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A SURVEY OF THE CHEMISTRY OF HIGH-VANADIUM OIL-ASH DEPOSITS IN NAVAL BOILERS

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ABSTRACT

High-vanadium oil-ash deposits taken from the boilers of destroyers and carriers have been examined and a survey made of the chemistry of their components. Three compounds of vanadium were identified: $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, which appeared in every high-temperature deposit examined, and $Na_2O \cdot 2V_2O_5$ and $NaVO_3$, both of which were found only on screen tubes of two 1200-pound boilers having deposits especially high in sodium sulfate. Other compounds present in detectable quantities were Na_2SO_4, $CaSO_4$, Fe_3O_4, $CaCO_3$, $Fe_2(SO_4)_3$, H_2SO_4, α-SiO_2, and elemental carbon. All deposits consisted of one or more of these compounds, but in various proportions.

The chemistry and physical properties of compounds in the system Na_2O-V_2O_5 were compiled after a literature search which was augmented by an appropriate laboratory investigation. Compilations were made of sources of information on systems containing vanadium oxides and the oxides of other elements, useful for the identification of the crystalline components of oil-ash deposits.

Three analytical methods for the determination of high concentrations of vanadium in oxide mixtures are described, as well as an x-ray diffraction method for estimating the relative quantities of crystalline $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ and $Na_2O \cdot 2V_2O_5$ in the presence of one another.

Some areas of research of probable immediate value toward solving the oil-ash deposition and corrosion problems are phase studies, sintering studies, and development of chemical cleaning processes.

PROBLEM STATUS

This is an interim report. Work on this problem is continuing.

AUTHORIZATION

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A SURVEY OF THE CHEMISTRY OF HIGH-VANADIUM OIL-ASH DEPOSITS IN NAVAL BOILERS

PART 1 - PROPERTIES OF VANADIUM OIL-ASH DEPOSITS AND THEIR OXIDE COMPONENTS

INTRODUCTION

The deposition of noncombustible matter on the heat-exchange surfaces of naval boilers is a serious problem. Not only are the deposits objectionable due to their relatively poor heat-transfer properties, but they may be extremely corrosive in locations where temperatures are above the melting point of the ash. Removal of deposits, once formed, may be all but impossible by ships' personnel, and complete retubing in repair yards is occasionally preferred to manual cleaning methods, because the ultimate cost and effort may be less.

The present work was intended to be a critical examination of the problem. It consisted of a thorough search of the scientific and engineering literature; visits to ships known to have had oil-ash problems, and to similar ships which did not; the collection of specimens firsthand; the analysis of specimens and identification of components by chemical and physical methods; discussions of the problem with shipyard maintenance workers, type commanders, ships' personnel, and shipyard laboratory personnel; and laboratory examination of chemical reactions in systems thought to represent those met in the boilers proper.

THE PHYSICAL NATURE OF OIL-ASH DEPOSITS

A portion of the incombustible matter originating in the fuel which is atomized into the combustion zones of naval steam boilers accumulates on the upstream surfaces of tubes which cross the gas stream. After prolonged operation of boilers a thin coating of hard, high-vanadium ash of the order of 1/8-inch thick is quite common on the surfaces of superheater tubes, although accumulations are occasionally massive and may cause blockage of gas passages. By far the greatest proportion of solid matter in oil passes through the boilers and, fortunately, out through the stacks.

The heaviest accumulations of debris occur in the economizers and on the top surfaces of water drums, and both of these areas require special treatment for the removal of foreign material. That which adheres to economizer tubes is removed by means of soot blowers during the operation of the boilers, and the water-drum deposits are removed by chemical and physical methods during maintenance outages.

Physically, water-drum and economizer deposits are similar, being for the most part earthy masses of material, quite different from the typical high-temperature deposits of the superheaters and screen tubes, which are almost vitreous in nature. There is nearly always a vitreous layer of high-vanadium content, however, near the surfaces of the generating tubes over the water drums, but this is usually buried beneath large amounts of loosely bound and less homogeneous material.

THE MICROSCOPIC NATURE OF OIL-ASH DEPOSITS

Portions of oil-ash deposit which are soft and crumbly are composed of random particles of more or less pure compounds concentrated in clusters. The vitreous, nearly

Fig. 1 - Crystals of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ making up black vitreous layer of oil ash. Reflected polarized light 75X.

black layers of material which are notoriously difficult to remove are composed of large, intermeshed crystals of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, which act as a ceramic bond for the hard layers. Other crystalline materials present in the hard layers can be observed as small particles enmeshed in a matrix of long needles of the vanadium compound (Fig. 1). In spite of the extreme hardness of these layers, the structure is not dense, and water-soluble fractions can be extracted from the interior regions of the deposits without noticeably affecting the hardness or disturbing the ceramic bonding of the layers.

From the fact that the longest, most perfectly developed crystals are consistently located in an intermediate position between the innermost layers of the deposit and the outermost surface it was concluded that these crystals are secondary in nature, not being due to crystallization of a melted mass, nor to the accumulation of material already crystallized. Many fernlike growths of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ can be observed with their points of origin toward the hot side, and radiating inward toward the cooler tube surfaces. Some of these can be traced over a distance of at least 1/4 of an inch, a fact which favors the conclusion that extensive crystal growth may have occurred after the deposits had accumulated.

THE CHEMICAL NATURE OF OIL-ASH DEPOSITS

The chemical compounds isolated and identified in this investigation were as follows: β-sodium-vandium oxide [$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ (approximately)], γ-sodium-vanadium oxide ($Na_2O \cdot 2V_2O_5$), sodium sulfate (Na_2SO_4), calcium sulfate ($CaSO_4$), magnetite (Fe_3O_4), calcium carbonate ($CaCO_3$), ferric sulfate [$Fe_2(SO_4)_3$], elemental carbon, sulfuric acid (H_2SO_4), and α-cristobalite (α-SiO_2). All deposits consisted of one or more of these compounds, but in various proportions.

There were, in addition to these identified compounds, traces of zinc, considerable quantities of nickel (as much as 1.45% in high-vanadium ash), and traces of manganese and titanium, all of which were detected but not isolated as solid compounds.

The probable sources of these compounds are as follows: vanadium compounds, from fuel oil; sodium compounds, from fuel oil or from ballast sea water via the burners, or from salt spray arriving with combustion air; calcium compounds, from fuel oil, where they may be present as calcium carbonate or sulfate, or from sea water (in flue gas at high temperatures calcium carbonate becomes calcium sulfate); iron compounds, mostly from corrosion of structural components, but small amounts are present in fuel oil; sulfur compounds, from fuel oil; silicon dioxide, from fuel oil, where it is in suspension, sea water, or from the atmosphere during operation in proximity to shore; and nickel and manganese compounds, from fuel oil and corrosion products of high alloy steel.

It should be noted that chromium was not detected, even in minute traces. This element is to be expected in the corrosion products of stainless steels used in naval boilers.

The chemistry of all the compounds listed, other than that of sodium-vanadium oxides, is covered in most elementary chemistry texts. No mention of sodium-vanadium oxides of the sort encountered in oil ash was found in any standard reference book, however, and great effort was expended in order to locate details concerning the sodium-vanadium oxide system in the chemical literature. For this reason the system is discussed separately below.

THE DISTRIBUTION OF CHEMICAL COMPOUNDS WITHIN BOILERS

The chemical and physical environments to which oil ash is exposed within boilers vary over wide ranges, and the compounds observed in slag samples taken from superheater tubes differ considerably from those which are found in cooler regions of boilers. There are many consistencies, however, as to the compounds which are found in equivalent locations of different boilers.

Compounds on Screen Tubes and Superheater Tubes

The carbonaceous, black deposits of the interior of furnaces are for the most part amorphous carbon, although there is often graphitization, which can be detected by x-ray diffraction methods. This material is actually unburned oil, and presumably accumulates when the burners are cut out.

Chalky white, water-soluble material coating the screen tubes, and which is sometimes hidden by carbon, is usually either sodium sulfate, or a mixture of sodium sulfate with sodium vanadate. (Material containing sodium vanadate gives an alkaline solution with water, while sodium sulfate is neutral.)

Purple-black layers on screen tubes and superheater tubes are invariably composed of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, sometimes mixed with small amounts of $Na_2O \cdot 2V_2O_5$ or sodium

sulfate. These layers are the most difficult to remove by present cleaning methods if they are tightly bonded to the metallic surfaces because they are not appreciably soluble in water and dilute acids. This is also the material which, when molten, is an excellent solvent for most materials of construction of boilers.

