

1945

# The composition of the water soluble fraction of some ceramic clay deposits of Iowa

Averill John Hammer  
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THE COMPOSITION OF THE WATER SOLUBLE FRACTION  
OF SOME CERAMIC CLAY DEPOSITS OF IOWA

by

Averill John Hammer

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

**Approved:**

Signature was redacted for privacy.

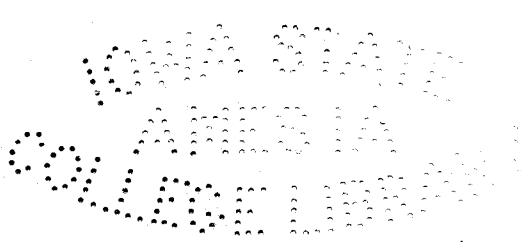
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Iowa State College

1945



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## I. INTRODUCTION

The water soluble materials in ceramic clays have been of interest to the manufacturers and users of structural clay products for many years. These materials are responsible for the formation of the white coating or efflorescence which is often seen on the surfaces of brick and tile walls and they also cause various difficulties in the manufacture of clay wares.

From what is now known concerning the causes of efflorescence, one may conclude that it has been appearing on brick walls since man first used burned clay for construction purposes, provided atmospheric conditions were such as to allow its formation. It was not until the reign of Napoleon III of France (1852-1871) that the phenomenon of efflorescence was brought to the attention of scientists. The emperor offered a reward of \$100,000 to anyone who would discover a means of preventing its occurrence (1-2). This stimulated a scientific study of the problem and, in a few years, papers began appearing in the various scientific journals of Europe describing the causes and remedies of efflorescence.

Since 1877 numerous papers have appeared in the ceramic, chemical and geological literature of both Europe and America on the efflorescence of structural clay products

and the relationship of the soluble salts in clays to the formation of efflorescence. The subject of efflorescence has been reviewed by a number of writers (3-19) and Jackson (20) has published a comprehensive bibliography on the subject which covers the literature between the years 1877 and 1924.

In America the first published notice of efflorescence appeared about the year 1882, at which time there was an unusual amount of it noticed on buildings both here and abroad. It appeared not only on buildings under construction, but also on those never known to have been troubled before. Among the several scientific societies which took up the problem in America was the Academy of Natural Sciences of Philadelphia. The Academy investigators reached the conclusion that the cause of the trouble was principally magnesium sulfate (21) present in the bricks which was carried to the surface in solution and there deposited as a white encrustation. At the first meeting of the American Ceramic Society in 1899, the problem of efflorescence was one of the chief subjects of discussion (22).

Hans Guenther, one of the early German investigators (23), laid particular emphasis on the role that pyrite plays as well as on the reactions which take place between the salts in the brick and those in the mortar. He is also thought to have recognized that oxidation products of pyrite lead to the formation of various soluble sulfates.

Gerlach (24) was one of the first to state the possible reactions of lime in the brick with the sulfur in the kiln gases and to show the influence of these reactions on the formation of efflorescence.

Seger (25, 26) was among the first of the ceramists who studied the problem. He concluded that efflorescence is composed chiefly of the sulfates of the alkalies and alkaline earths rather than salt peter as had been believed by some.

These incrustations are known to form on the surfaces of stone, concrete, gypsum, plaster and other building materials as well as those of clay origin (27-37). A variety of names has been given to this formation (5, 18, 37-40). They include "efflorescence", "florescence", "bloomings", "tile scum", "scum", "dry house scum", "drier scum", "kiln scum", "incrustation", "exerescence", "wall cancer", "stack white", "exudations", "salt peter", and "alkali". All of these refer to a crystalline deposit on the surface of the clay body. The term "efflorescence" has been adopted by the majority of manufacturers of ceramic products, probably because it was one of the first used to describe the phenomenon. Several have restricted the use of this term to deposits of soluble material from the raw clay, or to compounds brought to the surface in certain stages during the manufacture of the ware.

