The Nature and Distribution of Fluorine in the Hydrochloric Acid Processing of Florida Phosphate Pebble.

Curtis Locke Meredith

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://repository.lsu.edu/gradschool_disstheses

Recommended Citation

This Dissertation is brought to you for free and open access by the Graduate School at LSU Scholarly Repository. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Scholarly Repository. For more information, please contact gradetd@lsu.edu.
This dissertation has been microfilmed exactly as received

MEREDITH, Curtis Locke, 1932—
THE NATURE AND DISTRIBUTION OF FLUORINE IN THE HYDROCHLORIC ACID PROCESSING OF FLORIDA PHOSPHATE PEBBLE.

Louisiana State University, Ph.D., 1965
Chemistry, general

University Microfilms, Inc., Ann Arbor, Michigan
THE NATURE AND DISTRIBUTION OF FLUORINE IN THE HYDROCHLORIC ACID PROCESSING OF FLORIDA PHOSPHATE PEBBLE

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

Curtis Locke Meredith
B.A., David Lipscomb College, 1954
M.S., Louisiana State University, 1962
May, 1965
ACKNOWLEDGEMENT

It is a pleasure for the writer to express sincere appreciation to Dr. Hulen B. Williams, who guided this research, for his many contributions and helpful suggestions.

Gratitude is acknowledged to The Dow Chemical Company for their financial support. Particular note is taken of the pleasant association with and assistance of Mr. L. D. Hoblit of the Louisiana Division and Dr. E. R. Wright of the Texas Division.

The generosity of the Dr. Charles E. Coates Memorial Fund of the L.S.U. Foundation, donated by George H. Coates, in defraying part of the expense of manuscript preparation is gratefully acknowledged.

Finally, the writer must make known the debt owed his wife. As a test of a wife's patience and understanding, few things compare with a husband in graduate school. She not only endured, but encouraged, assisted, and inspired.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL METHODS</td>
<td>11</td>
</tr>
<tr>
<td>III. EXPERIMENTAL DATA AND DISCUSSION ON OF RESULTS</td>
<td>24</td>
</tr>
<tr>
<td>IV. CONCLUSIONS</td>
<td>106</td>
</tr>
<tr>
<td>V. SELECTED BIBLIOGRAPHY</td>
<td>112</td>
</tr>
<tr>
<td>VI. VITA</td>
<td>116</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Representative Analysis of Florida Land Pebble</td>
<td>29</td>
</tr>
<tr>
<td>II</td>
<td>X-Ray Diffraction Pattern of Florida Land Pebble</td>
<td>30</td>
</tr>
<tr>
<td>III</td>
<td>Fluorine Distribution Between Residue and Liquor</td>
<td>33</td>
</tr>
<tr>
<td>IV</td>
<td>Liquor Extraction Results</td>
<td>36</td>
</tr>
<tr>
<td>V</td>
<td>X-Ray Pattern of the Residue</td>
<td>45</td>
</tr>
<tr>
<td>VI</td>
<td>Digestion Results in the Presence of Various Substances</td>
<td>58</td>
</tr>
<tr>
<td>VII</td>
<td>Effect of the Amount and Concentration of Digestion Acid on the Fluorine Distribution</td>
<td>66</td>
</tr>
<tr>
<td>VIII</td>
<td>Initial Analytical Data of Heated Residues</td>
<td>71</td>
</tr>
<tr>
<td>IX</td>
<td>Analytical Data of Heated Residue Samples</td>
<td>74</td>
</tr>
<tr>
<td>X</td>
<td>Results of Elemental Analysis</td>
<td>76</td>
</tr>
<tr>
<td>XI</td>
<td>Analytical Data on Dynamically Heated Residue</td>
<td>83</td>
</tr>
<tr>
<td>XII</td>
<td>Results Calculated from the Data of Table XI</td>
<td>83</td>
</tr>
<tr>
<td>XIII</td>
<td>Molar Composition of the Residue</td>
<td>94</td>
</tr>
<tr>
<td>XIV</td>
<td>Normalized Molar Composition of the Residue</td>
<td>97</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thermogram of the Digestion Residue</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>Thermogram of CaSO₄·2H₂O</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>Thermogram of CaSiF₆·2H₂O</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>Thermogravimetric Curve of CaSiF₆·2H₂O</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>Effect of the Acid to Ore Ratio on the Fluorine Distribution and Quantity of Residue</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>Thermogram of the Digestion Residue</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>Thermogravimetric Curve of the Digestion Residue</td>
<td>81</td>
</tr>
</tbody>
</table>
ABSTRACT

An industrial method of phosphoric acid production exists that employs hydrochloric acid for phosphate ore digestion followed by liquid-liquid extraction for separation of phosphoric acid from the crude reaction mixture. Fluorine is an important constituent of phosphate ore but its presence as an impurity in phosphoric acid is usually objectionable. Investigation of the hydrochloric acid/extraction process was undertaken to determine the fluorine distribution between the insoluble residue and digestion liquor, the distribution between the liquor and various organic phases associated with the extraction processes, the effect of variables associated with these distributions, and the formation and chemical nature of the insoluble residue.

Digestion with a slight excess of acid placed slightly over half of the fluorine in the residue, but this distribution was markedly altered by the addition of fluorine-complexing agents and barium to the digestion medium. As the acid:ore ratio decreased, the reaction of the ore was less complete, the amount of residue increased,
and the amount of fluorine in the residue increased. At a
given acid:ore ratio, a more concentrated digestion medium
resulted in a more efficient acid-ore reaction and more
insoluble fluorine. Increased calcium concentration in the
digestion medium was particularly effective in precipitating
fluorine.

The fluorine distribution between the aqueous
digestion liquor and tributylphosphate (TBP) was determined.
It was apparent from this work, where approximately thirty
percent of the total fluorine was placed in the organic phase
by a single extraction, that practically all of the soluble
fluorine would be extracted by a continuous, countercurrent
process.

A particularly interesting discovery was the
quantitative and specific nature of the extraction of HBF₄,
to the exclusion of HBF₃(OH), by an alamine solution.
Digestion of the ore in the presence of borax, followed by
amine extraction of the boron containing liquor prior to
TBP extraction, caused very little change in the fluorine
content of the TBP phase when compared to a normal digestion
and extraction. The equilibrium and reaction rate between
the two boron fluorides place a restriction on the amount of
fluorine that can be extracted by the alamine.
Characterization of the insoluble fluorine compound was the most fundamental result of this investigation and probably the most important contribution to understanding the distribution of fluorine between the residue and liquor.

The residue mainly consisted of a single compound, of high fluorine content, that was not an original constituent of the ore, but was formed in and precipitated from the digestion medium. The properties of the residue compound were not those of the more common fluorine compounds that one might expect to find in the residue. Elemental analysis of the residue was interpreted to include the elements of the more common compounds in the correct stoichiometric quantities. Digestion results in the presence of various substances indicated that precipitation of the residue components were interrelated.

The residue compound was characterized by X-ray diffraction, differential thermal analysis, thermogravimetry, and by other physical and chemical means. The decomposition characteristics of the compound, as determined by DTA, TGA, and elemental analysis, were interpreted in terms of a complex mineral-like structure. All experimental observations supported the existence of a compound of this type rather than the independent simultaneous precipitation of the individual components.
Elemental analysis of the residue led to the proposed formula

$$\text{CaSO}_4 \cdot 1.5 \text{CaSiF}_6 \cdot \text{AlF}_3 \cdot \text{CaF}_2 \cdot 12 \text{H}_2\text{O}.$$ 

No compound of this formula or properties has been previously reported, and attempts to prepare the compound under conditions other than digestion of the phosphate ore were unsuccessful. It was concluded that substitution of the ionic components of the residue compound into the decaying apatite structure may be the mechanism by which it is formed.
CHAPTER ONE
INTRODUCTION

This research was concerned with the fluorine distribution between the crude phosphoric acid and the insoluble residue that result from the hydrochloric acid digestion of Florida phosphate pebble, and with the form of the fluorine in these two phases. The distribution of the fluorine between phosphate liquors and organic phases that resulted from various extraction procedures were also investigated.

Phosphatic substances in the form of fish, bones, and guano have been utilized as fertilizers since the beginning of recorded history and today fertilizer still accounts for most phosphate production. As the chemistry and technology of ore treatment advanced, natural phosphate deposits replaced these earlier sources and in a little more than a century commercial phosphate production has reached three billion pounds (as phosphorus) per year. A comprehensive history of the development of the chemistry and technology of the phosphate industry is found in "Phosphorus and Its Compounds,"¹ John R. Van Wazor, editor, and "Phosphoric Acid,

Phosphates, and Phosphate Fertilizers"\(^{2}\) by W. H. Waggaman. These two sources provided much of the background material presented here.

Phosphate is an almost universal constituent of igneous rocks as a fraction of a per cent. Despite the fact that "Dana's System of Mineralogy"\(^{3}\) lists almost two hundred phosphate minerals, only one mineral family—the apatites, \(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{Cl},\text{F})_2\)—represents by far the major amount of phosphorus in the crust of the earth. Although phosphate minerals are found as concentrated igneous deposits, the majority of those deposits which are sufficiently rich for mining are marine or sedimentary deposits. It is believed by some that all phosphates are of igneous origin, but that weathering and dissolution, followed by redeposition, led to the sedimentary formations. The concentration of the sedimentary phosphates from dilute sea water has been described by Emigh\(^{4}\) as the phosphatization of aragonite \((\text{CaCO}_3)\) pellets on the ocean floor by the apatite saturated water with the resulting formation of the insoluble carbonate apatite, francolite. The fluorine necessary for the


francolite formation is believed to have originated from volcanic activity.\(^5\)

There are four primary types of phosphate deposits, presumably formed in the following ways. The **igneous deposits** consist of fluorapatite, \([\text{Ca}_10(\text{PO}_4)_6\text{F}_2]\), formed by differentiation from cooling basic magma. The francolite, \(\text{CaF(Ca,C)}_4[\text{P,C}(0,\text{OH,F})_4]\) or \([\text{Ca}_3(\text{PO}_4)_2]\)\(_3\)\(\text{CaF}_2\cdot\text{XCaCO}_3\), of the **marinol deposits** was constituted by phosphate replacement of carbonate in aragonite pellets. The replacement of limestone or clay by phosphate from overlying marine phosphorites or guano produced the francolite and hydroxy apatite, \([\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2]\), and other minerals of the **phosphate rock deposits**. The **guano deposits** consist of hydroxy apatite and other minerals formed from accumulations of sea fowl or bat excreta.

The land pebble phosphate fields of west central Florida are fairly complex marine deposits. The lower Hawthorne formation (Miocene) consists of residual phosphorites left behind after decay of slightly phosphatic marine limestone. The overlying Bone Valley formation (Pliocene) is composed of phosphate released by weathering of the cementing carbonate of the lower Hawthorne formation. The phosphate thus released was later concentrated mechanically by the action of surface water. Above these phosphate matrices

lies the leached zone, an overburden of sand mixed with phosphatic clays. These clays, mostly wavelite, 
\[ \text{[Al}_3\text{(OH)}_3\text{(PO}_4\text{)}_2\cdot5\text{H}_2\text{O]} \], and pseudowavelite, \[ \text{[CaAl}_3\text{(PO}_4\text{)}_2\text{(OH)}_8\cdot\text{H}_2\text{O]} \], were formed by weathering of the upper part of the Bone Valley formation.

Approximately 70% of the phosphate production is used for phosphate fertilizer, most of which is manufactured through some modification of the century old Lowes method of treating the ore with sulfuric acid. In this process the insoluble apatite is formed into an acid slurry, which during continued digestion, hardens to a granular mixture of citrate soluble monocalcium phosphate, \( \text{Ca(H}_2\text{PO}_4\text{)}_2 \), and anhydrite, \( \text{CaSO}_4 \). This mixture is known as superphosphate. Enriched superphosphate may be obtained by partial substitution of phosphoric for sulfuric acid in the digestion. The use of phosphoric acid alone yields triple superphosphate which is mostly the water soluble dicalcium phosphate, \( \text{CaHPO}_4 \).

Minor modifications of the basic process which yields superphosphate fertilizer leads to the so called "wet process" for the production of phosphoric acid. Although in 1954 nearly equal quantities of phosphoric acid were produced by the wet process and electric furnace methods, in 1964 two-thirds of the three million tons \((\text{P}_2\text{O}_5)\) of phosphoric acid produced came from the wet process.\(^6\) In fertilizer production,

the amount and concentration of sulfuric acid is adjusted to obtain complete reaction with the ore and to form a dry product, whereas in phosphoric acid production, the digestion slurry is maintained at a fluid consistency by the addition of weak recycled phosphoric acid. The gypsum, CaSO₄·2H₂O, formed during the digestion is separated from the crude phosphoric acid by filtration. Most of this wet process acid is used captively for the production of fertilizer and sodium phosphates. Phosphoric acid made by oxidation of elemental phosphorus condensed in the electric furnace is used chiefly for the production of phosphate derivatives and particularly for applications where high purity is necessary.

A method of phosphoric acid production has recently been developed that employs hydrochloric acid for the ore digestion and liquid-liquid extraction for the phosphoric acid separation. A detailed description of this process, which is the basis of the present work, is presented following a discussion of some of the more important problems associated with the older methods of ore treatment.

A major disadvantage of the Lowes process of superphosphate production is the large quantity of calcium sulfate in the final product which materially increases the handling and transportation cost. Triple superphosphate, with its higher phosphate content, overcomes this disadvantage but phosphoric acid, usually wet process acid, is required for its production. A more economical means of obtaining crude
phosphoric acid could therefore receive wide application in the fertilizer industry.

Calcium sulfate formed in the manufacture of phosphoric acid by the wet process is one of the basic problems of production. The separation of the dihydrate by filtration is, in some plants, the limiting factor in plant capacity. Many of the controls necessary in the digestion of the ore are for the express purpose of obtaining an easily filterable form of the dihydrate. Formation of calcium sulfate on the surface of the ore particles at high acid to ore ratios reduces the reaction rate and places a practical restriction on the ratio used for the digestion. The factors which prevent the production of a crude acid with a $P_2O_5$ content greater than 33% can ultimately be traced to calcium sulfate formation. The amount of dihydrate formed during the digestion is slightly in excess of the ore used. Disposal itself is a problem of some magnitude.

A considerable amount of heat is evolved in the wet process digestion procedure and cooling is required in some cases. The temperature reached during the digestion causes volatilization of about 15% of the fluorine in the ore and magnifies the problems connected with this ore component. Approximately one-half the heat released is due to dilution of the sulfuric acid.

Fluorine not only occupies a prominent role in the geological formation of the phosphate deposits but its presence is quite evident in the processing of phosphate rock and is
usually objectionable in the final product. It is ironic that the element that is in a large measure responsible for the accumulation of the phosphate deposits, through the formation of the insoluble fluorapatites, should be so detrimental to the end uses of the phosphate. The transformation of the insoluble fluorapatite into a concentrated "available" phosphate is the main concern of phosphate fertilizer industry. The fluorine content of phosphate ores averages 0.110 parts of fluorine per part of $P_2O_5$ with a variation from 0.06 to 0.15 parts in ores from different locations. The fluorine required by the stoichiometry of fluorapatite is 0.095 parts. The elimination of this fluorine is necessary for those end uses that involve human consumption and low fluorine levels are required for animal nutrition uses. The cost of phosphate products is increased because of the necessity for removal and disposal of fluorine.

The toxicity of fluorine and its compounds in many cases requires the installation of costly and elaborate water scrubbing systems and dust collecting equipment that must be operated and monitored continuously. The magnitude of this problem is indicated by the one-half million tons of fluorine handled by the phosphate industry in 1957. Only a small fraction of this amount was recovered and it has been estimated that the fluorine discarded annually in phosphate manufacture was equal to the tonnage of fluorine mined.\(^7\)

The importance of fluorine in phosphate manufacture is reflected in the rather voluminous literature dealing with its elimination and disposal in the older methods of phosphate production.

The acidulation of phosphate rock with hydrochloric acid has long been known and a patent was issued on this process in 1936. Initially, utilization of the process was commercially impractical since both the phosphoric acid and calcium chloride formed in the reaction were soluble in the aqueous medium, and their separation was extremely difficult by then known procedures. Development of liquid-liquid extraction of the phosphoric acid with alcohols proved to be an economical method of separation and was patented by the Israeli Mining Industries, Tel Aviv. The use of tributylphosphate as the organic phase was a refinement introduced by the Dow Chemical Company. The acid produced contains 80% phosphoric acid, equivalent to 58% P$_2$O$_5$, compared to 32-42% P$_2$O$_5$ obtained from the conventional wet process and in addition is said to be of higher purity.

---

There are a number of advantages of the hydrochloric acid-solvent extraction process: (1) use of hydrochloric acid in areas where a cheap source is available, (2) a faster reaction of acid with ore is obtained, (3) elimination of the filtration step and handling of solid calcium sulfate is achieved, (4) an economical means of obtaining a crude acid for triple superphosphate manufacture is presented, and (5) a more concentrated acid that is competitive with conventional wet process acid in pure acid applications is obtained. Two industrial plants presently are known to be using hydrochloric acid-solvent extraction process. One is operated by the Dow Chemical Company and the other by the Israeli Mining Industries.