Compounds on Generating Tubes, Economizer Tubes, and the Top Surfaces of Water Drums

Generating-tube deposits are similar to superheater deposits in chemical composition, but show fewer signs of high-temperature effects. There are seldom indications of complete melting and flow. Compounds usually found are sodium sulfate, $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, and sometimes small amounts of $Na_2O \cdot 2V_2O_5$. Next to tube surfaces there is usually a small amount of white ferrous sulfate, which turns yellow (ferric sulfate) on being exposed to the air. Such deposits give an acid reaction on being treated with water.

The troublesome massive deposits which have been observed on the top surfaces of water drums are almost identical to those which accumulate on the fins of economizer tubes. The earthy material which yields to water washing is usually high in sodium and iron sulfates, while the purple-black layers in close proximity to tubes where they enter the drum and the powdery residue from water washing are almost entirely identical with the shell-like layers taken from superheater and screen tubes, i.e., they are mostly $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$.

Compounds in Uptakes, Breeching, and Stacks

In general, it can be stated that dustlike material deposits in gas passages beyond the boilers, and that liquid sulfuric acid accumulates when the temperature of the gas stream falls below a certain minimum value which is dependent on the firing procedures. The dustlike material is usually noncrystalline, and aside from a high percentage of adsorbed sulfuric acid, is essentially composed of unburned carbon.

The sulfuric acid may contain sufficient sulfate to qualify as "fuming sulfuric acid" while the boilers are operating, but this rapidly changes to the highly corrosive dilute sulfuric acid on long standing, or under the influence of a blast of moist air from the blowers when the boilers are down. Invariably, the corrosion products from ductwork can be found as water-soluble sulfates and water-insoluble spinels on the surfaces of corroded metal.

Miscellaneous Compounds Occurring in Minor Percentages

The following compounds have been found distributed at random in trace amounts in naval boiler deposits: silica (α-cristobalite); magnetite (Fe_3O_4), presumably a high temperature corrosion product; and calcium sulfate ($CaSO_4$). Calcium carbonate has been found in water-drum and economizer deposits in trace amounts.

THE CHEMISTRY OF VANADIUM COMPOUNDS IN OIL-ASH DEPOSITS

General Considerations

Choice of a single phase diagram which truly represents the state of vanadium under boiler-operating conditions is difficult because of the complexity of the environment in which the oil ash is found. Three compounds of vanadium have been isolated and identified

in this laboratory, the compound $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ appearing in every boiler examined, and $Na_2O \cdot 2V_2O_5$ and $NaVO_3$ appearing on screen tubes of two 1200-pound boilers having deposits especially high in sodium sulfate. It is concluded, therefore, that the system Na_2O-V_2O_5 should include most of the compounds of vanadium appearing in oil ash of the types studied to date, and since it had been found that sodium sulfate loses sulfur and oxygen on being heated with vanadium pentoxide, the ternary oxide diagram, Na_2O-V_2O_5-SO_3, would explain most of the thermal behavior of oil-ash compounds. Use of the ternary oxide diagram would be complicated, however, by the fact that some of the pentavalent vanadium is reduced to tetravalent vanadium merely by being heated with an appropriate quantity of sodium oxide, and by the fact that sulfur trioxide dissociates into sulfur dioxide and oxygen in the presence of certain catalysts, especially the vanadium oxides containing sodium. For practical purposes, therefore, the phase diagrams of the systems V_2O_5-$NaVO_3$ and V_2O_5-Na_2SO_4 as given by Illarionov (1) are being used at this time for the interpretation of effects observed during the study of oil-ash deposits (Figs. 2 and 3). Neither is claimed to be an equilibrium diagram, but each is based on experimental data obtained by heating mixtures of pure starting materials in the presence of air.

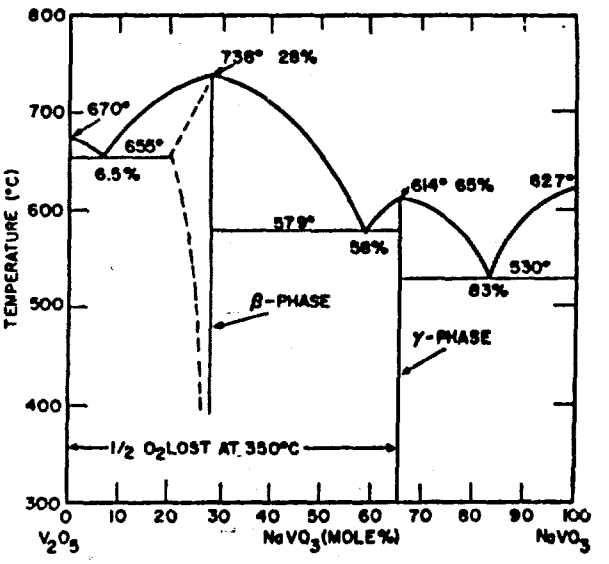

Fig. 2 - Phase diagram for the system $NaVO_3$-V_2O_5 (1)

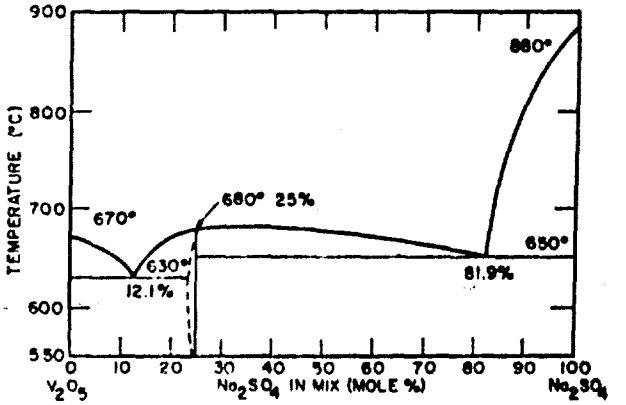

Fig. 3 - Phase diagram for the system Na_2SO_4-V_2O_5 (Obtained from heating curves. Systems not at equilibrium.) (1)

High-Temperature Properties of Systems Containing Sodium and Vanadium Oxides

Melting and Sintering Characteristics – When a mixture containing sodium vanadate and vanadium pentoxide is heated, a reaction in the solid state occurs at 265°C (509°F) and a compound containing 65 mole percent $NaVO_3$ forms. To this compound may be given the formula $Na_2O{\cdot}2V_2O_5$* (See Fig. 2).

If the temperature is raised further to 350°C (662°F) a second reaction occurs in the solid state. The $Na_2O{\cdot}2V_2O_5$ which first formed reacts with any excess of V_2O_5 to form a new compound, $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$. The second reaction is accompanied by a loss of oxygen.

The melting points of compounds in this system are: V_2O_5, 670°C (1238°F); $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, 738°C (1360°F); $Na_2O{\cdot}2V_2O_5$, 614°C (1137°F); and $NaVO_3$, 627°C (1160°F).

The melting points of eutectics in this system, which are the temperatures at which initial melting begins in the presence of two compounds, are as follows: between V_2O_5 and $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, 655°C (1212°F); between $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ and $Na_2O{\cdot}2V_2O_5$, 579°C (1074°F); and between $Na_2O{\cdot}2V_2O_5$ and $NaVO_3$, 530°C (986°F).

Melting and Sintering Characteristics in the Presence of Sulfates – The system Na_2SO_4-V_2O_5 (Fig. 3) differs from the system $NaVO_3$-V_2O_5 in that transition points and eutectic points are displaced. Phases equivalent to $Na_2O{\cdot}2V_2O_5$ and $NaVO_3$ do not appear in this system. The phase $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, which also appeared in systems without sulfate, crystallizes with small amounts of sulfate in a form which shows only slight changes in lattice parameter from the sulfate-free crystals, these changes being detectable only by precision x-ray methods.

In this system the compound $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ (with sulfate) melts at about 680°C (1256°F), the mixture not being at equilibrium. The eutectic temperatures are as follows: between V_2O_5 and $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, 630°C (1166°F), and between $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ and Na_2SO_4, 650°C (1202°F).

When a mix containing Na_2SO_4 and V_2O_5 is heated, a solid state reaction begins at 526°C (978°F) with the loss of SO_3 and oxygen and the formation of $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ (with sulfate).

To summarize the differences between the behavior of mixtures which contained, initially, $NaVO_3$, as opposed to Na_2SO_4, the presence of sulfate tends to raise the temperature at which the solid state reaction to form $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ occurs, while lowering the temperature at which initial melting occurs. The final melting occurs at a lower temperature in the presence of sulfate.

