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RP-1 Thermal Stability and Copper Based Materials Compatibility Study

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ABSTRACT

A series of electrically heated tube tests was performed at the NASA Glenn Research Center's Heated Tube Facility to investigate the effect that sulfur content, test duration, and tube material play in the overall thermal stability and materials compatibility characteristics of RP-1. Scanning-electron microscopic (SEM) analysis in conjunction with energy dispersive spectroscopy (EDS) were used to characterize the condition of the tube inner wall surface and any carbon deposition or corrosion formed during these runs. Results of the parametric study indicate that tests with standard RP-1 (total sulfur ~23 ppm) and pure copper tubing are characterized by a depostion/deposit shedding process producing local wall temperature swings as high as 500 °F. The effect of this shedding is to keep total carbon deposition levels relatively constant for run times from 20 minutes up to 5 hours, though increasing tube pressure drops were observed in all runs. Reduction in the total suflur content of the fuel from 23 ppm to <0.1 ppm resulted in the elimination of deposit shedding, local wall temperature variation, and the tube pressure drop increases that were observed in standard sulfur level RP-1 tests. The copper alloy GRCop-84, a copper alloy developed specifically for high heat flux applications, was found to exhibit higher carbon deposition levels compared to identical tests performed in pure copper tubes. Results of the study are consistent with previously published heated tube data which indicates that small changes in fuel total sulfur content can lead to significant differences in the thermal stability of kerosene type fuels and their compatibility with copper based materials. In conjunction with the existing thermal stability database, these findings give insight into the feasibility of cooling a long life, high performance, high-pressure liquid rocket combustor and nozzle with RP-1.

INTRODUCTION

NASA, under its Space Launch Initiative's Next Generation Launch Technology Program, is investigating the feasibility of developing a highly reliable, long-life, liquid oxygen/kerosene (RP-1) rocket engine for future launch vehicles. One of the top technical risks to the program is the potential for RP-1 thermal stability and material compatibility problems to occur under the high-pressure, high-temperature conditions required for regenerative fuel cooling of the engine combustion chamber and nozzle. With chamber pressures (and heat load) in the engine expected to more than double those of current regeneratively cooled hydrocarbon rocket engines, the ability to keep wetted wall temperatures in the combustion chamber liner at or below the coking limit of the fluid becomes exceedingly more difficult.

Experience has shown that hydrocarbon fuels, such as RP-1, at sufficiently high temperatures begin to decompose resulting in the formation of gums and solids that can deposit on wetted fuel surfaces. The deposit then acts as an insulating layer, causing a further increase in wall temperature, which can eventually lead to loss of structural integrity and propulsion system failure. Excessive deposits may also reduce the coolant flow area and increase surface roughness resulting in increased coolant pressure drop or reduced coolant flow rate. The rate at which the deposition process occurs is driven by many factors such as wall temperature, fuel composition (e.g. sulfur and oxygen content), velocity (residence time), and coolant passage material. At the present time, the interaction of these effects is not completely understood and the prediction of deposition remains difficult. However, it is generally accepted that at lower temperatures, less than about 900 °F, the deposition process occurs as the result of auto-oxidation reactions, whereas the deposition process at higher temperatures is driven by the pyrolysis of the hydrocarbon molecules.[1] Rule of thumb design guidelines for RP-1 place the coking limit of the fuel between 600 and 700 °F.

An additional complication has also been reported for hydrocarbon fuels containing fuel-bound sulfur components when they are used to cool copper and copper alloy structures. The sulfur reacts with the copper to form copper sulfides. This sulfide corrosion can both damage the copper surface and disturb the flow. In references 2-5, which contain heated tube test results performed under rocket engine conditions, dendritic structures were observed protruding from copper or copper alloy surfaces. Analysis indicated that these dendrites were composed largely of copper and were also referred to as "copper wool." In experiments reported in reference 4, the possibility that the dendritic structures were caused by reaction of the fuel-bound sulfur with the copper in the test section surface was investigated by doping fuels (RP-1, methane, propane) with additional sulfur compounds (thianaphthene, benzyl disulfide), and indeed an increase in the dendritic formations was observed after increasing the fuel sulfur content. In addition, the dendrite formations were identified as copper sulfides.

The purpose of this investigation was to use electrically heated tube sections to parametrically study the effect that sulfur content, test duration, and tube material play in the overall thermal stability and materials compatibility of RP-1. The tests were run under conditions similar to those that would be encountered in a next-generation, reusable, high-pressure rocket engine. Another goal of the study was to obtain limited heated tube data on the copper alloy GRCop-84. GRCop-84 is a copper alloy containing chromium and niobium and may be a replacement for materials currently considered for thrust chamber construction such as NARloy-Z.