No investigation has previously been reported on the behavior of the fluorine from phosphate ore under the conditions that occur in the hydrochloric acid-solvent extraction process of phosphoric acid production. One objective of the research reported here was to determine the fluorine distribution between the residue and liquor during the acid digestion of Florida land pebble phosphate, the variables related to this distribution, and possible methods of elimination and recovery of the by-product fluorine. A second objective was to determine the fluorine distribution between the crude phosphoric acid, or liquor, and tributyl phosphate, and also between other aqueous-organic systems that arise from the extraction process. A third problem,
one related to the first objective and fundamental to the hydrochloric acid-extraction process, was the question of the chemical nature of the residue that remained after digestion of the ore. This too was investigated.
CHAPTER II
EXPERIMENTAL METHODS

The materials used in this work were, for the most part, normal laboratory reagents available from a number of commercial sources. One reagent, alamine 336, primarily a tricaprylyl amine, was a product of General Mills, Inc., Chemicals Division. A full description of the phosphate ore, a high grade Florida land pebble flotation concentrate, is given in Chapter III.

The liquid-liquid extraction procedures were simple and employed a separatory funnel for agitation and separation of the two phases. When the crude phosphoric acid liquor was extracted with tributylphosphate, equal volumes of the two phases were used. In those cases where the liquor was extracted with a five percent solution of alamine 336 in toluene, two and one-half volumes of the alamine solution were used for each volume of the liquor. In most cases where the fluorine distribution between phases was to be determined, an entire phase was quantitatively recovered and analyzed.

Petrographic examination was done with a Bausch and Lomb petrographic microscope. Index of refractions were determined by noting the Becke line movement in a series of standard immersion oils.
Mass spectra data of the gaseous decomposition products of the digestion residue were obtained with a spectrograph, Model 21-620, manufactured by the Consolidated Engineering Company. The gas collection apparatus was arranged to provide simultaneous gas evolution analysis and differential thermal analysis.

The ore digestion procedure employed a 26% solution of hydrochloric acid for the phosphate pebble digestion, 255 ml of acid per 100 g of ore. This was sufficient acid to react with 100 g of Ca₃(PO₄)₂ plus a 5% excess. No difference in fluorine distribution between residue and liquor was observed when glass or polyethylene vessels were used as the reaction containers. The digestion was normally conducted by slowly adding the ore to the acid solution with vigorous stirring. Hydrogen sulfide was evolved during the reaction. The digestion mixture was allowed to settle five to ten hours after which the major portion of the liquor was removed by decantation. The remaining liquor was separated from the solid residue by filtering through the use of a medium fritted glass crucible and aspiration. Initially, the residue was thoroughly washed and dried at 100-110°C, but it was later found necessary to dry the residue under vacuum without heat to prevent decomposition of residue components. The weight of the residue normally amounted to 10% of the ore digested.

The liquor normally had a light yellow color following digestion; however, there was a reversible change
to light green on dilution. When the liquor was allowed to
stand for one to two weeks, a flocculent precipitate formed.
This appeared to be hydrous silica and has been interpreted
by Fox and Hill\(^1\) to be due to the hydrolysis of SiF\(_6\)\(^-\) and
the formation of a soluble aluminum fluoride.

**X-ray analyses** were obtained with a Norelco instru-
ment made by Philips Electronics, Inc. A wide range
goniometer, scintillation counter, and recorder were used
for the signal detection and display. A copper target was
used for the radiation source with a nickel filter just be-
fore the detector. The instrument settings were:

- Rate of scan: 1°/minute (26)
- Time constant: 4
- Slits: 1°, 0.006 inches
- Multiplier: 0.6
- Scale factor: 2

Powdered samples were used in all cases. Identification of
powder diffraction patterns was made by comparison with those
in the ASTM X-ray Powder Data File.

**Differential thermal analysis** and **thermogravi-
metric analysis** utilized the DuPont 900 DTA and 950 TGA
instruments. Samples of approximately 3 mg were used in the
DTA work and 10-50 mg samples were used in the TGA studies.

\(^1\) E. J. Fox and W. L. Hill, *Agric. and Food Chemistry*,
Heating rates of 20°C per minute were used in both cases although the measured heating rate decreased above 800°C with the TGA instrument.

Because of the different sample arrangements of the DTA and TGA instruments with respect to a purging gas stream, small but discernible differences were noted in the reaction temperature when gaseous products were evolved. The DTA samples were placed in the bottom of a one inch, 2 mm OD tube and gases produced by a reaction were removed from the sample primarily by thermal expansion and diffusion. A purging gas stream moved directly over the TGA sample, and gaseous products were removed much more efficiently. The TGA reaction temperatures were slightly lower due to the decreased vapor pressure of the decomposition products.

A rapid chemical attack on the chromel-alumel thermocouples occurred when residue samples of the acid/ore reaction were heated to the fusion temperature, about 700°C. To prevent failure of the thermocouples, which failed after only one run, the thermocouples were placed in 2 mm OD glass tubes with glass beads as a heat transfer medium. The glass enclosed thermocouple was then inserted in a 4 mm OD tube which contained the sample. The reference thermocouple was similarly arranged. Glass beads were used as a reference material in all DTA experiments.

The analytical procedures used in this study were, for the most part, recognized and proved methods. Only a general description of the methods, along with the
reference(s), will be given unless the published procedure was modified to conform to the system involved.

**Fluorine analysis** played a major role in this investigation and was the most important single source of information. During the course of this work some ninety-five quantitative fluorine analyses were made, each of which required from two to two and one-half hours.

Two methods were used for the qualitative determination of fluorine. The hanging drop test was used for the specific detection of gaseous $\text{SiF}_4$ through observation of gelatinous silica produced by fluosilicate hydrolysis in a drop of water.² The second qualitative test also depended on $\text{SiF}_4$ evolution, usually brought about by heating the sample in the presence of sulfuric acid and $\text{SiO}_2$. The gases were partially absorbed in a drop of NaCl solution, the drop evaporated, and detection of fluorine made by observation of the six pointed stars or hexagonal crystals of NaSiF₆. The test limit was given as 10 μg of fluorine.³

The method used for the quantitative analysis of fluorine was that first proposed by Willard and Winter,⁴ but


with a modified titration procedure. Fluorine, as SiF₄ or H₂SiF₆, was steam distilled from a perchloric acid solution at 135°C to prevent interference in the titration step. Aliquots of the distillate were titrated with thorium nitrate solution using sodium alizarin sulfonate as the indicator. Thorium, which forms a strong fluoride complex, gives a pink color with the indicator when all fluorine has been complexed. A detailed description of the procedure is given in Methods Used and Adopted by the Association of Florida Phosphate Chemists.

The procedure as described was primarily designed for solid samples. Difficulty was encountered with liquid samples, particularly when sulfuric acid replaced perchloric acid in the distillation. This substitution was necessary when the liquid samples contained organic material. When digestion liquor samples were added to the sulfuric acid, considerable heat was produced by the dilution, a copious quantity of CaSO₄ precipitated, and a considerable amount of HCl was evolved. Up to fifty percent of the fluorine was evolved at the same time. To prevent loss of fluorine through the neck of the distillation flask, pipettes and separatory funnels used to admit liquid samples were fitted with stoppers to provide an air-tight seal. Due to a lack of steam flow through the system, fluorine could also be lost.

5 M. P. Matuszak and D. R. Brown, Ibid., 17, 102 (1945).
6 Methods Used and Adopted by the Association of Florida Phosphate Chemists, (1960).
through an open condenser. The condenser was therefore fitted with an adaptor that extended into a slightly basic solution. Silver sulfate was also added to the distillation to prevent HCl evolution and the sweeping action it produced.

A second modification of the basic procedure was necessary when samples which contained boron and aluminum were analyzed. Due to the strong fluoride complexes formed by boron and aluminum, a higher distillation temperature was required for fluosilicate evolution. The necessary temperature was achieved by a tandem double distillation, the first from sulfuric acid at 160-165°C and the second from perchloric acid at 135°C. A distillate of 350 ml was collected under these conditions.

Since the conclusions of this investigation depended quite heavily on fluorine analysis, numerous checks of the techniques were made to insure accurate results. At least three aliquots of each distillate were titrated; additional aliquots were titrated if the titration volumes differed by more than 0.05 ml.

Fluoborate analyses utilized nitram, 4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole, for the

---

8 W. Lange, Ber., 59, 2107 (1926).
gravimetric determination of HBF$_4$. The procedure as published was followed in those cases where the analyzed sample did not contain chlorine. The published procedure could not be followed in samples such as the digestion liquor that contained a high chloride ion concentration. When attempts were made to precipitate nitron·HBF$_4$ from boron fluoride containing liquors, the entire precipitating solution formed a gel. On drying, the precipitate was observed to have two melting regions, at 230° - 240°C and 252° - 257°C. The reported melting point of crystalline nitron·HBF$_4$ was 227.5°C and a sharp melting point of 230.0 was observed for crystals precipitated from a NaBF$_4$ solution. Crystals that precipitated from a liquor that contained no HBF$_4$ and from a CaCl$_2$ solution were found to melt at 256-258°C and 250-265°C, respectively. It was possible to "melt" the gel by raising the temperature of the ice cold precipitating solution to 50°C, but the gel again formed in 100 ml of solution at approximately 10° above room temperature.

The nitron·HBF$_4$ crystals were recovered from boron-liquor samples in the following manner. The initial precipitation was made at 0°C from 100 ml of solution as recommended. The resulting gel was dried at 105°C for 24 hours and then dissolved by heating in 400 ml of nitron·HBF$_4$ saturated (room temperature) water. The green crystals (m.p. 227° - 231°C) were recovered after the solution had cooled to room temperature. When the suggested solubility
correction of 18.9 mg per 100 ml was applied to the total of nitron·HBF$_4$ precipitated, it is so indicated in Chapter III.

A *separation scheme* was required prior to the analysis for some of the components of the digestion residue. X-ray analysis indicated that fluorine, sulfate, calcium, and SiO$_2$ were present in the residue. Chlorine, phosphate, and elemental carbon were suspected due to the composition of the ore and the digestion medium. A spectrographic analysis, obtained by courtesy of Dow Chemical Company, Louisiana Division, indicated that aluminum, iron, and titanium were present in significant amounts and identified Be, B, Cr, Cu, Mg, Mn, Ni, and Na as trace elements. No attempt was made to obtain quantitative data for the trace elements.

The separation scheme used for analysis of the residue was almost identical to a scheme that has since been reported for analysis of phosphate rock.$^{10}$ An added complication was the presence of a large amount of fluosilicate in the residue. As was shown by qualitative analysis and other data, fluosilicate accounted for about one-half of the silicon content of the residue. It was necessary to ignite the residue prior to other elemental analyses to prevent interference from the hydrous silica formed by fluosilicate hydrolysis.

The SiO₂ and insoluble silicate content, reported as SiO₂, was determined gravimetrically after ignition by H₂SO₄/HF treatment. The residue was then treated with a HNO₃/HCl solution, one part each of concentrated nitric acid, hydrochloric acid, and water, then twice taken to dryness to expel fluorine. A few drops of H₂SO₄ or HClO₄ were added in the last evaporation. The remaining solids were then dissolved with hydrochloric acid and the solution diluted. Sodium carbonate or pyrosulfate fusion was used, if necessary, to obtain complete solution. The solution so obtained was used for iron, titanium, calcium, sulfate and phosphate analysis, with the stipulation that no sulfate be introduced if that analysis was to follow. Iron was determined colorimetrically as the 1,10-phenanthroline complex at 508 μm, and titanium, also colorimetrically, with hydrogen peroxide at 425 μm. A Beckman DU spectrophotometer was used in both analyses.

Calcium, sulfate, and phosphate were determined gravimetrically; calcium as the sulfate after precipitation.

---

11 Methods, op. cit., p. 40


13 Ibid., p. 870.
from an alcoholic solution, sulfate as barium sulfate, and phosphate as the molybdate (dried at 110°C). Even though calcium was not supposed to interfere with the titrimetric method used for aluminum, a sharper end point with improved reproducibility was obtained if calcium was first removed. Aluminum, iron, and titanium were separated from the other components of the residue solution by a double benzotri precipitation. The separation of iron and titanium from aluminum was achieved by precipitation with cupferron, nitrosoephelhydroxylamine. In retrospect, it is believed that the two metals could have been separated from aluminum just as efficiently, and in less time, by \( \text{CCl}_4 \) extraction of the cupferron complexes.

Aluminum was determined by a method first proposed by Sajo. The procedure employed a back titration of excess EDTA with a zinc solution followed by a replacement titration after addition of fluoride. The ferro-ferricyanide/3,3'-dimethylphosphitic redox indicator provided a sharp end point with a pH-5 buffer.

The water and elemental carbon contents of the residue were determined with a Coleman, Model 33, Carbon-Hydrogen Analyzer. An ignition temperature of 750°C was used.

Chlorides were determined gravimetrically as AgCl. The analysis was carried out on a solution obtained by heating the residue in a slightly basic solution at ninety degrees for one hour.

The analyses for the total silicon content of the residue by the usual wet chemical methods were unsatisfactory. Analyses for the \( \text{SiO}_2 \) content of the residue, after ignition of the sample showed good precision, but scattered results were obtained for the total silicon content. The poor precision was quite obviously caused by only a partial recovery of that silicon originally present as flusilicate.

References:

14 Methods, op. cit., p. 33.
15 Ibid., p. 42.
16 Ibid., p. 27.
18 Ibid., p. 106.
Dissolution of the sample was achieved by heating in an HCl/\nH_3BO_3 solution, followed by repeated evaporation to dryness

to precipitate hydrous silica and evolve fluorine as boron

trifluoride. In view of the high fluorine content of the

residue, it was not surprising that some fluorine was evolved

as silicon tetrafluorine. The insoluble silicon was
determined gravimetrically by H_2SO_4/HF treatment. In those
cases where a total silicon content is indicated, the highest
value obtained by the wet chemical method is quoted. Silicon
values for two samples were obtained by neutron activation
analysis through the courtesy of Dr. Frank Iddings of Esso
Research Laboratories.
CHAPTER III

EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

The phosphate ore used in this work was a commercial Florida land pebble flotation concentrate mined in the Plant City, Florida area. Calcining of the ore, at a temperature of 650°C, was done by the Louisiana Division of the Dow Chemical Company. Representative analyses of Florida land pebble are given in Table I. Not included in the table are some twenty-four trace metals also present in the ore. Analyses of the calcined ore gave fluorine contents of 3.98, 3.98, 4.03, 4.13, and 4.07% for an average of 4.04%.

The X-ray powder diffraction pattern, Table II, of the ore gave the reflections expected of the apatite crystal structure. The unit cell of the apatites consists of vertical -Ca-O-Ca-O-Ca- columns, crosslinked by oxygen atoms and phosphate groups, which form a hexagonal channel lined with oxygen atoms. Additional calcium and phosphorous atoms lie in holes in the column wall with fluorine, chlorine, or hydroxyl groups occupying the center positions in the channel. This rather complicated structure was first determined by Szabo\(^1\) in 1930, and has been confirmed by a number of

\[^1\] Naray Szabo, *Z. Kristallogr.*, 75, 387 (1930).
The X-ray diffraction pattern of the ore consisted of fifty-one peaks, forty-three of which could be assigned to SiO$_2$ or one of the various apatite forms: fluorapatite, [Ca$_3$(PO$_4$)$_2$]·CaF$_2$; hydroxyapatite, [Ca$_3$(PO$_4$)$_2$]·Ca(OH)$_2$; or francolite, CaF(Ca,C)$_4$[(P,C)(O,OH,F)$_4$]$_3$; as determined by the ASTM X-ray Powder Data File. Of the remaining eight peaks, six had a visual I/Io value of two or less which indicated that components other than the apatites and SiO$_2$ were present in only minor quantities.

