Manual on

REQUIREMENTS, HANDLING, AND QUALITY CONTROL OF GAS TURBINE FUEL

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H. vonE. Doering, chairman
J. A. Vincent, co-chairman

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Foreword

The Symposium on Gas Turbine Fuel Requirements, Handling and Quality Control was presented at the Seventy-fifth Annual Meeting of the American Society for Testing and Materials held in Los Angeles, Calif., 25-30 June 1972. The symposium was sponsored by Committee D-2 on Petroleum Products and Lubricants, Technical Division D02.C on Turbine Oils. H. vonE. Doering, General Electric Co., presided as the symposium chairman, and J. A. Vincent, Standard Oil of Calif., served as the co-chairman.

Related
ASTM Publications

Effect of Automotive Emission Requirements on Gasoline Characteristics, STP 487 (1971), $9.50, 04-487000-12

Contents

Introduction

Trace metals in fuels can be detrimental to the operating reliability of gas turbines particularly with the use of higher firing temperatures and stronger but less corrosion resistant hot section alloys.

Limiting these trace metals in distillate fuels by specifications on refinery production does not assure that the fuel is free of trace contaminants as delivered to the turbine because such impurities may be introduced during transportation and storage. Clean fuels free of troublesome trace metals are more likely to be available to turbine users if careful handling, appropriate cleanup procedures particularly at the point of use and routine trace metal analysis of the fuel are employed.

The purpose of this symposium, held in Los Angeles, 28, 29 June 1972, was to give the user, the transporter, and the refiner both fundamental and practical aspects of what can be done to provide cleaner fuels to gas turbines. It explored the nature and source of impurities, their measurement and effect on turbine performance as well as their control and removal. No single set of procedures can be recommended for all installations. However, none can be effectively selected or employed, unless the principles, capabilities, and limitations are understood.

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Operation of Gas Turbines on ASTM 3-GT Fuel

REFERENCE: Hussey, C. E., Lee, S. Y., and Young, W. E., "**Operation of Gas Turbines on ASTM 3-GT Fuel,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 3–21.

ABSTRACT: In 1965 two Westinghouse W171 gas turbines at the Miraflores station of the Panama Canal Co. were overhauled and put into service burning a locally available "Low Vanadium Special Fuel." The purchase specification was: sodium (less than 10 ppm), vanadium (less than 4 ppm), calcium (less than 10 ppm), and sulfur (less than 1.8 percent). Although some corrosion, even at the reduced turbine inlet temperature of 1375°F was anticipated, it was hoped that the damage would be minimal, thereby justifying the use of this fuel with its definite price advantage. However, after 6375 h of operation, an inspection indicated that corrosion had become extensive.

In 1966 the turbines were again overhauled and put back in service on the same fuel but in a treated state. Periodic sampling and analysis was carried out, and except for one brief excursion, the vanadium averaged 2.5 ppm and the sodium less than 0.5 ppm. After nearly 5000 h of operation, an examination showed only minor corrosion to a completely acceptable extent and the machines have continued to run under these conditions since 1967.

During this period, extensive laboratory tests were made in a pressurized passage which simulates gas turbine operation to set safe operating limits for the use of various grades of fuel in actual engines. In addition, an attempt was made to obtain quantitative corrosion measurement of the actual turbine blade by means of a device called "dipstick." It was shown that with a surface temperature of 1500°F together with a 5 ppm sodium/2 ppm vanadium fuel an excessive amount of attack would occur.

It may be concluded that in a modern high temperature gas turbine operating under base load conditions the use of a type 3-GT fuel as defined in ASTM Specifications for Gas Turbine Fuel Oils (D 2880-71) will lead to frequent blade and diaphragm replacement. Under some conditions, the turbine will tolerate a fuel with as much as 1 ppm each of sodium and vanadium. Satisfactory operation should result with a fuel as high as 2 ppm in vanadium content if the sodium is lowered by appropriate treatment to less than 0.5 ppm.

KEY WORDS: gas turbines, corrosion, fuels, specifications, heat resistant alloys, sulfidation, vanadium, sodium

From a combustion standpoint, gas turbines are capable of burning almost any type of liquid or gaseous fuel. However, it has been found that certain other fuel characteristics are overriding causing such deleterious effects as corrosion and

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fouling, when fuels other than light distillates, No. 2 distillate, and natural gas are burned. This corrosion may take place as oxidation or sulfidation and is intensified by certain contaminants in the fuel such as organic vanadium and alkalis such as sodium and potassium salts. During combustion, vanadium may form a corrosive pentoxide, and the alkali metals may form sulfates which are both corrosive and deposit forming. In some instances, the vanadium and sodium may combine to form an even more corrosive sodium vanadate. All of these compounds have low melting points which is a prerequisite for deposit formation or catastrophic corrosion or both.

For several years the gas turbine has played a major role as a peak power generator, and in this type of service its use of higher grade fuels was acceptable. There is now, however, an increasing tendency to run gas turbines for longer than peak schedules, approaching sometimes base load operation. The use of lower grades of fuel then becomes economically desirable. There has emerged a family of low sulfur heavy fuels containing a low level of contaminant such as the ASTM No. 3-GT class as listed in ASTM Specification for Gas Turbine Fuel Oils (D 2880-71). The specification permits up to 5 ppm sodium and 2 ppm vanadium. Certain crudes, high-boiling distillates, and even some residuals can meet this specification. There is also a true residual grade fuel, namely, ASTM No. 4-GT, but it is recognized that such a fuel will require treatment in the form of water washing or chemical addition or both to make it suitable for gas turbine consumption. Therefore, it is of interest to explore the possibilities of using No. 3-GT fuels with low contaminant levels, setting safe operating limits for the gas turbine. This review brings together past work [*1-3*][3] that concerned itself with the evaluation of the high temperature corrosive effects of fuels that are close to or at the limits set out by ASTM D 2880-71 for No. 3-GT fuel oil. The first section [*1*] will deal with actual gas turbine experience with fuels close to the ASTM No. 3-GT specification considering the limits for potentially corrosive chemical elements. Next section will report on experiments [*2,3*] that were designed to measure the corrosive effects of sodium and vanadium at the suggested levels of the specification as an aid in setting safe operating conditions. Finally, a "dipstick" is described. This is a device that was installed in an operating gas turbine in an effort to determine when the level of corrosive attack was becoming excessive.

Gas Turbine Operational Experience

Ratings

The two gas turbines under consideration in this review are Westinghouse type W171G each with a rated output of 10.8 MW at a nominal turbine inlet temperature of 1375°F. Peak temperatures at the first stage stators may be 1450°F due to normal stratification of the gas stream at the discharge of the

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[3] The italic numbers in brackets refer to the list of references appended to this paper.

combustion system. The materials in the gas turbine blade path that are of particular interest with respect to corrosion are:

First Stage	stator vanes	Udimet 500
First Stage	rotating blades	INCO 700 (Turbine No. 1) Udimet 520 (Turbine No. 2)
Second Stage	stator vanes	Udimet 500
Second Stage	rotating blades	Inco 700
Remaining	stator vanes	AISI 310
Remaining	rotating blades	Inco X

Early Experiences

The initial operation of these gas turbine units was with a fuel known as Navy Special. This fuel required a water wash system to remove sodium, and a magnesium additive system for treatment of the high vanadium content in the fuel. During the first year of operation with this fuel, operational difficulties were encountered due to deposit buildup in the turbine blade path resulting from the additive used for the inhibition of corrosion from the vanadium attack. Since the operation of these gas turbines was essentially base load, which precluded frequent cleaning (or shutdown to spall off deposits) of the turbine blade path to restore power, it was decided to change to a locally available fuel, known as a "Low Vanadium Special," which would possibly require no treatment and yet have a similar price structure to the Navy Special Fuel. The purchase specification for this fuel was: sodium (less than 10 ppm), vanadium (less than 4 ppm), calcium (less than 10 ppm), and sulfur (less than 1.8 percent). Although some corrosion, even at the reduced turbine inlet temperature of 1375°F was anticipated, it was hoped that the damage would be minimal, thereby justifying the use of this fuel with its definite price advantage.

First Year of Operation on Low Vanadium Special Fuel (1965 to 1966)

After an overhaul the two turbines were placed on line with the Low Vanadium Special Fuel and one turbine was inspected after 2480 h operation, when it was reported that no major deterioration had taken place on the stators, that is, no visible corrosion. The first-stage rotating blades, however, showed a pitted surface on the pressure side and the entire blade path was reported to be coated with a gray-green deposit. A further visual inspection was made through a combustor basket after an additional 2700 h when it was observed that the first-stage diaphragm showed serious damage. The gas turbines were shut down for general overhaul after 6375 h operation.

Condition at Overhaul

The general condition of the turbines after this year's inspection disclosed that extensive corrosion had occurred on the first stator vanes of Udimet 500; the vane sections were ragged where metal had been eaten away to the hollow core.

The second-stage Udimet 500 stator vanes showed heavy surface corrosion similar to the first stage, but the general condition was less severe. Both the first and second row turbine blades showed heavy oxidation scale with evidence of surface corrosion. Figures 1 and 2 illustrate the general condition.

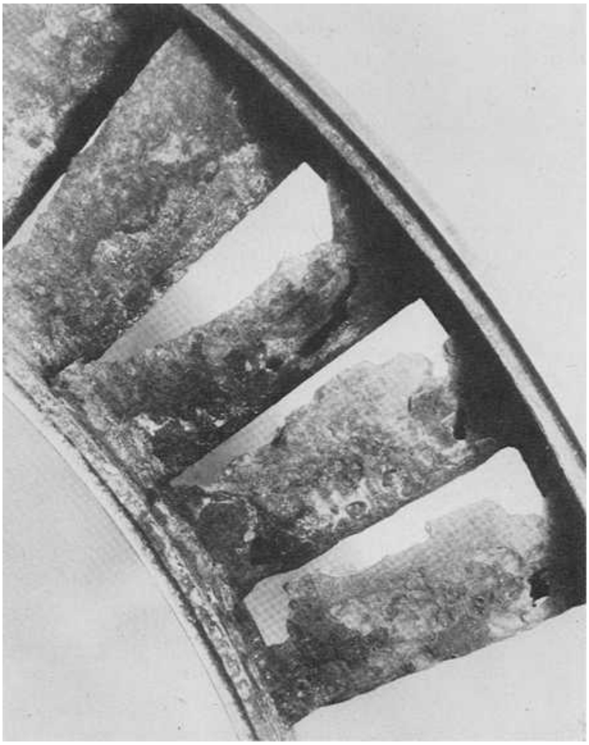


FIG. 1–*First-stage Udimet 500 stator, 1965 to 1966.*

Reviewing the operational history and analyses of the fuel as supplied by the refinery showed the average vanadium content to be 2.8 ppm with peaks to 3.8 ppm. The sodium content averaged 2 ppm except for 6 out of 22 shipments where this value ranged from 4 to 10 ppm. The average water content was 0.1 percent. The analyses carried out by the operator generally agreed with those from the refinery except for a few exceptions which are worthy of note.

Early in the year's operation it was discovered that an appreciable amount of sea water was present at the bottom of the fuel storage tanks. The tanks were drained and cleaned out at this time. Also, several of the operators' analyses showed vanadium concentrations of up to 11.5 ppm and these tended to coincide with the transportation of residual fuel, which had a vanadium levels of the order of 200 ppm, through the common pipeline from the tankers to the station.

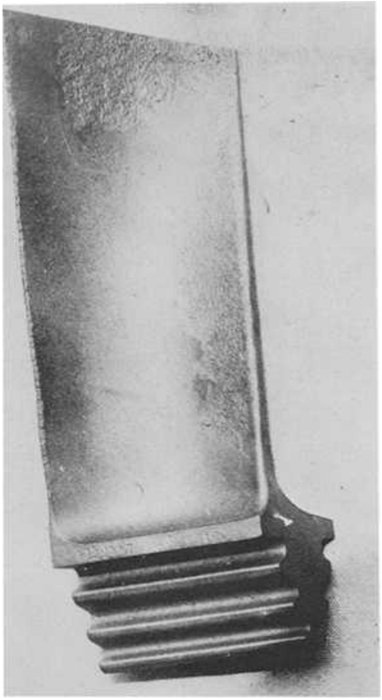


FIG. 2–*First stage Inco 700 rotating blade, 1965 to 1966.*

When the turbines were opened up for overhaul, deposits were collected from locations throughout the flow path and were submitted for detailed chemical analysis; and sample vanes and blades were obtained for metallographic analysis.

In general, these analyses showed that the turbine blade materials had suffered from a type of attack that has been typically described in the literature as hot corrosion or sulfidation. In particular, metallographic analysis of the first-stage stator of U-500 showed that a large proportion of the affected area next to the unaffected alloy contained gray islands of CrS_x that are typical with this type of corrosion. In addition, there was evidence of thick oxide layers. X-ray diffraction analysis of the deposits indicated some compounds, either singly or in combination, that are known to be corrosive. Table 1 lists the compounds that were found in the turbine blade path.

Of most interest in Table 1 is the compound, sodium vanadyl vanadate. This compound has been reported in the literature [*4,5*] as being extremely corrosive at temperature levels above 1200°F. In addition, vanadium pentoxide and sodium metavanadate are known to be corrosive. The corrosion mechanism of all these compounds is described as essentially an accelerated oxidation process. The presence of the magnesium and sodium compounds in the form of sulfates could alone account for the observed sulfidation corrosion.

TABLE 1–*X-ray diffraction analysis of deposits collected from locations throughout the flow path after 1965 to 1966 operation.*

Na_2SO_4	sodium sulfate
$Na_2Mg(SO_4)_2 \cdot 4H_2O$	sodium magnesium sulfate tetrahydrate
$MgSO_4$	magnesium sulfate
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	sodium vanadyl vanadate
$Na_2O \cdot V_2O_5$	sodium metavanadate
V_2O_5	vanadium pentoxide
$(VO)_2SO_4 \cdot 16H_2O$	vanadyl sulfate-hexadecahydrate
$V_{12}O_{26}(2V_2O_4 \cdot V_2O_5)$	vanadyl vanadate
NiO	nickel oxide

Thus, it appeared from these analyses that the corrosion was one of sulfidation due to the sulfate compounds that were present and that this sulfidation corrosion process had been enhanced by an accelerated oxidation process in presence of complex sodium vanadium vanadates.

Since a precise knowledge of the turbine environment was not known during this experience, it was recommended to the operator that certain precautions be taken for in the future use and that a carefully controlled operation be carried out to more fully evaluate the effects of operating with this particular fuel. These recommendations were:

1. Overhaul the turbines to the "as new" condition.
2. Reduce the allowable sodium in the fuel to 5 ppm.
3. Reactivate the water-washing plant to further reduce the sodium level to a minimum.
4. Pay particular attention to pipeline purging and drainage of storage tanks.
5. Institute regular fuel analysis.
6. Monitor the intake air.

Second Year of Operation (1966 to 1967)

Both machines returned to service after the overhaul and were shut down for inspection after completing an additional 5000 h. The results showed a major improvement over the previous year's operation, although the two machines did show slight differences.

Turbine No. 1

On the No. 1 machine, which was inspected first, the first-stage diaphragm showed some evidence of corrosion on the blades with the greatest concentration being on the pressure side of the blades at areas corresponding to the horizontal joint in the diaphragm. Only two leading edges showed any evidence of corrosion. There was virtually no visible evidence of corrosion on the remaining stationary or rotating blades.

Turbine No. 2

After No. 1 turbine was shut down, the No. 2 turbine was operated for an additional 450 h. The general condition was good by comparison to the previous year, but not quite as good as the No. 1 turbine. After vapor blasting, the pressure sides of the first-stage stator showed general corrosion as shown in Fig. 3. Interestingly, the suction side, as shown in Fig. 4, does not show any visible surface attack.

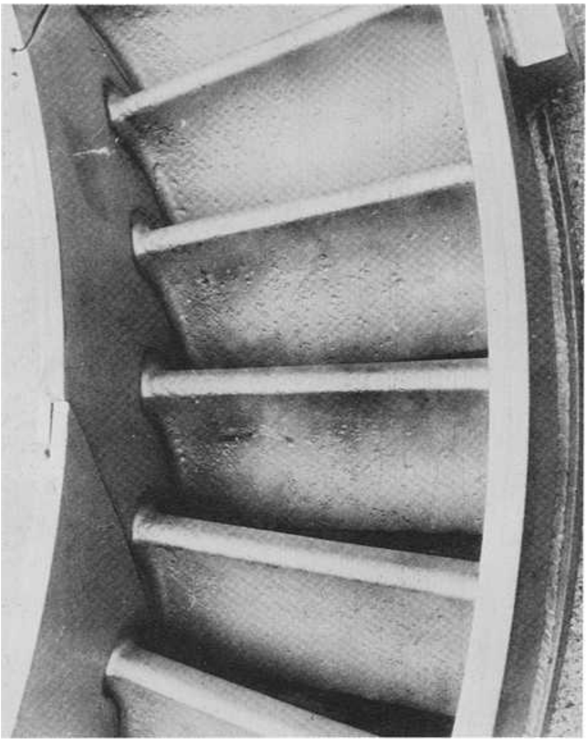


FIG. 3–*First-stage Udimet 500 stator pressure side, 1966 to 1967.*

The remainder of the turbine was in excellent condition with no visible corrosion as illustrated by Fig. 5 showing the condition after vapor blasting of the first-stage rotating blades.

This rate of corrosion experienced after the second year of operating appeared to be more in line with what might be expected with the level of corrosive contaminants found. Deposits were collected throughout the flow path, together with sample rotating blades for chemical and metallographic analysis, which is discussed later in the paper.

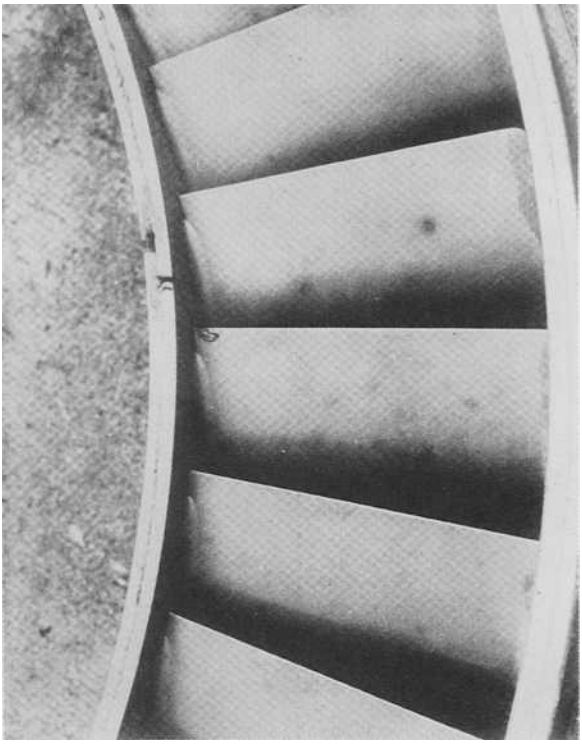


FIG. 4–*First-stage Udimet 500 stator, 1966 to 1967.*

Fuel, Deposit and Metallographic Analyses

Fuel Supply and Analysis

At the particular location in question the fuel is pumped from a tanker some five miles away, to a storage tank at the site. The fuel then passes through a water wash fuel treatment plant to lower the sodium concentration and then to a smaller storage tank from which it is delivered to the two gas turbines.

Weekly fuel samples were obtained by the operator who analyzed for water content, sodium, and vanadium in his own laboratory. In addition, monthly fuel samples were returned to Westinghouse for full chemical analysis. The correlation between the two sets of analyses were within 0.5 ppm for sodium and within 1 ppm for vanadium, which is considered satisfactory. The average concentration for sodium plus potassium, which is limited by the proposed ASTM specification, was 0.85 ppm. The average for vanadium was 1.97 ppm. A summary of the average physical and chemical properties of the fuel used for the 1966 to 1967 operation is given in Table 2, together with a comparison of the ASTM fuel specifications for No. 3-GT fuel.

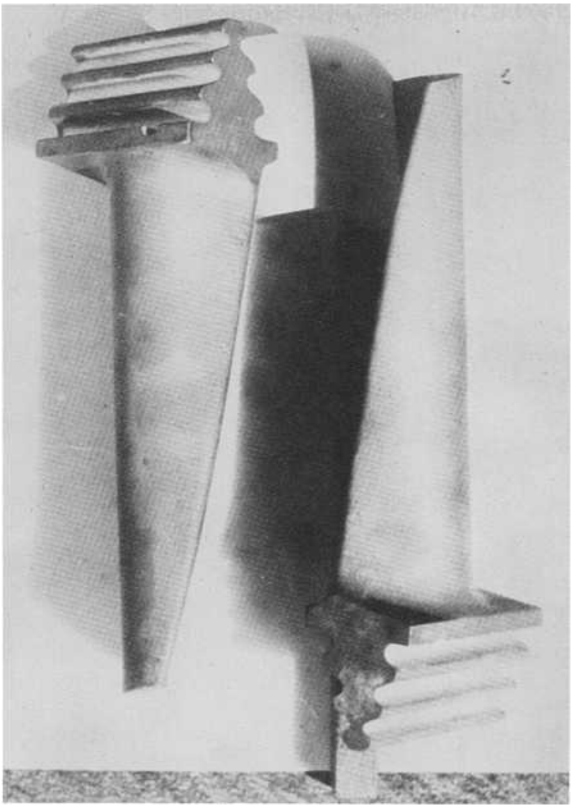


FIG. 5–*First-stage Udimet 520 rotating blade, 1966 to 1967.*

TABLE 2–*Average fuel properties for 1966 to 1967.*

	Gas Turbine Fuel	ASTM D 2880-71
Physical Properties		No. 3-GT
Specific gravity, deg API 60/60° F	27.4	. . .
Viscosity, SUV at 100° F	145	300 max.[a]
Water and sediment percent by volume	0.12	1.0
Ash percent by weight	0.001	0.03
Chemical Properties		
Sodium plus potassium, ppm	0.85	5
Vanadium, ppm	1.97	2
Calcium, ppm	0.38	10
Lead, ppm	0.02	5
Magnesium, ppm	0.26	. . .
Sulfur, percent by weight	1.2	0.7

[a] Furol at 122° F.

Because these turbines were located relatively near the sea and also because of the proximity to the gas turbine intake of a chemical treatment plant using sodium compounds, the intake air was also monitored during this year's operation. However, no significant ingestion of harmful chemical elements was noted—the sodium level was less than 0.02 ppm equivalent in the fuel.

Deposit and Metallographic Analysis

From the summary of fuel oil and inlet air analyses that were determined during the course of this year's operation, it appears reasonable that these conditions represent the average environment under which the observed corrosion occurred. It is interesting to compare these results with those of previous years, in light of deposits and metallographic analyses.

First, the deposit level was considerably less than had been observed previously. An X-ray diffraction analysis of these deposits is shown in Table 3.

TABLE 3—*X-ray diffraction analysis of deposits obtained after 1966 to 1967 operation.*

$NiFe_2O_4$	nickel iron oxide
$3Nio \cdot V_2O_5$	nickel orthovanadate
Fe_2O_3	iron oxide
$Ni(VO_3)_2$	nickel vanadate
NiO	nickel oxide
V_2O_5	vanadium pentoxide
V_2O_4	vanadium tetroxide
$Na_2Mg(SO_4)_2 \cdot 4H_2O$	sodium magnesium sulfate tetrahydrate
$CoSO_4 \cdot 6H_2O$	cobalt sulfate
$3CoV_2O_5$	cobalt orthovanadate

Aside from the fact that more corrosion products were distinguished in the analyses as compared to those listed in Table 1, the conspicuous absence of any of the complex sodium vanadium vanadates is noteworthy. As stated before, it is believed that these compounds can accelerate the corrosion process to catastrophic levels. Any combination of circumstances which will reduce the propensity for the formation of the sodium vanadate compounds should reduce the rate of corrosion attack. This is believed to be the case in the observed difference in corrosion rates. However, it can be seen that vanadium is still observed as the oxide and as a participant in the corrosion products. Thus, at an average level of 2 ppm of vanadium, it would appear that vanadium (in the form of V_2O_5) can still be a factor for inducing corrosion attack.

Additional Operation

The turbines were examined visually again in 1968 after a total operating time of approximately 12 000 h. No further corrosion was noted at this inspection, nor at any time since then.

Despite the small amount of observed corrosion, the diaphragms were returned to service after this inspection. The type of corrosive attack seen on the first-stage stators could not be positively identified. However, it is probable any sulfidation type of attack would have been identified in addition to corrosion from a combination of vanadium type products. This inference can be drawn first from microprobe work on a first row rotating blade that was returned for analysis, and secondly from the fact that sodium magnesium sulfate was detected in the deposits although at a much reduced level from that observed before. While the rotating blades did not show any signs of what might be called visible corrosion, a closer metallographic analysis with the microprobe did show some small sulfide inclusions in the affected alloy zone as well as the presence of vanadium in the oxide scale.

The presence of the compound sodium magnesium sulfate $Na_2Mg(SO_4)_2 \cdot 4H_2O$ is significant since it is believed that this compound is important in situations where sulfidation type corrosion alone is operative. This compound has been identified when equal mole mixtures of Na_2SO_4 and $MgSO_4$ have been heated to their melting point, subsequently cooled, and analyses made of the mixture by X-ray diffraction. Importantly, the 50-mole percent mixture has been found to be at a eutectic point for this system, with a melting point in the range of 1250°F. Thus, there are alkali metal compounds with fusion temperatures in the region of interest for gas turbine operation. In fact, coatings with 50/50 mixtures of sodium and magnesium compounds have been used to evaluate sulfidation resistance of gas turbine alloys [*6*].

The evidence developed from this investigation indicates that the corrosion observed at this inspection was due to sulfidation in combination with an oxidation process that was enhanced by the presence of vanadium products, specifically V_2O_5. The question as to whether the observed rate of corrosion would occur independently in the presence of either alkali compounds or the vanadium compounds (but not both) at this level of contamination was not known at the time. However, by carefully controlling the alkali metals and keeping a close watch on any excursions in the vanadium content, a significant improvement in corrosion performance has been obtained. This is probably at an acceptable level considering the large price differential of the fuel to No. 2 distillate fuel.

Laboratory Tests

In order to obtain corrosion data for superalloys under closely controlled laboratory conditions. Westinghouse maintains gas turbine test facilities in the Combustion Laboratory at the Research Center. Most of the tests are carried out in pressurized test passages (also called gas turbine simulators) which closely approximate operating conditions of the actual industrial gas turbines. Details of the test apparatus can be found elsewhere [*2*]. Briefly, the Combustion Laboratory is equipped with four test stands with pressurized test passages for corrosion and combustion testing. Air is supplied by a bank of 300-hp rotary compressors, each capable of 2 lb of air per second at pressures up to 7 atm. The compressed air passes through indirectly fired air preheaters giving temperatures up to 1000°F to simulate inlet air temperatures characteristic of gas turbine combustors. As shown schematically in Fig. 6, the preheated compressed air is fed into a 6-in.-diameter film cooled combustor which can be operated at a 1000°F inlet and 2000°F exit temperature. Fuel is injected through a bayonet-mounted nozzle in the upstream end and ignited by a torch. When liquid fuels are burned, both air and mechanical atomization are provided. At the combustor exit, thermocouple arrays for measuring stream temperature profiles and sampling ports for gas analysis may be seen. Beyond the sampling port a transition section reduces the flow area to a 2 by 3 3/4 in. rectangular section and increases the velocity to that characteristic of gas turbine inlets, that is, 500 ft/s. It is at this location that the specimens are exposed to the gas stream containing corrosive combustion products. A test section holds a set of eight 1/4 in. diameter pins (Fig. 7*a*), four air foil shaped paddles (Fig. 7*b*), or two internally cooled cylindrical sleeves 1 in. in diameter and 2 in. long (Fig. 7*c*). The cylinder has 12 holes drilled lengthwise to various depths to accomodate thermocouples which measure the specimen temperature. Beyond the test section, a valve located in the passage maintains typical turbine pressure, and finally the combustion products enter a water spray section for cooling and thence to a muffler.

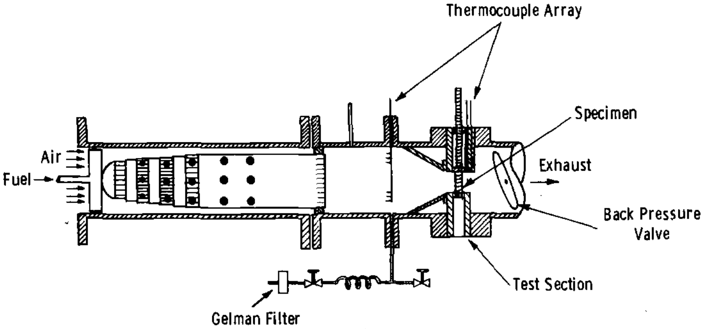
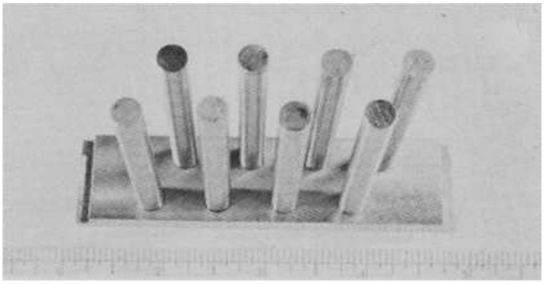
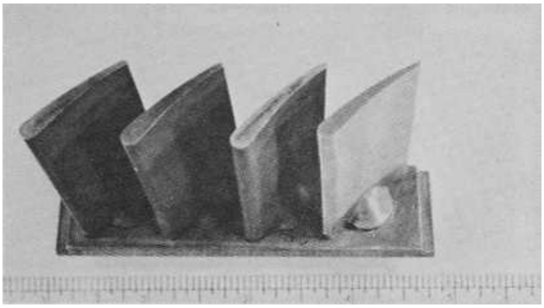


FIG. 6—*High pressure corrosion test passage.*

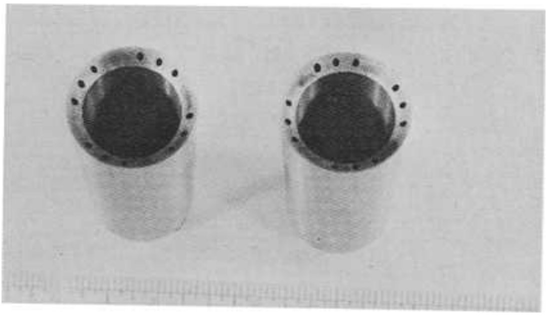
A number of tests have been made with several commercial alloys currently used in gas turbines operated on fuels with various contaminant levels. Tests were made with diesel fuel (Gulf Dieselect) containing various concentrations of vanadium (0 to 10 ppm) at a constant sodium level, and various concentrations of sodium (0 to 5 ppm) at a constant vanadium level. Sulfur in the form of ditertiary butyl disulfide was added to bring the sulfur level up to one weight percent. Vanadium and sodium were added to the fuel in the forms of oil soluble naphthenates and carboxylates. Most of the tests were of 150 to 300 h duration at temperatures of 1400 to 1500°F simulating first stage vane and blade metal temperatures of present and future gas turbines.



(a) ¼" Diameter Pins



(b) Air Foil Shaped Paddles



(c) Cooled Cylyinders with Eluxed
Holes for Thermocouples

FIG. 7–*Several specimen geometries used for hot corrosion tests.*

In most cases, the degree of attack is determined by a loss of weight (following cathodic descaling by immersing in molten sodium hydroxide and sodium carbonate with an application of electric current), or by metallographic examination when the attack is nonuniform or exhibiting deep intergranular penetration.

Test Results and Discussion

Corrosion Due to Presence of Vanadium

Corrosive effects of small amounts of vanadium (2 to 10 ppm present in the fuel) on turbine alloys were investigated in the pressurized passage at 1500°F. Two different vanadium concentrations of 2 and 10 ppm in the fuel were used. Results of these tests are shown graphically in Fig. 8. Descaled weight loss data are plotted against concentrations of vanadium in the fuel. The concentration of vanadium has an almost exponential effect on the corrosion rate of both X-45 and U-500. On the other hand, an increased concentration of vanadium above 2 ppm has a minor effect on other alloys such as In713 and In738X.

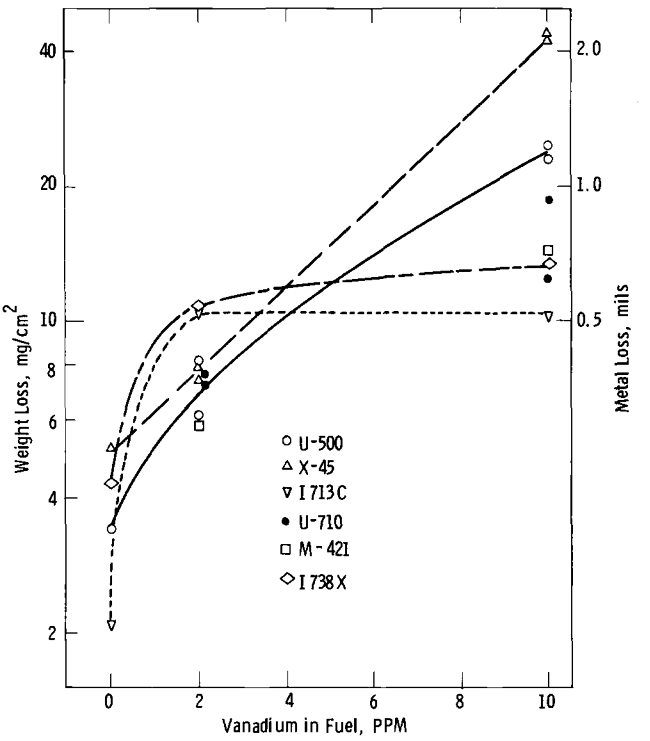


FIG. 8—*Effect of vanadium (with no sodium) on various alloys tested in the pressurized passage at 1500°F metal temperature and 3 atm pressure for 150 h.*

Metallographic examination showed that there was minor subscale sulfidation on the trailing edge of the 2 ppm specimen, but no evidence of it on the 10 ppm vanadium test specimen. Electron microprobe analysis of deposits revealed the presence of trace sodium, but no sulfur, indicating complete absence of sodium sulfate. Although no sodium was added to the fuel, a small amount of sodium (0.1 to 0.2 ppm) was present in the fuel itself. However, the absence of sodium sulfate indicates that sodium in such small quantities probably will not cause a large scale sulfidation attack on superalloys.

Figure 9 is a plot of weight loss versus test duration for a 2 ppm vanadium and no sodium[4] condition. This condition simulates an actual operating gas turbine when the fuel is water washed to eliminate sodium. For X-45 the corrosion rate was constant, showing no sign of decreasing. Data scatter for the U-500 test results is large, but it also indicates a constant rate of corrosion. An extrapolation of the present rate to an average life span of a turbine blade

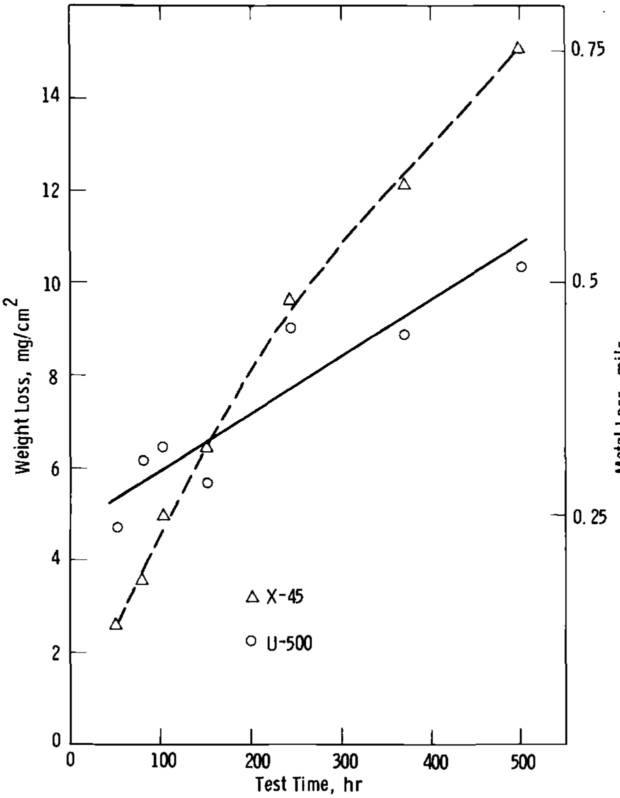


FIG. 9—*Corrosion rates of X-45 and U-500 tested in the passage with 2 ppm vanadium and no sodium at 1500°F and 3 atm pressure.*

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[4] No sodium added to the fuel. Dieselect contains 0.1 to 0.2 ppm background sodium.

indicates that no serious corrosion problem will be encountered at 1500°F if the concentration of vanadium is limited to 2 ppm, and sodium concentration is maintained at fraction of a ppm. This finding agrees with the Panama experiences reported earlier.

Sodium (Sea Salt) and Vanadium Combination

Corrosion due to the presence of both sodium (sea salt) and vanadium is much more severe than due to either sodium or vanadium alone. Figure 10 summarizes the results of tests made in the pressurized passage at 1500°F at several levels of sodium concentration keeping the vanadium at a constant level of 2 ppm. Weight loss data indicate that combined effects of 5 ppm sodium and 2 ppm vanadium is three times that of 5 ppm sodium alone and five times that of 2 ppm vanadium alone. Metallographic examination revealed a significant subscale sulfidation present in both nickel-base and cobalt-base superalloys. Penetration measurements at various sections of the specimens tested at 5 ppm sodium and 2 ppm vanadium show extensive attack on In713C, and intolerable local penetrations of 10 mils on U-500 and 6 mils on X-45 in 150 h of test time.

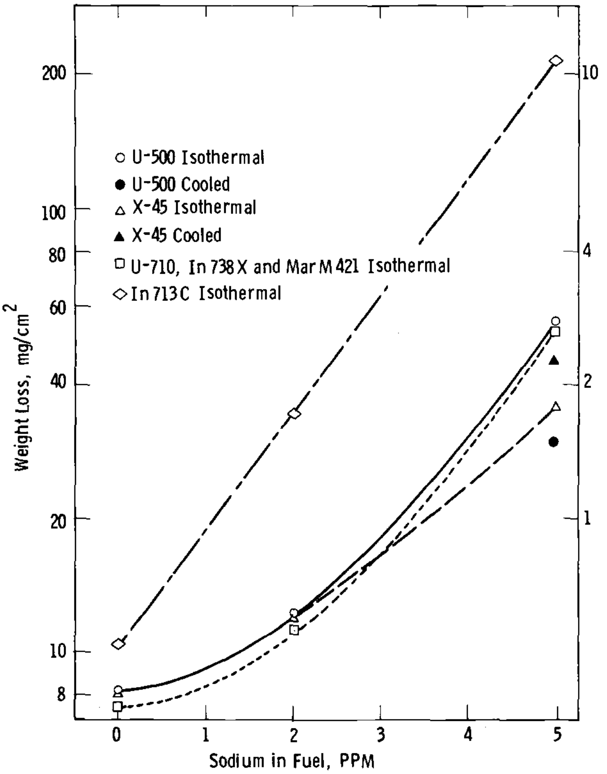

FIG. 10–*Effect of sodium (with 2 ppm vanadium) on various alloys tested in the pressurized passage at 1500°F metal temperature and 3 atm pressure for 150 h.*

Unless the effect of sodium is eliminated from the fuel by a technique such as water-washing or corrosion reducing additives, No. 3-GT fuel containing 2 ppm vanadium and 5 ppm sodium will lead to frequent blade replacement.

Comparison Between Laboratory Results and Field Tests

In order to obtain a meaningful comparison between laboratory test results and field experience, it is necessary to obtain quantitative corrosion data from the actual gas turbine. However, quantitative corrosion measurements on the actual turbine blade are very difficult to make. In order to overcome this difficulty, a device called a corrosion "dipstick" was installed in the Panama machines to monitor the progress of corrosion without disruption of the turbine operation. As shown in Fig. 11, the corrosion "dipstick" used an ordinary supervisory thermocouple located at the turbine inlet position to carry accurately sized rings representative of turbine hot part materials. The dipstick with its metal samples then is easily removed at any time to provide long term corrosion data, an impossible task in laboratory tests. However, the dipsticks have shortcomings in that the metal samples are necessarily small so that each sample along the thermocouple is subject to temperature variations in the combustor outlet gas stream, resulting in wide scattering of data. In addition, the dipstick is located in the transition section so that the exact aerodynamic condition at the turbine blade is not simulated. Nevertheless, the dipsticks were exposed for 3000 and 7300 h when the turbine was operating with fuel containing 2 ppm vanadium and 0.8 ppm sodium. At the same time a 300 h turbine simulator test was made with temperature and fuel composition duplicating Panama machine conditions. The laboratory test specimens and the

FIG. 11–*Corrosion dipstick.*

dipstick specimens were examined metallographically, and the results are shown in Fig. 12 for alloys U-500 and In700. Metal regression rates obtained from the dipstick specimens are less than those from the laboratory test specimens indicating that direct one to one relationships are not achieved between the two tests. However, corrosion rates in both cases are very small confirming qualitative observation of corrosion rates on the Panama machines operated with fuel containing low sodium and vanadium levels.

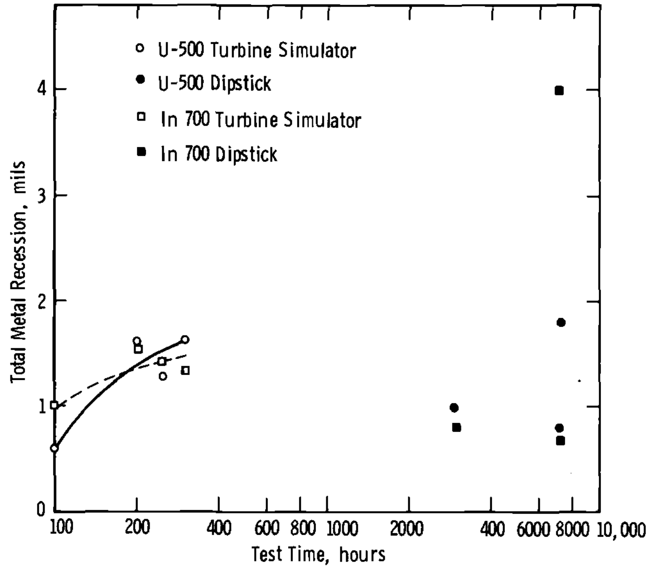

FIG. 12–*Turbine simulator and dipstick test data with fuel containing 2 ppm vanadium and 0.8 ppm sodium at 1370°F.*

Summary and Conclusions

ASTM D 2880-71 defines four grades of liquid fuel for gas turbines from No. 1-GT to No. 4-GT. Of current interest is the grade No. 3-GT which has economic advantages over the more highly refined grades No. 1-GT and No. 2-GT if it can be used without causing damage to the hot turbine components. No. 3-GT presently permits up to 5 ppm sodium and 2 ppm vanadium.

Westinghouse gas turbines have operated for several years in Panama with fuels approaching the No. 3-GT specification. During the first year of operation the vanadium content averaged 2.8 ppm, but the sodium level occasionally reached 10 ppm. Extensive corrosion resulted. During the second year the fuel quality was more carefully controlled. Vanadium averaged less than 2 ppm and alkali metals less than 1 ppm. A slight amount of corrosion, well within acceptable limits, resulted. The machines have continued to operate with no further problem.

Laboratory tests under simualated gas turbine conditions were made as an aid in setting safe turbine operating limits. Vanadium levels up to 10 ppm and sodium levels to 5 ppm were investigated. It was concluded that no serious corrosion should occur at metal temperatures of 1500°F if the vanadium concentration is limited to 2 ppm and the sodium concentration is reduced to less than 1 ppm. However, use of a fuel meeting the present specification for No. 3-GT, that is, 5 ppm sodium and 2 ppm vanadium, without some sort of fuel treatment or sodium removal or both, will lead to extensive attack and frequent blade and diaphragm replacement. These conclusions are in agreement with the Panama field experience.

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H. vonE. Doering[1]

Effect of a Heavy Distillate Fuel on U-700

REFERENCE: Doering, H. vonE., "**Effect of a Heavy Distillate Fuel on** U-**700**," *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531*, American Society for Testing and Materials, 1973, pp. 22-27.

ABSTRACT: Uncoated R77 (U-700) first stage buckets have seen 8800 h of satisfactory service in a General Electric model MS-5000 gas turbine at Progil burning a heavy distillate fuel. Although this alloy is quite sensitive to hot corrosion by sodium sulphate, these buckets emerged in excellent condition as shown by metallographic examination. Levels of sodium, vanadium, etc., in the fuel were reported to be less than 0.1 ppm for most of the shipments. It appears that thoughtful handling can maintain distillate fuels clean enough to permit satisfactory operation.

KEY WORDS: fuels, gas turbines, corrosion, fuel contamination

In August of 1969 the first of eight General Electric Model MS-5000 gas turbines went on stream at PROGIL, a chlorine producer at Pont DeClair near Grenoble, France, to generate electricity and supply waste heat for processing and steam. These units burn a heavy, waxy vacuum distillate fuel, which contains 1.8 percent sulfur. Although the first stage bucket alloy is U-700 and is thus sensitive to hot corrosion by sodium, potassium, lead, vanadium, etc., no deterioration has been observed in over 20 000 h of operation as of this writing.

Fuel and Fuel Handling

The fuel handling has been reported[2] and will only briefly be described here. Fuel from the refinery is shipped to the gas turbine in insulated railroad tank cars which are owned by the operator and are dedicated only to the service of supplying fuel. From a main storage tank the fuel is pumped to a day tank in which the fuel is heated to 175°F to maintain a viscosity of 12 centistokes suitable for air atomization in the turbine.

Careful handling and sampling of the fuel is maintained at all times. Table 1 summarizes the results of chemical analyses of fuels delivered from July 1969

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[1] Manager, Fuels and Corrosion Unit, Technical Resources Operation, General Electric Co., Schenectady, N.Y. 12345.

[2] Tintori, J., Schiefer, R. B., and Taylor, J. R., "A Fuel for Total Energy," ASME paper 71-GT-55, American Society for Mechanical Engineers.

TABLE 1–*Chemical analysis of fuels shipped between July 1969 and March 1970.*

Date	Number of Samples Reported	V	Na	Pb	K	Ca
July 8, 1969	1	0.34	<0.1	<0.1	<0.1	0.5
23	1	0.4	<0.1	<0.1	0.2	<0.1
Aug. 6	1	0.16	0.1	0.12	0.2	0.1
13	1	0.16	0.1	0.4	0.1	0.1
20	1	0.1	0.1	<0.1	<0.1	<0.1
Sept. 11	1	<0.1	<0.1	<0.1	<0.1	<0.1
23	1	<0.1	0.3	0.3	<0.1	<0.1
Oct. 2	1	<0.1	<0.1	0.2	<0.1	<0.1
9	1	<0.1	<0.1	<0.1	<0.1	<0.1
24	1	<0.1	<0.1	<0.2	<0.1	<0.1
30	1	<0.1	<0.1	0.1	<0.1	<0.1
Nov. 4	1	<0.1	<0.1	0.2	<0.1	<0.1
19	1	<0.1	<0.1	<0.2	0.1	<0.1
26	1	0.1	<0.1	0.1	<0.1	<0.1
29	1	<0.2	<0.1	0.3	<0.1	<0.1
Dec. 3	1	<0.1	<0.1	0.5	<0.1	<0.1
10,24	2	<0.1	<0.1	<0.5	<0.1	<0.1
18	1	0.1	<0.1	<0.1	<0.1	<0.1
27	1	<0.1	<0.1	<0.1	<0.1	<0.2
31	1	<0.1	<0.1	<0.1	<0.2	<0.2
Jan. 1, 1970	1	<0.1	<0.1	<0.1	<0.1	<0.1
3	1	0.1	<0.1	<0.1	<0.1	<0.1
7	1	<2.0	<2.0	<5.0	<3.0	<10.0
10	1	<0.1	<0.1	0.3	<0.1	<0.1
14, 21	2	<0.1	<0.1	<0.1	<0.1	<0.1
17	1	<0.1	<0.1	<0.25	<0.1	<0.1
28	1	<0.1	<0.1	. . .	<0.1	<0.1
Feb. 4-25	10	<0.1	<0.1	<0.1	<0.1	<0.1
Mar. 11-25	9	<0.1	<0.1	<0.1	<0.1	<0.1

through March 1970. Of the 239 entries in that table, 209 values are reported as "less than" a given quantity and 195 of the entries show a level of less than 0.1 ppm for each of the five elements of interest sodium, potassium, vanadium, lead, and calcium. Without exact values it is therefore difficult to extract from these data a precise level of trace metal contamination that can be tolerated by U-700.

U-700 First Stage Buckets

Two first stage buckets-were removed after 8800 hours of operation for metallurgical examination. The bucket from this machine is pictured in Fig. 1, and an example of the microstructure at the surface through the airfoil is shown

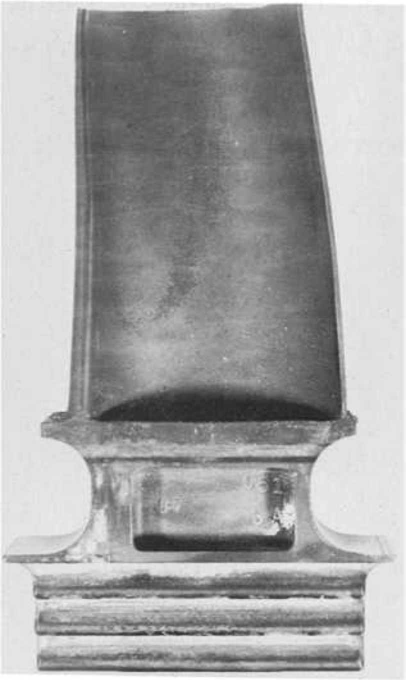
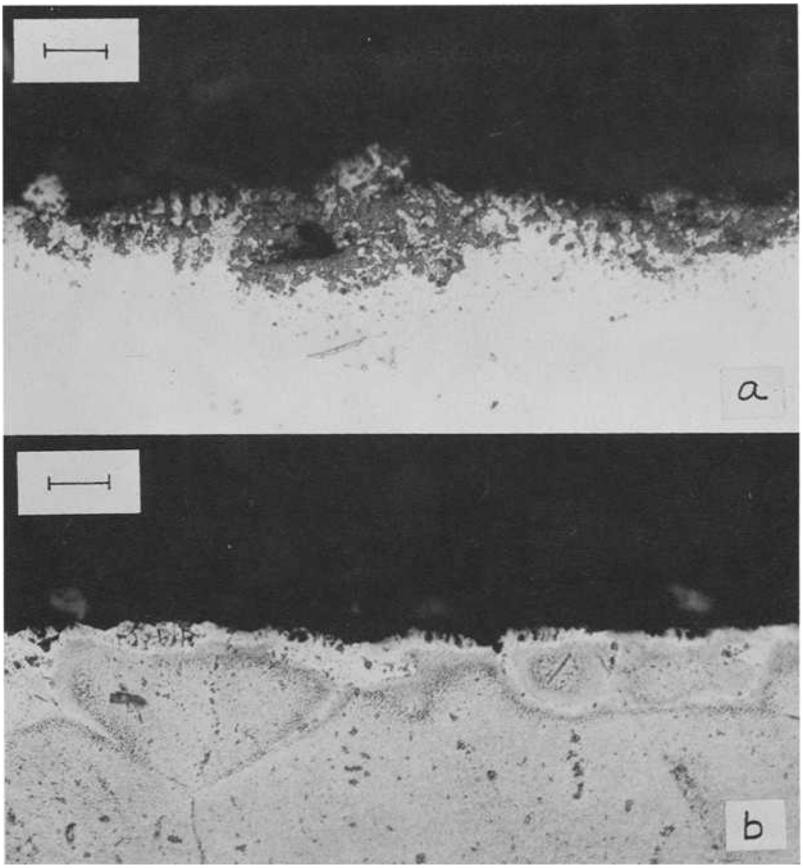


FIG. 1–*U-700 first stage turbine bucket after 8800 h service.*

in Fig. 2*a* and 2*b*. It should be noted that there is no gross hot corrosion distress on this bucket; however, some minute sulfides to a maximum depth of 0.004 in. are noticeable in Fig. 2b. The sulfides are very small and do not intersect the surface as is often seen in more severe cases of hot corrosion. These sulfides may in part be due to the 1.8 percent sulfur which is higher than in most distillate fuels. A chromium depleted zone (white) can be noted in Fig. 2*b* where in the strengthening phase γ' has returned to solution in the matrix. This phenomenon is usually observed with hot corrosion and to a lesser extent with oxidation alone. It should be noted that the thickness of this depleted zone does not exceed 1 mil in areas where sulfides are present indicating that the sulfides in this case are not indicative of severe or catastrophic hot corrosion.