EXPERIMENT

DESIGN OF EXPERIMENT

The baseline test condition chosen for this matrix was a target average tube inner wall temperature of 675 °F, the upper end of the rule of thumb coking limit range for RP-1, and an average flow velocity of 75 ft/sec. The inlet temperature for the baseline tests was left at ambient (~50 °F) while the outlet temperature was set at approximately 400 °F. This corresponds to a heat flux of 3.8 BTU/in^2-sec. All of the tests in the matrix were run at 1000 psig. Using this baseline condition, the primary variables investigated in these experiments were test duration, fuel total sulfur content, and wetted wall material.

Four different test durations were included in the matrix ranging in length from 20 minutes up to 5 hours, with the five hour duration test being representative of 100 cycle engine operating life. By investigating the effect of time on the deposition process it was hoped that insight into the ability to extrapolate trends from short duration tests would be gathered along with the validity of reporting deposition results in rate form (μg/cm^2-hr) which has been common in the literature.

RP-1 with three different sulfur levels was procured for testing. The first of the three sulfur levels was current production grade RP-1. This is the product currently delivered by the vendor for testing or launch operations and was designated in this matrix as standard grade. Two lower level sulfur contents were also tested due to the significance of copper sulfide corrosion problems that have been reported in the literature. A TS-5 grade RP-1 (TS designating total sulfur content and 5 representing less than 5 ppm) was chosen as a mid level sulfur fuel and has a total sulfur content similar to that of JP-7. Finally, a UL (Ultra-Low) grade RP-1 with a total sulfur content of < 0.1 ppm was procured. It was expected that at one of these lower sulfur levels the corrosion observed in past testing could be eliminated.

The two tube materials tested in the matrix were pure copper tubing (OFE) and GRCop-84. Finally, a wall temperature excursion was run with UL grade RP-1 in pure copper tubing at an average wall temperature of 820 °F. For this test, the outlet temperature of the fluid was raised to 450 °F and the tube heat flux was 4.8 BTU/in^2-sec. The test matrix is summarized below in Table 1 with the actual recorded average wall temperatures for each run.

Table 1: Test Matrix Summary

RP-1 Sulfur Level	Tube Material	Wall Temperature (°F)	Average Velocity (ft/sec)	Test Duration (hr)
		Time		
Standard	OFE	685	75	0.33
Standard	OFE	680	75	1.0
Standard	OFE	689	75	2.5
Standard	OFE	670	75	5.0
		Sulfur Level		
TS-5	OFE	680	75	1.0
UL	OFE	676	75	1.0
		Tube Material		
Standard	GRCop-84	675	75	1.0
UL	GRCop-84	670	75	1.0
		Wall Temperature Excursion		
UL	OFE	820	75	1.0

FACILITY AND HARDWARE

All heated tube tests were conducted at the NASA Glenn Research Center heated tube facility (HTF) in Cleveland, Ohio using the combustible liquid flow system. A simplified schematic of the facility architecture is shown in Figure 1.[2]

Flow rate and test section pressure are regulated by setting the nitrogen pressure in the supply tank to the desired level and then activating a control system that utilizes a Coriolis flow meter and two control valves (one back pressure and the other flow control) to continually maintain the desired test section flow and pressure conditions. The fuel, upon leaving the test section, is cooled using a water heat exchanger and is then stored in a scrap tank that is vented to the atmosphere. Electrical power is supplied to the test section from up to four 80 VDC, 1500 Ampere welding power supplies. Further details on this facility, details concerning run procedures, and details concerning data reduction methodology can be found in Reference 2.

