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AN INVESTIGATION OF THE EFFECTS OF ALKALINE PHOSPHATE SOLUTIONS AT ELEVATED TEMPERATURES ON COMPOUNDS PREPARED AT ROOM TEMPERATURE

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ABSTRACT

A study has been made of the effects of elevated
temperatures and pressures exceeding the saturation
pressure of water on compounds of some elements
known to be present as contaminants on the water
side of naval boilers. These compounds were, spe-
cifically, the gelatinous precipitates which are pro-
duced when sodium phosphate solutions react with
solutions of the chlorides of iron, copper, calcium,
and magnesium, as well as certain oxides of iron
which are the principal components of rust.

PROBLEM STATUS

This report completes one phase of the problem;
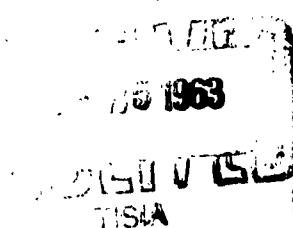work on other aspects is continuing.

AUTHORIZATION

AN INVESTIGATION OF THE EFFECTS OF ALKALINE
PHOSPHATE SOLUTIONS AT ELEVATED TEMPERATURES
ON COMPOUNDS PREPARED AT ROOM TEMPERATURE

INTRODUCTION

In the normal operation of ships' boilers a small amount of contamination in the feedwater is to be expected and when the boilers are operated under abnormal conditions, large quantities of undesirable matter may accumulate. In the presence of feedwater chemicals, which are ordinarily alkaline sodium phosphates, chemical reactions occur and the solids which are produced are not necessarily identical to those which were introduced as contaminants. Even in the absence of phosphates the effect of water at high temperatures and pressures may be such that new crystalline materials are produced.

Since there have been few reports on the effects of high pressures and temperatures on those compounds which might form when salts in solution react with water-treatment chemicals, an experiment was devised which would produce sufficient quantities of material for x-ray diffraction identification of crystalline compounds made in the presence of water under conditions approaching those found in boilers. In order that the experimental results be of future use to the Navy, reagents and procedures were related as closely as possible to those encountered aboard ships, with allowances for the fact that the laboratory experiments were scaled down to a miniature size compared with that of boilers. Consequently, a prior knowledge of the nature of deposits actually taken from the waterside of boilers was invaluable, and when precipitates prepared in the laboratories were identical in physical and chemical properties to actual deposits, it was concluded the size of the apparatus had little to do with the chemistry of the systems studied, and the experiments were sufficiently realistic for the purpose at hand.

Two types of experimental apparatus were used: 3-inch-long sealed capsules and 1-foot-high thermal convection loops, the latter for experiments where gas evolution was expected, because they allowed the release of pressure, and for use when circulation was thought to be desirable. With few exceptions there was no difference between reactions conducted in loops and those conducted in capsules. Both were operated at pressures equal to or above the natural saturation pressure of water.

Reagents were chosen on the basis of some of the more obvious types of feedwater contamination, which are sea water, rust, corrosion products of metals other than steel, contaminated or improperly used chemicals, residues from cleaning operations, and residues from manufacturing and maintenance operations. The various metallic elements known to be present in sea water were assumed to be chlorides for the purposes of this research, although any soluble salts would have been satisfactory. Corrosion products from iron were examined as individual compounds as well as in the accidental mixture which occurs during rusting of mild steel in salt water at room temperature.

Since the experimental setup and the handling of chemicals were nearly the same for each of the systems studied, the usual procedures and the description of the apparatus are discussed below, while deviations from the normal are discussed in conjunction with the appropriate portion of the investigation in which they were applied.

CONSTRUCTION AND OPERATION OF THERMAL CONVECTION LOOPS

One-foot-high thermal convection loops having a volume of 10 cubic inches were constructed of 1/4-inch stainless steel tubing, using standard pressure fittings throughout (Fig. 1). The heated zones were machined from 1-1/4-inch round stainless steel barstock, in order to raise the ratio of external (heated) surface to internal surface. The cooled zones were constructed by passing the "downcomer" portion of the loops through heat exchangers. Heating rates, obtained electrically, were as high as 110,000 Btu/sq ft/hr. The loops were air cooled on the "downcomer" side, using compressed air.

As a pretreatment, an appropriate concentrated acid was passed through the completed and wired loop, followed by dilute acid of the
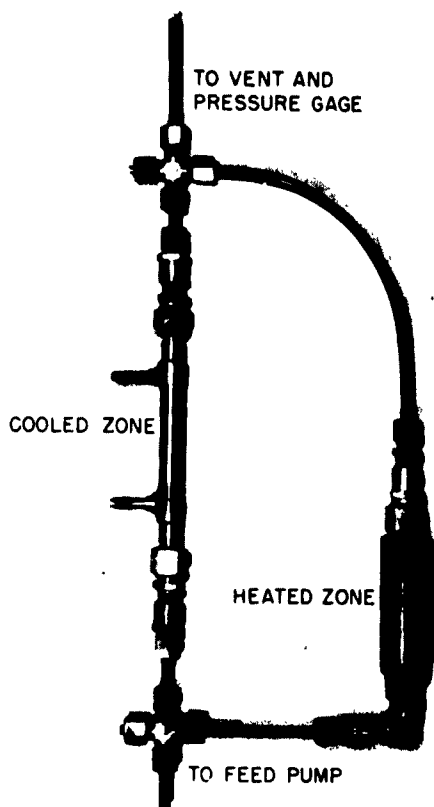
TO VENT AND
PRESSURE GAGE

COOLED ZONE

HEATED ZONE

TO FEED PUMP

Fig. 1 - Photograph of minia-
ture loop before being wired
and insulated

same type. The system was then rinsed and
neutralized with dilute sodium hydroxide, and
after further rinsing was pressure tested (cold)
at above 2000 psi. The test solution was then
introduced and the system pressurized several
times and vented to release entrapped air.

With the heater operating at 900 watts, the
temperature and pressure rose rapidly, but
venting kept the system at safe pressures. (At
no time did the pressure on the system drop be-
low the saturation pressure at the temperature
in question.) As the test temperature was
approached, cooling was initiated on the "down-
comer" side. In conjunction with careful venting,
it was possible to bring the circulating water to
a definite temperature, with the pressure being
held above a certain minimum value. These
startup operations were performed in less than
1 hour; loops were operated for a minimum of
4 hours.

The pressure dropped rapidly when the heat
supply was curtailed, but cooling required at
least one-half hour before the pressure connec-
tions could be broken. The loop was drained and
rinsed, and solid matter was collected and dried.

FABRICATION AND USE OF CAPSULES

A portion of the suspension introduced into
the loop was placed in capsules made from short
lengths of stainless steel tubing sealed at both
ends with a combination of standard fittings.
After having been held at some constant, ele-
vated temperature for a prescribed length of
time, they were cooled, opened, and the solid
material filtered off and dried prior to x-ray
diffraction analysis.