Deposits from the bucket surface were examined and are listed in Table 2. Very little of any of the troublesome metals sodium, vanadium, etc., are found. Nickel oxide (NiO) is expected as a product of oxidation of the bucket. The presence of copper is unaccounted for, and the silicon is undoubtedly a constituent of ingested dust generated by nearby earth moving and construction projects.

U-700 is a low (14 percent) chromium alloy and more sensitive to hot corrosion attack compared to alloys containing 15 to 19 percent chromium. However, its survival under these circumstances speaks for the efforts to maintain cleanliness of fuels with appropriate handling.



(a) Unetched showing minute sulfides (grey). (Scale mark indicates 0.001 in.).

(b) Etched showing chromium depleted zone (white) and minute sulfides (grey). (Scale mark indicates 0.001 in.).

FIG. 2–*Micrographs of U-700 first stage turbine bucket after 8800 h service.*

Air Quality

Although fuel is often blamed for the sole source of contaminants that cause hot corrosion, contaminants in the form of airborne particulates cannot be overlooked.

Samples of deposits taken from the intake house louvres were spectrographically examined and reported in Table 3.

The major and minor quantities of silicon, iron, aluminum, and calcium indicate the presence of soil. Na was reported only as a trace and potassium as a minor component. $PO_4^{\equiv}$ and $CO_3^{=}$ ions were found. The $PO_4^{\equiv}$ ions are possibly contributed by steam from a reported leak near the air inlet. To the author's knowledge, no sampling of the air to assess the concentration of particulates has

TABLE 2–*Deposits from bucket qualitative spectrographic.*

Concentration	From Base of Airfoil	From Recession Between Airfoil and Dovetail
Major	Ni, Co	Si
Minor	Cu, Ca	Ca, Co, Ni
Trace plus	V	Cu
Trace	Si, Mn, Mg, Pb Cr, Fe, Al, Mo Zn, Na, Ba, Ti	Mn, Mg, Pb, Cr Fe, Al, Ag, Na Ba, Ti
Faint trace	Sn, Ag	Sn, Mo, V, Zn
	X-Ray Diffraction and Ion Spot Tests	
	NiO	γ $CaSiO_3$, NiO $PO_4^{\equiv}$, $S^{=}$, $SO_4^{=}$

TABLE 3–*Deposits from inlet louvres qualitative spectrographic.*

Concentration	Elements
Major	Si, Fe, Ca
Minor	Mg, Al, K[a]
Trace Plus	Mn, Ti, Ba
Trace	Na, Pb, Sn, Ni Mo, V, Cu, Zn
Faint Trace	Co
	Positive Ion Spot Tests
	$PO_4^{\equiv}$, $S^{=}$, $SO_4^{=}$

[a] K was wet chemically analyzed since it is insensitive to emission spectrographic method.

been made. However, the dust loadings can only be assessed as minor since the entire machine has been reported to be quite clean.

Conclusion

A hot corrosion susceptible first bucket alloy, U-700, has successfully operated in a gas turbine burning a heavy, waxy distillate for nearly 9 000 hours without any distress. Although the fuel contained 1.8 percent sulfur and might have contained trace amounts of the corrosive elements sodium, vanadium, and potassium, these were held to an acceptable minimum by adequate attention to handling practice and frequent chemical analysis. The history of this case makes clear that proper fuel handling practices and frequent chemical analysis for trace metals can ensure long hot section component life in gas turbines.

M. F. Winkler[1]

Management of the Gas Turbine Fuel Systems

REFERENCE: Winkler, M. F., "**Management of the Gas Turbine Fuel Systems,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 28–44.

ABSTRACT: This paper identifies fuel handling problems and the complete fuel system. The greatest single factor contributing to distress of the high temperature turbine is shown to be fuel contamination. The management of gas turbine fuel systems is described to be based on maximum equipment utilization and on minimum maintenance downtime and minimum maintenance costs.

KEY WORDS: fuels, gas turbines, quality control, contamination, trace elements, microorganisms

The high performance gas turbine has achieved wide acceptance in many applications in recent years despite the use of fuels in the middle distillate range. The gas turbine has proved itself to be a competitive prime mover as dependable as the more conventional steam turbine and reciprocating engines. No small part of this acceptance can be attributed to the highly successful application of gas turbines in military and commercial aircraft and to the millions of hours logged as an aircraft powerplant. Distillate fuels with their low metals and low ash characteristics, match the requirements of high temperature, high performance gas turbines. The strong trend toward minimizing atmospheric pollutants and minimizing maintenance downtime has also contributed to the increased use of distillate fuels and correctly managed fuel handling systems. As technology advances, as gas turbines fire at higher temperatures, and as the atmospheric air quality controls tighten, the use of lower grades of fuels such as residuals will all but disappear!

Distillate fuels are well suited to gas turbine operation for industrial and marine service. The industrial gas turbine engine has operated successfully at high termperatures and high efficiencies on a wide variety of gaseous and liquid fuels, including naphtha, gasoline, kerosine, burner and diesel fuels, and heavy distillate fuels. Fuel contamination is the greatest single threat to the long life of the gas turbine. Therefore, the dependable operation of the gas turbine engine can be supported by the management of the complete fuel handling system. The problem areas and the techniques required for successful fuel system operation are discussed.

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Industrial fuel specifications are intended to provide guidance to users and to indicate fuels for specific climates and anticipated duty cycles. Specific fuel properties causing reduced gas turbine life, increased smoke levels, or decreased reliability must be controlled. Many of the flight fuel requirements are not needed for the industrial gas turbines; however, other properties must be specified.

Background

More recently, however, the aircraft derivative gas turbine has been used successfully in many industrial and marine applications. During the past eleven years, Turbo Power and Marine Systems (TP&MS) has installed over 70 engines for gas pipeline pumping, over 425 engines for electrical peaking service, over 18 engines for miscellaneous industrial services, and 27 engines for commercial and military marine services. Figure 1 shows the basic FT4 gas turbine in cross section. The total number now in service exceeds 550 units and covers the power range from 4000 to 30 000 shp.

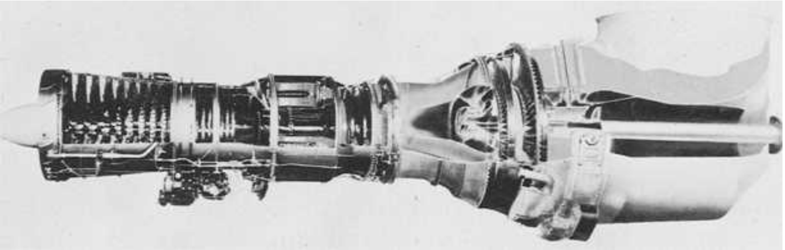

FIG. 1–*Cross section of basic FT4 gas turbine.*

The high performance gas turbine has achieved wide acceptance in many applications in recent years, using fuels in the middle distillate range. Management of the middle distillate fuel system is necessary for dependable operation and long life. Industrial gas turbine fuel specifications are designed to indicate suitable fuels for specific climates and anticipated duty cycles. Through these specifications, the fuel properties causing reduced gas turbine life, increased smoke levels or decreased reliability, are controlled. The ASTM gas turbine fuel classification is shown as Table 1. Many of the flight fuel requirements are not needed for industrial gas turbines; however, there are other properties that must be specified. The strong trend toward regulations minimizing atmospheric pollutants and toward minimizing maintenance downtime has also contributed to the concept of fuel system management. Since high-output gas turbine engines used large volumes of middle distillate fuels and fuel cleanup was required, a major program was indicated.

TABLE 1–*ASTM gas turbine fuel classification.*

Designation	Description	Fuel Types	Approximate Boiling Range or Viscosity	
No. 1-GT	volatile distillate of 550°F max 90% distillation temperature	light naphtha	90-300°F	
		JP-4	150-550°F	
		JP-5	320-550°F	
		kerosine	300-600°F	
No. 2-GT	medium volatility distillate of low ash with 540°F min and 675°F max 90% distillation temperature	marine diesel (MIL-F-16884F) No. 2 diesel No. 2 fuel oil	400-700°F	
No. 3-GT	low volatility, low ash fuel which may contain some residual components	navy distillate fuel (MIL-F-24397)	viscosity range of 85 to 225 SUS @ 122°F	←heavy distillates
No. 4-GT	low volatility fuel containing residual components and having higher vanadium content than No. 3-GT			

There is a significant difference between aircraft gas turbine fuels and industrial gas turbine fuels. The aircraft gas turbine fuels have many stringent requirements that are associated mostly with high altitude flying rather than with the requirements of the gas turbine themselves. Low temperature freeze points, high thermal stability, sufficient fluidity and volatility for altitude relight, extreme cleanliness, and freedom from water are all flight fuel requirements. The aircraft derivative industrial and marine gas turbine powerplant, on the other hand, is quite unique in its relative insensitivity to a broad range of fuel properties when applied to nonflight duty. The industrial gas turbine fuels do not have many restrictive requirements; however, control of metallic contaminants is considered necessary. The types of fuels used in industrial gas turbines (Fig. 2 shows the industrial FT4 gas turbine) range from gaseous fuels to naphtha, to unleaded gasoline, to kerosine, to No. 2 fuel oils, and on to heavy distillate fuels. The gas turbine in the marine environment normally would use either Navy diesel fuel or the new Navy distillate fuel.

Gaseous fuel has long been recognized as the ideal industrial gas turbine fuel. The lack of the need for vaporization and the low metallic contaminant levels generally found in these fuels are the major reasons for the long, uninterrupted, industrial gas turbine life experienced when gaseous fuel is used. Industrial gas turbines operate mostly on distillate fuels. This is true because distillate fuels are more widely available and easily handled. The naphtha fuels, with their high volatility and low contaminant levels, are superior liquid fuels. The industrial kerosine fuels, while similar in basic structure to aircraft kerosine fuels, have far less restrictive controls placed upon them and are generally more widely available at a lower cost. The No. 2 fuels used in industrial gas turbines cover a wide range of physical properties and contaminant levels. These fuels can range from high quality, high speed diesel fuel to the low quality, highly contaminated burner fuels.

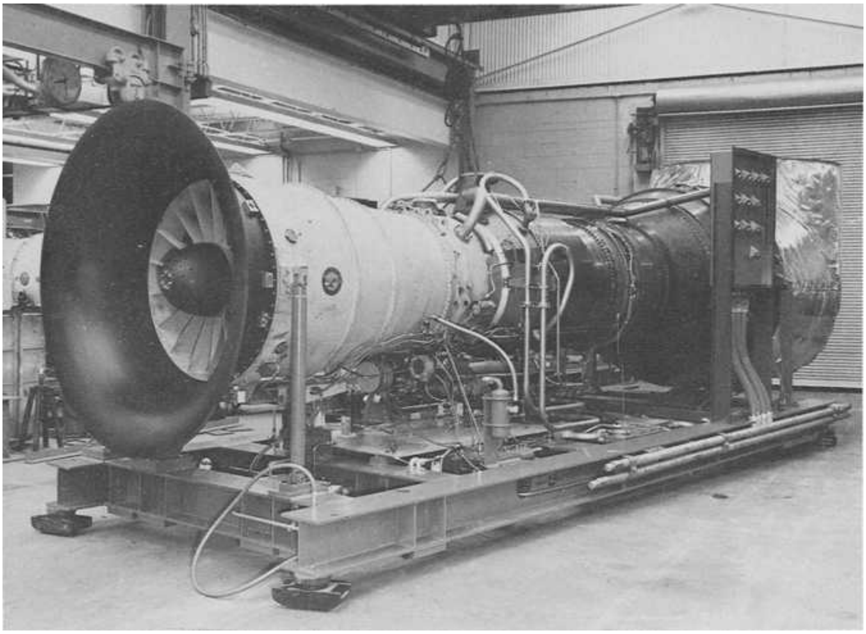

FIG. 2—*Industrial FT4 gas turbine.*

The contamination of gas turbine fuel is usually introduced during transportation by pipeline, barge or tanker, or by truck transport. The contamination in a pipeline usually takes the form of water, scale, previous fuel product, or previous additive packages. The contamination introduced by barges and tankers is predominantly salt water (ballast) and sediment, with minor amounts of previous products and chemical cleaning agents. Truck transport can add water, sediment, and previous product to the otherwise clean fuel.

The contamination introduced into the fuel via transport requires more cleanup equipment if the particulate and liquid contamination coexist with the fuel for long storage periods. These contaminants may catalyze the fuel degradation process further, thus increasing the cleanup load. The heavy distillate fuels selected for use in the industrial environment are fuels that have much lower volatility than the light and middle distillates, but they do have similar low-ash and metal contaminant levels so necessary to high availability, low maintenance costs, and long life. Navy diesel fuel is the marine equivalent of a good grade of No. 2 diesel fuel, and Navy distillate fuel is similar to a lighter version of the typical industrial heavy distillate fuel.

Critical Fuel Properties

The control of critical distillate fuel properties is important to long, trouble-free engine operation [*1*].[2] Selective control of fuel properties can almost eliminate corrosion and performance deteriorating deposits [*2*]. Critical distillate fuel properties and their effect on engine performance are discussed in detail.

Combustion Characteristics

The control of combustion characteristics minimizes carbon deposition in burner liners and on stationary turbine hardware, and minimizes burner liner temperatures caused by incandescent carbon radiation. Luminous flames radiate more heat to these metal surfaces than do nonluminous flames, resulting in higher metal temperatures and a reduction in parts life [*3*]. Luminometer number, smoke point, and hydrogen content indicate fuel combustion characteristics. By selectively filtering high boiling point insoluble materials from the fuel, the fuel burns more completely within the combustor and reduces the deposits in the combustor and in the turbine.

Distillate Range—The distillation range is the most defining of all characteristics, and the 10 and 95 percent points are of particular interest. The 10 percent distillation temperature is an index of the fuels "front end" volatility which is important to an engine's initial combustion. Most testing with heavy distillate has been with fuels having 10 percent distillation points above 500°F. In the opposite direction is the 95 percent point of the fuel, which, more than any other characteristic, determines whether a fuel is classified as a light, medium, or heavy distillate. The capability of a gas turbine engine to burn heavier fuel as cleanly as diesel fuel from the standpoint of visibility of exhaust emissions and to burn it completely and efficiently without forming combustion section deposits or hot section distress has been demonstrated.

Viscosity—The viscosity will affect the engine's low power operation as influenced by the capability of the engine to atomize the fuel. Experience with gas turbine engines under test has indicated that viscosity and atomization are inversely proportional in a direct mechanical atomizing nozzle.

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

The ability of a gas turbine to operate at low power output with a distillate fuel is dependent on the compressor discharge temperature. Below a certain temperature, flame quenching occurs prematurely, resulting in poor combustion efficiency and attendant increased smoke levels.

Volatility—The volatility is the range of temperatures within the various fuel components boil as measured by ASTM distillation. Front end volatility also may be controlled by vapor pressure limits. Gas turbine fuel volatility requirements can vary widely, depending on engine design factors and the application. Thus, volatility characteristics of distillate fuel have been controlled to assure that the liquid fuel delivered to the nozzle will have efficient combustion and flame propagation characteristics. The "tail-end" volatility is associated with the clean burning characteristics of distillate fuels.

Stability—Thermal stability of distillate fuels is a measure of the ability of a fuel to withstand temperatures of 250 to 400°F for short periods of time without forming deposits that can foul heat exchangers or plug fuel spray nozzles. Obviously these occurrences can adversely affect engine performance as well as contaminate the environment through additional exhaust emissions. The relative absence of cracked stock or unsaturated hydrocarbons or both has resulted in a long storage life even under the severe condition of heated storage.

Carbon Residue—This is the residue of carbon remaining after evaporation and pyrolysis of the fuel. It is expressed as a percentage of the total sample or of the bottom 10 percent of the sample after distillation. This fuel property is intended to provide an approximate index of the fuel's tendency to form carbon deposits in the engine during the combustion process. Although correlations are not established, formation of carbon on the fuel nozzles can interfere with the fuel spray pattern and eventually lead to thermal distress in the turbine section. If allowed to continue, it could result in turbine damage. Somewhat related is the accompanying problem of the accelerated formation and shedding of hard carbon deposits causing erosion of turbine coatings and air seals.

Sulfur—Sulfur reacts with trace metals in the fuel to form compounds corrosive to the turbine surfaces. Additionally, sulfur compounds can cause poor thermal stability at fuel temperatures approaching 300°F. The recommended maximum sulfur level of distillate fuel with 1.00 percent sulfur content have shown, over many years, no detrimental effects attributed to that level of sulfur. Sulfur alone is not a problem to the gas turbine. After testing many alloys at various temperatures, it was concluded that a practical reduction in sulfur would not yield significant benefits. The sulfur levels in distillate fuels currently comply to most local and federal limits for air pollution control. Once again, the distillate fuels fit into the advancing gas turbine technology as well as complimenting the federal clear air programs.

Fuel Contaminants

Gas turbines, as well as steam powerplants, operate best on clean fuel. Therefore, fuel contamination is a problem which requires protection for all types of fuels and all types of gas turbines. However, gas turbine engines (high horsepower/weight and bulk) can be more sensitive to particulate matter, water, and metallic fuel contaminants from other types of combustion machinery. Gas turbines operating at higher average metal temperatures and higher pressures are more prone to corrosion and erosion.

There are several reasons for this difference. The efficiency of the gas turbine increases with higher turbine inlet temperature. If some of the fuel nozzles become plugged, the fuel flow control system will still operate on a total fuel volume basis, and higher than normal quantities of fuel will be supplied to the remaining operable nozzles. This can result in overheating of the combustion cans or a rise in turbine inlet temperature or both. Significant damage due to high temperatures can occur more rapidly to the combustion cans and turbine blades of a gas turbine than to the diesel engine, where the greater bulk of metal can better dissipate excess heat. Although the gas turbine engine is somewhat critical of fuel contaminants, special equipment for the removal of water and particulate matter can be used to control these contaminants.

Types of contamination include metals, residuum, water, particulates, other fuels, surfactants, microorganisms, and refinery carry-over. The effect of these contaminants on engine performance is discussed in detail in the following.

Metals—Gas turbines are susceptible to corrosion from reaction products of sulfur, oxygen, and metals such as sodium, calcium, potassium, vanadium, copper, and lead [*4,5*]. Sodium from sea water or treating solution carry-over can react to form sodium sulfate, a highly corrosive material. Vanadium and sodium together with oxygen react to form another highly corrosive compound, sodium vanadyl vanadate. Vanadium and sodium, alone or in combination, can severely lower the ash melting point of a distillate fuel and increase turbine corrosion significantly. Copper and lead form compounds which can cause corrosion, cause filter problems, and can plug fuel nozzles.

Vanadium—Vanadium is the most controversial limit to be established. There has been limited experience with vanadium in high temperature gas turbine engines. The limit of 0.2 ppm is the combined result of a survey of distillate fuel sources and considerations of dependable and long gas turbine life [*6*].

A rapid increase in corrosion rate occurs as the vanadium content increases. Good grade, distillate-type fuels contain 0.2 ppm of vanadium or less. The rate of corrosion at these concentrations is low.

Sodium—Sodium in gas turbine fuel causes rapid turbine deposit formation as well as corrosion [*5,7*]. Besides naturally contained sodium, seawater contamination during transportation introduces the major percentage. It is the author's opinion that sodium (salt water) contamination has *not* received the proper attention. Although some level of sodium can be expected to remain after the refining process, the presence of sodium in large part is due to seawater contamination during transport. It seems pointless to remove all the sodium at the refinery because of the subsequent salt water contamination which can occur in transport. Salt towers or salt dryers can also introduce salt into an otherwise clean fuel. Reduction in the sodium content of the fuel results in a marked reduction in deposition rate. Deposits can be almost eliminated by keeping both the sodium and the calcium content reasonably low. Figure 3 shows the reduced deposits by effective fuel system management. The sodium and calcium metals appear in the turbine deposits in about the same proportion as they are found in the oil ash [*4*]. Additionally, corrosion by sodium sulphate is influenced strongly by the presence or absence of carbon, as well as by the presence of chlorides.

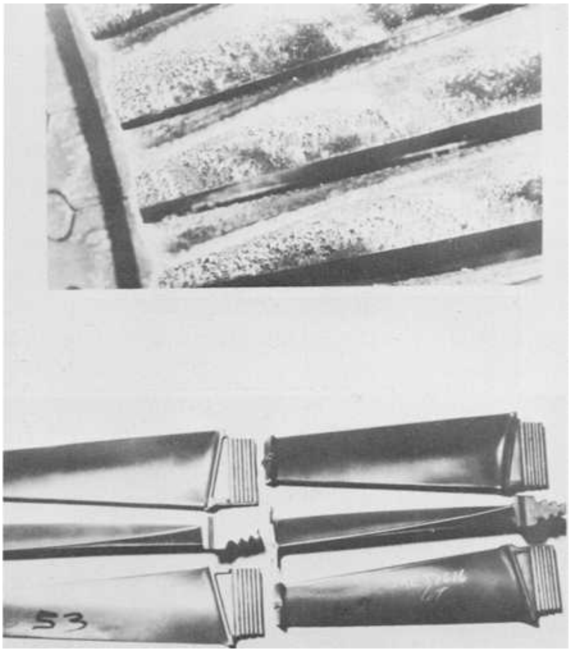

FIG. 3–(top) *Turbine blades without adequate sodium removal by the fuel handling system,* and (bottom) *turbine blades with adequate fuel system management.*

Lead–Lead in sufficient quantities can cause corrosion by itself. The high ash oil seems to be able to tolerate a larger quantity of lead than the low ash heavy distillates. It is suggested that the lead content of the gas turbine fuel be limited to approximately 0.5 ppm.

Copper Contamination–The effects of copper on the thermal stability of kerosine and marine diesel fuels are well known. As little as 125 ppb of copper would affect the thermal stability of kerosine, marine diesel, and distillate fuels

[*7*]. The presence of even trace amounts of copper acts as a catalyst and accelerates the rate of gum and sediment formation by initiating oxidation and polymerization reactions within the fuel.

The presence of metal deactivators may offset the gum forming role of copper by complexing the copper with an organic compound.

Residuum Contamination—There is concern over contamination by residual fuel since it always contains corrosive metals such as vanadium and sodium, which can accelerate engine corrosion [*1,8*]. Additionally, the sulfonates found in the residuum can rapidly degrade the performance of coalescing filters. It is highly desirable to eliminate residuum contamination.

Water—Water can be present in fuel in two forms, dissolved water and free water. Dissolved water is always present and is of concern, mainly because it becomes free water when the fuel is cooled. Free water is associated with fuel tank corrosion, microbiological growth, plugged fuel filters (due to ice), engine power loss, and flame out. Also, salt water, which is prevalent in marine operations, can cause corrosive damage to the turbine.

Particulate Matter—Suspended dirt or particulate matter can cause plugging of fuel system components and wear of moving engine components. The accepted level of distillate particulate contamination for industrial gas turbines is approximately 24 mg/gal. An increase in particulate load decreases static filter and coalescer element life, and can necessitate frequent time-consuming cleaning of centrifugal purifiers.

Other Fuel—Contamination with fuels other than that designed for a particular engine operation can present severe problems [*9*]. As an example, tetraethyl lead from gasoline and vanadium from residual fuels can cause damage to the turbine blades, vanes, and air seals. Since distillate fuels may require heated fuel for firing, the contamination by light fuels such as naphtha and gasoline can lower the flash point to a dangerous level.

Surfactants—Recently, considerable interest has been focused on the fuel surfactant problem. Briefly defined, a surfactant (short for surface active agent) is a polar-nonpolar material which lowers the interfacial tension of the fuel-water interface, promoting formation of very fine droplets. Surfactants tend to inhibit water settling, water stripping, and coalescing and tend to stabilize the formation of emulsions [*1*].

Microorganisms—Microbial growth (bacteria and fungi) is a potential source of contamination during the storage of distillate fuel. Microorganisms are always present, and, if conditions are conductive to their growth, they may accumulate as a slimy deposit which will clog the gas turbine fuel system. One type, sulfate-reducing bacteria, can create corrosive sulfur compounds in the fuel.

Water is required for growth of microorganisms. Most of these grow in tank water bottoms, feeding on nutrients in the water or on hydrocarbon at the fuel-water interface. Certain types are known to feed on tank coatings, leaving the base metal surface exposed to corrosive attack. However, even these types require moisture.

The most important single control to prevent microbial growth is good housekeeping techniques. Essentially, this requires judicious use and maintenance of equipment, and procedures to prevent the introduction of dirt and water in the fuel. This method is preferred to the use of biocides, since it incorporates techniques which will improve other aspects of fuel quality, such as water separability, and reduction of sediment content, fuel sludges, metallic content, and residuum contamination [*1*].

Treating Solution Carry-Over—Treating solution carry-over can occur from improper operation of refinery processes employed to remove undesirable sulfur compounds. Copper and lead contaminants carried over from these processes have been linked with filter plugging, engine hot parts deposits, and wear in fuel control systems. Both of these metals can catalyze fuel oxidation reactions or react with sulfur and nitrogen compounds in the fuel or both. Also, caustic carry-over from neutralization steps can react with acidic material in the fuel to form insoluble deposits which are harmful to the engine as well as the fuel handling system.

In the latter instance, the caustic reaction products, which may be surfactant in nature, can plug or disarm filter coalescer-separator units and permit passage of dirt and water into the engine fuel system. Corrosion or microbiological growth problems or both may then result.

Current Fuel Systems

The typical, distillate fuel handling system consists of a pretank filter, a fuel storage tank, a fuel pump, a depth type main filter, and a last-chance filter just prior to the engine fuel inlet. The fuel tank prefilter is a small capacity filter located ahead of the fuel storage tank and is designed to trap large quantities of water (primarily salt water) and sediment before they enter the fuel tank. A fuel storage tank should be designed to minimize the agitation of the tank bottoms by the action of the incoming fuel from the fill line and to provide a floating suction on the discharge line from the fuel tank. The main fuel filter used in this system is a Nelson/Winslow unit with an absorbent, depth type medium designed to control the majority of the hard particulate contamination, the semiliquid contamination, and the liquid contamination [*10*]. (Figure 4 is a schematic review of fuel filtration systems.)

The solid particulates are in the form of rust, scale, metal wear particles, and silica. The semisolids include fuel sludges, asphaltines, lacquers, and so forth. The liquid contaminants include water, organic acids, varnishes, and gums. (Figure 5 shows a typical filter installation.) The last-chance filter has been installed to act as a final device for controlling pipe scale and stray contamination that might break loose between the main filter and the engine enclosure. On large multi-engine installations, the distance from the main filter to the engine enclosure can be several hundred feet and, therefore, the control of stray contamination by the last-chance filter is strongly recommended.

The fuel pump should be of centrifugal design to minimize pressure-control systems and to minimize pressure surges in the fuel system.

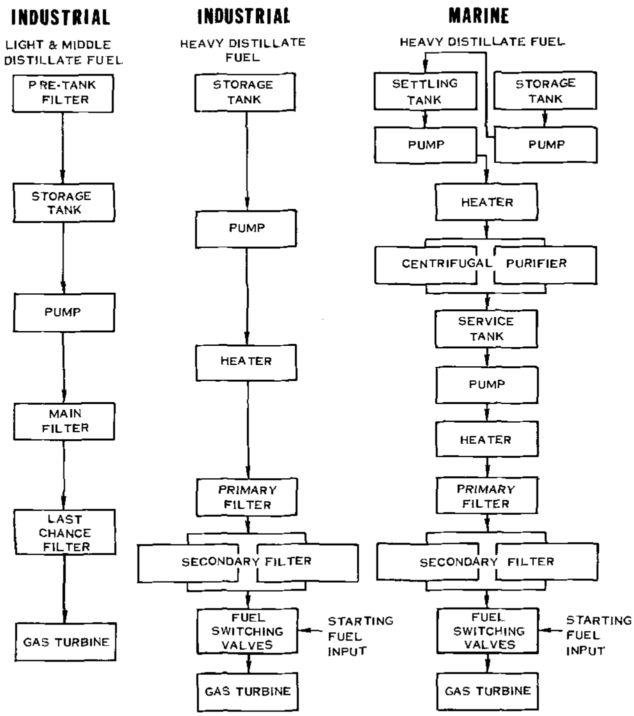

FIG. 4–*Gas turbine fuel handling system.*

FIG. 5–*Typical filter installation.*

The marine fuel handling system is identical to the industrial system except for additional system elements used as precautions to control large amounts of sea water ballast that can cause problems in the fuel handling system and compromise gas turbine life [*11*]. The approach has been to utilize settling tanks, floating suctions, and centrifugal purifiers to control large slugs of sea water.

Fuel System Management

The management of gas turbine fuel systems is based on maximum equipment utilization and on minimum maintenance downtime and minimum maintenance costs. Gas turbine performance, dependability, and life are affected by fuel contamination and fuel quality.

Gas turbines operate best on clean fuel. Fuel contamination is a problem that requires protection for all types of fuels [*9*]. Gas turbine engines (high horsepower/weight and bulk) are more sensitive to particulate matter, water, and metallic fuel contaminants than are other types of combustion engines. Gas turbines operate at higher average metal temperatures and higher pressures, and are thus more prone to corrosion and erosion.

The management of the fuel storage system begins with the receipt of the fuel for storage. Sampling the fuel upon delivery can provide many benefits in precluding the receipt of highly contaminated batches of fuel. A sample of fuel can be subjected to a single "sensory" inspection or can be sent to a laboratory for a complete, rigorous analysis. The sensory inspection compares color, haze, sediment, and odor against known standards. With the addition of a simple membrane test, such as "millipore," and a water detection kit, such as "aqua-glow," the field samples can be checked quickly and easily. The random sampling of incoming fuel samples can all but eliminate contaminated batches of fuel. When the fuel is accepted for storage, the fuel is pumped through tank prefilters designed to remove coarse particulate contamination and separate large slugs of water. The tanks themselves are a very important and often overlooked portion of the fuel storage system and can be used very effectively as aids to fuel cleanliness if they are properly designed and effectively maintained.

After the tank is built, the inner walls should be sandblasted to remove excessive scale and the walls then should be wiped down immediately with oil to prevent rusting. All sandblast material should be very carefully and thoroughly removed from the tank walls and tank bottom. To improve long-time fuel storage, the tank should have no copper, zinc, or vanadium alloys in contact with the fuel.

The fuel fill line to the tank should be located 18 in. or more from the bottom of the tank. The fill line should be directed so as not to agitate the bottom settlement of the tank and should include a velocity diffuser to minimize the jet effect of the incoming fuel. The discharge line from the tank should be fitted with a floating suction device to remove fuel from the top of the tank. The result is fuel that has a maximum settlement time and minimum particulate carry-over. This becomes particularly important in cold weather when the increased fuel viscosity hinders contaminant settling.

Typically, No. 2 fuels settle at about 1 ft/h so that a floating suction is a very valuable asset when tanks are used and filled often. The use of two tanks in place of one can also provide improved fuel settlement time. The concept of filling one tank and running from the other tank in a two-tank system provides a maximum settlement time and has proved to reduce filter maintenance significantly. The effective use of storage tank settlement time cannot be emphasized enough. After 24 to 48 h of undisturbed settling time, a significant quantity of the water and particulates settle below the floating suction pickup. The tank bottoms should have either a cone-down bottom or sumps to allow water to be drawn off on a weekly maintenance basis. This minimizes the amount of water in contact with the fuel and can significantly reduce the problems associated with microbial growth. Tank coatings have also been used successfully to minimize the scaling effect of the inside of the tank and to minimize bare metal surfaces in contact with the fuel.

If the liquid fuel is stored for periods exceeding one month, the use of nitrogen inerting is recommended [*12*]. The use of nitrogen to inert the interface between the fuel and the air greatly reduces degradation of the fuel by preventing oxygen absorption.

From fuel storage, the fuel filtration is through the main, absorbent, depth-type filter that is designed to control heavy contaminant loading with a slow, predictable differential pressure increase. The TPM filtration system has been developed through a cooperative test program with the Nelson/Winslow Engineering and Manufacturing Company of Wisconsin. During this program, the system was modified and optimized until a system was found that was most compatible with high temperature gas turbines. The absorptive type of depth media filtration was found to be best, and is the basis for the new system [*10,13*]. The depth type elements have 7 to 11 times the absorptive area of the finest paper type elements for removing liquid contaminants. This capability is not found in surface filter media. (Figure 6 shows a typical membrane filter analysis.)

To date, this type of fuel filtration has provided superior gas turbine protection to other types that have been tried. The treated, depth type filter is constructed to remove progressively a gradation of particle sizes, to remove a maximum quantity of free water, and to remove oxidized matter, providing a service life far beyond those of previously tested systems. Most types of filtration systems can, to a degree, remove gummy, oxidized material; but in doing so, the filter life and its effectiveness is seriously compromised. The graduated density in these filter elements allows the soft, asphaltic, carbonaceous matter (often saturated with water) to be reduced effectively without the rapid filter filming (surface sealing) action that occurs with fiberglass and pleated paper or stacked paper media-disk type of filter elements [*7*].

The depth type elements are designed to control 5 to 10 μm particle solids. A chemical treatment acts to reduce the detrimental action caused by unsaturated, unstable fuel radicals, and also serves as flocking agent. The reduction by absorption and neutralization of oxidized materials from the fuel is an important factor that greatly reduces turbine blade fouling.

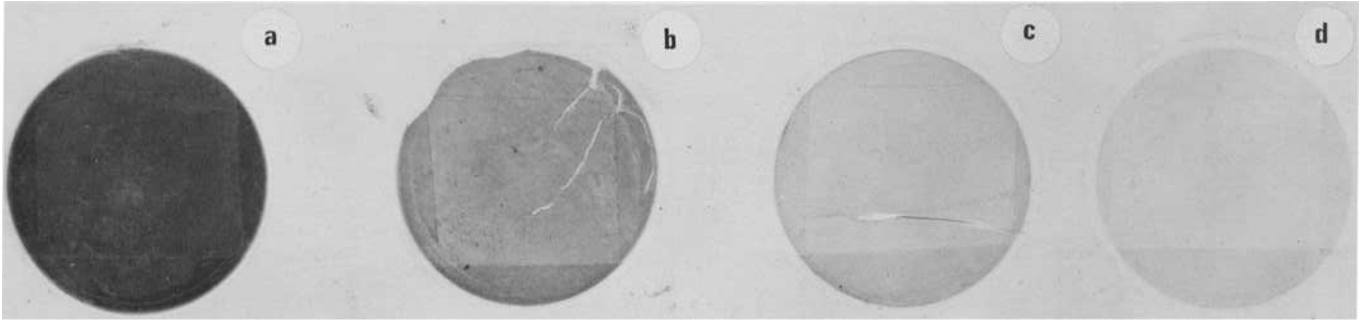

FIG. 6–(a) *From bunkering tanks to purifiers;* (b) *after purifiers and before Winslow primary filter;* (c) *after Winslow primary and before Winslow secondary filter; and* (d) *after secondary filter.*

The element-filtering media and the method of construction was developed to prevent early peripheral surface sealing (surfacting) caused by certain fuel additives, high molecular paraffinic compounds, long-chain hydrocarbon groups, and water-solids combinations. Due to the irregular element media surface, even ice particles formed in the fuel (during freezing weather) will have a minor effect on the performance life of the fuel elements.

Element changes may be required because of acid absorption levels before a delta "P" physical change is indicated by the differential pressure gauges [*13*]. Normally, the filter elements are changed when the differential pressure reaches 18 psi. Element service life, depending on levels of fuel contamination, is expected to be 3000 h.

Some systems use coalescer-separator to remove water from industrial fuels. Since "effective" coalescer filters are inherently fine filters, the life of the coalescer will be generally shorter than the life of the depth filter. The final filtration characteristics of coalescers and the presence of waxes and surfactants in the fuel can be the downfall of this filter, if located improperly in the fuel system [*6,14*]. The coalescer should be installed downstream of full-flow purifiers or depth type absorbent filters or both; in this position they have given good performance and reasonable life. The main depth filter is designed to minimize the heavy, oxidized ends of the fuel that can cause premature coalescer element change-out.

There are surfactant and filming materials present in small quantities in most industrial fuels. These materials have a preferential attraction for surface-type filters and fiberglass coalescers. Surface active materials, either singularly or combined, can cause disarming of filtration equipment by virtue of their plating or coating effect on the fiberglass media. This causes the reversal of preferential wetting and the loss of efficient coalescing action. In some instances, the loss of water coalescing action can occur much sooner than the differential pressure indicates. The combination of the normally fine degree of filtration and the use of synthetic fibers and resins can cause the coalescers to "blind-off" rapidly.

All filters should have the water drained from the sump at least every week. This includes depth type units as well as coalescer-separator filters.

The problems attributed to surfactants are principally related to their tendency to prevent the coalescer from performing its function, that is, removing water. The surfactants may come from the refinery in the form of naphthenic and sulfonic acids, sodium naphthenates, sulfonates, and many types of fuel additives such as anti-rust, anti-oxidants, storage stabilizers, detergents, dispersants, and pour point depressants. Tankers and barges can introduce seawater. The seawater and naphthenic acids can combine to form the undesirable sodium naphthenate. Also, a miscellaneous group of common surfactants include soaps, detergents, and chemical cleaning agents. Rust preventatives and descaling chemicals usually act as surfactants or can combine to form surfactants.

The last-chance filter in the system is designed to provide protection from scale and slag introduced in the piping runs from the coalescer-separator up to the engine fuel pump.

The fuel pumps used in the fuel handling system are of a centrifugal design and provide long life and minimum pressure surges in the fuel system. Positive displacement pumps should be avoided, since the greater pressure pulsations can cause premature "wash-out" of the insoluble contamination retained within the depth media filter elements and the coalescer elements.

Summary

The increase in use of the large, combustion gas turbine for electrical peaking is due to the recognition that this prime mover provides the economic incentives to reduce total capital investment per kilowatt installed or per kilowatt hour generated. Additional advantages, such as short installation time, remote, unattended operation, quick starting, and black starting capability provide further incentives. The successful management of the fuel system will complement the choice of the combustion gas turbine by providing maximum equipment utilization and minimum maintenance costs.

Experience has shown fuel contamination to be the greatest single factor contributing to distress of the high temperature turbine. The fuel handling problem areas have been identified and the complete fuel system has been described in detail. The remaining aspects of fuel system management rests upon the gas turbine user to follow routine precautionary control procedures in the procurement and use of the fuel.

Acknowledgements

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Experience with Distillate Fuels in Gas Turbines

REFERENCE: Del Favero, R. and Doyle, J. J., "**Experience with Distillate Fuels in Gas Turbines,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 45-56.

ABSTRACT: Con Edison uses more than 2000 MW of gas turbines to produce both peaking and base load power. In 1971, these units consumed approximately 6 million barrels of No. 2 oil and kerosine. This paper discusses fuel experiences with aircraft derivative engines and industrial engines. Data is presented from a fuel quality study at Con Edison. Conclusions and recommendations cover methods of fuel purchasing transportation, on-site fuel cleanup, and recommended housekeeping procedures.

KEY WORDS: fuels, gas turbines, trace elements

Currently about 2500 of Con Edison's 9500 MW of generating capacity are supplied by gas turbines (GTs). Originally purchased to provide capability for startup from blackout conditions and for peaking power, they were quickly pressed into service, more often than not, as base loaded units. Licensing problems for nuclear units, unanticipated outages, delays in construction, and deratings of units converted from coal to oil combined to make gas turbines look like the quickest solution to our immediate power problems.

Current Demands for Distillate Fuels

Gas turbines comprise about 26 percent of our generating capability, and provided about 10 percent of our electric generation in 1971. The increase in their contribution to electric production from 1 percent in 1969, to an estimated 15 percent for 1972 may explain why we have encountered some difficulties. The rush to provide additional generating capacity in the face of delays in construction of nuclear units and unanticipated outages which delayed maintenance on, and consequently reduced reliability of other conventional equipment, left little time for refinements.

We currently use two liquid fuels in gas turbines, kerosine and No. 2 oil. Approximately 50 percent of our GTs have gas burning capability, and so we also use natural gas when available. Kerosine is burned in the aircraft derivative engines exclusively (40 percent of our turbine capacity) and No. 2 oil in the

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industrial units with the exception of our latest 350 MW of barge mounted gas turbines, which burn kerosine. In 1971, we consumed about 6 million bbl (42 gal) of gas turbine fuel. In 1972, we expect to use about 10 million bbl.

To accommodate this large distillate demand, we maintain approximately 45 operating hours of on-site storage at each location serviced by barge and 30 h of storage at truck delivered sites. We have recently acquired additional tankage which in combination with existing storage will permit us to store a total of 100 h (based on peak summer load operation) of fuel supply for all our gas turbines. We maintain a smaller inventory for gas turbine fuels, which are purchased on yearly contracts either delivered or FOB New York Harbor, than we do for residual oil which originates offshore.

Problems with Fuel Quality

Prior to 1971, No. 2 oil was burned in many of the aircraft derivative engines. With the imposition of very stringent fuel purchase specifications by an engine manufacturer, covering trace metal contents and Luminometer Number (LN), properties not normally checked in No. 2 oil, we were unable to get complete coverage of our GT fuel requirements. We did get coverage with more liberal specifications, but the fuel was something less than ideal for the aircraft engines. In purchasing turbine fuel this year we did not encounter as many difficulties as we did in 1971.

After approximately 1200 h of operation, the aircraft engines experienced serious hot end corrosion and sulfidation attack in the hot gas path blading, as well as abrasion. These problems were attributed in part to fuels with low LN (with its high radiant heat), to fuels with high sodium, lead, and copper content (all of which help to catalyze sulfidation), and to fuels with high particulate levels (which cause nozzle and filter plugging). A study was instituted to determine just how bad or good fuel quality was, and where, if at all, it could be improved. Since the main problems seemed to be associated with metals, LN, and particulates, we concentrated our study on these items. Data for the study was obtained by analyzing samples obtained from our supplier's terminals, in barges, at our stations, and from other users and suppliers at various locations. (See Appendix I for description of analysis for trace metals.)

Analysis

Table 1 shows various metal contents of fuel oil as delivered to our stations. It is broken down to show the differences in metals content between kerosine and No. 2 oil, and among dedicated[2] and nondedicated barges and trucks. This table does not show the metal levels prior to delivery, or contaminants picked up enroute.

Table 2 shows metal contents of gas turbine fuel as sampled in the suppliers'

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[2] A dedicated barge was chartered exclusively for Con Edison's use, and steam cleaned before being used to carry kerosine and No. 2 oil. This particular barge was equipped with a double bottom which minimized the possibility of leakage.

TABLE 1–*Metals content by supplier. Original study data (May to July, 1971).*

	Number of Samples	Method of Delivery	Metals Contents, ppm					
			Cu	V	Pb	Ca	Na	K
			Kerosine					
Supplier A	7	dedicated barge	0.03	0.04	0.14	0.20	0.67	0.19
Supplier C	6	truck	0.01	0.04	0.66	0.12	0.43	0.04
Supplier D	4	truck	0.02	0.05	0.47	0.15	0.36	0.19
Supplier L	1	truck	0.02	0.03	0.34	0.21	0.29	0.02
	Average, all barges		0.03	0.04	0.14	0.20	0.67	0.19
	Average, all trucks		0.01	0.04	0.56	0.14	0.38	0.10
			No. 2 Oil					
Supplier A	11	dedicated barge	0.02	0.03	0.08	0.22	0.67	0.14
	1	regular barge	0.01	0.03	0.17	0.13	0.27	0.12
	Supplier A, average		0.02	0.03	0.09	0.21	0.64	0.14
Supplier E	1	dedicated barge	0.02	< 0.03	0.26	0.08	0.42	0.03
	7	regular barge	0.02	0.03	0.37	0.14	0.51	0.04
	Supplier E, average		0.02	0.03	0.36	0.13	0.50	0.04
	Dedicated barge, average		0.02	0.03	0.09	0.21	0.65	0.13
	Regular barge, average		0.02	0.03	0.34	0.14	0.48	0.05
	Average, all barges		0.02	0.03	0.19	0.19	0.58	0.10
Supplier C	2	truck	0.06	0.04	0.35	0.38	0.33	0.03
Supplier H	2	truck	0.03	0.05	0.30	0.12	0.38	0.23
Supplier G	4	truck	0.08	0.10	0.26	0.16	0.81	0.08
	Average, all trucks		0.06	0.08	0.29	0.20	0.58	0.10

TABLE 2–*Metals pickup due to barge transportation.*

	Dedicated Barge												
	In Supplier Tanks, ppm							In Barge Alongside Station, ppm					
Date	Cu	V	Pb	Ca	Na	K		Cu	V	Pb	Ca	Na	K
Supplier A, No. 2 Oil													
6/10	0.01	0.03	0.08	0.04	0.37	0.01		0.04	0.06	0.11	0.06	0.29	0.03
6/17	0.03	0.03	0.05	0.11	0.55	0.01		0.01	0.03	0.05	0.19	0.40	0.01
6/25	0.01	0.03	0.05	0.05	0.18	0.01		0.01	0.07	0.05	0.07	0.17	0.01
6/29 split shipment	0.03	0.03	0.12	0.26	0.67	0.08	Delivery point 1, 6/29	0.02	0.04	0.12	0.29	0.78	0.09
Average	0.02	0.03	0.07	0.12	0.44	0.03							
							Delivery point 2, 7/1	0.02	0.02	0.08	0.13	0.54	0.03
							Average delivered	0.02	0.04	0.08	0.15	0.44	0.03
Supplier A, kerosine													
6/18	0.01	0.03	0.05	0.14	0.54	0.01		0.01	0.03	0.05	0.04	0.36	0.01
7/2	0.02	0.04	0.14	0.18	0.49	0.05		0.05	0.03	0.25	0.25	0.49	0.12
7/10	0.03	0.03	0.14	0.16	0.66	0.05		0.02	0.03	0.12	0.14	0.67	0.06
Average	0.02	0.03	0.11	0.16	0.58	0.04	Average delivered	0.02	0.03	0.14	0.14	0.51	0.06
							Regular Barge						
Supplier E, No. 2 Oil													
6/25	0.04	0.03	0.33	0.16	0.30	0.01		0.01	0.03	0.46	0.11	0.26	0.01
6/26	0.02	0.03	0.26	0.10	0.26	0.01		0.02	0.06	0.45	0.13	0.20	0.01
6/29	0.03	0.05	0.36	0.20	0.47	0.06		0.03	0.05	0.25	0.14	0.66	0.07
7/2	0.04	0.03	0.37	0.23	0.68	0.08		0.02	0.03	0.39	0.16	0.58	0.07
7/12	0.03	0.02	0.37	0.11	0.56	0.05		0.02	0.02	0.35	0.22	0.75	0.04
Average	0.03	0.03	0.34	0.16	0.44	0.04	Average delivered	0.02	0.04	0.38	0.15	0.49	0.04
Supplier A, No. 2 Oil													
6/24	0.01	0.03	0.05	0.14	0.26	0.12		0.01	0.03	0.17	0.15	0.27	0.03

tanks and samples of the same oil as delivered in barges to Con Edison's sites. In addition to these two items, this table compares samples of kerosine and No. 2 oil from different suppliers, and from dedicated and nondedicated barges.

Table 3 shows analyses of samples from other large users and suppliers, and

TABLE 3–*Metals content of distillate fuel, other users.*

Identification	Metals Content, ppm Cu	V	Pb	Ca	Na	K
At Supplier C Terminal						
Jet A, Buffalo loading rack	0.03	0.02	0.05	0.12	0.39	1.03
Jet A, N.Y. barge terminal	0.01	0.72	0.05	0.09	0.39	0.03
After Cleanup At Airport						
Jet A, refueler Buffalo	0.06	0.02	0.02	0.10	0.37	0.03
Jet A, JFK	0.01	0.01	0.18	0.09	0.41	0.03
Jet A, JFK	0.03	0.07	0.38	3.05	0.66	0.20
Average fuel after cleanup at airport	0.03	0.03	0.19	1.08	0.48	0.09
Large eastern utility samples from station tanks for GTs						
Location 1, not identified	0.01	0.02	0.07	0.12	0.34	0.02
Location 2, 50/50 kerosine and No. 2	0.02	0.04	1.08	0.20	0.39	0.03
Location 3, No. 2 oil	0.02	0.02	0.46	0.14	0.39	0.02
Location 4, No. 2 oil	0.02	0.01	0.65	0.24	0.87	1.50
Location 5, No. 2 oil	0.03	0.03	0.53	0.22	0.45	0.04
Location 5, No. 2 oil	0.02	0.04	0.47	0.24	0.31	0.07
Location 6, No. 2 oil	0.01	0.08	0.51	0.25	0.53	0.02
Location 6, No. 2 oil	0.03	0.02	0.41	0.30	0.44	0.06
Location 7, 50/50 kerosine and No. 2	0.11	0.02	0.70	0.14	0.39	0.02
Average	0.03	0.03	0.54	0.21	0.46	0.22

Table 4 shows data subsequent to the original study. Table 5 is a statistical analysis of sodium in our distillate fuel for the period 1 July 1971 through January 1972.

It should be noted that this data has been numerically averaged rather than weighted by size of shipments. However, truck delivery data are monthly composites and are usually comparable in volume to a single barge delivery.

Results

From this data, reinforced by subsequent data, we drew the following conclusions:

1. Based on the data in Tables 1 and 4, kerosine and No. 2 oil are essentially equivalent with regard to metals content. While there are small variations in metals from supplier to supplier, there is little real difference between fuels. The sodium and lead content appear to have the widest variations. A summary of metal content for the period May 1971 to March 1972 is tabulated in Table 6.

TABLE 4–*Metals content by supplier (Aug. 1971 to March 1972).*

Supplier	Number of Samples	Method of Delivery	Metals Contents, ppm					
			Cu	V	Pb	Ca	Na	K
Kerosine								
Supplier A	64	barge	0.02	0.02	0.11	0.11	0.39	0.02
Supplier B	33	barge	0.02	0.05	0.24	0.11	0.39	0.05
Supplier C	24	truck	0.02	0.02	1.50	0.12	0.43	0.02
Supplier D	16	truck	0.01	0.02	0.44	0.10	0.40	0.04
	5	barge	0.02	0.05	0.21	0.10	0.50	0.04
	Supplier D, average		0.01	0.02	0.39	0.10	0.42	0.04
	Average, all barges		0.02	0.03	0.16	0.11	0.39	0.03
	Average, all trucks		0.02	0.02	1.08	0.11	0.42	0.03
No. 2 Oil								
Supplier E	44	barge	0.02	0.02	0.28	0.17	0.61	0.06
Supplier A	46	barge	0.02	0.02	0.15	0.16	0.71	0.04
	3	truck	0.02	0.02	0.22	0.08	0.61	0.03
	Supplier A, average		0.02	0.02	0.16	0.15	0.70	0.03
Supplier F	16	barge	0.01	0.01	0.11	0.10	0.43	0.03
Supplier G	12	truck	0.14	0.03	0.51	0.16	1.00	0.06
	2	barge	0.03	0.02	0.32	0.08	0.40	0.06
	Not averaged, vendor is reseller, bargeloads not from his stock.							
Supplier C	8	truck	0.02	0.04	0.41	0.10	0.50	0.04
Supplier H	7	truck	0.05	0.03	0.41	0.15	0.70	0.04
Supplier I	6	barge	0.06	<0.10	0.14	0.17	0.88	<0.10
Supplier J	5	barge	0.04	<0.10	0.12	0.12	0.39	<0.10
Supplier K	3	barge	0.03	0.02	0.37	0.19	1.04	0.03
	Average, all barges		0.03	0.02	0.21	0.16	0.66	0.05
	Average, all trucks		0.08	0.03	0.43	0.13	0.76	0.05

TABLE 5 – *Sodium content. Kerosine and No. 2 oil deliveries combined (July 1971 to Jan. 1972).*

Supplier	Number of Samples	Mean Sodium, ppm x 100	Standard Deviation, ppm x 100
A	75	45.9	34.7
E	50	57.6	34.4
C	28	39.4	28.0
D	15	35.9	22.3
G	15	69.5	36.6
F	15	42.8	18.8
B	25	38.3	20.0
H	7	63.6	42.3
		Mean average = 48.0	

TABLE 6–*Summary–metals content, May 1971 through March 1972.*

All Deliveries	Number of Samples	Cu	V	Pb	Ca	Na	K
Kerosine	161	0.02	0.03	0.42	0.12	0.41	0.04
No. 2 Oil	164	0.04	0.03	0.26	0.16	0.66	0.06

2. The use of a dedicated barge does not offer any material advantages insofar as controlling metallic contaminants is concerned. The data in Table 2 shows that the metals present in the supplier's tanks remain at the same levels upon delivery, regardless of which barge is used. Exposure to contamination would, however, be greater with a nondedicated barge due to the inability to control the nature of previous service.