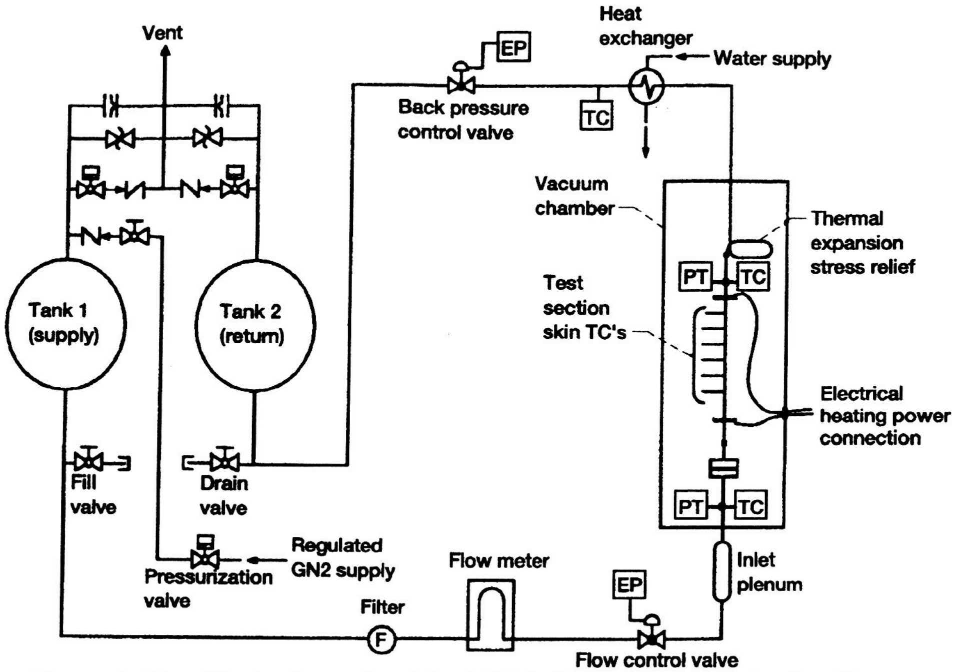

Figure 1. Simplified schematic of the NASA Glenn Heated Tube Facility.

The test sections were fabricated from drawn tubing of pure copper (OFE) and GRCop-84. The test section dimensions and are shown in Table 2. All of the test pieces were instrumented with eight K-type thermocouples equally spaced along the length of the tube and torch brazed to the outer wall. It is important to note that the surface roughness measurements for the two different tube materials are identical.

Table 2: Test Pieces Dimensions

Material	**Outer Diameter** (in)	**Inside Diameter** (in)	**Heated Length** (in)	**Surface Roughness**† (μin)
OFE	0.125	0.061	17.0	15
GRCop-84	0.125	0.060	17.0	15

† 2 mm stylus drag

FUEL ANALYSIS

Each of the fuels tested in this study was delivered with a vendor test report verifying that they met the requirements set in the current RP-1 military specification. Since sulfur was one of the primary variables in this test matrix, it was necessary to have accurate characterization of the fuel sulfur contamination. In general, the standard sulfur analyses required by the specifications were not sufficiently accurate for these low sulfur fuels. Thus, additional analyses for total fuel-bound sulfur (e.g. disulfides, mecaptans, thiophenes) were conducted according to standard ASTM test methods. The standard grade and TS-5 level sulfur fuels were analyzed using the ASTM D 5453, while a variation of the ASTM D 5623 test was performed on the UL grade sample. Total sulfur content of the fuels is shown in Table 3.

Table 3: Fuel Total Sulfur Content

Fuel	**Total Sulfur Content** (ppm)
Standard	23 †
TS-5	3 †
UL	26 ppb *
† ASTM D 5453	* modified ASTM D 5623

The reproducibility of the ASTM D 5453 test method is dependant upon the amount of sulfur in the sample. For the ranges seen in these tests it is approximately 2 ppm. The reproducibility of the modified ASTM D 5623 method is unknown. A standard ASTM 5623 speciation test was also performed on the standard grade RP-1 and showed that the only sulfur compounds above the detection limit (0.2 ppm) were thiophenes at 10 ppm. Speciation tests for the TS-5 and UL grade RP-1 were not performed due to the low levels of sulfur in these fuels.

MICROSCOPIC ANALYTICAL TECHNIQUES

Segments of each test section were milled to expose the interior surface for examination under a scanning electron microscope (SEM) as shown in the sketch in figure 2. In conjunction with the SEM imaging, energy dispersive spectroscopy (EDS) was utilized to perform elemental composition analysis on the inner wall of the tube samples. The EDS technique works by measuring the number and energy of X-rays emitted by the sample after being irradiated by an electron beam. By matching the energy of the emitted X-rays to the known characteristics of each element, the composition of the sample can be determined. It is important to recognize that the highly irregular surfaces analyzed in this investigation are not optimal for EDS analysis and that corrections for the atomic number, absorption, and possible fluorescence of the elements are all possible sources of errors in the quantification process. Even with these limitations, the qualitative information provided by the EDS analysis provides significant insight into the deposition and corrosion processes.

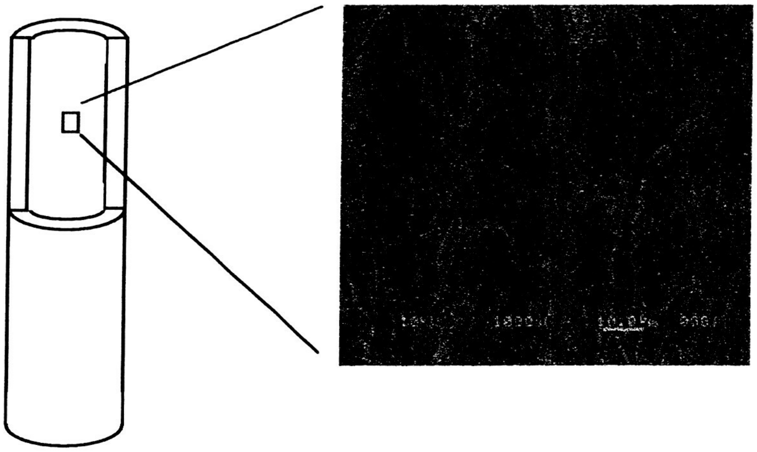

Figure 2. SEM micrograph of a clean section of OFE copper tubing showing the as delivered internal surface due to the drawing process.