Parmelee (18) believes that the term "efflorescence" should be restricted to surface deposits due to the soluble



salts in the clays or burned wares and "scum" be used to describe surface deposits formed by the action of furnace gases upon the wares during drying or burning. McIntire and Schaffer (41) and Lovejoy (42) have classified the various formations under four headings: I. Cryptoflorescence, the crystallization of salts below the surface of fired wares during long exposure to weather causing rupture of the bond and spalling of the surface. II. Efflorescence, a coating of soluble salts on the surface of clay bodies brought in solution from within or through the bodies by capillarity and deposited by evaporation. III. Inflorescence, a white coating of soluble salts deposited on the surface of fired ware prior to constructional use, from sources outside the ware. IV. Scum, a dirty white coating on the surface of fired ware, developed in the firing from efflorescence on the dry ware.

Although there are several factors which influence the formation of this deposit on clay wares, it has long been recognized that the water soluble compounds present in the raw clay are responsible for a large part of the efflorescence. In so far as is known, no information is available concerning the water soluble material in the various Iowa ceramic clays. The only mention of the matter of efflorescence in the studies of the ceramic clays of Iowa (43-45) was by Beyer (43, p.341) who ascribes it to materials in the fuel used in burning the ware.

The object of this investigation was (I) to obtain data on the chemical composition of the soluble salt fraction of a list of representative Iowa ceramic clays. This necessitated (II) a study of the various methods of determining the soluble salts in clays. Another object (III) was to review the literature and arrive at conclusions concerning the modes of origin of soluble salts in the finished clay body.

## II. THE ORIGIN OF SOLUBLE SALTS IN NATURAL CLAYS AND SHALES

### A. The Origin of Clays and Shales

Clay may be defined as an earthy substance of fine texture containing a mixture of hydrous aluminum silicates, with fragments of other minerals such as silicates, oxides, carbonates, etc., and colloidal material which may be either organic or mineral in character (46). From the ceramist's viewpoint, clay is a naturally occurring earthy substance which will mold when wet, retain its shape when dry, and harden to a rock-like substance upon cooling after being subjected to a sufficiently high temperature, a process known as firing or burning (45). The petrographer has a tendency to consider clay as a mixture of the various clay minerals which impart physical properties such as plasticity, bonding strength, shrinkage, retention of form, etc. to the material while all other materials are considered as impurities (47).

Clays are derived from crystalline rocks and the processes responsible for the transformation into deposits of clay or shale are both chemical and mechanical in nature, with the chemical processes of natural weathering having the greatest influence on the conversion of rock fragments or mineral grains into clays. The grinding effect of streams rolling stones and rock fragments over one another; glaciers

grinding small rocks and boulders against the bed rock; abrasion of exposed rocks by wind-blown sand; disruptive effect of frost and unequal expansions due to alterations of heat and cold; and chemical decomposition due to water, oxygen, carbon dioxide and other constituents present in the atmosphere all play important parts in the pulverizing of rocks to fine powder and converting a part or all of the powder into new minerals, some of which are quite soluble in water (48).

The decomposition of rocks by carbon dioxide and water was studied by Rogers (49) in 1848 and the effect of water and carbon dioxide on feldspar was investigated by Headen (50). The feldspars, e.g. orthoclase ( $KAlSi_3O_8$ ) and other silicates may be converted into a group of hydrated aluminum silicates which are prominent in clay composition. Among these hydrated aluminum silicates is kaolinite whose formation may be illustrated by the following equation:



The literature on the formation of clays in general and kaolin in particular is voluminous (51-59). Rosler's paper (54) is very thorough and includes a bibliography of 303 references.

Although the theories concerning the origin of kaolin and other hydrated aluminum silicates usually consider their formation from feldspars by the action of water and carbon dioxide, there is evidence that under certain conditions they

may be formed by reactions between colloidal alumina and silica in the presence of water (60-61). Schwarz and Walcker (60) have found that when aluminum hydroxide and silica are mixed in water in the proportions  $Al_2O_3:6SiO_2$ , a substance is precipitated which has the formula  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$  and which on keeping becomes similar to kaolin. Others (61) have found that when colloidal  $SiO_2$  and colloidal  $Al_2O_3$ , no matter what the ratio, are mixed in water the alumina and silica are always precipitated in the ratio 1:2, which is the same as that of a number of clays.

Each clay bears witness to its geological history; its parent igneous rock; the mechanical and chemical disintegration of past ages; the leaching out of soluble salts and the infiltration of other salts; the transportation by water, wind or ice and subsequent sedimentation in stream channels and quiet lakes or coagulation in the saline waters of the ocean (62).