CHEMICAL METHODS

The problem of placing quantities of rea-
gents sufficient to produce amounts of reaction
products adequate for x-ray diffraction analysis
into small capsules and loops was resolved in
the following manner: solutions of chlorides
were allowed to react with concentrated solu-
tions of trisodium phosphate (Na_3PO_4) or were
titrated to certain pH value with sodium hydrox-
ide after the introduction of appropriate amounts
of phosphate. The slurries obtained were either
washed free of entrained liquids by repeated de-
cantation or placed in the high-pressure appa-
ratus while still contaminated. Because several
of the systems become acid as a result of the
crystallization of basic phosphates, such exper-
iments were repeated under conditions which
remained alkaline for the duration of the runs.

IRON

Rust and Other Iron Oxides

Oxides of iron (x-ray data in Appendix A,
Table A1) are found on the inner surfaces of
boiler tubes in all cases. The stable oxide in
contact with water or with steam under normal
operating conditions is magnetite (Fe_3O_4). Un-
der unusual conditions wüstite (FeO) or hematite
(α-Fe_2O_3) are formed or may even make up the
bulk of material coating boiler tubes on shut
down. When these compounds are detected, how-
ever, it is probable that abnormal conditions
have prevailed in the boiler.

Not only may iron oxides originate as the
high-temperature oxidation products of the mild

steel from which most boilers are constructed, but they may also be due to corrosion of the boiler feedwater system at low temperatures. The compound lepidocrocite (γ-FeOOH), which made up the bulk of the corrosion product when mild steel corroded in air-saturated salt water at room temperature, invariably covered a thin layer of magnetite (Fe_3O_4). In the presence of a limited supply of air at low temperatures or in hot salt water, the corrosion product was magnetite alone.

The hydrated forms of iron oxide lose water on being heated open to the air. Thus, lepidocrocite and goethite (α-FeOOH), another hydrated oxide of iron, dehydrate in the following manner:

$$2\ \alpha\text{-FeOOH} \longrightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O}$$

$$2\ \gamma\text{-FeOOH} \longrightarrow \gamma\text{-Fe}_2\text{O}_3\ (\text{maghemite}) + \text{H}_2\text{O}$$
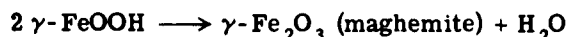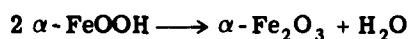
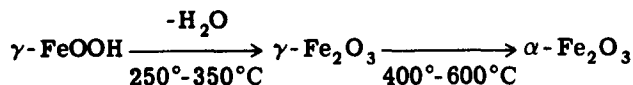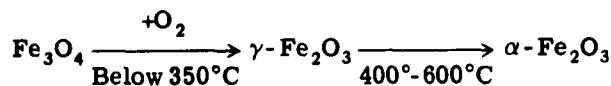Since water is one of the reaction products, it might be expected that high water pressures would tend to prevent the decomposition of the hydrated oxides. This is true in the case of goethite, for which stability-field boundaries have been reported (1,2). The effect of pressures up to 2000 atmospheres on the decomposition temperature of this hydrate in contact with neutral or alkaline solutions is of small order, that is, less than 5°C per thousand atmospheres in 0.1M NaOH solutions, the decomposition temperature being nearly constant at 165° ± 5°C. In neutral suspensions at pressures of one or two atmospheres the decomposition temperature is about 130°C (3-5), while in acid suspensions the decomposition temperature is said to be about 100°C (6).

The stability field boundaries for lepidocrocite have apparently not been studied in detail, although conditions under which lepidocrocite can be dehydrated to maghemite have been investigated (7-15). In spite of numerous inconsistencies in the literature, it may be stated with some certainty that when lepidocrocite is heated in air, adsorbed water is lost at about 100°C (212°F), constitutional water is gradually evolved over a range of temperatures from about 250° to 350°C (480° to 660°F), and recrystallization of the maghemite (the product of dehydration of lepidocrocite) occurs over a temperature range of from 400° to 600°C (750° to 1110°F) giving hematite as a final reaction product. These temperatures are by no means fixed points, since they may be raised or lowered by the presence of other materials, such as the other iron oxides, especially hematite (4,12) and silica (16). Other factors affecting these transition temperatures are the degree of crystallinity

(4,10,12), the original method of preparation of the synthetic compound (12), and pressure (17).

The chemistry of the oxides of iron applicable to this study may be summarized as follows. The usual low temperature oxidation products or iron are magnetite and lepidocrocite. Heated to high temperatures in the air these compounds undergo the reactions:

$$\text{Fe}_3\text{O}_4 \xrightarrow[\text{Below }350°\text{C}]{+\text{O}_2} \gamma\text{-Fe}_2\text{O}_3 \xrightarrow{400°\text{-}600°\text{C}} \alpha\text{-Fe}_2\text{O}_3$$

$$\gamma\text{-FeOOH} \xrightarrow[250°\text{-}350°\text{C}]{-\text{H}_2\text{O}} \gamma\text{-Fe}_2\text{O}_3 \xrightarrow{400°\text{-}600°\text{C}} \alpha\text{-Fe}_2\text{O}_3$$

At pressures above one atmosphere lepidocrocite is dehydrated directly to hematite (5).

In order to determine the effects of elevated temperatures and pressures on the compounds formed during the rusting of iron at room temperature, the following experiment was conducted: a few grams of low-temperature corrosion product was prepared by allowing mild steel to rust while immersed in aerated salt water. This rust was washed free of chloride, placed into a capsule with distilled water, and the sealed capsule heated to 230°C (446°F) for four hours.

Whereas the original rust gave an x-ray pattern for a mixture of magnetite and lepidocrocite, the material taken from the capsules at the end of the experiment gave an x-ray pattern of a mixture of magnetite and hematite. This result was not entirely unexpected because magnetite is known to be unaffected by these conditions and lepidocrocite has been reported to be dehydrated directly to hematite, rather than maghemite, at water pressures above one atmosphere (5).

Since it had been stated in the literature that synthetic lepidocrocite can absorb up to 8.15% of its weight in phosphate and that ferric oxide gels can absorb up to 21.28% phosphate when placed in acid solutions of water-soluble phosphates (18), a test was made to find whether rust would give the same reaction products when heated in the presence of sodium phosphate solutions, but under alkaline conditions. Accordingly, a slurry of rust in sodium phosphate solution (100 ppm PO_4 at pH 10.6) was heated to 230°C (446°F) for one-half hour and the residue examined by x-ray

diffraction techniques.* The results were no dif-
ferent from those in which distilled water was
used and the reaction products were again mag-
netite and hematite.