3. As can be seen from Table 3, fuel from other suppliers and from other large users, while admittedly smaller samplings, appear to contain metals at the same levels as fuel delivered to us.

Changes in Fuel Specifications

The conclusions drawn from the study, completed in July 1971, have been reinforced by additional data collected since that date. There have been changes in individual supplier's quality, as we outstripped our contracted fuel requirements by a factor of three which forced our suppliers, in some cases, to make operational adjustments. There have also been changes because we added fuel suppliers, and because barging firms used different equipment. But none of these changes has been significant–the magnitude of metal levels remained constant (see Table 4). One trend, not indicated in our tables, was an increase in sodium content over the last few months, which appeared to be due to normal inventory reduction at the end of the heating season–we've gotten tank bottoms on occasion.

Luminometer Number

The Luminometer Number problem was solved, but not without additional cost. While we could not secure sufficient high LN No. 2 oil to meet our needs, we were able to obtain kerosine to burn in our aircraft derivative engines. This fuel has apparently worked out very well. The high LN of kerosine (mid 40s) has given us a lot less problems in our aircraft engines than did the No. 2 oil (LN is low to mid 20s). We recently ran identical aircraft engines on No. 2 oil and kerosine for 1000 to 1200 h in the same type of service. Some test data is tabulated below. As can be seen there was little difference in fuel quality other than LN.

		PPM					
Fuel Type	LN	Cu	V	Pb	Ca	Na	K
Kerosine	45	0.02	0.10	0.12	0.13	0.47	0.10
No. 2 Oil	25	0.04	0.10	0.22	0.10	0.61	0.10

The engines using No. 2 oil exhibited serious hot section deterioration, as evidenced by badly corroded inlet guide vanes which required replacement. The engines on kerosine did not exhibit any unusual wear or deterioration. Since metals content was approximately similar, and the units underwent the same type of service, the difference could only be attributed to the LN. The test results have justified the changeover of our aircraft engines to kerosine.

Particulates

When our laboratory discovered that the major particulate contaminants in some of our fuel samples were from dirty sample cans due to particulates in the ambient air, we realized we would need more sophisticated equipment to properly sample for particulates. We made rough checks by field monitoring fuel input through filters, and determined that fuel met specifications with regard to particulates. It was also determined that existing filters were undersized.

We are now working on our present sampling system. We currently take "grab" samples out of a flowing line, or obtain "running" samples from each barge compartment. However, the reliance upon a manual sampling system with incorrectly taken, or missed samples can create as many problems as it was designed to detect. In-line samplers which will take a composite sample automatically are currently being installed.

Metals Levels

As a result of our data gathering, we have determined a range of metal levels, covering ten suppliers, for over 6 million bbl of gas turbine fuel delivered in slightly over one year. We have found average metals levels of less than 0.10 ppm for vanadium, copper, and potassium, between 0.10 and 0.20 ppm for calcium. We have found lead to vary from 0.10 to 1.0 ppm, and sodium from 0.40 to 1.0 ppm.

The sulfur content of No. 2 oil ranged from 0.15 to 0.30 percent until October 1971 when legal requirements reduced allowable sulfur content to 0.20 percent maximum. Our No. 2 oil now runs between 0.15 and 0.20 percent sulfur. Kerosine has typically ranged between 0.01 and 0.06 percent sulfur.

Typical metals specifications for the various engines are shown in Table 7, as well as specifications for ASTM GT-1 and GT-2.

TABLE 7–*Typical metals specifications for various engines and for ASTM GT-1 and GT-2.*

				Metals, ppm			
Specification	Cu	V	Pb	Ca	Na	K	Na+K
GT-1	...	2	5	5	...	...	5
GT-2	...	2	5	10	...	...	5
Industrial engine, No. 2 oil[a]	...	2	5	10	...	...	5
Industrial engine, No. 2 and kerosine[b]	...	0.5	5	5	...	...	2
Aircraft engine No. 2 and kerosine	0.02	0.10	0.10	0.10	0.10	0.10	...

[a] Specifications for engines purchased during 1969 through 1971.
[b] Specifications for engines purchased for 1972.

After more than one year of monitoring kerosine and No. 2 oil deliveries we have found only two or three isolated instances where industrial engine specifications were apparently not met. During that same time, not one of the many hundreds of samples analyzed (whether from our own suppliers, airports, or other large users) has ever met the aircraft engine specification for metals.

We have been unable to meet the stringent aircraft engine metals specification, and do not believe fuels meeting that specification can be purchased in New York Harbor. We have therefore directed our attention to proper fuel housekeeping, and to preventing acceptance of those occasional obviously contaminated shipments.

Program Objectives and Recommendations

Our program is to initially purchase a specified clean, low metals fuel. Secondly, we try to keep it clean in transit by inspection of the vessel before loading and discharging. Thirdly, we try to follow proper handling procedures once the fuel is in our system.

Have we got a good working system now? Unfortunately, not yet. Combinations of the following have been recommended at various sites: filter separators, automatic samplers, floating suction, cone bottom tanks, coated tanks and lines, increased settling time, water drawoffs, and, of course, additional storage. While these improvements would allow us to put together a decent oil handling system, most of it is difficult to install in an operating installation which is in service at least five days per week, and does not easily permit downtime. Therefore, we are forced to operate within the framework and restrictions of our existing system.

As mentioned previously, petroleum inspectors check each barge prior to loading, and sample each barge delivery for water prior to discharging. As a result of these cross checks, we uncovered a practice we have since prohibited. We ocasionally found samples with high water and high sodium, while the inspection report showed no unusual amounts of water in the storage tanks. How then could we explain the samples? In checking with the barging company, we found that compartments are occasionally flushed with sea water to clean and purge them. Although these compartments are then stripped, if the deck lines are not properly drained an initial sample taken before lines are cleared will contain sea water. Four to eight gallons of sea water provides enough sodium to contaminate a 20 000-bbl barge load of kerosine so that it will not meet specifications for aircraft derivative units.

Filter separators have been recommended, and in some cases have been installed on fill lines. These serve to remove entrapped and suspended water golbules and foreign matter, but are not foolproof since they allow slugs of water to pass. Periodic draining of water in storage tanks has also been initiated to remove that water which passes through the separators and, of course, the condensation formed as the tanks "breathe." We have found that the interface between the water layer and product is an excellent breeding ground for bacteria and slime which contribute to plugging of the fine (5 μm) final fuel filters. Several samples from our tanks, during a period of filter plugging, and prior to regular tank draining programs, showed bacteria counts between 1 and 9 million bacteria per ml.

Present Conditions

Unfortunately at present, at a number of our gas turbine sites we operate with insufficient settling time, and have, on occasion, been forced to draw out of a tank at the same time it is being filled. Filling, of course, stirs up any water and impurities which have settled to the bottom. These impurities then either plug filters or are carried into the engines unless given sufficient time to settle out. Additional storage tanks to allow adequate settling time, and providing each tank with floating suctions will mean a large improvement in our handling system. Floating suctions are a relatively inexpensive improvement and should be installed in every turbine fuel tank. Installation of larger capacity disposable fuel filters on the tank discharge line (in parallel if required operationally) would also improve fuel quality at the turbine inlet.

If the recommendations are implemented, we are confident that metals, particulates, and water will be kept to a minimum. We doubt, however, that the metals specifications can ever be consistently met for the aircraft derivative engines.

Our laboratory recently obtained some air samples near one of our gas turbine sites, which are adjacent to water. These samples as well as data from other sources indicate that the turbine inlet air can carry significant quantities of sea salt. Since about 60 times as much air as fuel by weight is used, more total salt can be introduced from the air than from the fuel even when the concentration of salt in the air is lower. While the turbine hot section components may respond differently to salt depending on whether it is ingested with air or with fuel, the magnitude of the salt contribution by the air can raise a question as to the relative importance attributed to the metals content of the fuel. Users and manufacturers should be made aware that air quality may have a measurable significance on corrosion. We suggest that a study be made comparing corrosion in identical units having like operating conditions and similar fuels, operating in marine and nonmarine environments.

Conclusions

Since our success in substituting kerosine for No. 2 oil, we feel that LN, or more correctly the radiant heat output of the fuel, may be of greater importance than metals content for certain equipment designs. If the LN is sufficiently high, the combustion chamber metal temperatures will be low, and the engines will be better able to withstand metals contamination from any source. The substitution of a higher quality (and more expensive) fuel is, of course, an economic balance, weighing differential fuel costs against maintenance costs, providing that one can afford the option of increased turbine downtime required by operating on a lower quality fuel. However, the use of a higher quality fuel appears to have paid off for us in our aircraft derivative engines.

We, therefore, recommend a high quality fuel, and a good cleanup system at the site. We also recommend that serious consideration be given to the effect of salt laden sea air on the operation of gas turbines, and the means to reduce the amounts of airborne contaminants carried into the engines.

APPENDIX I

Procedures for the Analysis of Trace Metals in Jet Fuels and Comments on Accuracy and "Repeatability"

Samples are prepared by "dry ashing" as described in the following procedure:

Procedure for Preparing Jet Fuels for Trace Metals Analysis

1. Weigh a clean 150 ml beaker to 1 mg.
2. Measure about 100 ml of jet fuel sample into the beaker.

3. Reweigh the beaker to 1 mg.
4. Record weight of oil as the difference.
5. Heat the beaker on a hot plate, and ignite the oil with a Bunsen burner when hot. Let the oil burn itself out.
6. Ignite the beaker with the carbonaceous ash in a furnace at 900°F overnight.
7. Let the beaker cool, and rinse the sides of the beaker with 5 percent nitric acid. Boil gently for a few minutes.
8. Let cool and wash into a 50 ml volumetric flask with 5 percent nitric acid–bring to volume with same.

The acidified ash solution is used to determine vanadium according to standard colormetric method as described in the American Society for Testing and Materials, using the Technicon Auto-Analyzer, and to determine copper, calcium, magnesium, lead, sodium, and potassium by means of atomic absorption spectrophotometry. Use of this instrument for the determination of trace cations is recognized and approved by ASTM.

Accuracy, "repeatability," and "reproducibility" are not stated in ASTM for these tests. We can, however, state approximate lower detection limits for each test and an estimate of "repeatability."

Our data upon which to base this estimate is fragmentary and we cannot make any judgment at all as to the "reproducibility" of procedures. Any errors inherent in the preparation of the samples are not included in these considerations.

TABLE 8–*Trace metals detection limits and repeatability.*

Trace Metal	Lower Detection Limit, ppm	Estimated "Repeatability," ppm	ASTM References[a]
Na	0.001	0.006	D 2788-72
K	0.01	0.06	D 2788-72
Ca	0.01	0.06	D 2788-72
Mg	0.001	0.006	D 2788-72
Pb	0.03	0.18	D 2788-72
Cu	0.001	0.006	. . .
V	0.01	0.06	D 2787-72 D 1548-63 D 2788-72

[a] Part 17, *1972 Annual Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, Pa.

J. C. Bradley[1]

Clean, Bright, and Dry

REFERENCE: Bradley, J. C., "**Clean, Bright,** and **Dry,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 57–72.

ABSTRACT: At the inception of the gas turbine, it was generally advertised by the uninitiated and ill-advised that gas turbines could "run on anything." This thesis did not attempt to answer for how long – how well – how reliably – and most importantly, how economically.

Experience, after millions of hours of turbine operation in both aviation and ground units, has proved that the turbine engine does indeed require some sophisticated attention to its "care and feeding," and that the proper attention to its diet is of utmost importance.

It is the purpose of this paper to pinpoint some of the sources and types of fuel contamination and to outline precautions and procedures currently in use by the industry to preclude the possibility of contaminated fuel from reaching the turbine. In this connection, practices used in the aviation sector of the industry will be explored in detail since millions of gallons of jet fuel daily are being supplied to aviation turbines clean, bright, and dry with utmost reliability of product quality. Similar procedures applied to ground and marine units can assure dependable and economical operation.

KEY WORDS: fuels, fuel storage, quality control, fuel contamination

The subject of this paper is "clean, bright, and dry" which refers to certain qualities we are looking for when accepting distillate fuels for consumption in combustion or gas turbines. These words have become a byword of the aviation industry, because the turbojet aircraft engine requires a high degree of fuel quality.

Because of the fact that the aircraft turbine is by far and away the largest consumer of turbine fuel (some 7¼ billions of gallons per year in the United States alone) as against ground units, because its operating environment is so hostile, and because its needs are so critical, I will attempt to outline some of the steps my company and the aviation industry take to assure jet fuel quality to aircraft turbines. Obviously, these same quality assurance procedures, when applied to ground turbine fueling systems, will provide superior quality product and thereby superior operating performance and reliability to all power generation equipment whether it flies, floats, runs on rails, rubber tires, or merely stands still.

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It is a corollary in the oil business that crude oil is where you find it. By and large, with some few exceptions, it is feasible to refine crude oil near to where it is produced. As luck would have it, points of major consumption are seldom near either the production or refinery source, so that finished products must of necessity be transported over long distances via various methods–all of which can and do alter our criteria of clean, bright, and dry.

Types of Contamination

Most distillate fuels today, in their travels from refinery to the tail pipe of the engine, are exposed to either tanker or pipeline transportation and sometimes both in various permutations and combinations. They also enter and leave numerous break-out and storage tanks in their travels and almost certainly are carried, at some point in the trip, by transport truck or tank car.

Tankers, barges, etc., can be, if carelessly operated and maintained, serious contaminators of distillate fuels. Fresh or salt water or both are the most serious pollutants, with rust, mill scale, and various and sundry rust inhibitors a close second, but often more serious than water contamination. Pipelines can be, but are not always, even more serious contaminators than tankers, depending on their operating characteristics and the mix of products they are handling.

Strangely enough in this connection, a pipeline like the largest in the world stretching 1500 miles from the Texas Gulf Coast to New York, handling product at 48 000 bbl/h (2 000 000 gal/h), is a far less severe problem contaminationwise than is a much slower (4000 bbl/h) connecting line of almost the same size. The slower line gives more time for the interfaces between products to collapse and intermingle, allows inhibitors and gasoline additives more residence time to plate-out on pipe walls to be picked up by the following jet fuel, and allows water to remain in solution longer. However, both lines can present us with many and varied problems at any time, and the price of quality integrity of product from either type of line is eternal and continual vigilance by all concerned.

It is one thing to protect the product against contamination during primary transportation, but it is another to keep it clean and water-free in our own tanks and in our own terminals once we get it there. Here again, fuel is subjected to new and additional contamination if tanks are not maintained in clean condition–water bottoms are not drained regularly and pump suction intakes are not kept high off the bottom of the tanks.

If, after all this exposure to contamination, we still have clean product or are able to make it clean by filtration, then we always have at least one more, and possibly two more, good opportunities to foul it up; that is, by use of a dirty, wet transport truck from terminal to customer storage or by a customer's dirty storage tank.

In the aviation fuel quality assurance program, we protect our product quality by filtering through Fuller's earth filters and coalescer-separator filters downstream of our terminal storage tanks and into transport trucks. Transport trucks to customer's storage at airport's are dedicated units and in rare cases where a dedicated unit cannot be used, careful flushing and cleaning procedures are used before the truck is loaded with jet fuel. White pail tests are made before the truck leaves the terminal and again before unloading at the airport. When the truck is unloaded into airport storage, the product is filtered through coalescer-separator filter into airport storage. Similarly, it is again filtered through coalescer-separator filters in out-of-airport storage into either refueler trucks or airport hydrant system and then through one more filter on the refueler or hydrant cart while refueling the aircraft. Where pipeline deliveries are made direct to airport storage, the product is almost invariably filtered through Fuller's earth prior to entering storage.

Importance of a Quality Assurance Program

Now, just why are we so concerned with such redundancy of filtration and why are we so concerned with all this cleanliness, brightness, and dryness?

First, the aircraft engine's fuel controller is a highly sophisticated and complicated piece of equipment subject to failure from fuel containing particulate matter, water, corrosive bacteria, or other contaminants. Similarly, the aircraft's fuel system consisting of valves, tanks, manifolds, etc., is prone to problems due to deposits left by large volumes of fuel handled over extended periods of time. Freezing of free water is an obvious hazard since fuel tank temperatures can drop as low as -38°F under some conditions after long "soaks" at altitude and under some operating conditions, tanks don't get much above freezing for months at a time. Dissolved water also comes out of solution as fuel temperature drops, causing further complications.

By and large, we are not concerned with petroleum additive contamination of jet fuel *per se.* Most gasoline dispersants, additives, pipeline corrosion inhibitors, anti-icing compounds, etc., however, are surface active agents or "surfactant" by nature. As such, they act as a disarming agent to water coalescer filters and render such filter elements useless for water removal and even tend to promote particulate matter migration through the filter. Fuller's earth filtration, therefore, is used primarily to remove these surfactants, and therefore, to protect the coalescer's ability to remove water. In ninety-nine cases out of a hundred, a distillate which shows a Water Separometer Index Modified (WSIM) of above 85 is a relatively surfactant-free fuel; and in the event it is carrying water, it should be able to be handled by the coalescer. You will note that I have said ninety-nine cases out of a hundred. As in everything else, it has been the one percent that has given us some real bad moments. Some household detergents, water soluble and introduced by river water getting into a barge of jet fuel, do not respond to the WSIM test criteria and will disarm a coalescer regardless of the WSIM figure.

Water in jet fuel and heavier distillates is the source of microbacteriological contamination. This growth is particularly dangerous to aircraft, not only from a fuel filter plugging standpoint, but from an aluminum corrosion standpoint. This corrosion can, and has caused, entire wing plank or spar or both replacement in transport, military, and private aircraft wings. Obviously, it cannot be tolerated from either an economic or safety standpoint, and it certainly should not be tolerated in fuel systems supplying power generation ground installations, diesel fuel installations supplying diesel engines, or for that matter, heating oil installations supplying oil burners.

Bacterial Contamination

All of the just-mentioned areas of activity have had their epidemics caused by bacterial contamination and these crises have been enormously expensive to those who have experienced them. Basically, there is no real reason to be plagued by any such phenomenon since the records are full of the illness, and the cure is elementary–good common sense design of tankage and piping and routine elementary good housekeeping. Bacteria require water in which to live; therefore, keep the system dry and you will have no bacterial problem. There are any number of additives which will help in the control of bacterial contamination, but no additives can do the job as well as keeping the system dry and clean. Tank cleaning should be done every two years at least and tank walls wiped down, by hand, with a solution of chlorox or hypochlorite solution and water. Never wash down a tank with water containing soap or detergent since these are surfactants and are next to impossible to flush out of the system. Adequate ventilation and protective clothing should be employed when handling hypochlorite solutions. All cylindrical tanks (lying on their sides) should be sloped at least 2 in. in 10 ft. so that water will collect in one end where it can be removed by a sump pump or drain, if above ground, and water should be removed daily. If possible, a sump should be placed at the low end of the tank so that water removal can be complete.

For tanks on end, conical bottoms with sumps and water draw-off are ideal, but if tanks are flat-bottomed with no sump, eternal vigilance and occasional fresh water flushing is the only answer. Floating suctions are a good investment any time, but are almost a necessity for the flat-bottomed tank. Floating suctions have been known to sink, so some method of checking the float is desirable so long as it does not present a static or sparking problem. It goes without saying that grease-lubricated plug valves should never be used since grease is a surfactant and will cause filter disarming.

What we are saying here is that there is nothing highly sophisticated nor complicated about an adequate and reliable fuel system–just a little good engineering, good plumbing, good housekeeping, and common sense.

I can go on at considerable length with reference to the pitfalls in the distribution system which can cause serious contamination problems, but at this point, it may illustrate my object better if we simply follow a tender of jet fuel from the refinery to the tail pipe of an aircraft and the various steps we take to protect and assure its quality at destination.

Quality Control System

Distribution System

Figure 1 is a typical distribution system. Jet fuel is manufactured at the refinery and held in refinery storage tanks until either tanker, barge, or pipeline space is available for shipment. The product must meet refinery specifications and must be certified by the refinery chemist before shipment. Included in this specification is a particulate matter specification of no more than 2 mg/gal by weight. Assuming that the product is carried by common carrier pipeline, it is accepted by the carrier, and after transmission it goes into pipeline company break-out storage. The pipeline company monitors the tender into its tank, running gravity, flash, and a Millipore monitor, using matched Millipores to determine not only the color of the monitor but the particulate matter expressed in mg/gal. In short, the pipeline company is charged with delivery of the same quality product that was tendered to them. These tests give them, within limits, the assurance that they have fulfilled their contract. When customer's terminal tanks are ready, the product is pumped from the pipeline break-out tank to the customer's terminal tanks. We now have the product in our hands, and we promptly quarantine and padlock the tank until a sample is taken, sent to Gulf Research & Development Company, and a complete type AB analysis is run. The results of the type AB analysis (Fig. 2) are wired to the regional technical service engineer who has responsibility for evaluating the analysis and either releasing the tender for use or rejecting it.

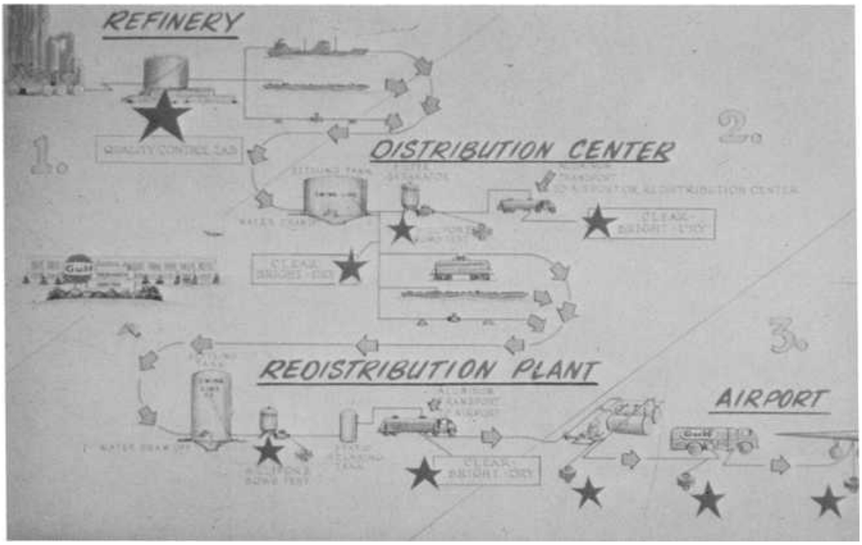
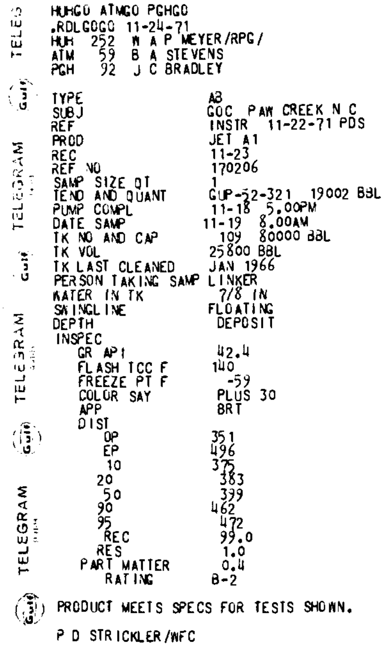


FIG. 1–*A typical distribution system.*



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HUHGO ATMGO PGHGO
.RDLGOGO 11-24-71
HUH  252  W A P MEYER/RPG/
ATM   59  B A STEVENS
PGH   92  J C BRADLEY

TYPE                     AB
SUBJ                     GOC  PAW CREEK N C
REF                      INSTR  11-22-71 PDS
PROD                     JET A1
REC                      11-23
REF NO                   170206
SAMP SIZE QT             1
TEND AND QUANT           GUP-52-321  19002 BBL
PUMP COMPL               11-18  5.00PM
DATE SAMP               11-19  8.00AM
TK NO AND CAP             109  80000 BBL
TK VOL                   25800 BBL
TK LAST CLEANED          JAN 1966
PERSON TAKING SAMP LINKER
WATER IN TK               7/8 IN
SWINGLINE                FLOATING
DEPTH                     DEPOSIT
INSPEC
    GR API                42.4
    FLASH TCC F          140
    FREEZE PT F            -59
    COLOR SAY             PLUS 30
    APP                   BRT
    DISI
       OP                351
       EP                496
        10               375
      20                  383
       50                 399
      90                 462
      95                  472
       REC                99.0
      RES                 1.0
    PART MATTER           0.4
       RATING            B-2

PRODUCT MEETS SPECS FOR TESTS SHOWN.

P D STRICKLER/WFC
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FIG. 2–*Results of the type AB analysis.*

As the product is called for by the customer, it leaves the terminal storage, is filtered through Fuller's earth to remove possible surfactants, and passes through coalescer-separator filter for water and particulate matter removal into the transport truck for delivery to the airport. If deliveries to the airport are on a more or less frequent and constant schedule, Millipore tests are run daily in order to monitor filter performance. Daily water checks and draining of tank sumps and filter sumps are made and permanently recorded. Before each truck leaves the loading rack, a white pail test is made and if pail shows water or bad color, the truck is not dispatched.

Airport Storage

On arrival at the airport, the truck driver and a representative of the customer perform another white pail test and a gravity check before unloading into customer storage. The product is then unloaded through a coalescer-separator filter into airport storage. Daily water checks, differential pressure check, and weekly Millipores are run on this filter as a performance monitor. The product is then passed from airport tankage through yet another coalescer into either the refueling truck or airport hydrant system. Airport refuelers or hydrant carts or both are also equipped with coalescer-separator filters as a final protection against contamination reaching the aircraft. All filters in the system are checked and logged daily for water and differential pressure. Excessive water or wide variations in differential pressure are red flags to trouble and are acted on promptly.

The previous operating procedures are performed by terminal personnel and supervisors trained in quality control and operating under the instructions contained in various applicable operating manuals, copies of which are shown in Fig. 2. Company-owned pipelines, tankers, barges, and refrineries all operate under similar manuals written by their own people.

I might add here that all airlines are required by the FAA to have similar operating manuals to which they adhere. The FAA makes periodic checks at airports to ensure adherence to airline operating manuals, and records of all items called for by these manuals must be on file, at the installation, at all times. An inspector can then easily determine when filter cartridge changes were made, what differential pressure readings were made, when and how much water was drained from tanks, filter housing, etc.

We, in our company, have a similar routine and a department to perform this inspection function. It is staffed by five field engineers who spend 100 percent of their time inspecting and checking all facilities, records, and people employed in the manufacture, transportation, storage, and end use of aviation fuels. These Field Engineers are equipped with several items of equipment with which they can check and trouble-shoot.

Quality Tests

Figure 3 is a Millipore monitor. This tool is used to monitor a running stream of product for both color and, if matched membranes are used, weight, as expressed in milligrams of particulate matter per gallon. It is probably the most

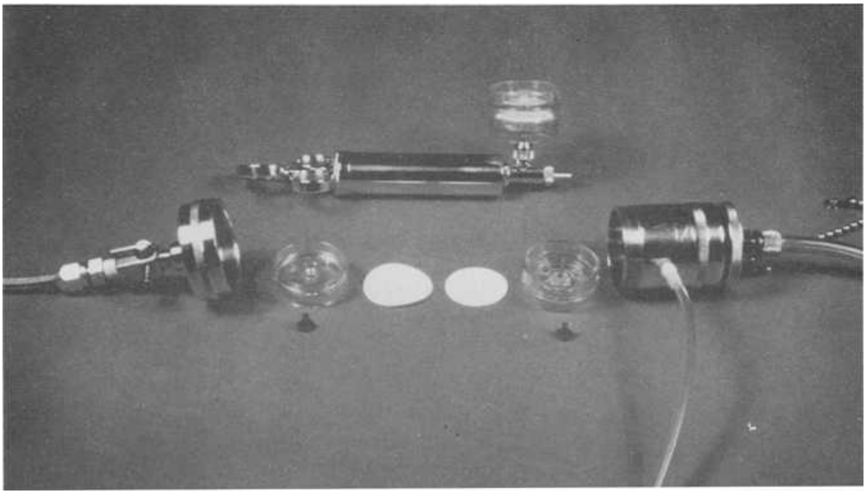

FIG. 3–*A Millipore monitor.*

valuable tool in the field engineer's kit. Figure 4 is a section of the membrane and holder in detail, and Fig. 5 is a display of membranes showing varying degrees of color experienced in the field. Figure 6 is an illustration of different colors and indicates the points at which we question a particular fuel and reject it as unsuitable for use in aircraft.

Figure 7 is a Thermo-Hydrometer used to identify quickly the type of fuel in question; that is, No. 2 Fuel Oil, kerosine, or gasoline. It, of course, measures specific gravity or API gravity or both. It is very useful in monitoring a pipeline cut at the interface of two different products or, in some cases, two different brands of the same product where the gravity varies.

Figure 8 is an instrument used to measure free water in jet fuel and is called an Aqua Glo. It can measure water at from 1.5 ppm and is an exceedingly useful tool. A measured sample of fuel is passed through a paper pad treated with sodium fluorescein on its upstream face. The pad is then compared with a fluorescing standard under ultraviolet light.

Figure 9 is illustration of a Surfactometer which can be used in the field as a fairly reliable indicator of the presence of surfactants. Its readings can be correlated with some degree of accuracy with those obtained from a WSIM laboratory instrument. It has a tendency to be "fail safe;" that is, a high reading indicating no surfactants is reliable—a low reading may or may not be, but warns the inspector to go for a more sophisticated laboratory determination. You will note that I have used the word "tendency." In the aviation industry, nothing should be taken for granted—everything is suspect!

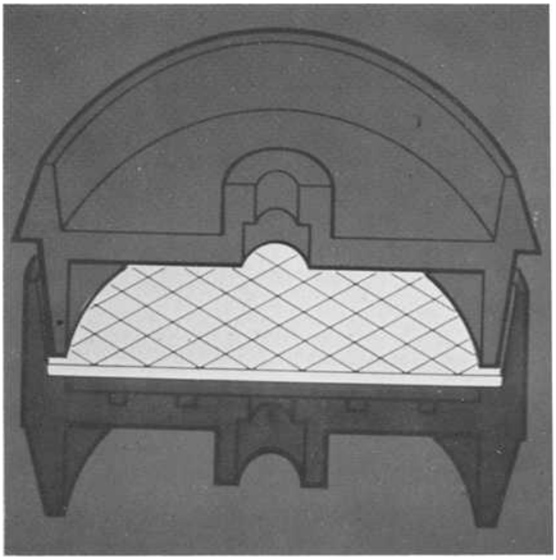

FIG. 4–*Section of the membrane and holder in detail.*

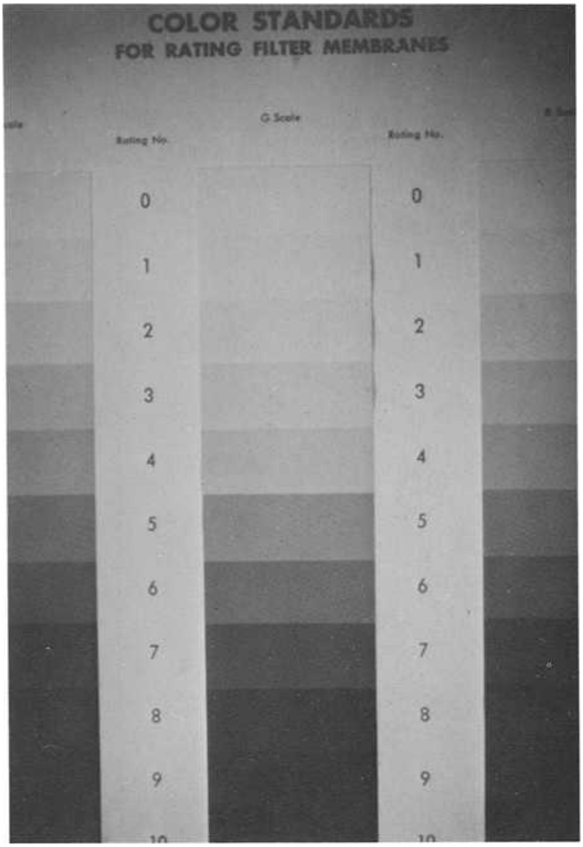

FIG. 5–*A display of membranes showing varying degrees of color experienced in the field.*

Figure 10 is the most important tool of all–a plain, everyday, run-of-the-mill, white bucket–preferably porcelain coated and absolutely clean. In the hands of an experienced man with good eyes, this ridiculously simple tool has probably saved more grief than all the other instruments combined. A white pail test should always be your final acceptance of product into your tanks. Figure 11 shows classic examples of soap contamination and microbial slime. Figure 12 illustrates floating suction, a daily check to see that it's still floating. Figure 13 shows the inside of a Fuller's earth filter (bag type). Note that casing is coated. Fuller's earth filters are normally located upstream of coalescer-separators since the latter will catch any Fuller's earth fines which might migrate downstream or be released downstream by a broken bag or cartridge. Fuller's earth is a surfactant remover and should not be used for removing large quantities of particulate matter since this has a tendency to coat the outside of the bags, thus preventing good penetration of the media by the surfactant. Fuller's earth

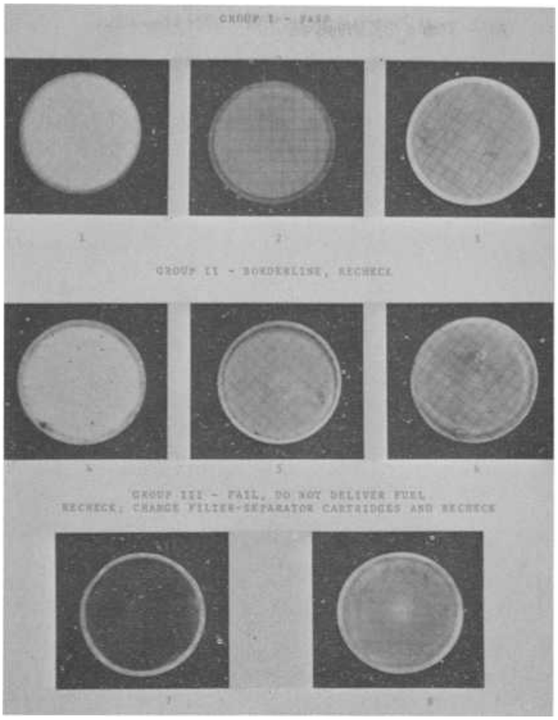

FIG. 6–*Illustration of different colors used to indicate the points of a particular fuel.*

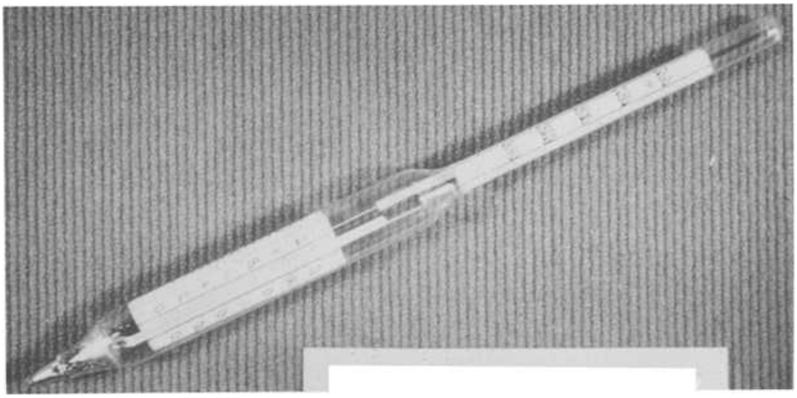

FIG. 7–*Thermo-Hydrometer.*

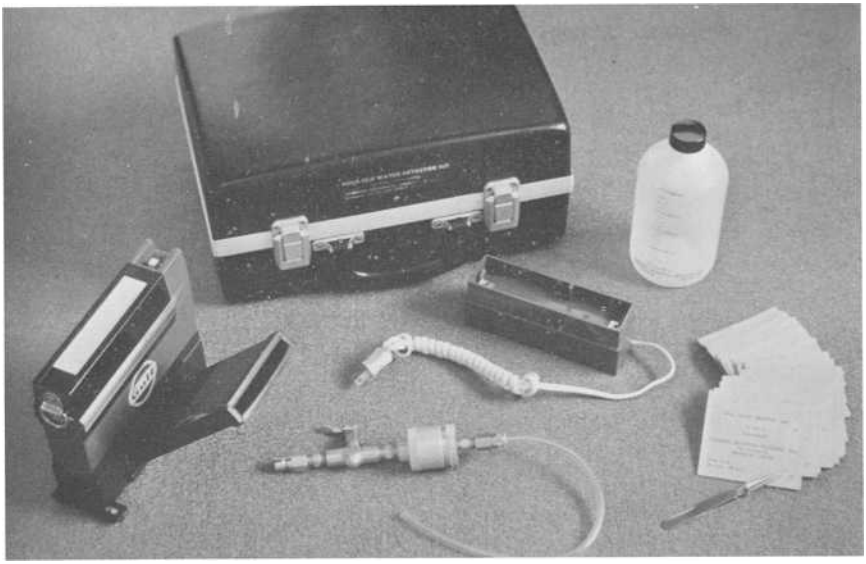

FIG. 8–*Aqua Glo.*

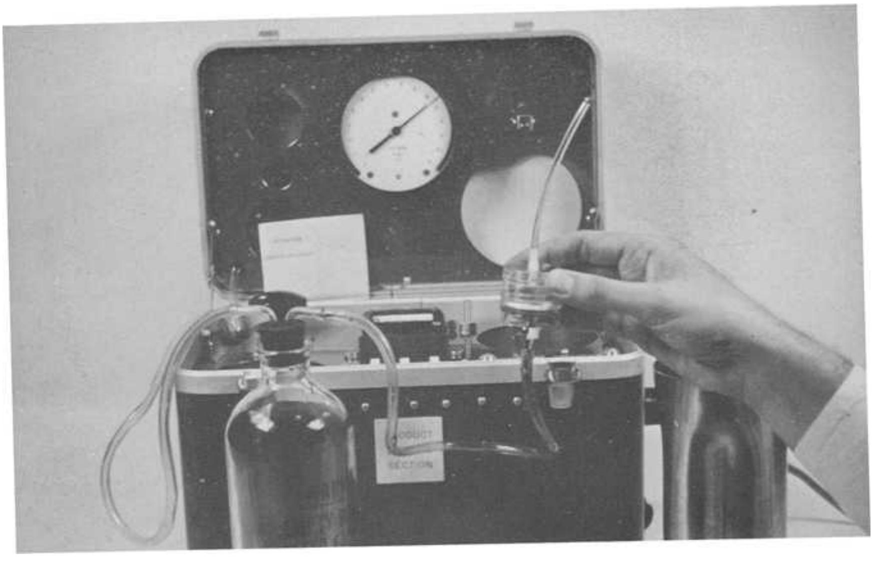

FIG. 9–*Surfactometer.*

FIG. 10–*White bucket.*

FIG. 11–*Soap contamination and microbial slime.*

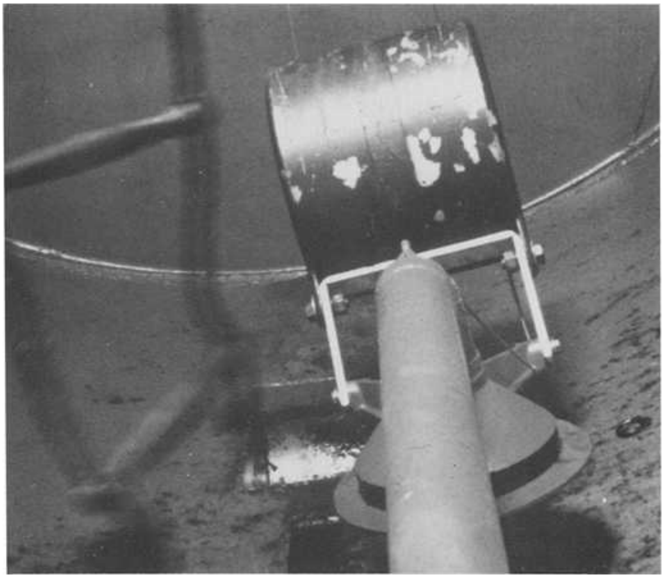

FIG. 12–*Floating suction.*

FIG. 13–*Inside of a Fuller's earth filter (bag type).*

cartridges are expensive and are time-consuming to change. Thus, if the product is heavily loaded with particulate matter, a prefilter should be installed ahead of the Fuller's earth. In these cases, a prefilter is an excellent investment. Figure 14 is a diagrammatic sketch of coalescer-separator filter.

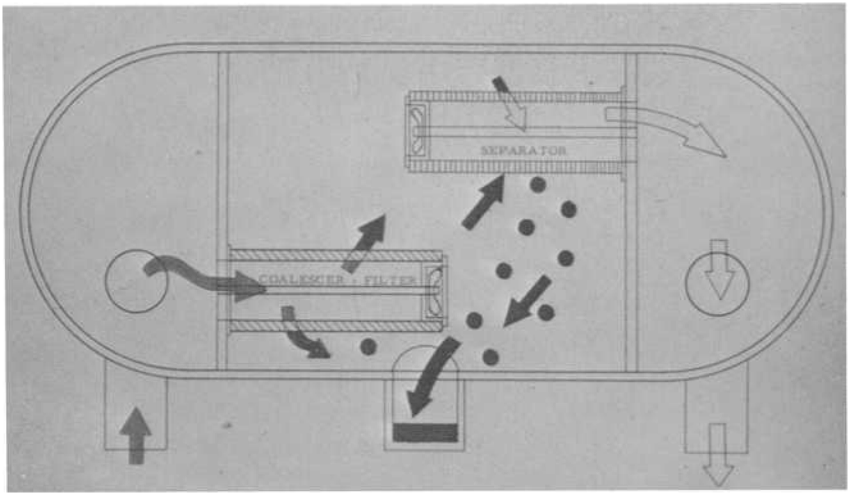

FIG. 14–*Diagrammatic sketch of coalescer-separator filter.*

Figure 15 shows the single element test rig. The coalescer element is the one with the "sock" on and the separator is pleated paper. Distillate and water enter the inside of coalescer cartridge and flow to the outside. Notice how water drops grow from smaller to larger and drop to bottom. When this coalescer and separator become "disarmed" from surfactant, water drops do not agglomerate and water stays in fine particles and in suspension, passing right through separator element. The surfactant also has a tendency to "lubricate" filter fibers allowing particles of dirt to pass. If the filter is already coated with particulate matter when surfactant hits, elements have a tendency to "unload." This can be noted from outside casing on differential pressure gauge which is one of the reasons differential pressure readings should be made and logged daily. Sudden differential pressure drop across filter also indicates ruptured or bypassing cartridges.

Figures 16 and 17 show the inside of Lockheed Jet Star Corporate Aircraft wing tanks' severe bacterial contamination with subsequent corrosion. A number of these wing planks had to be replaced.

There is absolutely no reason to permit a situation like this to exist. Good management and a little care can prevent it all.

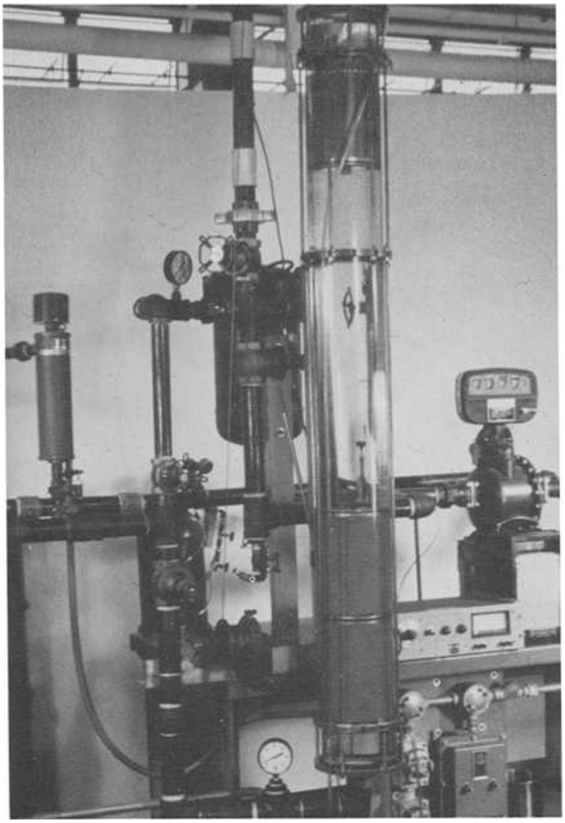

FIG. 15–*Single element test rig.*

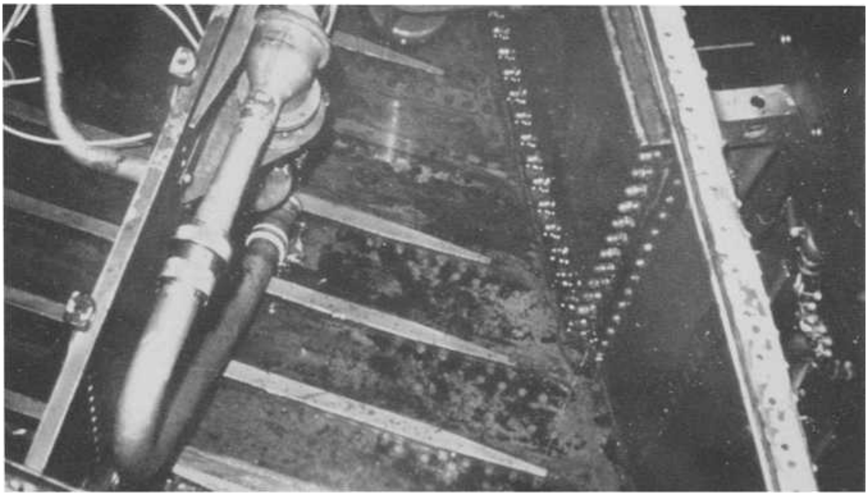

FIG. 16–*Inside of Lockheed Jet Star Corporate Aircraft wing tanks.*

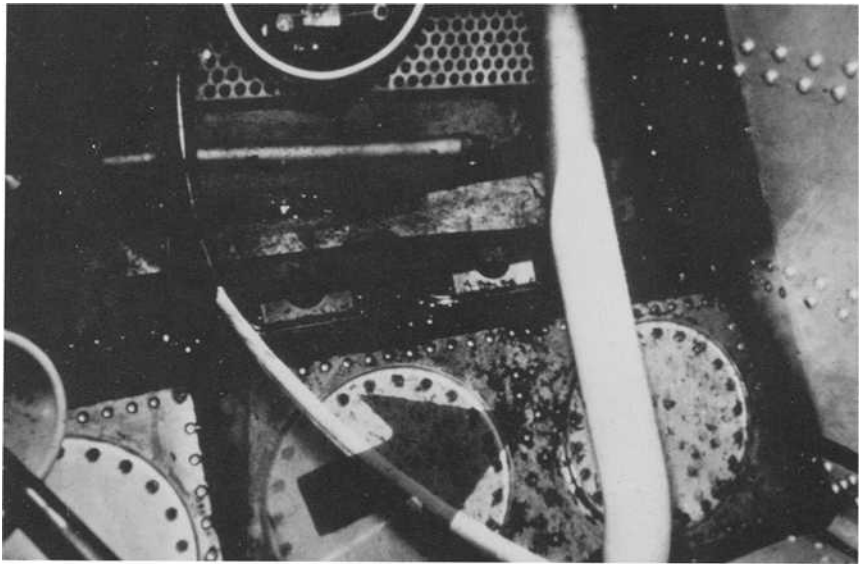

FIG. 17–*Inside of Lockheed Jet Star Corporate Aircraft wing tanks.*

Conclusions

Quality control of petroleum distillates intended for use in gas turbines provides definite benefits to the purchaser in the form of increased reliability of equipment, lower maintenance costs on equipment, and lower costs of fuel handling. Nothing in the quality control program must be sophisticated or expensive. The use of good engineering, good plumbing, good housekeeping, and common sense is all that is required.

R. W. Greenlee[1] *and R. N. Lucas*[2]

Electrical Purification of Gas Turbine Fuels

REFERENCE: Greenlee, R. W. and Lucas, R. N., "**Electrical Purification of Gas Turbine Fuels,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 73-104.

ABSTRACT: Transportation of low-ash fuels can so increase the levels of sodium and other ash-forming compounds as to cause serious corrosion and deposition problems in gas turbines burning these contaminated distillates. Electrostatic separation provides an advantageous alternative to more familiar methods of on-site fuel treatment used to restore fuel quality. The theory and applications of electrically effected phase separation are described in this paper. On-site purification by electrical means can achieve sodium levels of 1.0 to 0.2 ppm in candidate low-ash fuel oils. Sufficient data are presented to facilitate cost estimates for this approach to purification of gas turbine fuels.

KEY WORDS: gas turbines, corrosion, fuels, quality control, purification, desalting, washing, fuel transportation, fuel contamination, distillates, crude oil, residual oils, sedimentation, filtration, centrifuging, emulsions, coalescing, electrostatic separators

Hot corrosion and deposition problems experienced by gas turbines burning liquid fuels are attributed to contamination by minor amounts of certain metals—particularly sodium and vanadium—which form compounds during combustion that condense on metal parts in the hot gas path. These deposits promote accelerated corrosion, reduce power output, and may interfere with internal cooling of critical turbine parts. Increased expense for inspection and maintenance is required to ensure that the impurity-caused deposits do not force unscheduled outages resulting from component failure.

Fuel contamination problems with gas turbines burning high-ash oils have a rational solution in adequately removing the sodium (and other water-soluble) salts, and inhibiting the vanadium by chemical additives. Although suitable techniques have been known for a number of years, expected installation cost, operating expense, and various complications which could arise in operating a fuel purification system have limited commercial application of the conventional processes. Problems with fuel contamination, even though considerably lower levels of both sodium and vanadium are involved, have been more recently experienced by gas turbines burning low-ash fuels. While the conventional

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methods have been applied with reasonable success in some cases, there remains considerable reluctance to add purification equipment to the turbine installation. Aside from the cited objections, there is particular resistance to making provision for on-site restoration of contaminated fuel to purity levels available at the refinery.

The petroleum industry produces fuel oils having very low levels of contaminants through the use of electrical separation equipment. The authors believe that this established electrical separation technology provides an alternative to more familiar methods of on-site fuel treatment which offers sufficient technical and economic advantage to meet previous objections. In this paper, the petroleum-refinery technique of electrostatic phase separation is considered in detail. The nature and source of important impurities in distillate gas-turbine fuels have been reviewed, and the record of their successful removal by electrical means in various refinery processes has been traced. The operating principles of electrostatic separation processes have been examined and compared with those of alternate processes. Finally, several specific examples of electrostatic separation process applications to on-site purification of three classes of gas turbine fuels have been cited.

Electrostatic Purification in the Petroleum Industry

Besides hydrocarbons, crude oil has a variety of organic and inorganic components, some of which can be identified as impurities representing the source of corrosion and deposition problems when derived fuels are burned in gas turbines. The major portion of produced water and associated inorganic materials are separated from the crude petroleum in an oil field operation called "dehydration"; most of the remaining water-soluble inorganic components, principally sodium chloride, are washed from the crude oil in a refinery operation called "desalting." Refinery distillation processes concentrate any inorganic materials not removed by desalting into heavy oil fractions which become major components of 4-GT class fuels. Distillation, however, is not able to segregate organic impurities (such as sulfur compounds and organic acids) into particular distillate streams. Instead, these impurities (together with small amounts of water and vanadium) are fractionated into the various products which become the major components of distillate gas turbine fuels. Reduction of these organic impurities to levels appropriate for use in distillate-fuel gas turbines often involves "scrubbing" the raw refinery distillates with reactive chemicals such as aqueous solutions of sodium hydroxide. Such process steps must be followed by careful separation of the aqueous phase from the hydrocarbon stream if low levels of metallic contaminants, particularly sodium, are to be maintained. Such phase separations in refineries—from desalting through all phases of distillate treating—are almost entirely effected by electrical treating methodology.

Electrostatic phase separation, initially applied in 1909, was developed to resolve connate water from its natural emulsified form in heavy petroleum oils (sp gr 0.985) produced in the San Joaquin Valley of California. The techniques were subsequently (1935) modified to facilitate removal of deposit and corrosion-causing inorganic components, primarily sodium salts and particulate matter, from crude oils charged to petroelum refineries; additional modifications (1950) extended refinery applications of electrostatic techniques to the removal of organic impurities (compounds of sulfur, nitrogen, and oxygen) from petroleum distillates.