The particles making up a clay deposit are extremely small. In the mechanical analysis of sediments, the clay particles are considered to be the smallest in the series. There is some variation among authors as to the limit of particle size below which all clay particles should fall. Boswell (63) gives 0.01 mm. as the lower limit of particle size for silt and the upper limit of particle size for clay. Marshall (64) gives this value as 0.002 mm. while others (65) prefer 1/256 mm.

Clay particles are easily carried by running water to ponds, lakes or the ocean where they settle out in the quiet water as a fine sediment. As time goes on, the layer of fine sediment may be covered with other types of material and finally consolidated either by pressure or the cementing of the particles together. Consolidated clay is called shale, and this upon grinding and mixing with water often becomes as plastic as an unconsolidated clay.

#### B. The Mineral Composition of Clays and Shales

Although more than a thousand mineral species are known to science, only a relatively small number of them are in any sense abundant or to be reckoned as essential constituents of rocks (66). The possible number of primary or original minerals which find their way from an igneous rock to a clay deposit is probably large but unless the particles are comparatively large, many are soon altered to secondary minerals. Although a number of primary minerals have been identified in clay deposits (67-74), their identification has been made difficult because of the size of the mineral grains and also because the grains are often surrounded by decomposition products. The great bulk of secondary minerals found in clays are the various hydrated aluminum silicates which are responsible for the properties of a ceramic clay. Howe (75) has listed sixty-one hydrous aluminum silicates which had

been described in the literature up to 1914 and Wherry (76) has added to the list. Because of the importance of these minerals, they have been studied in considerable detail with reference to their chemical properties (77), structure, physical and optical properties (78). There have been several attempted classifications suggested for this series of minerals based upon dehydration studies (79), on solubility in HCl and H<sub>2</sub>SO<sub>4</sub> (57) and on the Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> ratio (80). Grim (78) lists the illite group, the montmorillonite group, and the kaolinite group as being the most important among the clay minerals. He also includes four groups which are considered as being of minor importance, the halloysite group, the attapulgite group, the allophane group and the chlorite group.

Among the minerals either directly or indirectly responsible for the formation of scum or efflorescence on ceramic products, the various sulfate and sulfide minerals, particularly the sulfides of iron, are the most important (81-83). The action of water and carbon dioxide on various silicates has been known since 1835 (84). This may result in partial or complete solution of the mineral in water (85-90), or decomposition of the mineral resulting from the combined action of water and carbon dioxide (49, 91). The products of the action of water alone or the action of water and carbon dioxide on silicates, however, are not considered as important as those resulting from the decomposition of

the various sulfides of iron. A number of chemical analyses of the water soluble fractions of clays show a preponderance of sulfates (66, 92). The reactions of the sulfide minerals of iron during atmospheric oxidation often forms sulfuric acid which in turn reacts with basic materials to form a large group of sulfates, the majority of which are sufficiently soluble to produce efflorescence. Lindgren (93) found 117 p.p.m. of free sulfuric acid, in addition to other sulfates, in the water seeping into a coal mine. Clarke (66,p.647) also reports free sulfuric acid ranging up to 251.7 p.p.m. in certain mine waters. His tables of the analyses of spring waters, river waters, and mine waters show a preponderance of sulfate. The average sulfate content of the river waters of North America was calculated to be 15.31 p.p.m., while mine waters have been found to contain as high as 71,053.3 p.p.m. of sulfate. These analyses show that sulfates are common in ground waters and particularly in waters which percolate through deposits rich in sulfides.

Theories concerning the origin of the mineral sulfides of iron (94-109) usually assume the iron to be carried to the clay deposit in solution while the sulfur originates from the organic material present in the clay and is released by bacteria. According to Doss (99) the iron is carried in solution to waters where organic material is abundant. Here the iron is precipitated, either directly as black colloidal hydrous ferrous sulfide by reaction with hydrogen sulfide



liberated by bacteria from organic matter; or as ferric hydroxide by iron bacteria. Under reducing conditions, the ferric hydroxide is then converted to ferrous monosulfide. By the loss of water and the addition of sulfur present in the mud, the latter is changed to melanikovite which gradually alters to pyrite as the enclosing mud becomes consolidated.