By observation of the digestion through a microscope, the quantity of gas released suggests that a considerable amount of the ore was composed of francolite. This agreed with the analysis of the ore and the conclusion of a number of authors.$^{11-14}$ While the structure of the other

---

7 C. A. Beevers, B. D. McIntyre, Mineralogical Magazine, 27, 254 (1946).
13 Methods Used and Adapted by the Association of Florida Phosphate Chemists, (1950).
apatites is firmly established, some controversy exists as to the manner in which carbonate substitutes into the apatite structure to form francolite. Most of those knowledgeable in this field, however, consider the francolite a separate, identifiable, crystallographic species.\textsuperscript{11,15-19}

Another point of controversy related to the ore concerns the chemical nature of the fluorine present. If one assumes that all of the phosphate in the ore is present as fluorapatite, calculations using the phosphate and fluorine analysis of the ore indicate that almost 20\% of fluorine is in excess of that required by the stoichiometry of the crystalline structure. In addition, it has not been possible, in a neutral aqueous medium, to prepare synthetic apatite that contains more than 73\% fluorapatite, the remaining 27\% being present as hydroxyapatite.\textsuperscript{20,21} If the ore used in this work is assumed to contain the fluorapatite to hydroxyapatite ratio indicated above, then 43\% of the fluorine must

\textsuperscript{17} \textit{Industrie Chim. Belg.} 20, Special No., 582 (1955).
\textsuperscript{21} Kirk and Otmer, \textit{op. cit.}, p. 399.
be in some form other than fluorapatite. Excess fluorine is not limited to Florida land pebble as 12-52% in excess of that required for fluorapatite is found in domestic phosphate rock.\textsuperscript{22} Evidence that two different forms of fluorine were present in phosphate rock has been reported in the literature.\textsuperscript{22,23,24} Conflicting claims have been made as to the identity of the second fluorine form with CaF\textsubscript{2} and CaSiF\textsubscript{6} having been suggested.\textsuperscript{25,26,27} Despite the evidence summarized above, it was suggested in the last reference given that all the fluorine in phosphate ore is present as fluosilicate.

Roughly 90\% of the ore exhibited no crystalline character under petrographic investigation, yet the ore was quite crystalline as shown by X-ray diffraction. The pebbles were aggregates of submicroscopic crystalline particles called collophane.\textsuperscript{28} The majority of the pebbles were

\begin{footnotes}
\footnotetext[22]{George R. Mansfield, \textit{Am. J. Sci.}, 238, 863 (1940).}
\footnotetext[24]{F. Coufalik and M. Odehnal, \textit{Chem. Prumysl.}, 7, 465 (1957).}
\footnotetext[25]{Mansfield, \textit{op. cit.}}
\footnotetext[26]{Kirk and Otmer, \textit{op. cit.}, p. 411.}
\footnotetext[27]{E. J. Fox and W. L. Hill, \textit{Agric. and Food Chem.}, 7, 478 (1959).}
\footnotetext[28]{Clifford Fondel, \textit{Am. Mineralogist}, 28, 215 (1943).}
\end{footnotes}
opaque-white but they also existed in a wide range of colors from translucent orange to the clear yellow of the massive fluorapatite crystal. This range of colors was produced by small red and yellow crystals embedded in the white collophane matrix. Also present were a number of red and black particles, clear SiO₂, and other trace minerals.

On calcining, the white amorphous particles turned black and some crystal orientation was produced. These phenomena, however, were largely a surface effect occurring with particles larger than 40 mesh. The black color, which remained in the residue on digestion, was carbon that resulted from carbonization of organic material in the ore. The decrease in digestion frothing brought about by the calcining process was believed to be due to elimination of CO₂ from the ore rather than destruction of the organic compounds. Recent literature data substantiated this conclusion.28 No significant changes in the X-ray pattern were produced by calcining.

A density separation of the ore was attempted in order to remove trace minerals and, hopefully, to achieve isolation of fluorine compounds other than fluorapatite. Since the collophane particles had a wide density range, 2.2-3.2 g/cc, the X-ray patterns of the various density fractions were only slightly different.

---

TABLE I

Representative Analysis of Florida Land Pebble

<table>
<thead>
<tr>
<th>Element</th>
<th>Florida Land Pebble</th>
<th>Florida Land Pebble, Representative</th>
<th>Florida Land Pebble, High Grade</th>
<th>Florida Land Pebble Flotation Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_2O_5)</td>
<td>30-36%</td>
<td>35.5</td>
<td>34.42</td>
<td>36.3</td>
</tr>
<tr>
<td>CaO</td>
<td>46-50</td>
<td>48.8</td>
<td>49.44</td>
<td>48.0</td>
</tr>
<tr>
<td>F</td>
<td>3.8-4.0</td>
<td>4.0</td>
<td>3.52</td>
<td>3.7</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>1.5-4.4</td>
<td>1.7</td>
<td>3.41</td>
<td></td>
</tr>
<tr>
<td>(SO_3)</td>
<td>0.2-1.5</td>
<td>2.4</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>(Al_2O_3)</td>
<td>0.7-1.1</td>
<td>0.9</td>
<td>0.74</td>
<td>1.1</td>
</tr>
<tr>
<td>(Fe_2O_3)</td>
<td>0.7-2.6</td>
<td>0.7</td>
<td>0.77</td>
<td>1.4</td>
</tr>
<tr>
<td>(TiO_2)</td>
<td>0.03-0.08</td>
<td>0.03-0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(SiO_2)</td>
<td>2-10</td>
<td>6.4</td>
<td>5.08</td>
<td></td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>0.25-0.40</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


4 Ibid., p. 1036.

5 The Dow Chemical Company, Louisiana Division, private communication.
**TABLE II**
X-Ray Diffraction Pattern of Florida Land Pebble*

<table>
<thead>
<tr>
<th>d</th>
<th>I/Io (Visual)</th>
<th>d</th>
<th>I/Io (Visual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.04</td>
<td>5</td>
<td>1.795</td>
<td>10</td>
</tr>
<tr>
<td>3.87</td>
<td>5</td>
<td>1.768</td>
<td>10</td>
</tr>
<tr>
<td>3.45</td>
<td>37</td>
<td>1.747</td>
<td>10</td>
</tr>
<tr>
<td>3.16</td>
<td>12</td>
<td>1.726</td>
<td>10</td>
</tr>
<tr>
<td>3.06</td>
<td>15</td>
<td>1.636</td>
<td>3</td>
</tr>
<tr>
<td>2.791</td>
<td>100</td>
<td>1.607</td>
<td>1</td>
</tr>
<tr>
<td>2.700</td>
<td>53</td>
<td>1.503</td>
<td>1</td>
</tr>
<tr>
<td>2.628</td>
<td>25</td>
<td>1.466</td>
<td>3</td>
</tr>
<tr>
<td>2.518</td>
<td>4</td>
<td>1.453</td>
<td>3</td>
</tr>
<tr>
<td>2.291</td>
<td>5</td>
<td>1.423</td>
<td>2</td>
</tr>
<tr>
<td>2.246</td>
<td>20</td>
<td>1.400</td>
<td>1</td>
</tr>
<tr>
<td>2.136</td>
<td>5</td>
<td>1.293</td>
<td>1</td>
</tr>
<tr>
<td>2.064</td>
<td>4</td>
<td>1.276</td>
<td>1</td>
</tr>
<tr>
<td>1.936</td>
<td>22</td>
<td>1.259</td>
<td>2</td>
</tr>
<tr>
<td>1.883</td>
<td>10</td>
<td>1.233</td>
<td>4</td>
</tr>
<tr>
<td>1.839</td>
<td>27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*SiO₂ and other low density minerals removed by density separation.
Petrographic investigation did not distinguish among the fractions but did provide positive identification of the massive apatite crystals.

After digestion of the ore with 26% HCl solution, the residue was approximately 10% by weight of the ore digested and contained an average of 54.5% of the total fluorine (Table III). The same quantity of residue, containing 67% of the fluorine, has been reported with nitric acid digestion.30 As noted in Table IV, the addition of borax or aluminum chloride to the digestion medium left substantially less fluorine in the insoluble residue. A corresponding decrease in the amount of residue was expected but was observed only in the latter case. The usual amount of residue (10% of ore weight) which resulted from the first borax digestion was attributed to the precipitation of hydrous silica from fluosilicate hydrolysis. Petrographic and X-ray examination showed that less than 1% of the phosphate pebbles do not react during the digestion.

The slow sedimentation rate of the residue, which persisted even after repeated washing, was due to the sequestering action of phosphoric acid. The strongly absorbed acid was removed by washing with acetone or ethyl alcohol.

By washing the residue through a 325 mesh screen, SiO₂, silicates, and other acid insoluble minerals which

30 Mane Kate, et. al., Japan, 14, 355 (1960).
amounted to 23% by weight of the residue were removed. Partial separation of the carbon in the residue could be achieved by sedimentation.

The residues obtained from the first three digestions shown in Table III were dried in an oven at 110°C. Residues obtained from all other digestions were dried under vacuum without heat.

The volume of the liquor amounted to 280 ml after the digestion of 100 g of ore with 255 ml of 26% HCl. The approximate concentration of some of the components of the liquor are given below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>1.8 M/L</td>
</tr>
<tr>
<td>Phosphate</td>
<td>2.9</td>
</tr>
<tr>
<td>Acidic hydrogen</td>
<td>7.3</td>
</tr>
<tr>
<td>Chlorine</td>
<td>7.3</td>
</tr>
<tr>
<td>Fluorine (if all fluorine in liquor)</td>
<td>0.75</td>
</tr>
<tr>
<td>(if 45.5% in liquor)</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The liquor contained an average of 45.5% of the fluorine in digestions 2-5 of Table III. These digestions, in which only the ore and 26% HCl (255 ml per 100 g of ore) were added to the reaction vessel, will be termed normal digestions. In digestions 4 and 6, the first a normal and the second a boron digestion, particular care was exercised in order to obtain a quantitative recovery of both the insoluble residue and the aqueous liquor. The material balance of the fluorine thus obtained showed that essentially no fluorine was volatilized during the digestion.
TABLE III
Fluorine Distribution Between Residue and Liquor

<table>
<thead>
<tr>
<th>Residue Wt. % of Ore</th>
<th>Percent of Total Fluorine in Residue</th>
<th>Percent of Total Fluorine in Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 10.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 9.97</td>
<td>52.6</td>
<td>47.4(d)</td>
</tr>
<tr>
<td>3 10.20(a)</td>
<td>57.4(d)</td>
<td>42.6</td>
</tr>
<tr>
<td>4 10.39</td>
<td>53.36</td>
<td>46.64</td>
</tr>
<tr>
<td>5 10.68</td>
<td>53.13(d)</td>
<td>46.87</td>
</tr>
<tr>
<td>6 10.03</td>
<td>3.22</td>
<td>96.73</td>
</tr>
<tr>
<td>7 -</td>
<td>less than 1.5 (x)</td>
<td>greater than 98.5(d)</td>
</tr>
<tr>
<td>8 10.20</td>
<td>55.8</td>
<td>44.2(d)</td>
</tr>
<tr>
<td>9 4.44</td>
<td>0.6(d)</td>
<td>99.4</td>
</tr>
</tbody>
</table>

(a) amorphous       (d) by difference (x) by X-ray

1. Digestion of uncalcined ore.
2. First digestion of calcined ore.
4. Third digestion of calcined ore.
5. Fourth digestion of calcined ore.
6. First digestion of calcined ore in presence of borax (400% excess if BF$_4^-$ formed).
7. Second digestion of calcined ore in presence of borax (50% excess if BF$_4^-$ formed).
8. Digestion of calcined ore in the presence of Al$_2$O$_3$ (insoluble--did not enter reaction).
9. Digestion of calcined ore in the presence of AlCl$_3$ (100% excess if AlF$_6^{3-}$ formed.)
The color of the liquor after digestion was invariably a deep yellow. During the steam distillation of the liquor, required by the fluorine analysis procedure, the yellow color soon disappeared. The reappearance of the color on addition of HCl was taken as evidence that the formation of the yellow FeCl\textsuperscript{4-} complex was responsible for the color. Extraction of the liquor with alamine solution, which is effective in removing iron, also resulted in a clear liquor. At high dilutions the solution was a light green color which probably was due to vanadium. The increased concentration of phosphate ions at high dilution was sufficient to cause the formation of an iron-phosphate complex instead of an iron-chloride complex.

The investigation of the fluorine that remained in the liquor after digestion of the ore was primarily concerned with its distribution between the aqueous liquor and organic phases after extraction procedures. Tributylphosphate (TBP) and Alamine 336 (a tricaprylylamine) were the organic materials used in this study.

The results of extracting three different liquor solutions with TBP and subsequent extraction of the TBP phases with water are shown in Table IV. The first two liquor solutions were obtained by digesting the ore with 26% HCl while the third resulted from digestion with 26% HCl to which borax has been added.

The formation of a soluble boron-fluorine compound or compounds in the boron digestion was suggested by the
vastly different fluorine distribution between the residue and liquor, as well as the distribution following the liquid-liquid extractions with TBP. Under the normal digestion conditions with 26% HCl, approximately 45% of the total fluorine was found in the liquor and approximately 2/3 of this was subsequently extracted by the TBP. When boron was added to the digestion medium, c.a. 97% of the fluorine was in the liquor and of this, 8/10 was extracted by the TBP.

As practically all of the fluorine was found in the liquor following the borax digestion, and presumably in the form of a boron-fluorine complex, its removal was attempted by extraction. A tertiary amine in the form of a 5% solution of tricaprylylamine in toluene was used for this purpose.

An extraction of the boron liquor was carried out with the alamine solution as follows. The liquor was first extracted with an equal volume of TBP. The TBP phase was then extracted with water which left 75.8% of the fluorine in the organic phase. An equal volume of the alamine solution subsequently extracted 81.8% of the remaining fluorine from the aqueous phase. Thus, in every case where the fluorine was believed to be in the form of a boron-fluorine complex, at least 75% of the fluorine was found in the organic phase after extraction. This was not the case when the alamine solution was used for extraction of the boron liquor.

When the boron liquor was extracted with 2-1/2 times its volume of the alamine solution, only 54.4% of the fluorine was found in the alamine solution (see C of Table IV).
TABLE IV

Liquor Extraction Results

(All data are percentages of the fluorine present in the ore.)

<table>
<thead>
<tr>
<th>Ore (100% F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>digestion with 26% HCl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquor</th>
<th>Alamine</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>2)* 47.4%</td>
<td>79.8%</td>
<td>19.6%</td>
</tr>
<tr>
<td>3) 42.6</td>
<td>76.5</td>
<td>22.9</td>
</tr>
<tr>
<td>6) 96.8</td>
<td>Alamine extraction</td>
<td></td>
</tr>
<tr>
<td>9) 99.4</td>
<td>Alamine extraction</td>
<td></td>
</tr>
</tbody>
</table>

Organic to liquor ratio, 1:1
a) single extraction
b) double extraction

c) 42.4% | d) 41.9 |
| e) 41.4 |

Organic to liquor ratio, 2.5:1

c) single extraction
d) double extraction
e) double extraction

extraction with TBP
(equal volumes)

<table>
<thead>
<tr>
<th>Liquor</th>
<th>TBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>2) 13.3%</td>
<td>34.1%</td>
</tr>
<tr>
<td>3) 16.3</td>
<td>26.3</td>
</tr>
<tr>
<td>4) 15.7</td>
<td>81.1</td>
</tr>
</tbody>
</table>

*Experimental conditions of digestion are given in Table III.
It was known that alamine was effective in removing HCl from the liquor and, to preclude the possibility that the acid was being preferentially extracted, two double extractions (d and e) were made. In the first, the total extraction of the fluorine was 54.9%, and in the second, 55.4%. Thus, the distribution of the fluorine between the liquor and residue following digestion in the presence of borax suggested that all of the soluble fluorine was in the form of a soluble boron fluorine complex. At the same time, the small increase in fluorine extracted in the double extractions, as compared to a single extraction, suggested that at least two fluorine species were present in the liquor after a borax digestion. Although it was realized that the extraction system was far from ideal, the data obtained from the boron liquor extractions could best be interpreted by the postulation of one fluorine species for which alamine was specific and a second species which was not extracted by the alamine solution.

Other anomalies of fluorine distribution were noted after alamine extraction. The alamine phase in the first double extraction above was washed with water to improve the recovery of the aqueous phase. By following this procedure erroneous results would be obtained unless there was no distribution of fluorine between water and the alamine phase. The close agreement of the results obtained from the two double extractions indicated that no distribution did occur. Precipitation experiments with nitron further indicated that there was little transfer of the BF$_4^-$ ion between
a neutral NaBF₄ solution and the alamine solution. As will be shown below, the transfer of the tetrafluoroborate ion was quite rapid with highly acidic aqueous solutions.

The specificity of the alamine solution for a particular boron-fluoride complex was further indicated by extraction results on a solution made from a residue sample dissolved with a borax/HCl solution. A single alamine extraction removed 79.8% of the fluorine from a filtered aqueous solution obtained by dissolving 1.0056 g of digestion residue in 40.0 ml of 26% HCl containing 0.7211 g of borax. A double extraction from a sample of the same solution gave 79.4%. A second solution was made as before but with the fluorine to boron mole ratio reduced from 2 to 1. Only 65.2% of the fluorine was extracted by the alamine in a single extraction. The fluorine concentration in the first residue solution was 0.0048 g/ml and 0.0050 g/ml in the second so that the differences in fluorine distribution most probably arose from the difference in the fluorine to boron ratio.

The second residue solution was neutralized as much as possible with CaO, i.e., until a precipitate began to form. An alamine extraction yielded 68.7% of the fluorine under these conditions.

In order to establish more firmly that a boron-fluoride complex was being extracted by the alamine solution, extractions were attempted from liquors which contained no added boron. The relatively small amounts, 4.1% and 3.5%,
that were extracted from the second and third calcined liquors, respectively, support the above conclusion.