Current refinery desalting operations routinely reduce the sodium content of crude oil to the 3 ppm level in a single stage, and below 1 ppm in two stages of electrically-aided separation. World-wide, more than 500 electric desalters are in operation, processing 25 million barrels of crude oil per day (B/D). A typical unit capacity is 100 000 B/D (3000 gal per min (gpm)) although units are conventionally furnished with capacities ranging from 20 000 B/D (600 gpm) to 200 000 B/D (6000 gpm). About 350 electric distillate treaters are in operation, with capacities typically varying from 2000 B/D (60 gpm) to 40 000 B/D (1200 gpm). This equipment, processing a daily total of 3.5 million barrels of distillate, routinely reduces sodium level below 1 ppm.

Although the petroleum industry extensively uses electrostatic phase separation equipment to achieve low levels of contamination in various crude oils and distillates, certain finishing operations and, more significantly, product transportation can substantially increase the contamination levels. Further refinery steps to enhance product purity would be unlikely to compensate for the contamination experienced by the fuels after they leave the refinery.

Significant Impurities in Gas Turbine Fuels

The adverse effects on gas turbine performance which are caused by various impurities in candidate fuel oils have been recognized for several years and have stimulated interest in the selective control of certain critical fuel oil properties. The success of gas turbine applications in military and commercial aircraft can be attributed in part to use of fuels characterized by virtual freedom from these recognized impurities. Unfortunately, this cleanliness is accomplished by specialized methods which substantially increase the cost of the fuel. These include severe restrictions upon the initial distillation and subsequent processing steps, followed by careful control of the entire fuel handling system. Such means have been found too expensive for fuels intended to compete in the industrial and utility markets.

In order to provide more economical fuels which will still allow dependable operation and long life of gas turbines in non-aviation applications, quality limits for various gas turbine fuels are provided by general industry standards (for example, ASTM Specification for Gas Turbine Fuel Oils (D 2880-71)), specifications of individual turbine manufacturers, and certain users' requirements (for example, military specifications). For ease in comparing these quality limits with the more restrictive aviation fuel specifications, characteristic properties of typical industrial gas turbine fuels have been summarized in Table 1. The fuels have been classified, for convenience, into those of high, medium,

TABLE 1—*Selected characteristics of gas turbine fuels.*

Identification		Physical Properties			Oleophilic Materials				Oleophobic Materials			
Specification	Source	Minimum Gravity, °API	Viscosity, CS at 100°F	90% Distillation Temperature, °F	Acid[a] Cu.No.	Mercaptan[b] S, ppm	Sulfur, %	Vanadium, ppm	Na+K, ppm	Ca, ppm	H_2O, ppm	Ash, ppm
					Aviation Fuels							
522-F[c]	Manuf[g]	37	. . .	. . .	1	50	0.30	. . .	. . .	. . .	. . .	. . .
JP-5	MIL	35	. . .	464	1	10	0.40	. . .	. . .	. . .	. . .	. . .
Jet A	Refinery	42	. . .	472	1	10	0.05	. . .	. . .	. . .	. . .	. . .
					High Volatility Fuels							
1-D	ASTM	. . .	2.2	550	3	. . .	0.50	. . .	. . .	. . .	. . .	100
1-GT	ASTM	35	2.5	550	. . .	. . .	0.50	2.0	5.0	5.0	500	100
532A[c]	Manuf	. . .	. . .	350	1	50	0.30	. . .	. . .	. . .	. . .	. . .
Kerosine	Refinery	41	1.6	477	. . .	. . .	0.01	0.1	0.1	0.1	. . .	. . .
					Medium Volatility Fuels							
2-D	ASTM	. . .	4.3	640	3	. . .	0.5	. . .	. . .	. . .	500	100
2-GT	ASTM	30	4.3	640	. . .	. . .	0.5	2.0	5.0	10.0	500	100
527C[c]	Manuf	. . .	3.0	675	1	. . .	1.0	0.1	0.2	0.1	100	50
G272[d]	Manuf	. . .	11.0	657	. . .	. . .	1.3	0.5	0.5	. . .	50	50
GE41047D[e]	Manuf	. . .	5.8	. . .	. . .	. . .	. . .	2.0	5.0	10.0	1000	100
F24397	MIL	27	10.0	765	2	. . .	1.3	0.5	. . .	. . .	200	100
MGO[d]	Refinery	36	2.7	560	. . .	. . .	0.3	0.1	0.1	. . .	100	100
No. 2	Refinery	32	2.9	592	. . .	. . .	0.2	0.1	0.5	0.1	. . .	. . .

					Low Volatility Fuels							
3-GT	ASTM	. . .	1500.0	. . .	. . .	. . .	. . .	2.0	5.0	10.0	10000	300
539[c]	Manuf	. . .	11.0	. . .	. . .	. . .	1.3	0.2	0.6	. . .	100	100
GE41047D[e]	Manuf	. . .	1500.0	. . .	. . .	. . .	. . .	2.0	5.0	10.0	10000	300
West.26717[f]	Manuf	26	45.0	675	. . .	. . .	2.0	2.0	2.0	10.0	. . .	100
MDO[d]	Refinery	30	6.2	728	. . .	. . .	1.0	1.0	0.8	. . .	8000	50
ESSO[d]	Refinery	. . .	18.0	. . .	. . .	. . .	0.2	0.3	1.5	. . .	1500	60
Crude oil	Libya	39	5.7	. . .	. . .	. . .	0.4	3.0	5.0	. . .	. . .	25
Crude oil	Nigeria	38	. . .	. . .	. . .	. . .	0.2	3.0	. . .	. . .	. . .	. . .
Crude oil	Sumatra	38	14.0	. . .	. . .	. . .	0.1	0.7	7.8	2.0	2500	20
Crude oil	Arabia	33	8.2	. . .	. . .	. . .	1.3	12.0	1.0	. . .	. . .	270

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[a] ASTM Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test (D 130-68).

[b] ASTM Test for Mercaptan Sulfur in Aviation Turbine Fuels, Color Indicator Method (D 1219-61).

[c] Pratt & Whitney Aircraft Specification.

[d] Specification cited by Brubaker and Calvino [*18*].

[e] General Electric Company Fuel Specification.

[f] Westinghouse Electric Company Fuel Specification.

[g] Manuf = manufacturer.

and low volatility [*1*][3]. The quality limits have been grouped according to whether specifications apply to the physical properties, the amount of oleophilic (largely organic) impurities, or the oleophobic (inorganic) impurity content, as explained later.

Characteristic Properties

The selected physical properties—API gravity, viscosity, and 90 percent distillation point—are determined both by characteristics of the precusory crude oil and by the refinery fractionation process. The temperature at which 90 percent of the distillate becomes a vapor is a convenient physical index of its cost. The fuel viscosity affects pumping and related fuel handling problems, while the density (together with the viscosity) largely determines the ability of the fuel to retain water and other inorganic impurities.

The oleophilic impurities mentioned have their origins in the precursory crude oil; the amounts found in a particular distillate are completely determined by the initial distillation and the subsequent refining steps. Organic acids (principally naphthenic acids, mercaptans, and phenols) can promote corrosion in the fuel handling system and will react with certain metals to create oil-soluble metal salts. These acids, together with sulfur compounds and unsaturated hydrocarbons, can promote the formation of gums and sludge in the fuel oil. Although sulfur alone is not a major obstacle to successful gas turbine operation, air pollution legislation may restrict the allowable content of sulfur in the fuel. Vanadium occurs in petroleum largely in oil-soluble forms, for example, vanadium porphyrins. Vanadium reacts during fuel combustion processes to form metal oxides which, either alone or in combination with other ash ingredients, are corrosive to metal surfaces within the hot gas path. The levels found in distillates depend on properties of the original crude oil, the distillation temperature, and the subsequent refining steps. By suitably restricting the distillation temperature and by employing more expensive refining processes, substantially all of the vanadium can be eliminated from distillates.

The inorganic impurities—inorganic solids, soluble salts, and water—are of predominant importance to ash deposition problems and corrosion which attend the burning of distillate fuels in gas turbines. Ash deposits are largely metal oxides and sulfates formed from metal-containing impurities during combustion. Oxides of sodium and potassium, reacting with sulfur and vanadium oxides which are also combustion products, form molten ash deposits which are corrosive by one or more mechanisms. Water, harmless in the combustion gases, may promote microbiological growth in stored fuels which can clog filters and cause corrosion of the fuel delivery system.

Sources of Impurities

It is convenient to associate the oleophilic impurities found to be present in distillate gas-turbine fuels with their major source, the precursory crude oils. By

[3] The italic numbers in brackets refer to the list of references appended to this paper.

contrast, the inorganic contaminants do not stem from connate sources, but are *primarily* introduced during the refining process and the subsequent transportation steps. The inorganic materials still present in crude oil as received at the refinery are largely removed by the electrical desalting process; during the subsequent crude oil distillation step, most of the remaining inorganic impurities (including sodium) are concentrated into the residual fractions. Asphaltenes and all of the debris from incomplete desalting (except chloride and water) are generally not volatile enough to be distilled into the lighter fractions, but they are fairly easily entrained into lower distillate fractions such as gas oils. Unfortunately, organic compounds of sulfur and oxygen found in crude oils have a range of volatilities which place them in substantially all distillates. Thus, the expected impurities in petroleum distillates include organic acids (principally oxygen compounds), sulfur compounds, vanadium compounds, and water.

Efficient elimination or conversion of the organic impurities–which are responsible for the objectionable odor and color of raw distillates, for their corrosive nature, and for storage instability–is the goal of refinery distillate treating processes. Certain of these compounds (naphthenic acids, mercaptans, and phenols) are sufficiently acidic that they can be removed by the action of alkaline reagents. Other sulfur compounds, basic nitrogen derivatives, certain oxygen compounds, some of the asphaltenes and porphyrins, and most of the other compounds which cause storage instability, are removed by the actions of acidic reagents–the acid-treated distillates being subsequently neutralized with aqueous caustic solution. In some cases, sulfur-containing compounds are more advantageously converted to less offensive sulfur compounds rather than removed. Such "sweetening" processes are either carried out in a caustic alkaline environment or are followed by an alkaline wash. Copper and lead sweetening agents are also used, and the undesirability of these elements in distillate fuels is well established. However, the product distillates are almost invariably washed with water to reduce copper and lead concentrations below the ppm level. In summary, removal or conversion of these organic impurities by various refining processes involves introduction of aqueous reagents, which results in water imbibition or sodium contamination or both.

Following each of these chemical treatment processes, the refined distillates are ordinarily processed to remove free and suspended water, with the objective of providing a final product that is "clear and bright." This is often accomplished by processing the distillate through a salt dryer–a bed of solid sodium chloride–which desiccates the hydrocarbon. Sodium compounds can be introduced into the distillate by this drying process.

All of these distillate refining processes offer the possibility of contaminating the fuel with sodium and certain other metals. In spite of these numerous opportunities for contamination, the wide-spread refinery use of electrostatic precipitation consistently maintains the sodium level in treated distillates below 1.0 ppm up to the final drying stage. Thus, most of the sodium in excess of 1.0 ppm observed in delivered turbine fuel probably results from contamination during transportation (especially from shipboard bilges); however, contributions from the salt drying step cannot be excluded. Essentially all of the calcium, potassium, water, and ash contamination occurs in the same way, reflecting post-refinery handling of the fuels.

Refinery Processes for Impurity Removal

It appears that most of the inorganic impurities found in distillate fuels result from contamination encountered during transportation from the refiner to the user, especially from contamination by seawater. However, it is instructive to examine more closely the refinery process for impurity removal to establish two points: (1) the extent to which contamination of distillate products by refinery "treating solutions" can be expected to impose limits on fuel oil specifications, and (2) the impurity levels routinely achieved by refiners through the use of electrostatic phase separators on refinery streams which are candidate gas turbine fuels.

Petroleum is a complex blend of hydrocarbons along with smaller amounts of substantially oil-soluble compounds of sulfur, nitrogen, oxygen, and metal complexes. All crude oils contain sulfur in one or another form, including the element itself. The sulfur content may range from 0.1 percent up to 5 percent by weight. But since the sulfur atoms are characteristically small parts of relatively large hydrocarbon-derived molecules, compounds containing sulfur constitute as much as one third of some crude oils. Like sulfur, nitrogen is found in all crude oils, in amounts ranging from 0.1 to 2.5 percent. Including the attached hydrocarbon structures, nitrogen compounds can represent as much as one fifth of the crude oil in some cases. The principal oxygen-containing compounds found in crude oils are carboxylic acids and phenolic compounds; amounts of the latter are much increased during certain refinery processing steps. Except for water-soluble salts, especially those of sodium and calcium, important parts of the metals found in crude oils (notably nickel, iron, and vanadium) are combined in stable organometallic complexes called porphyrins. These are understood to include remnants of biologically produced chelate compounds, such as chlorophyll or hemoglobin, present in the hydrocarbon source material.

It is evident that the major refinery processes are directed to separating and converting hydrocarbons into distillate fractions which can be efficiently used as fuels. A large part of the total refining effort is directed at removing or modifying the extraneous nonhydrocarbon materials. This is done largely to reduce their adverse effects, including unpleasant odors, corrosive activity toward metals, or storage instability, on the finished products of the refinery. The objective of such refinery efforts, often called "treating," is to eliminate or convert these extraneous materials. In this way, the finished product will not only be satisfactory to an immediate customer, but will also have a long-term storage stability.

Numerous processes have been developed through the years for such treating of petroleum distillates. Methods which have survived in common use are characteristically those which are easily adapted to various crude oil stocks, require inexpensive chemicals, operate in a continuous mode, and have effluents which cause few disposal problems. The process known as "electric desalting" [2] may be considered as the model for all treating processes. Fresh water, certainly a cheap chemical, is first intimately mixed into crude petroleum to contact the finely dispersed inorganic material, and the resulting mixture is then separated through the combined influence of electrostatic and gravitational fields. The separated phases are: (*a*) a refinery charge stock substantially purified of inorganic impurities, and (*b*) a predominately aqueous effluent containing the impurities. The distillate treating processes use, as chemical reagents, caustic and acid (and, occasionally, oxidizing agents) in addition to water. These aqueous phase components extract and modify the materials which adversely affect the utility, stability, and aesthetic appeal of refinery products. The effectiveness of treating processes of this kind [3] is enhanced by the application of a high potential electric field to separate the treating reagent or process by-products from the bulk hydrocarbon phase. To illustrate the wide-spread utilization of electrical phase separation, several examples have been selected. In each case, oils which have been used as gas turbine fuels are cited to provide clear indications of the utility of similar equipment to a fuel consumer.

Desalting

In addition to the oleophilic impurities, crude oils received at a refinery always contain water, inorganic salts, and finely divided inorganic solids dispersed in the continuous oil phase. To minimize the corrosion and fouling deposition which would accompany attempts to process oils containing these materials, standard refinery practice is to subject all crude oils to one or two stages of water washing and electrical separation.

The electrical desalting process, as illustrated in Fig. 1, is relatively simple. To crude oil at an appropriate temperature, fresh water is first added and then uniformly dispersed throughout the contaminated oil. The resulting dispersion of fresh water, brine, and particulate matter is then exposed to a high potential

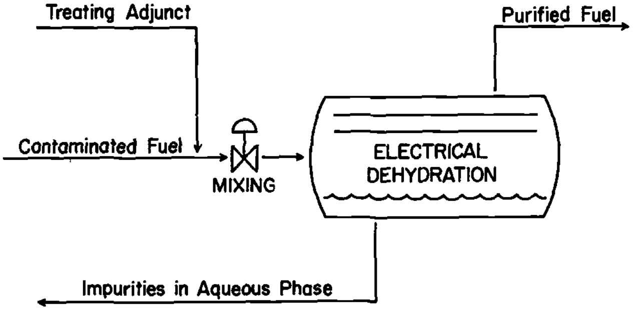

FIG. 1–*Electrostatic purification system.*

electric field which promotes coalescence of the dispersed water droplets, after which enlarged droplets gravitate from the oil. To the extent that the water droplets make contact with and extract the crude oil contaminants, separation of the water phase purifies the oil.

In many refineries, two stages of counter-current water washing are used to achieve very low levels of impurities in crude oils. The data of Table 2 illustrate results which can be accomplished by this process on crude oils which have been used as gas turbine fuels.

Distillate Treating

As previously indicated, substantially all of the oleophobic impurities (except water) are excluded from raw distillates by the refinery fractionation steps. The organic impurities, to varying degrees, are distilled into the several fractions. Efficient elimination-conversion of these oleophilic but nonhydrocarbon compounds are the goals of all distillate treating processes.

Except for hydrogen treating, the more common distillate treating processes can be divided into three major classes according to the particular treating reagents employed. Sulfuric acid is used to reduce the sulfur content of distillates, to extract the instability-promoting components of certain fuels and to remove nitrogen and metal-containing compounds from process feedstocks. In every case, acid-treating must be followed by an alkaline neutralization step (or an adsorption step) to remove trace amounts of acidic products. Dilute caustic (NaOH or KOH solution) is used to extract acidic components, that is, hydrogen sulfide, naphthenic acids, and the more acidic (or less oil-soluble) mercaptans from distillates. More concentrated caustic solutions are required to extract the less acidic organic materials, such as phenols (for example, cresylic or "tar" acids); water is also effectively removed by concentrated caustic. In other processes, mercaptans of low acidity are generally converted to disulfides which either remain in the oil or are extracted by sulfuric acid. Water is also used as a reagent to remove small amounts of metal contaminants, particularly residual caustic and trace metals, from prior treatments.

The distillate treating processes which utilize electrical phase separation are similar to the desalting process. As illustrated in Fig. 1, a chemical reagent is added to the raw distillate, dispersed by a mixing device to promote good contact with the distillate, and then separated with the aid of an electric field which promotes coalescence of the dispersed reagent droplets.

Summarized in Table 2 are results selected from installations processing various distillates which have been used as gas turbine fuels. Aviation fuels were selected for the first two examples, a 1-D diesel and a kerosine were selected for two examples of high volatility fuels, a 2-D diesel and a No. 2 fuel were selected to illustrate processing medium volatility distillates, and one heavy oil was selected to illustrate processing low volatility fuels.

Aviation Fuels—A Gulf Coast refinery produces a raw distillate which is suitable for use as JP-5 fuel except that the levels of organic acidity and mercaptans are excessive. The organic acidity, measured in terms of neutrali-

TABLE 2–*Refinery products from electrostatic treating.*

Identification		Physical Properties			Oleophilic Materials				Oleophobic Materials			
Specification	Source	Minimum Gravity, °API	Viscosity, CS at 100°F	90% Distillation Temperature, °F	Neut.[a] No.	Mercaptan[b] S, ppm	Sulfur, %	Vanadium, ppm	Na + K, ppm	Ca, ppm	H_2O, ppm	Ash, ppm
					Aviation Fuels							
JP-5	Refinery	44.0	1.5	460	0.006	1	. . .	. . .	1.0	. . .	. . .	. . .
Jet A	Refinery	43.0	1.4	420	0.002	4	. . .	. . .	0.5	. . .	10	. . .
					High Volatility Fuels							
Kerosine	Refinery	41.0	1.6	. . .	0.02	. . .	0.009	. . .	0.1	. . .	10	. . .
1-D	Refinery	36.0	2.1	580	0.02	. . .	. . .	. . .	0.3	. . .	10	. . .
					Medium Volatility Fuels							
No. 2	Refinery	32.0	2.3	. . .	. . .	. . .	. . .	. . .	1.0	. . .	30	. . .
2-D	Refinery	33.0	2.3	635	0.013	. . .	. . .	. . .	0.8	. . .	30	. . .
					Low Volatility Fuels							
Fuel oil	Refinery	28.0	16.0	. . .	. . .	. . .	. . .	. . .	1.0	. . .	90	. . .
Crude oil	Libya	37.7	52.0	. . .	0.02	. . .	0.30	1.2	0.2	. . .	1000	119
Crude oil	Nigeria	39.2	36.0	. . .	. . .	. . .	0.11	0.2	0.2	. . .	1000	. . .
Crude oil	Arabia	35.0	44.0	. . .	. . .	. . .	0.17	11.0	0.8	. . .	1000	. . .

[a] ASTM Standard Method of Test for Neutralization Number by Color Indicator Titration (D 974-64).
[b] See footnote[b], Table 1.

zation number (conventionally measured by ASTM Test for Neutralization Number by Color Indicator Titration, D 974-64), is reduced by washing with dilute sodium hydroxide, while the mercaptans are converted to disulfides by a copper sweetening process. Acid and copper carry-over from the sweetening process is controlled by washing the sweetened distillate with dilute sodium hydroxide. In this case, 43 000 B/D of distillate at 110°F is mixed with 0.25 percent of 6° baumé (Bé) caustic which is later separated in a 10-ft-diameter electric treater. The neutralization number is reduced from 0.09 to 0.006 and the sodium content is less than 1.0 ppm. After the copper sweetening process, the distillate at 100°F is washed with 0.25 percent of 2° Bé caustic which is then separated in a 10-ft-diameter electric treater. The product oil contains less than 1.0 ppm of sodium and less than 0.15 ppm of copper.

A mid-continent refinery produces a raw distillate which is suitable for use as Jet A fuel except that the levels of organic acidity and mercaptans are too high. The oganic acidity is reduced by washing with dilute caustic while the mercaptans are converted to disulfides by a lead sweetening process. Metal carry-over from the "Doctor" sweetening process is reduced by washing the product distillate with water. In this example, 15 000 B/D of distillate at 135°F is mixed with 0.12 percent of 5° Bé caustic which is then separated in an 8-ft-diameter electric treater. The neutralization number is reduced from 0.02 to below 0.002 and the sodium content is maintained below 2.0 ppm. The sweetening process reduces the mercaptan content from 44 to 2 ppm; the product is "doctor sweet." The product distillate is washed with 5.0 percent fresh water; the sodium carry-over is reduced below 0.5 ppm, there is no detectable lead content, and the free water carry-over is maintained below 10 ppm.

High Volatility Fuels—A southern refinery produces a virgin kerosine which has excessive amounts of organic acidity and sulfur. The 41° API distillate is contacted with 93 percent sulfuric acid to reduce the sulfur content; the spent acid, now containing the sulfur reaction product, is separated from the oil in an electrostatic treater. The acid-treated oil is then washed with dilute sodium hydroxide to remove residual acidity and is finally washed with water to reduce the sodium level. Sulfuric acid at the rate of 8 lb/bbl is mixed with 20 000 B/D of kerosine at 100°F. This dispersion is then separated in a 10-ft-diameter electrostatic treater; the sulfur is reduced from 367 to 94 ppm. Dilute caustic is mixed into the oil and separated in a second 10-ft-diameter electric treater; the neutralization number is reduced from 0.07 to 0.02. The distillate is then washed with 8 percent fresh water which is separated in a third 10-ft-diameter treater; the product oil contains less than 0.1 ppm of sodium and less than 10 ppm of free water at 100°F.

A Gulf Coast refinery produces a distillate which is suitable for use as a 1-D diesel fuel except that the level of organic acidity is high. Because of this, the oil will promote corrosion and will retain suspended moisture (haze). Reduction of the organic acidity can be accomplished by contacting the oil with dilute caustic to saponify the organic (naphthenic) acids and then separating the resulting sodium naphthenates and excess caustic from the oil. To achieve adequate reduction of the organic acidity, the neutralization number specification of 0.05 is imposed; to ensure adequate removal of the reagent and the reaction products, a sodium limitation of 1.0 ppm is also specified. These twin limits are achieved by very intense mixing of the caustic into the oil to react with and extract the organic acids, followed by substantially complete separation in an electric field of the spent caustic and the reaction products from the distillate. Typical results reveal a neutralization number reduction from 0.08 to 0.02 and a sodium carry-over of 0.3 ppm, with less than 10 ppm of free water in the treated oil.

Medium Volatility Fuels–A mid-continent refinery produces a 32° API blend of coker and catalytically cracked distillates which is suitable as a No. 2 fuel oil except that storage stability is unsatisfactory due to an excess of organic acidity (phenols and thiophenols). This weak organic acidity can be extracted by means of strong (50° Bé) caustic. Some 16 000 B/D of blended distillate at 80°F is first charged to a 12-ft-diameter electrical dehydrator which lowers water content from 150 down to 30 ppm. Approximately 5 percent by volume of strong caustic is mixed into the distillate which is then separated in a 10-ft-diameter electrostatic treater. The phenols are reduced from 300 to 100 ppm and the thiophenols are reduced from 98 to 9 ppm, which adequately improves storage stability. The distillate is then charged to a third electrostatic treater which reduces the sodium content below 1.0 ppm.

A Gulf Coast refinery produces a 33° API virgin distillate which is suitable for use as a 2-D fuel except that there is an excess of organic acidity, principally from naphthenic acids. These somewhat stronger organic acids can be extracted by means of weak caustic. Approximately 23 000 B/D of straight-run distillate at 188°F is contacted with 0.5 percent of 5° Bé caustic and is then charged to a 10 by 17-ft horizontal electrostatic separator. The neutralization number of the distillate is reduced from 0.25 to 0.013, while the sodium carry-over is maintained below 0.8 ppm; there is approximately 30 ppm of free water in the oil. One measure of the effectiveness of this caustic wash is the observed increase in interfacial tension. Against water, the interfacial tension of the raw distillate is 27 dynes/cm; the value for the treated distillate is 43 dynes/cm.

Low Volatility Fuels–A mid-continent refinery produces a light cycle oil which could be used as a heavy distillate fuel except that the levels of phenols and thiophenols are high enough to preclude satisfactory storage stability. These levels are reduced by extracting with strong (46° Bé) caustic. Heavy distillate, in the amount of 5000 B/D, is charged at 80°F to a 6-ft-diameter dehydrator which reduces the water content from 700 to 90 ppm. The dehydrated distillate is contacted with strong caustic and separated in a second 6-ft-diameter treater; the phenols are reduced from 160 to 40 ppm while the thiophenols are reduced from 30 to 2 ppm. The product oil is charged to a third electrostatic dehydrator which reduces the sodium content below 1.0 ppm.

Finishing and Additives

As previously indicated, the treated distillates contain a small amount (10 ppm) of free water as well as being saturated with dissolved water at prior process temperature. In addition, there are modest amounts of impurities in the distillates which have not been extracted or converted in the treating processes. Various drying steps are used to remove free and dissolved water to produce a product which is "clear and bright." Chemical oxidation inhibitors and dispersants may be added to the oils to combat the effects of these oleophilic impurities. Unless the chemical additives contain harmful amounts of metals, the only refinery finishing operation which could potentially *add* contaminants is a desiccation process called "salt drying."

Salt-dryer desiccant systems are widely used in the petroleum refining industry to reduce the "haze point" of distillates, that is, to remove sufficient dissolved water so that cooling which occurs during transportation will not cause water to precipitate as a fine water-in-oil dispersion. There is relatively little information [*4,5*] in the open literature concerning the design, operation, or expected performance of such units. However, the usual salt dryer consists essentially of a steel tank enclosing a bed of rock salt. As fuel containing water moves through the salt, the oil is desiccated and brine is formed which percolates, as brine droplets, to the bottom of the tank. This brine is withdrawn manually or automatically and salt is periodically replaced. Except for these two operations, salt dryers require little attention or monitoring. It is reported that a salt dryer is typically expected to desiccate the oil to a final haze point 25 to 30°F below the operating temperature of the salt tower, normally 100°F. Under these circumstances, the dried distillate should contain no free water even when cooled to 75°F.

The possibilities of sodium contamination during this drying operation have received relatively little attention. However, in the 1970 report to the Dallas ASTM meeting, the Section III Task Force on Gas Turbine Fuel Oils provided the following information.

1. Full-scale experience with salt dryers on jet fuel revealed that these units add no sodium to the fuel—the sodium content before and after salt drying being 0.1 to 0.2 ppm.
2. Pilot scale tests with No. 2 fuel oil produced oils containing 0.2 to 8 ppm of sodium, with most results in the 1 to 4 ppm range.

As indicated by Porter et al [*5*], disturbances of the tower salt bed (even surge-flow incidents) can result in sodium carry-over of crystalline salt particles. Two weeks may be required to reestablish stability after recharging or startup of commercial units.

Summarized in Table 3 are results recently observed at four refinery salt dryers. Comparisons between the sodium content of the influent versus product distillate streams illustrate how significant sodium contamination of distillate fuels can occur, at least occasionally. While these data are too limited to justify broad conclusions about the effect of such final processing of distillates, they do suggest that possible sodium contamination by salt drying should be taken into account.

Other conceivable sources of "contamination" of finished distillate fuels by organic or metal compounds are fuel oil additives. These are provided to improve

TABLE 3–*Results from salt dryers.*

	Sample Identification			Sodium Content of Hydrocarbon	
Refinery Location	Type	Gravity, °API	Date	Salt Tower Feed, ppm	Salt Tower Product, ppm
Gulf Coast	kerosine	43.	3/15/72	0.03	5.8
			4/11/72	0.19	0.85
Gulf Coast	kerosine	41.	3/17/72	0.42	2.7
			3/22/72	0.08	2.8
West Coast	diesel fuel	32.	3/17/71	8.0	7.1
			5/19/71	7.2	25.5
Gulf Coast	cycle oil	23.	3/15/72	16.3	19.1

various appearance, stability, or performance characteristics of the fuels [*6*]. Such substances generally contain few ash-forming compounds, and alkali metals are *not* a component of major significance. However, alkaline earth metals like barium, largely as essentially oil-soluble sulfonates, have been offered as aids to combustion and as sludge dispersants. Probably of more general significance as gas turbine fuel contaminants, however, are surface active additives. Certain types of such agents, deliberately added for other purposes, may exhibit one or more undesirable effects on distillate fuels. Because of interfacial activity and consequent solids-wetting effects, normally hydrophilic filter elements may fail to exclude water droplets from fuel streams. Surfactants in fuels may also interfere with retention of solid particulates in other filter elements. Finally, surfactant additives, in some cases, may stabilize dispersions of water and sediment, registering in poor water tolerance values and, again, in filtration problems. Such possible "contamination" of distillates of interest as gas turbine fuels by important fuel additives is summarized in Table 4.

Principles of Dispersion Stability and Electrostatic Separation

Dispersions which consist of two immiscible liquids having differing densities are unstable in a gravitational field; that is, the two liquids will eventually separate. If the interfacial tension is appreciable, the dispersion is also thermodynamically unstable with respect to the two bulk liquid phases. Thus, any such dispersion will eventually resolve into its constituent phases. The key word here is "eventually," since the time required for a dispersion to undergo resolution is often found to be unacceptably long. Natural repulsive forces are insufficient in dispersions to prevent gradual creaming to closely packed droplet arrays. However, attractive forces alone are ordinarily too small, even after such close approach, to ensure coalescence or even to prevent redispersion of the droplets. Close approach which establishes irreversible droplet contact is a fundamental requirement of general methods for resolving liquid-liquid dispersions.

TABLE 4–*Fuel oil additives as possible sources of distillate gas turbine fuel contamination.*

Additive Type	Generic Identity of Major Components	Typical Use Conc., ppm	Possible Significance as Fuel Contaminant
Antioxidants	arylene polyamines, aliphatic amine derivatives, bisphenol compunds	5 to 50	minor surfactant effects
Biocides	phenol derivatives, quaternary ammonium salts	5 to 25	designed to inhibit bacterial growth, surfactant effects may interfere with filter action
Cetane-number improvers	alkyl nitrate	500 to 5000	provided for diesel unit starting, neutral nitrogen compound, no contamination effects
Combustion improvers	Barium sulfonates, manganese derivatives	50 to 100	Ba, Mn, as sulfates, could have undesirable effect on gas-turbine ash problems
Dyes	anthraquinone, azo dyes	1 to 5	colorants for identification, no contamination effects
Metal deactivators	Schiff's base compounds, salicyaldehyde-alkanepoly-amine	5 to 10	reduce corrosivity, inactivate copper and other heavy metal ions; minor surfactant effects
Pour point depressants	olefin, alkenyl acylate, and alkyl alkylacylate copolymers and terpolymers, hydrocarbon polymers, and chlorinated hydrocarbons	50 to 5000	designed to lower pour point, polymeric material may cause serious emulsion problems (poor water tolerance)
Rust inhibitors	Polycarboxylic acids, amine/acid condensates, alkylamine phosphates, polyamine sulfonates	3 to 30	rust preventatives may give surfactant effects on filters and cause emulsion problems
Sludge dispersants	barium sulfonates, acrylate ester copolymers with nitrogen monomers, nitrogen derivatives of polycarboxylates	10 to 50	barium as sulfate may contribute to gas turbine ash problems, significant effects may be registered along with emulsion problems
Sludge inhibitors	aliphatic amines and amine derivatives are predominant	5 to 50	important additives, basic nitrogen reacts with unstable components and organic acids to give oil-soluble products, including soluble gums. Some emulsion-problem side effects are seen.
Water tolerance agents	Oil-soluble demulsifiers, usually non-ionic surfactants	5 to 10	designed to correct emulsion problems, may give surfactant effects on filters

Dispersion Stability

Accepting the thermodynamic certainty that such dispersions will eventually resolve, the study of their stability is, in reality, the evaluation of factors which influence the rate of resolution. These belong to two distinct groups, one involving the sedimentation rate of droplets in a gravitational field, the other concerning the flocculation and eventual coalescence of the droplets. For a better appreciation of these two (quite different) rate phenomena, it is convenient to consider them separately. Because sedimentation is common to settling tanks, centrifuges, and electrostatic separators, it is appropriate to discuss it before considering coalescence.

Gravitational Sedimentation—Since the initial publication by Stokes, in which slow fluid flow past a sphere is described by the Navier-Stokes equations, it has been customary to relate the sedimentation rate of droplets in a gravitational field to the density difference between phases by means of Stokes' law:

$$V = k\,\frac{|\rho_w - \rho_o|}{18\,\mu_0}\,g\,d^2 \tag{1}$$

where

V = droplet velocity in the continuous phase (in./min),
d = the diameter of the droplet (micrometers),
μ_o = the continuous phase viscosity (centipoise),
ρ_w and ρ_o = the specific gravities of the phases, and
k = a proportionality constant.

Consideration of this equation reveals that droplet diameter is the most significant variable affecting separation velocity. Doubling the average droplet diameter will cause a four-fold increase in sedimentation rate; enlarging the characteristic droplet size from 1 to 10 μm will increase the settling rate of the dispersion by a factor of 100. Such considerations demonstrate why those methods of emulsion resolution favored from practical experience by the petroleum industry are directed at increasing the size of the discrete phase elements. For example, in an appropriate electric field, the characteristic droplet size is increased by 10 to 100 fold, resulting in rapid resolution of the dispersion.

Discrete Phase Coalescence—As measured by interfacial tension, dispersions are thermodynamically unstable with respect to the bulk phases of oil and water. In analogy to the approach used in chemical reaction kinetics, it is generally understood that an activation energy barrier exists between the thermodynamic states of discrete element dispersion and the coalesced homophases; this energy barrier must be overcome or reduced before coalescence can occur. Analogous physicochemical barriers are also observed as stemming from the nonhydrocarbon components of oil phases. As previously mentioned, organic impurities consisting of oxygen, nitrogen, and sulfur derivatives of hydrocarbons are usually present in distillates in at least small concentrations. By virtue of the fact that they are chemically functional species, these compounds exhibit varying degrees of surface activity, in terms of interfacial tension lowering and film formation. Such films often have dispersion stabilizing properties [7]. Finely divided, oil-wetted inorganic solids can have a similar effect; they, too, are functionally interface-active, and may provide the substance of emulsion films that are extremely resistant to rupture by coalescence.

Coalescence occurs in petroleum emulsions when close contact is established between droplets whose interfacial films are "wetted through" by the liquid of the internal phase [*8*]. Although contacting water droplets experimentally survive in pure hydrocarbon media for less than 1 min, water droplets in typical crude oil systems may register average survival times of 60 min or more; survival of oil droplets in the brine phase observed in such cases is typically only 1/10 to 1/20 that of the brine droplets in oil [*9*]. These effects indicate that the film substance is hydrophobic; that is, it is "wetted through" only when oil is the internal phase. The overall stabilization also appears to involve kinetic factors of droplet approach which are related to oil viscosity as well as specific coalescence resistance from films.

Thus, the details of droplet protection against coalescence involve first the prevention of close mechanical contact between the aqueous droplets (since coalescence cannot occur until intimate contact is established), and, second, a mode of stabilization which depends on the nature of the hydrophobic film itself (since coalescence is the result of water penetration of this film). Separation of the two modes of film stabilization is not always possible in real emulsions but is a conceptual necessity for better understanding of the process. Dispersions of water in oil may therefore be considered to have both an inertial and a specialized film-barrier type of stabilization, the former reflecting the overall characteristics of the oil phase, the latter depending upon formation of a hydrophobic film of organic substances or of partially oil-wetted inorganic solids at the oil-water interface. Petroleum dispersions of this type are apparently seldom stabilized by electrostatic double-layer repulsion, as the double layer is too diffuse to prevent droplet approach [*10*].

Electrical Resolution Processes

As indicated by Stokes' Law, the rate of resolution can be increased by causing small droplets to coalesce into larger ones which then separate more rapidly in a gravitational field. An electric field promotes faster droplet coalescence both by sharply increasing the attractive force between individual droplets and by overcoming mechanical barriers at the oil/water interface. The changes are illustrated in Fig. 2. As an oil-continuous emulsion first enters an electric field, the dispersed phase is present as individual spherical droplets which are separated by an average distance of several micrometers. The electric field distorts the shapes and charge distributions of the droplets. Distortions in shape disturb and weaken the interfacial stabilizing film. Perturbations of charge distribution on the droplets induce strong attractive forces (dipole interactions) between adjacent droplets. As a result, there is a sharp rise in the energy and frequency of contacts between droplets which, at once, are less resistant to coalescence. Thus, the electric field has the effect of sharply increasing the rate of coalescence, producing large droplets which rapidly settle from the oil.

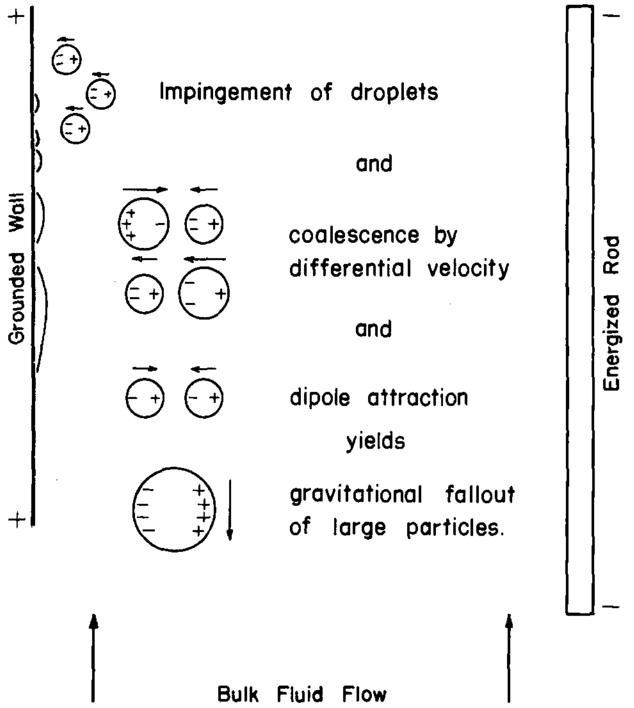

FIG. 2–*Electrostatic phase separation.*

Coalescence rate and overall efficiency of electrostatic separations are often enhanced by a process additive, usually an oil-soluble, non-ionic demulsifier added at low concentration (5 to 100 ppm).

Coalescence by electrical means is eventually limited by the gradual reduction in number density of the dispersed droplets. As the volume fraction of the dispersed phase is reduced from higher levels down to the range of 0.1 percent, electrical process efficiency falls off rapidly. If a further reduction of the impurity level is required, it is necessary either to employ an electrical process based on an electrophoretic principle or to increase the number density of the discrete phase by adding additional material (usually water) to coalesce with and dilute the residual impurities. The former process is used in treating petroleum distillates while the latter is used in crude oil desalting.

It is generally believed that the primary mechanisms responsible for electrically induced phase separations in petroleum distillates stem from both electrostatic and electrodynamic forces. Although the electrostatic forces resulting from induced dipole interactions are usually more significant, electrophoresis and dielectrophoresis may acquire principal roles in the electrical separation of treating reagents from petroleum distillates. Both types of forces can act in a purely mechanical way (for example, distortion of the interfacial film) as well as introduce long range attractive forces (induced dipole interactions) which promote coalescence.

Distortion of Droplets–Droplets of the dispersed phase in all emulsions assume spherical shape, a configuration which minimizes the surface energy of the interface. When, however, an electric field is applied to this system, electrical stresses are induced which distort the drop into an elongated spheroid resembling a football. This occurs because resultant outward pressures are induced in the direction of the field, so that, within the constraint of interfacial tension, the drop becomes elongated in the direction of the field and contracted in directions perpendicular to it. A typical result of the application of an electric field to a droplet is illustrated in Fig. 3. Under fairly reasonable assumptions [*11*], the shape of a droplet in an electric field can be described by a complex relation

$$F(a,b) = E\left[\frac{r_0}{\sigma}\right]^{1/2} \qquad (2)$$

where

E = the electric field,
r_0 = the radius of the undistorted drop,
σ = the interfacial tension,
a = half the length of the major axis,
b = half the length of the minor axis, and
$a = b = r_0$ when the applied field is zero.

The relationship is graphically illustrated by Fig. 3, in which the elongation (a/b) is plotted as a function of the field strength, interfacial tension, and droplet size. It can be seen that the maximum distortion occurs when the ratio $E(r_0/\sigma)^{1/2}$ has a value of 1.625 which produces an elongation of 1.850. The increase in surface area which accompanies this change in shape (from a/b = 1.00 to a/b = 1.85) is sufficient to weaken or rupture interfacial films which ordinarily tend to hinder coalescence.

Droplet Motion–Within electric fields, dispersed droplets will be decelerated by the action of fluid frictional forces, and will be either accelerated or decelerated by the action of external forces. The frictional force depends on the local velocity of the element relative to that of the continuous phase; the external forces include those due to gravity, electrophoresis, and dielectrophoresis. It is the resultant of these forces which determines the trajectories of the particles in the electric field.

In an electric field, particles having a net charge move normal to planes of constant potential; this motion is generally called electrophoresis. There is some uncertainty as to whether the net charge on such droplets is acquired by interaction of the particle with the oil, by different rates of charging and discharging in the field, or by a limiting mechanism in which it charges until there is a nil gradient at the interface. Particle motion due to the weak translational force which bears on a dipole in a nonhomogeneous (converging) electric field is called dielectrophoresis. The direction of movement is toward

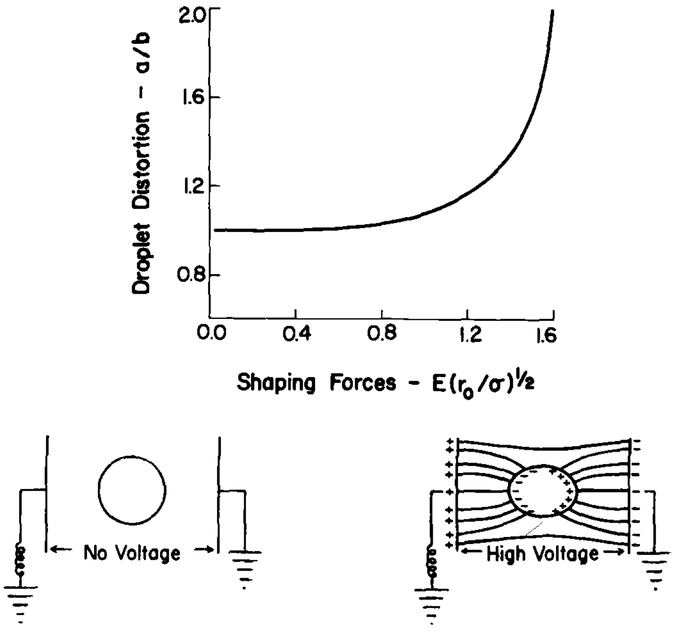

FIG. 3–*Droplet distortion in an electric field.*

field convergence and is independent of polarity. The force is proportional to the field intensity, to its divergence, and to the difference in dielectric constant between the particle and the continuous phase. The requirement for high divergence limits the practical treating volume; except at points or sharp edges, divergence in commercial-scale electrical coalescers is so modest that the overall influence is small.

A solution to equations governing droplet trajectories demonstrates that larger droplets tend to overtake smaller ones. In a sufficiently strong field, they will coalesce. Due to sparceness of the droplet population, too long a period might be required for droplets to grow large enough to settle against the bulk fluid motion. This is avoided (Fig. 2) by providing fixed surfaces, parallel to the direction of fluid flow, upon which droplets may impinge and coalesce. The result is a stream of aqueous phase which can drain down against the rising distillate.

Induced Dipole Coalescence–Two adjacent conductive droplets, regardless of charge, will experience an attractive force if they are exposed to an impressed electric field. This results from the imaging effects of the dipoles induced by the field, which causes charge separation in each drop. Moreover, the attractive force increases as the effective field between the droplets increases. In order to coalesce two droplets, it is ordinarily possible to generate a force which will overcome any of the usual barriers to coalescence by adequately intensifying the field.

It is well known that the effective field between adjacent droplets increases as the impressed field increases, and as the separation between droplets decreases. The effective field is enhanced by a factor of four as the droplet separation is decreased from one to one tenth of a droplet diameter, but is decreased by a factor of two as the separation is increased from one to four diameters. Beyond four diameters, there is virtually no enhancement of the field by imaging effects, and it becomes necessary to impress higher fields to promote coalescence. Since most distillate dispersions enter the region of uniform field with a separation greater than seven droplet diameters (1000 ppm), it is necessary to employ high fields (typically 10 kV/in.) for efficient coalescence action.

Evaluation of Dipole Attraction Forces—To understand the attractive forces experienced by droplets exposed to an electrostatic field, it is sufficient to consider the situation indicated in Fig. 4, namely, that of two uncharged droplets in a uniform electrostatic field of intensity E. As illustrated in the figure, the droplets are polarized by the electric field so that charges of opposite sign appear on the neighboring surfaces. Due both to the imaging effect of these separated charges on the opposing droplets and to the attraction of opposite charges for each other, there is an increased density of field lines between the droplets. This results in an enhanced field between the droplets and a mutual force of attraction. If the direction of the field were reversed, there would be a complete interchange of all the signs, but the mutual force of attraction would remain. Under certain reasonable conditions, it can be shown [*12*] that the attractive force F between two conducting spheres of radius r whose surfaces are separated by a distance ℓ in a medium of dielectric constant $\epsilon_0\epsilon$ and in an electric field of gradient E can be represented by the expression

$$F = \epsilon_0\epsilon \, E^2 \, r^2 \, \Psi\left(\frac{\ell}{r}\right) \tag{3}$$

in which Ψ (ℓ/r) represents a complex series which can be approximated by the ratio $6r^4/\ell^4$. The dimensionless plot of Fig. 4 graphically illustrates the manner in which this force increases as the droplets come closer together. A scaling factor $(Er)^2$ has been removed from the ordinate so that the values plotted depend neither on the specification of the field nor on the size of the drop. To obtain the attractive force for any given separation it is necessary only to multiply the ordinate value by the square of the product of the droplet radius and the applied field.

Electrical Versus Gravitational Forces—To gain some appreciation of the magnitude of electric field force, it is interesting to compare it with gravitational force. It can easily be shown [*13*] that this ratio is given by

$$R_{e/g} = \frac{k \, \epsilon_0\epsilon \, d^2 \, E^2}{\Delta\rho g d^3} = \frac{k \, \epsilon_0\epsilon \, E^2}{\Delta\rho g d} \tag{4}$$

For a water droplet having a diameter of 50 μm in an oil of dielectric constant 2.2 and a density of 0.8 exposed to an electric gradient of 2.5 kV/in., the ratio of electrostatic forces to gravitation forces is found to be 10, that is, $R_{e/g} = 10$.

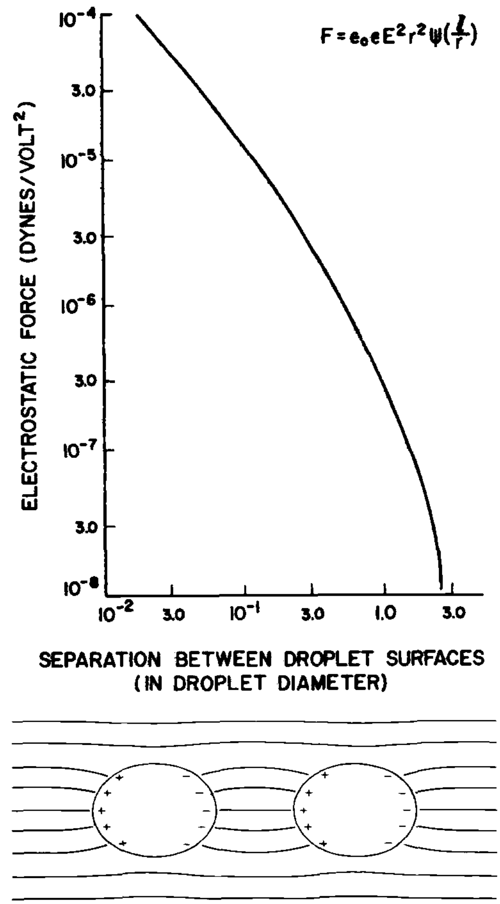

FIG. 4–*Attractive force between droplets in an electric field.*

Thus, in this particular case of a large water droplet in a fairly light hydrocarbon, the electric forces are some ten times greater than the gravitational forces. For smaller droplets or smaller density differences, this ratio becomes large enough to account for further substantial increases in relative efficiency observed with electric phase separations under these conditions.

In addition to the phase separation provided by settling in fuel-storage tankage, both filters and centrifuges have previously been employed to remove various types of impurities from distillate fuels for gas turbines. Although more detailed explanations of the theoretical mechanisms can be found elsewhere, it is interesting to compare and contrast the principles and limitations of these systems with those of electrical separation.

Sedimentation–Fuel tankage can be used to separate entrained water from fuel oils [*14*]. The sedimentation mechanism is described by Stokes' law. Provided that adequate duration (24 to 48 h) of undisturbed settling time is available, significant amounts of water and particulate matter can be separated from fuel oils by simple sedimentation.

The improvement effected by an electrostatic field is readily apparent. While the typical settling rate [*15*] for a No. 2 fuel is reported to be 0.2 in. per min, under the same conditions in an electric field the typical rate is 20 in. per min. This 100-fold increase in settling rate is a result of electrically induced coalescence action which, in this case, increased the characteristic diameter of water droplets from 50 to 500 μm.

Filtration—Various types of filters can be used to remove free water (containing sodium chloride and other water-soluble materials) and particulate matter (including both abrasive solids and semi-solids such as sludges and gums) from contaminated distillates. Water is generally removed in a two-stage apparatus called a coalescer/separator [*16*]. The coalescer section contains hydrophilic elements, often composed of fiberglass, which can be wetted by water. The water-wetted surfaces promote the coalescence of fine droplets into larger ones which grow on the element surfaces until they eventually detach themselves and are carried by the fuel to a second stage. This second section contains hydrophobic elements which are intended to block passage of the larger water aggregates but to allow relatively free flow of oil. Particulate matter is removed by different types of filters which rely on one of two mechanisms: (1) straight-forward screening action by which particles larger than the pores bridge or block the openings, and (2) a surface attraction mechanism by which particles smaller than the pores impinge on the fibers and are retained by surface forces. Particulate matter retained by either mechanism forms a "cake" which traps additional particulate matter and eventually limits flow of fluid.

According to Winkler and Bacher [*15*], the performance of a coalescer/separator is somewhat inferior to that expected from depth-type absorbent filters. Data they report from a marine distillate fuel-purification system indicate that a coalescer/separator reduced the suspended water content from 6.0 to 1.5 ppm. By contrast, primary and secondary stages of depth filtration of the same fuel reduced the water content from 6.0 to 2.5 ppm in the first stage and to 0.7 ppm in the second stage. Data they report from an industrial distillate fuel-purification system indicate that the combination prefilter and coalescer/separator reduced the sodium content from 0.15 to 0.06 ppm.