Electrical Properties of Systems Containing Sodium and Vanadium Oxides – The paper of Flood and Sorum (3) announced the discovery of a new type of electrical semiconductor, namely the "β-phase" in the system sodium-vanadium oxide. It had been found in this laboratory that fused mixtures of sodium-vanadium salts are good conductors, but from the work of Flood and Sorum it is apparent that the solid compounds are conductors, also. The maximum conductivity at room temperature is of the order of ten percent of that of graphite, or is nearly equivalent to that of iron oxide (Fe_3O_4). (See Table 1.)

*The formula given by Foster et al. (2) is $Na_2O{\cdot}3V_2O_5$, but this is based on x-ray data alone, as opposed to the formula $Na_2O{\cdot}2V_2O_5$ of Illarionov (1) which is based on thermal data.

Table 1
Table of Electrical Conductivities

Material	Conductivity (ohm^{-1} cm^{-1})
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	60
Tungsten Bronze	10
Vanadium Pentoxide	10^{-3}
Magnetite (Fe_3O_4)	100
Lead Sulfide	10 - 100
Graphite	800

The maximum conductivity in the system sodium vanadate-vanadium pentoxide occurs in the mixture which is lowest in oxygen content, which also coincides with the composition of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ (see Fig. 4). Flood and Sorum compared this compound with tungsten bronze, and suggested that it is a semiconductor for the same reasons that magnetite and tungsten bronze are semiconductors. (Details in the crystal structure of the so-called "vanadium bronzes" are reported by Wadsley (4).)

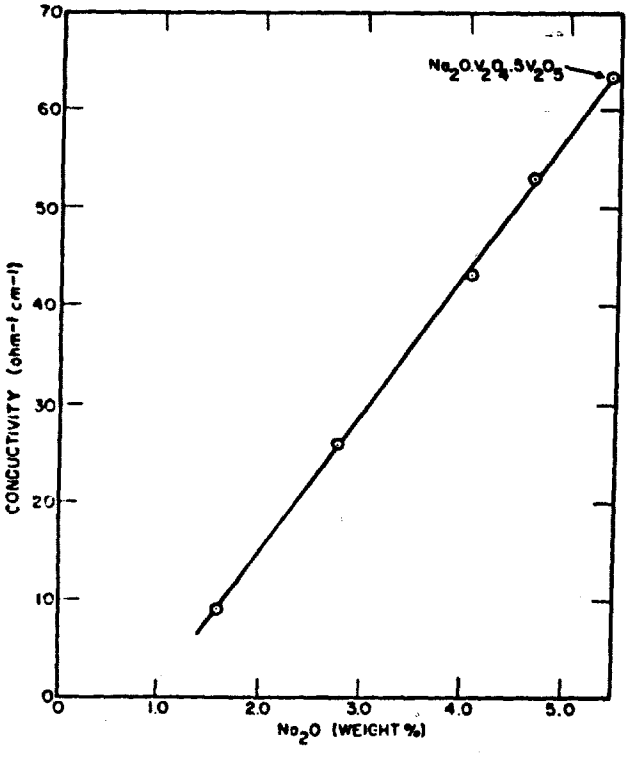

Fig. 4 - Electrical conductivity as a function of sodium content in the system Na_2O-V_2O_5 (3)

The Evolution of Gases on Heating of Solids and Cooling of Melts – The formation of the $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ in the system sodium vanadate-vanadium pentoxide is accompanied by the evolution of oxygen. According to the work of Flood and Sorum (3) the composition at which the greatest volume is evolved coincides with that of the stoichiometric compound $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, which was described above as having the greatest conductivity and the highest melting point in the system $NaVO_3$-V_2O_5. A graph of oxygen evolution compared with composition of the mix is shown in Fig. 5. The data have been verified by Illarionov (1) and have been shown by both Flood and Illarionov to be related to the oxidation state of the vanadium remaining behind in the solid.

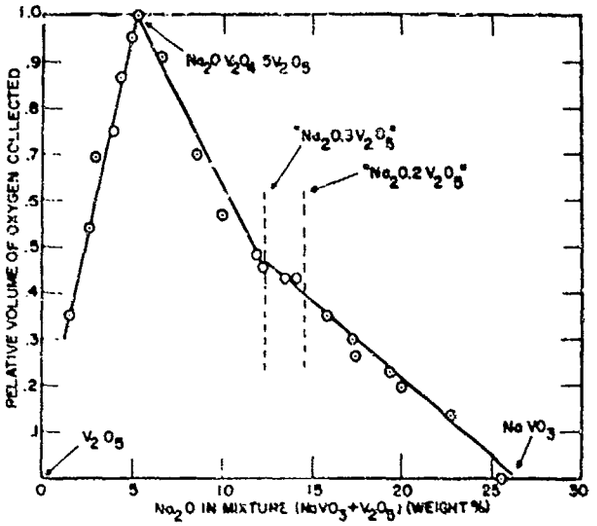

Fig. 5 - Oxygen evolution as a function of sodium content of melts containing sodium and vanadium oxides (3)

Gases are evolved the first time mixtures of vanadium pentoxide and sodium salts of volatile acids are heated to the melting point. On cooling, additional gases are evolved. This phenomenon was studied in detail in 1908 by Prandtl (5). One of his conclusions was that the spitting must be due to the evolution of oxygen, since a portion of the vanadium in the solids had been reduced to the tetravalent state.

A very brief laboratory investigation on systems containing vanadium pentoxide, initially, and salts of sodium containing anions which are volatile at elevated temperatures indicated that the compound $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ results when the proper proportions of the following sodium-containing compounds are heated with vanadium pentoxide: sodium peroxide (Na_2O_2); sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium bromide (NaBr), and sodium vanadate ($NaVO_3$). The gas which was missing from the final solids was evolved during reactions in the solid state and immediately after resolidification, at which time the solid material remelted with effervescence, and then recrystallized. A qualitative test of the gases showed the presence of oxygen from sodium peroxide; carbon dioxide from sodium carbonate; sulfur dioxide, sulfur trioxide, and oxygen from sodium sulfate; and the gases chlorine and bromine from the corresponding chloride and bromide reactions. No gas was evolved on solidification after the melting of pure $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ under vacuum

High-Temperature Properties of Systems Containing Oxides of Other Elements In Addition to Sodium and Vanadium Oxides

From the standpoint of usefulness in the prediction of the chemical effects of additives a knowledge of compounds formed between the vanadium compounds found in oil ash and the oxides of potential additives would be extremely valuable. The literature search revealed that very little work has been done in this area, in spite of the vast number of patents issued and the papers written on the subject of additives.

Systems Containing Vanadium Oxides and Other Metal Oxides

Data concerning the systems containing vanadium oxides and other metal oxides are scattered throughout the literature. An attempt has been made to compile sources of information in Appendix A.

In general, it may be stated that pentavalent vanadium oxide behaves as an acid in its properties (relative to silica) and that the more basic the oxide with which it is reacting, the greater is the tendency toward compound formation. There is little or no reaction between silica and vanadium pentoxide, nor between boron trioxide and vanadium pentoxide.

Trivalent vanadium forms spinels with the same oxides as iron oxide or aluminum oxide. [Most of the reactions of tetravalent vanadium listed in Appendix A were taken from a single paper (6) which gives data in direct conflict with other papers on the same subject.] In all cases reported, the melting points of reduced oxides containing vanadium are considerably higher than those in which the vanadium is in the pentavalent state.

Room Temperature Reactions of Compounds Formed at High Temperatures

Although vanadium pentoxide and sodium vanadate have appreciable solubility in water at room temperature, the two compounds which can be formed from mixtures of the two, that is $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ and $Na_2O \cdot 2V_2O_5$, are only slightly soluble in water. These compounds are quite soluble in hot, concentrated hydrochloric acid, forming first a deep red solution which turns green on standing. The final state of the vanadium is the +4 oxidation level, which accounts for the green coloration.

Organic reducing acids, such as citric and tartaric acids, dissolve sodium-vanadium oxides very slowly, giving deep blue solutions. Oxidizing agents such as permanganate, dichromate, and persulfate have little effect, either in acid or alkaline solutions.

The relatively weakly oxidizing hydrogen peroxide gives a violent reaction which goes to completion rapidly if the temperature is allowed to rise spontaneously, and results in a deep red solution. This reaction is one of the qualitative tests for vanadium. The coloration is said to be due to the formation of a peroxy compound with pentavalent vanadium. Once formed, this peroxy compound catalyzes the rapid decomposition of any unreacted hydrogen peroxide.