RESULTS AND DISCUSSION

Upon completion of the test runs, the test pieces were sectioned for deposition analysis. One-inch tube sections were removed around each of the thermocouples for carbon deposition analysis while small lengths of tube between these sections were kept for SEM and EDS analysis.

Carbon deposition measurements were made by first removing any residual fuel left in the tube sections with a heptane rinse followed by a vacuum drying process. A Leco RC-412 Carbon Determinator was then used to measure the carbon remaining in the sectioned pieces. The Leco measures the carbon dioxide evolved from the sample in an oxidizing environment using an infrared cell. For a one-inch tube section, the process has a sensitivity of about 10 µg.

Carbon deposition results from the four different time duration tests are presented in Figure 3. The thermocouple locations in the figure represent roughly the beginning, middle, and end of the test section. The carbon deposition results have been normalized by the surface area of the sample and it can be seen that the results are largely independent of both test duration and the axial station along the tube where the sample was taken. In all cases, the total deposition that was observed (on the order of 30 µg) is not much higher than the level of the clean tube and on the order of the sensitivity of the measurement process. The data shown in Figure 3 has been recast into rate form in Figure 4. The figure clearly shows that for these tests, extrapolating carbon deposition levels from short duration tests would be extremely misleading, resulting in errors as high as a factor of 20.

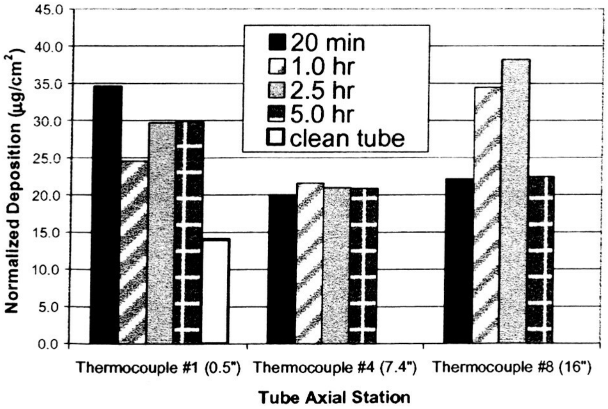

Figure 3. Effect of time on the deposition process for standard grade RP-1 in pure copper tubes

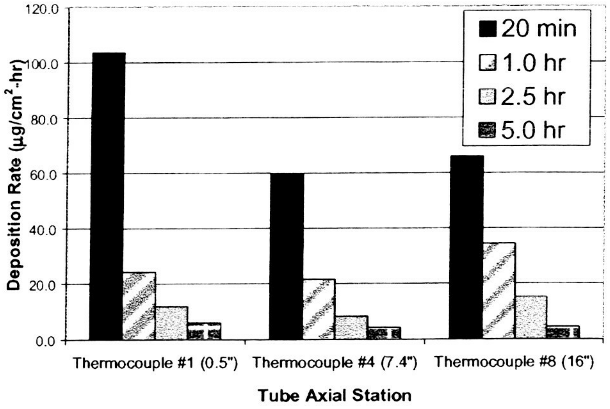

Figure 4. Comparison of deposition rates for standard grade RP-1 in pure copper tubes

The tube inner wall temperature histories at the first thermocouple along with an SEM image (30X magnification) for both the 20 minute duration test and the 5 hour duration test are shown for comparison in Figures 5 and 6. These photos were taken at the first thermocouple. Significant shedding of deposits can be inferred to occur in both tests as indicated by the sudden temperature drops recorded by the wall thermocouples. Although the largest drop shown below is approximately 400 °F, in other tests temperature swings as high as 500 °F were recorded. It appears from Figure 6 that as the shedding process continues the average wall temperature at each thermocouple is actually decreasing, probably due to the corrosion process increasing the local surface roughness. The EDS analysis of the SEM images shown in figures 5 and 6 indicated that the dark region of the tube wall was characterized by larger levels of elemental carbon while the lighter region was found to be high in elemental sulfur content. The loose nature of some of the deposits is particularly evident in Figure 5.