In comparing the filtration and electrostatic mechanisms, two points should be particularly noted. Filters are essentially passive devices, depending on fluid flow to bring impurities to specially conditioned surfaces at which coalescence, adsorption, or blocking is expected to occur. In contrast, electrostatic systems actively impose long-range forces which both concentrate impurities in certain regions and increase the attractive forces between water droplets. The filtration mechanisms depend heavily on surface properties, and filters are particularly sensitive [*15*] to the presence of trace amounts of surface active materials in the oil which lower the interfacial tension relative to water. In contrast, the mechanisms of the electrostatic systems are substantially independent of surfactant effects on interfacial tension. One particular demonstration of this fact can be found in the previously cited example of the 33° API virgin distillate. The raw distillate displayed an interfacial tension of 27 dynes/cm relative to water, but because the aqueous "treating" phase was a weak caustic solution which reacted to form sodium naphthenates, the equilibrium interfacial tension of the system during electrical separation was only 0.4 dynes/cm. However, despite this interfacial tension reduction by nearly two orders of magnitude, operation of the electrostatic unit was substantially independent of this change, the sodium carry-over being only 0.8 ppm.

Centrifugation—In contrast to settling tanks and filters, centrifuges are active devices which impose an external force on discrete elements of a fuel in an effort to concentrate them in a particular region. Both water and particulate matter can be removed in the same apparatus which, in principle, can operate on a continuous basis.

According to Ambler [*17*], the performance of a centrifuge can be described by considering a single particle in equilibrium with the external force supplied by the centrifuge under the usual conditions of Stokes' law. The centrifuge acts to increase the effective gravitational force so that the rate of settling is described by the equation

$$V = k \, \frac{|\rho_w - \rho_0|}{18\mu_0} \, d^2 g \Sigma \qquad (5)$$

where Σ is proportional to the factor by which gravitational force is increased due to the centrifuge; all other symbols are as previously defined. It is reported that industrial centrifuges achieve Σ values of 6000 to 9000 from the corresponding increase in effective gravitational force.

In comparing the separation mechanism of centrifuges with those employed by electrostatic systems, significant differences are noted. The external force supplied by the centrifuge affects the settling rate in a linear fashion; a 100-fold increase in the external force (corresponding to $\Sigma = 100$) increases the rate of settling by a factor of 100. In contrast, the electric force acts to increase the diameter (d) of the droplets. Because the diameter term enters the Stokes relation quadratically, it requires only a factor of 10 diameter enlargement to obtain the same 100-fold increase in settling rate. In actual practice, the electric field is observed to enlarge characteristic droplet diameters by factors up to 100, so the effective settling rate may be increased 10 000-fold.

Brubaker and Calvino [*18*] report data from two systems employing both centrifuges and filters. On the gas-turbine vessel *Callaghan*, a purification system consisting of a settling tank, three centrifuges, and a coalescer/filter at 85°F typically reduced the water content of a low ash heavy (33° API) distillate from 50 to 2 ppm with occasional excursions to 10 ppm. On *Euroliner* class vessels, a purification system consisting of a settling tank, four centrifuges, and filters typically reduced the water content of a lighter (37° API) distillate from 20 to 2 ppm; with greater contamination (60 ppm), the water content was reduced to 10 ppm.

It is interesting to note that the single system of electrostatic separation not only achieves the same required degree of distillate purification as filter-centrifuge combinations, but does so without need for moving parts, and has no requirement for periodic "dump" sequences or element changes which characterize centrifugal and filtration systems. Specifically, the electric units are able to operate in a fully continuous fashion; on a practical basis, both centrifuge and filter operation is occasionally interrupted (or bypassed) because of accumulated debris or other service problems. Also, since centrifuges generate their gravitational force by high-speed rotation, maintenance and operation costs are relatively high.

On-Site Electrical Treatment of Gas Turbine Fuels

Although electrostatic phase separation equipment has been commercially employed to remove sodium and other inorganic impurities from residual and crude oils for use as gas turbine fuels, such equipment has not been employed to remove similar contaminants from distillate fuels at a gas-turbine site. Provided below are descriptions of installations projected for this purpose, along with indications of their anticipated performance.

Installation

Assuming that the distillate fuel initially had met its use specifications at the refinery, then a single stage of electrical processing is expected to reduce the sodium, potassium, and sediment introduced by seawater contamination to 0.5 ppm of alkali metals (sodium plus potassium) and 10 ppm of solids larger than 0.8 μm. As shown in Fig. 1, the installation provides a single stage of electrical separation. Fresh water is added to the distillate, dispersed by a mixing valve throughout the fuel, and then separated in the electric field. By varying the amount of fresh water added, this system will cope with relatively massive levels of seawater contamination, for example, in excess of 20 ppm of sodium. If more restrictive sodium limits of 0.1 ppm are imposed, two stages of water-washing and electrical separation, as indicated in Fig. 5, are required. As this is a counter-current washing operation, water needs are equal and other requirements are little more than for the single stage system.

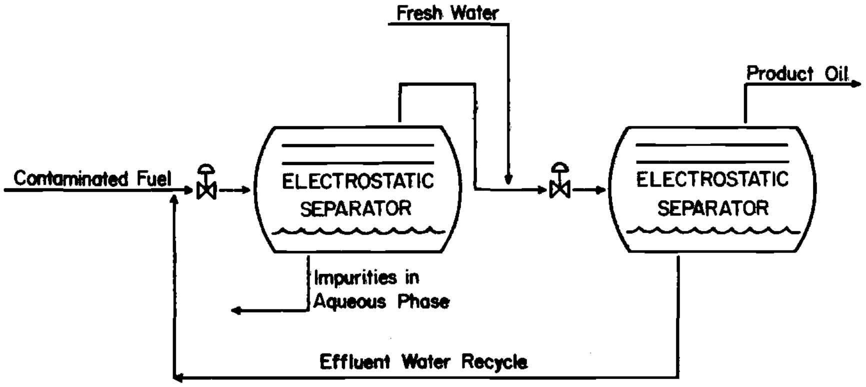

FIG. 5–*Electrical treating system for turbine fuels.*

Expected Performance

As previously indicated, electrostatic separation equipment is used commercially to process the components of typical turbine fuel blends but has not been employed to process the materials as received, for example, at a barge terminal. To simulate the fuels which might be received, several distillate fuel oils were purchased, deliberately contaminated with various levels of seawater and sediment, and then processed in pilot plant equipment. Results of several such tests, outlined below, are more fully described in Table 5.

Case A—A 40.8° API kerosine was mixed with 5 percent Persian Gulf water which has a sodium content of 5600 ppm. Processing through an electrostatic pilot plant simulating commercial operation gave an oil with less than 0.1 ppm of sodium and less than 0.001 percent free water.

Case B—A 32.2° API No. 2 fuel oil was mixed with seawater to produce a fuel contaminated with 25 to 30 ppm of sodium and 0.3 percent water. Processing through an electrostatic pilot plant under standard operating conditions produced an oil containing less than 0.5 ppm of sodium and less than 0.003 percent free water.

Case C—A 35.9° API No. 2 diesel fuel was mixed with a synthetic seawater blend to produce a fuel contaminated with 60 ppm of sodium and 0.1 percent water. Processing through a single stage of electrostatic separation equipment produced an oil containing less than 1.0 ppm of sodium and less than 0.002 percent free water. A second stage of processing provided an oil containing less than 0.02 ppm of sodium, and less than 0.002 percent free water.

Case D—A 28.7° API gas oil containing 4 ppm of solids (as retained on a 0.45 μm filter paper) was processed, after adding water, by an electrostatic pilot plant to yield a product oil containing less than 1 ppm of sediment and less than 0.002 percent free water. There was no detectible sodium in the feed or in the product oil.

Case E—A 32.2° API distillate containing 24 ppm of solids (as retained on a 0.45 μm filter paper) was similarly processed by a pilot plant unit. The product oil contained less than 6 ppm of sediment and less than 0.002 percent free water.

Case F—Samples of Libyan crude oil were obtained from several sources. The oil with the highest sodium content was processed with high mixing intensity through two stages of electrical desalting. With 5.0 percent of fresh water (55 ppm sodium) added counter-currently, the sodium level of the fuel was reduced below 0.5 ppm; water carry-over (0.1 percent) and effluent water quality were satisfactory at an operating temperature of 95°F. To determine the effects of contamination during transportation, seawater was blended into a sample of the oil. After a short period of settling, the decanted crude oil was found to contain 8.0 ppm of sodium. A single stage of electrical desalting reduced the sodium content to the 1.0 ppm level; a second stage reduced the sodium content below 0.5 ppm.

Case G—Samples of 39° API Nigerian crude were processed through two stages of electrical desalting. With high mixing intensity, 5.0 percent fresh water was

TABLE 5—*Electrostatic decontamination of candidate gas-turbine fuels.*

			Contaminant Content								
Fuel Processed			In Feed			First Stage			Second Stage		
Case	Name	Gravity, °API	Na, ppm	Sediment, ppm	H_2O, %	Na, ppm	Sediment, ppm	H_2O, %	Na, ppm	Sediment, ppm	H_2O, %
A	kerosine	40.8	280	...	5.0	$<$0.1	...	0.001	...	...	...
B	No. 2	32.2	30	...	0.3	0.3	...	0.001	...	...	...
C	diesel	35.9	60	...	0.1	0.8	...	0.001	0.015	...	0.001
D	gas-oil	28.7	...	4	...	...	0.8	0.001	...	...	...
E	distillate	32.2	...	24	...	...	6.0	0.001	...	...	...
F	Libyan crude	37.7	8	...	0.1	1.0	...	0.100	0.200	120.	0.100
G	Nigerian crude	39.2	22	...	0.4	1.0	...	0.100	0.200	...	0.100

added counter-currently to the crude oil containing 22 ppm of sodium. The two-stage process reduced the sodium level below 0.5 ppm; water carry-over (0.1 percent) and effluent water quality were satisfactory at an operating temperature of 80°F.

Cost Estimates

Based on correlations established between pilot plant data and results obtained from commercial units, pilot plant results of the type described in the previous section can be used for accurate calculations of sizes and costs of electrostatic phase separation equipment required to achieve specified performance levels. These relations are illustrated in Fig. 6; the cost figures are estimated for equipment of the type schematically indicated in Fig. 5, and may vary with specific construction codes, optional equipment, etc. These units are ordinarily supplied by the manufacturer in almost fully assembled form, complete with associated piping, valves, and instrumentation. A maximum of 500 man-hours may be required to prepare the equipment for service.

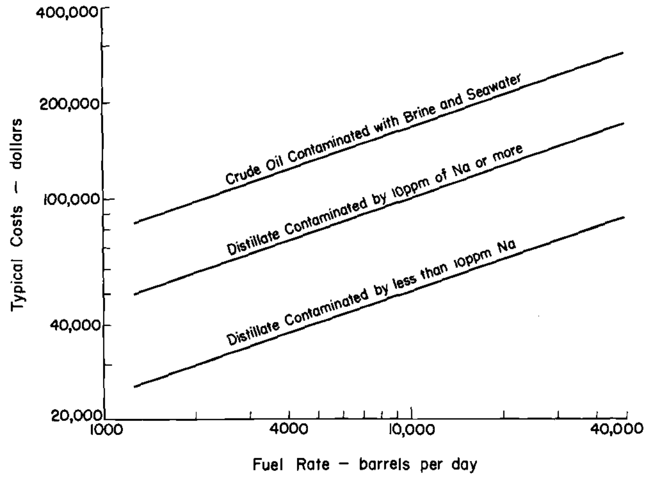

FIG. 6—*Cost-capacity relationships for electrostatic fuel purification systems.*

Specific Applications of Electrostatic Separation Equipment

To deal more explicitly with costs, operating characteristics, and expected performance of electrostatic phase separation equipment, several specific applications are described later in detail. Each example represents a system currently installed or proposed to reduce the contamination found in a candidate low-ash gas turbine fuel to levels required for acceptable turbine operation. For convenience, the applications have been divided into those processing fuels of low volatility, medium volatility, and high volatility; within the first classification, applications involving crude oils have been separated from those involving distillates. In each of the applications, the expected contamination levels and the performance requirements are first indicated, followed by an outline of the equipment required. Where possible, operating details, including actual product quality results, are supplied.

Low Volatility Fuels

Case I (Crude Oil)–At a remote location in Canada, a light (40° API) crude from a pipeline supplies fuel for two relatively large industrial gas turbines used for base-load operation. A two-stage electrostatic phase separator was installed to maintain the sodium content below 5.0 ppm; the sodium content of the crude in the pipeline was observed to fluctuate up to 100 ppm. The electrical equipment principally consists of a single vessel, divided into two compartments, which contains the means for establishing the electrical field. The cylindrical treater, approximately 6 ft in diameter and 18 ft long, is energized by two 10 kVA transformers. Some 1800 B/D of crude oil, heated at 250°F and mixed with 5 percent fresh water, is charged to this vessel; the product oil typically contained less than 2.0 ppm of sodium during more than two years of operation.

Case II (Crude Oil)–At a power station in the eastern United States, a light (38° API) low-sulfur crude oil is used as fuel for four large industrial turbines intended for an intermediate duty cycle. Although field testing of this crude indicated that the sodium content rarely exceeded 5 ppm, the possibility of contamination during tanker shipment was considered appreciable. A two-stage electrostatic phase separator, consisting of two separate vessels 8 ft in diameter and 20 ft long, was installed to maintain the sodium content below 1.5 ppm. During operation, 4 percent fresh water is added to 350 gpm of crude at 95°F and then separated in the electrostatic field at an electrical consumption rate of only about 5 kW. Sodium levels in the product oil are maintained below 1.0 ppm, even though the sodium content of the tanker shipment averaged 11 ppm (sampled after 48 h of settling). The treated oil is inhibited with an oil-soluble magnesium compound before it is burned as turbine fuel.

Case III (Crude Oil)–A power station in the western United States is considering the use of a variety of low-sulfur crudes for a projected multi-turbine installation. A two-stage electrostatic phase separator for 25 000 B/D has been proposed to maintain the sodium content below 0.5 ppm for delivered fuel containing up to 20 ppm of sodium. Two separate vessels, each 10 ft in diameter and 35 ft long and powered by a 50 kVA transformer, and the related equipment required for unattended operation were recommended.

Case IV (Heavy Distillate)–A location in South America plans to use a 28° API diesel oil which may become contaminated with a small amount of seawater. A single-stage electrostatic phase separator for 1500 B/D of the contaminated distillate has been proposed to maintain the sodium content below 0.2 ppm for delivered fuels containing up to 2.0 ppm of sodium. Approximately 1.3 gpm of fresh water is to be added to the oil at 100°F and separated in a 40-in.-diameter vessel which is 16 ft tall and energized by a 5 kVA transformer. The product oil is expected to contain less than 0.2 ppm of sodium and less than 100 ppm of suspended water at the operating temperature of 100°F.

Case V (Heavy Distillate)—A Caribbean island location uses a 27° API distillate that becomes contaminated with seawater to the extent of 10 to 12 ppm of sodium. A single-stage electrostatic phase separator for 3500 B/D of contaminated distillate has been proposed to maintain the sodium level below 2.0 ppm. Approximately 3 gpm of fresh water is to be added to the contaminated distillate and then separated in a vertical vessel 6 ft in diameter, 13 ft high, and powered by a 5 kVA transformer. An oil-soluble additive containing magnesium is to be injected into the product oil to inhibit corrosion associated with the vanadium content of 4 ppm.

Medium Volatility Fuels

Case VI (Middle Distillate)—A power plant in the eastern United States receives a 35° API distillate by barge. Contamination with seawater occurs so that occasional shipments are found to contain from 5 to 9 ppm of sodium. Since increased duty cycles have expanded the fuel consumption, the amount of settling time available in existing tankage had been sufficiently reduced to allow sodium levels in excess of 0.6 ppm to reach the turbines. To treat this No. 2 fuel as it is being discharged from barges at the rate of 32 000 B/D, an electrostatic separator was proposed which is 12 ft in diameter, 23 ft long, and powered by a 5 kVA transformer. With the addition of 3 percent fresh water, the electrical unit is expected to maintain the sodium level below 0.6 ppm.

Case VII (Middle Distillate)—An electric utility receives by barge a No. 2 distillate which is contaminated by seawater so that the resultant sodium content varies from 0.5 to 2.0 ppm. To process 5600 B/D of this distillate to a sodium specification of less than 0.2 ppm, a single electrostatic separator 8 ft in diameter, 14 ft long, and energized by a 5 kVA transformer has been proposed. In addition to a maximum sodium content of 0.2 ppm, the product oil is expected to contain not more than 100 ppm of insoluble water at the operating temperature of 60 to 80°F.

High Volatility Fuels

Case VIII (No. 1 Distillate)—A power plant receives barge shipments of kerosine which is contaminated by seawater. To process this contaminated fuel at the rate of 18 000 B/D, a two-stage electrostatic separator has been proposed. At 70°F, up to 5 percent of fresh water is added counter-currently to the kerosine; the mixture is separated in two vessels, each 12 ft in diameter and 20 ft long, energized by two 5 kVA transformers. This installation is expected to keep the sodium level below 0.2 ppm when the feed is contaminated with up to 50 ppm of sodium.

Conclusions

Installed at an operating turbine site, a properly designed electrostatic purification system is capable of restoring contaminated fuel oils to sodium levels meeting all current and anticipated commercial or military specifications for gas turbine fuels. Installation costs are relatively modest, especially for larger turbine installations, and operating costs (including maintenance) are comparatively negligible. Performance, reliability, and consistency expectations from electrostatic phase separation equipment exceed that of alternative means for on-site purification of turbine fuels.

Acknowledgments

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A. S. Zambone[1] and C. Y. Lee[1]

Centrifugal Liquid-Liquid Separation as Applied to Alkali Metal Reduction in Liquid Fuels by Aqueous Extraction

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REFERENCE: Zambone, A.S. and Lee, C.Y., "**Centrifugal Liquid-Liquid Separation as Applied to Alkali Metal Reduction in Liquid Fuels by Aqueous Extraction,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531*, American Society for Testing and Materials, 1973, pp. 105–120.

ABSTRACT: Liquid-liquid separation within a high speed centrifuge is reviewed. The interrelationship between counter current, liquid-liquid extraction and liquid-liquid separation unit operations are discussed. Alkali metal removal as a function of the physical parameters of the hydrocarbon fuel and theoretical centrifuge capacity, sigma, is analyzed.

KEY WORDS: fuels, gas turbines, hydrocarbons, washing, corrosion

Nomenclature

a	Distance between adjacent discs measured normal to surface of disc
c	Heavy phase concentration at the radius
C	Sodium concentration
d	Droplet diameter
d	Mean droplet diameter
f	Partial specific volume of the heavy phase
g	Acceleration of gravity
G	Ratio of centrifugal acceleration to acceleration of gravity
K	Constant
n	Number of discs
P	Pressure
Q	Volumetric rate
r	Radius
R	Gas constant
t	Time during which feed is under centrifugal force
T	Absolute temperature of the suspension
v	Velocity
V	Volume
W	Weight of water
x	Distance parallel to the disc surface from the outside edge of the disc
Δ	Difference

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μ	Viscosity
M	Molecular mass
ω	Angular motion
ρ	Mass density
Σ	Theoretical capacity factor
θ	Half included disc angle

Subscripts

B	Bottle centrifuge
c	Fuel after centrifuging
CY	Cylindrical section
D	Disc stack
e	Interface between heavy and light phases
F	Original fuel
h	Heavy phase
l	Light phase
s	Settling velocity of a particle in a centrifugal field
W	Wash water
1	Inner radius
2	Outer radius

Fuel washing, the contacting of a liquid hydrocarbon with water followed by the separation of the water phase from the continuous hydrocarbon phase, is carried out to reduce the content of the alkali metals sodium and potassium. The procedure also serves to varying, but uncertain, degrees to reduce the content of calcium and lead which are also frequently observed in fuel analyses. All the foregoing metals, but particularly sodium and potassium, especially in combination with vanadium, have adverse affects on gas turbine operation. These affects and their mechanism are discussed at length elsewhere and are of importance here simply because they are the reason for fuel washing.

Corrosive Metals

Sodium, of all the foregoing metals, is the most difficult problem. This is the result of its abundance and broad distribution as much as it is the result of its corrosive compounds. Potassium and lead, although presenting severe problems when present in the several parts per million range are relatively rare. The fact that sodium constitutes approximately 1.05 percent of sea water by weight frequently ensures introduction into fuel supplies during shipboard transport before and after refining. The high solubility of all inorganic salts of the alkali metals in an aqueous medium recommends water as the obvious "solvent."

Figure 1 illustrates the schematic flowsheet of a fuel washing process employing a water washing or mixing and extraction step, and a centrifugal liquid-liquid separation step. Contacting of the continuous fuel phase with the water phase is effected in a mechanical mixer to a degree sufficient to ensure

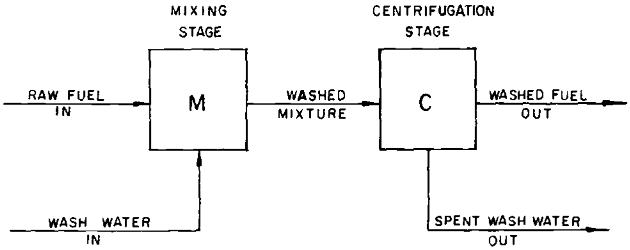

FIG. 1–*Fuel oil washing flow scheme.*

near uniform distribution throughout the aqueous phase of the sodium present in the washed mixture.

Moreover, contacting must be such as to maximize transfer into aqueous solution of those metal salts present as undissolved suspended (crystalline) solids. Clearly, generation of maximum interfacial surface area will maximize transfer rate. This approach, usually through prolonged or violent mixing, often, but not always creates a liquid-liquid separation problem by: (1) formation of stable emulsions in which, due to the presence of natural emulsifiers, oil-water/water-oil emulsions form which resolve so slowly as to render separation impractical; (2) generation of an aqueous phase with droplet diameters below the range of economic capture; and (3) some combination of one and two.

Effective inhibition of emulsion formation is aided by employment of one or more of a very wide variety of surface active agents at relatively low concentrations. The selection and function of such agents is beyond the scope of this paper.

Control of mixing intensity must also be practiced in every case and even when no tendency toward emulsification exists, to ensure generation of droplet diameters suitable for both sodium extraction and for subsequent separation.

Centrifugal Liquid-Liquid Separation

It is now convenient to consider the separation of the aqueous phase from the hydrocarbon phase while under centrifugal force in some detail. The system will then be briefly considered as a process. The discussion will basically proceed along theoretical lines. Therefore, an effort will be made to cite major weaknesses in the theory at salient points.

Any discussion of liquid-liquid separation under centrifugal force must logically begin with Stokes law. We will then proceed with derivation of the sigma definition of centrifuge size according to Ambler, but also Hebb and especially Lavanchy [*1-3*].[2]

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

A liquid droplet, in this case water, suspended in the hydrocarbon phase is subject to the following major influences: gravity, viscous drag, and Brownian motion.

If a particle diameter is sufficiently great to permit neglect of Brownian motion, as does Stokes law, the particle will settle, being accelerated by the force of gravity until the viscous drag force balances that of gravity and terminal velocity is reached. We will discuss somewhat later why, indeed, Brownian motion can be neglected in our case.

Stokes law states:

$$v_g = \frac{\Delta\rho d^2 g}{18\,\mu} \tag{1}$$

where

v_g = droplet settling velocity at one earth gravity
$\Delta\rho$ = ρ_h - ρ_l, the difference in density between the heavy (aqueous) and light (hydrocarbon) continuous phase,
d = droplet diameter; spherical shape assumed,
g = acceleration of gravity, and
μ = viscosity of the continuous (hydrocarbon) phase.

In the special case of centrifugal liquid-liquid separation under consideration, we may substitute the centrifugal acceleration term for the gravitational term, giving:

$$v_s = \frac{\Delta\rho\, d^2\ (\omega^2\, r)}{18\,\mu} \tag{2}$$

where

v_s = settling velocity of the droplet in the centrifugal field,
ω = angular velocity of the particle in the centrifuge, and
r = radius at which the settling velocity is determined.

It has been noted [3] that the velocity just described is relative to the continuous phase and that if that phase, in this case the fuel phase, is also in motion, then a vector summation should be carried out to fully define droplet motion. This, in turn, requires full characterization of continuous phase motion inside the centrifuge. Rigorous definition of such motion in commercial equipment at practical rates is not yet possible, and because of this fact one of the major error sources in the theoretical fabric is introduced.

However, in the laboratory bottle centrifuge such effects are minimized. It is, therefore, the convenient and general practice to consider the droplet now settling in Fig. 2 under centrifugal force [3]. This droplet is settling as described in Eq 2 or as it may also be expressed:

$$v_s = v_g\ \frac{(\omega^2\, r)}{g} \tag{3}$$

Also consider that the droplet has a velocity which may be expressed as $v_s = dr/dt$ then:

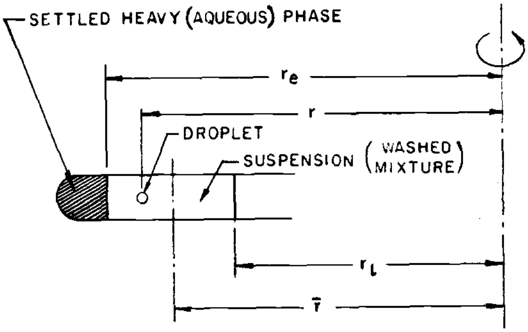

FIG. 2–*Bottle centrifuge tube.*

$$dr/dt = v_g \frac{(\omega^2 r)}{g}$$

and

$$\int_r^{r_e} \frac{dr}{r} = \int_0^t v_g \frac{\omega^2}{g} \, dt \qquad (4)$$

Integrating:

$$\ln (r_e/r) = v_g \frac{\omega^2}{g} t \qquad (5)$$

or

$$t = \frac{\ln (r_e/r)}{v_g \, \omega^2/g}$$

where t is the time the droplet is under centrifugal acceleration while still in suspension, and r_e is the radius from the centerline of rotation to the heavy liquid, light-liquid interface or the boundary between the volume in which liquid-liquid separation is being conducted and that in which it is, in theory, completed.

Bottle Centrifuge

One may now attempt to define the theoretical capacity of the bottle centrifuge. This is done by making the following assumptions known to be erroneous or largely so even in the bottle centrifuge: (1) all water droplets are spherical and uniform in size, (2) all droplets are uniformly distributed in the hydrocarbon phase and there is no interaction between particles, and (3) there is no remixing or turbulence.

It has then been conventional to arbitrarily choose a condition known as the "50 percent cutoff point." This refers to a condition which assumes that 50 percent of all droplets suspended in the supernatant "wash mixture" at time $t = 0$ are sedimented into the heavy phase after time t. This, in turn, requires a definition of $\bar{r}$, a radius which from Fig. 2 can be described as

$$\bar{r} = \frac{r_e + r_l}{2}$$

and which, because of uniform water droplet distribution in the fuel phase, defines both the mean and average droplet radius in the wash mixture undergoing liquid-liquid separation at time $t = 0$.

The actual centrifugal capacity Q_0, of a bottle centrifuge (tube) can be considered as the ratio of the volume, V, undergoing separation, in this case the liquid-liquid suspension or washed mixture and the .time in the centrifugal field, t, or:

$$Q_0 = \frac{V}{t} \tag{6}$$

substituting directly from Eq 5

$$Q_0 = v_g \frac{\omega^2}{g} \frac{V}{\ln (r_e/\bar{r})} \tag{7}$$

but on the basis of the cutoff assumption and as it is conventionally written:

$$Q_0 = 2v_g \frac{\omega^2}{g} \Big/ 2 \ln \left[\frac{2r_e}{(r_e + r_l)}\right] \tag{8}$$

Conventional treatment now considers v_g, a characteristic of the material under centrifugation, as apart from the remainder of the expression which, in fact, describes the centrifuge itself. This term is used as a capacity factor and is called Σ and in the prior case of the bottle centrifuge:

$$\Sigma_B = \frac{\omega^2 V}{2 g \ln \left[\frac{2r_e}{(r_e + r_l)}\right]} \tag{9}$$

Note that the 50 percent cutoff assumption, although convenient as a method of visualization, and the expressions that are derived from it are no more or less valid than a 100 percent cutoff or "x" cutoff assumption. Since in practice the ultimate use of Σ is not to predict actual recoveries but simply to predict relative performance on similar suspensions between centrifuges of similar geometry, any consistent basis is suitable.

The Σ term, as in Eq 9, has the dimensions of an area and is considered as describing a gravity settling tank having an equivalent area giving a performance equal to the centrifuge when settling equivalent feeds.

Disc Centrifuges

Thus far only the bottle centrifuge has been considered, the simplest case, because of its batch nature of operation and the quiescent settling conditions which thus can be expected. Fuel washing liquid-liquid separation, while studied in the laboratory with bottle centrifuges, is invariably effected commercially by use of disc centrifuges. Although other types of centrifuges can also effect a separation, they will not be considered due to their lack of practical importance in fuel washing.

The derivation of Σ, the centrifuge capacity factor, for a disc centrifuge is similar in all basic respects to that carried out for the bottle centrifuge except that: (1) a batch condition no longer holds, and the flow of fluid through the centrifuge must be considered, and (2) the varied geometry in the settling region must be considered.

As can be seen from Fig. 3, the characterizing feature of the disc centrifuge is the stack of trunco-conical lamina which fill the interior of the rotor. The similarly shaped volumes between these lamina or discs are the regions in which the bulk of liquid-liquid separation takes place within a disc machine. It has been the practice in the determination of disc centrifuge Σ, to base the Σ value entirely upon the disc stack Σ calculation, neglecting the Σ of the unit outside the stack. This is largely justified in a theoretical treatment but the importance of the region outside the stack cannot safely be dismissed from a practical study due to a variety of effects which must, necessarily, be omitted in the theoretical treatment. This important region will be considered briefly later.

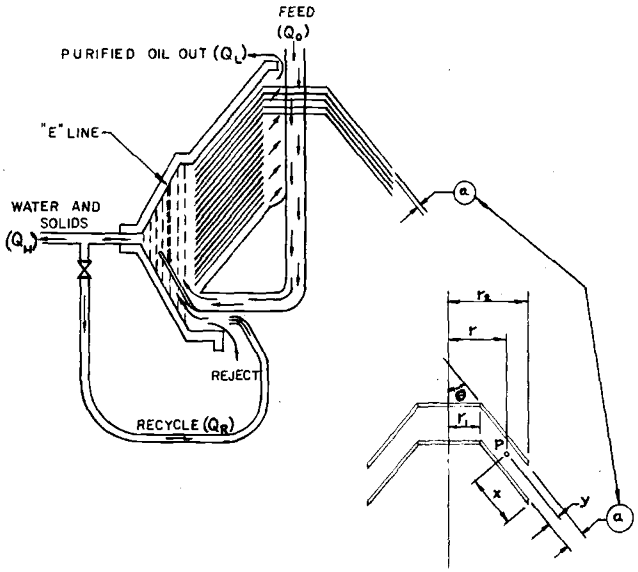

FIG. 3–*Disc centrifuge, Gravitrol Configuration.*

Consider the flow of "washed mixture" or feed into the centrifuge bowl in Fig. 3 and then the flow of a representative portion, both as regards composition and flow distribution up thru the channel described in Fig. 3. Now, making all previous assumptions regarding sedimentation in the bottle centrifuge as well as assuming the liquid-liquid mixture "up to speed," that is, with the same angular velocity as the disc stack, the flow velocity up thru the disc stack of the fuel-water mixture will be [*3*]:

$$\frac{dx}{dt} = -\frac{dr}{dt \sin\theta} = \frac{Q_0}{2\pi nra} \tag{10}$$

where

x = distance parallel to the disc surface from r_2 the outside edge of the disc,

t = time interval starting from the moment the continuous liquid element enters the disc space,

r = radial position of this liquid element at time t,

a = perpendicular clearance between adjacent discs, and

θ = half the included angle of the discs.

The complete derivation of the disc stack Σ from Eq 10 can be found by reference to Lavanchy [*3*].

As was the case with the bottle centrifuge, the expression for disc centrifuge capacity can be broken into two parts, that dealing with the settling properties of the feed and that dealing with the centrifuge. In this case those terms referring to the centrifuge alone refer more specifically to the disc stack alone. On this basis:

$$Q_0 = 2v_g \Sigma_D \tag{11}$$

and

$$\Sigma_D = 2\pi \frac{n}{3} \frac{\omega^2}{g} \cot\theta \, (r_2{}^3 - r_1{}^3) \tag{12}$$

where

Σ_D = Σ of the disc stack, and

n = number of discs in the stack.

Therefore, any comparison of Σ_D between two centrifuges is a comparison of their disc stacks alone. Such comparisons are extremely valuable but are not complete comparisons.

Liquid-Liquid and Liquid-Solid Separation

Thus far, a considerable amount of attention has been devoted to characterizing the ability of a centrifuge to separate the two immiscible phases being considered, fuel and water. Consider the general dispositions of these two phases in a disc centrifuge under equilibrium operation.

The rotor illustrated in Fig. 3 shows a liquid-liquid and liquid-solid separator in the Gravitrol configuration in which the washed mixture of fuel and water is fed to the centrifuge into the lower portion of the rotor, accelerated by a feed zone accelerator to a point outside the disc stack. Note that the "E line" or theoretical interfacial layer between the two separating phases lies well outside the disc stack and close to the bowl wall. This permits: (1) the full Σ_D to be brought to bear on separation of alkali metal bearing water phase from the hydrocarbon phase; (2) maximum centrifugal force to be placed at the "E line", or more practically defined, the interfacial zone, where emulsion stability most frequently interfers with separation; and (3) maintainance of the emulsion layer completely outside the disc stack, preventing stack plugging due to "disc bridging" by stiff emulsions.

E line position in a centrifuge bowl is maintained by a hydrostatic balance directly comparable to that between two immiscible liquids in a U-tube as described in Fig. 4. Rotating the U-tube about an axis as described in Fig. 5

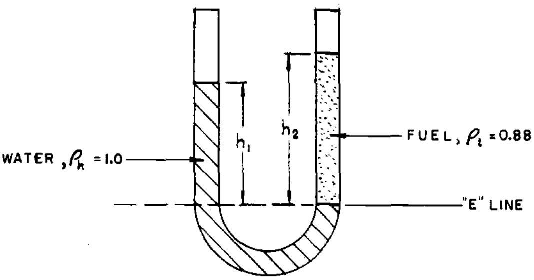

FIG. 4–*Liquid-liquid pressure balance; gravity.*

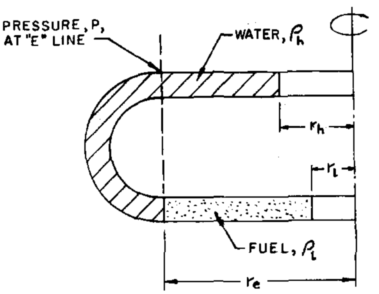

FIG. 5–*Liquid-liquid pressure balance; centrifugal force.*

permits description of the pressure at radius r_e as

$$P = \frac{\rho_l}{2}\ (\omega^2)\ (r_e^2 - r_l^2) = \frac{\rho_h\,\omega^2}{2}\ (r_l^2 - r_h^2)$$

the pressure due to the light or heavy phase at the E line.
Then

$$\frac{\rho_h}{\rho_l} = \frac{r_e^2 - r_l^2}{r_e^2 - r_h^2} \tag{13}$$

The depth of the liquid crest at point of discharge or the change in the free surface radius of the light or heavy phase at point of discharge can and should be considered at high flow rates. The preceding equation is then modified according to Trowbridge [*4*].

$$\frac{\rho_h}{\rho_l} = \frac{r_e^2 - r_l^2 + \left(\dfrac{Q_l}{K\omega}\right)^{3/2}}{r_e^2 - r_h^2 + \left(\dfrac{Q_h}{K\omega}\right)^{3/2}} \tag{14}$$

The E line radius is varied in actual practice by:

1. Varying r_l or r_h or both the point of light or heavy phase discharge. This is often, but not necessarily, accomplished by a change in ring dam diameters. It may also be effected by relocation of a skimmer tube or indirectly by a change in centripetal pump back pressure.

2. Varying of ρ_h or ρ_l. ρ_h is the most frequently varied but ρ_l may also be varied by similar techniques. Loading of the heavy (aqueous) phase by use of a suitable inorganic salt is a technique developed with specific reference to fuel washing as is density adjustment, particularly heavy phase density adjustment, by precise temperature control [*5, 6*].

Aqueous phase density control by soluble salt loading was originally conceived as an aid to liquid-liquid separation by increasing $\Delta\rho$ and thereby increasing the range of fuels which can be washed into the region of bunker fuels having densities equal to or greater than water. This remains its most important function in view of the fact that fuels having API gravities as low as twelve may be washed and separated to satisfactory alkali metal levels by use of proper E line position and Q/Σ ratios without recourse to aqueous phase weighting either as an aid to separation or E line adjustment [*7*].

Note that Q is flow rate, and Σ is considered as describing a gravity settling tank having an equivalent area giving a performance equal to the centrifuge when settling equivalent feeds. Q/Σ is equal to two times the droplet settling velocity, V_g, at one gravity field. The mean droplet with V_g settling velocity will be captured when assuming 50 percent cutoff.

It must now be observed that with the E line located outside the disc stack no Σ_D remains to act on the aqueous phase. It must not be assumed that any oil droplets entrained in the continuous aqueous phase must, therefore, discharge with the aqueous phase. The reason this does not occur is the appreciable Σ term which exists in the cylindrical volume outside the disc volume, Σ_{CY}. This term derived in similar fashion to the Σ_B and Σ_D may be written [3]

$$\Sigma_{CY} = 2\pi L \frac{\omega^2}{g} (3/4\, r_{CY}^2 + 1/4\, r_e^2) \tag{18}$$

where

r_{CY} = radius of inner cylinder wall,
r_e = radius of E line, and
L = length of cylinder.

If equal separation is required for each phase then:

$$\frac{Q_l}{\Sigma_D} = \frac{Q_h}{\Sigma_{CY}} \tag{19}$$

where:

Q_l = the hydrocarbon phase flow, and
Q_h = the aqueous phase flow.

In practice $Q_h \leqslant 0.1\, Q_l$, a condition which gives more than adequate alkali metal extraction. Therefore, generally

$$\frac{Q_l}{\Sigma_D} > \frac{Q_h}{\Sigma_{CY}}$$

despite the relatively low value of Σ_{CY} and the limiting capacity of the liquid-liquid centrifugation remains Q_l and the limiting Σ, Σ_D.

It should be noted that the above ratio assumes a constant Σ_{CY} as well as a constant Σ_D. Solids accumulation in either volume reduce Σ not only as a result of decreased separating volume but by interference with proper flow pattern. This is particularly true within the disc stack itself. The volume outside the stack is not equally sensitive to solids accumulation. It is frequently observed that an equilibrium solid deposit in this volume only, once established, gives little evidence of decreasing Σ.

Brownian Motion

The disposition of both hydrocarbon and aqueous phases inside a typical disc centrifuge bowl have been considered as well as some of the major factors giving rise to the liquid-liquid separation itself. It was noted at the outset however, that Brownian motion is neglected by Stokes law and the subsequent derivations. The validity of this assumption is confirmed by considering the expression from Svedburg [8]

$$\frac{dc}{c} = \frac{N \frac{\pi}{6} d^3 (\rho_s - \rho)\, \omega^2\, rdr}{RT} \tag{20}$$

where

c = heavy phase concentration at the radius,

d = particle diameter,
N = Avogadro constant,
ρ_s = density of particle,
ρ = (mass) density of the light (continous) phase,
R = gas constant,
T = absolute temperature of the suspension,
ω = angular velocity, and
r = radial position at which concentration is computed developed from Eq 20.

Integrating Eq 20 obtains

$$\ln \frac{C_1}{C_2} = \frac{N \frac{\pi}{6} d^3 (\rho_s - \rho)}{RT} \omega^2 \frac{1}{2} (r_1^2 - r_2^2)$$

or

$$\frac{C_1}{C_2} = e^{\frac{-N \pi d^3 (\rho_s - \rho)(\omega^2 \bar{r})}{6\,RT} (r_2 - r_1)}$$

On a commercial fuel oil washing system the $(\rho_s - \rho)(r_2 - r_1)$ is close to unity. At room temperature the above equation is further simplified as

$$\frac{C_1}{C_2} \approx e^{-1.29 \times 10^{13} d^3 (\bar{r} \omega^2)} \tag{21}$$

Based on Eq 21, Fig. 6 shows the drop size versus centrifugal force for various concentration gradients when the diffusion by Brownian motion is balanced by sedimentation velocity in a centrifugal field.

It will be observed that only at droplet diameters of 100 millimicrons (mμ) or less does Brownian motion become significant, a value over two orders of magnitude less than the droplet diameter range anticipated in a typical fuel washing process. Thus, Brownian motion can indeed be safely neglected.

However, although the droplet diameters at which Brownian motion becomes important are not encountered in the system under consideration, a calculation of the range of aqueous droplet diameters in hydrocarbon suspension subject to capture during fuel washing is of interest. Figure 7 illustrates the droplet diameter at the 40 percent cutoff point versus Q/Σ_D. The cross hatched area

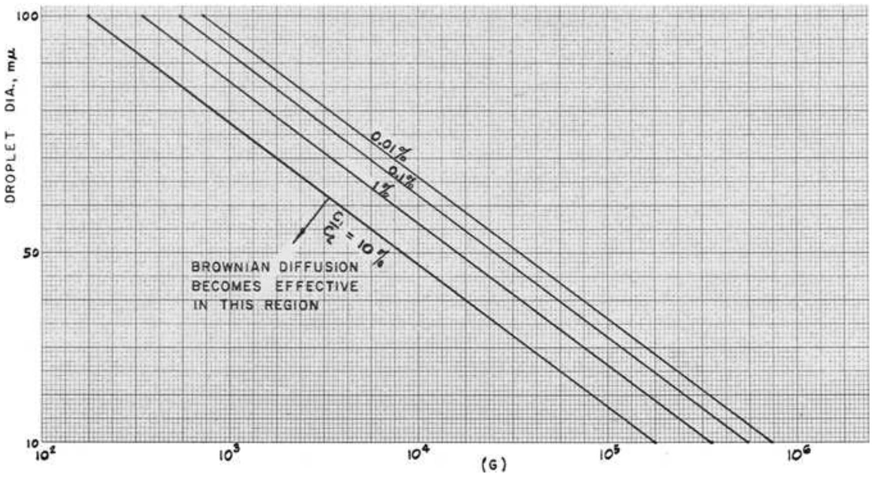

FIG. 6–*Brownian motion effect.*

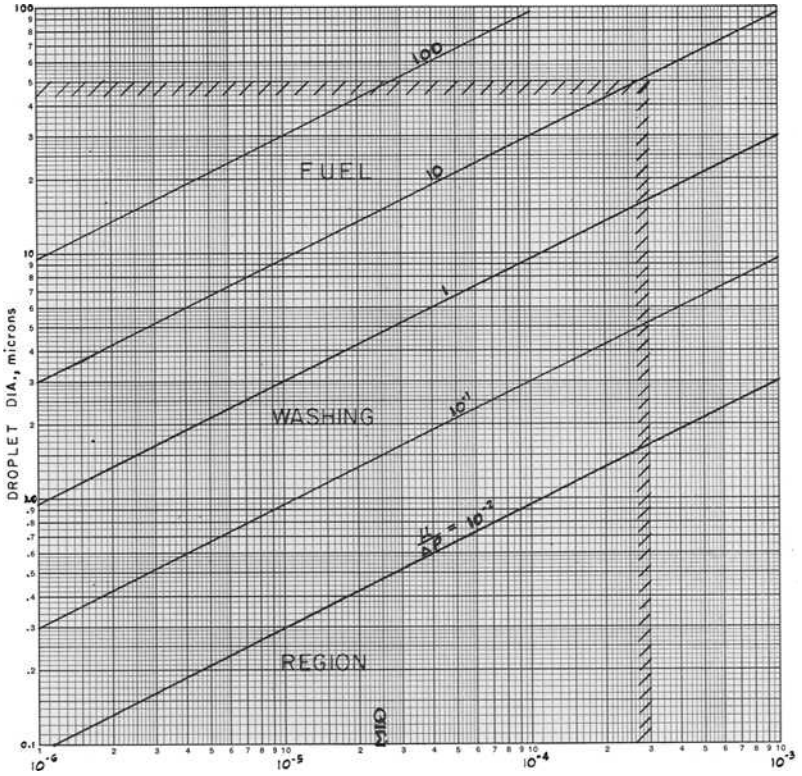

FIG. 7–*Effective fuel washing region.*

labeled "Fuel Washing Region" outlines those limiting values most probably generated with the systems under consideration. Since Fig. 7 is derived by calculation only, directly from Stokes law, it is necessary to apply a suitable centrifugal efficiency factor, determined from experience, in order to estimate actual droplet diameter at the 50 percent cutoff point. The purpose of this factor is to compensate for the error introduced by assumptions known to be invalid and already discussed as well as the following assumptions known to be invalid, at least in part.

1. No re-suspension of heavy phase.
2. Uniform distribution of feed through the disc stack.
3. Symmetrical and uniform distribution and removal of heavy phase.
4. Turbulent flow confined to the feed zone, where feed acceleration occurs.
5. No difference in angular velocity between feed and discs or between phases.

However, a centrifuge efficiency term neglects any emulsification tendency of the fuel, mixing efficiency coalescence effects, and other process variables. Of these process variables the emulsification tendency of the fuel and the strength or stiffness of the resulting emulsion is of great importance [*9*]. This is particularly true with regard to the stiffness of the interfacial emulsion within the centrifuge bowl which can be expected despite the use of various types of emulsion breaking surfactants.

The degree to which any given fuel will present a serious emulsion problem varies greatly and is determined by actual laboratory tests if specific experience is lacking.

It can be seen from the foregoing discussion that the liquid-liquid separation step is affected to one degree or another by a wide number of variables. Intensity and type of mixing is one of these mentioned earlier. Due to the large number of variables affecting and interacting with the mixing and separation operations, the optimum degree of mixing required in fuel washing has been selected on an empirical basis.

It is assumed that alkali metal extraction or washing is carried out by counter current extraction in two stages, by a straight material balance the water needs can be expressed

$$W_W = -\frac{W_F}{2} + \left(\frac{W_F^2}{4} + W_c W_F \frac{C_F - C_c}{C_c - C_W} \right)^{1/2}$$

where

W_F = weight of water in original fuel,
W_W = weight of water used in washing,
W_c = weight of water in washed fuel after centrifuge,
C_F = sodium concentration in original fuel,
C_W = sodium concentration in wash water, and
C_c = sodium concentration in washed fuel.

Then, it is possible to obtain the amount of wash water required when operating in the described mode if the amount of water remaining after centrifugation is known, by reference to Fig. 8, based on calculation and data obtained from

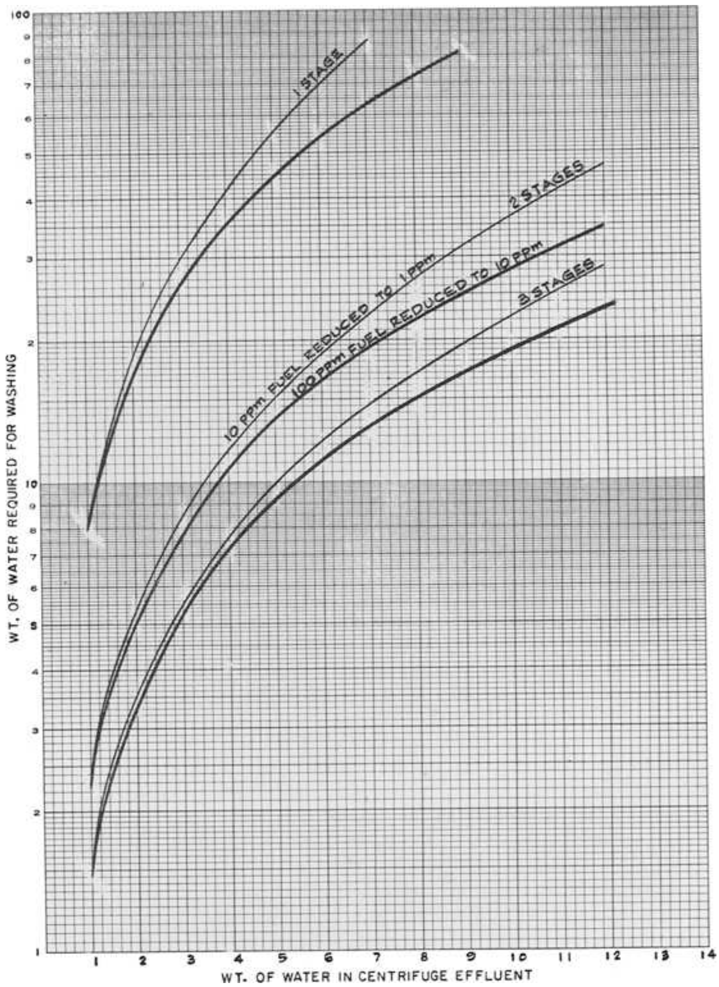

FIG. 8–*Fuel washing water requirements.*

operating experience with a specific fuel stream [*10*].

However, the precise degree of water removal effected by the centrifuge, as is now evident, cannot be predicted from theory alone. The viscosity-density relationship is important and useful in predicting water removal to be expected, yet direct experience with the fuel in question is most preferable. This experience should cover the behavior of the fuel during mixing and extraction as well as centrifugation. Once a data base with a given fuel has been established, projection of the degree of alkali metal removal expected at varying metal contents, flows, and temperatures is readily made via proper application of theory. In those cases where such projections can be made, selection of centrifugal and other process equipment can be carried out with confidence.

Should no data base be available, while theory is still a useful guide, qualifications are so numerous that study of the fuel in question is clearly indicated. In those instances where such study is not possible, often due to uncertainty as to what fuels will actually be employed, the fuel consumer imposes upon himself an unnecessary economic penalty in the form of the large safety margins which must necessarily be incorporated into the fuel washing system design.

Conclusion

Centrifugal separation theory, based on the sigma concept, is a most useful tool when predicting disc centrifuge capacity factors on liquid fuel systems of known washing characteristics. However, the physical chemical nature of any two fuels can vary so greatly that washing performance estimates, based on differences between viscosity-density and centrifuge design parameters alone, must be considered as theoretical projections.

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F. H. Hilts[1]

Purification of Fuel Oils by Centrifugal Force

REFERENCE: Hilts, F. H., "**Purification of Fuel Oils by Centrifugal Force,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531*, American Society for Testing and Materials, 1973, pp. 121-132.

ABSTRACT: This paper defines the type of centrifuge to use depending on fuel oil to be purified, and also describes performance on distillate and heavy fuels for straight purification systems. More extensive fuel washing and inhibition treatment is discussed for residual oils.

KEY WORDS: fuels, gas turbines, contaminants, centrifuges, separation

The economics of today's gas turbines require clean fuel, whether it be distillate or residual type fuel. Distillate fuel is, for all intents and purposes, clean when it leaves the refinery. In the course of transportation and storage, however, it is liable to pick up contaminants which impair its properties. Both water and sediment are commonly found in distillate fuels at point of use.

Heavy fuels consist of residual oil only, or a mixture of residual oil and distillate, the proportion being determined by specification requirements. Apart from impurities which have entered the oil during transportation and storage, such as slag, scale, rust, sand, dirt, water, etc., these fuel oils contain impurities which come with the crude oil from the oil wells. Such impurities vary according to the source of the crude but usually consist of abrasive substances which are very harmful to the gas turbine, such as silica, metallic oxides, and small sodium chloride crystals. All such solids are difficult to remove from the oil, particularly when the oil has both a high specific gravity and a high viscosity.

Nevertheless, centrifugal purifiers are used to treat both distillate and heavy fuel oils, with excellent results. Each type of fuel, distillate or heavy, requires different handling, and sometimes different types of centrifuges. We shall therefore consider these fuels separately.

Historical Background

Historically, the use of centrifugal force for the removal of contaminants is well established. Biblical references to the slinging of honey and the obtaining of olive oil are among the first recorded references to the exploitation of

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centrifugal force. The ancient Chinese are said to have used a container on the end of a rod, rotated about its center of gravity, and in this manner separated cream from milk in a considerably shortened time.

The first continuous centrifugal separator was invented in 1877 by Dr. Gustav De Laval, and it was applied to the continuous separation of cream from milk. The second major application for the centrifuge, a few years later, was in the purification of mineral oils. Today, there are tens of thousands of centrifugal separators purifying mineral oils throughout the world.