AREAS IN WHICH FURTHER BASIC RESEARCH WOULD BE OF IMMEDIATE VALUE

As a result of this survey of the chemistry of fireside deposits in naval boilers it is apparent that there is a complete lack of factual information in certain fields of chemistry which have either been uninvestigated or unreported. For other subjects much of the data is incomplete, faulty, or merely represents speculation, not necessarily based on

experimental observation. Some of the subjects in which factual information would have immediate utility are discussed below.

There is a need for the determination of phase relationships in systems containing sodium and vanadium oxides in combination with other oxides. There has been some work with systems containing vanadium pentoxide and additional oxides, this work supposedly being applicable to the chemistry of boiler additives, but the fact remains that vanadium pentoxide was not one of the components of the deposits taken from naval boilers. Data from phase diagrams prepared by melting mixtures of additional oxides with the two vanadium compounds which are actually present in most boiler deposits, that is $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ and $Na_2O \cdot 2V_2O_5$, would be useful for predicting the physical and chemical effects of the use of appropriate additives.

The observation was made during this investigation that very hard layers containing large crystals of the mixed sodium-vanadium oxides mentioned above showed no indications that these crystals had grown during the cooling of a melt. There were definite signs of ceramic bonding, however, and there are reasons to believe that crystal growth had occurred in the solid state. It is concluded, therefore, that a detailed study of the sintering characteristics of compounds found in oil ash using the methods of the ceramists would be extremely useful for determining the conditions necessary for the formation of boiler deposits of this type.

It is self-evident that research toward the development of cleaning processes using the room temperature reactions of vanadium compounds with solutions of appropriate chemicals would be aided by accurate knowledge of the actual chemical reactions involved.

These three types of research, that is, phase studies, sintering studies, and solution-chemistry studies, are not the only areas which would have immediate utility in the search for an ultimate solution to the boiler-deposit problems. There is a definite possibility that modifications of existing equipment and changes in present operating procedures could do much to alleviate the problems, but these subjects are outside the scope of this report.

PART 2 - SPECIAL LABORATORY METHODS USED IN THESE INVESTIGATIONS

STANDARD X-RAY PATTERNS OF COMPOUNDS DETECTED IN HIGH-VANADIUM OIL ASH AND THEIR SIGNIFICANCES

The following x-ray powder diffraction patterns were used for the identification of the crystalline components present in specimens of oil ash taken from naval boilers. The problem of identification was not always straightforward, however, because of the great difficulty encountered in finding standard patterns sufficiently reliable to be used for positive identification of vanadium oxides. There was the added problem, also, of identifying complex mixtures of materials.

In many instances it was possible to isolate crystalline materials by means of physical and chemical methods, but without changing the crystalline structures. When chemical means were used for separations, care was taken to check the x-ray pattern of the original sample for the presence of major lines of the compounds identified in concentrated fractions.

It was possible by heating fragments of deposit in concentrated hydrochloric acid to isolate the acid-insoluble silicon dioxide known as α-cristobalite, since such silicon compounds are not rapidly attacked by strong acids. Likewise it was possible to concentrate the vanadium-containing fractions of a few deposits by means of a simple water extraction, since of the three vanadium compounds encountered, only sodium metavanadate ($NaVO_3$) is water soluble. Although the material going into solution could be identified by recrystallization from the water, and this was done routinely, such a recrystallization did not give an indication of the nature of the soluble compounds before the water extraction. It was found, however, that the water-soluble fractions were also lighter than bromoform, a liquid with a density of 2.89, and that a physical separation could be accomplished in many cases by centrifuging the pulverized samples suspended in the heavy liquid.

Vanadium Compounds (Table 2)

The compound vanadium pentoxide V_2O_5 was not identified as a component of oil ash sampled during this investigation. Since the "X-Ray Powder Data File" published by the American Society for Testing Materials does not include data for the three vanadium compounds detected, and since the data of the literature were inconsistent, and in some cases definitely in error, the compounds were prepared from analytical reagents, weighed in the proper stoichiometric proportions, and crystallized from melts by slow cooling. In this manner $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, $Na_2O{\cdot}2V_2O_5$, and anhydrous $NaVO_3$ were prepared in a crystalline form.

The compound being designated as $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ is equivalent to the compound of the same formula reported by Prandtl (5); the "NV_6" of Foster (2); the β-phase in the systems $NaVO_3$-V_2O_5 and Na_2SO_4-V_2O_5 described by Flood (3) and Illarionov (1); the "Compound X," thought to be $Na_2SO_4{\cdot}6V_2O_5$, of Cunningham (7); and solid solutions of the general formula $Na_{2-x}V_6O_{15}$ for which a detailed structural analysis has been prepared by Wadsley (4).

The compound designated as $Na_2O{\cdot}2V_2O_5$ is equivalent to the γ-phase of Flood (3) and Illarionov (1), found in the system Na_2O-V_2O_5; and is the "NV_3" of Foster (2). The

Table 2
X-ray Diffraction Data for Sodium Vanadium Oxides
of High Vanadium Content (Copper K_α Radiation)

$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$		$Na_2O \cdot 2V_2O_5$		$NaVO_3$*	
d(A)†	I/I_o‡	d(A)	I/I_o	d(A)	I/I_o
9.6	15	7.05	100	4.92	75
8.2	5	5.86	2	4.67	100
7.3	100	5.03	10	3.56	65
5.1	10	4.78	2	3.40	55
4.77	20	3.90	5	3.23	100
3.87	5	3.68	1	3.11	100
3.64	50	3.C4	2	2.64	45
3.49	35	3.52	10	2.43	25
3.40	5	3.45	2	2.27	25
3.22	5	3.28	5	2.23	20
3.17	5	3.23	2	2.16	75
3.076	95	3.16	10	1.95	50
3.015	5	3.12	5	1.85	25
2.928	20	3.025	30	1.79	50
2.728	2	2.806	1	1.74	55
2.53(wide)	1	2.688	1	1.64	20
2.378	5	2.439	2	1.57	25
2.268	1	2.331	10	1.50	40
2.182	40	2.276	20	1.45	40
1.928	1	1.974	2	1.40	55
1.916	2	1.959	2		
1.819	5	1.833	1		
1.809	5	1.809	1		
1.689	1	1.770	1		
1.674	5	1.726	1		
1.584	1	1.654	2		
1.543	1	1.510	5		
1.536	5				
1.493	2				

*G.W. Cunningham and A. deS. Brasunas, Corrosion 12:389t-4[illegible]t (1956).
†Lattice spacing in angstroms.
‡Line intensity relative to strongest line.

formula was chosen to indicate that two, rather than three moles of vanadium oxide are combined with one mole of sodium oxide because a melt of the oxides in the mole ratio of one to two gave an x-ray diagram with no spurious lines, while a melt in the ratio of one to three contained extra lines indicating the presence of the compound $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$.

The x-ray powder pattern of anhydrous sodium metavanadate, $NaVO_3$, as stated by Cunningham (7) includes three lines with an intensity of 1.00 (equivalent to a value of 100 under the system in use here). Although it is improbable that this is a true situation, the data are included here because it is very difficult to take this x-ray powder pattern without special procedures, due to the extreme hygroscopicity. This same difficulty was encountered by Sörum (8), who was unable to perform single-crystal structure analysis of the compound without having coated his crystals with collodion.

This instability of the anhydrous compound in contact with air would indicate that the detection of crystalline, anhydrous sodium metavanadate in oil ash is a virtual impossibility; consequently, in the work reported above, the presence of sodium metavanadate was considered to be verified if a water extraction of a melt gave an alkaline solution containing water-soluble vanadium in the pentavalent condition. No crystalline sodium metavanadate was detected, even in the form of the monohydrate.

Sodium Sulfate (Table 3)

Identification of crystalline forms of sodium sulfate is complicated by the fact that early investigators were not in agreement on nomenclature. The ASTM X-ray Powder Data File retains the designation suggested by Kracek and Ksanda (9) although it was necessary to refer to the original paper in order to learn the significance of that designation, which is as follows:

Sodium sulfate crystallizes from water at room temperature as the decahydrate, $Na_2SO_4{\cdot}10H_2O$, for which the ASTM index includes a card, Number 11-647, which gives values slightly lower than those given by Kracek and Ksanda.

The decahydrate loses its water of crystallization spontaneously on standing open to the air, and a new, anhydrous crystalline material known as "thenardite" forms. The data for this compound which are given on ASTM Index Card Number 5-0631 agree very closely with that for the same compound listed by Kracek and Ksanda.