In a separate series of experiments run in
capsules at much lower temperatures with syn-
thetic lepidocrocite as a starting material it was
found that partial dehydration to mixtures of
hematite and maghemite had occurred after 16
hours at 102°C (216°F). At as low a tempera-
ture as 90°C (194°F) a trace of hematite could
be detected after 16 hours at temperature.

As a result of these experiments and from
the chemistry of this system taken from the
literature it can be concluded that iron oxide
hydrates from low temperature corrosion are
changed, ultimately, into hematite under boiler
conditions. It is inferred that the presence of
hematite in a boiler deposit may lead to the
erroneous conclusion that the boiler metal had
been attacked by feedwater of high-oxygen con-
tent, when in fact the hematite may have been
due to low-temperature corrosion of the feed-
water lines or of the boiler when it was not
operating. It is inferred, also, that the existence
of lepidocrocite and maghemite in boiler deposits
under operating conditions is a virtual impossi-
bility, and that the presence of these compounds
in locations which are normally under pressure
implies that corrosion and oxidation have oc-
curred between the time of shutdown and the
time of laboratory examination of the deposits.

Iron II and Iron III Phosphates

When an alkaline solution of a water-soluble
phosphate, such as sodium phosphate, is added
to a solution of a water-soluble iron salt there
is an immediate precipitation of a gelatinous,
insoluble "hydroxide" which is noncrystalline
with respect to x-rays and has an indefinite
composition. If the iron was originally present
in the trivalent oxidation state, the effect of dis-
solved oxygen in the solutions is negligible, but
if divalent iron is present when the solution is
made alkaline, the white precipitate which first
forms soon turns green and then black, as micro-
crystalline magnetite (Fe_3O_4) forms. (Although
it is sometimes claimed that precipitated mag-
netite contains water of hydration, even a fresh
preparation is attracted by a magnet, but such
material differs from coarsely crystalline mag-
netite in that it is rapidly oxidized by hydrogen
peroxide solutions.)

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*This test was run in a loop in order to ensure
intimate contact between the oxides and the
phosphate solution.

Because of the existence of two series of
iron phosphates and the differences in how the
chemical reagents had to be handled, due to the
ease of oxidation of Fe^{++} in alkaline solution,
two series of experiments were conducted.

Solutions containing trivalent iron required
no special handling. The reaction between iron
III chloride solution and a solution containing
trisodium phosphate (Na_3PO_4) in an amount suf-
ficient to supply 100 ppm $PO_4^=$ gave a creamy,
yellow noncrystalline precipitate, but when the
pH was adjusted to a value of 10.6 with sodium
hydroxide, the color became brown. A slurry
of this precipitate in the mother liquor, heated
to 230°C (446°F) in either a capsule or in a loop,
resulted in a crystalline compound which con-
tained no phosphate, but which was identified as
well-crystallized hematite (α-Fe_2O_3).

Solutions containing iron II chloride initially,
and containing 100 ppm $PO_4^=$, turned green and
then black after having been made alkaline in
the presence of air. This black precipitate
changed into well-crystallized magnetite (Fe_3O_4)
on being heated in closed systems while sus-
pended in the mother liquor.

When iron II chloride solutions were car-
ried through an identical series of operations,
but in the absence of air,* the results were en-
tirely different. Although the initial pH of the
suspensions was 10.6, the systems were decidedly
acid after being heated under pressure to 230°C,
and a mixture of two distinct crystalline phases
appeared. In the absence of comparable data in
the usual compilations of x-ray patterns no im-
mediate identification could be made. It was
possible, however, to make a separation of these
two crystalline phases on the basis of the rela-
tive rates of settling of the individual, bladelike,
cream-colored crystals and the rosettes of
green crystals in the mixture. Each of these
phases gave a characteristic x-ray powder dif-
fraction pattern (Appendix A, Table A2).

Although it was virtually impossible to
achieve complete separation of the two com-
pounds, a fact which prevented an identification
by means of quantitative chemical analysis, the
cream-colored crystals gave an x-ray pattern
and optical data similar to those of the mineral
called "wolfeite" (19), which in nature contains

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*This was accomplished by placing metallic
iron powder in the iron II chloride solution in
order to reduce any iron III ions which might
have been present, and by bubbling oxygen-free
hydrogen through the phosphate and hydroxide
solutions. Capsules and loops were filled under
an atmosphere of hydrogen.

manganese as well as iron. Because of this similarity the synthetic iron II phosphate is thought to have the formula Fe_2PO_4OH. The precipitation of this basic phosphate would explain the change in pH from a value of 10.6 to an acidic value (actually about 6.6 and 6.7) in two experimental runs, since such a precipitation removes hydroxyl ions from solution. Similar pH changes occurred when magnesium, calcium, and copper basic phosphates crystallized from solutions.

The green rosettes were not identified for lack of x-ray and optical data for comparison. A second compound in the form of well-defined green octahedra crystallized from more acidic solutions (final pH = 4.0), but these, also, were not identified. Since these compounds were found in contact with solutions known to be acid, and since such systems were beyond the scope of this work, the identification was not pursued further.

The high temperature experiment was repeated, but under conditions which guaranteed that reactions occurred in the absence of oxygen but in alkaline solutions. For this purpose iron II chloride solutions were added to solutions containing 2% trisodium phosphate, which resulted in a pH value above 11.0 after the reaction at elevated temperatures. As a result of this treatment a new crystalline sodium iron phosphate was produced, and since a compound giving an identical, but unidentified x-ray diffraction pattern (Appendix A, Table A3) had been found in large quantities on the surfaces of badly corroded generating tubes of a boiler (20), considerable effort was made to achieve an identification based on the relatively pure material at hand, and to determine some of the chemical properties of this compound.

On the basis of the chemical analysis it is concluded that the compound which crystallized from strongly alkaline solutions has the formula $NaFePO_4$* (Table 1). This compound hydrolyzed rapidly in water, giving an alkaline solution containing sodium phosphate, and a residue of magnetite. In the alkaline mother liquor $NaFePO_4$ remained unoxidized and unchanged over a period of a week, but after one year, two of the three major lines of the x-ray powder pattern had disappeared and two new major lines had made their appearance (Appendix A, Table A3).

*It should be noted that $NaFePO_4$ was also obtained by the direct reaction of metallic iron with concentrated trisodium phosphate solutions.

Table 1
The Analysis of the Sodium Iron
Phosphate Crystallizing
From Strongly Alkaline Solutions

Element	Found (%)	Calculated* (%)
Na^+	13.0	13.2
Fe^{++}	30.3	32.2
Fe^{+++}	1.4	Nil
$PO_4^=$	54.6	54.6
	99.3	100.0

*Based on the formula $NaFePO_4$.