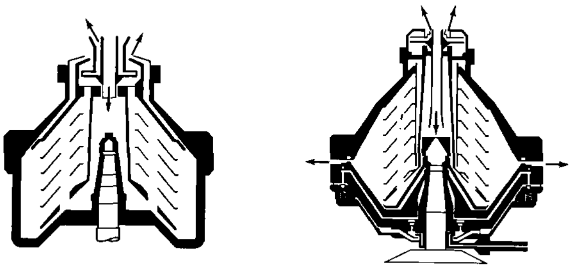
More recently, fuel treatment systems and extensive automation capabilities have resulted in the use of centrifugal fuel washing systems for removal of harmful salts as well as sediment and water from gas turbine fuel oils. Fuel washing will be discussed as our third application of centrifugal force to fuel treatment.

Types of Centrifuges

The common types of centrifuges which are used to purify fuel oils fall into two categories: (1) solid bowl centrifuges (sludge retaining), and (2) solids-ejecting centrifuges (self-cleaning).

The solid bowl centrifuge is illustrated in Fig. 1. This type of unit continuously discharges the purified oil and separated water phases. The solids are retained against the bowlwall, and must be periodically and manually removed from the bowl. This type is routinely used for distillate oil purification because of the relatively low solids content of distillate fuel.

The water droplets and solids, being heavier than the oil, move horizontally toward the outer wall of the bowl. The oil moves inward toward the center of the bowl. Each liquid phase is discharged from separate outlets, continuously and to the degree that they are displaced within the bowl by incoming liquid.



Conventional
Solid Bowl

Self-cleaning
"PX" Bowl

FIG. 1–*Bowl design–conventional versus self-cleaning.*

If the feedstream to the bowl is stopped, discharge from the bowl will stop and it will continue to rotate full of liquid. If 1 gal of pure oil is fed into the bowl, only 1 gal of oil will discharge. If 1 gal of an oil/water emulsion (50 percent each) is fed into the bowl, ½ gal of each will discharge from the bowl.

The separation itself takes place within the disc stack. The discs are usually spaced about 0.030 to 0.050 in. apart. Although *g* force controls the speed of particle separation, the discs control the distance that the particle must travel to be separated. Therefore, the use of discs in a bowl increases the capacity many times greater than a similar one without discs.

The space between the bowl wall and the edge of the disc stack is sludge holding space. Since the separation takes place within the disc stack, the efficiency of the separation is not changed by build up of a solids cake on the wall. The machine must be stopped, opened, and the solids removed, at such time as the cake has built up to the edge of the discs.

The solids-ejecting centrifuge was developed about 15 years ago. In that short a time it has become the dominant centrifuge for oil purification. It is self-cleaning, reliable, and easily automated. It is widely used for remote installations where there is no operator in attendance.

Until the development of the solids-ejecting centrifuge, the nozzle type centrifuge was used for oils with high solids content. However, the far greater reliability, versatility, capability for unattended operation, its equal efficiency and lower maintenance costs, soon displaced the nozzle bowl unit in almost all applications involving oil.

The solids-ejecting centrifuge bowl is also shown in Fig. 1. The bowl wall (sometimes called a split bowl) is tapered outward so that the solids are retained at this outer "V" shaped wall. The bowl bottom actually consists of an outer stationary bowl and an inner sliding bowl bottom. In the lowered position, the sliding bowl bottom exposes a wide opening around the entire bowl wall. This slot may be 3/8 to 1/2 in. wide and thereby very positively discharges the accumulated sludge cake.

The space between the stationary and sliding bowl bottom is filled with water, termed operating water. The hydraulic force upward, generated by the *g* force in the rotating bowl, upon the operating water, is approximately double the hydraulic force downward by the oil in the bowl. This force keeps the bowl tightly closed. At such time as the sludge space is filled, the operating water is rapidly and automatically released from beneath the sliding bowl bottom. The sliding bowl bottom drops downward, exposing the discharge slots, causing ejection of the solids. This ejection cycle is most commonly initiated by a timer and requires only seconds to complete.

The separation of oil, water, and solids within the bowl occurs similar to that of the manually cleaned solid-bowl centrifuge.

Several techniques are available for elimination of oil from the discharged sludge. The choice is somewhat dependent on the installation site, economics, or customer preference. Among them, the most popular is commonly called a bowl purge. This is accomplished by blocking the water outlet, injecting water, displacing all the oil from the bowl, and then initiating the ejection cycle. This "purge" cycle may be automatic and adds only a few seconds to the cleaning sequence. On fuel oils the ejection cycle may vary from once every 2 h to once every 12 h, depending on the cleanliness of the oil handled.

Selection of Centrifuge Type

The purification efficiency of the solid-bowl and solids-ejecting centrifuges are equal. The choice of one over the other is therefore made for one or more of the following reasons: (1) quantity of impurities in the oil, (2) centrifuge cost versus labor cost, and (3) plant requirements for automated equipment.

In general, distillate fuels have low quantities of suspended solids. A solid-bowl centrifuge costs approximately 65 to 75 percent as much as the automatic solids-ejecting type. Therefore, unless point 3, just mentioned, provides an overriding factor, the solid bowl centrifuge will usually be selected.

It is a common fact that sludge and impurity content as well as the specific gravity increases with the viscosity. Therefore, the heavier the fuel oil used, the more likely it will be that a solids-ejecting type centrifuge will be necessary. Generally, the following figures are found to be valid:

Viscosity, SSU at 100°F	500 to 4200
Specific gravity at 60°F	0.93 to 0.99
Sludge, percent by volume	0.02 to 0.08

Figure 2 illustrates the interval between sludge evacuation from the centrifuge bowl, either by manual or automatic means, as a function of sludge content of a fuel oil. The variable band results because of the slight variation between

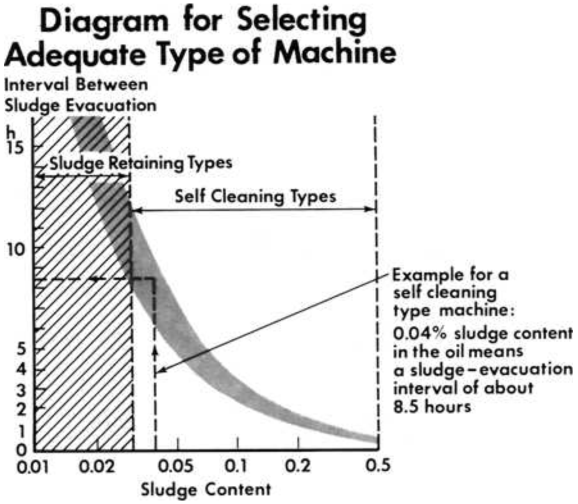


FIG. 2–*Diagram for selecting adequate type of machine.*

machines capacity versus sludge holding space. A 2000 gallons per hour (gph) machine does not necessarily have twice the sludge holding space of a 1000 gph unit.

From this illustration one can observe that if it is desired that the purifier be cleaned only once per 8 h shift, a manual unit may only operate on oil with solids content up to 0.03 percent. Over 0.03 percent the manual unit may be oversized one or more models in order to obtain the necessary larger sludge space of the larger machine. This, of course, may then result in equipment cost equal to, or higher than that of the automatic self-cleaning unit.

Purifier Installation

Both a solids-retaining centrifuge and a solids-ejecting centrifuge are installed in the same general manner. The units are both equipped with suction and discharge pumps, temperature and pressure gauges, sampling cocks for both unpurified and purified oil, and all necessary strainers, valves, and fittings to make the unit a self-contained purification system.

The purifier is installed between the raw fuel storage tank and the gas turbine day tank. The purifier withdraws oil from the storage tank using its own pump, purifies it, and pumps it to the day tank. The purifier is often permited to operate 24 h per day, regardless of the length of time of operation of the turbine. An overflow line returns excess purified oil from the day tank back to the storage tank. By such an arrangement, a full day tank is always assured, and when the turbine is not operated the storage tank is purified.

This arrangement was used aboard the *MSC G.T.S. Admiral Wm. Callghan* and has proven enormously successful. Details of purification performance are outlined later in this paper.

Another popular system arrangement is to automatically start and stop the purifier from a level control in the day tank. This, of course, is easily accomplished with the modern self-cleaning type centrifuges.

Temperature Requirements

Light distillate fuel, such as No. 2, is purified at room temperature. Heavy fuel is heated prior to centrifugation. The heater is placed in the line between the centrifuge's suction pump and the centrifuge inlet, as shown in Fig. 3. The temperature is raised to a level at which the viscosity is again returned to approximately 100 SSU. By so doing, the settling rate again approaches that of the distillate and the purification rate will be maintained high.

In both manually cleaned and self-cleaning type centrifuges, the heater is commonly supplied as an integral prepacked part of the purification device.

Prepackaged and Automated Systems

Both the solids-retaining type centrifuge and the solids-ejecting type are available in prepackaged, pretested modules, complete with all necessary accessories and controls such that the module forms a complete purification

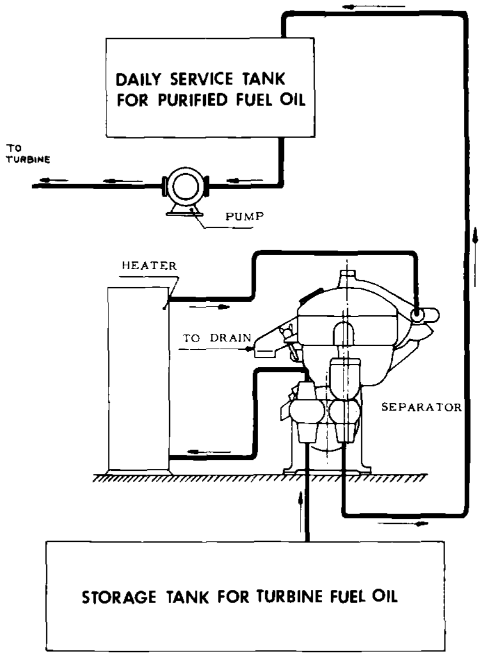


FIG. 3–*Storage tank for turbine fuel oil.*

system. Installation requires a minimum amount of space, and requires connections only to outside piping, power, and utilities. Malfunction detection, alarms, and reactive logic are easily built into all fuel treatment systems. The solids-ejecting unit especially lends itself to such total control, and may thereby be installed in remote areas with no operator attendance whatsoever. Inspection is limited only to monthly maintenance.

Automatic start, locally or remote, may be utilized. Automatic malfunction detection may be provided against such possibilities as vibration, low water pressure, low air pressure, failure to eject solids, failure of the bowl to close, oil discharge from water outlet, and feed flow failure. Each of these malfunctions are programmed to sound an alarm and take protective reaction steps to prevent disruption of system operation.

The unit shown in Fig. 4 is such an automated fuel oil purifier, complete with all electrical controls and malfunction detection devices mentioned previously. It is equipped with a compact steam heater. This unit is also equipped with a sludge collecting tank built into the base, a level control in that tank, and a sludge transfer pump controlled by the liquid level control in the tank. The platform is semiportable; that is, it may be moved quickly to new positions by fork lift truck.

Purification Performance

I mentioned earlier the installation of two centrifuges aboard the *Admiral*

FIG. 4–*Fuel oil purifier.*

Callaghan. These units are intended for primary purification of the gas turbine fuel oils, thereby extending the life of the down stream filters.

Reported performance indicates that the oil as delivered to the vessel contained an average of 410 ppm water and 300 ppm suspended solids. The purifier, a solids-ejecting centrifuge, removed 80 percent of the water per single pass and 60 percent of the solids. A surprising and desirable occurrence, yet to be explained, is that the purifier is removing 70 percent of the vanadium. It was reduced from 0.2 to 0.07 ppm.

The purifier is operating at twice the demand rate of the turbine and half of the purified oil is recycled from the day tank back to the storage tank. The purifier is therefore handling a mixture of purified and unpurified oil.

Accordingly, the purity of the oil discharged from the centrifuge shows only 4 ppm water, and trace solids. At times, a water level as low as 1 ppm has been recorded.

Prior to installation of the centrifuges, the life of the downstream cartridges was 3 to 4 days. Since installation, the filter life has been extended to 10 to 14 days.

A typical performance for a centrifuge on Navy distillate and heavy fuel oils is shown in Fig. 5. These are excerpts from certified test reports on actual installed units. Please note the low levels of residual moisture in the oil and the negligible amount of solids. Further, on heavy fuel, there is some reduction of sodium since most of it is present in the water phase.

Time in Min.	10	20	30	40	50	60	Ave
Oil Temp °F	120	120	118	117	116	116	118
Oil Feed GPH	700	700	700	700	700	700	700
%Water in Feed	3.0	3.3	3.0	3.0	3.2	3.1	3.1
%Sediment in Feed	.01	.008	.01	.01	.01	.009	.095
%Water in Oil Discharge	.01	.015	.01	.015	.005	.01	.01
%Sediment in Oil Discharge	Trace	Trace	Trace	Trace	Trace	Trace	Trace
%Cuff in Oil Discharge	None	None	None	None	None	None	None

	Feed	Discharge
Specific Gravity @ 60°F	.963	.963
A.P.I. Gravity @ 60°F	15.4	15.4
Viscosity @ 100°F, SSU	1135	1127
Viscosity @ 210°F, SSU	91	90
% Water (by Volume)	13.5	
% Solids (by Volume)	0.5	
Water by Distillation, % by Weight	13.9	0.02
Sediment, Hot Filtration, % by Weight	0.54	0.22
Sodium (Uranyl Acetate), % by Weight	0.0090	0.0037

FIG. 5–(top) *Excerpt from a certified test report on distillate fuel; and* (bottom) *excerpt from a certified test report on heavy fuel.*

In a recent study employing the electron microscope, the effectiveness of a centrifugal purifier was closely evaluated. Figures 6 and 7 show the impurities before and after centrifugation. The oil under study was a 600 SSU at 100°F oil. The microscopic slides illustrate not only the effective removal of solids by quantity, but indicates that the residual solids had an average size of 2 μm.

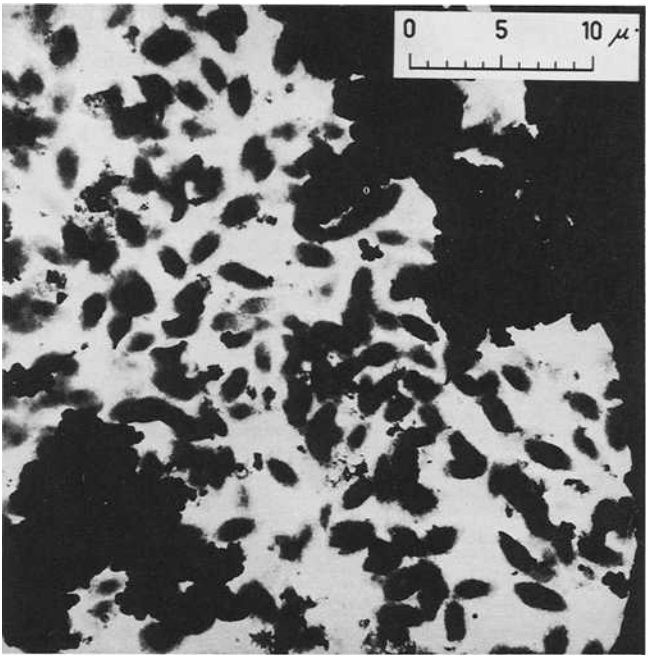


FIG. 6–*Impurities before centrifugation.*

It should be noted that many distillate and heavy fuel oils are high in wax and resinous materials. Unless an oil temperature is maintained above the melting point of these waxes, they will remain as suspended solids in the oil. Although they do have Btu value and may be suitable for combustible fuel in the turbine, they can create severe problems in the suspended semisolid state. They will severely shorten the life of filters and cause fouling problems of associated controls and hardware. However, a centrifuge will normally treat these suspended waxes or resins as solid contaminants and remove them from the oil. Thus, the downstream system is protected from not only solids and water, but the blinding and fouling effects of resinous or waxy material.

Fuel Wash Systems

For heavy fuel with high alkali metal content, a centrifugal system was developed in 1960 for the washing and inhibition of gas turbine fuel. The basic

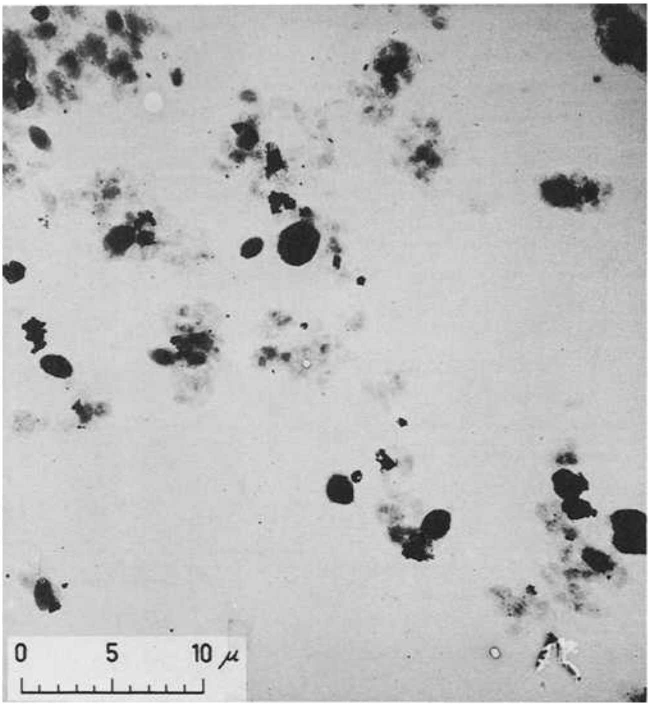


FIG. 7–*Impurities after centrifugation.*

work on such a system was performed at Central Vermont Public Service Corporation at Rutland, Vt. Since then, more than a dozen such systems have been installed around the world. The centrifuge, with its proven ability to handle a very wide variety of oils, from distillate to worst case residual, and from low contaminant level to high contaminant level, is an ideal device around which to design a fuel wash system. Such a system may be operated on whatever washable fuel is readily available at the moment, crude, distillate, or residual.

To remove or reduce corrosive deposits it is necessary to eliminate or inhibit the action of sodium and vanadium. Sodium is normally present in the oil in the form of finely divided droplets of an aqueous solution of sodium chloride (NaCl). The concentration of sodium in the droplet is estimated at 1 percent. Thus, it is theoretically possible to remove these droplets of salt solution by treatment in a centrifugal separator, since no extraction of sodium from the oil is involved, the problem being purely and simply one of separation. In actual fact the sodium content of the oil can be reduced by ordinary separation of water, but the final sodium concentration achieved in this way is not low enough. This is because some very fine droplets of highly concentrated NaCl solution remain in the oil. One can improve the separation result by injecting fresh water and mixing this water into the oil well enough to ensure that as many as possible of the salt solution droplets come into contact with the wash water. The purpose of this procedure is two-fold: (1) to swallow up the small, often emulsified salt-solution droplets in the larger droplets of wash water; and (2) to reduce the salt content of the droplets by dilution.

To finely distribute the wash water, it has to be stirred vigorously into the oil almost to the point of emulsification. The emulsion formed must, however, be broken; that is, small droplets must be made to coalesce into larger units so that they can be separated out again effectively. A demulsifier must therefore be added to the oil, preferably at the earliest possible stage; namely, before the addition of water–and uniformly distributed throughout the entire volume of oil.

In regard to the salt content of the wash water, it should be noted that this will hardly ever be equal to zero in actual practice. For pure tap water, a figure of 11 to 15 ppm sodium is acceptable. Such a sodium content is unlikely to increase the final amount of sodium in the washed oil by more than a fraction of 1 ppm. In certain cases, where the water supply is limited, recirculation of part of the wash water need not necessarily be ruled out, but such a procedure would require careful consideration in each individual case, particularly with reference to the degree of freedom from sodium demanded.

The washing process may be carried out in either one or two stages. If the viscosity of the oil and the initial concentration of sodium are high and the desired final concentration of sodium low, washing should take place in two stages in series. Accordingly, it has been demonstrated that heavy fuel (3000 to 5000 SSU at 100°F), having 100 ppm of sodium, can be reduced to less than 1 ppm. Distillate fuels can be reduced to 1 ppm or less quite easily.

When it comes to combatting vanadium corrosion, there are unfortunately not the same possibilities as in the case of sodium. The vanadium compounds in oil are oil soluble, but not water soluble, and it is therefore normally not possible to wash out and separate vanadium. In the previously reported case of the *Admiral Callaghan* it might appear that under some unique situations, yet to be defined, it is possible to separate out part of the vanadium compounds together with the oil sludge in the separator. However, under ordinary circumstances and based upon present technology, vanadium must not be considered removable by washing techniques.

To frustrate the corrosive attacks of vanadium, one has to add certain chemicals to the washed oil which react chemically with the vanadium and increase the melting point of the vanadium ash, thus preventing corrosion and deposits. The best known and most widely used additives in practice are magnesium sulphate and magnesium oxide. Good results have also been obtained with kaolin, zinc oxide, ethyl silicate, and other compounds. Oil-soluble additives such as magnesium naphthenate have also been tried. According to Russian sources, good results have been obtained in laboratory trials by the addition of organic, oil-soluble magnesium compounds and by the injection of ammonia into the air intake of the turbine. At moderate gas temperatures (up to about 670°C), a silicon-based product called Perolin 602 GT and Petrosene D, a magnesium-based product, have given good results under service conditions.

It is difficult to compare the effectiveness and limitations of the various additives, since so much depends on such factors as the quality of the oil, the temperature of the gas, the cost of the additive, etc. Moreover, some additives are good corrosion inhibitors but at the same time tend to promote the formation of deposits. Of all the inhibitors tried to date, $MgSo_4$ has been most successful, and this compound is used in the great majority of installations.

Earlier plants were equipped with minimum system automation. More recent plants have featured extensive automation and system control. A fuel wash plant normally includes all equipment for heating, demulsification, water washing, inhibition, and fuel forwarding. Also, most systems include facilities to weigh the wash water when oils of close to 1.0 specific gravity are encountered. Most users prefer that such plants be modularized and pretested.

Summary

In conclusion, centrifugal purification of fuel oils offers effective removal of water, solids, and other contaminants heavier than the oil. It does so under ordinary conditions as well as extreme conditions of gross water and solids. There is no continuing cost of media, and it is well proven to be reliable. It is a compact device, and is available in many sizes. Finally, it is available in automatic self-cleaning designs which open up a wide range of applications including unattended or remotely installed power stations, pumping plants, or engine rooms.

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C. C. Ward[1]

Survey of Trace Metals in Distillate Fuels

REFERENCE: Ward, C. C., "Survey of Trace Metals in Distillate Fuels," *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 133–142.

ABSTRACT: The amounts of trace metals in distillate fuels are receiving increased attention, especially those of metals that cause corrosion of gas turbine blades.

Published information on the levels of trace metals in distillate fuels is scarce, so members of Section D02.E on Burner, Diesel, and Gas Turbine Fuel Oils of ASTM Committee D-2 on Petroleum Products and Lubricants agreed to pool information available in individual laboratories. Twelve laboratories furnished data on 408 samples of kerosines, diesel fuels, burner fuels, aviation turbine fuels, and gas turbine fuels. Data on trace metals content included that of sodium, potassium, vanadium, calcium, lead, magnesium, and copper. Some laboratories did not report data on all metals.

This survey to pool information available on the amounts of trace metals in random samples of distillate fuels does not lend itself to statistical treatment of the data. However, it does show that the level of trace metals in currently produced distillate fuels is much lower than the amounts presently allowed in ASTM Specification for Gas Turbine Oils (D 2880-71).

KEY WORDS: fuels, trace elements, turbine blades, gas turbines

The amounts of certain trace metals in distillate fuels are receiving increased attention, especially those in fuels intended for aircraft and gas turbine engines. ASTM Specification For Gas Turbine Fuel Oils (D 2880-71) sets maximum values for the amounts of vanadium, sodium plus potassium, calcium, and lead, and both a minimum and a maximum ratio of magnesium to vanadium because of the effects of these metals on turbine blades. Despite the interest in these metals there is little published information on the trace metals content of distillate fuels. Information was available in individual laboratories, so members of Section D02.E on Burner, Diesel, and Gas Turbine Fuel Oils, of Committee D-2 on Petroleum Products and Lubricants agreed to pool information available in their laboratories.

Data on trace metals in 408 distillate fuels were furnished by 12 laboratories. The metals included sodium, potassium, vanadium, calcium, lead, copper, and magnesium in samples of kerosine, diesel fuels, burner fuels, jet fuels, and gas

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turbine fuels. Information on the methods used for the analyses was also furnished.

Some of the laboratories did not furnish data on all of the metals. Also, many of the metals were reported as being present in "less than" a certain value. This method of reporting prevented a statistical study of the data or even making a distribution curve, so the data are reported for each type of fuel on the basis of the number of samples having individual metals within certain ranges of parts per million. Reporting the data as "less than" results in bias showing more of a metal than is actually present. For example, samples reported as <0.1 ppm of a metal are included in the range 0.06 to 0.10, whereas some of them may be less than 0.06.

The trace metals contents are discussed for each type of distillate fuel for which data were reported.

Kerosines—Data on 151 samples were received from five suppliers, but 128 of these samples showed analyses only for lead and copper. Table 1 shows distribution of the 392 metals and analyses, which included 181 by atomic absorption, 126 photometric, 54 emission, and 31 by methods not reported. Actual values were reported for only 27 of the determinations, and the others were reported as "less than" a certain value, which results in metals contents being reported higher than actual. For example, 123 samples were reported to contain <1.0 ppm of a trace metal. These are reported in Table 1 in the range 0.51 to 1.00, but many of them may have contained less than 0.51 ppm.

TABLE 1—*Distribution of kerosines according to content of individual metals.*

	Number of Fuels in Each Metal Content Range						
Metal Content	Na	K	V	Ca	Pb	Mg	Cu
Range, ppm							
<0.01 to 0.01	1	3	1	2	2	1	7
0.02 to 0.05	...	7	10	2	10	...	9
0.06 to 0.10	21	12	13	11	10	...	7
0.11 to 0.30	2	...	...	...	1	...	...
0.31 to 0.50	...	...	...	...	...	...	...
0.51 to 1.00	...	...	...	7	121	1	126
>1.00	...	...	...	...	5	...	1
Minimum, ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maximum, ppm	0.12	<0.10	<0.10	<1.0	3.0	<1.0	4.0

Diesel fuels—Data were received for trace metals from eight suppliers on 152 diesel fuels. These included data on the vanadium contents of 95 samples of Navy fuel MIL-F-24397, which is a heavy distillate having an allowable maximum 95 percent distillation point of 765°F.

One hundred and forty-one of the 344 metal determinations on commercial fuels tabulated in Table 2 were reported as "less than" the maximum of the ppm

TABLE 2–*Distribution of diesel fuels according to content of individual metals.*

	Number of Fuels in Each Metal Content Range						
Metal Content	Na	K	V	Ca	Pb	Mg	Cu
Range, ppm							
<0.01 to 0.01	6	14	22	9	6	6	6
0.02 to 0.05	4	9	40	6	8	1	29
0.06 to 0.10	34	32	69	32	31	...	10
0.11 to 0.30	10	1	20	1	3	...	7
0.31 to 0.50	...	...	1	1	1	...	1
0.51 to 1.00	3	...	...	7	3	...	2
1.01 to 3.00	...	...	...	...	2	...	...
>3.00	...	...	...	...	2	...	...
Minimum, ppm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Maximum, ppm	1.0	0.3	<0.5	<1.0	<5.0	<0.05	1.0

brackets in which they are tabulated. Therefore, the table is biased to indicate metal contents higher than actual. Twenty of the 95 vanadium values from Navy fuels also were reported as less than.

Analytical methods were not reported for vanadium in the Navy fuels, but of the 344 metals determinations reported on commercial fuels, 257 were by atomic absorption, 80 by emission, six by X-ray, and one by flame photometry.

Burner Fuels–Five suppliers furnished data on 82 samples of burner fuels. One hundred and sixty of the 478 values were reported as 0.0 ppm, and only 179 were reported as less than a specific value. Thus, the values on the top line of Table 3 may reflect a bias toward lower than actual. This is the reverse of the probable bias reported for the other fuels. Four hundred and eight of the 478 results were obtained by atomic absorption, 42 by emission spectroscopy, 23 by a photometric method, and five by X-ray spectroscopy.

TABLE 3–*Distribution of burner fuels according to content of individual metals.*

	Number of Fuels in Each Metal Content Range						
Metal Content	Na	K	V	Ca	Pb	Mg	Cu
Range, ppm							
<0.01 to 0.01	32	33	40	33	21	33	30
0.02 to 0.05	...	7	11	...	8	...	23
0.06 to 0.10	29	29	29	29	22	...	11
0.11 to 0.30	11	2	1	2	4	...	6
0.31 to 0.50	3	...	...	1	1	...	2
0.51 to 1.00	3	...	1	7	2	...	...
1.01 to 3.00	2	1	...	...	14	...	...
>3.00	3	...	...	...	1	...	...
Minimum, ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.002
Maximum, ppm	6.4	1.2	0.7	<1.0	3.5	<0.01	0.42

Aviation Turbine Fuels—Data were received on only ten aviation turbine fuels, and nine of these were from one supplier. Fifty-nine of the 60 values in Table 4 were reported as less than, so the indicated distribution means little. No data were reported on the magnesium content. Fifty-seven of the values for trace metals were by emission spectroscopy and three by X-ray.

TABLE 4—*Distribution of aviation turbine fuels according to content of individual metals.*

	Number of Fuels in Each Metal Content Range						
Metal Content	Na	K	V	Ca	Pb	Mg	Cu
Range, ppm							
<0.01 to 0.01	...	...	1	...	...	...	1
0.02 to 0.05	1	10	9	1	9	...	...
0.06 to 0.10	9	...	...	...	...	...	9
0.11 to 0.30	...	...	...	...	...	...	...
0.31 to 0.50	...	...	...	...	...	...	...
0.51 to 1.00	...	...	...	9	...	...	...
>1.00	...	...	...	...	1	...	...
Minimum, ppm	<0.02	<0.02	<0.01	<0.02	<0.05	...	<0.01
Maximum, ppm	<0.10	<0.05	<0.05	<1.0	<2.0	...	<0.10

Gas Turbine Fuels—Data on trace metals in gas turbine fuels were reported on only 13 fuels. Ten of these were from one supplier and included five each of Grades 1-GT and 2-GT. Fifty-four of the 88 determinations in Table 5 were reported as "less than" a certain value, which results in a bias toward higher values than indicated in the tabulation. However, the amounts of metals are much lower than the maximum presently allowed by ASTM D 2880-71. The values for Grade 2-GT are slightly higher than those for 1-GT. Most of the values for sodium and potassium were obtained by flame photometry, values for most of the other metals were by atomic absorption.

TABLE 5—*Distribution of gas turbine fuels according to content of individual metals.*

	Number of Fuels in Each Metal Content Range						
Metal Content	Na	K	V	Ca	Pb	Mg	Cu
Range, ppm							
<0.01 to 0.01	1	1	1	2	...	5	8
0.02 to 0.05	...	...	...	3	3	2	1
0.06 to 0.10	1	6	12	4	7	3	4
0.11 to 0.30	1	5	...	4	2	...	...
0.31 to 0.50	2	1	...	...	...	...	...
0.51 to 1.00	4	...	...	...	...	...	...
>1.00	4	...	...	...	1	...	...
Minimum, ppm	<0.02	<0.02	<0.01	<0.01	<0.02	<0.01	<0.01
Maximum, ppm	1.9	0.33	<0.10	<0.20	<2.0	<0.1	<0.10

Discussion of Data

A review of information submitted by 12 suppliers on the trace metals content of 408 distillate fuels shows that data were included from 1457 individual metal determinations. Table 6 shows that atomic absorption, some of which were on ashed samples, accounted for more than 60 percent of the determinations, and most of the remainder were by emission spectroscopy or by an extraction and photometric technique. Flame photometry was used on several samples for determining sodium and potassium, and a few metals analyses were made by X-ray.

Unfortunately, one-half (816 out of 1457) of the analyses were reported as "less than" a certain value rather than as specific parts per million. This precluded any attempt at a statistical treatment of the data or even a distribution curve of metals content. No data were included on replicate determinations, so no information is available on repeatability. Although the samples were obtained from locations such as laboratories, pipelines, tankers, and loading racks, the data were not definitive enough to draw any conclusions that sample handling increased the metals content. Many of the analyses were made on refinery samples, so the values probably are lower than would have been found on fuels that had gone through the normal distribution system before delivery to the point of use.

Only 13 of the 408 fuels were designated specifically as turbine fuels, but several contributors stated that the data were submitted on other types of fuels that are being used in gas turbines. In addition to the individual fuels listed, one contributor provided data on the range and average values of 22 No. 2 fuel oils that have been used as gas turbine fuels. The levels of trace metals in these fuels were in the same range as those that are tabulated.

Even though one-half the values were reported as "less than" a certain value, which resulted in a bias showing higher metal levels than reported, the values indicate that the levels of trace metals are much lower than the maximum values allowed in the present specifications for gas turbine fuels. However, gas turbine engine manufacturers report that modern high-temperature gas turbine engines are less tolerant of trace metals than engines that were in use when ASTM D 2880-71 was first published. Therefore, Section D02.E is reviewing the fuel requirements of these engines to determine if the amounts of trace metals allowed in ASTM D 2880-71 are realistic.

Acknowledgements

This survey was made possible by contributions of data from the following laboratories: American Oil Co., Continental Oil Co., Gulf Research and Development Co., Humble Oil and Refining Co., Lion Oil Co., Mobil Oil Corp., Naval Ships Engineering Center, Phillips Petroleum Co., Standard Oil Co. (Ohio), Texaco, Inc., Turbo Power & Marine Systems, Union Oil Co. of Calif., and Westinghouse Electric Corp.

TABLE 6—*Frequency of use of each analytical method.*

			Analytical Methods, Times Used					
Fuel	Samples, Number	Suppliers, Number	Atomic Absorption	Emission Spectroscopy	Photometric	X-Ray	Flame Photometer	Not Reported	Total
Kerosine	151	5	181	54	126	. . .	. . .	31	392
Diesel fuel	152	8	257	80	. . .	6	1	95	439
Burner fuel	82	5	408	42	23	5	. . .	. . .	478
Aviation turbine	10	2	. . .	57	. . .	3	. . .	. . .	60
Gas turbine	13	3	62	3	. . .	3	20	. . .	88
Total	408		908	236	149	17	21	126	1457

Discussion

J. A. Vincent[1] *and D. L. Beers*[1] *(written discussion)*–The prospective purchaser of fuel for a gas turbine, whether automotive, industrial or marine, will probably find No. 2 Grade diesel fuel the most readily available product. Considerable information concerning the trace metals present in such fuel has been reported by C. C. Ward in this paper. Additional information about No. 2 Grade diesel fuel has been obtained through a recent field survey. An important objective was to determine to what extent fuels "pick-up" additional metals between the refinery and the customer.

Figures 1 through 5 summarize the results of the survey with specific regard to those metals considered detrimental to the continuous operation of industrial gas turbine engines.

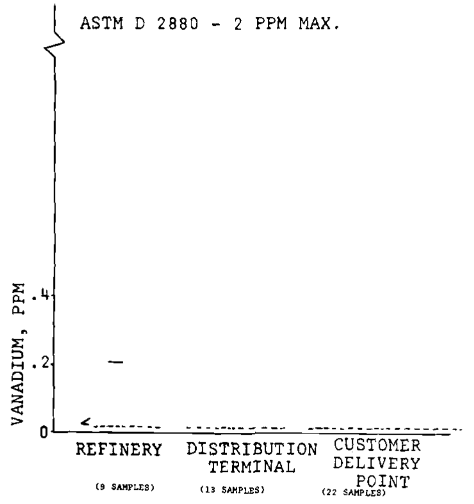

FIG. 1–*No. 2 diesel fuel trace metal survey on vanadium.*

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[1] Senior product engineers, Product Engineering Dept., Standard Oil Company of California, San Francisco, Calif.

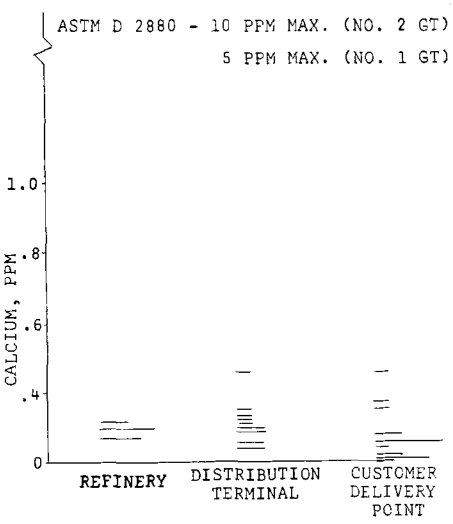

FIG. 2—*No. 2 diesel fuel trace metal survey on calcium.*

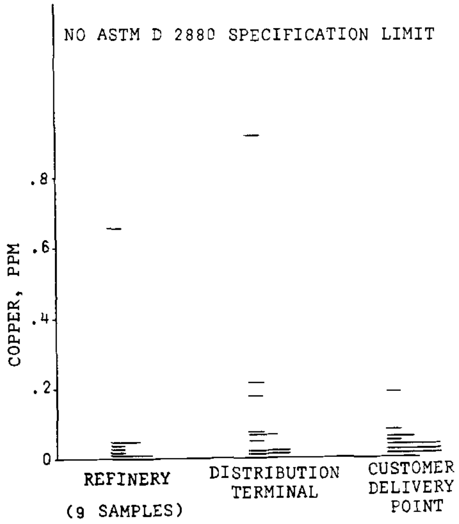

FIG. 3—*No. 2 diesel fuel trace metal survey on copper.*

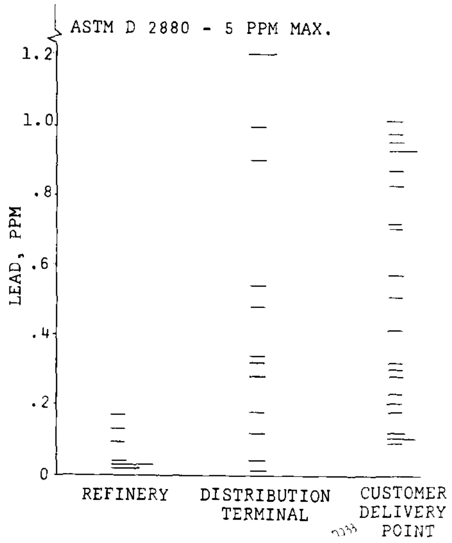

FIG. 4—*No. 2 diesel fuel trace metal survey on lead.*

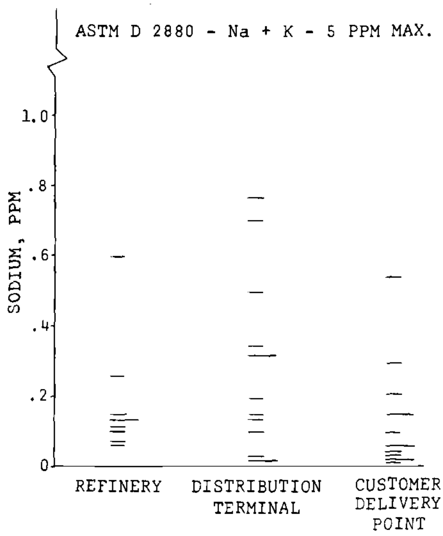

FIG. 5—*No. 2 diesel fuel trace metal survey on sodium.*

Samples were obtained during the period March through June 1972. Special glass sample containers were supplied to the sampling locations to minimize sample contamination.

Samples were from four different refineries; eight different distribution terminals, representing tanker, barge, pipeline, and truck shipments; and 13 different customer delivery points (fuel distributors and truck stops) including eight different petroleum suppliers.

Samples were analyzed using emission spectrographic techniques with the following minimum limits of resolution in ppm:

Ca	Cu	Na	Pb	Vn
0.01	0.01	0.01	0.01	0.03

All samples were also analyzed for potassium content by atomic adsorption. No potassium was detected with this technique which has minimum limit of resolution of 0.10 ppm. Thus, values shown for sodium content should be a reasonable approximation for sodium plus potassium.

It is readily evident that distribution contamination takes place particularly with regard to the Pb level. However, all samples were well below the ASTM D 2880-71 maximum limits presently established for these metals.

It is also evident that the very low levels of these metals (in the order of 0.10 ppm) proposed by gas turbine engine manufacturers will require a much more sophisticated and costly distribution system than is presently adequate for No. 2 diesel fuel.

C. C. Ward (author's closure)—The amounts of trace metals reported in this survey indicate the values are much lower than the allowable limits in ASTM D 2880-71. This is not unexpected because most of the analyses were made on fuels sampled at the refinery or at loading docks where the fuels were still under refinery control. Analyses that have been made in the author's laboratory on refinery distillates and on distillates prepared from crude oils having a high content of trace metals show that distillation effectively reduces the level of trace metals below that presently allowed in ASTM D 2880-70. Information by J. A. Vincent and D. L. Beers in their discussion of this survey paper shows that metal contamination occurs during the handling, storage, and transportation from the refinery to the point of use. Additional data are needed on the levels of trace metals in gas turbine fuels at the customer delivery point to provide information needed to develop realistic values to replace the tentative levels of trace metals now specified in ASTM D 2880.

E. W. White[1]

Storage Stability of Distillate Fuels for Ships

REFERENCE: White, E. W., "**Storage Stability of Distillate Fuels for Ships,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuels, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 143–166.

ABSTRACT: A program to evaluate the storage stability of the Navy's new distillate fuel is described and cumulated data are presented. The outdoor storage location is shown to be a factor in the aging process, on the basis of data obtained from fuel stored in Maine, Maryland, and Florida. The use of tinned cans is shown to be unsuitable for long term storage tests of Navy distillate fuel. The results obtained in accelerated tests such as a 110°F beaker test or the ASTM Test for Stability of Distillate Fuel Oil (Accelerated Method) (D 2274-70), are shown to be indicative of results obtained in long term tests outdoors. From available data it appears that one week of storage at 110°F is equivalent to about 1¼ months outdoors at ambient temperature.

KEY WORDS: fuel storage, fuels, accelerated storage tests, fuel aging, total gum, insolubles, adherent gum, temperature effects, quality control

During the past several years the Navy has been converting selected ships to the use of a new distillate fuel, Navy Distillate (ND) (MIL-F-24397). This ND fuel is a higher boiling distillate than such other Navy fuels as JP-5 and Diesel Fuel Marine (DFM). It is intended to serve both as the Navy's boiler fuel for ships and also ultimately as a fuel for the Navy's gas turbine and diesel ship propulsion engines.

The stability of a fuel during storage is an important consideration in both commercial and military fuel supply systems. Degradation products such as gums and sediments can cause deposits in fuel systems and can lead to filter and fuel nozzle plugging. This can be very critical in gas turbine and diesel engine fuel systems, but must also be considered in boiler fuel systems.

Consequently, a study was initiated in 1969 at the Naval Ship Research and Development Center, Annapolis Laboratory, to ascertain whether the new distillate fuel is likely to present problems associated with storage stability and to determine whether accelerated aging tests are usable as predictors of storage stability for any given batch of fuel. This paper describes the test program and presents results obtained through mid-April 1972.

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Technical Background

Stability Definitions

The term "fuel stability" implies the general resistance of a fuel to change. It can refer to oxidative stability, gum formation, increasing viscosity, thermal stability, corrosivity, and even compatibility. Each relates in some manner to the environments and materials to which a fuel may be exposed during its life from refinery to ultimate combustion. The primary purpose of the study described in this report is to ascertain the "storage stability" of the Navy's new distillate fuels for ships. Storage stability refers to the relative chemical reactivity of the fuel and its tendency to form degradation products of such a nature and in such quantities as to cause operating problems through depositon in storage tanks, in distribution systems, and in the combustion system.

The Basis of Instability

The stability of fuel depends on such factors as crude source, boiling range, type and severity of refining processes, and the hydrocarbon composition [*1*].[2] With respect to the last of these factors (hydrocarbon composition), chemical stability decreases in the order: paraffins, naphthenes, aromatics, olefins, and diolefins. An organic sediment, the most common evidence of instability, probably results from oxidation and chemical reactions such as polymerization involving unsaturated hydrocarbons (such as olefins) and reactive organic compounds of sulfur, nitrogen, and oxygen present in the fuel. Sometimes the formation of mercaptide gels is associated with instability. Such clear, usually amber-colored, gels are thought to result from a reaction between fuel mercaptans and copper (or other reactive metal) present in metal parts, to yield metal mercaptides which in turn from a gel in contact with fuel and small amounts of water and oxygen. Inorganic sediment, such as rust, may also develop in the stored fuel from storage system corrosion products.

A number of investigators have studied the factors which determine the degree of storage stability exhibited by a fuel, and some investigators have proposed mechanisms by which organic sediment is formed. Representative of such studies are those reported by Offenhauer et al [*2*] Nixon and Thorpe [*3*], Ward and Schwartz [*4*], and Sauer et al [*5*]. Offenhauer et al, from their studies of catalytically cracked distillate fuel oils, concluded that most of the sediment is formed through oxidation of part of the aromatic thiols present in the fuel to sulfonic acids, a reaction which, in the presence of air, leads to a condensation of pyrroles [*2*].

Nixon and Thorpe studied the possible use of cracked stocks in jet fuels. They concluded that the instability of gas-oil components of jet fuel is influenced by such species as aromatic olefins, alkyl thiophenes, conjugated dienes, and pyrroles [*3*].

Ward and Schwartz, from studies of hydrocarbons and other compounds

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

present in motor gasoline, reported that olefins in the presence of thiols were the most reactive hydrocarbons tested. Further, they noted that gum formation is not a simple addition reaction of sulfur compounds with hydrocarbon, but rather the sulfur compounds may be initiators of oxidation-type reactions [*4*].

Sauer et al studied sediment formation in heating oils [*5*]. Chemical, infrared, and mass spectrometer analyses indicated the presence of oxygen in ester type linkages in the sediment. An experimental study of the kinetics of sediment formation and aromatic thiol reaction at 212°F revealed an 8 to 10 h induction period before much sediment was formed; by the end of the induction period the aromatic thiols had almost entirely disappeared and the disulfide concentration had reached a constant value. On the basis of these and other experimental facts, and drawing on a hydroperoxide, decomposition mechanism proposed by Durham and coworkers [*6*], Sauer et al postulated the following mechanism of sediment formation:

Step 1—The side chain oxidation of reactive hydrocarbons, nitrogen, and sulfur-compounds is catalyzed by thiols to form hydroperoxides.

Step 2—These partially decompose by splitting out water to form aldehydes.

Step 3—The aldehydes react with other hydroperoxides to form peroxyhemiacetals.

Step 4—The peroxyhemiacetals decompose by two reaction paths to form monomeric oxidation products by one path and condensed, esterified products of higher molecular weight by the other.

The second path of Step 4 is said to be catalyzed by acids and to form simple esters; further oxidation of the initial ester side chains yields more ester bonds and eventually sediment and color bodies.

The Effect of Temperature on Sediment Formation

Increasing the temperature is known to increase the rate at which many reactions proceed. This principle has been used in developing accelerated storage stability tests and an Arrhenius type equation has been used to predict results of storing fuels at temperatures other than that at which data were obtained. Unfortunately, laboratory-scale accelerated tests at elevated temperatures are not always very accurate in predicting the results of bulk storage at ambient temperatures. Surface-to-volume effects, the presence of corrosion products in bulk storage fuels, the loss of volatile components in accelerated tests, and different effects of temperature on the individual chemical reactions associated with instability combine to create differences in the degradation processes. Moreover, if the sediment formed is used as a measure of stability and is ascertained by filtration, the weight of sludge retained by a filter of given porosity is dependent on sludge particle size as well as on the amount of sludge in the fuel. Despite such factors, correlations between accelerated and long-term storage results have been reported in the technical literature.

Nixon and Cole [*7*] subjected MIL-F-5624 JP-3 type aircraft jet engine fuels to three aging conditons:

1. Desert storage in sealed 55-gal drums.

2. Hot room storage (110°F) in sealed, amber-glass gallon bottles.
3. Accelerated aging at 212°F in an oxygen bomb under 100 psig oxygen pressure.

Correlations among the results of aging under these three sets of conditons were based upon total gum formation. Reasonably high correlation coefficients were obtained. In another series of experiments, a plot of the log of the induction time versus the reciprocal of the absolute temperature was found to be linear as implied by the Arrehenius equation. Including the effect of the bomb oxygen pressure, they obtained:

$$\log (t_1/t_2) = 4500 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) - 0.52 \log (P_1/P_2) \qquad (1)$$

where t_1 and t_2 are the times required to obtain the same amount of total gum under two conditions of temperature (T_1 and T_2, in degrees Rankine) and of pressure (P_1 and P_2, in psia).

Milsom and Rescorla [*8*] working with 17 No. 2 fuel oils noted that, after insolubles reached the 2 mg/100 ml level, the rate of formation of additional insolubles increased; that is, the 2 mg/100 ml level marked the end of an induction period. Samples of the fuel oils were stored at four temperatures (110, 150, 180, and 212°F) maintained at ±0.1°F in bottles. Periodically, a bottle was removed from the storage oven and the insolubles in the fuel were determined. For each fuel tested a linear relationship was obtained between the logarithm of the time to reach 2 mg/100 ml insolubles and the reciprocal of the absolute temperature (°R = 460 + °F). The line obtained with any of the fuels was parallel to that obtained with any other fuel. Further, the investigators found they could predict with a precision of two weeks or less the time to reach 2 mg/100 ml in drum storage of these fuels at 100°F from accelerated tests at 180°F.

Tests

The number of storage stability tests that have been described in the technical literature seems as great as the number of investigation teams. Hogin and Clinkenbeard [*1*] listed three accelerated aging tests, four long-term storage tests, two filter-plugging tests, and two copper gel tests as examples of the myriad tests pertinent to distillate heating oils. The following is thus only a sampling of the work that has been done in the field. It is presented to provide an appreciation of the differences that exist among the various procedures.

The studies of Nixon and Cole [*7*] on the storage stability of JP-3 jet fuel and cracked blending stocks in the 87 to 536°F boiling range have been noted during the discussion of the effects of storage temperatures. Their accelerated test employed an oxygen bomb assembly in which a sample of fuel was stored under 100 psig of oxygen at 212°F for 5, 10, or 16 h. Steam-jet residue gum was used as a measure of stability.

The Milsom and Rescorla [*8*] use of stoppered bottles to age No. 2 fuel oil samples at elevated temperatures has also been noted. By daily introducing air to the stoppered bottles and by close control of the storage temperature, they were able to predict the rate of buildup of insolubles in the same fuel in drum storage.

Personnel at the Bureau of Mines Petroleum Experiment Station, Bartlesville, Okla., have made major contributions to the literature on petroleum and its products. In one study, Bureau of Mines [*9*] working with 34 distillate fuels and 250 blends at 110°F in vented bottles, compared bottle and drum storage at ambient temperature with 110°F bottle storage. The 34 fuels were middle distillates having initial boiling points (IBP) generally above 300°F and end points (EP) generally between 600 and 697°F. For the hot aging tests the fuels were stored in vented, 1-pt bottles 80 percent filled with sample. To promote breathing and replenishment of air in the bottles, the storage room temperature was allowed to drop to about 90°F (from the normal 110°F) for a 2-h period each day. They reported that bottle storage at 110°F for 13 weeks is approximately equivalent to either drum or bottle storage at ambient temperature for one year.

Christian, Johnson, and Carhart [*10*] stored eleven distillate fuels in ovens in glass bottles loosely capped with aluminum foil. The ovens were equipped with automatic timers to allow the fuels to cool (from the normal 130°F) and breathe for 6 h each day. They found that soft glass retarded aging but that Pyrex glass is essentially inert. Hence, the latter should be used in fuel aging studies.

Anderson, Jones, and Glassman conducted extensive evaluations of the storage stability of Navy marine fuels (MIL-F-16884) at the Naval Ship Research and Development Center, Annapolis Laboratory. Special attention was given to predictive tests, and Anderson reported that the best ranking of fuel stability, compared with results obtained in long-term glass column storage, was obtained in a 16-h, 210°F accelerated test when both soluble and insoluble gums are used to measure fuel change.

Loveland et al [*11*] noted the ambiguity inherent in sludge-weight methods and recommended concurrent use of light-scattering, electron microscopy, and polarography for understanding stability problems in oils. They identified the limitations of the methods used singly with No. 2 fuel oil samples and with transformer oils.