According to Harder (110), ferrous sulfide may be formed in four distinct ways: (A) Hydrogen sulfide formed by the decomposition of sulfur-bearing proteins under action of decay-producing bacteria may react upon ferrous salts in solution, forming ferrous sulfide. This is probably a common manner of formation. (B) Certain bacteria, known as sulfate reducers, have the ability, in the presence of decaying organic matter, to take oxygen from sulfites, sulfates and thiosulfates, and to form sulfides. (C) If the sulfides thus formed are other than iron sulfide, they may react with carbon dioxide and water to form hydrogen sulfide, which in turn reacts with ferrous salts in solution to form ferrous sulfide. (D) Some bacteria in the presence of decaying matter may act directly on free sulfur to form hydrogen sulfide, which acts upon ferrous salts in solution forming ferrous sulfide.

Twenhofel (107) lists bacteria of the following species as having the ability to reduce sulfates: *Vibrio hydro-sulfureus*, *V. thermodesulfuricans*, *Bacterium hydrosulfureum ponticum*, *Proteus vulgaris*, *Bacillus mycolides*, *Spirillum*

desulfuricans, *Microspira aesturarii*, and *Bacterium sulfureum*. Another group of bacteria has the power to oxidize hydrogen sulfide to free sulfur and sulfuric acid, the latter immediately uniting with bases to form sulfates. Rudolfs (111) has found that the mineral pyrite may also be oxidized to sulfates by certain bacteria. Glick (112) and Stover (113) have found that bacterial growth in clays is an important factor in the aging of ceramic clays because of their influence on the decomposition of sulfides.

In 1912 Allen, Crenshaw and Johnston (95) advanced an hypothesis for the formation of iron disulfides in sedimentary deposits based upon the formation of thiosulfates. According to this hypothesis, the iron disulfide of igneous origin is oxidized under surface conditions to ferrous thiosulfate by direct addition of oxygen. The ferrous thiosulfate is transported by circulating waters to some point where it is reduced again to its former condition.

Other possible reactions involving thiosulfates would be their formation from the natural oxidation of pyrite, which under certain conditions, may form  $SO_2$ :



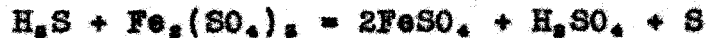
The sulfur dioxide may then react with alkaline hydroxides such as KOH formed by the decomposition of feldspar with water:



to form the corresponding sulfite:



Free sulfur may originate from a number of sources in the deposit, such as the reaction of hydrogen sulfide on ferric sulfate:



The alkali sulfite may then react with the free sulfur to form the alkali thiosulfate which in turn reacts with ferrous sulfate to form iron disulfide:



Ferrous thiosulfate may also be formed by the reaction between ferrous sulfate and an alkali thiosulfate. This may then react with an alkali thiosulfate to form iron disulfide.



Stokes (114) believes that pyrite and marcasite are decomposed by circulating waters which leave hematite or hydrated ferric oxide and carry away the sulfur in the form of alkali sulfides and thiosulfates.

Foreman (115) did not find that pyrite dissolved in sodium sulfide solutions but Stevens (116) found that pyrite is attacked by solutions of sodium sulfide, forming pyrrhotite and sodium polysulfide. Pyrrhotite is also formed when hydrogen sulfide, alkali sulfides, or their solutions when weak in polysulfides, react with ferrous salts under hydrothermal conditions.

The reactions of monohydrated ferric oxide and ferric hydroxide with hydrogen sulfide have been studied under laboratory conditions (102,117).  $\text{Fe}_2\text{S}_3$ , formed by the primary reaction, decomposed to give the mono- and disulfides of iron. The formation of  $\text{FeS}_2$  under these conditions has been thought to be a process by which pyrite may be formed in nature (105). Woodland (108), in discussing the development of pyrite grit in mudstones, considers  $\text{FeS}$  to be present in the sediments. This diffused to points of crystallization where it was converted to  $\text{FeS}_2$  with separation of iron and reduction in volume. The iron formed magnetite, more or less according to the equation:

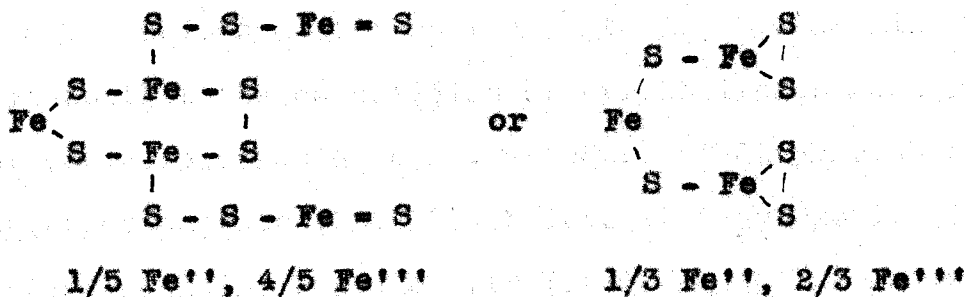


Although pyrite may crystallize direct from magmas, both pyrite and marcasite found in sedimentary deposits have crystallized from water solution. Tarr (106) has found that pyrite requires a neutral to slightly alkaline solution and a temperature range of from cold to 100 degrees C. for its formation, while marcasite requires an acid solution and a much narrower temperature range. In Tarr's experiments, he found that 1.18 per cent sulfuric acid and a temperature of 100 degrees C. were the most satisfactory for the formation of marcasite.

The iron sulfides that have been identified in sedimentary deposits are hydrotroilite ( $\text{FeS}\cdot\text{H}_2\text{O}$ ), melnikovite ( $\text{FeS}_2$ ), marcasite ( $\text{FeS}_2$ ), pyrite ( $\text{FeS}_2$ ) and pyrrhotite which

has a variable composition ( $\text{Fe}_7\text{S}_8$  to  $\text{Fe}_{11}\text{S}_{12}$ ). Linstrom (118) believes that the composition of pyrrhotite is best represented by the formula  $\text{Fe}_7\text{S}_8$ . Because of its variable composition, some authors (93,119) believe that pyrrhotite is a solution of S in FeS. Roberts (120) made a thermal study of the system FeS-S and reported that this system forms a series of solid solutions extending from the compound FeS to a sulfur rich solution of approximately the composition  $\text{FeS}_{1.14}$  at 300 degrees C. X-ray powder spectra of these solid solutions at room temperature show that a continuous series is formed from FeS to the sulfur rich limit (121-123). The sulfide  $\text{Fe}_2\text{S}_3$  or  $2\text{Fe}_2\text{S}_3 \cdot 3\text{H}_2\text{O}$  has been prepared in the laboratory (102,117,124) but it decomposed spontaneously into FeS and  $\text{FeS}_2$ .

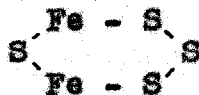
Of the five common natural sulfides of iron, marcasite and pyrite are the most common and have been studied in considerable detail by chemists and mineralogists. Both minerals are represented by the same chemical formula but there is sufficient difference in their physical and chemical properties to indicate that there is less similarity in these minerals than their chemical formulas would indicate. Brown (92) made a comparative study of the chemical behavior of these minerals and proposed the following structural formulas for pyrite:



His formula for marcasite shows the simple iron disulfide:



Arbiter (119) studied the reactions of these minerals with hydrogen peroxide and concluded that the formula for pyrite is:



while the formula for marcasite is:



Plummer (125) concludes that the iron in both pyrite and marcasite is in the ferrous condition and the structure of both minerals is represented by the formula:



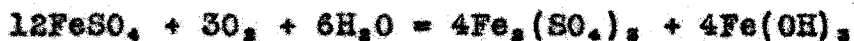
Buerger (126), after a study of the crystal structure of pyrite and marcasite, concludes that pyrite is ferrous disulfide while marcasite is ferric disulfide.

From the chemical point of view, there is little difference in the atmospheric oxidation of pyrite and marcasite.

It is known that marcasite weathers more rapidly than pyrite but the final products of weathering will be as varied in one case as in the other, and will depend upon the conditions under which the oxidation took place. The reactions representing the various types of atmospheric oxidation of  $\text{FeS}_2$  may be illustrated by the following equations:



The ferrous sulfate formed by the oxidation of  $\text{FeS}_2$  may be oxidized further to  $\text{Fe}_2(\text{SO}_4)_3$  and this compound may hydrolyze to form ferric hydroxide or hydrated ferric oxide (93):



There is also a possibility of the  $\text{FeS}_2$  reacting with the ferric sulfate:



Sulfur may also be formed by the reaction of  $\text{H}_2\text{S}$  with  $\text{Fe}_2(\text{SO}_4)_3$ :



or by the reaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ :



It will be noted that sulfuric acid is a common product from the atmospheric oxidation of  $\text{FeS}_2$ . This may react with

a number of basic compounds in the clay to form a wide variety of sulfates, a large percentage of which are sufficiently soluble to be classed as "soluble" sulfates.