When a specimen of thenardite prepared by drying the decahydrate is heated above 220°C (428°F) a phase change occurs. The new structure is stable to at least 700°C (1292°F). Although there is a spontaneous phase change at 220°C on cooling, the high temperature modification can be "stabilized" down to room temperature by traces of sodium carbonate. Sodium sulfate examined by x-ray techniques at temperatures between 220° and 700°C or after stabilization is called Na_2SO_4(I) and metathenardite (Card Number 1-0990), or α-Na_2SO_4(I) (Card Number 3-0280).

Specimens of sodium sulfate which have been heated to a high temperature in the absence of a stabilizing foreign salt, when cooled to room temperature give an x-ray pattern different from the original thenardite or from that of the stabilized high-temperature form, and this was called Na_2SO_4(III) by Kracek and Ksanda. The data on ASTM Card Number 8-31 is that of Fischmeister (10) who made a detailed structural investigation of this compound.

It has been reported that calcium sulfate ($CaSO_4$) stabilizes the high temperature form of sodium sulfate, also, and that when calcium sulfate and sodium sulfate are fused together complete solid solubility over a very wide range of compositions occurs, but the structure is essentially that of sodium sulfate (I)(11).

Table 3
X-ray Diffraction Data for Sodium Sulfate (Copper K_α Radiation)

Na_2SO_4 from Efflorescence of $Na_2SO_4 \cdot 10H_2O$ (Thenardite)		α-Na_2SO_4(I) Stabilized High-Temperature Form		Na_2SO_4(III) Modification from Heated and Cooled Thenardite	
ASTM Card 5-0631		ASTM Card 3-0280		ASTM Card 8-31	
d(A) *	I/I_o †	d(A)	I/I_o	d(A)	I/I_o
4.66	73	4.68	30	4.74	60
3.84	18	3.92	100	4.47	30
3.178	51	3.62	60	3.91	90
3.075	47	2.86	90	3.76	90
2.783	100	2.70	90	3.48	80
2.646	48	2.35	20	2.80	100
2.329	21	2.21	20	2.63	90
2.211	5	1.96	70	2.46	10
1.919	4	1.81	20	2.37	80
1.891	4	1.58	20	2.23	30
1.864	31	1.56	30	2.18	20
1.841	6	1.50	40	2.12	40
1.798	4	1.35	20	2.10	30
1.680	12			2.08	40
1.662	8			2.06	30
1.605	5			1.958	80
1.589	3			1.877	60
1.553	10			1.764	30
1.537	1			1.738	80
1.512	2			1.691	30
1.497	5			1.631	10
1.465	1			1.619	30
1.429	5			1.607	20
1.386	3			1.580	70
1.324	3			1.559	70

*Lattice spacing in angstroms.
†Line intensity relative to strongest line.

From these facts it is concluded that the presence of thenardite is virtually an impossibility in a boiler which has just been shut down, but if an ash which contains sodium sulfate is first wet and then dried, this form is a probability.

The presence of sodium sulfate crystallized in form I would indicate that the material has been to a high temperature while in the presence of a material such as calcium sulfate, which will stabilize this high-temperature form, and conversely, its presence in form III implies heating in the absence of the effects of calcium sulfate and other stabilizers.

Calcium Sulfate (Table 4)

Special effort was required to isolate sufficient calcium sulfate from boiler deposits for the identification of its crystalline state. The phase which was identified was "anhydrite,"

Table 4
X-ray Diffraction Data for Calcium Sulfate
(Copper K_α Radiation)

$CaSO_4$ (Anhydrite)		$CaSO_4 \cdot 2H_2O$ (Gypsum)	
ASTM Card 6-0226		ASTM Card 6-0046	
d(A)*	I/I_o†	d(A)	I/I_o
3.87	6	7.56	100
3.498	100	4.27	51
3.118	3	3.79	21
2.849	33	3.163	3
2.797	4	3.059	57
2.473	8	2.867	27
2.328	22	2.786	5
2.208	20	2.679	28
2.183	8	2.591	4
2.086	9	2.530	1
1.993	8	2.495	6
1.938	4	2.450	4
1.869	15	2.400	4
1.852	4	2.216	6
1.749	11	2.139	1
1.748	10	2.080	10
1.648	14	2.073	8
1.594	3	1.990	4
1.564	4	1.953	2
1.525	4	1.898	16

*Lattice spacing in angstroms.
†Line intensity relative to the strongest line.

the anhydrous variety of $CaSO_4$ which is normally insoluble in water, but which could be extracted from boiler deposits with water, presumably because of its very small particle size. Recrystallization of the water solutions gave gypsum ($CaSO_4 \cdot 2H_2O$) even in cases where crystalline calcium sulfate was not detected in the original ash.

Silica (Table 5)

Every specimen dissolved in concentrated hydrochloric acid left a small residue of silica in the crystalline form known as α-cristobalite, α-SiO_2. This material can be prepared artificially by heating quartz (sand) to a temperature of 1260°C (2300°F) in the absence of fluxes such as sodium sulfate, or calcium sulfate. (In the presence of fluxes, silica is detected at room temperatures as α-tridymite, which gives an entirely different x-ray diffraction pattern.)

Iron Compounds (Table 6)

Corrosion-product iron oxides are usually detected as magnetite (Fe_3O_4) or as hematite (α-Fe_2O_3). Although a second form of ferric oxide known as maghemite

Table 5
X-ray Diffraction Data for α-Cristobalite (α-SiO_2) (Copper K_α Radiation)

α-SiO_2	
ASTM Card 11-695	
d(A)*	I/I_o†
4.05	100
3.53	3
3.135	11
2.841	13
2.485	20
2.465	5
2.340	1
2.118	5
2.019	3
1.929	5
1.870	7
1.757	1
1.730	1
1.690	3
1.634	1
1.612	5
1.600	3
1.571	1
1.567	1
1.533	3

*Lattice spacing in angstroms.
†Line intensity relative to the strongest line.

(γ-Fe_2O_3) has been reported as a component of an oil-ash deposit (12), the presence of this modification is highly improbable because maghemite is converted quantitatively into hematite on being heated above 350 C (632° F). Precision x-ray methods are required to distinguish between magnetite and maghemite since both are spinels with x-ray powder patterns which differ only in minor details. It is assumed, therefore, that the iron spinel normally found in corrosion products associated with oil ash is magnetite.

Crystalline ferrous and ferric sulfates or their hydrates were not detected in this study, although the presence of these compounds was implied by the presence of water-soluble iron compounds giving a test for sulfate.

Carbon

Under ordinary conditions carbonaceous materials lose volatile gases on being heated with insufficient air for complete combustion, leaving a residue of amorphous carbon, which scatters x-rays without diffracting them. Specimens of "soot" taken from uptakes, however, gave an x-ray pattern having a single very broad peak with its boundaries at half height at about 23 and 28 degrees (copper radiation). The peak, therefore, occurred very nearly coincidental with the expected major diffraction line for graphite, and on this basis it is concluded that the carbonaceous material was somewhat graphitized.

Table 6
X-ray Diffraction Data for Iron Oxides
(Cobalt K_α Radiation)

Fe_3O_4 (Magnetite)*		α-Fe_2O_3 (Hematite)	
ASTM Card 11-614		ASTM Card 6-0502	
d(A)†	I/I_o‡	d(A)	I/I_o
4.85	40	3.68	70
2.966	70	2.69	100
2.530	100	2.51	80
2.419	10	2.20	70
2.096	70	2.07	10
1.712	60	1.837	70
1.614	85	1.691	80
1.483	85	1.634	10
1.327	20	1.596	40
1.279	30	1.484	70
		1.451	80
		1,348	20
		1.309	40
		1.255	30
		1.224	10

*The compound γ-Fe_2O_3 and many other spinels give almost identical patterns.
†Lattice spacing in angstroms.
‡Line intensity relative to the strongest line.

PROCEDURE FOR THE DIRECT GRAVIMETRIC ANALYSIS OF HIGH PERCENTAGES OF VANADIUM IN OIL ASH

The following gravimetric method of analysis for vanadium was devised in order to fill a need which has developed; that is, for the analysis of oil ash taken from naval boilers, in which the vanadium content, calculated as the pentoxide, may be of the order of 80 percent.

The basic idea for the precipitation was obtained from the work of Morette and Gaudefroy (13) who reported that vanadium (IV) hydroxide and sodium vanadate ($NaVO_3$) are precipitated quantitatively by sodium bicarbonate when the vanadium salts are in a solution containing 50-percent acetone. It was reasoned that if ammonium hydroxide were substituted in the precipitation, ammonium vanadate should be precipitated, and that this, on ignition could be converted into vanadium pentoxide and the vanadium weighed as such. Although any tetravalent vanadium precipitated would be oxidized to the higher oxidation state on ignition, it was felt that prior oxidation with hydrogen peroxide would be desirable because this would place any iron present in a condition suitable for separation before precipitation of the vanadium.