Fairly conclusive evidence that a boron-fluoride complex was the extractable species, and insight as to which species, was provided by extractions from the third calcined digestion liquor after the addition of boron. Sufficient boron was added in the form of borax to give a total fluorine to boron mole ratio of two. The amounts of fluorine extracted by the alamine solution were found to be a function of the reaction time at room temperature, and at 1, 1.5, and 12 hours were 3.5, 25.6, and 54.6%, respectively. The time dependence of the quantity of fluorine extracted and the close similarity of the amount extracted after 12 hours, 54.6%, with the 54.4% (average value from two boron liquors) extracted from the boron liquors was indicative of a reaction slow in reaching equilibrium.

Such a reaction equilibrium has been suggested by Wamser\(^{31}\) to include the following steps:

\[
\begin{align*}
(1) & \quad H_3BO_3 + HF \rightarrow HBF(OH)_3 \\
(2) & \quad HBF(OH)_3 + HF \rightarrow HBF_2(OH)_2 + H_2O \quad \text{very fast} \\
(3) & \quad HBF_2(OH)_2 + HF \rightarrow HBF_3(OH) + H_2O \\
(4) & \quad HBF_3(OH) + HF \nleftrightarrow HBF_4 + H_2O. \quad \text{slow}
\end{align*}
\]

Wamser determined the equilibrium constant for the last reaction under various conditions of concentration, fluorine to boron mole ratio, and pH. Hydrolysis of HBF_4 was decreased

by high concentration, large F/B ratio, and low pH. If an equilibrium of the type shown in reaction (4) above is presumed to exist in the boron fluoride solutions dealt with in this work, an extrapolation of Wamser's data would predict hydrolysis of HBF₄ to be of the order of 20-30%. Also, in view of the above reactions, the increasing amounts of fluorine extracted from the borax/HCl/residue solutions as the reaction time increased indicated that HBF₄ was the species extracted by the alamine solution. The hydrolysis that would be predicted by the alamine extraction data was in poor agreement with that from Wamser's data, but a closer correlation would probably be fortuitous due to the differences in the systems involved.

The fluoborate analyses with nitron were undertaken to provide an independent quantitative estimation of the fluoborate-hydroxyfluoborate equilibrium. While the difficulties encountered with chlorine interference reduced the accuracy of the analysis, useful results were obtained. A nitron analysis of the boron liquor indicated that 44.4% of the fluorine was present as the tetrafluoborate, a value substantially different from the percentage of fluorine extracted by the alamine solution, 54.4%. If the suggested correction of 18.9 mg per 100 ml of precipitating solution was applied, the nitron analysis for HBF₄ indicated that 50.5% of the fluorine was present as HBF₄. While this provided a closer agreement between the extracted percentage
and nitron analysis, more conclusive proof that the alamine solution did extract the tetrafluoborate ion or acid was desired.

Proof was obtained by formulating a solution that approximated the boron liquor in phosphate, fluoborate, and hydrogen ion concentration. This solution was prepared by dissolving 2.0410 g of NaBF₄ in 12.30 ml of 85% H₃PO₄ and 5.25 ml of H₂SO₄, and diluting to 100.0 ml. A nitron analysis of the solution indicated that 48.3% (50.9% with the solubility correction) of the fluorine was present in the solution as tetrafluoborate. A second portion of the approximated boron liquor solution was extracted with 2-1/2 times its volume of alamine solution just prior to the nitron analysis. No precipitation of nitron•HBF₄ occurred. After five days, however, a nitron•HBF₄ precipitate, which amounted to about one-fourth of the original tetrafluoborate present, had settled from the extracted solution.

From these results it was concluded that the alamine solution was essentially specific and quantitative in the extraction of the tetrafluoborate ion or acid under the highly acidic conditions which existed in the boron liquor. The absence of any appreciable fluorine transfer between a neutral fluoborate solution and alamine solution, or between a fluoborate alamine solution and water, would imply that the acid was the extractable species. Both the specificity and quantitative nature of the extraction were substantiated by the insignificant difference in the results of single and
double extractions—a phenomenon shown from two different solutions that contained boron and fluorine. The precipitation experiments with nitron supported the specificity and quantitative arguments and established the identity of the extractable species.

No direct data were obtained which showed that all of the fluorine in the boron liquor was in the form of boron fluoride complexes. This supposition was, however, inferred indirectly by a number of observations. First, an obvious change in fluorine distribution between the residue and liquor occurred when borax was added to the digesting acid. The fluorine distributions in the TBP-liquor and alamine-liquor extraction systems were also markedly influenced by the presence of boron. Second, about the same amounts of nitron·HBF$_4$ were found in a boron liquor and in a formulated liquor where all the fluorine was initially introduced as a tetrafluoborate. Third, nearly equal amounts of fluorine were extracted by alamine from a boron liquor and a liquor to which boron was added after the digestion. Fourth, HCl/borax solutions dissolved a normal residue and subsequent alamine extractions removed 65-80% of the fluorine from this solution depending upon the fluorine to boron ratio.

Analysis of the ore for aluminum revealed that a sufficient amount of this element was present to react with 61.5% of the fluorine if AlF$_6^{3-}$ was formed or 41.0% if AlF$_4^-$ was formed. It was therefore conceivable that after a normal digestion with hydrochloric acid, the aluminum was associated
with the soluble fluorine form. Digestion in the presence of aluminum did place nearly all of the fluorine in a soluble form. Aromatic extractions of the aluminum liquor were made as shown in Table IV and the amount extracted, almost 20%, was five times as much as was extracted from a normal liquor. This difference was large enough that it seemed very unlikely that an aluminum fluoride complex could constitute more than a minor portion of the fluorine in the normal liquor. A double extraction (see Table IV, 6) of the aluminum liquor increased the fluorine extracted by only 3%, a result that suggests the same type of equilibrium as was noted in the boron liquor.

The supposition of Fox and Hill,\(^\text{32}\) that the fluorine in the liquor was present as the hexafluosilicate ion, can most probably be extended to the HCl digestion system although their work was concerned with sulfuric acid digestions. No evidence to the contrary was found. The fluosilicate ion was observed to be sufficiently soluble in the HCl digestion system to account easily for the fluorine found in the liquor.

Investigation of the residue after partial removal of the SiO\(_2\) showed that it consisted of minute (1-10 microns) isotropic by-pyramid hydroscopic crystals with an index of refraction of approximately 1.42 and a density of less than

The crystals were insoluble in dilute HCl, concentrated HNO₃, NaOH, and NH₄OH, but were slowly soluble in concentrated HCl. They were readily decomposed by heat and rapidly soluble in hot HNO₃, concentrated H₂SO₄, basic EDTA solution, and in 26% HCl to which aluminum or boron had been added. Neutralization of a nitric acid solution of the residue yielded a considerable quantity of NaF and CaF₂. Evaporation of the liquid following dissolution with an AlCl₃/HCl solution yielded fluorine as Al(OH)₂F and Al(OH)F₂. The decomposition with aluminum was much slower than with boron.

The "d" and visual "I/Io" values of the residue powder X-ray pattern are given in Table V. Despite prolonged efforts to identify the pattern from the ASTM card index in conjunction with the Trimetex system and the literature, the only assignable peaks were those of SiO₂. These are not included in the table. The X-ray pattern of Roscherite, reported to be (Ca,Mn,Fe)₃Be₃(PO₄)₃(OH)₃·2H₂O by Lindberg, gave the closest match with the observed residue pattern. However, there was no agreement between the elemental analysis of the residue and the composition required by the mineral formula and there was no similarity between solubility characteristics. Efforts were also made to analyze the X-ray pattern of the residue as a mixture.

---

TABLE V

X-Ray Pattern of the Residue

<table>
<thead>
<tr>
<th>d</th>
<th>I/Io (visual)</th>
<th>d</th>
<th>I/Io (visual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.65</td>
<td>100</td>
<td>1.915</td>
<td>4</td>
</tr>
<tr>
<td>5.93</td>
<td>55</td>
<td>1.824</td>
<td>15</td>
</tr>
<tr>
<td>5.04</td>
<td>25</td>
<td>1.748</td>
<td>2</td>
</tr>
<tr>
<td>4.18</td>
<td>20</td>
<td>1.714</td>
<td>2</td>
</tr>
<tr>
<td>3.84</td>
<td>7</td>
<td>1.675</td>
<td>2</td>
</tr>
<tr>
<td>3.41</td>
<td>10</td>
<td>1.557</td>
<td>2</td>
</tr>
<tr>
<td>3.212</td>
<td>35</td>
<td>1.511</td>
<td>2</td>
</tr>
<tr>
<td>2.956</td>
<td>5</td>
<td>1.464</td>
<td>3</td>
</tr>
<tr>
<td>2.824</td>
<td>16</td>
<td>1.411</td>
<td>4</td>
</tr>
<tr>
<td>2.641</td>
<td>17</td>
<td>1.353</td>
<td>2</td>
</tr>
<tr>
<td>2.548</td>
<td>25</td>
<td>1.277</td>
<td>3</td>
</tr>
<tr>
<td>2.337</td>
<td>8</td>
<td>1.243</td>
<td>1</td>
</tr>
<tr>
<td>2.231</td>
<td>20</td>
<td>1.194</td>
<td>1</td>
</tr>
<tr>
<td>2.173</td>
<td>30</td>
<td>1.178</td>
<td>2</td>
</tr>
<tr>
<td>1.968</td>
<td>7</td>
<td>1.137</td>
<td>1</td>
</tr>
<tr>
<td>1.928</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*May be due to silicates.
Only the identification of the aforementioned SiO$_2$ resulted. A residue obtained from the Dow Chemical Company and a nitric acid digestion residue also exhibited the pattern shown in Table V. When aluminum, boron, or silicic acid was present in the digestion medium or when the residue was treated with an HCl/borax or HCl/AlCl$_3$ solution, CaSO$_4$ and SiO$_2$ were the only crystalline components remaining other than acid insoluble trace minerals.

As previously stated, the residue readily decomposed by heat. The residue, which was white to gray depending upon the amount of carbon removed, when placed in a crucible and heated with a small bunsen flame, evolved a considerable amount of gas and turned a dark gray color. At the point of darkest color, the X-ray pattern showed that a completely amorphous stage had been reached. On continued heating there resulted a white ignition product, composed of crystalline CaF$_2$ and CaSO$_4$. On strong ignition with a Fisher burner, the ignition products fused into a pink mass.

Positive results of the "hanging drop" test showed that, along with water vapor, SiF$_4$ was one of the gaseous products. This result was substantiated by silicon and fluorine analysis before and after heating. Carbon dioxide was the only additional gaseous decomposition product found when the gases were examined by mass spectroscopy.

It was unexpectedly found that the residue would slowly decompose at a temperature as low as 145°C. An initial determination of the thermal decomposition was made at
100-110°C on a vacuum dried sample obtained from Dow. For three days there was a smooth rapid weight loss which amounted to 11% of the original weight. The weight loss after 10 days had reached 21.6%. For the next 21 days the change was very slight and after 31 days of heating, there resulted a total weight loss of 22.8%. A similar decomposition was carried out using a smaller residue sample with considerably more exposed surface area from the third calcined digestion. A rapid weight loss of 20.0% was observed after 40 hours at 110°C and reached 20.8% after 90 hours. When the sample came to equilibrium with the atmosphere, only 79.5% of the weight loss was regained. Thus, an irreversible decomposition rather than a simple dehydration was indicated.

These preliminary characterizations of the residue disclosed some properties that might be expected of a mixture of CaSiF₆·2H₂O and CaSO₄ or of CaSiF₆·2H₂O, CaSO₄·2H₂O, and CaF₂. Indeed, one could reasonably suspect that CaSiF₆·2H₂O and CaF₂ might constitute the insoluble fluorine compounds in the residue. The results of elemental analysis of the residue were interpreted to include these elements in ratios suggested by the above stoichiometry; these specific compounds, however, were not believed to be present. Instead, the experimental evidence led to the postulation of a complex mineral-type compound as the major component of the residue.

Detailed thermal decomposition data was obtained using the DuPont 900 Differential Thermal Analyzer and Thermo-gravimetric Analyzer. The initial thermal data was gained
through the courtesy of Dr. Conrad of the U. S. Department of Agriculture, Southern Regional Laboratories, with an instrument made by R. L. Stone and Company. The thermogram of the third calcined digestion residue displayed three thermal reactions below 500°C (Figure 1). There was a strong endothermic reaction with an extrapolated onset of 165-167° and peak at 168-170°, a weak endothermic reaction with the extrapolated onset at 356-357° and peak at 372-373°, and a weak exothermic reaction with the peak at 428-431°. Under a "vacuum of 30 in." the strong endothermic peak shifted to 119-124° and the extrapolated onset occurred at 102-105°. A weak, broad band at 166-175 appeared to be a doublet. (After holding the temperature at 154° for one hour, no reaction was noted in the 170° region when the temperature was raised.) The other peaks were little affected by the pressure change with the weak endothermic reaction extrapolated onset occurring at 357-360° and the peak at 369-372°. The exothermic peak occurred at 426-428°. No difference in any peaks were noted under a nitrogen atmosphere. Two endothermic peaks were evident at higher temperature, one at 740° and the second at 800°. These latter two thermal reactions were believed associated with fusion of the sample.

Knowledge of the nature of thermal decomposition of the residue was considerably extended by obtaining the diffraction pattern of samples that had been heated through specific thermal reactions in the DTA instrument. Thus, X-ray patterns were obtained from samples that had been heated to
the following temperatures: 200°, just after the strong endothermic peak; 320°, prior to the second endothermic peak; 390°, between the second endothermic peak and the exothermic peak at 428°, and 500°, after the exothermic reaction was completed. Diffraction patterns of these samples revealed that crystallinity of the residue was completely destroyed (except for the SiO₂) by the thermal reaction at 170° and that the residue remained in an amorphous state until the endothermic reaction at 370°. This latter reaction gave rise to crystalline CaF₂ and the 428° exothermic reaction produced β-CaSO₄.

A thermogram of CaSO₄·2H₂O (Figure 2) exhibited endothermic peaks at 155° and 197° and a weak, broad peak at 414-443°. The first two peaks, corresponding to water loss by the di- and hemihydrate respectively, and the last to the γ to β transition, were in good agreement with results reported by Ljunggren. This worker gave the peak values of 155°, 195°, and 420°C.³⁴ West and Sutton reported 180°, 215°, and 360°C.³⁵ The dehydration of the hemihydrate, CaSO₄·0.5H₂O, has also been reported to occur at 200-210°C for an α form and at 170-180°C for a β form.³⁶ Although the exothermic peak at 428°C was weak and ill defined using the DuPont instrument, a strong peak at 440°C was displayed by the Stone

---

instrument, and there can be no doubt that the formation of $\beta$-CaSO$_4$ from the amorphous residue is responsible for this exothermic reaction.

The weak exothermic reaction at $372^\circ$ was associated with the formation of crystalline CaF$_2$.

The decomposition of CaSiF$_6$·2H$_2$O involved dehydration, SiF$_4$ evolution, and the formation of CaF$_2$. This behavior closely resembled the action of the residue when heated. The loss of the water of hydration by CaSiF$_6$·2H$_2$O has been reported to take place at $145^\circ$ with SiF$_4$ evolution and crystalline CaF$_2$ formation occurring at 380-400°C.\textsuperscript{37} Differential thermal analysis of CaSiF$_6$·2H$_2$O revealed a large endotherm at 154-160° with the extrapolated onset at 140-147° which corresponds to the dehydration, and the decomposition was indicated by a strong endothermic peak at 332-338°. Thermogravimetric analysis confirmed the assignment of the peaks (see Figures 3 and 4). Under a vacuum of 30 in. these peaks occurred at 139-144° and 285-288°. A mixture of CaSO$_4$·2H$_2$O and CaSiF$_6$·2H$_2$O gave the same results as the individual samples.

Notwithstanding some similarities between the properties of the residue and CaSiF$_6$·2H$_2$O or a mixture of CaSiF$_6$·2H$_2$O and CaSO$_4$, the experimental evidence indicated that neither of these compounds was present in the unheated

residue. Neither the X-ray pattern, thermogram, nor the thermogravimetric data of the residue in any way resembled that of CaSiF₆, CaSO₄, or their hydrates.

There are a number of experimental observations which indicated that the bulk of the residue was composed of a single compound. There was a uniform decrease in intensity of all the peaks in the X-ray diffraction pattern of the residue, except those due to SiO₂, during thermal decomposition. A comparison of the X-ray pattern of a partially decomposed sample with the pattern of an unheated sample revealed a decrease of 49 ± 5% in intensity for all peaks which initially had an I/I₀ value of 10 or greater. The rapid transformation of the residue from a crystalline to an amorphous state by the endothermic reaction at 170°C was strong support for a single compound.

