioxide would be present at the lower test temperature.

Several furnace experiments were performed with NaCl on platinum at shorter exposure times to determine if perhaps more sulfate was formed initially at higher temperatures but because of a more rapid vaporization rate of both NaCl and Na_2SO_4 , less sulfate would be detected than at 650°C . Such is not the case, as demonstrated by the data presented in Figure 16. The initial sodium chloride deposit varied between 10 and 13 mg/cm^3 . The dense smooth surface of platinum is unique among all the surfaces tested at high temperatures. Perhaps when a liquid phase is formed in the salt deposit on platinum there is less surface area of sodium chloride for reaction and fewer pores for access to the sulfur atmosphere compared to the other surfaces tested at elevated temperatures.

An experiment was set up to determine if, by artificially increasing the sulfur trioxide partial pressure by placing platinized alumina upstream of a NaCl -coated sample, the amount of sulfate converted from NaCl would increase. Duplicate experiments in which platinized alumina filled the entire cross section of the quartz tube furnace just upstream of NaCl coated silica did not result in any increase in the amount of sulfate detected. Perhaps the sulfur trioxide needed must be produced at the salt metal interface as would occur

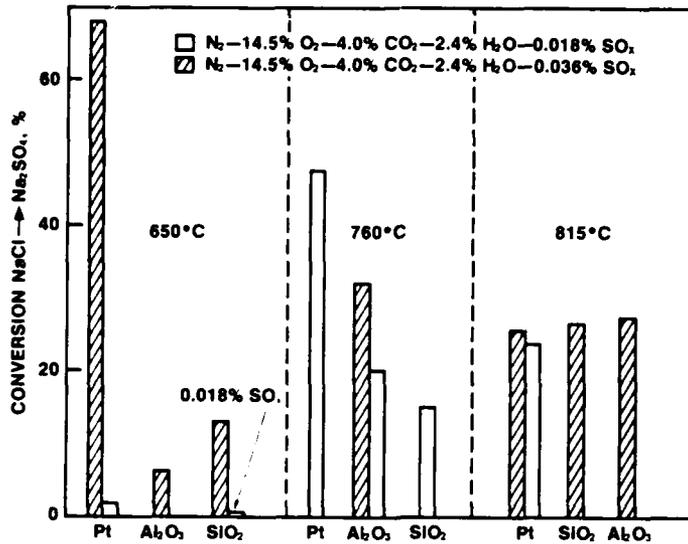


Figure 14. Conversion of NaCl to Na₂SO₄ on Fully Dense Substrates After One Hour Exposures to Synthesized Gas Turbine Combustor Exhaust

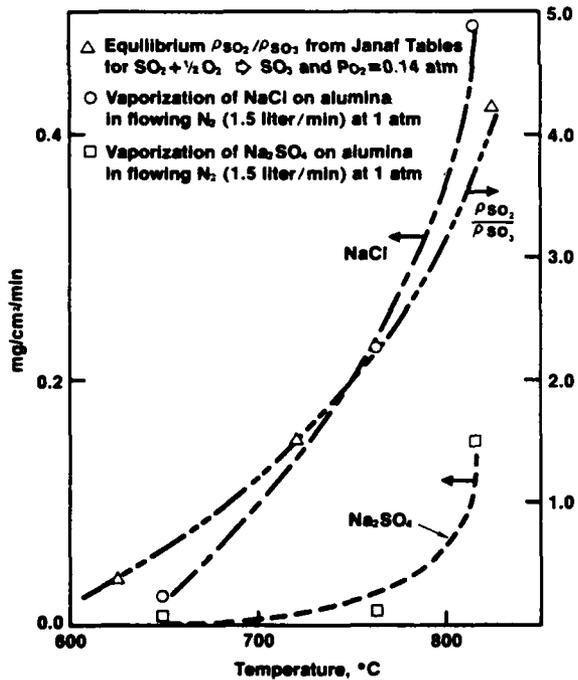


Figure 15.

Characterization of Experimental Salt Vaporization and Equilibrium Sulfur Oxide Ratios as a Function of Temperature

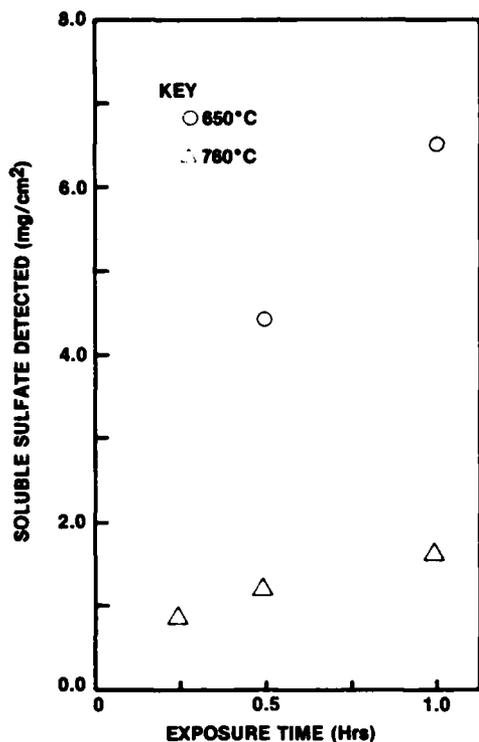
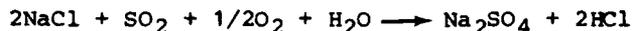


Figure 16.