The method of analysis is as follows:

A 0.3-gram portion of the sample is reduced to a powder and dissolved in 50 ml of concentrated HCl while being heated nearly to boiling. After the solution has become a clear green color, 50 ml of water is added, and the residue (mostly silica) is filtered off.

To the cool filtrate is added 10 ml of concentrated (30 percent) hydrogen peroxide, and the mixture warmed gently until the violent effervescence subsides, and the solution has become deep red in color.

To this oxidized solution is added sufficient concentrated ammonium hydroxide to neutralize the acid, and then 5 milliliters more. At this point any rust-colored precipitate represents the R_2O_3 group along with a small amount of occluded vanadium hydroxide. (In the present work it has not been found necessary to recover this vanadium.) If a precipitate forms, the solution is filtered. The residue can be analyzed as R_2O_3 if desired.

To the cooled filtrate is added an equal volume of acetone. A white turbidity appears immediately, and after having stood for at least twenty minutes, this can be filtered off quantitatively. This residue, which is mostly ammonium vanadate, contains some ammonium chloride. It may be washed free of entrained liquid with as much as 100 ml of 85 percent acetone without rendering the vanadium soluble.

The filter paper containing the precipitated vanadium must be dried and ignited carefully in order to prevent the expulsion of vanadium oxides along with the ammonium salts, and to prevent too great a reduction of the vanadium oxides. The residue is ignited under oxidizing conditions in a weighed quartz-glass crucible at a temperature sufficiently high to melt vanadium pentoxide. This compound should be a clear, red liquid, containing no signs of solid particles at a red heat. On cooling, the vanadium is weighed directly as vanadium pentoxide.

ANALYSIS OF HIGH PERCENTAGES OF VANADIUM IN OIL ASH USING X-RAY FLUORESCENCE TECHNIQUES

Two x-ray methods were used for the rapid analysis of the vanadium content of oil ash in specimens containing very high percentages of vanadium. One is based on the assumption that the intensity of secondary x-rays emitted by a specimen is a function of the concentration of the particular element being assayed.

The other method is based on the fact that the secondary K_β radiation of chromium is absorbed by vanadium in the specimen, and that this absorption is proportional to the concentration of vanadium. This method of analysis was suggested by the fact that chromium had not been detected in any boiler deposit and by the fact that vanadium filters are chosen by x-ray diffractionists for the absorption of chromium K_β radiation.

The Estimation of Vanadium by the Measurement of Chromium K_β Absorption (Method 1)

A series of samples containing known quantities of sodium sulfate and vanadium pentoxide was prepared. Exactly 0.4300 gram of each of the mixes was mixed with exactly 0.0218 gram of chromium oxide under trichloroethylene and then dried.

Each of these prepared mixes was added to exactly 0.700 gram of methoxycellulose and mixed thoroughly (while dry). Pellets were pressed in a conventional metallographical specimen press using one-inch dies.

With the x-ray fluorescence unit operating at 40 kv and 10 ma, and with the scaler at a time constant of 2 seconds, a scan was made over the spectrum of secondary radiations at the rate of one degree per minute. A lithium fluoride crystal was used as a diffraction grating.

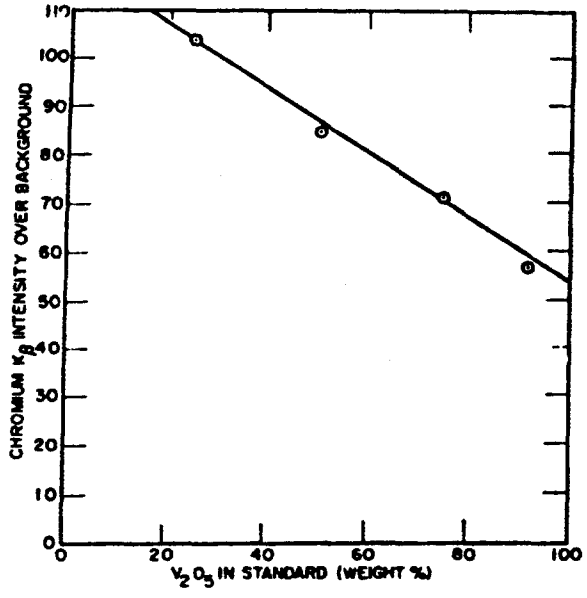

Fig. 6 - Typical calibration curve for estimating vanadium content of oil ash by absorption of chromium K_β radiation

The x-ray intensities of chromium K_β radiation from each of the standard samples, when plotted as a function of the known vanadium content, gave an empirical graph (Fig. 6) for the estimation of the vanadium content of unknowns which were prepared in the same manner.

The Direct Measurement of Vanadium Secondary Radiation as a Means of Estimating Vanadium Content of Oil Ash (Method 2)

A calibration curve for the estimation of vanadium in oil ash was prepared from samples containing known amounts of vanadium and sodium sulfate, made by mixing weighed portions of pure compounds under trichloroethylene, followed, after drying, by pelletizing in methoxycellulose. The proportions of mix used were 0.4309 gram of mixed oxides with 0.70 gram of methoxycellulose.

With the x-ray machine operating at 40 kv and 10 ma, and with the scaler at a time constant of 2 seconds, a scan was made over the secondary spectrum at the rate of two degrees per minute. A lithium fluoride crystal was used as a diffraction grating.

When the x-ray intensity of vanadium K_α radiation was plotted as a function of vanadium content, an empirical curve (Fig. 7) was obtained for the estimation of vanadium in unknowns prepared by the same procedure.

THE QUANTITATIVE ANALYSIS OF CRYSTALLINE $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$ and $Na_2O{\cdot}2V_2O_5$ IN THE PRESENCE OF ONE ANOTHER USING X-RAY POWDER DIFFRACTION METHODS

The absence of $Na_2O{\cdot}2V_2O_5$ from several oil-ash specimens which contained both $Na_2O{\cdot}V_2O_4{\cdot}5V_2O_5$, and Na_2SO_4 in substantial percentages, but which could be partially converted into this compound on being melted, pointed out the need for an estimation of the limits of detection of this vanadium compound in the presence of the other.

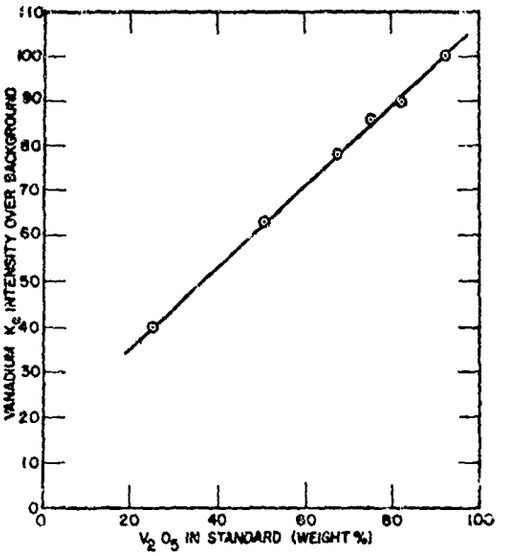

Fig. 7 - Typical calibration curve for estimating vanadium content of an oil ash by direct measurement of secondary vanadium radiation

The two compounds were prepared by fusion of appropriate amounts of $NaVO_3$ and V_2O_5 (with allowances for the fact that commercial reagent labelled "$NaVO_3$" was actually $NaVO_3 \cdot H_2O$). The crystalline material obtained on cooling the melts was reduced to pass through a 200-mesh sieve and then tested for homogeneity by x-ray powder-diffraction techniques.

Weighed portions of the two pure compounds were mulled together under trichloroethylene, followed by evaporation of this solvent. These standard mixes containing various levels of concentration of the two compounds were pressed into a glass powder-specimen holder, and a scan made of the powder pattern. Although the most intense diffraction lines have a tendency to overlap at very high percentage compositions, the calibration curve is empirical, and the accuracy of the analytical method is not affected by this interference.

The characteristic spacings which are compared in order to obtain a numerical value which is a function of the percentage composition of the specimens are the two most intense lines. That which was chosen to represent $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ has a value of about 7.3 A, while that chosen to represent $Na_2O \cdot 2V_2O_5$ has a value of about 7.0 A. Neither of these lines appears in the diagram of the other compound, contrary to the data of Foster (2), whose compound "$Na_2O \cdot 3V_2O_5$" actually is a mixture of the two.