There was no difficulty in identifying CaSO₄ and CaF₂ as the ignition products by X-ray analysis. Furthermore, CaSO₄ or one of its hydrates was quite evident in the X-ray pattern of the solid residue that remained after a borax or AlCl₃ digestion or when the normal residue was decomposed with the fluorine complexing agents in a strong acid solution. Since CaSO₄ and CaF₂ were easy to detect by X-ray analysis, but were not evident in a normal residue X-ray pattern, and the thermal properties of the residue differed from CaSiF₆ and the decomposition products, the conclusion was reached that the sulfate and fluoride in the residue were bound in a complex mineral-type compound.
Figure 1. Thermogram of Digestion Residue
Figure 2. Thermogram of CaSO₄•2H₂O
Figure 3. Thermogram of CaSiFe\textsubscript{2}•2H\textsubscript{2}O
Figure 4. Thermogravimetric Curve of CaSiF₆·2H₂O
There were indications that the residue compound was not present as such in the ore, but was formed and precipitated during the digestion of the ore. Since the residue compound decomposed at a relatively low temperature, beginning as low as 110°C, if it were present in the ore, the calcining process at 650°C would be expected to produce its decomposition products. Less than 1% of the ore particles were as small as the residue compound crystals (1-10 microns), although the possibility of their being embedded in the phosphate rock pebbles exists. Additional evidence that the residue compound was precipitated from (formed in) the digestion medium came from the second digestion of calcined ore. Contrary to the normal procedure, the acid was added to the ore in this digestion and produced a residue that was amorphous to X-ray investigation. This residue gave the normal ignition products of CaF₂ and CaSO₄. Such a supersaturated digestion medium should have no effect on the residue compound if the latter was an unchanged and undissolved ore residue. An amorphous precipitate of the residue compound might be expected if precipitation occurred in its supersaturated solution.³⁸

The results of the examination of the residue by X-ray and thermal methods as given above indicated that CaSO₄, CaSiF₆, and CaF₂ did not exist as the simple or

---

hydrated compounds in the residue. The possibility was recognized that residue components other than sulfate or fluorine compounds might give rise to the observed X-ray pattern. Evidence that both sulfate and fluorine were necessary components of the residue compound was obtained by introducing various substances into the digestion medium. Marked changes were produced in the fluorine distribution between the solid and liquid phases of the digestion mixture and in the properties of the residue under these conditions. The results and conditions are shown in Table VI.

Digestion of the ore in the presence of boron, aluminum, or silicic acid solubilized practically all of the fluorine and examination of the residues by X-ray diffraction revealed no trace of the normal residue diffraction pattern.

The mechanism that caused the change in the fluorine distribution was believed to be the same in each of these cases, i.e., the formation of a soluble metal-fluorine complex with a greater stability than the normal residue fluorine form. Presumably, soluble complex formation was also responsible for the dissolution of a normal residue in a HCl/AlCl₃ or HCl/H₃BO₃ solution. These results clearly indicated that fluorine was a constituent of the compound that produced the X-ray diffraction pattern given in Table V.

When the insoluble residues that remained after digestion of the ore in the presence of fluorine complexing agents, or the residues left after dissolution by a HCl/AlCl₃
TABLE VI

Digestion Results in the Presence of Various Substances

<table>
<thead>
<tr>
<th>Digestion</th>
<th>% F in Liquor</th>
<th>% F in Residue</th>
<th>X-Ray Analysis of Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Normal</td>
<td>45.5</td>
<td>54.5</td>
<td>SIO₂, residue compound (RC)</td>
</tr>
<tr>
<td>2. Boron</td>
<td>96.8</td>
<td>3.2</td>
<td>SIO₂, no RC (γ CaSO₄ ppt'd from liquor)</td>
</tr>
<tr>
<td>3. Aluminum</td>
<td>99.4</td>
<td>0.6</td>
<td>SIO₂, no RC (CaSO₄ evident on heating)</td>
</tr>
<tr>
<td>4. Silicic Acid</td>
<td>100.0</td>
<td>0</td>
<td>SIO₂, no RC (CaSO₄ evident on heating) (γ CaSO₄ settled from liquor)</td>
</tr>
<tr>
<td>5. Barium</td>
<td>75.6</td>
<td>24.4</td>
<td>SIO₂, BaSO₄, no RC</td>
</tr>
<tr>
<td>6. Sulfate</td>
<td>61.7</td>
<td>38.3</td>
<td>SIO₂, RC CaSO₄·2H₂O</td>
</tr>
</tbody>
</table>

Conditions of Digestions:

1. 26% HCl
2. 26% HCl, borax - molar ratio B/F = 1
3. 26% HCl, AlCl₃ - molar ratio Al/F = 0.33
4. 26% HCl, Si(OH)₄ - 2% of ore weight, molar ratio Si/F = 0.5
5. 26% HCl, BaCl₂ - molar ratio Ba/SO₄ = 2
6. 26% HCl, H₂SO₄ - molar ratio SO₄/F = 0.5
or HCl/H₃BO₃ solution were heated and then examined by X-ray diffraction, crystalline CaSO₄, but not CaF₂, was evident in each case.

In the boron digestion, γCaSO₄ was evident before heating, and hydrated forms of CaSO₄ remained behind after dissolution of a normal residue with the acid/metal solution. The ability to detect CaSO₄, or its hydrates, under these conditions, coupled with the absence of CaF₂, which is easier to detect, strongly suggested that the fluorine and sulfate were both bound in a mineral-type compound.

More conclusive evidence that precipitation of fluorine and sulfate from the digestion medium was not independent was provided by digestion in the presence of barium chloride. If the sulfate in the residue was associated with the residue compound and its X-ray diffraction and thermal properties, the addition of a soluble barium compound to the digestion medium should cause a profound change in the X-ray diffraction pattern of the resulting residue. If the sulfate and fluorine were both components of the residue compound, digestion of the ore in the presence of barium ions could be expected to produce a different sulfate distribution and, indirectly, a different fluorine distribution between the liquor and residue than that found after a normal digestion.

Nitric acid of the same normality as 26% HCl was used for the acidulation only after it was determined that its use produced no change in the usual residue X-ray diffraction pattern. When barium ions were added to the nitric
acid digestion, X-ray analysis showed the presence of the residue compound and Ba(NO$_3$)$_2$ but no BaSO$_4$. Ignition produced CaF$_2$, CaSO$_4$, and BaClF. The amount of BaCl$_2$·2H$_2$O added to the digestion acid in this case was 5% of the ore weight. The barium evidently precipitated as Ba(NO$_3$)$_2$ prior to the digestion reaction. Precipitation of BaSO$_4$ was observed when HCl was used in the acidulation.

In the first barium/HCl digestion, the BaCl$_2$·2H$_2$O (3.4% of the ore weight) added to the 26% HCl solution was the molar equivalent of the sulfate normally found in the residue. All of the BaCl$_2$ did not dissolve in the 26% HCl prior to the digestion reaction but none was found in the residue which contained the residue compound and BaSO$_4$. After ignition, CaF$_2$, CaSO$_4$, and BaSO$_4$ were present. Although there seemed to be a decrease in the intensity of residue compound diffraction pattern, no firm conclusions could be drawn from these observations since both the residue compound and BaSO$_4$ were present in the residue and both CaSO$_4$ and BaSO$_4$ were in the ignited residue.

In the second barium/HCl digestion where the BaCl$_2$·2H$_2$O content of the acid was increased to 7.5% of the ore weight, the digestion produced a residue containing primarily BaSO$_4$ and only a trace of the residue compound. After ignition BaSO$_4$ and a trace of CaF$_2$ were found, but no CaSO$_4$ or residue compound.

The fluorine distribution that resulted from this last digestion, 75.6% in the liquor and 24.4% in the residue,
is shown in Table VI and compared with other distributions. Overnight, a fine precipitate, identified as BaSiF₆, settled from the initially turbid liquor. This precipitate contained 14% of the fluorine content of the ore. The turbidity was a characteristic of all the barium digestions. The results of this series of experiments were just those expected if sulfate and fluorine were necessary for the formation of the residue compound during the ore digestion.

Digestion with 26% HCl to which silicic acid had been added, left no fluorine in the residue (Table VI). The amount of silicic acid used was sufficient to form SiF₆²⁻ with the fluorine that was normally found in the liquor, i.e., 45% of the total fluorine content of the ore. This fluorine distribution allowed a number of conclusions to be drawn if it is accepted that the silicic acid resulted in the formation of the hexafluosilicate ion. The formation of the hexafluosilicate is the normal result of a reaction between silicic acid and an acidic fluoride solution. It is recognized that the formation of the SiF₆²⁻ ion from silicic acid proceeds through the step-wise replacement of the hydroxyl groups. The intermediate ions have not been observed as stable ions in aqueous solution, however, and the intermediate reaction steps are believed to be very rapid.³⁹

The reaction rate of fluorine with the Si(OH)$_4$ in the silicic acid/HCl solution obviously was considerably greater than the reaction rate with crystalline quartz. Otherwise, the quartz that is present in the ore would have caused the same fluorine distribution as found in the silicic acid digestion.

This digestion experiment clearly showed that an increased concentration of reactive silicon in the digestion medium did not lead to a greater amount of fluorine in the insoluble residue. The absence of fluorine in the residue under the conditions of this digestion indicated that fluorine in the form of calcium fluosilicate, per se, does not precipitate from the digestion medium. The residue was separated from the liquor twelve hours after the ore and acid were mixed. A further precipitate did settle from the liquor after four days, but it consisted mostly of CaSO$_4$ and contained only 1-2% of the total fluorine. The absence of a CaSiF$_6$ precipitate from this liquor suggested that the fluosilicate ion might be the soluble fluorine form that results from a normal digestion.

In addition, the absence of any residue compound indicated that non-complexed fluorine, or fluorine in a complex of lower stability than SiF$_6^{2-}$, was necessary for the formation of the residue compound.
Fox and Hill\textsuperscript{40} concluded from their work that all the fluorine found in phosphate rock was present as calcium fluosilicate. Their conclusion seemed at variance with the results of the study. Digestion of the ore with the silicic acid/HCl solution changed the normal residue to liquor fluorine distribution of 55 to 45\% to 0 to 100\%. If the normal 55:45 distribution did result from an ore in which all the fluorine was present as fluosilicate, the addition of a small amount of silicic acid to the digestion medium would be expected to cause little, if any, change in this distribution. Only a small amount, 2\%, of the fluorine settled from the silicic acid digestion liquor after four days even though the fluorine, calcium, and reactive silicon concentrations were much higher than in the normal liquor concentration. As previously stated, this observation strongly suggested that calcium fluosilicate does not precipitate from the digestion medium. If calcium fluosilicate was the only fluorine compound in the ore, little or no fluorine would be expected in the residue after a normal digestion with HCl in view of these results.

A digestion with twice the amount of acid solution normally used resulted in a residue that contained no fluorine and none of the residue compound. While these results supported the conclusion that the residue compound precipitated

\textsuperscript{40} Fox and Hill, \textit{op. cit.}
from the aqueous digestion medium, they further suggested that formation of the residue compound, and the fluorine distribution, might be influenced by a mass action effect. The fluorine distribution and amount of precipitate formed was observed to be a function of the acid to ore ratio used for the digestion.

Since the volume of the acid used for the digestion might also be expected to influence the fluorine distribution, two different means of changing the acid to ore ratio were used. In one case, a constant volume of acid solution (255 ml per 100 g of ore) of different concentrations were used to obtain the desired acid to ore ratio. Thus, 26.0, 23.5, and 20.9% HCl solutions were used to obtain acid to ore ratios of 1.05, 0.95, and 0.85, respectively. The ratios were calculated so that 100% of the theoretically required acid was 1.0. The second means of achieving the desired acid to ore ratio was to use different volumes of the same concentration of acid solution. Thus, 255 and 230 ml of 26% HCl solution per 100 g of ore gave acid to ore ratios of 1.05 and 0.95. These two means of adjusting the acid to ore ratio permitted, to some extent, the observation of the separate effects of initial acid concentration and initial acid volume.

The results of ore digestion under the above conditions are shown in Table VII and Figure 5. These data show that both the gross amount of the residue and the amount of fluorine in the residue increased as the acid to ore ratio decreased. The increased amount of residue was partly due to
unreacted ore when the weaker acid solutions were used; un-
re acted ore was particularly evident in the residue at the 
0.85 acid to ore ratio.

A comparison of the results of the two digestions 
at an acid to ore ratio of 0.95 revealed that the stronger 
acid solution resulted in considerable more insoluble fluorine 
while the gross amount of residue was almost the same for the 
two digestions. This comparison would imply that the in-
creased concentration of the liquor components was the more 
important factor in making the fluorine less soluble.

The specific effect of an increase in calcium con-
centration in the digestion medium was shown by the digestion 
in which CaCl₂, amounting to 15.1% of the ore weight, was 
added to the acid solution. The increase in insoluble fluorine 
from 54.5%, in the case of a normal digestion, to 65.7%, when 
the calcium concentration was increased, was readily ascribed 
to a mass action effect.

The effect of the addition of a small amount of sul-
fate to the digestion medium was not so easily explained. It 
has been previously shown that the precipitation of sulfate 
from the digestion medium with barium resulted in less 
insoluble fluorine than found after a normal digestion. One 
might expect, therefore, that additional sulfate in the 
digestion medium would produce more insoluble fluorine. The 
opposite was found experimentally. The quantity of sulfate, 
1% of the ore weight, equaled that normally found in the resi-
due and was added to the usual amount of 26% HCl solution.
### TABLE VII

**Effect of the Amount and Concentration of Digestion Acid on the Fluorine Distribution**

<table>
<thead>
<tr>
<th>Digestion Conditions</th>
<th>Amount of Acid*</th>
<th>Acid Concentration</th>
<th>Percent of Fluorine in Liquor</th>
<th>Percent of Fluorine in Residue</th>
<th>Amount of Residue (% of Ore Wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10</td>
<td>(26.0% HCl)</td>
<td>100%</td>
<td>0%</td>
<td>3.56%</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>26.0% HCl</td>
<td>45.5</td>
<td>54.5</td>
<td>10.34</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>26.0% HCl</td>
<td>40.6</td>
<td>59.4</td>
<td>11.39</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td>23.5% HCl</td>
<td>43.8</td>
<td>56.2</td>
<td>11.58</td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>26.9% HCl</td>
<td>39.9</td>
<td>60.1</td>
<td>13.22</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>26.0% HCl</td>
<td>34.3</td>
<td>65.7</td>
<td>10.58</td>
<td></td>
</tr>
</tbody>
</table>

(CaCl$_2$ addition to ore
15.1% of ore wt.)

The amount of acid is given in units so that 1.0 equals 100% of the theoretically required amount of acid.
Figure 5. Effect of Acid to Ore Ratio on the Fluorine Distribution and Quantity of Residue

CaCl₂ Addition

- 26% HCl
- 21% HCl
- 23.5% HCl

Amount of Residue (Wt. % of Ore)

Acid to Ore Ratio
After digestion, the residue amounted to 10.67% of the ore weight and contained 38.34% of the fluorine. The residue X-ray pattern indicated the presence of the residue compound and CaSO₄·2H₂O.

A possible explanation of the results may be as follows. The sulfate digestion was the only experiment where CaSO₄·2H₂O was observed to precipitate from a digestion medium. In all other cases, both digestion and after dissolution of the residue, the sulfate was in the form of γ-CaSO₄ or a highly hydrated form. The excess sulfate may have caused the formation of the dihydrate early in the digestion and after being thus seeded, sulfate was precipitated in this form. The formation of the residue compound was thereby inhibited and less fluorine in the residue resulted.

Elemental composition of the residue was obtained by analytical methods described in Chapter I. For the most part, the necessary elemental analyses were routine in nature and obtained by recognized and proved methods. The widest variation in results, except for total silicon content (see Table X), occurred in the aluminum analyses, and although the procedure was neither simple nor rapid, reproducible results could be obtained by careful attention to detail and technique in both the separation and titration procedures. The variation of results in the chemical analysis for total silicon undoubtedly was caused by interference from the large amount of fluorine in the residue. The total silicon contents obtained by chemical analysis was not given in the following tables.
No difficulty was encountered in obtaining the SiO₂ and insoluble silicate content of the residue; differences in the total silicon analyses were due primarily to silicon present as fluosilicate.

Attempts to determine the silicon which was present as fluosilicate by analysis of the gaseous decomposition products were unsuccessful. The attainment of any degree of accuracy by this method was prevented by hydrolysis of the gaseous silicon tetrafluoride on contact with moisture in the gas train. Introduction of moisture into an initially dry gas train was inevitable since water was the first decomposition product evolved during ignition of the residue. Silicon present as fluosilicate was determined by assuming that fluorine lost during ignition of the residue was evolved as SiF₄. This was a logical conclusion in reasonable agreement with the analytical results and believed justified by other experimental data.