By way of comparison, the synthetic wolfeite (Fe_2PO_4OH) was unaffected by water, as would be expected from the fact that a mineral of similar composition occurs in nature. It was found, however, that all of the crystalline iron II phosphates obtained from high-pressure apparatus were readily soluble in dilute acids.

Whereas no iron II phosphate was detected after alkaline solutions containing Fe^{+++} and phosphate had been raised to high temperatures while under pressure, at least three compounds formed when Fe^{++} solutions were treated in this manner. The identity of the iron II phosphate was a function of the surroundings; thus, in the presence of high concentrations of trisodium phosphate the double phosphate $NaFePO_4$ was obtained, while the compounds appearing from solutions containing trisodium phosphate in quantities just sufficient to give an initial pH value of 10.6 included the basic phosphate Fe_2PO_4OH which is thought to be related to the mineral known as "wolfeite," and a second unidentified compound containing Fe^{++} and phosphate.

Of these compounds only the sodium iron phosphate $NaFePO_4$ has been detected in boilers, and this under very unusual circumstances in which extremely high concentrations of sodium and phosphate were present during operation. Coincidental with the accumulation of $NaFePO_4$ there had been catastrophic corrosion of generating tubes. Since it was found in this investigation that solutions containing a high concentration of trisodium phosphate react with powdered iron to give $NaFePO_4$, it may now be concluded that accumulations of this compound in the failed boilers were actually the result of the corrosion and the cause was almost certainly the high concentration of ordinary water-treatment

chemicals, or of some improper chemical additive which gives sodium phosphate under boiler conditions.

An additional finding which may be significant is the fact that $NaFePO_4$ hydrolyzes in water to give alkaline sodium phosphate solutions and, in the presence of air, magnetite. The behavior of this compound would make it suspect in connection with the problem of "phosphate hideout," which was investigated by Straub (21). This author postulated that the loss of phosphate under high boiler loads, followed by the reappearance under low loads, may be due to the formation of "a complex sodium phosphate of low solubility which was forming at high temperatures, but was not stable at low temperatures."

Although Straub was able to produce deposits containing sodium phosphate, no identification was obtained by x-ray methods. Since he reported no x-ray data in his paper, it is impossible to tell whether the compounds produced by Straub are the same as those found during this investigation. An analyst's report quoted by Straub, however, is in part as follows:

"...We did not find this (material) to be readily soluble in water. It appears to decompose in water at room temperature, slightly faster when heated to 70° to 80°C. It is readily soluble in dilute acids and decomposes in hot dilute NaOH solutions. The exact composition was not determined, but qualitative tests show sodium, orthophosphate, and ferrous iron to be present in appreciable quantities. From these tests the scale is believed to be a sodium ferrous phosphate..."

These statements are also applicable to the compound identified here as $NaFePO_4$.

CALCIUM

The presence of a light yellow powder on the waterside surfaces of boiler tubes is a very common occurrence when alkaline phosphates are used as water-treatment chemicals. In most cases this yellow powder gives an x-ray diffraction pattern for hydroxylapatite $[Ca_5(PO_4)_3(OH)]$ (Appendix A, Table A4) although there is a report in the literature that phosphorite $(Ca_3P_2O_8 \cdot H_2O)$ and whitlockite $(\beta\text{-}Ca_3P_2O_8)$ (Ref. 22) have been identified in boilers (23).

It was found in this investigation that the insoluble precipitate obtained when a sodium phosphate solution was added to a calcium

chloride solution, followed by adjustment of pH to a value of 10.6 with sodium hydroxide, gave a weak diffraction pattern for hydroxylapatite, and that after treatment under pressure at elevated temperatures this pattern had become very intense. Other phosphates of calcium were not detected.

COPPER

Because low-temperature heat exchangers aboard ships contain alloys of copper, it is not surprising that this element is found as a component of waterside deposits. The means by which it is thought to be transported from the point of origin to the point of destination have been discussed at length by Corey (24), who claimed that this subject is "highly controversial, speculative, and confused," and who stated that some authors feel that copper has nothing to do with the generating-tube corrosion with which it is often associated, while others feel that it is the cause of the corrosion of tubes.

In the absence of conclusive evidence concerning the means by which copper is transported to the heat-transfer surfaces, and in the absence of reports on controlled experimental investigations, it is difficult to guess the correct explanation for the transport of this element from one location to another. It is known that the source is invariably a metallic surface containing elemental copper; copper is carried in some manner suspended or dissolved in water; copper remains suspended or dissolved during the adjustment of the phosphate and alkalinity to some prescribed values; copper enters the boilers; and after operation it may be found on the surfaces of tubes as metallic copper, plated in a coherent sheet or as "nuggets," as a dust-like metallic component of an oxide boiler deposit, or as one of the common copper oxides. This sequence of events assumes that the deposition occurs during normal boiler operation.

An alternative means by which copper could be carried from source to final resting place is in the form of dissolved or suspended salts in acids used for cleaning boilers.

The present investigation was not intended to touch on the problem of the transportation of copper, but rather to gather facts concerning the changes occurring when compounds precipitated at low temperatures by alkaline sodium phosphate solutions are heated to elevated temperatures under steam pressure and in the presence of such alkaline solutions. Since it was known that copper is usually detected in

the metallic form, but that it has also been found as Cu_2O, and CuO, the equipment and experimental procedures were modified as described below in order to illustrate ways in which these forms of copper can be produced in the presence of water.

Experiments Involving Precipitated Phosphates

The reaction between copper II chloride solution and a solution containing trisodium phosphate in an amount sufficient to supply 100 ppm $PO_4^{\equiv}$, and with pH adjusted to a value of 10.6 after reaction, led to the precipitation of a pale blue gel which gave a very faint x-ray diffraction pattern of the hydrated copper phosphate, $Cu_3(PO_4)_2 \cdot 3H_2O$ (Appendix A, Table A5). When a slurry of this gel in the mother liquor was heated to 230°C (446°F) in either a capsule or in a loop the resulting compound was well-crystallized pseudomalachite $(Cu_5(PO_4)_2(OH)_4$.

The formation of pseudomalachite (25), a basic phosphate, led to a decrease in the pH of the liquid contents of the systems, and when the proportion of solids was high, the final pH approached or reached acid values, and metallic copper was found as a reaction product. The inner surfaces of the containers were corroded in such cases. Metallic copper was not found when the final pH was 10.6 or higher, although the limiting pH value for the reduction of copper under the experimental conditions was not determined.

Experiments Involving Copper Oxide

Copper phosphates are not the usual compounds of copper found in waterside deposits, and since neither of the common copper oxides was produced as a result of the precipitation of soluble copper salts in alkaline solutions, a series of experiments was conducted using solid copper II oxide (CuO) as a starting material.

Sealed in capsules and loops and heated to 230°C (446°F) in the presence either of water, of alkaline solutions of sodium phosphate (pH = 10.6), of alkaline solutions containing ammonium ion, or of alkaline solutions containing only sodium hydroxide, the copper II oxide was recovered unchanged.