A filter located downstream of the test section was able to catch some of the particles that were shed during each of the runs. These particles were then prepared for SEM and EDS analysis. Spine-like growths were found to be present on some of the particles as seen in Figure 7. The corresponding EDS spectrum indicates a very strong sulfur and copper return with weaker returns for carbon and oxygen. This gives strong evidence to support the assumption that copper sulfide was being created at the tube wall. Unfortunately, crystallography performed on the samples was not able to conclusively identify the sulfide structure due to the limited amount of sample that was available for analysis. Finally, it should be noted that although deposit shedding kept the carbon deposition levels roughly constant regardless of test duration, this was not the case with the corrosion and deposition induced tube pressure drop increases. Table 4 shows the percentage increase in tube pressure drop as a function of time. The pressure drop increase of nearly 30% recorded in the five hour run would be unacceptable for an operational engine.

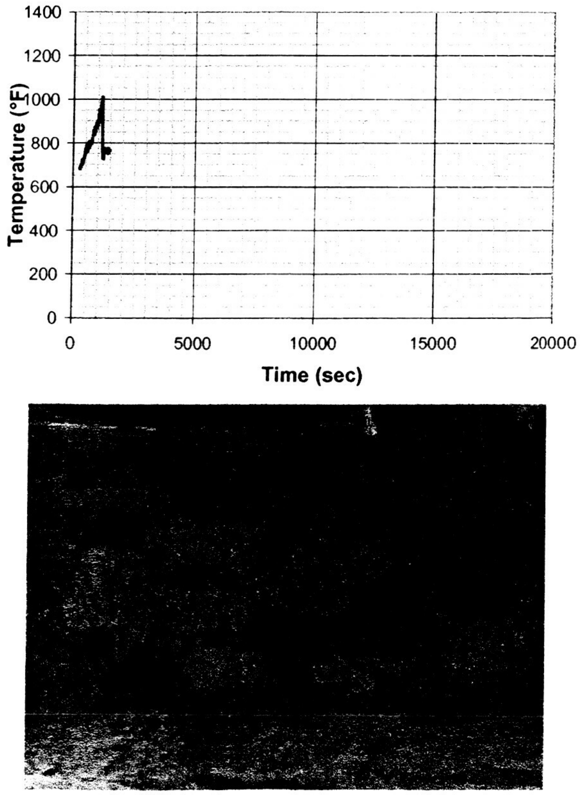

Figure 5. Temperature history and SEM (30X) for 20 minute duration standard RP-1/OFE copper tube test (Thermocouple #1 0.5")

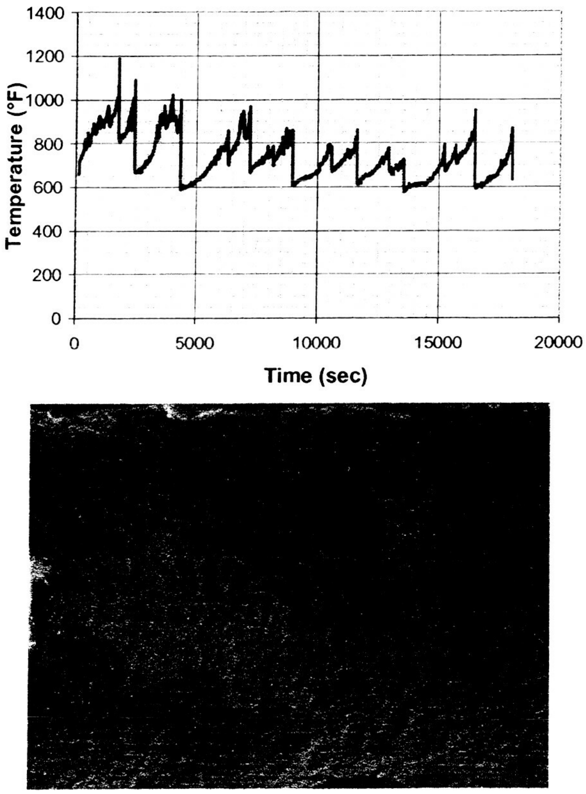

Figure 6. Temperature history and SEM (30X) for 5 hour duration standard RP-1/pure copper tube test (Thermocouple #1 0.5")