The presence of fluorine, sulfate, calcium, and quartz in the residue was shown by X-ray analysis. Chlorine, phosphate, carbon, and water were suspected due to the composition of the ore and the digestion medium. Results of spectrographic analyses, shown below, identified aluminum as a major component and iron and titanium as relatively minor components.
<table>
<thead>
<tr>
<th>Bulk residue</th>
<th>Calcium</th>
<th>Silicon</th>
<th>Aluminum</th>
<th>Iron</th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.8%</td>
<td>11.8%</td>
<td>2.3%</td>
<td>0.26%</td>
<td>0.49%</td>
</tr>
<tr>
<td>Ignited residue</td>
<td>26.2</td>
<td>6.5</td>
<td>2.5</td>
<td>0.36</td>
<td>0.34</td>
</tr>
<tr>
<td>Ignited residue--some SiO2 removed</td>
<td>31.8</td>
<td>4.8</td>
<td>4.0</td>
<td>0.15</td>
<td>0.23</td>
</tr>
</tbody>
</table>

In addition, Be, B, Cr, Cu, Mg, Mn, Ni, and Na were present in trace quantities.

During elemental analysis and characterization of the residue, attention was given to the fluorine content of the dehydrated residue and the amount of fluorine lost on ignition. The first attempts along these lines of investigation resulted in the data in Table VIII. Sample I was a residue from which no SiO2 had been removed. Samples IV and V indicated that the fluorine content of the dehydrated residue was at least 38% and the silicon analysis of IV clearly showed that silicon was present in more than one form. The data obtained from the two decompositions of sample III were reproducible and consistent with the decomposition data of Sample II. Although nearly equal percentages of fluorine were lost from Samples II and III when relatively mild heating conditions were employed, the strong ignition of Sample V indicated that considerably more of the fluorine could be volatilized. In view of thermal analysis of comparable residues, it is probable that incomplete decomposition occurred in the first two cases.
TABLE VIII
Initial Analytical Data of Heated Residue Samples

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>21.02%</td>
<td>28.40%</td>
<td>33.01%</td>
<td>37.31%</td>
<td>37.73%</td>
</tr>
<tr>
<td>Fluorine (after heating)</td>
<td>15.10</td>
<td>32.79</td>
<td>33.98</td>
<td>33.30</td>
<td>27.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.29</td>
<td>4.25</td>
<td>4.43</td>
<td>3.17</td>
<td></td>
</tr>
<tr>
<td>Total Si (as SiO₂)</td>
<td>25.3</td>
<td>11.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight Loss, Percent</td>
<td>40.88</td>
<td>37.46</td>
<td>30.0</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>Fluorine Loss, Percent</td>
<td>32.68</td>
<td>35.65</td>
<td>35.63</td>
<td>46.0</td>
<td></td>
</tr>
</tbody>
</table>

Description of Residue Samples:

I. Residue from first calcined digestion, no SiO₂ removed. Dried at 95°C for 48 hours.

II. Residue sample obtained from the Dow Chemical Company, Louisiana Division. Large particles, mostly SiO₂, which amounted to 16.3% of original sample weight, were removed from the sample with a 325 mesh wire screen. Vacuum dried.

III. Same as II, except 15.8% of weight removed by 325 mesh screen and by sedimentation separation. Dried at 110° for 10 hours.

IV. Same as III, except dried at 110°C for five weeks.
TABLE VIII (Cont'd)

V. Same as IV, except that additional SiO₂ removed by a second sedimentation separation. The sample was heated at 145°C for 2 days prior to the ignition. Some decomposition probably occurred during this period.

Ignition Conditions:

Samples II, III, and IV were slowly and intermittently heated with a Tirril burner using no more heat than was necessary to completely oxidize the carbon. The ignited residues were white.

Sample V was strongly ignited with a Fisher burner. A pink, fused product resulted.
The effects of ignition were of importance because ignition preceded most analytical elemental analyses to eliminate interference by fluorine and hydrous silica. Of greater importance was the accuracy of determining the fluosilicate content of the residue from the fluorine lost on ignition. Numerous ignitions and thermal analyses of residue samples were therefore carried out to determine the effects of ignition.

The results obtained by ignition of residue samples in a muffle furnace are given in Table IX along with the data of Sample II. The calculated SiF₄ and associated silicon contents are included as well as the water contents obtained. Data for Samples VI and VII were obtained under carefully controlled conditions in view of knowledge gained by differential thermal analysis and thermogravimetric analysis.

A close examination of the percentage weight losses of Samples VI and VII in Table IX indicated that the percentage loss was not only a function of the temperature and time of ignition, but was also a function of the sample size. If the fluorine analyses after ignitions (f) and (g) were assumed to be correct, a non-homogeneity of the ignited sample was indicated. Thermal analysis indicated that fusion of the residue occurred at 700°- 800°C. The weight loss at this point was about 40% and continued heating to 1200°C caused an additional weight loss of 8%. It was possible that fusion produced a non-homogeneous sample after static heating at 500°C for a long period.
### TABLE IX

Analytical Data of Heated Residues

<table>
<thead>
<tr>
<th></th>
<th>II</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss</td>
<td>40.88% (a)</td>
<td>39.50% (b)</td>
<td>39.74% (h)</td>
</tr>
<tr>
<td></td>
<td>39.39%</td>
<td>39.39%</td>
<td>39.75%</td>
</tr>
<tr>
<td></td>
<td>39.21%</td>
<td>38.00%</td>
<td>38.94%</td>
</tr>
<tr>
<td></td>
<td>39.14%</td>
<td>38.94%</td>
<td>38.94%</td>
</tr>
<tr>
<td></td>
<td>38.62%</td>
<td>39.76%</td>
<td>40.33%</td>
</tr>
<tr>
<td></td>
<td>38.40%</td>
<td>38.14%</td>
<td>39.05%</td>
</tr>
<tr>
<td></td>
<td>38.07%</td>
<td>38.87%</td>
<td>38.14%</td>
</tr>
<tr>
<td></td>
<td>40.64%</td>
<td>38.26%</td>
<td>37.87%</td>
</tr>
<tr>
<td>Percent fluorine in heated residue</td>
<td>32.79 (a)</td>
<td>26.31% (b)</td>
<td>25.78% (h)</td>
</tr>
<tr>
<td></td>
<td>26.51%</td>
<td>26.46</td>
<td>25.82%</td>
</tr>
<tr>
<td></td>
<td>30.62%</td>
<td>27.94%</td>
<td>27.94%</td>
</tr>
<tr>
<td></td>
<td>25.35%</td>
<td>28.51%</td>
<td>27.81%</td>
</tr>
<tr>
<td>Fluorine loss</td>
<td>32.68% (a)</td>
<td>42.05% (b)</td>
<td>44.00% (h)</td>
</tr>
<tr>
<td></td>
<td>41.51%</td>
<td>41.78</td>
<td>43.93%</td>
</tr>
<tr>
<td></td>
<td>31.7%</td>
<td>37.87%</td>
<td>43.67%</td>
</tr>
<tr>
<td></td>
<td>44.5%</td>
<td>43.4%</td>
<td></td>
</tr>
<tr>
<td>Calculated SiF&lt;sub&gt;4&lt;/sub&gt; content</td>
<td>12.91 (a)</td>
<td>15.73% (b)</td>
<td>16.71% (h)</td>
</tr>
<tr>
<td></td>
<td>16.73%</td>
<td>16.71%</td>
<td>16.60%</td>
</tr>
<tr>
<td></td>
<td>14.45%</td>
<td>14.45%</td>
<td></td>
</tr>
<tr>
<td>Calculated Si content</td>
<td>3.48 (a)</td>
<td>4.24% (b)</td>
<td>4.51% (h)</td>
</tr>
<tr>
<td></td>
<td>4.51%</td>
<td>4.51%</td>
<td>4.48%</td>
</tr>
<tr>
<td></td>
<td>3.91%</td>
<td>3.91%</td>
<td></td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O content by difference</td>
<td>26.04% (a)</td>
<td>22.40% (b)</td>
<td>22.01% (h)</td>
</tr>
<tr>
<td></td>
<td>22.59%</td>
<td>22.59%</td>
<td>21.42%</td>
</tr>
<tr>
<td></td>
<td>24.87%</td>
<td>24.87%</td>
<td></td>
</tr>
</tbody>
</table>
TABLE IX (Cont'd)

The values enclosed by brackets indicate data obtained from two independent experiments. Values underlined indicate overages. A description of the samples is given in Table XII.

(a) 3.0 g sample heated with a Tirril burner. See Table VIII for a more detailed description of heating procedures.

(b) 0.14 g samples heated in a muffle furnace at 450°C for 4-1/3 hours.

(c) 1.0 g samples heated in a muffle furnace at 450°C for 11 hours.

(d) 2.0 g samples heated in a muffle furnace at 450°C for 4 hours.

(e) 1.0 g samples heated in a muffle furnace at 450°C for 1-1/2 hours. Same samples used in (c).

(f) 3.5 g sample heated for 6 hours at 500°C in a muffle furnace.

(g) Same as (f) but heated for an additional 12 hours at 500°C. The fluorine analyses are duplicate analyses on the same ignited sample.

(h) 0.12 g samples heated in muffle furnace at 450°C for 3 hours.

(i) 1.0 g samples heated in muffle furnace at 400°C for 2-1/2 hours.

(j) 1.0 g sample heated with Tirril burner.

(k) 1.0 g sample heated in muffle furnace:
   16 hours at 350°C
   1-3/4 hours at 400°C
   1/2 hour at 475°C.

(l) Same as (k) but heated in muffle furnace at 450°C for an additional 2 hours.
<table>
<thead>
<tr>
<th></th>
<th>Dow, Vacuum Dried Residue</th>
<th>Third Calcined Residue</th>
<th>95% Acid Digestion Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>F</strong></td>
<td>29.25, 28.40% 26.82</td>
<td>27.60, 27.35 27.47</td>
<td>27.73, 27.76 27.75</td>
</tr>
<tr>
<td><strong>PO(_4)</strong></td>
<td>1.15, 1.13, 1.14</td>
<td>1.54, 1.72, 2.10 1.79</td>
<td>2.83, 2.80 2.82</td>
</tr>
<tr>
<td><strong>Ca</strong></td>
<td>18.59, 18.38, 18.49</td>
<td>17.14, 17.24, 17.19</td>
<td>18.30, 18.61 18.46</td>
</tr>
<tr>
<td><strong>Al</strong></td>
<td>(2.60), (2.40), (2.88), 3.04, 3.02, 3.03</td>
<td>2.92, 2.66, 2.45 3.09, 2.70, 2.77</td>
<td>(3.28), 2.72, 2.70 2.71</td>
</tr>
<tr>
<td><strong>Fe</strong></td>
<td>0.14 0.17 0.16 0.16</td>
<td>0.13</td>
<td>0.13, 0.12 0.13</td>
</tr>
<tr>
<td><strong>Ti</strong></td>
<td>0.13 0.15 0.14</td>
<td>0.24</td>
<td>0.19, 0.19 0.19</td>
</tr>
<tr>
<td><strong>Cl</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SiO(_2)</strong></td>
<td>4.61, 3.94, 4.31 4.29 (3.78), 4.29</td>
<td>8.07, 7.97, 7.93 7.95, 7.98</td>
<td>5.68, 5.58, 5.58 5.61</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
<td>2.25, 1.61, 1.93</td>
<td>1.33, 1.34, 1.28 1.32</td>
<td>(1.94), (1.88), 1.02 0.99, 1.07 1.03</td>
</tr>
</tbody>
</table>
TABLE X (Cont'd)

<table>
<thead>
<tr>
<th></th>
<th>26.04 (by difference)</th>
<th>25.46, 25.72, 25.56</th>
<th>25.99, 26.21, 26.29, 26.16</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>25.78, 26.06 25.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>3.48</td>
<td>4.24</td>
<td>4.51</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.21</td>
<td>98.98</td>
<td>98.85</td>
</tr>
</tbody>
</table>

Sample

II A residue obtained from the Dow Chemical Company, Louisiana Division, 26% HCl used for digestion. SiO₂, which amounted to 16.3% of the original weight of the bulk residue, was removed with a 325 mesh screen.

VI The residue that remained after the third digestion of calcined ore with 105% of the theoretically required amount of 26% HCl. SiO₂ and other insoluble minerals, which amounted to 23% of the bulk residue weight, were removed with a 200 mesh screen. The residue contained 53.4% of the fluorine present in the ore.

VII. Residue that remained after digestion of calcined ore with 95% of the theoretically required amount of 26% HCl. SiO₂ and other insoluble minerals, 22.2% of the bulk residue weight, were removed with a 270 mesh wire screen. The residue contained 59.4% of the fluorine originally present in the ore.

Underlined values are averages. Those values in parentheses were not used in calculating the averages.
Definite non-homogeneity was visually observed with large samples strongly ignited with a Fisher burner. On three different occasions during this work, fluorine analysis before and after ignition indicated that the fluorine loss exceeded the weight loss of the sample. This paradox could have resulted from inaccurate fluorine analyses but the magnitude of the error required was some ten times the usual uncertainty of the analysis.

For this reason, the elemental analyses that required elimination of silicon and fluorine by heating were carried out after complete solution of the sample. Sodium carbonate fusion was utilized when necessary. Ignitions and fluorine analyses, (b) and (h) of Table IX, used to determine the fluosilicate content of the residue Samples VI and VII, employed small quantities of residue and the entire ignited samples were analyzed to determine the fluorine content.

The total silicon content of Sample VI obtained by wet chemical methods was 7.1%. If the assumption was correct that all fluorine lost during ignition was lost as SiF₄, the total silicon content would be 7.97%. Silicon dioxide would account for 3.73% Si and the remaining 4.24%, as determined from ignition (b), would be present as fluosilicate. The silicon content of Sample VI was also determined by neutron activation analyses (NAA). The value obtained was 7.7% with an estimated accuracy of ± 5%. A NAA silicon analysis was also obtained after heating; see ignition (f), Table IX.
Fluorine analysis of the ignited sample indicated that 40% of the silicon was lost on ignition and NAA silicon analysis indicated 36% was lost. Although the agreement between the two methods could be better, NAA clearly implied that the fluorine lost on ignition was almost, if not entirely, evolved as SiF₄.

Thermogravimetric analysis (TGA) of the residue, in conjunction with the previously discussed differential thermal analyses (DTA) and X-ray analysis, was particularly useful in establishing the chemical formula of the residue compound. As noted in the elemental analysis, Table X, the residue contained a considerable amount of water. Thermal analysis was used to determine the nature of this water, i.e., whether the water was absorbed or chemically bound. Additional data obtained by this method identified SiF₄ as the chemical species associated with the fluorine lost on ignition.

A thermogravimetric curve and differential thermogram of the third calcined residue are given in Figures 6 and 7 respectively. The correlation of the endotherms of the DTA curves with the weight loss shown by the DTA curves was apparent for the endotherms at 170°C and 372°C, and the fusion reaction at about 700°C. There were no obvious indications in the DTA curve, however, which corresponded to the weight loss noted between 180° and 380°C.
Figure 6. Thermogram of Digestion Residue
Figure 7. Thermogravimetric Curve of Digestion Residue
An interpretation of the thermal data was possible by correlation with fluorine analysis of samples dynamically heated, i.e., at a constant rate of temperature increase, to temperatures indicated by the thermogravimetric curve to be of particular interest. The temperatures chosen were 185°, 360°, and 600°C. The choice of 600°C was somewhat arbitrary since the thermogravimetric curve exhibited a very gradual slope change between 450° and 600°C. Instead of dynamically heating to 185°C, a sample was heated isothermally at 140°C to minimize any effects of the gradual weight loss that normally occurred in the 185° to 380°C range.

These data were obtained in the following manner. Fifty milligrams of residue were placed in the sample holder and heated (TGA) under a nitrogen atmosphere to the desired temperature or until the desired weight loss had occurred. The sample was then removed from the furnace and rapidly cooled to room temperature. Had there been any weight changes during the cooling period, they could have been observed, but none occurred. The precision of the weight measurements under the conditions of the experiment was ±0.1 mg. A quantitative transfer of the sample, including the platinum holder, was made to a distillation flask and the entire sample analyzed for fluorine. The results of this series of experiments are given in Table XI.
### TABLE XI

**Analytical Data of Dynamically Heated Residue**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temperature Range</th>
<th>Weight Loss</th>
<th>Fluorine Content</th>
<th>Fluorine Lost (Percent of Total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isothermal-140°C for 80 minutes</td>
<td>22.0%</td>
<td>35.95%</td>
<td>1.8%</td>
</tr>
<tr>
<td>2</td>
<td>25° to 358°C</td>
<td>28.4</td>
<td>34.89</td>
<td>13.4</td>
</tr>
<tr>
<td>3</td>
<td>25° to 360°</td>
<td>28.2</td>
<td>34.15</td>
<td>14.2</td>
</tr>
<tr>
<td>4</td>
<td>25° to 630°</td>
<td>38.4</td>
<td>30.31</td>
<td>35.0</td>
</tr>
<tr>
<td>5</td>
<td>25° to 550°</td>
<td>37.5</td>
<td>29.62</td>
<td>35.8</td>
</tr>
</tbody>
</table>

### TABLE XII

**Results Calculated From the Data of Table XI**

<table>
<thead>
<tr>
<th>Temperature Interval</th>
<th>Weight Loss Per 100 g</th>
<th>Fluorine Loss Per 100 g</th>
<th>SiF₄ Loss Per 100 g</th>
<th>Moles of SiF₄ per 100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>25° to 185°</td>
<td>22.6 g</td>
<td>0.0 g</td>
<td>0.0 g</td>
<td>0.0</td>
</tr>
<tr>
<td>185° to 360°</td>
<td>5.7</td>
<td>3.8</td>
<td>5.2</td>
<td>0.05</td>
</tr>
<tr>
<td>360° to 590°</td>
<td>9.6</td>
<td>6.1</td>
<td>8.4</td>
<td>0.08</td>
</tr>
<tr>
<td>185° to 590°</td>
<td>15.3</td>
<td>9.9</td>
<td>13.6</td>
<td>0.13</td>
</tr>
</tbody>
</table>
The fluorine content of the residue sample, from the third calcined digestion, was 28.56%. By averaging the results of runs 2 and 3, and 4 and 5, the weight loss due to fluorine and silicon tetrafluoride was calculated and compared with the experimental weight loss for the temperature intervals (see Table XII). The weight loss, 22.0%, found for the isothermal run at 140°, closely corresponded to the weight loss, 22.6%, observed for dynamic heating at 185°C (Figure 7). As a consequence, the temperature of 185°C was used for the upper limit of the first interval in the table. The small amount of fluorine lost during the isothermal run at 140°, 1.8% of the total, was included in that lost during the second interval. When the carbon content of the residue sample, 1.32%, was added to the calculated SiF₄ weight loss, 13.6%, the calculated weight loss of 14.9% was in good agreement with the experimental value of 15.3% for the 185°-590°C temperature range, and further justified this method of determining the fluosilicate content of the residue compound.