Mixed with powdered, metallic iron and sealed in a loop along with a solution containing 100 ppm $PO_4^{\equiv}$ and at a pH of 10.6 (adjusted with sodium hydroxide), a trace of copper I oxide

(Cu_2O) was produced. Since it was possible that the reduction of copper II oxide to copper I oxide may have involved an indirect reaction with hydrogen gas from the oxidation of metallic iron by water, the following series of experiments was conducted.

Two 10-ml capsules were connected by a tube to form a reaction vessel. The lower capsule was filled with copper II oxide suspension, and after the system was evacuated, hydrogen gas was bled in and then raised to 50 pounds pressure. After having been valved off, the entire unit was placed in a furnace at 230°C (446°F) for 4 hours. At the end of this time the cooled capsules were no longer under pressure, and the surface layer of the copper oxide, which had settled to the bottom, was metallic in appearance. The x-ray diffraction pattern, however, indicated that this copper-colored layer was entirely Cu_2O, and no metallic copper was detected.[*] Below the surface the starting material was unchanged.

A second experiment in the absence of liquid water was conducted by pressurizing a system containing dry copper II oxide with 50 pounds hydrogen pressure while the capsule was held in a furnace at the elevated temperature. In this case about 10% of the CuO had been reduced to Cu_2O in 30 minutes, but again no metallic copper was detected.

MAGNESIUM

Magnesium compounds are not usually found as components of naval boiler deposits, although brucite $(Mg(OH)_2)$, forsterite (Mg_2SiO_4), and serpentine $(3\,MgO \cdot 2\,SiO_2 \cdot 2\,H_2O)$ have been reported as components of deposits in shore-station boilers (23). Since water-soluble compounds of magnesium make up a substantial proportion of the total solids of seawater, however, the effect of water-treatment chemicals on soluble magnesium compounds was investigated.

In general it may be stated that although a number of hydrated magnesium normal, acid, and basic phosphates have been reported (26-30), these are either unstable even at moderate temperatures or decompose when washed with water.

In the absence of water at least three magnesium phosphates appear in the system magnesium oxide-phosphorus pentoxide at high

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[*]The limit of detection of metallic copper in the presence of CuO by x-ray methods is about 2%.

temperatures, these being $3MgO \cdot P_2O_5$, $2MgO \cdot P_2O_5$, and $MgO \cdot P_2O_5$ (31). There is also a mixed calcium-magnesium phosphate, $Ca_3Mg_3(PO_4)_4$, which is said to give an x-ray diffraction pattern almost identical with that of $\alpha\text{-}Ca_3(PO_4)_2$ (32,33).

In spite of the vast amount of work reported on systems containing magnesium and phosphorus oxides, x-ray-diffraction and optical-crystallographic data are scarce. This fact was a distinct handicap in the identification of the magnesium phosphates precipitating from alkaline solutions in the present study.

When magnesium chloride solutions were titrated into a solution containing trisodium phosphate (Na_3PO_4) at an initial pH of 11.6 until the pH had dropped to a final value of 10.6, a curdy, white precipitate giving no x-ray diffraction pattern was obtained. This material could be made crystalline either by being boiled in water, heated in capsules and loops in the as-precipitated condition, or by being heated in capsules and loops after having been washed free of soluble reaction products, but in each case mixtures of different compounds were produced. For want of standard x-ray patterns no identification was attained, although numerous preparations of magnesium phosphates were made, based on methods taken from the literature. The x-ray diffraction patterns of the unknown magnesium phosphates and some phosphates prepared by known methods have been listed in Appendix A, Tables A6-A8.

There were at hand samples of a previously unidentified magnesium phosphate taken from an experimental boiler (34); operating under conditions which simulated normal boiler operation, except for the presence of "synthetic sea water." Since the x-ray pattern of this compound (Appendix A, Table A9) also differed from those of the newly prepared compounds, random mixtures of various magnesium phosphates were treated in capsules at elevated temperatures and in the presence of water until the pattern of the unidentified phosphate appeared. It was found empirically that mixtures containing stoichiometric proportions of magnesium oxide (MgO) and magnesium phosphate $(Mg_3(PO_4)_2)$ in the ratio of one to one reacted to give patterns which indicated the absence of ordinary magnesium hydroxide and phosphates in the reaction products. On this basis it is concluded that the formula for the new compound must approximate $MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$ (Appendix A, Table A10). On ignition this compound lost 7.5% in weight, and the resulting material gave an x-ray pattern of anhydrous $Mg_3(PO_4)_2$ having spacings shifted

slightly toward higher values, which infers solid solubility of MgO in the phosphate structure. Lines of magneisum oxide were absent from the powder pattern of the ignited material.

It was found, also, that this compound formed in the presence of a 2% solution of Na_3PO_4 when a slurry containing stoichiometric proportions of the magnesium oxide and phosphate were heated in sealed systems to a temperature of 230°C (446°F). No compound containing both sodium and magnesium was detected even after reactions at high temperatures.

In conclusion, the reaction of solutions of magnesium salts and alkaline solutions containing phosphates results in the precipitation of poorly crystallized, insoluble compounds containing magnesium, phosphate, and water. On being heated to high temperatures these are converted into well-crystallized magnesium basic phosphates if the original pH was sufficiently high, and there is a corresponding drop in pH. The formation of double phosphates between sodium and magnesium was not indicated.

DISCUSSION

Much of the chemistry which is applied to the operation of boilers is the result of long established traditions based on the fact that certain problems could be controlled by the use of certain chemicals at certain times. In many cases empirical findings have later been put on a scientific basis, while in more recent times the scientific method has preceded the employment of new chemicals. One of the areas of research which has been more or less overlooked has been the investigation of the chemistry of materials which find their way into boilers unintentionally, and reactions which might occur between such foreign materials and the chemicals which are now accepted as being suitable for the prevention of high-temperature reactions between steel and water.

There is little question but that contamination by sea water and by corrosion products of structural alloys results in the removal of phosphate from the boiler water as insoluble phosphates precipitate from solution. As a result, it is often difficult for boiler operators to maintain dissolved phosphate concentrations at prescribed levels, and continual chemical analysis of boiler water is a necessity. Furthermore, the depletion of boiler chemicals is accompanied by the accumulation of water-insoluble solids which must be discharged from the boiler by periodical blowdowns in order to

protect heat-transfer surfaces from buildup of thermally nonconducting solids. The present work was intended to illustrate some chemical reactions which might possibly occur under boiler conditions and to characterize some of the reaction products.