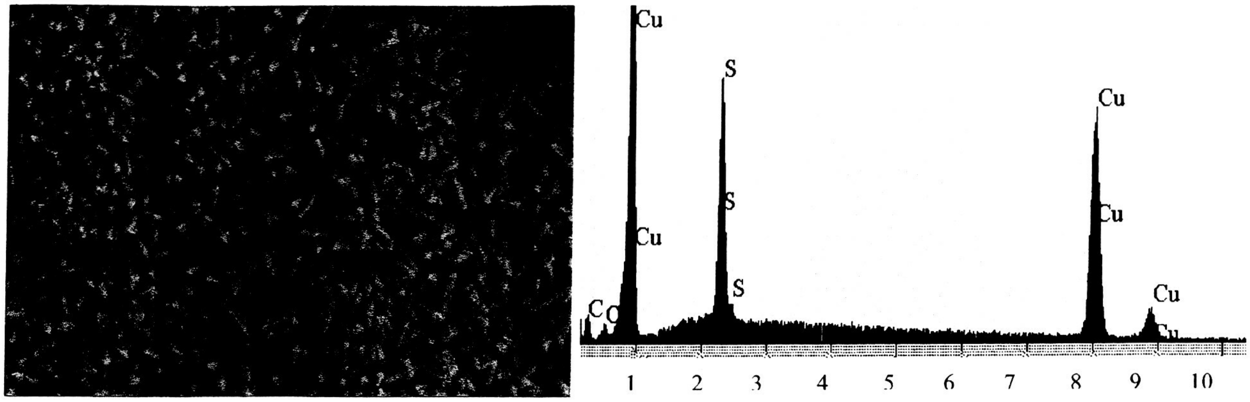

Figure 7. SEM (2500X) and EDS shed particle analysis

Table 4: Effect of run duration on tube pressure drop rise

Test Duration (hours)	**Pressure Drop Increase** (%)
1/3	4.5
1.0	11
2.5	23
5.0	28

With the one hour test conducted with standard grade RP-1 and pure copper tubing selected as a benchmark, the effect of reducing the fuel total sulfur content was investigated by repeating this test with the TS-5 and UL grade sulfur levels. Shown in Figure 8 is a comparison of the normalized deposition levels for all three sulfur level fuels in 1 hour duration tests. With the exception of the fourth thermocouple in the TS-5 run, it appears that reducing the sulfur content of the fuel also reduces the level of carbon deposition. This is probably due to the fact that increasing levels of hydro treating were performed on the TS-5 and UL grade fuels to reduce their sulfur content. This additional hydro treating in turn would have reduced the unsaturated hydrocarbon content of the fuel which is known to be particularly susceptible to forming deposits.

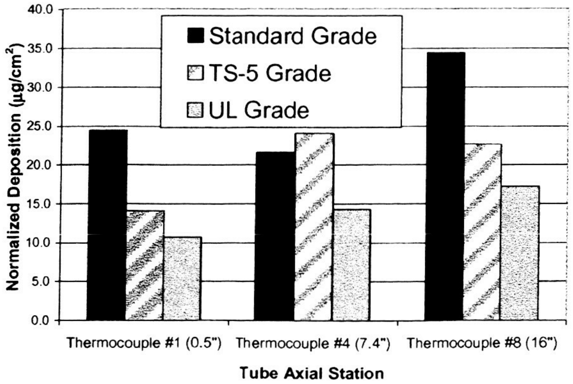

Figure 8. Effect of sulfur content on deposition levels in 1 hour duration tests

At the TS-5 level, the wall temperature histories and down stream filter both showed no sign of deposit shedding, although a nearly linear increase in the local wall temperature was observed at the middle and end of the tube. The amount of this increase was particularly significant near the end of the test section at 100 °F. By further reducing the total sulfur content of the fuel, both shedding and significant wall temperature increases were eliminated. The 1 hour UL grade RP-1 test showed a maximum wall temperature increase of 20 °F at one thermocouple location while all other wall temperature histories were unchanged over the course of the test. The impact of virtually eliminating the sulfur content of the fuel can be seen in Figure 9 which is an SEM (30X) photo and the corresponding temperature history for the first thermocouple on the test section. The corresponding EDS analysis indicated no elemental sulfur present at the tube wall. The debris that is present on the wall in Figure 9 was found from EDS to be copper and is most likely debris that was left from the sawing process used to section the tubes. Table 5 summarizes the effect of reducing RP-1 total sulfur content on wall temperature variation, deposit shedding, and tube pressure drop increases. The effect of reducing the sulfur content of the fuel from 23 ppm down to less than 0.1ppm is dramatic producing a total elimination of deposit shedding and only modest increases in tube wall temperature and pressure drop. Furthermore, the reduction in sulfur content of the fuel to the TS-5 level may not be sufficient for an engine that is designed for a 100 mission life.