Using copper K_α radiation from a Norelco tube operating at 35 kv and 18 ma, the x-ray pattern was traced at the rate of one-half degree a minute over the "2θ" region from 11 to 13 degrees, using a time constant of 4 seconds. The intensities over background were estimated in chart divisions, and a ratio taken of the intensity of the line due to $Na_2O \cdot 2V_2O_5$ vs that due to $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$. A plot of this ratio against the percentage composition with respect to one of the compounds gives a curve (Fig. 8) which may be used for estimating the relative amounts of the two compounds in a mixture.

The diffraction efficiency of the $Na_2O \cdot 2V_2O_5$ is so much greater than that of $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ that an x-ray pattern having major lines for the two compounds of equal intensity actually contains only 15 percent $Na_2O \cdot 2V_2O_5$. A mix containing 6.7 percent $Na_2O \cdot 2V_2O_5$ gave a major line intensity of 1/3 full scale, indicating that this compound is detectable in quantities of the order of one percent.

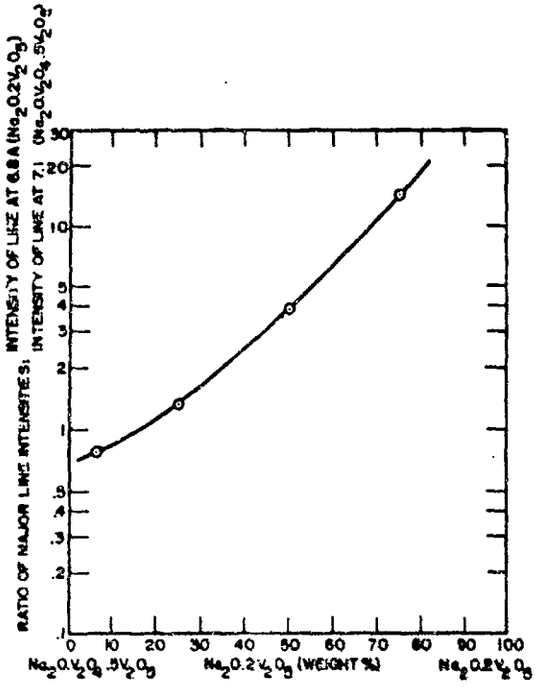

Fig. 8 - Calibration curve for the estimation of two oxides of sodium and vanadium by an x-ray powder diffraction method

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APPENDIX A

SOURCES OF DATA ON SYSTEMS CONTAINING VANADIUM OXIDES

Systems	Type of Investigations	Type of Data Given	Compounds	References
Aluminum				
Al_2O_3-V_2O_5	Additives	Phase diagram, X-ray	$AlVO_4$	A1
Al_2O_3-V_2O_5	Additives	Liquidus diagram via Seger cones		A2
Al_2O_3-V_2O_3	Phase Study	Phase diagram	$(Al,V)_2O_3$	A3
Al_2O_3-V_2O_5	Ceramics research	Petrographic	$2Al_2O_3 \cdot V_2O_5$	A4
Al_2O_3-V_2O_4	Ceramics research	Petrographic	$Al_2O_3 \cdot V_2O_4$	A4
Antimony	No pertinent references			
Arsenic	No pertinent references			
Barium				
BaO-V_2O_5	Chemical	Minimum temp for reaction		A5
BaO-V_2O_5	Ceramics research	Petrographic	Glass	A4
BaO-V_2O_5	Preparation of vanadates	Chemical	$3BaO \cdot 2V_2O_5$	A6
BaO-V_2O_4	Ceramics research	Petrographic	Compound (?)	A4
Beryllium				
BeO-V_2O_5	Additives	Liquidus diagram via Seger cones		A2
BeO-V_2O_5	Ceramics research	Petrographic	$BeO \cdot V_2O_5$	A4
BeO-V_2O_4	Ceramics research	Petrographic	$BeO + V_2O_4$ (?)	A4
Bismuth	No pertinent references			
Boron				
B_2O_3-Na_2CO_3-V_2O_5	Gas evolution	Chemical		A7
Cadmium	No pertinent references			
Calcium				
CaO-V_2O_5	Additives	Liquidus diagram via Seger cones		A2
CaO-V_2O_5	Phase study	Phase diagram	$CaO \cdot V_2O_5$ $2CaO \cdot V_2O_5$ $3CaO \cdot V_2O_5$	A8
CaO-V_2O_5	Chemical	Minimum temp for reaction		A5
CaO-V_2O_4	Iron-refining slags	Chemical	None exists	A9
CaO-V_2O_4	Ceramics research	Petrographic	Two compounds	A4
CaO-V_2O_5	Iron-refining slags	Chemical	$CaO \cdot V_2O_5$ $2CaO \cdot V_2O_5$	A9

Systems	Type of Investigations	Type of Data Given	Compounds	References
Cerium				
CeO_2-V_2O_5	Ceramics research	Petrographic	$CeO_2 \cdot V_2O_5$	A4
CeO_2-V_2O_5	Chemical	Minimum temp for reaction		A5
CeO_2-V_2O_4	Ceramics research	Petrographic	$2CeO_2 \cdot V_2O_4$	A4
Cesium				
Cs_2CO_3-V_2O_5	Gas evolution	Chemical		A7
Cs_2CO_3-V_2O_5	Preparation of vanadates	Chemical	$Cs_4V_2O_7$	A6
Cs_2SO_4-V_2O_5	Preparation of vanadates	Chemical	$Cs_2O \cdot 2\ V_2O_5$	A6
Cs_2SO_4-V_2O_5	Catalysis	X-ray	$Cs_2SO_4 \cdot V_2O_5$	A10
$CsVO_3$-CsCl	Phase study	Thermal	None	A11
Chromium				
Cr_2O_3-V_2O_5	Additives	Liquidus diagram via Seger cones		A2
Cr_2O_3-V_2O_5	Crystal study	X-ray data	$CrVO_4$	A12
Cr_2O_3-NiO-V_2O_5	Additives	Liquidus curve via Seger cones		A2
Cr_2O_3-V_2O_3	X-ray study	Phase diagram, X-ray	$(Cr,V)_2O_3$	A3
Cobalt				
Co_3O_4-V_2O_5	Additives	Liquidus diagram via Seger cones		A2
CoO-V_2O_3	Electrolytic preparation of spinels	X-ray	$CoO \cdot V_2O_3$	A13
Copper				
CuO-V_2O_5	Phase study	X-ray data	$CuO \cdot V_2O_5$ $2CuO \cdot V_2O_5$ $3CuO \cdot V_2O_5$ $4CuO \cdot V_2O_5$ $5CuO \cdot V_2O_5$	A14
CuO-V_2O_5	Additives	Liquidus curve via Seger cones		A2
CuO-V_2O_5	Chemical	Minimum temp for reaction		A5
Iron				
Fe_2O_3-V_2O_5	Phase study	Phase diagram and X-ray data	FeV_2O_6 FeV_2O_4	A15
Fe_2O_3-V_2O_5	Additives	Liquidus curve via Seger cones		A2

Systems	Type of Investigations	Type of Data Given	Compounds	References
Iron (cont'd.)				
$FeO-V_2O_3$	Preparation of vanadium spinels	X-ray data	$FeO\cdot V_2O_3$	A16
$FeO-V_2O_3$	Studies on vanadium spinels	X-ray data	$FeO\cdot V_2O_3$	A17
$FeO-V_2O_3$	Electrolytic preparation of spinels	X-ray data	$FeO\cdot V_2O_3$	A13
$Fe_2O_3-V_2O_5$	Oil ash corrosion	Phase diagram and x-ray data	$FeVO_4$	A18
Lead				
$PbO-V_2O_5$	Chemical	Minimum temp for reaction		A5
Lithium				
$Li_2CO_3-V_2O_5$	Oxygen evolution	Chemical	$4Li_2O\cdot V_2O_4\cdot 7V_2O_5$	A7
$Li_2CO_3-V_2O_5$	Oxygen evolution	Chemical	$LiVO_3$ $Li_4V_2O_7$	A19
$Li_2CO_3-V_2O_5$	Preparation of vanadates	Chemical	Li_3VO_4	A6
$Li_2CO_3-V_2O_5$	Preparation of vanadates	Chemical	$4Li_2O\cdot 5V_2O_5$	A6
$LiVO_3-V_2O_5$	Phase study	Phase diagram and x-ray data	$LiVO_3$ $Li_2O\cdot 3V_2O_5$	A20
$LiVO_3-LiCl$	Phase study	Phase diagram	None formed	A11
Magnesium				
$MgO-V_2O_5$	Ceramics research	Petrographic	$3MgO\cdot 2V_2O_5$ $MgO\cdot V_2O_5$	A4
$MgO-V_2O_5$	Additives	Liquidus curve via Seger cones		A2
$MgO-V_2O_5-Na_2SO_4$	Oil ash problem	X-ray	Unidentified	A21
$MgO-V_2O_4$	Ceramics research	Petrographic	$4MgO\cdot V_2O_6$ $MgO\cdot V_2O_4$	A4
$MgO-V_2O_5$	Preparation of vanadium spinels	X-ray data	$MgO\cdot V_2O_5$	A16
$MgO-V_2O_5$	X-ray study of spinels	X-ray data	$MgO\cdot V_2O_5$	A17
$MgO-V_2O_5$ (etc)	Phase study	X-ray data	MgV_2O_4 $MgVO_3$ Mg_2VO_4	A22