Precipitation reactions of water-soluble compounds of iron, calcium, copper, and magnesium with solutions of trisodium phosphate (Na_3PO_4) gave virtually noncrystalline reaction products at room temperature, but when these gelatinous materials were heated to high temperatures with water in sealed systems, crystallization occurred, which permitted the characterization of the compounds by x-ray powder diffraction methods. Summaries of the experiments and the compounds identified in the solid reaction products are given in Tables 2 and 3. It may be stated, briefly, that insoluble phosphates were formed in the presence of Fe^{++}, Ca^{++}, Mg^{++}, and Cu^{++}; solutions of Fe^{+++} gave a precipitate of insoluble, hydrated oxides which became α-Fe_2O_3 (hematite) at elevated temperatures; the corrosion products of iron changed, ultimately, into Fe_3O_4 (magnetite) and

α-Fe_2O_3; and in the presence of a large excess of Na_3PO_4 in solution metallic iron and precipitated iron phosphates changed into $NaFePO_4$, which is unstable in water at room temperature.

The problem of copper precipitation in boilers was touched upon but not resolved. It was not possible under the conditions of these experiments to produce metallic copper except from acid solutions, the end products from alkaline solutions being Cu_2O (cuprite) or $Cu_5(PO_4)_2$ $(OH)_4$ (pseudomalachite).

RECOMMENDATIONS

This concludes one phase of the investigation of boiler water chemistry. Some of the areas of research which were considered have been reported upon in great detail in the literature, while for others data on prior work was practically nonexistent. There is a specific need for further research: (a) on the problem of copper deposition in boilers and the significance of the copper on heat-transfer surfaces, (b) on the stability-field relationships of γ-$FeOOH$, (c) on

Table 2
A Summary of Compounds Identified After Room Temperature Precipitations and
After Recrystallization at Elevated Temperatures in the Presence of Water

Element	Product of Room Temperature Reaction with Na_3PO_4 (final pH = 10.6)	Special Conditions	Solid Reaction Product After Having Been Heated Under Pressure
Fe^{+++}	Brown gel (first ppt cream-colored gel)	–	α-Fe_2O_3
Fe^{++}	White gel, turning green and then black	–	Fe_3O_4 + $NaFePO_4$
Fe^{++}	White gel	Absence of oxygen*	Fe_2PO_4OH + Unidentified green crystals (rosettes)
Fe^{++}	White gel	Excess Na_3PO_4 (2%), absence of oxygen	$NaFePO_4$
Fe^{++}	White gel	Insufficient Na_3PO_4†	Unidentified green prisms
Ca^{++}	White $Ca_5(PO_4)_3$ (OH) gel	–	$Ca_5(PO_4)_3(OH)$
Cu^{++}	Pale blue $Cu_3(PO_4)_2 \cdot 3H_2O$ gel	–	$Cu_5(PO_4)_2(OH)_4$
Mg^{++}	White gel	–	Unidentified phosphates

*The pH after high-temperature reaction was 6.7.
†The pH after high-temperature reaction was 4.0. Capsules contained high pressure of hydrogen due to reaction of acid with steel fittings.

Table 3
A Summary of Changes Occurring When Solids Were Heated
or Reacted at a Temperature of 230°C (446° F)

Solid Compounds	Solutions and Special Conditions	Solid Reaction Product After Having Been Heated Under Pressure
Rust	Water or phosphate at pH of 10.6	α-Fe_2O_3 and Fe_3O_4
Fe_3O_4	Same as above	No change
α-Fe_2O_3	Same as above	No change
γ-Fe_2O_3	Same as above	α-Fe_2O_3
α-FeOOH	Same as above	α-Fe_2O_3
γ-FeOOH	Same as above	α-Fe_2O_3
Fe (powder)	Same as above	Fe_3O_4 and $NaFePO_4$ (trace)
CuO	Water, Na_3PO_4 at pH 10.6, NH_4OH or NaOH at pH 10.6	No change
CuO + Fe (powder)	Na_3PO_4 at pH 10.6	Cu_2O
CuO	Na_3PO_4 at pH 10.6, 50 pounds H_2 pressure at start	Cu_2O
CuO	Continuous 50 pounds H_2 pressure, dry reaction	Cu_2O
MgO	Water	$Mg(OH)_2$
$Mg_3(PO_4)_2$ (anhydrous)	Water	$Mg_3(PO_4)_2 \cdot 5H_2O$
$Mg_3(PO_4)_2 \cdot 5H_2O$	Water	No change
MgO + $Mg_3(PO_4)_2$	Water, Na_3PO_4 at pH 10.6, or 2% Na_3PO_4	$MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$
6 MgO + $Mg_3(PO_4)_2$	Na_3PO_4 at pH 10.6	$Mg(OH)_2$ + $MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$
MgO + 1.1 $Mg_3(PO_4)_2$	Na_3PO_4 at pH 10.6	$MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$ + $Mg_3(PO_4)_2 \cdot 5H_2O$

the basic orthophosphates of magnesium, (d) on the identity of compounds actually found on the waterside of boilers for which x-ray data have not been reported, and (e) scientific studies on corrosion reactions, especially at high temperatures and under normal boiler conditions.

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APPENDIX A

X-RAY POWDER DIFFRACTION DATA

Table A1

X-Ray Powder Diffraction Data for Oxides and Hydrated Oxides of Iron

α-Fe$_2$O$_3$ (hematite)		γ-Fe$_2$O$_3$ (maghemite)		Fe$_3$O$_4$ (magnetite)		FeO (wüstite)		α-FeOOH (goethite)		γ-FeOOH (lepidocrocite)	
d(Å)	I/I$_o$	d(Å)	I/I$_o$	d(Å)	I/I$_o$	d(Å)	I/I$_o$	d(Å)	I/I$_o$	d(Å)	I/I$_o$
3.68	70	5.90	2			2.486	80	5.0	20	6.26	100
2.69	100	4.82	5	4.85	40	2.153	100	4.21	100	3.29	90
2.51	80	4.18	1			1.523	60	3.37	20	2.79	10
2.20	70	3.73	5			1.299	25	2.69	80	2.47	80
2.07	10	3.41	2			1.243	15	2.57	20	2.36	20
1.837	70	2.95	34	2.966	70	1.077	15	2.48	20	2.09	20
1.691	80	2.78	19	2.530	100	0.988	10	2.44	70	1.937	70
1.634	10	2.52	100	2.419	10	0.9631	15	2.25	20	1.848	20
1.596	40	2.41	1					2.18	40	1.732	40
1.484	70	2.32	6					2.09	5	1.566	20
1.451	80	2.23	0.5	2.096	70			2.00	10	1.535	20
1.348	20	2.08	24					1.920	10	1.524	40
1.309	40	1.87	0.5	1.712	60			1.803	20	1.496	10
1.255	30	1.70	12	1.614	85			1.774	5	1.449	10
1.224	10	1.61	33					1.719	50	1.433	20
1.205	10	1.55	0.5					1.689	20	1.418	10
1.187	30	1.53	1	1.483	85			1.660	10	1.389	10
1.160	30	1.48	53					1.602	20	1.367	30
1.137	40	1.43	1	1.327	20			1.563	30	1.261	10
1.100	40	1.32	7					1.507	20	1.213	20
ASTM Card 6-0502 Co Kα Radiation		ASTM Card 4-0755 Fe Kα Radiation		ASTM Card 11-614 Co Kα Radiation		ASTM Card 6-0615 Co Kα Radiation		ASTM Card 8-97 Fe Kα Radiation		ASTM Card 8-98 Co Kα Radiation	