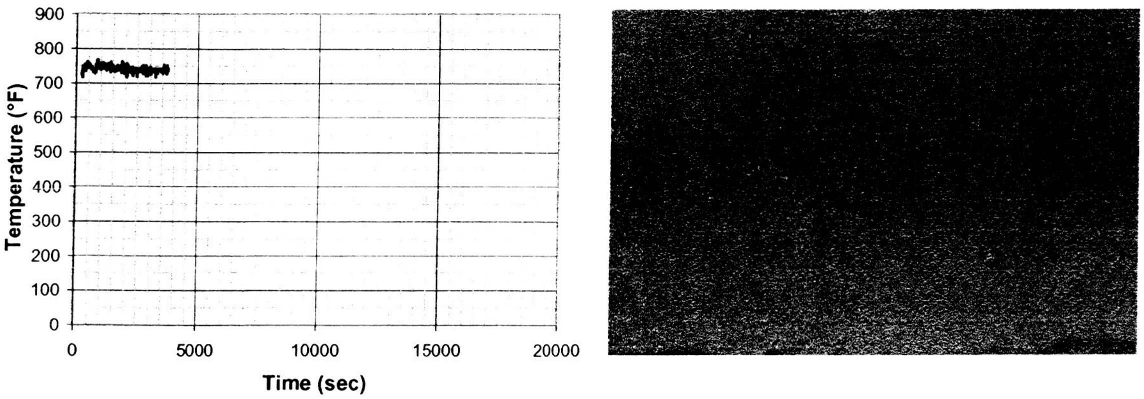

Figure 9. SEM (30X) and temperature history for 1 hour duration UL Grade RP-1/pure copper tube test (Thermocouple #1 0.5")

Table 5: Effect of sulfur content on tube pressure drop rise, deposit shedding, and wall temperature variation in 1 hour duration tests in OFE tubing

Sulfur Level	Shedding	Wall Temperature Variation (°F)	Pressure Drop Increase (%)
Standard	YES	+400	11
TS-5	NO	+100	9
UL	NO	+20	2

Carbon deposition results comparing the effect of wall material on the deposition process in 1 hour tests are shown in Figure 10. It can be seen that for both standard grade and UL grade RP-1, the GRCop-84 tubing exhibited higher levels of carbon deposition than the same tests run in pure copper tubing. It is also interesting to note that UL grade fuel in GRCop-84 had higher deposition levels than standard grade RP-1 in pure copper tubing.

Unlike tests done in pure copper tubing, the significant amounts of deposit shedding that were observed with standard grade RP-1 were not found to occur in GRCop-84 tubing. Shown below in Figure 11 is a SEM image (1000X) from the standard grade RP-1/GRCop-84 test along with the corresponding wall temperature history. The spine-like structures observed in the pure copper tubing deposit analysis are again seen on the wall of the GRCop-84 tubing. The EDS analysis performed on these structures, as with those in the pure copper tubing, showed strong signs of sulfur but very weak returns for carbon and oxygen, ndicating copper sulfide production. From the temperature trace it is also seen that the increase in local wall temperature is significant at about 350 °F. As with the pure copper tubing tests, the UL grade RP-1 test in GRCop-84 showed slight local wall temperature increases and almost no tube pressure drop increase. The wall temperature variations, increases in tube pressure drop, and deposit shedding of the GRCop-84 tests are summarized in Table 6.

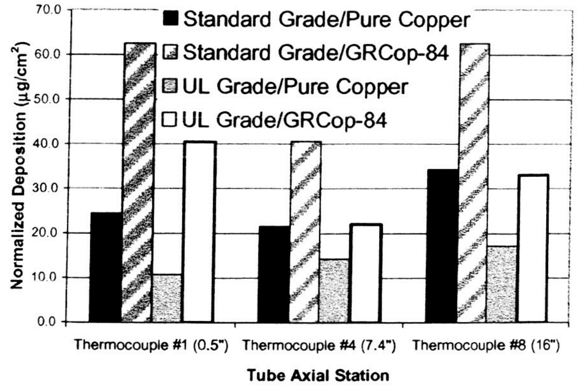

Figure 10. Effect of wall material on carbon deposition process in 1 hour duration tests

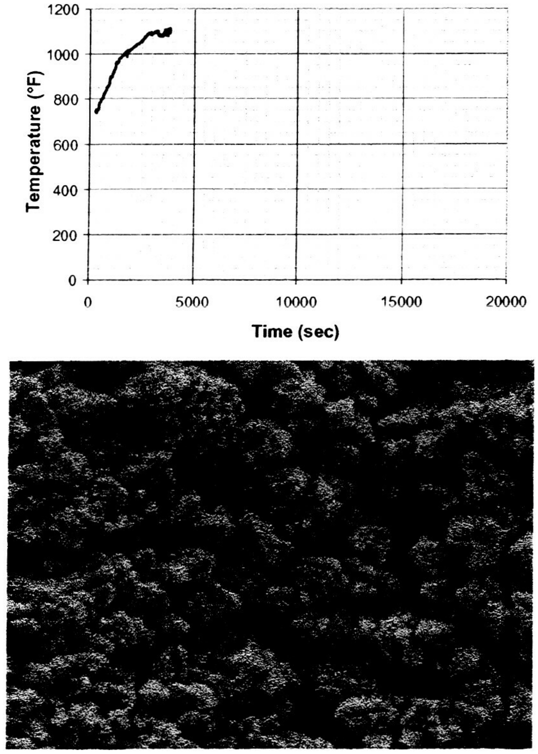

Figure 11. SEM (1000X) and temperature history for 1 hour duration standard grade RP-1/GRCop-84 test (Thermocouple #1 0.5")