Although the American Society for Testing and Materials (ASTM) has accepted several accelerated tests for evaluating petroleum products [*12*], only the ASTM Test for Stability of Distillate Fuel Oil (Accelerated Method) (D 2274-70) is directly applicable to distillate fuel oils. The other stability tests are designated for gasoline ASTM Test for Oxidation Stability of Aviation Fuels (Potential Residue Method) (D 525-55), aviation fuels ASTM Test for Oxidation Stability of Gasoline (Induction Period Method) (D 873-65) (1970), and steam turbine oils ASTM Test for Oxidation Characteristics of Inhibited Steam-Turbine Oils (D 943-54) (1968) and ASTM Test for Continuity of Steam-Turbine Oil Oxidation Stability by Rotating Bomb (D 2272-67) (1972). Of these ASTM D 525-55, D 873-65, and D 2272-67 employ an oxygen bomb at 212°F for the first two, and 302°F for the last. Method D943-54 uses a bubbling oxygen technique at atmospheric pressure at 203°F in the presence of water and an iron-copper catalyst.

ASTM D 2274-70, which applies to distillate, uses apparatus identical to that used in ASTM D 943-54, but eliminates the uses of water and the iron-copper catalyst. The test is identical to that used by Anderson at the Annapolis Laboratory, except for the use of a 203°F temperature instead of Anderson's 210°F. Oxygen is bubbled at a fixed rate through a measured volume of filtered fuel held at 203°F for 16 h. The weight of insolubles formed during this time is measured.

This brief review has indicated that accelerated test results can be related to long-term storage results and can indicate the less stable fuels. There is reason to expect the general experience of Anderson et al with MIL-F-16884 Navy diesel fuel marine (DRM) to extend to the new distillates.

Test Procedures

Fuels in Test Program

Four distillate fuels are being used in a long-term storage stability test program involving two test procedures. The same four fuels have been subjected to accelerated storage stability tests. They are identified and characterized in Table 1.

Fuels A, C, and D are considered Navy distillate fuels meeting the requirements of either Military Specification MIL-F-24376 or Military Specification MIL-F-24397. Fuel B is a light catalytic cycle stock potentially usable as a blending component in preparing the new Navy distillates. It was included in the storage program as a material having low inherent storage stability since it is a cracked stock. It was expected to accentuate the degradation products such as sludges resulting from aging.

Long-term Storage Tests

Three types of long-term storage stability tests have been initiated. These are termed "column tests," "bottle tests," and " can tests" after the containers in which the fuels are stored.

Details of the storage columns are shown in Fig. 1. The column array consists of four Pyrex-glass columns mounted in brackets on an outside wall of a building and enclosed in a ventilated light-proof box as shown in Fig. 1*a*. Each column is made up from two 10-ft (3.05-m) lengths of standard 2-in. glass pipe plus an 8-in.-long bottom section. The lower 4 in. of this bottom section is tapered from 2 to 1 in. in diameter. A 1-in.-diameter glass side arm, 4 in. above the bottom, leads to a 1/4-in. IPS pipe standard adapter and drain valve assembly (Fig. 1*c*). The top of each column is fitted with a gooseneck breathing tube and a thermocouple fitting. A 206-in. (5.23-m) length of 16 gage W & M (0.0625-in. diameter) mild steel wire is suspended from the top plate of each column. In a column filled with fuel, the 206-in. length of 1/16-in.-diameter wire is wetted by the fuel for about 197 in. (5 m) of its total length. Consequently, the ratio of

TABLE 1–*Inspections and analyses of fuels used on storage tests.*

	Fuel			
Inspection Test	A	B	C	D
	Physical Properties			
Gravity, deg API, 60/60°F	28.9	21.4	30.6	32.2
Viscosity, cSt at 100°F	6.1	2.7	6.0	4.8
Pour point, deg. F	+25	-30	+15	+15
Flash Point, Pensky-Martens Closed cup, °F	190	225	205	196
Interfacial tension, dynes/cm at 77°F	20	32	22	23
	Distillation Data			
10% distilled point, °F	472	476	508	. . .
50% distilled point, °F	593	508	623	564[a]
90% distilled point, °F	726	549	719	644[b]
95% distilled point, °F	770	. . .	742	. . .
98% distilled point, °F	. . .	. . .	781	. . .
End point, °F	. . .	582	. . .	. . .
	Chemical Analysis			
Ash, %	0.01	. . .	0.005	Trace
Water and sediment, %	0.05	. . .	0.02	<0.02
Sulfur, %	1.22	0.10	1.05	0.14
Carbon residue, %	0.4[c]	0.02[c]	0.07[c]	<0.10
Neutralization No., mg KOH/g	1.42	0.03	0.85	0.11
Vanadium, ppm	0.2	. . .	0.05	<0.01

[a] Mid-boiling point.
[b] 87% distilled.
[c] On 10% bottoms.

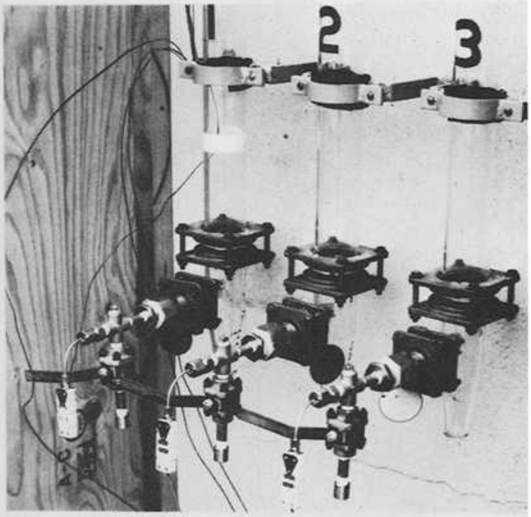
wetted area to fuel volume is 11.5 in.^{2} per gal, roughly that in a half-full 10-ft-diameter by 10-ft-high cylindrical storage tank.

There are three copper-constantan thermocouples to determine temperatures for each column. One terminates about an inch below the liquid level (top of the column). The second enters through the side arm of the tapered bottom section and terminates at the axis of the column. The third is taped to the outside of the column at a point just below the midpoint bracket. The leads from these thermocouples pass through the wall of the building to a 12-point temperature recorder mounted on the inner wall. The temperature and relative humidity of the air in the enclosure are recorded by a hygrothermometer resting in the bottom of the enclosure.

Before a fuel is introduced into a column, the column is cleaned by flushing with a series of solvents in the following sequence: water, isopropyl alcohol, benzene, isopropyl alcohol, and acetone. After the acetone has evaporated by air

(a) Overall View

(b) Top Details



(c) Bottom Details

FIG. 1—*Storage columns.*

convection, 3.35 gal (12.7 liters) of fuel is poured into the column through a 100-mesh screen as insurance against introducing gross particulate contaminants in case such contaminants are inadvertently present in the fuel drums. Except for weekly signal inspections, the fuel remains undisturbed in the column for three years. It is then drained from the column and subjected to tests and analyses to ascertain how storage under ambient conditions affects the fuel. Temperature and relative humidity records are kept for a possible relationship to observed visual changes in a fuel, for example, wax formation when ambient temperatures drop below the cloud point of the fuel.

Because it is considered undesirable to withdraw samples from the glass columns prior to the completion of the three-year storage period, it is necessary to run other tests to follow the aging process. A 1-gal sample is minimal for running desired analytical and inspection tests and for a reserve in case of accidental losses of any of the aliquot portions drawn for these tests. Further, since temperature and humidity may affect the aging process, additional storage tests under different climatic conditions should be part of the program. Consequently, eight 1-gal batches of each fuel used for the column tests are stored at each of three geographic locations.

Four-liter Pyrex-glass bottles are used for the bottle storage tests. The bottles are prepared for storage by washing first with water and then with acetone. The acetone is allowed to evaporate. The bottles are then wrapped in heavy duty aluminum foil to eliminate light. A gallon of the test fuel, which is first passed through a 100-mesh screen, is then poured into each bottle. A solid Neoprene stopper is inserted into the mouth of each bottle and wired in place. (See the middle bottle of Fig. 2*a*.) The stopper and mouth of the bottle are covered by the aluminum foil.

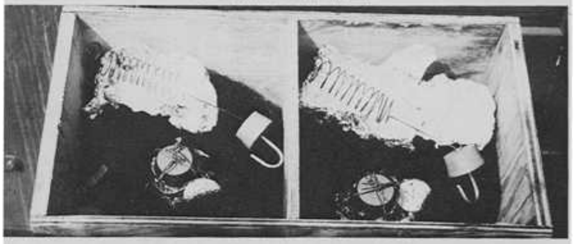
Two bottles are then placed in each shipping-storage box. The boxes (Fig. 2*b*) are so designed that the lids can be raised to open ventilation holes during storage but the holes are protected from rain and snow by an overhang. Drainage holes are provided in the bottoms of the boxes to prevent an accumulation of moisture from any source. The boxes are supported several inches off the ground. Boxes of bottles are shipped to Maine and to Florida; others are stored at the Annapolis Laboratory (Fig. 2*c*).

After the boxes arrive at their storage destinations, the solid stoppers are removed from the bottles and replaced with a stopper containing a stainless-steel gooseneck. A coil of mild steel wire, of a length to give the same steel surface-to-fuel-volume ratio as in the glass columns, is suspended from the stopper as shown in the right hand pair of test bottles of Fig. 2*a*. Aluminum foil is then secured around the stopper and gooseneck as shown in the left-most bottle. The box lids were placed in the ventilation position (Fig. 2*c*).

Boxes are withdrawn from storage sites, and the contents of the bottles are inspected and analyzed after 3, 6, 12, 18, 24, 30, and 36 months of storage. An eighth box provides either a duplicate for the 36-month inspections or a replacement if any of the samples are lost or destroyed.

The third type of long term storage test is the "can test." In place of the glass bottles, 1-gal, wide-mouth rectangular tinned steel cans are used. Goosenecks and 52-in. (1.32-m) wire coils are used, and the fuels are strained through a 100-mesh screen just as with the bottles. However, there are only eight cans in the test, four filled with Fuel A and four filled with Fuel B. The eight cans, each containing 3500 ml of fuel, are stored inside the glass-column enclosure at the Annapolis Laboratory where they are protected from the weather but subject to environmental temperature and humidities. One can of each fuel is removed after 6, 12, 24, and 36 months of storage. The contents are inspected and analyzed.

(b) Bottles Ready for Shipment



(c) Boxed Bottles in Storage

FIG. 2–*Bottle storage.*

Accelerated Storage Tests

Although long-term storage tests, such as the glass-column and 1-gal container tests just described are considered more indicative of field storage of fuels, it is not practical to wait for three years to ascertain whether a given batch of fuel will perform satisfactorily in storage. Therefore, two types of accelerated storage stability tests are run on each fuel in the storage program. The one type, ASTM D 2274-70, is called the "ASTM test." The other, a 110°F oven storage test, is called the "beaker test."

The ASTM test involves 16 h of oxidation at 203°F followed by filtration of the fuel to obtain adherent gum. ASTM D 2274-70 specifies evaporation, of solvent from the adherent gum, by the air-jet method (ASTM Test for Existent Gum in Fuels by Jet Evaporation (D 381-70)). However, because there was no jet evaporation apparatus available in the early days of the storage program, a slightly modified procedure was used initially. The tri-solvent was evaporated from the adherent gum on a low temperature hot plate.

In the beaker test a 500 ml sample of the fuel is placed in a beaker, covered with a watch glass, and the covered beaker is placed in a 100°F oven for the desired number of weeks. Three such samples are prepared for each fuel and one is removed after each of the following periods: 12, 24, and 36 weeks. On removal from the oven, the entire sample is filtered to determine insoluble gum and sediment. The beaker is rinsed with tri-solvent to obtain adherent gum (the solvent is evaporated as just described for the modified ASTM D 2274-70). The total insolubles (the sum of the insoluble gum-and-sediment, and adherent gum) are reported as milligrams per 100 milliliters.

Inspections and Analyses

Properties of each fuel in the storage program are determined both before and after a storage test. The properties measured and the procedures used for the measurements are shown in Table 2.

TABLE 2–*Procedures used for measuring fuel properties.*

Property	Procedure
Gravity, deg API	ASTM D 287-67 (1972)
Viscosity, kinematic, cSt at 100°F	ASTM D 445-72
Interfacial tension, dynes/cm at 77°F[a]	ASTM D 971-66 (1971)
Insoluble gum, mg/100 ml[b]	ASTM D 2274-70
Adherent gum, ml/100 ml[b]	ASTM D 2274-70
Emulsibility at 77°F, oil/water/emulsion, ml (30 min)	ASTM D 1401-67 (1972)
Neutralization No., mg KOH/g	ASTM D 974-64 (1968)

[a] Synthetic seawater prepared according to Procedure B of ASTM D 665-60 is used in the interfacial tension (IFT) determination.

[b] On samples from storage only.

Cumulative Results

Column Tests

From April 1969 through March 1972 the first two fuels were exposed to ambient relative humidities ranging from a low of 14 percent to a high close to 100 percent (saturation). Column temperatures ranged from 12 to 100°F. From March 1970 through March 1972 the second two fuels were exposed to relative humidities of 14 percent to close to 100 percent, and to column temperatures of 14 to 100°F.

The following observations regarding sludges in the bottoms of the columns were made in mid-April 1972:

Fuel A–1/4 in. (6 mm) sediment (black sludge),

Fuel B–3/4 in. (19 mm) sediment (black sludge),

Fuel C–7/8 in. (22 mm) sediment (1/4 in. grey sediment on bottom with 5/8 in. black sediment on top of the grey sediment), and

Fuel D–<1/8 in. (3 mm) sediment (black sludge). It should be noted that, during cold weather, a white material assumed to be paraffin wax appeared in the column containing Fuel D, but disappeared as the ambient temperature increased. Fuels A and B were withdrawn from the columns in mid-April 1972 after three years of storage, and are currently being inspected and analyzed for signs of deterioration.

Bottle Tests

Analytical inspection data on samples removed from bottle storage appear in Tables 3 through 6 for Fuels A, B, C, and D, respectively. Tables 3 and 4 (Fuels A and B, respectively) present data for 30 months of storage. Tables 5 and 6 (Fuels C and D, respectively) present data for 24 months of storage at the three locations.

Can Tests

Results from the tests in which fuel is stored in 1-gal tin cans rather than in foil-wrapped bottles are shown in Table 7. Only Fuels A and B were used in these tests.

Beaker Tests

Analytical inspection data on samples removed after oven storage in beakers at 110°F for 12, 24, and 36 weeks are shown in Table 8.

ASTM Tests

Results of the ASTM D 2274-70 accelerated storage stability tests for the four fuels are given in Table 9.

Discussion

Column Tests

The depths of sludges obtained in the column tests are compared with the results of accelerated tests in Fig. 3. Despite some scattering of data, it appears that the accelerated storage procedures give promise of correlating with sludge depths obtained during long term storage.

Bottle Tests

Fuel A (Table 3) is showing evidence of aging. Although gravity and viscosity show little change, the IFT values appear to be declining and the total gum levels are increasing. Similar evidence is noted for the aging of Fuel B (Table 4). Fuels C and D have not been in storage for as long as Fuels A and B, yet there is evidence of aging in the increased total gum levels.

The total gum data from samples recovered from the three storage locations reveal a location factor. Table 10 shows the total gum levels in all four fuels after 24 months of storage. The increasing levels of gum as the location of storage moves south to warmer climates is evident and consistent with the usual effect of temperature on reaction rates.

TABLE 3–*Analytical data on Fuel A bottle storage samples.*

	Physical Properties					Emulsibility, 30 min, 77°F, ml		
Storage Time, months	Gravity, deg API 60/60°F	Viscosity, cSt at 100°F	Interfacial Tension, dyne/cm at 77°F	Total Gum, mg/100 ml	Neutralization No., mg KOH/g	Oil	Water	Emulsion
				Fuel as Received				
0	29.2	6.1	20.0	. . .	1.4	35	0	45
				Fuel From Bottle Storage in Florida				
3	29.2	6.1	16.3	0.9	NA[a]	26	8	46
6	29.1	6.1	15.9	1.8	NA	32	4	44
12	28.9	6.1	13.9	3.7	1.6	39	7	34
18	29.5	6.1	12.5	5.2	1.7	30	8	42
24	29.2	6.0	12.5	3.4	1.6	35	30	15
30	28.6	6.2	NC[b]	9.6	1.4	37	22	21
				Fuel From Bottle Storage at Annapolis				
3	28.9	6.1	16.4	0.8	NA	28	0	52
6	29.0	6.1	16.3	0.9	NA	28	3	49
12	29.2	6.1	15.9	0.6	1.7	37	15	28
18	29.3	6.1	14.5	4.4	1.9	35	10	35
24	29.1	6.1	14.5	3.5	1.6	28	8	44
30	29.1	6.1	NC	3.5	1.5	33	15	32
				Fuel From Bottle Storage in Maine				
3	29.0	6.1	16.5	1.2	NA	28	8	44
6	29.4	6.0	16.7	1.2	1.5	32	3	45
12	29.3	6.1	16.5	0.8	1.5	38	12	30
18	29.4	6.1	13.9	3.6	1.5	30	10	40
24	NA[a]	6.1	14.6	1.0	1.5	38	12	30
30	29.4	6.1	15.0	2.9	1.4	33	12	35

[a] NA = not available.
[b] NC = not completed.

TABLE 4–*Analytical data on Fuel B bottle storage samples.*

	Physical Properties					Emulsibility, 30 min, 77°F, ml		
Storage Time, months	Gravity, deg API 60/60°F	Viscosity, cSt at 100°F	Interfacial Tension, dyne/cm at 77°F	Total Gum, mg/100 ml	Neutralization No., mg KOH/g	Oil	Water	Emulsion
				Fuel as Received				
0	21.5	2.8	31.3	. . .	0.03	41	39	0
				Fuel From Bottle Storage in Florida				
3	21.4	2.8	31.0	1.1	NA[b]	38	42	0
6	21.6	2.8	29.5	1.9	0.02	41	38	1
12	21.5	2.8	28.0	2.5	0.01	40	39	1
18	21.3	2.8	24.4	2.8	0.06	41	39	0
24	21.4	2.8	24.3	3.0	0.03	40	40	0
30	21.7	2.8	NC[a]	4.0	0.00	41	39	0
				Fuel From Bottle Storage at Annapolis				
3	21.0	2.8	29.3	2.8	NA	41	39	0
6	21.4	2.8	30.4	1.7	NA	41	32	7
12	21.5	2.8	30.2	1.2	0.02	41	39	0
18	21.3	2.8	26.9	2.2	0.06	41	39	0
24	21.3	2.8	27.3	2.0	0.01	40	33	7
30	21.2	2.8	NC	2.2	0.03	43	37	0
				Fuel From Bottle Storage in Maine				
3	21.4	2.8	31.1	0.9	NA	41	39	0
6	21.6	2.8	30.9	1.3	0.02	42	34	4
12	21.6	2.8	30.6	1.4	0.02	41	39	0
18	21.7	2.8	27.6	1.9	0.02	41	39	0
24	21.1	2.8	30.9	2.4	0.02	40	40	0
30	21.2	2.8	26.5	2.3	0.00	42	38	0

[a] NC = not completed.
[b] NA = not available.

TABLE 5—*Analytical data on Fuel C bottle storage samples.*

	Physical Properties					Emulsibility, 30 min, 77°F, ml		
Storage Time, months	Gravity, deg API 60/60°F	Viscosity, cSt at 100°F	Interfacial Tension, dyne/cm at 77°F	Total Gum, mg/100 ml	Neutralization No., mg KOH/g	Oil	Water	Emulsion
Fuel as Received								
0	30.4	6.0	21.5	NA[c]	0.9	41	39	0
Fuel From Bottle Storage in Florida								
3	31.1	6.1	20.0	1.7	0.9	40	40	0
6	30.7	6.1	16.5	1.0	NA[c]	40	40	0
12	30.9	6.1	17.6	2.4	0.9	41	39	0
18	31.0	6.1	16.9	7.4	0.9	40	40	0
24	30.8	6.2	NC[b]	4.6	0.8	40	40	0
Fuel From Bottle Storage at Annapolis								
3	30.9	6.1	20.1	0.5	0.9	41	39	0
6	30.9	6.1	20.1	1.2	0.9	40	39	1
12	31.2	6.1	18.5	1.8	0.9	40	40	0
18	30.4	6.2	17.8	1.8	0.8	40	40	0
24	31.2	6.1	17.4	2.4	0.8	41	39	0
Fuel From Bottle Storage in Maine								
3	31.2	6.1	20.1	1.2	1.0	40	40	0
6	31.1	6.1	17.7	0.8	0.9	NA[c]	NA[c]	NA[c]
12	SL[a]	. . .	. . .	. . .	. . .	. . .	. . .	. . .
18	SL	. . .	. . .	. . .	. . .	. . .	. . .	. . .
24	31.0	6.0	NC	2.0	0.8	40	40	0

[a] SL = sample lost in transit.
[b] NC = not yet completed.
[c] NA = not available.

TABLE 6—*Analytical data on Fuel D bottle storage samples.*

Storage Time, months	Physical Properties					Emulsibility, 30 min, 77°F, ml		
	Gravity, deg API 60/60°F	Viscosity, cSt at 100°F	Interfacial Tension, dyne/cm at 77°F	Total Gum, mg/100 ml	Neutralization No., mg KOH/g	Oil	Water	Emulsion
				Fuel as Received				
0	31.6	4.8	22.1	NA[c]	0.1	41	39	0
				Fuel From Bottle Storage in Florida				
3	32.0	4.8	21.1	0.8	0.1	39	41	0
6	32.0	4.8	18.6	1.9	NA[c]	40	40	0
12	31.8	4.8	21.0	0.4	0.1	40	40	0
18	31.7	4.7	20.2	0.6	0.1	40	40	0
24	32.1	4.8	NC[b]	1.0	0.1	41	39	0
				Fuel From Bottle Storage at Annapolis				
3	32.0	4.8	21.8	0.5	0.1	40	40	0
6	31.8	4.8	21.8	1.0	0.1	41	39	0
12	32.3	4.8	22.1	0.4	0.1	40	40	0
18	31.9	4.9	21.0	0.4	0.1	40	40	0
24	32.2	4.8	21.5	0.6	0.1	41	39	0
				Fuel From Bottle Storage in Maine				
3	31.7	4.8	22.1	0.3	0.1	41	39	0
6	31.8	4.8	20.7	0.8	0.1	NA[c]	NA[c]	NA[c]
12	32.0	4.8	NA[c]	0.8	0.1	41	39	0
18	SL[a]	. . .	. . .	. . .	. . .	. . .	. . .	. . .
24	32.1	4.9	NC	1.3	0.1	40	40	0

[a] SL = sample lost in transit.
[b] NC = not yet completed.
[c] NA = not available.

TABLE 7–*Data from can tests.*

Storage Time Months	Gravity, deg API, 60/60°F	Viscosity cST at 100°F	Interfacial Tension, dyne/cm at 77°F	Total Gum mg/100 ml	Neutralization No., mg KOH/g	Emulsion, 30 min		
						Fuel	Water	Emulsion
				Fuel A				
6	29.0	6.1	16.1	2.8	NA[a]	36	5	39
12	29.3	6.1	16.2	2.0	1.6	36	1	43
24	28.9	6.1	13.6	1.9	1.5	38	3	39
				Fuel B				
6	21.4	2.8	28.6	3.4	NA	41	39	0
12	21.3	2.8	28.5	4.1	0.02	41	39	0
24	21.6	2.8	27.7	1.8	0.05	41	38	1

[a] NA = not available.

TABLE 8–*Analytical data from 110°F beaker tests.*

Storage Time, weeks	Gravity, deg. API	Viscosity, cSt at 100°F	Interfacial Tension, 77°F	Total Gum	Neutralization No. mg KOH/g	Emulsibility, 30 min, 77°F, ml		
						Oil	Water	Emulsion
				Fuel A				
0	29.2	6.1	20.0	NA[a]	1.4	35	0	45
12	29.3	6.0	13.3	1.3	NA[a]	40	5	35
24	28.5	7.3	12.1	1.7	NA	38	2	40
36	27.7	7.4	6.4	3.9	1.7	40	0	40
				Fuel B				
0	21.5	2.8	31.3	NA	0.03	41	39	0
12	21.6	2.8	26.5	2.6	NA	40	39	1
24	21.4	2.8	23.6	4.4	NA	40	39	1
36	21.5	2.8	21.8	4.2	0.03	41	38	1
				Fuel C				
0	30.4	6.0	21.5	NA	0.9	41	39	0
12	31.5	5.4	16.7	2.8	0.9	41	39	0
24	30.5	6.8	11.6	3.7	0.9	39	41	0
36	30.3	6.4	10.9	4.5	1.0	39	41	0
				Fuel D				
0	31.6	4.8	22.1	NA	0.1	41	39	0
12	31.3	5.0	16.8	0.6	0.1	41	39	0
24	31.4	4.9	12.7	0.9	0.1	41	39	0
36	31.6	5.1	12.4	0.9	0.1	41	39	0

TABLE 9–*ASTM test results for four fuels.*

Fuel A	0.4 mg/100 ml
Fuel B	1.1 mg/100 ml
Fuel C	1.3 mg/100 ml
Fuel D	0.5 mg/100 ml

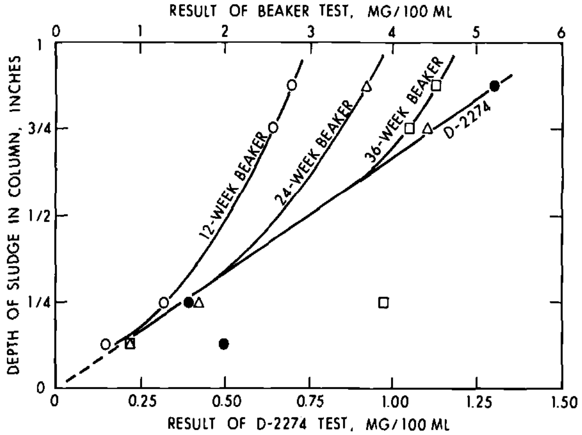


FIG. 3–*Results of accelerated tests compared with sludge depths in columns.*

TABLE 10–*Data showing location effect. Total gum levels in 24-month samples.*

Fuel		Maine	Annapolis	Florida
A		1.0	3.5	3.4
B		2.4	2.0	3.0
C		2.0	2.4	4.6
D		1.3	0.6	1.0
	Total	6.7	8.5	12.0

Can Tests

The gravities, viscosities, interfacial tensions, and neutralization numbers (Table 7) of the 6, 12, and 24-month can samples of Fuels A and B differ little from the same determinations on Annapolis bottle samples of a comparable age. However, Table 11 shows that the adherent gum levels, and consequently the total gum levels, of the can samples are appreciably higher than those of comparable bottle samples. It is suspected that the difference is due to corrosion of the tin can with the corrosion products appearing with the true adherent gum. Consequently, future storage tests should not be conducted in such tin cans.

TABLE 11–*Comparison of gum levels in can and bottle storage samples.*

Fuel	Storage Time, months	Can Samples, Gum, mg/100 ml		Bottle Samples, Gum, mg/100 ml	
		Adherent	Total	Adherent	Total
A	6	2.1	2.8	0.3	0.9
	12	1.2	2.0	0.1	0.6
	24	0.5	1.9	0.1	3.5
	Total	3.8	6.7	0.5	5.0
B	6	2.6	3.4	0.9	1.7
	12	3.6	4.1	0.4	1.2
	24	0.2	1.9	0.5	2.0
	Total	6.4	9.4	1.8	4.9

Beaker Tests

The effect of aging at 110°F in the beaker test is most evident in the increasing gum contents (Table 7) but may also be noted in decreasing interfacial tensions. Figure 4 reveals an erratic but general increase in the total gum contents of the four distillate fuels as storage time at 110°F increases. The data for the individual fuels are erratic, but the averages of the 12, 24, and 36 week data yield a relatively smooth trend line.

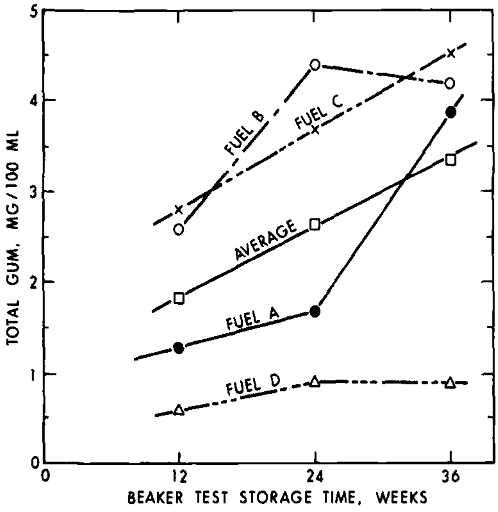


FIG. 4–*The effect of aging at 110°F, total gum formation in four distillate fuels as a function of storage time.*

The average beaker trends have been compared with the average bottle trends in Fig. 5. The 18-month and 30-month bottle results are seen to lie above the trend line established by the remaining bottle data. The 18 month average is based on limited data as the samples from Maine for Fuels C and D were lost in transit, so the point is based only on Annapolis and Florida data for these fuels. The 30-month average was also based on limited data, since Fuels A and B are the only ones that have reached this storage age.

The trend lines shown in Fig. 5 reveal that 12 weeks of beaker storage at 110°F is equivalent to average outdoor storage for 15 1/4 months (66 weeks). Further, if the two types of storage are compared on the basis of time to obtain 2 mg/100 ml of total gum, about 15 weeks of 110°F storage is seen to be equivalent to about 18.4 months of outdoor storage, that is, roughly 80 weeks. Thus, one week of beaker storage at 110°F is about equivalent to about 1¼ months of bottle storage. If the Arrhenius-type equation, Eq 1, is used without the pressure correction term to estimate the equivalent outdoor temperature, a value of 62°F is obtained. This calculated temperature appears to be a reasonable estimate for the grouped average annual temperature of the three locations.

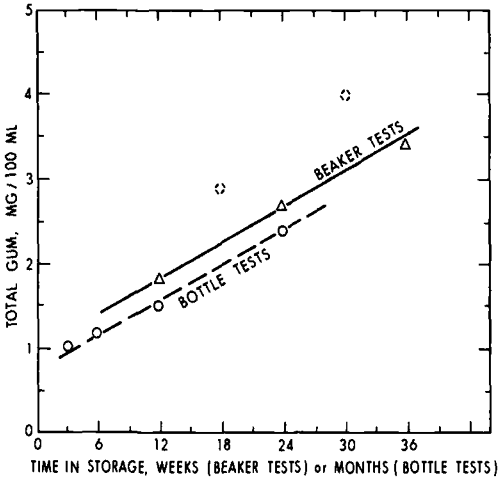


FIG. 5—*Comparison of total gum formed in beaker tests at 110°F with average total gum formed in bottle storage at ambient temperature.*

ASTM Tests

ASTM D 2274-70 test values for the four fuels are all below the 2.5 mg/100 ml maximum used in the specification for Navy marine diesel fuel (MIL-F-16884). The ASTM test results would suggest that the distillate propulsion fuels examined to date would possess sufficient storage stability for Navy needs.

The ASTM values are shown to be related to the gum values obtained in bottle storage and in beaker 110°F storage in Fig. 6 and 7, respectively. Although the data are scattered, the general upward trend of total gum with increasing ASTM test values lends encouragement to the proposition that the 16-h ASTM test can be used to distinguish between stable and potentially unstable Navy distillate fuels.

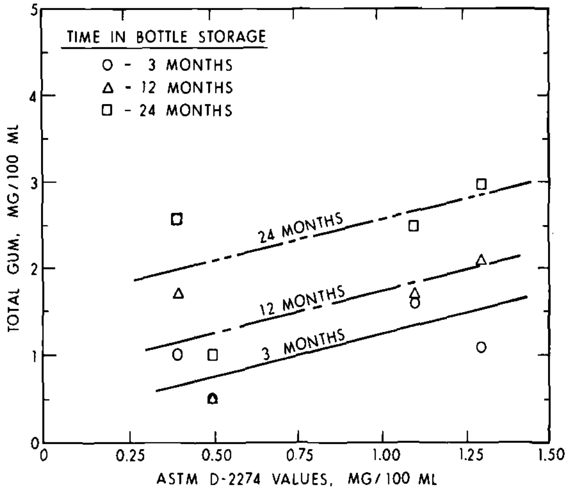


FIG. 6–*Relationship of ASTM D 2774-70 values to total gum levels in bottle storage. Note–the lines are intended to show trends only and are not best fits of the data points.*

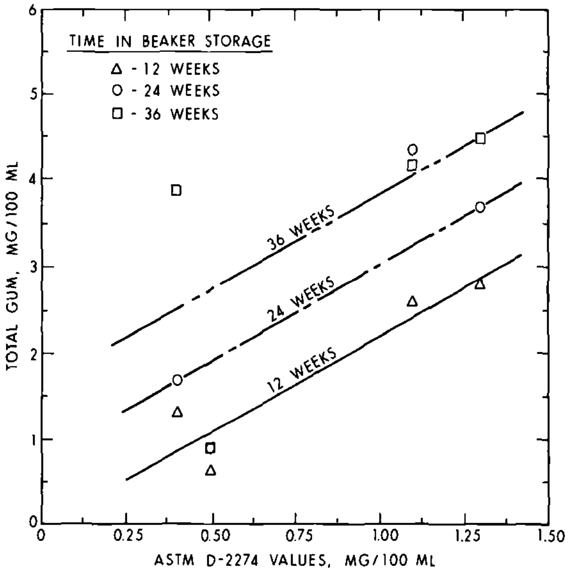


FIG. 7–*Relationship of ASTM D 2774-70 values to beaker storage data points. Note–the lines are intended to show trends only and are not best fits of the data points.*

Findings and Tentative Conclusions

The four fuels currently in the storage program are showing evidence of deterioration. The outdoor storage location appears to be a factor in the aging process on the basis of data from fuels stored in Maine, Maryland, and Florida. Differences are found in gum levels measured in samples stored in tinned cans compared with those measured in samples stored in bottles, probably as a result of can corrosion. The quantity of total gum found in bottle samples stored at ambient conditions are found to be generally related to values obtained in 110°F beaker storage and in the ASTM D 2274-70. One week of storage at 110°F in the beaker tests appears to be equivalent to about 1¼ months of average storage in bottles exposed to ambient outdoor temperatures.

Future Plans

The storage test program is continuing. Two or three new Navy distillates will be introduced into the program this year. The column samples of Fuels A and B are being inspected in detail after three years of storage.

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The ideas and opinions expressed in this paper are those of the author and do not necessarily represent those of the Navy or the naval establishment at large.

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Analysis of Fuel Oils for Trace Metals

REFERENCE: Braier, H. A., "Analysis of Fuel Oils for Trace Metals," *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531*, American Society for Testing and Materials, 1973, pp. 167–190.

ABSTRACT: The continuing trend toward lower tolerances for contaminants in oil products places a heavy demand on both well established and new analytical techniques. Some of the new techniques, in spite of the fact that they are uncommonly expensive and sophisticated, may be needed to comply with existing or future specifications. The first part of this paper presents general considerations on trace analysis, sampling, contamination, etc. The second part describes several techniques for the quantitative determination of vanadium, lead, sodium, potassium, calcium, and magnesium at the concentration levels indicated in the ASTM Specifications for Gas Turbine Fuel Oils (D 2880-71). Neutron activation, X-ray fluorescence, arc, spark and flame emission spectrometry, atomic absorption spectrometry, and spark source mass spectormetry are described in principle. Their characteristics are also intercompared as well as their general advantages and limitations.

KEY WORDS: fuels, gas turbines, trace elements, contamination, sampling, analyzing

In recent years analytical methods have increased in sensitivity. Therefore, a growing awareness has developed on how significant trace elements are and how important it is to detect them accurately. The demands of research and the availibility of modern instrumentation led to the development of new and specialized methods for the measurement of elemental composition at the parts per million (ppm) or parts per billion (ppb) levels. Thus, the distinctive field of trace analysis emerged within the realm of analytical chemistry.

General Considerations on Trace Analysis

The main feature of trace analysis is not the determination of a minute quantity of a substance—which, in general, is not a difficult task—but the determination of such small quantity in the presence of an overwhelming amount of other substances. These other substances, which are generally part of the sample matrix, may seriously affect the behavior of the trace constituent. A trace is generally and arbitrarily accepted as a constituent present in samples below a concentration of 100 ppm.

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The modern approach to elemental trace analysis is by means of physical methods. These methods are generally fast and require small samples which may need little or no processing. In most cases the elements are determined regardless of their oxidation state and chemical combination and usually many elements can be determined simultaneously. In general, physical methods produce some permanent record on photographic film of strip chart, which can be used for future reference or verification. But there are no universal methods. Every technique has its peculiar advantages and limitations.

Selection of an Analytical Method

The solution of a trace analytical problem lies in the selection of the analytical approach [*1,2*][2] will produce the quality of information required and whose limitations are unimportant to the solution of that particular problem. Considerable compromising is involved in the selection of an appropriate analytical technique.

Fundamental requirements such as the sensitivity and accuracy needed must be clearly established before looking for a solution to the problem. Sensitivity refers to the ability to see a small change in concentration. A closely related term is detection limit which is the lowest concentration that can be determined with a given degree of confidence. Accuracy refers to the reliability of the result, how close it is to the true value. Precision refers to the repeatibility of the result. Obviously, it is possible to have good precision with bad accuracy, but good accuracy implies good precision.

After one or more methods have been selected on the basis of their sensitivity and accuracy, it has to be established if their specificity is satisfactory. Specificity refers to the ability of measuring one element with no significant effects from other elements present in the system. In general, the conditions under which a method is specific are met by proper regulation of the chemical system and instrumental parameters. However, due to the nature of certain samples, these modifications cannot always be successfully applied.

Caution should be exercised when using information available in the technical literature about the terms just described. Sensitivity, precision, specificity, etc., as generally given by instrument manufacturers and some authors, are ordinarily measured when the element being determined is present alone in a pure solvent. This is an ideal situation far from what is found in real samples. As a rule of thumb, limits of detection given by instrument manufacturers should be multiplied by a factor of 2 to 10. The same applies to analysis time. In 1933, G.E.F. Lundell [*3*] published a paper entitled "The Chemical Analysis of Things as They Are" in which he complained that many talks and articles on analytical matters dealt with "The chemical analysis of things as they are not." The situation has not changed.

The following are considerations of variable importance in the selection of an instrumental method. Is the instrument available in our laboratory? If not, how much does it cost? What kind of space and utilities does it require? Can this

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

instrument determine one element at a time or various elements simultaneously? How is the sample to be presented to the instrument? Will our particular type of sample require processing? Can the instrument be operated by a technician? Can the data be directly transformed into concentration or must it be processed or interpreted? Useful information concerning reliability, frequency of adjustments, calibration, and repairs can be obtained from users whose names are usually provided by the manufacturer. And finally, an often forgotten consideration, is there in town a factory representative qualified to service the instrument?

Precautions in Trace Analysis [4, 5]

Contamination—Contamination in trace analysis may be a serious source of error, especially in the determination of common and widespread elements. A specimen exposed to atmospheric dust, for example, may gain as much sodium as was originally present. Contamination may occur from the moment of sampling to the last stage of the analytical procedure. It may be introduced by unclean containers, laboratory ware, reagents, atmospheric dust, distilled water, etc. Even dandruff, perspiration, fingerprints, and cosmetics are known to cause contamination in the trace analysis of some elements. If the sample must be chemically processed, a properly run blank will correct for contaminants contributed by laboratory ware and reagents. However, contamination experienced during sampling, transfer, storage, etc., will affect the sample before its analysis and will not be accounted for by the blank.

Sampling—Sampling which normally precedes analysis should be carefully planned and executed because its quality regulates the value of everything which follows. Generally, a laboratory sample is removed from the bulk product to be analyzed, and this sample is then divided into analytical subsamples. The quantitative result generated from an analytical subsample is limited by how well the subsample represents the bulk. Of course, the bulk may be only a portion of a larger volume.

Trace elements are generally not uniformly distributed in solids or nonhomogeneous materials like most fuel oils. Trace elements of interest in a fuel oil may be associated with the particulate matter or sediment, with the solution, or both. Highly sensitive instrumental techniques often require a very small specimen. This increases the danger that the specimen being analyzed may not constitute a representative portion of the original sample.

Sample and Standard Storage—Standards and laboratory samples are usually stored for variable periods of time. During storage, precautions must be taken to minimize changes such as particulate segregation, precipitation, oxidation, polymerization and other slow reactions, etc. Exposure to light, heat, air, and vibration should be avoided. Plastic containers should not be used to store liquid samples, especially if they are of organic nature. Containers should be tightly closed to avoid the evaporation of light components which will leave a concentrated sample. Also, trace metals can be adsorbed on the walls of the containers or contamination may occur from desorption of previously adsorbed contaminants.

Sample Processing—As it was already mentioned, many instrumental methods can handle a sample as it is. Sometimes processing is called for to comply with standardized procedures or to create conditions for the specific determination of a substance. In trace analysis, sample processing is performed to concentrate a trace constituent to a level at which it can be determined by a given instrumental technique or to eliminate interfering constituents, or both. Solvent extraction, evaporation, distillation, precipitation, ashing, etc., are some of the techniques used.

Conclusion

In chemical analysis and especially in trace analysis, every step no matter how simple is important, from sampling to the writing of the final report. Each operation contributes certain variability to the final result. A completed analysis can properly be compared to a chain, in the sense that no chain is stronger than its weakest link.

Analytical Methods

Figure 1 lists part of the specifications of ASTM Specifications for Gas Turbine Fuel Oils (D 2880-71). It must be realized that these are upper limits. Therefore, the analytical methods used must be suitable to accurately determine smaller concentration levels than those specified.

SPECIFICATIONS FOR GAS TURBINE FUEL OILS ASTM D2880

	PPM					Mg:V
FUEL OIL	ASH	V	Na+K	Ca	Pb	RATIO
No 1-GT	100	2	5	5	5	-----
No 2-GT	100	2	5	10	5	-----
No 3-GT	300	2	5	10	5	-----
No 4-GT	---	500	10	10	5	3.0-3.5

FIG. 1—*Specifications for gas turbine fuel oils ASTM D 2880-71.*

Determination of Ash

Ash is the noncombustible material in an oil. It may be part of the sediment or of water or oil soluble metallic compounds. Ash is determined by igniting the sample contained in a suitable vessel until ash and carbon remain. This residue is then completely reduced to ash by heating in a muffle furnace at high temperature, cooling, and weighing. This procedure is well described in ASTM Test for Ash from Petroleum Products (D 482-63), which covers the 10 to 2000 ppm ash range.

Methods of Elemental Analysis

What follows is a review of the general principles of some instrumental methods. These methods can be used to determine some or all of the trace elements listed in ASTM D 2880-71. A list of advantages and disadvantages is given for each technique described.

Some who have worked with these techniques may somewhat disagree with what, in the context of this presentation, is considered to be advantageous or detrimental. Of necessity, those who have worked for a long time in a given analytical field will sometimes favor their familiar approach at the expense of other good possibilities. The writer of this paper does not claim to be different and will not be surprised if he too is found in the predicament just described.

Neutron Activation Analysis

Neutron activation is a well established method of elemental analysis capable of attaining very low limits of detection for most elements [*6-8*]. It is not as widely used as other methods because to achieve low limits of detection large installations or complex machines are needed, although this is now changing with the advent of the californium-252 isotopic neutron sources. Of the elements listed in ASTM D 2880-71, vanadium is especially easy to determine by this analytical technique.

Advantages—Little or no sample preparation. Very high sensitivity for most elements. Interferences, if observed, can be eliminated by instrumental or chemical means or by the application of proper corrections. Analysis time can be very short, but this depends on the element to be determined and other factors. Neutron activation analysis on a service basis is available from a number of private and government laboratories throughout the country.

Disadvantages—Because of the use of radiation, special licensing, training of personnel, and controls are required. To achieve high sensitivities, high neutron fluxes are required which are expensive to obtain.

Cost and Space Needed—Cost and space needs can vary widely. About $35 000 and a medium size room are needed for a 1 mg californium-252 source system. Several hundred thousand dollars and a building are needed for a nuclear reactor. Particle accelerators are of intermediate cost and space requirements.

Principle—In neutron activation analysis, a sample is irradiated or bombarded with neutrons. Each atom which captures a neutron undergoes a nuclear reaction and could be transformed into an unstable or radioactive element. This unstable element, called radionuclide, becomes stable by releasing energy in the form of radiation. Each radionuclide is characterized by its rate of radioactive decay or half-life, type of radiation emitted, and energy of the radiation. These characteristics, like nuclear fingerprints, unambiguously identify the artificially created element; and by inference, the element in the sample that gave origin to it. Once the sample has been irradiated, two main approaches can be followed: chemical separation or instrumental analysis.

Chemical separation, which requires sample processing after irradiation, is time consuming and can be quite involved but it provides the lowest limit of detection afforded by activation analysis.

Instrumental activation analysis, which is widely practiced because it is fast and nondestructive, involves the use of gamma-ray spectrometry to study the gamma radiation emitted by the activated sample.

Instrumental neutron activation lends itself to on-stream applications. Figure 2 shows a schematic representation of on-stream and discrete sample instrumental activation analysis. In the on-stream example the sample flows through an irradiation coil and then through a counting coil. In the discrete sample application the sample, in a suitable container, is first irradiated and then taken close to the radiation detector. The radiation detection-analyzing system shown here is similar to the one described for energy dispersive X-ray spectrometry.

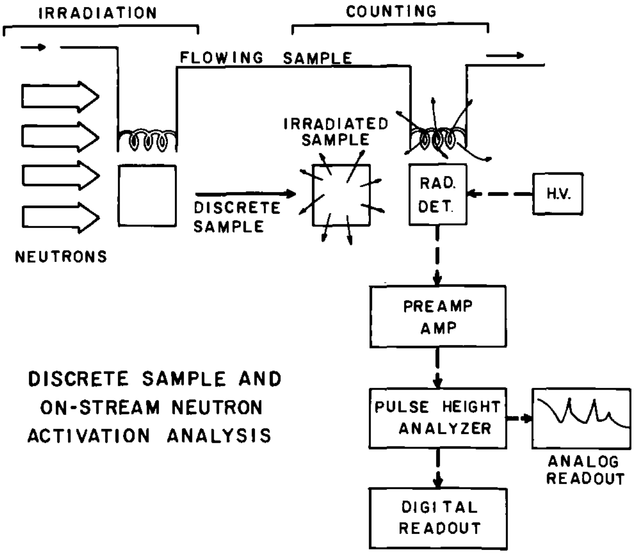

FIG. 2–*Discrete sample and on-stream neutron activation analysis.*

Neutron Sources–Neutrons are easy to produce. Being electrically neutral they easily invade the nuclear domain. For these reasons and because they react with most elements, neutrons are almost exclusively used in activation analysis. Neutrons can be obtained by means of nuclear reactors, particle accelerators, and isotopic sources.

Nuclear reactors are large and expensive to build and maintain, but they produce high neutron fluxes which facilitate the attaining of low limits of detection. Service irradiations and analysis can be obtained from a number of government, industry, and university owned reactors.

Particle accelerators are machines in which high speed charged particles collide with suitable target materials inducing nuclear reactions with the production of neutrons or other particles. Van de Graaff and Cockroft-Walton machines are typical of this group. The complexity of some of these machines can be realized by inspecting Fig. 3, which shows the 3-Mev Van de Graaff electron accelerator installation at Gulf Research and Development Company. Notice the four large rooms needed and the 5-ft thick solid concrete shielding wall.

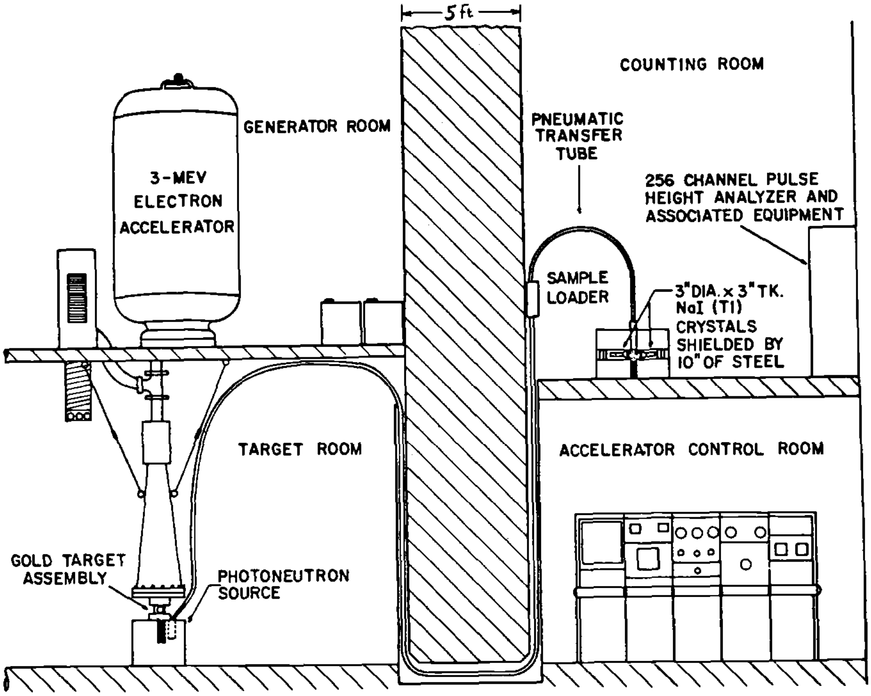

FIG. 3–*Facility for slow neutron activation.*

Isotopic neutron sources have the advantages of compactness, simplicity, and lack of moving parts. Also their neutron output is uniform, stable, and predictable. These characteristics make them ideal for on-stream applications. Until a few years ago the known sources of this type produced low neutron fluxes unsuitable for most applications.

Californium-252 Neutron Sources—For isotopic sources the picture has changed with the discovery in 1955 of californium-252, an artificial radionuclide which decays by spontaneous fission with an intense neutron production. Figure 4 shows the californium-252 source holder used at Gulf Research and Development Company. It is about 4 in. long and can contain several milligrams of the radionuclide. About 1 mg of californium-252, surrounded by an appropriate moderator, will produce approximately the same useful neutron flux as can be produced with the installation shown in Fig. 3. Californium-252 is commercially available from the United States Atomic Energy Commission.

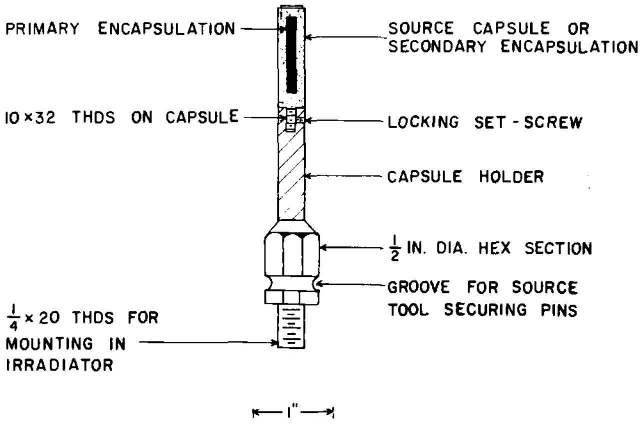

FIG. 4—*Californium-252 source holder.*

Figure 5 depicts an on-stream californium-252 irradiator in which space and radiation shielding requirements are reduced to a minimum by an underground location. Stream inlet and outlet are at ground level, while the irradiation coil surrounding the californium-252 source is about 2 ft below ground. A similar analyzer in an above-the-ground design can be seen in Fig. 6 which also shows the counting electronics, readout system, and inlet-outlet pipes on top of the tank. The 3-ft diameter steel barrel is filled with water for radiation shielding purposes. These on-stream irradiators can be easily adapted for the analysis of discrete samples. Figure 7 shows a calibration curve for vanadium in crudes obtained with the above-ground on-stream analyzer just described. The chart paper readout in Fig. 8 indicates how rapidly this analyzer reacts to a sudden change in vanadium concentration from 2.3 to 1.7 ppm. By changing operational parameters, vanadium can be determined from fractional ppm to percent concentrations.