An evaluation of both the thermogram and the thermogravimetric curve of the residue is now in order and will include the X-ray and analytical data that have been presented. The first question concerned the nature of the change that produced the large endotherm at 170°C. X-ray analysis showed that the crystalline structure of the residue compound was completely destroyed by this change and that an amorphous solid resulted.
The elemental analyses showed that water was the only gaseous decomposition product present in sufficient quantity to account for the large weight loss, and fluorine analysis showed that water was essentially the only gaseous product of this reaction. The weight loss did not begin until 90-95°C was reached and was slow below 130°C. Thermogravimetric curves of samples known to contain absorbed water showed that weight loss began at 50°C and had virtually ceased at 110°C. There was little doubt, therefore, that the weight loss that occurred between 90° and 185°C, and the endothermic reaction at 170°C, were primarily due to loss of chemically bound water. The dehydration was found to be irreversible.

The residue was shown to be amorphous at temperatures in the region between the two endothermic peaks at 170° and 372°C, and there were no indications of a thermal reaction in this temperature region. The fluorine analyses shown in Table XII indicated, however, that about 5.2 wt. % of the residue was lost as SiF₄ in this region.

The formation of crystalline CaF₂ occurred at the 372°C endotherm and the thermogravimetric curve showed a sharp increase in the rate of SiF₄ evolution at this temperature. The extrapolated onset of the endotherm was within 3°C of the slope change of the thermogravimetric curve. Only CaF₂ was evident in the X-ray diffraction pattern of a sample heated to 390°C (DTA), but βCaSO₄ formed during the exothermic reaction at 428°C. An X-ray pattern of a sample
heated to 500° exhibited the pattern of both crystalline substances. The intensities in the X-ray patterns of samples heated above 500°C increased, which suggested that part of the weight loss above this temperature may be associated with continued SiF4 evolution and formation of crystalline CaF2 and CaSO4.

A probable explanation for the gradual SiF4 evolution between 185° and 380° may be gained by a closer examination of the decomposition characteristics of the residue compound and the physical states produced by the decomposition. The amorphous state formed by the irreversible dehydration was a non-equilibrium state. This instability was evidenced by the gradual SiF4 evolution at a rate that was essentially independent of temperature over the 200°C range. No gradual weight loss of this type was observed during the decomposition of CaSiF6·2H2O. Another characteristic of the SiF4 evolution of the residue compound not paralleled in calcium fluosilicate decomposition was the effect produced by a vacuum. The 372°C endotherm of the residue compound was unaffected by a vacuum, whereas both endotherms of CaSiF6·2H2O and the dehydration endotherm of the residue compound shifted by 20-40°C to lower temperatures under these conditions.

If the residue compound was assumed to have a complex mineral-like crystalline structure, dehydration might well be expected to leave the remaining components as a tumbled array of molecules and/or ions incapable of reforming
into a crystalline structure. It was observed that as the temperature increased and SiF$_4$ evolution occurred, crystallization of the non-volatile components became more energetically favored. Although SiF$_4$ evolution began at about 185°C, X-ray examination showed that no crystalline CaF$_2$ was formed before the endothermic reaction at 372°C and no crystalline CaSO$_4$ was formed before the exothermic reaction at 428°C. The temperature of the first reaction, 372°C, was some 35°C higher than the endotherm caused by SiF$_4$ evolution and crystalline CaF$_2$ formation from CaSiF$_6$. The second reaction at 428°C was 10°C lower than the peak of the broad exotherm caused by the γ to β phase change of pure CaSO$_4$. The fact that no CaSiF$_6$, CaF$_2$, or CaSO$_4$ crystalline formation occurred over the 185°-380°C temperature region, although the molecular species were most probably present, strongly suggests that disorder and spatial arrangement of the amorphous state prevented aggregation of the species into the more energetically favored crystalline state. When sufficient energy was available to overcome the high entropy of the system, CaF$_2$ crystallization occurred.

It seems evident that although the quantity of SiF$_4$ evolved would influence the ultimate amount of crystalline CaF$_2$ produced, a much greater energy barrier existed between the amorphous and crystalline state than could be attributed to the reaction,

$$\text{CaSiF}_6 \rightarrow \text{CaF}_2 + \text{SiF}_4\uparrow.$$
In order to overcome the barrier, a temperature of 372°C was required. On crystallization, the energy released caused an increased rate of SiF₄ evolution and thereby, additional crystallization. The mechanism envisioned would be somewhat analogous to the seeding of a supercooled liquid. An added requirement, since no mixed crystals were observed, would be the ejection of foreign ions from the rapidly forming crystalline lattice.

An explanation of this type would account for the temperature difference noted for the endotherms due to CaF₂ crystallization and SiF₄ evolution in the residue compound and CaSiF₆. It would also explain the absence of any temperature shift in the 372°C endotherm of the residue compound under a vacuum. During CaF₂ crystalline formation, a simultaneous lowering of the energy barrier for CaSO₄ crystallization in the β form seemed to occur. Since the γ to β transformation of CaSO₄ was fairly broad, the formation of the latter modification at a temperature slightly below the normal transition temperature was not unexpected.

The changes in the thermograms of the residue compound and CaSiF₆·2H₂O caused by a vacuum (1 mm Hg) have been described. In general, the effect of a vacuum is to lower the vapor pressure of the volatile components of a reaction. In those cases where gaseous products are evolved, the temperature of the reaction would be expected to decrease
as the pressure is lowered. The exceptions to this statement are those reactions which are not effected by changes in the partial pressure of the volatile products and, therefore, are irreversible. Both endotherms of CaSiF$_6$·2H$_2$O and the dehydration endotherm of the residue compound shifted to lower temperatures when the pressure was reduced to 1 mm Hg. The reactions that produced these endotherms are therefore assumed to be reversible.

It will be recalled that dehydration of the residue compound has previously been described as irreversible. The assumption of irreversibility was based on the behavior of dehydrated residue that was exposed to the atmosphere until equilibrium with atmospheric moisture was attained. Twenty percent of the weight loss was not regained, and DTA indicated that the regained weight was mostly due to absorbed water. It is believed that the apparent contradiction concerning the nature of the dehydration supports the assumed complex mineral-like structure of the residue compound. The latter conditions under which it was indicated that the dehydration was reversible were such that the system was "not far" from equilibrium, the system crystalline, and thus the reaction responded in a normal manner to a change in the vapor pressure of the gaseous decomposition products. Under the former conditions, complete dehydration had occurred and reconstruction of the original crystalline structure, in which water was essential, from the "tumbled array" of the solid amorphous state was not possible.
The irreversible character of the 372° endotherm of the residue compound was established by the same line of reasoning, i.e., the temperature of the reaction was not a function of the partial pressure of tetrafluosilicate. As intimated previously, the increased rate of SiF₄ evolution would primarily be a result, rather than a cause, of the change from the amorphous to crystalline state.

A formula for the residue compound, based on the physical and chemical properties and the elemental analysis of the residue, will be suggested. The type of formula presented will resemble that encountered in mineralogy and will incorporate calcium, aluminum, fluorine, sulfate, fluosilicate, and water. No single compound that contained these components has previously been postulated and a brief summary of the most important results that led to the proposed formula will be given.

No substance was found described in the literature that corresponded to the chemical composition and physical properties of the residue. Prolonged efforts to match the X-ray diffraction pattern of the residue with that of a known compound or mixture of compounds were unsuccessful. The same X-ray pattern resulted from every residue, with two exceptions, that contained more than four percent of the fluorine originally in the ore. The first exception was an amorphous residue which was caused by a departure from the usual digestion procedure. The second exception occurred
when sulfate normally associated with the residue compound was preferentially precipitated as barium sulfate. The same X-ray pattern was exhibited by residues obtained by digestion with nitric acid as well as with hydrochloric acid and also by a residue sample received from the Dow Chemical Company.

A uniform decrease in intensity of the diffraction pattern as dehydration proceeded, with the ultimate formation of a completely amorphous state, suggested that the major portion of the residue was composed of a single compound. The decomposition characteristics of the residue compound were such that calcining of the ore would have completely destroyed the compound. The formation of an amorphous residue by changing the digestion procedure would further suggest that the residue compound was not an unchanged ore component, but was formed in and precipitated from the digestion medium.

X-ray examination identified CaF₂ and CaSO₄ as solid products of the residue decomposition; SiF₄, H₂O and CO₂ were shown to be gaseous products. The latter component resulted from oxidation of elemental carbon carried over from the ore. Both X-ray and thermal analysis indicated that the residue compound properties were not those of CaF₂, CaSO₄, CaSiF₆, or their hydrates. The decomposition characteristics of the residue compound were interpreted in terms of a complex mineral-like crystalline structure composed of calcium, fluorine, fluosilicate, and water. The conclusions drawn from the dehydration, reversible under one set of conditions
and irreversible under another, were particularly instructive in establishing the type of crystallographic composition proposed for the compound. Formation of an amorphous state upon dehydration, the different rates of SiF$_4$ evolution noted, and the temperature at which CaF$_2$ crystallization occurred, provided corroborative evidence that the residue decomposition products resulted from a structure in which each product was an integral part.

Digestion of the ore in the presence of fluorine complexing agents demonstrated that this element was necessary for formation of the residue compound. When boron, aluminum, or silicic acid was added to the digestion medium, less than three percent of the fluorine and none of the residue compound was found in the insoluble residue.

It was also found that no residue compound was formed when the ore digestion was carried out in the presence of barium ions. This series of experiments indicated that sulfate ions were necessary for formation of the residue compound and, by the altered liquor/residue fluorine distribution, that precipitation of fluorine and sulfate was not independent. This interdependence was also suggested by the precipitation of crystalline calcium sulfate from the digestion medium only in those cases where residue compound formation was blocked by the presence of fluorine complexing agents.

No residue compound formation occurred when a small amount of silicic acid was added to the digestion medium.
The results indicated that some form of fluorine other than hexafluosilicate ions was required; either the fluoride ion or a complex of lower stability than fluosilicate. Since aluminum, the only fluorine complexing element besides silicon present in quantity, forms a more stable fluorine complex than silicon, it was most logical to assume that silicic acid reacted with the fluoride ion. If this conclusion is accepted, the presence of some non-complexed fluoride ions becomes a necessary requirement for formation of the residue compound.

Despite qualitative evidence that various cationic and anionic chemical species were required for the formation of the chemical entity that has been referred to as the "residue compound," establishment of a chemical formula must ultimately rest upon quantitative analytical data and electrical neutrality of the whole. Translation of the elemental percentage compositions given in Table X and the H₂O and SiF₄ contents given in Table IX into molar quantities gave the data of Table XIII. The results are given as moles per 100 g of residue for two reasons; first, this presentation makes no assumption as to which elements were associated with the residue compound or which may have been present as impurities; secondly, the presentation is consistent with the manner in which data were presented in Tables VIII through XII and permits a direct comparison of results.
<table>
<thead>
<tr>
<th></th>
<th>Sample II</th>
<th>Sample VI</th>
<th>Sample VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>1.517</td>
<td>1.446</td>
<td>1.460</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.122</td>
<td>0.100</td>
<td>0.099</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.012</td>
<td>0.019</td>
<td>0.030</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.461</td>
<td>0.429</td>
<td>0.461</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.112</td>
<td>0.102</td>
<td>0.100</td>
</tr>
<tr>
<td>Iron</td>
<td>0.003</td>
<td>0.002</td>
<td>0.005</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.003</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td></td>
<td>0.014</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.427</td>
<td>1.427</td>
<td>1.452</td>
</tr>
<tr>
<td>(by difference)</td>
<td>1.445</td>
<td>1.243</td>
<td>1.221</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.124</td>
<td>0.151</td>
<td>0.161</td>
</tr>
<tr>
<td>(from fluorine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lost on ignition)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The residue samples chosen for complete elemental analysis, VI and VII, were selected from digestions carried out with different acid to ore ratios (and consequently a different liquor/residue fluorine distribution) so that differences might appear if the formula of the residue compound was influenced by the digestion conditions and/or fluorine distribution. The close agreement between the analytical results for Samples VI and VII were in a sense fortuitous, and did not reflect the original differences in the composition of the bulk residues. X-ray analysis had shown that the original calcium phosphate content of Sample VII was significantly greater than that of sample VI, but most of this residue component was removed by repeated washing. Thus, the total of calcium phosphate and SiO$_2$ percentages, neither of which was then thought to be associated with the residue compound, was nearly the same for the two samples. Since the total amount of these two residue components was approximately the same, although the phosphate and SiO$_2$ contents were different for the two samples, material not then believed associated with the residue compound constituted an equal part of each sample. The components which constituted the residue compound would be expected to be present in equal amounts under these conditions. Such a close agreement of the analytical data were observed and, of itself, inferred that the formula of the residue compound was not a function of the digestion conditions.
An examination of the data of Tables XIII and XIV indicated, as already suggested from the elemental percentage composition, but more dramatically, that iron, titanium, phosphate, and chlorine were present in the residue as minor components. Iron and titanium were most probably present as phosphates since the solubilities are quite low even in a highly acidic medium. Despite the high solubility of CaCl₂, the large concentration of these two ions in the liquor would permit chlorine to be present in this form. Quartz and carbon are not included in the table because they were obviously present as foreign matter.

The chemical and physical properties of the residue implied that the remaining residue constituents, except for aluminum, were combined to form the residue compound. The presence of aluminum in the residue was not surprising since its solubility properties very closely resemble those of iron and titanium. It was clearly evident, however, that insufficient phosphate was in the residue to account for more than thirty percent of the aluminum, even if no phosphate was required for iron and titanium. The value of thirty percent applied only to Sample VII, for Samples VI and II, values of twenty and twelve percent would apply. These figures also assumed that no calcium phosphate was in the residue, which would be unusual considering the medium in which the residue was formed.
### TABLE XIV

Normalized Molar Composition of Residue Samples

<table>
<thead>
<tr>
<th></th>
<th>II</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>1.04</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>CaSiF₆</td>
<td>1.04</td>
<td>1.50</td>
<td>1.61</td>
</tr>
<tr>
<td>AlF₃</td>
<td>0.94</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>CaF₂</td>
<td>1.90</td>
<td>1.14</td>
<td>1.00</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.10</td>
<td>12.3</td>
<td>12.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Excess</th>
<th>Excess</th>
<th>Excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄</td>
<td>0.040</td>
<td>Ca</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca</td>
</tr>
</tbody>
</table>

II. CaSO₄ · CaSiF₆ · 0.9 AlF₃ · 1.9 CaF₂ · 12.1 H₂O

VI. CaSO₄ · 1.5 CaSiF₆ · AlF₃ · 1.1 CaF₂ · 12.3 H₂O

VII. CaSO₄ · 1.6 CaSiF₆ · AlF₃ · 1.0 CaF₂ · 12.3 H₂O
Of the two remaining anions with which the aluminum could be combined, fluorine appeared the most logical choice. From results of X-ray examination of the heated residue, sulfate was obviously associated with calcium and it would be difficult to justify the formation of aluminum sulfate. A third possibility did exist, occurrence as aluminum silicate, but the weight of the evidence suggested that no only was aluminum present as the fluoride but that, as such, it was a constituent of the residue compound.