Table 6: Effect of wall material on tube pressure drop rise, deposit shedding, and wall temperature variation in 1 hour duration tests

Material	Sulfur Level	Shedding	Wall Temperature Variation (°F)	Pressure Drop Increase (%)
C101	Standard	YES	+400	11
GRCop-84	Standard	NO	+350	3
C101	UL	NO	+20	2
GRCop-84	UL	NO	+30	1

The final test that was performed in the matrix was a wall temperature excursion of about 150 °F using UL grade RP-1 in pure copper tubing. The 150 °F delta was chosen to represent the possibility of off design operation and give some insight into the sensitivity of the deposition process to changes in wall temperature. Figure 12 shows the carbon deposition results comparing the two wall temperatures. At all thermocouple locations, the hot wall condition was seen to increase the carbon deposition levels. Furthermore, at the eighth thermocouple location of the hoter wall test, there was an instance of deposition shedding which resulted in about a 200 °F wall temperature swing (Figure 13) none of which were observed at the 675 °F level. The sensitivity of the carbon deposition process to wall temperature changes is further observed in the fact that the hot wall condition produced a four fold increase in tube pressure drop rise when compared to the cooler 675 °F wall temperature condition (2% to 8% increase).

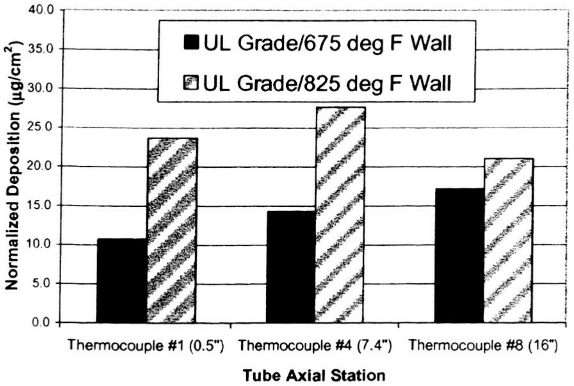

Figure 12. Effect of wall temperature on carbon deposition for UL grade RP-1 in 1 hour duration tests

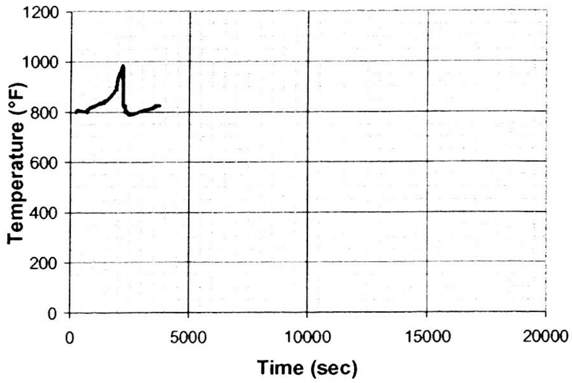

Figure 13. Deposit shedding observed in a UL grade RP-1/OFE copper test at 820 °F wall temperature (Thermocouple #8 16")

SUMMARY AND CONCLUDING REMARKS

A series of electrically heated tube experiments were conducted to investigate the effect of test duration, tube material, and sulfur content on the overall thermal stability and materials compatibility of RP-1. The results from this limited number of parametric tests are very consistent with previously reported data that indicated that small changes in fuel total sulfur content can lead to significant differences in the thermal stability of kerosene type fuels and their compatibility with copper based materials. Specific findings include:

- standard grade RP-1 (23 ppm sulfur content) and pure copper tubing tests are characterized by a deposition/deposit shedding process that can induce up to 500 °F wall temperature swings
- EDS analysis on shed particles indicates strong likelihood of copper sulfide formation
- TS-5 grade RP-1 (3 ppm total sulfur content) eliminated all signs of deposit shedding but local wall temperature increases and tube pressure drop increases still occurred
- UL grade RP-1 (26 ppb total sulfur content) eliminated all signs of deposit shedding and minimized wall temperature and tube pressure drop increases
- In identical tests, carbon deposition levels in GRCop-84 tubing were higher than those in pure copper tubing
- The carbon deposition process appears to be very sensitive to wall temperature changes. A 150 °F increase in wall temperature in UL grade RP-1/pure copper tubes was enough to induce deposit shedding and increase the tube pressure drop rise by a factor of 4

Finally, extrapolating carbon deposition results from tests where deposit shedding is significant, such as standard grade RP-1 and pure copper tubing tests, is not valid, the ability to do so in low sulfur level fuels tests should be further investigated.

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