Table A2
X-Ray Powder Diffraction Data for Iron II Phosphates

$Fe_2PO_4(OH)$ Synthetic (manganese-free)		Wolfeite* (natural)		Green Crystals Occurring With $Fe_2PO_4(OH)$		Green Crystals Occurring in Acid Under High H_2 Pressure (final pH = 4.0)	
d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o	d(A)	I/I_o
4.34	20	4.37	30	9.8	10	4.9	2
3.60	60	3.63	40	8.9	100	4.8	10
3.42	10 }	3.37	50	7.4	5	3.64	5
3.32	20 }			6.9	5	3.50	2
3.14	90	3.18	80	6.43	25	3.32	100
3.07	80	3.09	90	5.11	5	3.19	80
2.89	100	2.93	100	4.44	10	2.80	5
2.85	10	2.87	10	4.15	20	2.60	20
2.76	50	2.80	40	3.73	5	2.55	2
2.69	40	2.69	10	3.51	5	2.42	5
2.62	10	2.63	10	3.15	5	2.29	20
2.56	50	2.57	50	3.09	10	2.26	5
2.51	5 }	2.45	30	3.02	20	2.05	30
2.42	5 }			2.97	20	2.03	20
2.369	5	2.33	10	2.92	20	1.98	5
2.300	5	2.29	50	2.79	5	1.87	10
2.259	10			2.72	5	1.84	20
2.173	2	2.19	10	2.616	5	1.75	5
2.134	5	2.14	50	2.570	10	1.67	10
2.085	5	2.06	10	2.526	5	1.66	50
2.053	10	2.04	10	2.431	10	1.62	10
2.026	10	2.01	10	2.088	5	1.61	60
1.998	5	1.96	30	2.034	10	1.46	10
1.934	20	1.95	30	1.941	20	1.43	10
1.911	5	1.82	10	1.881	5	1.38	5
Film Cr Kα Radiation		ASTM Card 5-0612 Fe Kα Radiation		Film Cr Kα Radiation		Film Cr Kα Radiation	

*C. Frondel, Am. Mineral. 34:692-705 (1949).

Table A3
X-Ray Powder Diffraction Data for NaFePO₄ and a Deposit from a Ship's Boilers

NaFePO$_4$		Grey Deposit from Boilers of USS Edwards		NaFePO$_4$ (after standing open to the air for one year)	
d(A)	I/I$_o$	d(A)	I/I$_o$	d(A)	I/I$_o$
4.44	10	4.45	5		
4.34	10	4.37	10	4.50	40
3.71	5	3.73	10	4.40	40
3.66	10	3.67	20	3.70	5
3.40	5				
3.33	5	3.32	10	3.36	5
2.95	5	2.95	5		
2.80	2	2.80	5		
2.75	2				
2.71	60	2.71	80	2.73	5
2.69	60	2.69	80		
2.65	5				
2.62	5	2.59	5		
2.566	100	2.566	100	2.592	100
2.509	30	2.509	20	2.526	15
2.415	20	2.419	10	2.427	5
2.384	20	2.384	10		
2.236	5	2.236	10	2.247	15
2.188	5	2.191	5	2.199	5
2.082	20	2.085	20	2.097	5
2.050	5	2.052	10	1.678	5
2.021	5	2.029	10	1.518	5
1.974	2	1.976	5	1.513	5
1.920	2	1.920	5	1.497	20
1.872	30	1.872	30	1.466	10
1.843	40	1.845	50	1.287	5
1.712	20	1.711	30		
1.688	10	1.688	5		
1.672	10	1.672	5		
1.658	2	1.660	2		
Film Cr Kα Radiation		Film Cr Kα Radiation		Chart Cu Kα Radiation	

Table A4
X-Ray Powder Diffraction Data for Calcium Phosphate (Hydroxylapatite)

Ca$_5$(PO$_4$)$_3$(OH)* (hydroxylapatite)	
d(A)	I/I$_o$
8.17	11
5.26	5
4.72	3
4.07	9
3.88	9
3.51	1
3.44	40
3.17	11
3.08	17
2.814	100
2.778	60
2.720	60
2.631	25
2.528	5
2.296	7
2.262	20
2.228	1
2.148	9
2.134	3
2.065	7
2.040	1
2.000	5
1.943	30
1.890	15
1.871	5
1.841	40
1.806	20
1.780	11
1.754	15
1.722	20
ASTM Card 9-432 Cu Kα Radiation	

*The lines 2.814, 2.778, and 2.720 are not resolved by molybdenum radiation.

Table A5
X-Ray Powder Diffraction Data for Oxides and Phosphates of Copper

Cu$_2$O (cuprite)		CuO* (tenorite)				Cu$_3$(PO$_4$)$_2$·3H$_2$O (synthetic)		Cu$_5$(PO$_4$)$_2$(OH)$_4$ (pseudomalachite)	
		Precision Determination		Routine Determination					
d(A)	I/I$_o$	d(A)	I/I$_o$	d(A)	I/I$_o$	d(A)	I/I$_o$	d(A)	I/I$_o$
3.020	9	2.751	12	2.744	10	9.9	100	4.75	5
2.465	100	2.530⎫	49			6.9	25	4.48	100
2.135	37	2.523⎭	100	2.520	100	4.80	8	3.46	50
1.743	1	2.323⎫	96			4.32	15	3.27	5
1.510	27	2.312⎭	30	2.319	95	3.90	5	3.12	20
1.287	17	1.959	3	1.963	5	3.34	10	3.09	40
1.233	4	1.866	25	1.861	25	3.02	87	3.04	20
1.0674	2	1.778	2			2.65	20	2.97	40
0.9795	4	1.714	8	1.711	10	2.54	5	2.93	30
0.9548	3	1.581	14	1.581	15	2.49	5	2.85	10
0.8715	3	1.505	20	1.504	20	2.41	5	2.72	30
0.8216	3	1.418	12	1.416	10	2.34	5	2.56	10
		1.410	15	1.407	15	2.15	8	2.42	60
		1.375	19	1.376	15	1.93	8	2.39	80
		1.304	7	1.303	5	1.71	15	2.32	50
		1.265⎫	6	1.262	5	1.66	5	2.23	50
		1.262⎭	7			1.61	5	2.19	10
		1.1961	2			1.50	10	2.12	10
		1.1697⎫	5			1.43	5	2.09	30
		1.1620⎭	3			1.37	8	2.01	10
ASTM Card 5-0667 Cu Kα_1 Radiation		ASTM Card 5-0661 Cu Kα_1 Radiation		Norelco Spectrometer Cu Kα 1° slit scanned at 2° per minute with 1/2 second time constant.		ASTM Card 1-0054 Mo Kα Radiation		ASTM Card 8-163 Cu Kα Radiation	

*It should be noted that some types of x-ray equipment, particularly cameras, are not able to resolve the most intense lines of CuO. In such cases the lines have the apparent d-values and intensities stated as Routine Determination.