Systems	Type of Investigations	Type of Data Given	Compounds	References
Manganese				
$MnO-V_2O_5$	Phase study	X-ray and thermal data	$Mn(VO_3)_2$ $Mn_2V_2O_7$ $Mn_3(VO_4)_2$	A23
$MnO-V_2O_3$	Preparation of vanadium spinels	X-ray data	$MnO\cdot V_2O_3$	A16
$MnO-V_2O_3$	X-ray studies of spinels	X-ray	$MnO\cdot V_2O_3$	A17
$MnO-V_2O_3$	Electrolytic preparation of spinels	X-ray	$MnO\cdot V_2O_3$	A13
Nickel				
$NiO-V_2O_5$	Additives	Liquidus curve via Seger cones		A2
$NiO-V_2O_5$	Chemical	Minimum temp for reaction		A5
$NiO-Cr_2O_3-V_2O_5$	Additives	Liquidus curve via Seger cones		A2
Niobium				
$Nb_2O_5-V_2O_5$	Ceramics research	Petrographic	Solid solution +compound (?)	A4
$Nb_2O_5-V_2O_5$	Ceramics research	Petrographic	$2\ Nb_2O_5\cdot V_2O_5$	A4
Phosphorus				
$P_2O_5-NaVO_3-V_2O_5$	Oxygen evolution	Chemical		A7
Potassium				
$K_2CO_3-V_2O_5$	Phase study	Phase diagram and x-ray data	$K_2O\cdot 4V_2O_5$ $K_2O\cdot V_2O_5$ $16K_2O\cdot 9V_2O_5$ $2K_2O\cdot V_2O_5$ $3K_2O\cdot V_2O_5$	A24
$K_2CO_3-V_2O_5$	Preparation of vanadates		$K_4V_2O_7$	A6
$K_2CO_3-V_2O_5$	Oxygen evolution	Chemical	$2K_2O\cdot V_2O_4\cdot 9V_2O_5$	A7
$K_2SO_4-V_2O_5$	Oxygen evolution and phase diagram	Chemical	KVO_3 $K_4V_2O_7$ K_3VO_4	A19
$K_2SO_4-V_2O_5$	Catalysis	Chemical	$K_2SO_4\cdot V_2O_5$	A25
$K_2SO_4-V_2O_5$	Preparation of vanadates	Chemical	$2K_2O\cdot 3V_2O_5$	A6
$K_2S_2O_7-V_2O_5$	Catalysis	Chemical	Glass	A25
KVO_3-KCl	Phase study	Phase diagram	No compounds	A11
KVO_3-KBr	Phase study	Phase diagram	No compounds	A11

Systems	Type of Investigations	Type of Data Given	Compounds	References
Rare Earths				
R_2O_3-V_2O_5	Crystal study	X-ray data	RVO_4	A26
Rubidium				
Rb_2CO_3-V_2O_5	Preparation of vanadates	Chemical	$Rb_4V_2O_7$	A6
Rb_2CO_3-V_2O_5	Oxygen evolution	Chemical	No "bronze"	A7
Rb_2SO_4-V_2O_5	Catalysis	X-ray data	$Rb_2SO_4 \cdot V_2O_5$	A10
Rb_2SO_4-V_2O_5	Preparation of vanadates	Chemical	$Rb_2O \cdot 2V_2O_5$	A6
$RbVO_3$-RbCl	Phase study	Phase diagram	No compound	A11
Rhodium				
Rh_2O_3-V_2O_5	Crystal study	X-ray data	$RhVO_4$	A12
Silicon				
SiO_2-V_2O_5	Thermal analysis		No compound	A27
SiO_2-V_2O_5	Phase studies		No compound	A1
SiO_2-V_2O_5	Ceramic research	Petrographic	$SiO_2 + V_2O_5$	A4
SiO_2-V_2O_4	Ceramic research	Petrographic	No reaction	A4
SiO_2-V_2O_4	Iron-refining slags		No reaction	A9
Silver				
$AgNO_3$-V_2O_5	Oxygen evolution	Chemical	$Ag_2O \cdot V_2O_4 \cdot 5V_2O_5$	A7
Sodium				
$NaVO_3$-V_2O_5	Phase study	Phase diagram	$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ $Na_2O \cdot 2V_2O_5$	A28
$NaVO_3$-V_2O_5	Crystal study	X-ray data	$Na_{1+x}V_6O_{15}$	A29
$NaVO_3$-V_2O_5	Crystal study	X-ray data	$NaVO_3$	A30
$NaVO_3$-P_2O_5-V_2O_5	Oxygen evolution	Chemical		A7
Na_2CO_3-V_2O_5	Oxygen evolution	Chemical	$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	A7
Na_2CO_3-V_2O_5	Preparation of vanadates	Chemical	$2Na_2O \cdot V_2O_5$	A6
Na_2CO_3-V_2O_5	Phase study	Phase diagram	$NaVO_3$ $Na_4V_2O_7$ Na_3VO_4	A19
Na_2SO_4-V_2O_5	Phase study	Phase diagram and x-ray data	$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	A28
Na_2SO_4-V_2O_5	Oil-ash problem	Phase diagram and x-ray data	$Na_2SO_4 \cdot 6V_2O_5$ $NaVO_3$	A21
Na_2SO_4-V_2O_5	Preparation of vanadates	Chemical	$2Na_2O \cdot 3V_2O_5$	A6

Systems	Type of Investigation	Type of Data Given	Compounds	References
Sodium (cont'd.)				
$NaVO_3$-NaCl	Phase study	Phase diagram	No compounds	A11
Strontium				
SrO-V_2O_5	Ceramics research	Petrographic	Glasses	A4
SrO-V_2O_4	Ceramics research	Petrographic	Compound (?)	A4
SrO-V_2O_4	Vanadium spinels	X-ray data	SrV_2O_4	A22
Thallium				
Tl_2CO_3-V_2O_5	Phase study	Phase diagram	$TlVO_3$ $Tl_4V_2O_7$ Tl_3VO_4	A19
Titanium				
TiO_2-V_2O_5	Ceramics research	Petrographic	No compounds	A4
TiO_2-V_2O_4	Ceramics research	Petrographic	$(Ti,V)_2O_4$	A4
Uranium				
U_3O_8-V_2O_5	Ceramics research	Petrographic	$2U_3O_8 \cdot 3V_2O_5$	A4
U_3O_8-V_2O_5	Ceramics research	Petrographic	$(U,V)_2O_4$	A4
Zinc				
ZnO-V_2O_5	Additives	Liquidus curves via Seger cones		A2
ZnO-V_2O_5	Chemical	Minimum temp for reaction		A5
ZnO-V_2O_3	Vanadium spinels	X-ray data	$ZnO \cdot V_2O_3$	A16
ZnO-V_2O_3	Vanadium spinels	X-ray data	$ZnO \cdot V_2O_3$	A17
ZnO-V_2O_3	Electrolytic preparation of spinels	X-ray data	$ZnO \cdot V_2O_3$	A13
ZnO-V_2O_3	Spinels	X-ray data	$ZnO \cdot V_2O_3$	A22
Zirconium				
ZrO_2-V_2O_5	Phase study	Thermal data	Compound stable above 730°C	A31
ZrO_2-V_2O_5	Ceramics research	Petrographic	No reaction	A4
ZrO_2-V_2O_5	Vanadates	Thermal and x-ray data	ZrV_2O_7 and $Zr(VO_3)_4$	A32
ZrO_2-V_2O_4	Ceramics research	Petrographic	No reaction	A4

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