Effect of Exposure Time on Formation of Soluble Sulfate Deposit From Sodium Chloride on Platinum in $N_2-14.5\%O_2-4.0\%CO_2-2.4\%H_2O-0.036\%SO_x$ at Two Temperatures

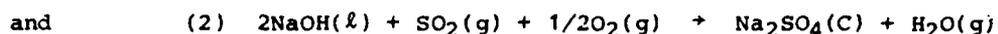
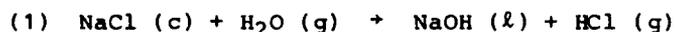
with a NaCl-coated platinum sample. A second alternative is that most of the sulfate is produced by reaction of NaCl with sulfur dioxide, as noted below:



The supposition that SO_2 contributes most of the sulfur in the formation of Na_2SO_4 is supported by the work of Fletcher and Gibson (Ref. 7). In their investigation iron oxide added as Fe_2O_3 presumably as a powder was found to greatly increase the rate of sodium sulfate formation from sodium chloride. The one test result for 1010 steel which would have an Fe_2O_3 scale during exposure at 650°C reported in this investigation did not indicate any increase in the amount of sulfate formed from sodium chloride. However the sulfur oxide content in the test gas used by Fletcher and Gibson was an order of magnitude higher than that used in this study. Gas flow rates used in this study were also 35 percent lower than in that investigation.

The importance of the sulfur oxide level in the test environment is demonstrated in Figures 7 and 14 by the amount of sulfate produced and percent conversion of chloride, respectively, on a platinum surface for two sulfur oxide levels. With the high amount of conversion indicated for platinum in Figure 14, a reduction in the sulfur oxide content by a factor of two must drastically reduce the probability of an SO_2 materials being absorbed on the surface of salt-coated samples for the necessary reaction.

The probability of reaction of SO₂ with a chloride salt would increase if intermediate reactions occurred such as



where "c", "l" and "g" refer to solid liquid and gaseous states respectively.

Although the free energy of formation of the first reaction is unfavorable [+31.3 kcal/mole at 627°C (Ref. 8)] there is evidence in the literature that the hydrolysis reaction does occur (Ref. 9, 10). Also the favorable thermodynamics of the second reaction [-81.9 kcal/mole at 627°C (Ref. 8)] will tend by mass action to drive reaction (1) to the right.

The importance of water vapor was indicated in Figure 5 on which the amount of sulfate detected in a sodium chloride deposit on platinum is less than 0.1 mg/cm² in a gas environment without water vapor. This data point is the result of duplicate tests. With the addition of water to the test vapor a high amount of sulfate was detected. This is further evidence of the necessity for the hydrolysis reaction to occur before the formation of sodium sulfate.

The results of the burner rig tests are not clear in the verification of surfaces on the production of sulfates from chlorides. When sodium chloride was applied to the surface of the test pins, a higher amount of conversion was detected on the MAR-M-421 pins at 650°C than on IN 713 pins which were pre-oxidized to produce an alumina scale on the surface. However, the analyses of salt deposits from chloride solution emulsified in the fuel do not support this ranking of surfaces. In fact, more sulfate was detected on the IN 713 surface in these experiments with surfaces maintained at 650°C than on the MAR-M-421 pins. Since the chlorides must be transported through the hotter gas flame before arriving on the cooler surface, the influence of gas phase reaction will be more important when the chloride solutions are emulsified in the fuel. Why more sulfate was detected on the IN-713 pins from the rig tests with salt emulsified in fuel is not known. Perhaps with so much salt entrained into the gas stream (5 to 8 gm of salt in an hour) there is a limit as to how much salt can be retained on the test pin surface. As soon as sodium sulfate is formed, a liquid phase is present in the sodium chloridesodium sulfate system above 1150°F (Ref. 4). The high shear forces on a liquid phase on rotating samples in a high velocity gas stream may limit the amount of salt that can be retained on the surface. This may explain why the total sulfate detected on pre-coated pins is nearly equivalent to sulfate detected on pins in which salt was continually supplied through the fuel.

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CONCLUSIONS

1. Conversion of condensed chlorides occurs rapidly in both a slow moving (0.2 m/sec) synthesized exhaust flow and a high velocity (500 m/sec) combustor exhaust. Assuming sodium sulfate was formed, most (74%) of the original NaCl coating was converted to sulfate in one 1-hour burner rig test.
2. Complete conversion or vaporization of NaCl occurred on test pins rotated in a high-velocity combustor effluent with NaCl emulsified in the fuel or coated on the pin surface before the test. Tests were performed for 1 hour at 650°C.
3. Surfaces affect the amount of conversion of sodium chloride to sodium sulfate and magnesium chloride to magnesium sulfate at 650°C.
4. The effect of surface on the conversion of chlorides to sulfates at test temperatures of 760 and 815°C is obscured by the higher vaporization rates of NaCl at these temperatures and therefore shorter residence times of condensed chlorides.
5. The amount of sulfate produced from chloride conversion in low velocity furnace tests is dependent upon the sulfur content of the gas environment.
6. The presence of water in the gas environment is critical, if not essential, to the formation of sodium sulfate from sodium chloride.

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