It was found by spectrographic analysis that the aluminum content was significantly higher in those residue samples from which SiO₂ and other large particles had been removed. The opposite was noted for iron and titanium. From considerations of the molar quantities of aluminum, calcium, silicon, and fluorine in Samples II, VI, and VII, it was obvious that aluminum and fluorine must be combined if a cation-anion balance was to be obtained. If aluminum was present as the fluoride, independent of the other residue components, its insolubility in the digestion medium was at variance with other observations. When aluminum was added to the digestion medium, nearly all of the fluorine was found in the liquor. This experiment would indicate that neither aluminum fluoride, as such, nor phosphate was insoluble to a large extent.

In a sense, the "pairing off" of cationic and anionic species was an academic undertaking if the species
were indeed constituents of a complex compound. Assumed incorporation of aluminum in the residue compound would resolve the perplexities discussed above and also provide an explanation for the equal molar quantities of aluminum and sulfate found in each residue sample. The equimolar occurrence of aluminum and sulfate was one of the strongest arguments for inclusion of aluminum in the formula for the residue compound. At no time was aluminum detected by X-ray analysis.

As noted in Tables IX and X, different amounts of water were indicated to be present in a given residue sample. The water contents of Samples VI and VII of Table X were obtained by gas analysis utilizing a commercial carbon-hydrogen analyzer. The samples were ignited at a temperature of 750°C, which was above the fusion temperature of the residue, and the percentages obtained were taken to be the total water content of the samples. The water contents given in Table IX, designated "by difference," were determined from weight losses observed after heating the residues in a muffle furnace at 450°- 500°C. The weights of carbon and SiF₄, the latter determined from the fluorine loss, were subtracted from the total weight loss to yield the water content.

Although there was good agreement among the ignition results shown in Table IX, only ignitions (b) and (h) were used to calculate the molar quantities in Table XIII. The
water content thus obtained by ignition was in fair agreement with the weight loss observed by isothermally heating residue samples at 110°C and in good agreement with the weight loss due to dehydration as determined by TGA.

The results for Sample VI are shown below.

22.50% -- Average H₂O content as determined by ignition, 450°-500°C.
21.6% -- Isothermal (110°C) weight loss after 30 days.
20.8% -- Isothermal (110°C) weight loss after 90 hours.
22.56% -- Weight loss due to dehydration as determined by TGA; average of five determinations.

The water content designated "by difference" was assumed to be chemically bound water. No weight loss was observed for any absorbed water. The water loss above 500°, which was in excess to the water of hydration, was probably associated with the weight loss at and above the fusion temperature of the sample. Some of the excess water could have been associated with hydrous silica which is known for its ability to hold absorbed water even at high temperatures.

The formalism used to obtain a cation-anion balance, and thus the "molecular components" of the residue, was as follows. The molar quantities in Table XIII were normalized by the time honored tradition of division by the lowest common denominator, in this case, the average of the sulfate and aluminum content. The phosphate was distributed between iron and titanium and any excess ascribed to calcium
phosphate. It was assumed that all sulfate was present as CaSO₄, and all aluminum as AlF₃. The CaSiF₆ content was determined by the silicon present. The remaining calcium and fluorine were then combined as CaF₂. The water of hydration required no such formalism.

The above procedure led to the following formulas for residue samples II, VI, and VII.

- **II.** 1.0 CaSO₄ • 1.0 CaSiF₆ • 0.9 AlF₃ • 1.9 CaF₂ • 12.1 H₂O
- **VI.** 1.0 CaSO₄ • 1.5 CaSiF₆ • 1.0 AlF₃ • 1.1 CaF₂ • 12.3 H₂O
- **VII.** 1.0 CaSO₄ • 1.6 CaSiF₆ • 1.0 AlF₃ • 1.0 CaF • 12.3 H₂O

The reasonable agreement between VI and VII is just as obvious as is their poor agreement with formula II. The difference between II and the other two formulas was a result of incomplete SiF₄ evolution on ignition as shown in ignition II(a) of Table IX. Ignition VI(f) will lead to results very similar to formula II above, but it was shown that in this instance, too, there was incomplete decomposition. Except for the fluorine distribution between CaF₂ and CaSiF₆, which would be strongly affected by incomplete ignition, good agreement exists between formula II and formulas VI and VII.

A consideration of formulas VI and VII indicated that

\[ \text{CaSO}_4 \cdot 1.5 \text{CaSiF}_6 \cdot \text{AlF}_3 \cdot \text{CaF}_2 \cdot 12 \text{H}_2\text{O} \]

was the probable formula for the residue compound. It should be noted that although only ignitions VI(b) and VII(h) were used to obtain formulas VI and VII, ignitions (g) and (l) led to the same results. The above formula could also be
represented as Ca$_3$.5AlSi$_{11}$.5(SO$_4$)F$_{14}$. The average experimental composition of the residue samples (excluding II) was Ca$_{4.43}$Al$_{1.01}$Si$_{11.55}$(SO$_4$)$_{0.98}$F$_{14.50}$. The 4.43 moles of calcium included all the calcium in the residue whether or not it was chemically part of the residue compound. There was not sufficient chlorine and phosphate in the residue, however, to account for the excess calcium. This excess calcium was most probably present in the residues as calcium silicate. The analytical procedures which were used would include any such calcium in the total, and the silicate would have been recorded as SiO$_2$, also not included in the formula for the residue compound.

The methods of analysis and interpretation of the results would have been greatly simplified had it been possible to obtain a pure sample of the residue compound. As it was, SiO$_2$, insoluble silicates, elemental carbon, iron, titanium, phosphate and chlorine, were present in all samples. Attempts to prepare the residue compound from solutions that approximated the digestion conditions were unsuccessful.

In one attempt, a residue was decomposed with concentrated HCl, filtered to remove SiO$_2$ and other insolubles, and the resulting solution slowly evaporated. The only crystalline component formed was CaSO$_4$·2H$_2$O. It was known that no fluorine precipitated if only one-half of the usual amount of ore was added to a given volume of 26% HCl. Such a dilute liquor was prepared, filtered, and an amount of
Ca₃(PO₄)₂ added that corresponded in phosphate content to the second half of the ore. No precipitation occurred. Most attempts to approximate a liquor which contained the correct quantities of residue compound components resulted in CaSO₄ precipitation in one form or another.

In a critical evaluation of the residue compound formula, one particular point should be made. Evidence was presented which indicated the requirement for each component in the formula. It cannot be categorically stated, however, that the total amount of each of these components found in the residue was part of the crystalline structure of the residue compound, i.e., a portion could have been present in an amorphous state or absorbed on the crystalline residue compound. The TGA curve could be interpreted to suggest that one-third of the fluosilicate was absorbed, and while some could have been, this quantity seemed excessive. Also, the TGA curves were reproducible and it appears unlikely that the same percentage of fluosilicate would have been absorbed on the residue compound in every digestion.

The proposed formula was fairly close to CaSO₄•1.5 CaSiF₆•1/2[Ca₃(AlF₆)₂] which would require an additional 0.5 moles of CaF₂. Sufficient calcium was available if none were present as the silicate, but the average fluorine content of Samples VI and VII was one-half mole less than the required total of fifteen.
It is interesting to speculate on some factors that could have been associated with the formation of the residue compound. From the lack of success in synthesizing the compound, it was apparent that rigid conditions were required for its formation. It seemed probable that the partially decayed apatite mineral lattice offered a number of spaces into which other chemical species could move in the formation of the residue compound. Non-complexed fluoride was already present in the apatite structure; also, sulfate and silicate are known to substitute for phosphate in this structure. The substitution is nearly complete in the mineral Ellestadite.\(^1\)

Minerals which are somewhat similar in composition to that proposed for the residue compound do exist. Below is a partial list of minerals that contain calcium, aluminum, and fluorine.

<table>
<thead>
<tr>
<th>Minaral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prosopite</td>
<td>CaF(_2)\cdot2\text{Al}(\text{F},\text{OH})_3</td>
</tr>
<tr>
<td>Pachnolite</td>
<td>NaCa((\text{AlF}_6)\cdot\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Gearksutite</td>
<td>CaAl((\text{F},\text{OH})_5)</td>
</tr>
<tr>
<td>Para-gearksutite</td>
<td>CaAl((\text{F},\text{OH})\cdot0.7\ \text{H}_2\text{O})</td>
</tr>
</tbody>
</table>

A description of these minerals can be found in most standard mineralogical references. The physical and chemical properties, including the X-ray diffraction pattern, differed from the corresponding properties of the residue compound.

Another mineral, Creedite, contained all components of the residue compound except the fluosilicate, also differed in the same basic properties. There exists some difference of opinion as to the correct formula for Creedite.

Frenzel quotes $2\text{CaSO}_4 \cdot 4\text{CaF}_2 \cdot 2\text{AlF}_3 \cdot 3\text{Al(OH)}_3$ whereas Fleischer, who characterized samples from five different localities by elemental analyses, DTA, and X-ray analysis, prefers $\text{CaSO}_4 \cdot 2\text{CaF}_2 \cdot 2\text{AlF}_3 \cdot 7\text{H}_2\text{O}$ or the general formula $\text{Ca}_3\text{Al}_2(\text{SO}_4)(\text{F}_8 \text{OH})_{10} \cdot 2\text{H}_2\text{O}$. The residue compound is therefore proposed as a previously unreported chemical entity of the formula

$$\text{CaSO}_4 \cdot 1.5 \text{CaSiF}_3 \cdot \text{AlF}_3 \cdot \text{CaF}_2 \cdot 12 \text{H}_2\text{O}.$$
CHAPTER IV
CONCLUSIONS

In any research endeavor, it is possible to draw conclusions of one type or another. It is most often the case that the conclusions themselves suggest areas of investigation that would be profitable for future consideration. This work was no exception. Considerations for future work will therefore be presented along with the summary of conclusions.

Initially, the primary objective of this investigation was to eliminate the fluorine impurity, easily and cheaply, at as early a stage as possible in the processing of Florida phosphate pebble for the manufacture of phosphoric acid. The course of the research progressed along four distinct lines of investigation: (1) a study of the formation and chemical nature of the insoluble digestion residue; (2) a determination of the fluorine distribution between the residue and digestion liquor; (3) a determination of the fluorine distribution between various liquid phases associated with the phosphoric acid extraction process; and (4) an investigation of the effects of variables related to the distribution in (2) and (3). Considerable progress was made along each line of investigation, and
although the initial objective was not achieved, some observations were made which led to conclusions that were possibly of an even more fundamental nature.

The fluorine distribution between the residue and liquor was determined under different digestion conditions of acid to ore ratio, acid volume and concentration, and in the presence of a number of different chemical substances. Under what has been termed normal digestion conditions, i.e., with a slight excess of acid, it was found that the reaction of the ore was essentially complete. The residue contained approximately fifty-five percent of the fluorine under these conditions, and the remaining forty-five percent was in the phosphoric acid liquor. As the acid to ore ratio was decreased, the reaction of the ore was less complete, the amount of residue increased, and the amount of fluorine in the residue increased. For a given acid to ore ratio, the more concentrated digestion acid resulted in less residue but more insoluble fluorine. Therefore, in general terms, at a given acid to ore ratio, a more concentrated digestion medium resulted in a more efficient acid-ore reaction and more insoluble fluorine.

Variation of the calcium concentration of the digestion medium showed that increased calcium concentration was particularly effective in placing more fluorine in the residue. A comparison of the effects of calcium addition to a normal digestion and the effect of reducing the acid to ore ratio of a normal digestion was instructive. When
sufficient calcium was added to a normal digestion to increase the calcium concentration of the digestion medium by two percent, there was a twenty percent increase in insoluble fluoride. When the volume of acid (26% HCl) used for a normal digestion was decreased by ten percent, there was a one and one-half percent increase in the calcium concentration of the digestion medium and a ten percent increase in insoluble fluoride resulted. When the acid to ore ratio was decreased by the same ten percent with no change in the digestion volume or calcium concentration, the insoluble fluoride increased by only three percent. The general effect of acid to ore ratio, of concentration in the digestion medium, and the specific effect of calcium concentration were clearly defined.

Elimination of fluorine during the digestion step would be most desirable. Considerably more fluorine could be removed by combining the different effects mentioned above. Increasing the amount of insoluble fluoride by decreasing the acid to ore ratio, by decreasing the volume of digestion acid, or by increasing the calcium concentration of the digestion medium, will have practical limits imposed by an acceptable efficiency of the acid-ore reaction and by formation of the insoluble calcium chlorohydrophosphate in highly concentrated solutions. A more detailed study of the effect of the above three factors, singly and in combination, should be undertaken. The use of recycled, extracted liquor would
appear to be a most advantageous way to increase the calcium concentration of the digestion medium.

The fluorine distribution between the aqueous digestion liquor and tributylphosphate was determined. It was apparent from this work, where approximately thirty percent of the total fluorine was placed in the organic phase by a single extraction, that practically all of the soluble fluorine would be extracted by a continuous, countercurrent process.

A particularly interesting discovery was the quantitative and specific nature of the extraction of HBF₄⁻, to the exclusion of HBF₃(OH), by the alamine solution. Digestion of the ore in the presence of borax, followed by alamine extraction of the boron containing liquor prior to TBP extraction, would cause very little change in the fluorine content of the TBP phase when compared to a normal digestion and extraction. The equilibrium and reaction rate between the two boron fluorides place a restriction on the amount of fluorine that can be extracted by the alamine. It would be possible, however, to recover the alamine extracted fluorine as tetrafluoboric acid or its salt and the fluoborate would be a less objectionable impurity than fluosilicate in some cases. It would also be possible to add borax to the liquor after separation of the residue and remove additional fluorine by alamine extraction.

Liquid-liquid extraction is an interesting and useful method of separation. The specificity of the alamine
solution for tetrafluoroborate is just one example of unique results and suggests that investigation of fluorine extraction by other organic phases might be profitable.

The characterization of the insoluble fluorine form was the most fundamental result of this investigation and probably the most important contribution to understanding the distribution of fluorine between the residue and liquor.

Evidence was presented to show that the residue compound was not an original constituent of the ore, but rather was formed in and precipitated from the digestion medium. It was shown that the properties of the residue compound were not those of the more common fluorine compounds that one might expect to find in the residue. While the elemental analysis of the residue could be interpreted to include the elements of the more common compounds in the correct stoichiometric quantities, digestion results carried out in the presence of various chemical substances indicated that the precipitation of the residue components were interrelated.

The residue compound was characterized by X-ray diffraction of powdered samples, differential thermal analysis, thermogravimetry, and by other physical and chemical means. The decomposition characteristics of the compound, as determined by DTA, TGA, and elemental analysis, were interpreted in terms of a complex mineral-like structure.
All experimental observations supported the existence of a compound of this type rather than the independent simultaneous precipitation of the individual components.

Elemental analysis of the residue led to the proposed formula

\[ \text{CaSO}_4 \cdot 1.5 \text{CaSiF}_6 \cdot \text{AlF}_3 \cdot \text{CaF}_2 \cdot 12 \text{H}_2\text{O}. \]

Minerals of a somewhat similar composition are known, but their physical and chemical properties differ from those of the residue compound.

Since no compound of this formula or properties has been previously reported, and attempts to prepare the compound under conditions other than digestion of the phosphate ore were unsuccessful, it was concluded that substitution of the ionic components of the residue compound into the decaying apatite structure might well be the mechanism by which it is formed.

Crystallography comprises one area where additional work is needed to fully characterize the compound. Determination of the crystalline family, point group, unit cell dimensions, and if possible, a complete crystallographic analysis should be undertaken.
SELECTED BIBLIOGRAPHY


Emigh. The Petrography, Mineralogy, and Origin of Phosphate Pellets in the Western Permian Formation and Other Sedimentary Formations, Dissertation, Univ. of Arizona (1956).


Hill, W. L. and Jacob, K. D. *Mining Eng.*, 6, 994 (1954).


Kate, Mane, et. al. *Japan*, 14, 355 (1960).


Lang, W. *Ber.*, 59, 2107 (1926).


Methods Used and Adopted by the Association of Florida Phosphate Chemists. (1960).


VITA

Curtis Locke Meredith was born in Ecru, Mississippi, in October of 1932. He received his elementary education at Utica and Hazlehurst, Mississippi. After graduation from high school at Hazlehurst in May, he entered David Lipscomb College in September, 1950, and was awarded a Bachelor of Arts Degree in June of 1954. He served in the United States Navy from September of 1954 to July of 1958 and began his graduate studies at Louisiana State University in September of that year. These studies were interrupted for one year, from October, 1961, to October, 1962, upon his recall to active duty in the U. S. Navy. In February, 1962, he was awarded a Master of Science Degree by Louisiana State University. He resumed his studies there in September, 1962.

Since July, 1964, he has been employed by Copolymer Rubber and Chemical Corporation in Baton Rouge, Louisiana. He and his wife, Gloria, have two children, a son, Curtis Locke, Junior, born in 1960, and a daughter, Deborah, born in 1961.
Candidate: Curtis Locke Meredith

Major Field: Chemistry

Title of Thesis: "The Nature and Distribution of Fluorine in the Hydrochloric Acid Processing of Florida Phosphate Pebble"

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

[Signature]

[Signature]

Date of Examination:

May 10, 1965