The use of No. 4-GT fuels requires the addition of magnesium to keep a 3.0 to 3.5 magnesium/vanadium ratio to inhibit corrosion. This could be easily achieved with the automatic continuous control system schematically described in Fig. 9, which features a californium-252 on-stream vanadium analyzer. The

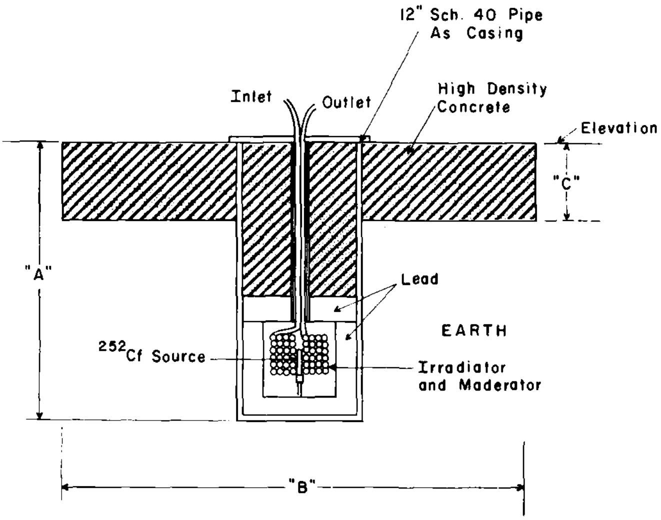

FIG. 5–*On-stream californium 252 irradiator in a below ground configuration.*

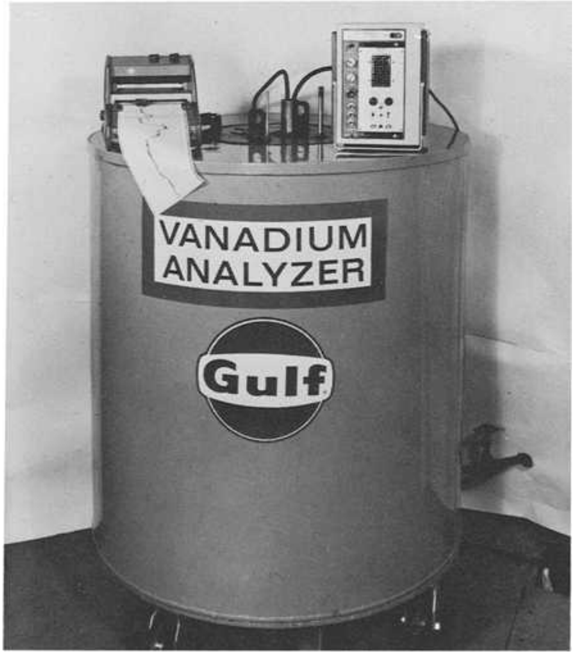

FIG. 6–*Above ground on-stream vanadium analyzer featuring a californium-252 source.*

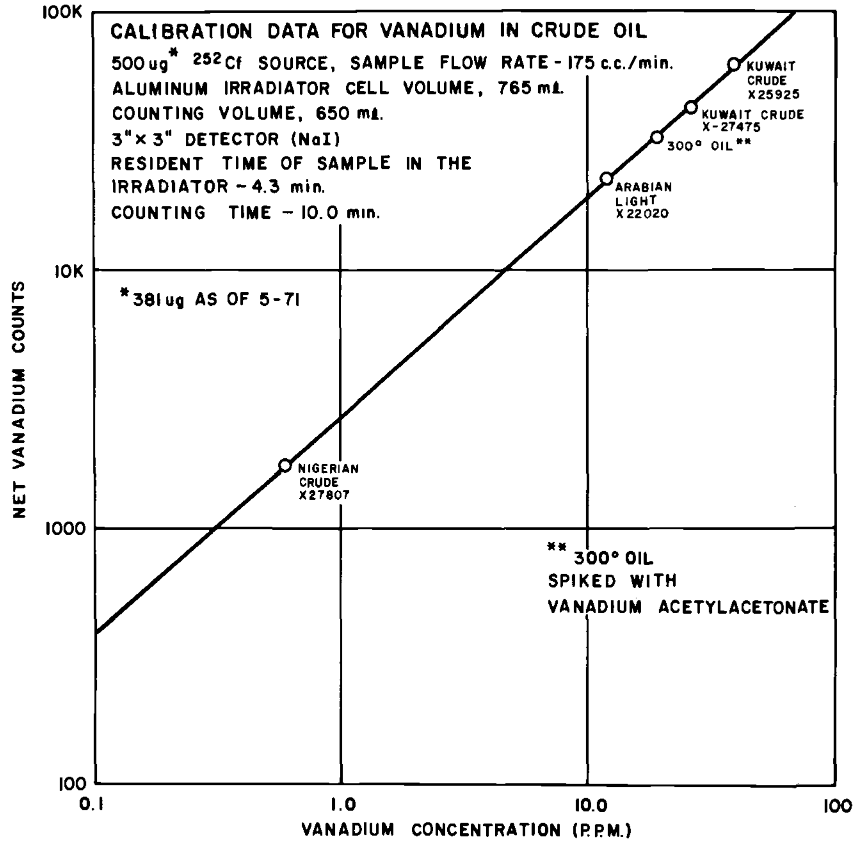

FIG. 7—*Calibration data for vanadium in crude oil.*

analog computer controller continuously processes input information on vanadium level and fuel flow rate. Its output signal, by activating a control valve or pump, adds the right amount of a stock magnesium solution to the fuel.

X-Ray Fluroescence

X-ray fluorescence is a well known and widely used method of elemental analysis [*9-11*]. It is directly applicable to solid or liquid samples of organic or inorganic nature.

Advantages—X-ray fluorescence analysis can be performed using rapid and simple techniques with little sample preparation for concentrations above 0.01 percent. It is an excellent method when applied to routine, run-of-the-mill samples.

Disadvantages—To determine low or fractional parts per million levels, most samples must be processed to concentrate the trace elements. The technique is not sensitive for sodium and lighter elements. Matrix effects are important and affect accuracy unless appropriate standards or corrections or both are used.

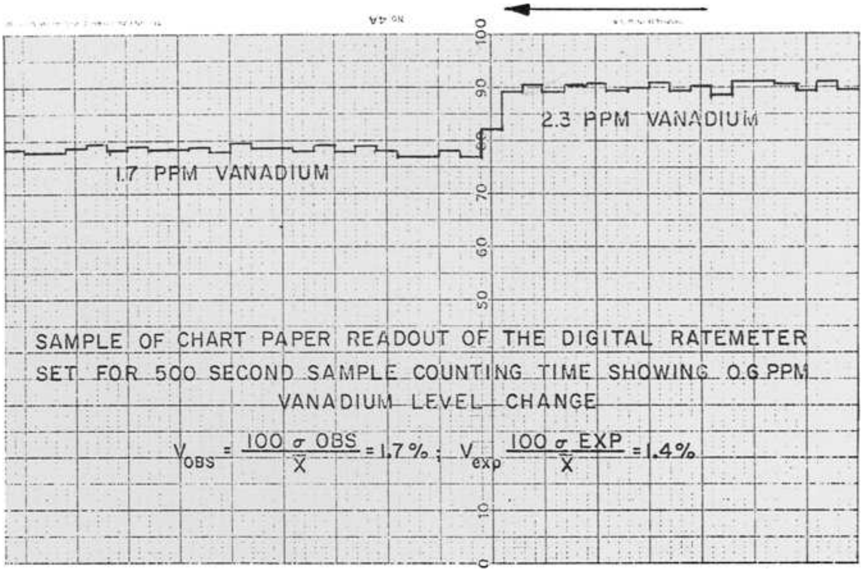

FIG. 8—*Recorder readout of a vanadium level change.*

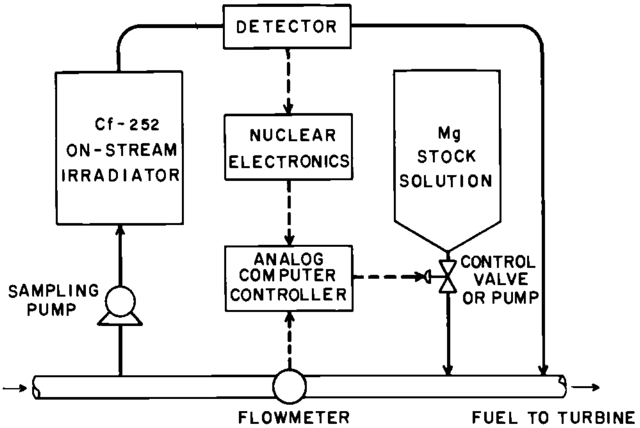

FIG. 9—*Automatic continuous control system for the determination of vanadium and addition of magnesium to No. 4 GT fuels.*

Cost and Space Needed—Prices range from \$20 000 to \$40 000 for a good instrument. The cost can be easily doubled by the addition of automatic features, computer operation, etc. For safety consideration it is desirable to have these instruments in a separate room.

Principle—When atoms are excited by X-ray bombardment, inner shell electrons are ejected. The vacancies thus created are immediately filled by outer shell electrons. These outer shell, energetic electrons move toward the lower energy inner shells by discrete jumps from energy level to energy level. The resulting decrease in their energy appears as X-ray photons with wavelengths which are characteristic for each element.

When a specimen is bombarded with X-rays, the elements present will emit their characteristic X-rays. For analytical purposes these X-rays must be resolved and their intensity measured. This is accomplished with an X-ray spectrometer of which there are two fundamental types, namely, the wavelength dispersive and the energy dispersive. Figure 10 shows a schematic diagram of these spectrometers.

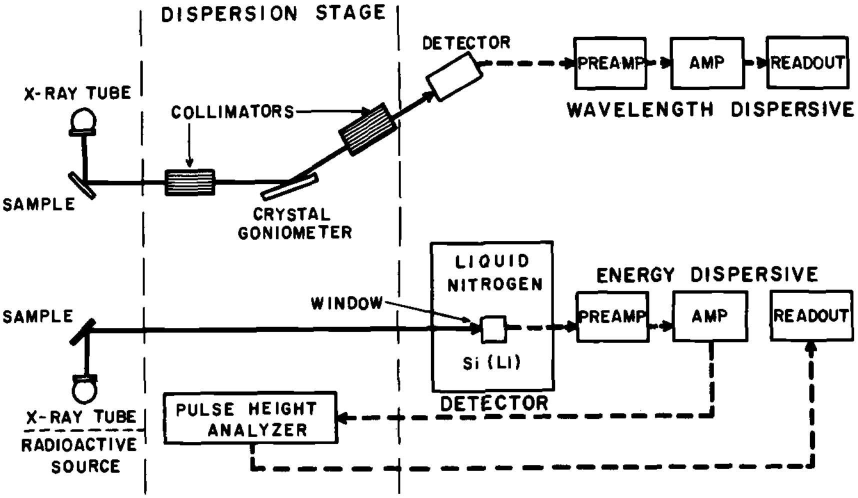

FIG. 10–*Comparison of wavelength dispersive and energy dispersive X-ray spectrometers.*

The wavelength dispersive spectrometer is the conventional optical instrument in which the photons are spatially dispersed by diffraction by means of a crystal goniometer. For each position of the goniometer, the detector sees only a narrow wavelength band. These spectrometers have good resolution but with them only one element at a time can be determined.

In energy dispersive instruments, all the characteristic X-rays from the specimen are first detected by a high resolution solid state detector. The detector output consists of electrical pulses of amplitude proportional to the energy of the detected photons. These pulses, once linearly amplified, are electronically sorted according to their amplitude by means of a pulse height analyzer. An advantageous consequence of this detection mode is that analysis of all chemical elements can be performed simultaneously. Since it eliminates the use of crystal goniometers and the X-rays are not spatially dispersed, this type of spectrometer is also sometimes referred to as nondispersive.

Atomic Emission Spectroscopy

There are different techniques in atomic emission spectroscopy [*6, 12*]. These are based upon the types of excitation and detection used. Under this heading arc and spark excitation and photographic and multi-photometric detection will be discussed. Flame photometry, although by principle belongs to this group, will be discussed together with atomic absorption spectrometry.

Advantages—Qualitative or quantitative determination of about 70 elements. All or most of these elements can be simultaneously determined. Analysis time can be very short as is the case with direct readers.

Disadvantages—Strong matrix effect. Poor sensitivity for volatile elements. Involved calibration required for precise quantitative analysis.

Cost and Space Requirements—Cost varies from about $30 000 for a relatively simple spectrograph and accessories to $100 000 for more sophisticated instruments. A medium size room is the minimum space required to house this equipment.

Principle—In atomic emission spectroscopy the atoms are excited by thermal or electrical means or both. The excited atoms and atomic ions emit their excess energy in the form of light of definite wavelengths. The emitted radiation is resolved by optical means in its individual wavelengths which are recorded photographically or photoelectrically as a definite pattern of spectral lines. The position of the spectral lines gives a qualitative indication of which elements are present. The intensity of the spectral lines gives a quantitative indication of the amount of each element in the sample.

Figure 11 shows the fundamental parts of an emission spectrograph. These are: a means to excite the sample, a dispersive element, and a detection system.

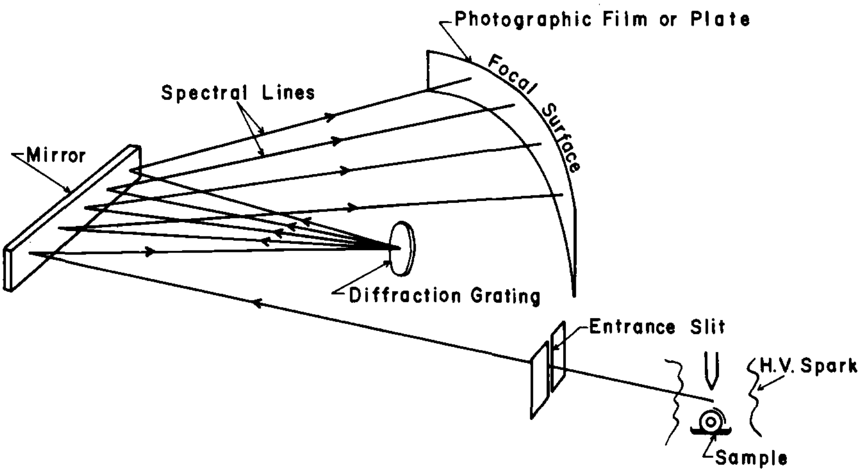

FIG. 11—*Schematic diagram of an optical emission spectrograph.*

Sample Excitation—There are three sources commonly used to vaporize and excite the elements in a sample: the flame, the electric arc, and electric spark discharge. Flames possess the lowest excitation energy producing a rather simple line spectra. Flame excitation will be discussed when dealing with flame photometry and atomic absorption.

In arc excitation vaporization occurs from the heating caused by the passage of electrical current. It produces a complex line spectrum due mostly to excited neutral atoms. The d-c arc is widely used because it can be applied to almost any kind of solid sample and because it exhibits the highest sensitivity for trace element detection. Its lack of stability results in somewhat poor precision.

The high voltage a-c spark gives higher excitation energies than the d-c arc with much less heating effect. It produces a complex line spectrum due mostly to excited atomic ions. Because it is a stable source, it is preferred when high precision rather than high sensitivity is required. It is easily applicable to liquid samples and solutions.

Dispersion—The most important component of a spectrograph is the dispersive element, which can be either a prism or a diffraction grating. It sorts out by wavelength the radiant energy coming from the excited atoms.

Detection—The dispersed radiation is photographically recorded on film or plate providing a permanent record for analysis. The slowness of the photographic process and subsequent evaluation led to the development of instruments known as direct-reading spectrometers.

Direct Reading Spectrometers—In a typical such instrument, schematically shown in Fig. 12, the photographic film is replaced with an opaque barrier which has several slits located at wavelengths appropriate to the elements to be analyzed. Behind each slit is mounted a photomultiplier tube which directly

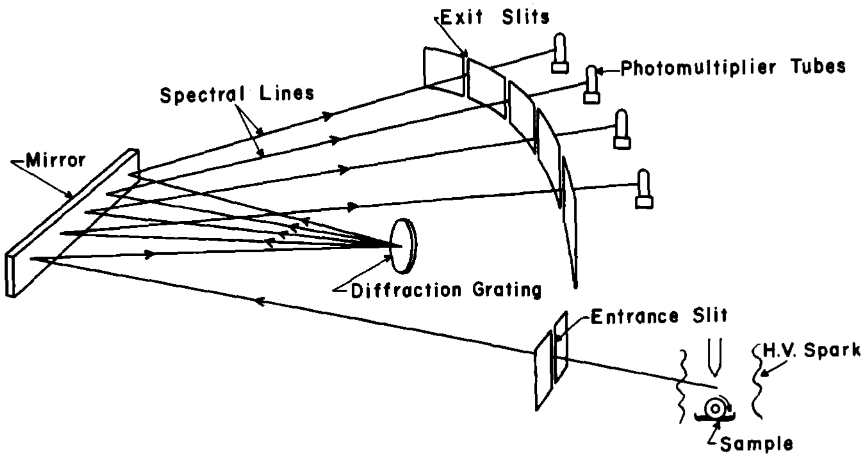

FIG. 12—*Schematic diagram of a direct reading optical emission spectrometer.*

converts radiant energy into electrical energy, permitting a rapid readout. Direct readers are very useful in high speed routine quantitative work. From few to many elements can be simultaneously determined.

Atomic Emission Flame Photometry and Atomic Absorption Flame Photometry [13]

Although these spectroscopic techniques are conceptually different, they have some points in common and will be discussed together to emphasize their similarities and differences. Both are well-known, widely used, and relatively inexpensive instrumental methods for the determination of metallic elements in organic or inorganic samples.

Advantages—Flame emission: very high sensitivity for some elements, rapid simple and inexpensive. Atomic absorption: good sensitivity for most metallic elements, rapid, simple, specific, with few interferences.

Disadvantages—Flame emission: spectral interferences and flame fluctuations affect precision and accuracy. Determines one element at a time. Sample must be in solution. Atomic absorption: determines one element at a time. Sample must be in solution although new flameless techniques like the carbon rod may change this requirement.

Cost and Space Needs—Prices range from $5 000 to $15 000 for an instrument that can perform both techniques, and considerably less for a flame emission spectrometer. Few feet of bench space is needed for either instrument.

Principle—As can be seen in Fig. 13, both methods use a burner, a flame, a monochromator, and a detector which generally is a phototube. A hollow cathode lamp and a chopper are added for atomic absorption.

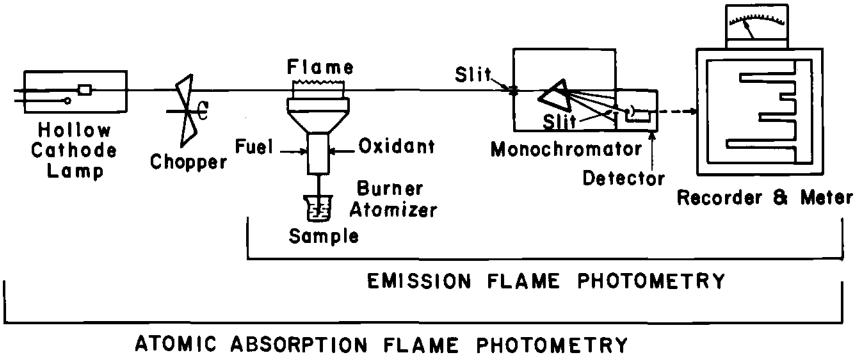

FIG. 13—*Comparison of emission and atomic absorption flame photometry.*

In flame emission as in atomic absorption a burner aspirates a solution of the sample and atomizes it into the flame. The heat of the flame and the kinetic energy of the combustion products break down the sample molecules into its component atoms. Close to 100 percent of these atoms are not excited but merely dissociated from their chemical bonds and placed into a non-ionized ground state. An important property of the ground state atoms of a given element is that they will absorb light of a specific wavelength. This light, known as resonant radiation, is the same that would be emitted by these atoms if they were excited. The resonant radiation of a metallic element is easily produced with a hollow cathode lamp whose cathode contains that metallic element. The excitation energy of the commonly used flames is low compared to that of arcs and sparks. Consequently, less than 1 percent of the metal atoms in the flame are mildly excited to emit a simple line spectrum. In both methods, the monochromator is used to isolate the analytical wavelength used for the analysis from all other unwanted light produced by the flame or hollow cathode lamp or both.

The conceptual difference between both methods is that in flame emission, what is measured is the *emission* from the excited atoms, which are only a small part of the metal atoms of a given element present in the flame. In atomic absorption what is measured is the *absorption* of a constant output of certain resonant radiation by the majority of the metal atoms of a given element present in the flame, which are those in the ground state.

In flame emission, spectral interferences are common and affect accuracy. Spectral interferences occur because the different elements excited emit their radiation simultaneously and the monochromator may not have the resolution to isolate an analytical line from the effect of a very intense or a very close interfering line. Precision also suffers because the population of excited atoms is affected by difficult to control flame fluctuations. Flame emission is extremely sensitive for the determination of the alkali metals, the alkaline earth metals, and a few other metallic elements.

Due to a combination of factors, spectral interferences are much less prevalent in atomic absorption than in flame emission. For example, by means of a chopper or other suitable device, the continuous output of the hollow cathode lamp is transformed into a modulated analytical signal. This signal is then separated electronically and measured independently from the continuous and interfering signal produced by the flame. Also, the lines from a hollow cathode lamp are few and narrow and are specifically absorbed. Therefore, a given element can only be determined when the lamp and the monochromator setting are both matched to that element analysis. Precision is not significantly affected by flame fluctuations because these have little effect on the population of ground state atoms. Atomic absorption is by no means free of interferences, but they are uncommon and, in most cases, can be recognized and overcome by the use of standard techniques.

New flameless methods for sample presentation to the instrument like the graphite rod and the tantalum boat are expanding the use and applications of atomic absorption spectrometry. In the first technique the burner is replaced by a graphite rod with a small well where a few microliters of sample are deposited and electrically heated by means of a controlled power supply. Important advantages of this procedure are that a very small sample is needed and the dilution of viscous samples is not required. Also, the absence of interfering flame background helps to obtain better sensitivity for many elements. In the boat technique the liquid sample is deposited in a narrow, boat shaped container, and carefully dried. The container is made of tantalum or another high melting point metal. The boat is placed under the light path of the hollow cathode lamp and the dried sample is vaporized by electrical heating or with a conventional acetylene-oxygen flame. This technique, although simple, is not free from interferences and offers better sensitivity for a few elements only.

Spark Source Mass Spectrometry

This is not a common or well-known technique of elemental analysis. Nevertheless, it has reached the point of refined development; instrumentation is commercially available and the technique has attractive features.

Advantages—It is the only method that offers high and uniform sensitivity for all elements with the exception of hydrogen and helium. Typical precisions are ±2 to 5 percent above the 1 ppm level and ±10 to 20 percent from 1 to 0.001 ppm. All elements can be determined simultaneously.

Disadvantages—It is a sophisticated instrument that requires the services of a professional. It is a relatively slow technique. Barring any difficulty, about ten oil samples a day can be analyzed. It is expensive. The instrument costs about $120 000 and requires considerable floor space.

Principle—As the name implies, this is a mass spectrometric technique. The principle of mass spectrometry can be briefly explained with the aid of Fig. 14 which shows the diagram of a double focusing instrument which is the type used in spark source mass spectrometry.

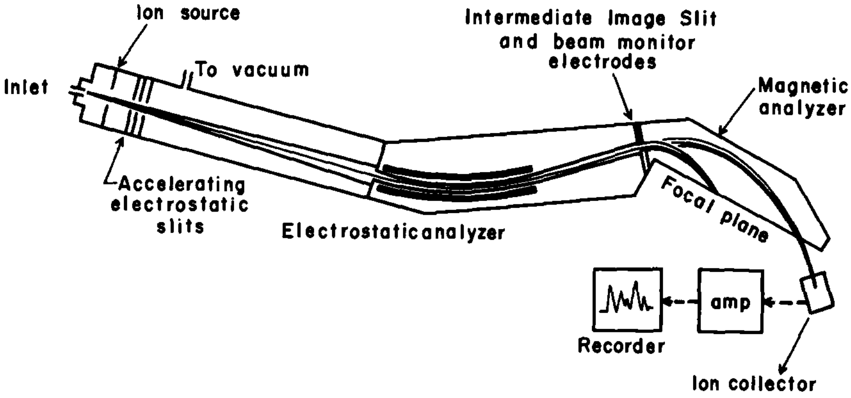

FIG. 14—*Double-focusing mass spectrometer.*

Mass Spectrometry in General—The mass spectrometer is an instrument which sorts out molecular or atomic ions according to their masses and electrical charges. Several methods of producing mass spectra have been devised and all of them have the following five parts in common.

(1) The inlet sample system. It provides the means for sample introduction. It is generally suited for gaseous and liquid samples and is usually heated to help vaporize the sample in the high vacuum of the instrument.

(2) The ion source. In this part the gaseous molecules are ionized and fragmented by electron bombardment.

(3) The accelerating system. It consists of a series of slits charged at decreasing potentials through which the ions formed at the ion source are accelerated.

(4) The mass analyzer. Separates and focuses the ions on a curved or plane surface according to their mass to charge ratio. The main difference among the different types of mass spectrometers lies in the design of the mass analyzer.

(5) Detection system. Detects the individual ion beams by means of an ion collector-amplifier-readout system. Photographic plate can also be used to detect and record the mass spectrum. The position of the spectral lines gives a qualitative indication of the elements or molecules present in the sample. The intensity of the spectral lines gives a quantitative indication of the amount of each element or molecule present in the sample.

Spark Source Mass Spectrometry—This is a technique adapted to the determination of elemental rather than molecular composition. The main difference between the instrument just described and the kind needed for this technique lies in the design of the sample inlet and ion source. The regular inlet is replaced with a rather large door which provides access to the ion source area and the ion source is replaced with electrodes made with the sample to be analyzed. If the sample is liquid, it is frozen on the outside surface of hollow metal electrodes through which liquid nitrogen is constantly circulated. In this manner, a film of frozen sample remains on the electrodes' surface even during excitation. A high voltage radio frequency spark, which provides energetic and cool excitation, is used to vaporize and ionize the elemental components of the sample. These elemental ions are then accelerated, analyzed, and detected as described, previously. Because of the characteristics of the spark excitation, the ion output varies little from element to element. This is why all elements can be determined with about the same sensitivity.

Conclusion

Table 1 represents an attempt to intercompare some characteristics of the instrumental techniques just described. It would be unfair and difficult to assign other than general values to these characteristics because they depend on many variables. Among such variables are the nature of the sample, the element to be determined, the particular instrument and perhaps most important, the ability of the analyst.

Some of the described instrumental techniques are complex and uncommon but offer very low limits of detection. Some others are simple and widely used. Nevertheless, they may become sophisticated and restricted if pushed to give the ultimate detection limits of which they are theoretically capable.

As new specifications establish lower tolerances, exotic instrumentation and

TABLE 1—*Comparison of analytical methods for the analysis of sodium, potassium, calcium, magnesium, vanadium, and lead in fuel oils.*

Characteristic	Neutron Activation Analysis	X-Ray Fluorescence	Emission Spectroscopy	Flame Emission	Atomic Absorption	Spark Source Mass Spectrometry
Sensitivity	very good: V good: Na, K, Ca, Mg poor: Pb	good: V, Pb Poor: Na, K, Ca, Mg	good to poor	good: Na, K, Ca, Mg poor: V, Pb	good	good
Accuracy	good	good	good to poor	good to poor	good	good to poor
Specificity	good	good	good	good to poor	good	good
Contamination	good	good	good	poor	poor	good
Analysis time	fast to slow	fast	fast	fast	fast	slow
Several elements simultaneously	yes	yes: E. Disp. no: W. Disp.	yes	no	no	yes
Instrument cost	$30 K up	$30 to 50 K	$30 K up	$2 to 4 K	$4 to 15 K	$120 K
Space needed	room-bldg.	room	room	bench	bench	room
Operation	simple to complex	simple	simple	simple	simple	complex
Interpretation	simple to complex	simple to complex	simple to complex	simple	simple	complex
On-stream capability	yes, for V	no	no	no	no	no

involved handling–not available elsewhere–may be needed to analyze fuel oils. In this regard the gas turbine fuel oil user should be prepared to send samples for analysis to laboratories far from his own location. If so, analytical results should not be expected sooner than a few days, or in some cases a few weeks.

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Discussion

J. B. Harrell[1] *(written discussion)*—To support our corporate effort in the area of fuel treatment to meet gas turbine specifications, it became necessary to develop a method for determining metal contaminants in these fuels. We found the available methods to be time consuming and difficult. To meet our needs and those of our customers, any new method would have to provide accurate metal detection in the range of 0.2 to 20 ppm while being rapid and precise. Applicability to both aqueous and nonaqueous impurities was also recognized as essential. In response to this need, we developed and tested a direct-dilution method based on atomic absorption spectroscopy which appears to meet these requirements. Our laboratory has successfully employed this technique to determine sodium, magnesium, calcium, potassium, iron, and lead in various hydrocarbon oils. The method is applicable to the analysis of any metal which is reasonably sensitive to analysis by atomic absorption spectroscopy methods. We have shown that the accuracy of the method for sodium in various oils is ±10 percent or ±0.2 ppm, whichever is larger. One man can analyze six samples in 1 h, whereas analysis of the same samples by ASTM Test for Sodium in Residential Fuel Oil (Flame Photometric Method), (D 1318-64) (1968), would require a minimum of 8 h. The basic method can be described briefly in the following way. An oil sample is diluted with an equal volume of a solvent which consists of an equal-volume mixture of isopropyl alcohol and xylene. This dilution-solvent dissolves water and water-soluble salts which may be in the oil, making it possible to employ the dilution as a working sample in the analysis. The metal to be determined is analyzed by atomic absorption spectroscopy, using the technique of standard additions.

In the course of our studies which resulted in the present method as applied to the determination of sodium in distillates, we found a water extraction/hydrolysis procedure to have certain advantages. In this procedure, samples are taken in plastic bottles containing a measured equal amount of deionized water, after which the sample is intimately mixed with the water. The dispersion is allowed to separate and metal analysis is performed on the aqueous phase. This may be done either by atomic absorption spectroscopy or by flame emission spectroscopy. If the sodium content of the oil is low, the sodium ion can be concentrated in the water by using a 3 to 1 or 4 to 1 ratio of oil to water.

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B. T. Hagewood, supervisor of Chemical Controls for Long Island Lighting Company, has done independent investigations in the use of a water extraction technique of this type. His work indicates that the sodium ion of ostensibly oil-soluble sodium compounds can be efficiently recovered from distillate samples using this water-extraction or hydrolytic principle or both as the basis for analytical determination of the sodium.

A case involving the operation of salt dryers in a Gulf Coast refinery graphically illustrates the need for an analytical method sensitive to water-soluble or water-extractable sodium salts in hydrocarbons. Our laboratory has made analytical studies of the effluent kerosine from a salt tower over a period of 25 days; included in this work was the careful monitoring of sodium level in the oil. Table 2 shows the results of sodium analysis by three methods on the 35° API kerosine. The results under "Petreco Extraction Method" in the table were obtained by taking the samples in bottles containing deionized water and analysing the water phase as just explained. The low results by ASTM Tentative Method of Test for Trace Metals in Gas Turbine Fuels (D 2788-69) obtained on 10 and 14 March prompted us to double check the Petreco Method by titrating water-extractable chlorides in the water extract. The excellent agreement seen between the sodium values by the Petreco Method and that calculated from chloride values (assuming NaCl) indicates that values by ASTM D 2788-69 are low. The low results were attributed to the absorption of sodium contained in the oil upon sample container walls. We have observed that this absorptive loss of sodium is particularly serious with light, virtually dry distillates.

TABLE 2–*Comparative results by three methods of sodium analysis in oil.*

		Sodium, mg/liter		
Date	Sample	ASTM D 2788-69	Petreco Extraction Method	NaCl Extracted, Chloride Titration
3/10/72	out of salt tower	0.2	1.1	...
3/14/72	out of salt tower	0.2	1.5	...
3/21/72	into salt tower	...	0.1	0.2
3/21/72	out of salt tower	0.2	2.8	2.9
3/24/72	into salt tower	...	0.3	0.7
3/24/72	out of salt tower	...	32.0	31.0

This sodium-loss effect is practically eliminated if original oil samples are taken in bottles containing a measured amount of isopropanol-xylene solvent. When this precaution is observed, dilution analysis may be performed on the oil with results virtually identical to those by the water extraction technique. This provides a more satisfying procedure in that the analysis is run on the *total* sample and not on an extract of the sample, thus reducing the likelihood of error. On this basis, we have evolved a final general procedure for atomic absorption spectroscopy dilution analysis for sodium and other metals as contaminants in various oils, especially distillates. The analytical method itself is described in full detail in Tables 3 and 4.

TABLE 3–*Petreco dilution method; determination of metals in hydrocarbon oils.*

PREPARATION OF DILUTION SOLVENTS

Dilution Solvent A–Equal volumes of isopropanol and xylene are mixed.

Dilution Solvent B–To a 1-liter volumetric flask add 20 ml of glacial acetic acid and 50 ml of isopropanol. Fill to the mark with methyl isobutyl ketone (MIBK).

PREPARATION OF STANDARD SOLUTIONS

Prepare a 500 ppm working solution of sodium in oil by placing 10.0 ml of the 5000 ppm sodium-in-oil standard solution in a 100-ml volumetric flask. Dilute to the mark with MIBK. Use this 500 ppm solution to prepare the remaining standard solutions.

1 ppm Standard–To a 500 ml volumetric flask, add 25 ml isopropanol, 10 ml glacial acetic acid. Add 1.0 ml of the 500 ppm sodium-in-oil working solution. Dilute to the mark with MIBK. Store the solution in a tightly capped plastic bottle.

2 ppm Standard–Repeat procedure above except add 2.0 ml of the 500 ppm sodium-in-oil solution.

SAMPLING AND INITIAL DILUTION

If possible, take sample in a container already containing a measured amount of Dilution Solvent A, such that the oil sample will be diluted by a known factor, approximately x2. The preferred dilution of the original oil samples is as follows:

Place 50 ml of Dilution Solvent A to a 100-ml glass-stoppered graduated cylinder. Add a representative oil sample to the cylinder to bring the total volume in the cylinder to 100 ml. Mix well.

PROCEDURE

Place 25 ml of the diluted sample in each of three 100-ml plastic bottles. Add 25 ml of Dilution Solvent B to bottle (1), add 25 ml of 1 ppm sodium standard to bottle (2), add 25 ml of 2 ppm sodium standard to bottle (3). This produces a series of solutions of the sample, each diluted 4 to 1 and containing 0, 0.5, and 1.0 ppm sodium, respectively. The samples are now ready for observation with the atomic absorption spectrophotometer.

INSTRUMENT CONDITIONS

Follow the manufacturer's instructions in setting instrument conditions for the analysis for the particular element to be determined. Set the instrument for zero absorbance while burning a mixture of 25 percent Dilution Solvent A, 25 percent metal-free blank oil, and 50 percent Dilution Solvent B.

Aspirate Solutions (1), (2), and (3), recording the absorbance on a strip chart recorder. Allow each solution to reach a steady reading before proceeding to the next. Aspirate the mixture used to set the instrument to zero between each sample solution to clean out the aspirator and burner, and to check the stability of the zero setting.

CALCULATION

Plot the absorbance of Solutions (1), (2), and (3) versus the ppm of sodium added to each solution. Draw a straight line through the three points. The intersection of this line with the concentration axis is equal to the amount of sodium in Solution (1). The intercept is multiplied by the dilution factor of 4 to give the concentration of sodium in the original sample in parts per million.

The following sample calculation is given as an example of a typical oil analysis.

Solution	Sodium Added (ppm)	Absorbance
(1)	0.0	0.10
(2)	0.5	0.15
(3)	1.0	0.20

Figure 15 shows the proper plot of the above data. The intercept of the line with the concentration axis is -1.0 ppm, indicating that 1.0 ppm corresponds to the sample absorbance of 0.10. Multiplying 1.0 ppm by the dilution factor of 4 gives 4.0 ppm sodium in the original sample. The dilution factors used and the parts per million of sodium added to the samples should be adjusted so that the absorbance of Solution (3) is 2 or 3 times as large as the absorbance of Solution (1). For best accuracy, the absorbance values should fall between 0.05 and 0.5.

TABLE 4–*Apparatus and reagents required.*

APPARATUS REQUIRED

Atomic absorption spectrophotometer with appropriate hollow cathode lamps

Strip chart recorder

Polypropylene bottles–screw cap, 100 and 500 ml capacity

Pipettes–analytical, 25.0 ml capacity

Volumetric flasks–analytical, 500 ml capacity

Glass-stoppered graduated cylinder–100 ml

REAGENTS REQUIRED

Sodium in oil–atomic absorption standard solutions, 5 000 ppm (Conostan)–available from Conoco, Ponco City, Okla.

Methyl isobutyl ketone–reagent grade or equivalent

Isopropanol–purified grade

Glacial acetic acid–reagent grade

Blank oil–metal free lubricating oil for atomic absorption analysis

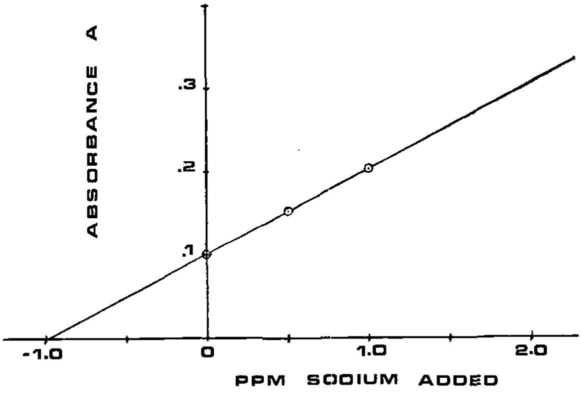

FIG. 15–*Graphical data treatment; method of standard additions.*

J. F. Boyle[1]

Problems Associated with Vanadium Determination in Heavy Distillate Fuels

REFERENCE: Boyle, J.F., "**Problems Associated with Vanadium Determination in Heavy Distillate Fuels,**" *Manual on Requirements, Handling, and Quality Control of Gas Turbine Fuel, ASTM STP 531,* American Society for Testing and Materials, 1973, pp. 191-198.

ABSTRACT: The introduction of the gas turbine as a marine propulsion plant has brought to light fuel contamination problems due to the presence of certain metals at low concentration levels. These metals have been found to cause corrosion, and with it, attendant operational problems. The source of these contaminants may be found in the heavier distillate fuels used in the gas turbine in an effort to reduce overall operational costs. Since the metals of interest occur at levels below 10 ppm, they present unique analytical problems, particularly with vanadium, the effects of which are considered deleterious even at levels below 2 ppm. This paper discusses the specific problems encountered with vanadium analysis in heavy distillate fuels.

KEY WORDS: fuels, gas turbines, vanadium, trace elements, contamination

The use of aircraft type gas turbines for ship propulsion has brought new challenges to the fuel analyst. In an effort to make the gas turbine competitive with the more traditional marine power plants, it is desirable to minimize operational costs. A fertile area for such cost reduction is in the fuel selection [*1*].[2] In the U.S. Navy, the search for cost reduction of fuels for marine gas turbines has turned to the use of heavy distillate fuels rather than the traditional kerosine fractions. The expanded use of heavy distillate fuels for gas turbines is of interest not only to the Navy, but to many others who anticipate greater use of the gas turbine for marine or other applications.

Discussion

Heavy Distillate Fuels

For a full appreciation of the use of heavy distillate fuels for gas turbine propulsion and the attendant analytical problems, it is appropriate to consider what is meant by the term heavy distillate fuel, since this term can be somewhat ambiguous. In the context of this paper, the heavy distillate fuels are confined to those fuels encountered in the Navy Distillate (ND) fuel program. In the last few

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

years, the U.S. Navy has taken the necessary steps to define a heavy distillate fuel for use in present and proposed marine propulsion systems. After a considerable cost and availability study, the characteristics of a heavy distillate fuel were established. It was, of course, recognized that any fuel improvement over the present boiler fuel would be beneficial for boiler maintenance, but that any degradation in fuel quality from the kerosine grades would affect its usage in the gas turbine. With the use of the gas turbine definitely in future Navy plans, it can be seen that it was the principal dictator in the definition of the fuel characteristics–consistent of course with cost considerations.

The culmination of these activities is shown in Table 1, MIL-F-24397, Fuel, Navy Distillate issued in January 1969. Of special significance is the permissible distillation levels at the 90 and 95 percent points; with these allowances, fuels having end points in the 800 to 825°F range can be anticipated.

TABLE 1–*Principal characteristics of navy distillate fuel MIL-F-24397.*

	Maximum
Pour point, °F	+25
Viscosity cSt 100°F	10
Carbon residue, % (10% BTMS)	0.4
Boiling range, °F 95% Point	765
Sediment/water, %	0.02
Vanadium, ppm	0.5
Sulfur, %	1.3
Residuum contamination	pass

Vanadium in Distillate Fuels

High end points, while desirable from the standpoint of fuel cost, also open up the possibility of vanadium contamination [*2,3*]. Prior to the inception of MIL-F-24397, the heaviest distillate fuel used by the Navy for consumption in gas turbines, was MIL-F-16884 with an end point of 725°F. It is this increase in end point of approximately 100°F that has introduced the problems of vanadium contamination. While one would not expect distillation of vanadium bearing complexes, even at these temperatures the possibility of "carry-over" increases as we push our distillation temperatures higher and higher.

The effects of trace amounts of vanadium in gas turbine hot corrosion has been demonstrated, even if the mechanisms of corrosion have not been fully understood. While there is general agreement among engine manufacturers that vanadium levels at the 2 to 5 ppm level is deleterious [*4*], there is also evidence that the critical levels exist below 1 ppm. It is from this consideration and the evidence that has been developed concerning vanadium levels that can occur in heavy distillate fuels, that the maximum vanadium level allowable under MIL-F-24397 has been set at 0.5 ppm.

Prior to the establishment of a vanadium limitation, the oil industry was contacted and requested to submit to the Navy, potential ND fuels and blending stocks that might be supplied under a heavy distillate specification.

A total of 14 fuels and 19 blending stocks were received. These products were analyzed for vanadium content, Table 2 is a summary of the results. Of the 14 fuels, only one fuel exceeded 0.5 ppm and of the 19 blending stocks, 16 were below 0.5 ppm. On the basis of these results, the level of 0.5 ppm was considered a reasonably attainable level and, it was therefore included in the specification.

TABLE 2–*Vanadium content of 33 ND fuels and blending stocks.*

Potential ND Fuels	
Number	ppm vanadium
9	<0.1
4	0.1 to 0.5
1	0.6 to 1.0
Blending Stocks for ND Fuels	
Number	ppm vanadium
10	<0.1
6	0.1 to 0.5
1	1.1 to 1.5
1	1.6 to 2.0
1	2.1 to 2.5

With the information on vanadium content of heavy distillate fuels shown in Table 2, it became of interest to know what the vanadium content was of the heaviest distillate in the Navy supply system at the time. This fuel, MIL-F-16884, Diesel Fuel, Marine (DFM) has a maximum end point of 725°F. Through the Navy Fuel Supply Office, samples of DFM from the world-wide stock system were obtained for vanadium analysis. A total of 78 samples, representing separate tanks in 20 storage depots were analyzed. In all cases the vanadium level was below 0.1 ppm.

Need for Low Vanadium Procedure

The term "trace metals" in fuels is a nebulous one when we consider what was "trace" and analytically unattainable yesterday, is recognized as gross today and well within the realm of detection.

The necessity for analytical tools and procedures to effectively monitor vanadium at low levels is evident. As such, it becomes another step in the unending challenge that is presented to the analytical chemist. While there is no doubt that procedures will be developed, it is a fact that these levels present a challenge today, and they have projected us into a new dimension of fuels analysis.

At the onset of the Navy Distillate fuel program and in the development of the fuel specification, it was necessary, of course, to define the analytical procedures required for the determination of each particular fuel characteristic. The normal procedure is to specify the appropriate American Society for Testing and Materials (ASTM) procedure. With a requirement of a maximum of 0.5 ppm vanadium in the specification, appropriate analytical procedures were necessary. The only ASTM procedure available at the time was ASTM Test for Vanadium in Navy Special Fuel Oil (D 1548-63). ASTM Test for Lead in Gas Turbine Fuels (D 2787-72) and ASTM Test for Trace Metals in Gas Turbine Fuels (Atomic Absorption Method) (D 2788-72) subsequently have been added.

The approaches employing wet ashing procedures were rejected primarily due to the fact that they were unwieldy and time consuming. A rapid analytical procedure was of particular importance due to the fact that the Navy was conducting full scale gas turbine tests with a distillate fuel somewhat of the same nature as MIL-F-24397. While the fuel was a heavy distillate, its vanadium content was in the order of 0.05 ppm. Since experience at the 0.5 ppm was desirable, vanadium in the form of vanadium Naphthenate was proportioned into the fuel prior to combustion. It was therefore necessary to have a rapid analytical procedure to monitor the efficiency of the vanadium addition. The time involved in wet ashing procedures was totally unfeasible. Our own experience with atomic absorption, as well as the results of the round robin studies conducted by RDIII indicated that atomic absorption techniques did not offer much encouragement. The alternative chosen at this time was to explore the use of the X-ray spectrograph as a means of a rapid instrumental procedure.

Experiences with X-ray Determination of Vanadium

It quickly became evident that this procedure was not sensitive enough to detect vanadium levels below 10 ppm when analysing the fuel as received.

It was therefore decided to explore the technique of sample concentration in an attempt to utilize the X-ray spectrograph. It was theorized that the vanadium that was present in the fuel was from high molecular porphorins and, the result of inefficient distillation. It was likewise postulated that a carefully controlled laboratory distillation using either ASTM Test for Distillation of Petroleum Products (D 86-67) or ASTM Test for Distillation of Petroleum Products at Reduced Pressure (D 1160-61) would effectively concentrate the vanadium in the distillation "bottoms." These distillation procedures were employed to reduce fuel samples to 5 or 10 percent bottoms, thereby effecting a 10 to 20 percent concentration of the higher boiling components. Continuing on the basis that this procedure would also effect a similar concentration of the vanadium bearing compounds, these reduced fuel samples were analyzed for vanadium content by the X-ray spectrograph. The procedure used is detailed in Appendix A of MIL-F-24397.

Material balances run on initial samples, distillate fractions and bottom concentrates confirmed the efficacy of this approach. An alternate concentration procedure was subsequently developed whereby a weighed amount of fuel is deposited dropwise on either a graphite or aluminum flat disc electrode resting on a heated surface. As each drop is fumed off the high molecular weight compounds are deposited on the surface. This electrode is subsequently placed in the X-ray spectrograph for analysis of the residue. By this procedure, concentration of vanadium in fuel at the 0.05 ppm level can be measured.

The use of concentration steps such as I have described raise the question of the danger of loss of vanadium by volatilization. While this is a possibility, it has not been evident from the work we have done to date where we have worked extensively with the addition of known amounts of vanadium to fuel stocks. While volatilization losses have not been evident, at the levels of interest, that is, < 1 ppm, some loss would have been acceptable in the desire to obtain a procedure that offered rapid results. This is particularly true in the light of alternate procedures.

In an effort to determine the validity of using the distillation technique as a means of concentrating the vanadium to a detectable level, analysis of distillate bottoms were made to determine if the vanadium remaining in the bottoms fraction was in agreement with the initial level as determined by wet ashing procedures. Data shown in Table 3 was seen as substantiation of the "concentration" approach.

TABLE 3—*Vanadium concentration by distillation.*

Sample	ppmV	Procedure
A (as received)	1.7	wet ash
A (concentrated to 5% by distillation)	31.5[a]	X-ray
B (as received)	2.4	wet ash
B (concentrated to 15% by distillation)	14.0[b]	X-ray

[a] Equivalent to 1.6 prior to distillation.
[b] Equivalent to 2.3 prior to distillation.

An interesting situation occurred where an engine manufacturer was conducting a program to qualify a gas turbine on the Navy Distillate fuel. In this case, the fuel supplier used a metallo-organic additive to raise the vanadium level to the 0.5 ppm level prior to delivery. While the refiner controlled the additive treatment, the treatment was also monitored by the use of an atomic absorption procedure. Samples of the fuel were taken periodically throughout the test and sent to our laboratory for analysis by the X-ray procedure. Table 4 is a summary of these analyses. While direct side by side comparison with the atomic absorption results was not possible, it does illustrate the utility of the X-ray procedure for monitoring operations.

TABLE 4–*Vanadium content of fuel during gas turbine test program.*

Fuel adjusted to 0.5 ppm vanadium (as determined by atomic absorption analysis). X-ray analysis of fuel at approximately every 200 h of engine operation.
0.31
0.25
0.38
0.38
0.38
0.43
0.43
0.43
0.47
0.45
0.47
0.47

Another utilization of the X-ray procedure occurred during an extended test stand run on a marinized aircraft gas turbine at the Naval Ship Engineering Center in Philadelphia. One of the aims of the program was to study the corrosive effects of vanadium on the turbine blades. Since the vanadium level of our test fuel was 0.05 ppm, it was necessary to provide an additive to bring the level up to 0.5 ppm, the level of interest for the test. This was accomplished by mixing vanadium naphthenate batchwise with test fuel in a stock solution to a level of 320 ppm and, by means of a proportioning pump set at a ratio of 1 to 640, the desired level of 0.5 ppm was attained. X-ray analysis of each "concentrate" batch was run to assure that the vanadium level which had been achieved by the addition of a 6 percent solution of vanadium naphthenate was maintained at the 320 ppm level.

Table 5 is a summary of the batch analyses taken throughout the program and while it is evident that this was not a "trace" analysis, it again demonstrates the utility of the X-ray procedure. In addition to the monitoring of the "concentrate" solutions, analyses were also made of the fuel going to the engine at the nominal 0.5 ppm level. Table 6 is a summary of these analyses. These samples were concentrated by the hot electrode deposition technique.

TABLE 5–*Vanadium content of stock solutions for gas turbine test.*

	Stock solution made to 320 ppm vanadium by addition of 6 percent van-naphthenate.	
Batch 1	322 ppm vanadium	(X-ray)
Batch 2	316 ppm vanadium	(X-ray)
Batch 3	307 ppm vanadium	(X-ray)
Batch 4	310 ppm vanadium	(X-ray)
Batch 5	342 ppm vanadium	(X-ray)
Batch 6	298 ppm vanadium	(X-ray)
Batch 7	325 ppm vanadium	(X-ray)

TABLE 6–*Vanadium content of fuel to gas turbine engine.*

Sample	ppm vanadium (X-Ray)	Sample	ppm vanadium (X-Ray)
1	0.45	16	0.40
2	0.60	17	0.40
3	0.55	18	0.40
4	0.50	19	0.50
5	0.45	20	0.55
6	0.65	21	0.55
7	0.55	22	0.50
8	0.40	23	0.50
9	0.45	24	0.40
10	0.50	25	0.40
11	0.65	26	0.50
12	0.50	27	0.50
13	0.45	28	0.45
14	0.50	29	0.40
15	0.40		

Table 7 presents a summary of comparison data accumulated during the Navy Distillate conversion program on various fuel stocks supplied. No specific attempt was made to carry out a designed program, therefore, these results represent comparison of the X-ray method with both wet ashing and spectrographic techniques.

TABLE 7–*Vanadium analysis (comparisons).*

	ppm vanadium	
	Supplier	NAVSEC
Refiner A		
High pour point diesel	<0.5	<0.1
Marine diesel (Caribbean)	<0.1	<0.1
Marine diesel (domestic)	<0.1	<0.1
Refiner B		
ND reference fuel (Caribbean)	0.2	0.1
ND blending stock (Caribbean)	0.02	<0.1
ND blending stock (Caribbean)	2.2	2.1
ND blending stock (Caribbean)	0.02	0.1
ND blending stock (Caribbean)	0.02	0.1
Refiner C		
ND reference fuel (Caribbean)	0.07	0.05

Summary

This has been a summary of experiences by the Naval Ship Engineering Center in facing the problems of vanadium determination in heavy distillate fuels. The techniques employed have been invaluable, without them we would not have been in a position to monitor our gas turbine testing programs. A gas turbine can consume large volumes of fuel very rapidly, therefore, in the interest of economy it was mandatory that necessary analytical information be made available as quickly as possible to optimize operational test conditions.

The competitiveness of the gas turbine with other propulsion systems is vitally linked to the use of low cost fuels. The development of engine components that are resistant to corrosion and deterioration is a continuing process and is inexorably linked to those fuel components that are deleterious to the system. It is therefore necessary for the maximization of these factors that we are in a position to detect and quantify those fuel components that affect the engine system.

While there are not as yet any alternatives within ASTM for a rapid sensitive procedure at the levels of interest in gas turbine fuels, it is known that within industry, individual laboratories [5] are using various methods for the analysis of low levels of vanadium. For example, an activation analysis procedure, using a californium-252 neutron source, has been developed as an on-stream procedure. In addition, new techniques have been recently developed in the atomic absorption field using unique methods of sample excitation. These new approaches offer an order of magnitude improvement in detection sensitivities of many trace metals and a significant improvement in vanadium detection. The use of the carbon rod and the tantalum strip would appear to be the most imminent weapons available to the analyst for rapid detection of today's "trace metals." It is almost axiomatic that the analytical challenge will continue as we endeavor to maximize the performance of our systems.

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