Table A6
Tabulation of X-Ray Diffraction Data of
Crystalline Magnesium Phosphate
Mixtures Initially Precipated at a pH
of 10.6 and Higher

Mg-PO$_4$ Slurry (boiled one hour)		Mg-PO$_4$ (reacted in capsule)	
d(A)	I/I$_o$	d(A)	I/I$_o$
6.81	80	7.3	40
5.79	100	5.8	10*
4.29	90	5.12	10*
3.61	10	4.82	10
3.386	15	4.50	30
3.22	5	4.17	10*
2.919	40	3.88	30*
2.882	90	3.75	30
2.753	10	3.66	30
2.660	10	3.42	20
2.486	5	3.34	40
2.390	20	3.24	10
2.325	5	3.17	70
2.189	5	2.95	80*
2.083	5	2.837	100
1.988	5	2.753	90*
1.836	10	2.642	30
1.806	10	2.547	30
1.685	20	2.513	30
1.614	5	2.460	10
1.569	5	2.378	20
1.309	20	2.366	10

*These lines were also present in patterns
of mixtures taken from the heated sur-
faces of loops. Over a period of a year
at room temperature the compound which
gave these lines vanished, and a new
series of lines corresponding to those of
Mg$_3$(PO$_4$)$_2$·8H$_2$O appeared. The rest of
the pattern did not change.

Table A8
X-Ray Powder Diffraction Data for Secondary Magnesium Orthophosphate and Its Hydrates

MgHPO$_4$·3H$_2$O (newberyite)		MgHPO$_4$* (from hydrate heated to 150°C)	
d(Å)	I/I$_o$	d(Å)	I/I$_o$
5.94	70	8.75	40
5.37	45	7.19	30
5.12	5	6.55	100
4.72	70	5.37	10
4.62	15	3.83	50
4.50	35	3.46	40
4.15	35	3.195	40
3.70	10	3.035	60
3.66	15		
3.59	15		
3.49	85		
3.195	15		
3.087	90		
3.046	100		
2.811	30		
2.794	30		
2.728	40		
2.583	40		
2.527	10		
2.434	5	(very weak pattern)	
Spectrometer Cu Kα Radiation		Spectrometer Cu Kα Radiation	

*The anhydrous material was hygroscopic, and the hydrate x-ray pattern returned after the specimen had stood open to the air overnight.

Table A7
X-Ray Powder Diffraction Data for Tertiary Magnesium Orthophosphate and Two of Its Hydrates

Mg$_3$(PO$_4$)$_2$·8H$_2$O (synthetic bobierrite*)		Mg$_3$(PO$_4$)$_2$·5H$_2$O† (reagent)		Mg$_3$(PO$_4$)$_2$ (reagent ignited at red heat)	
d(Å)	I/I$_o$	d(Å)	I/I$_o$	d(Å)	I/I$_o$
10.5	5	8.7	40	5.60	10
8.7	5	7.2	20	4.35	30
7.9	30	6.5	100	4.31	25
6.95	35	4.8	30	4.17	25
6.70	100	4.21	30	4.11	30
4.84	5	3.83	65	3.86	85
4.31	10	3.19	30	3.66	30
3.93	5	2.94	55	3.46	100
3.83	10	2.89	30	3.21	15
3.59	5	2.84	85	2.99	15
3.184	15	2.71	15	2.79	15
3.149	10	2.58	20	2.54	25
3.009	10	2.55	20	2.51	25
2.945	40	2.42	20	2.43	30
2.757	5	2.36	45	2.34	10
2.688	35	2.21	20		
2.619	5	2.10	20		
2.521	25				
2.424	15				
2.415	15				
2.313	5				
2.252	5				
2.210	10			(intense pattern)	
Spectrometer Cu Kα Radiation		Spectrometer Cu Kα Radiation		Spectrometer Cu Kα Radiation	

*Prepared by suspending Mg$_3$(PO$_4$)$_2$·5H$_2$O in water overnight.
†Specimen lost 21.9% of its weight on ignition (theoretical = 25.5%).

Table A9
The Identification of a Deposit Containing Magnesium,
Calcium, Iron, and Phosphate

X-Ray Powder Pattern of Material Submitted for Analysis		$MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$ (from Table A10)		$\alpha\text{-}Fe_2O_3$ (hematite) (from Table A1)		$Ca_5(PO_4)_3(OH)$ (hydroxylapatite) (from Table A4)	
d(A)	I/I₀	d(A)	I/I₀	d(A)	I/I₀	d(A)	I/I₀
8.0	10					8.2	11
5.79	50	5.81	70				
4.80	100	4.81	100				
4.15	65	4.14	95				
4.06	20	4.06	25				
3.88	15					3.88	9
3.75*	20						
3.70	10	3.69	5	3.68	70		
3.64	15	3.645	20				
3.42	20					3.44	40
2.97	45	2.974	25				
2.89	35	2.893	80				
2.81	35					2.814	100
2.77	20					2.778	60
2.72	30					2.720	60
2.69	35			2.69	100		
2.64	20	2.642	30				
2.62	25					2.631	25
2.56	5	2.569	5				
2.52	10			2.51	80		
2.49	5	2.498	5				
2.45	15	2.465	20				
2.41	10	2.415	25				
2.38	5	2.390	25				
2.35	10	2.362	30				
2.30⎫	20	2.307	35				
2.29⎭	20					2.296	7
2.26	20	2.263	25			2.262	20

*This line was not accounted for.

Table A10
X-Ray Powder Diffraction Data
for $MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$

$MgO \cdot Mg_3(PO_4)_2 \cdot xH_2O$ (slight excess of phosphate)	
d(A)	I/I_o
6.27	10*
5.81	70
4.81	100
4.15	95
4.06	25
3.69	5
3.645	20
2.974	25
2.893	80
2.642	30
2.569	5
2.498	5
2.465	20
2.415	25
2.390	25
2.362	30
2.307	35
2.263	25
Spectrometer Cu Kα Radiation	

*Residual $Mg_3(PO_4)_2 \cdot 5H_2O$.