In addition to sulfuric acid, the sulfates of iron are common products of the weathering of  $\text{FeS}_2$ . Although the list of recorded sulfates of iron is long and includes some of very complex composition, Posnjak and Merwin (127) have found that only a few of them are properly defined and represent single crystalline substances. The majority of these compounds, especially the basic salts, are described as "amorphous" substances, and undoubtedly are mixtures. All ferric sulfates decompose more or less readily in contact with water and the atmosphere, and are stable only in contact with solutions of certain concentrations, temperatures and pressures. Theoretically, at ordinary temperatures and in the presence of oxygen and water, the complete oxidation of pyrite gives the acid ferric sulfate which may crystallize completely to the mineral rhomboclase ( $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ).

A number of sulfate deposits have been studied with reference to their content of iron sulfate minerals (127-128). In 1907 Cameron and Robinson (129) reviewed the literature on ferric sulfates and published a list of thirty compounds which had been described since 1812. Of this number, seven were listed as minerals. The system  $\text{Fe}_2\text{O}_3$ - $\text{SO}_3$ - $\text{H}_2\text{O}$  has been studied by Posnjak and Merwin (127) and the compounds formed by the reactions of ferric oxide



and aqueous sulfuric acid have been investigated by Baskerville and Cameron (130).

Dana (131) lists the following ferric sulfate minerals:

Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Quenstedtite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$
Iheite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$
Castanite	$\text{Fe}_2\text{S}_2\text{O}_9 \cdot 8\text{H}_2\text{O}$
Copiapite	$\text{Fe}_2\text{S}_2\text{O}_{11} \cdot 18\text{H}_2\text{O}$
Utahite	$\text{Fe}_2\text{SO}_4 \cdot 1 \frac{1}{3}\text{H}_2\text{O}$
Amaranite	$\text{Fe}_2\text{S}_2\text{O}_9 \cdot 7\text{H}_2\text{O}$
Fibroferrite	$\text{Fe}_2\text{S}_2\text{O}_9 \cdot 10\text{H}_2\text{O}$
Raimondite	$\text{Fe}_2\text{S}_2\text{O}_{11} \cdot 7\text{H}_2\text{O}$
Carphosiderite	$\text{Fe}_2\text{S}_2\text{O}_{11} \cdot 10\text{H}_2\text{O}$
Glockerite	$\text{Fe}_2\text{SO}_9 \cdot 10\text{H}_2\text{O}$

Dana also lists the ferrous sulfate melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and castanite ( $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ ). There are also a number of double sulfates of iron containing sodium, potassium, magnesium or calcium. In the various saline residues formed by the evaporation of mineral waters such as the Stassfurt and Searle's lake deposits, approximately fifteen sulfate minerals of calcium, magnesium, sodium and potassium have been identified (66,98) in addition to various chlorides, borates and nitrates.

It is evident that the number of sulfate minerals resulting from the weathering of iron sulfides in the presence of clay is great. The number and amount of soluble minerals

in any given clay will depend upon its geological history but the available chemical analyses indicate that the sulfates of magnesium and calcium are the most prominent among the various water soluble minerals while the sulfates of sodium potassium and iron are also usually present (132).

### III. THE ORIGIN OF SOLUBLE SALTS IN BURNED WARES

#### A. The Decomposition and Oxidation of Sulfides during the Burning of the Ware

The thermal decomposition of the sulfides of iron in various atmospheres has been investigated by a number of writers. The papers on this subject which have appeared in the literature between 1820 and 1935 have been summarized by Mellor (133). Although the greater part of this work was done with the minerals pyrite and marcasite, the results obtained would be assumed to be similar to those obtained by heating these minerals in the presence of clay. Some differences would be expected, however, such as the formation of a number of sulfates other than those of iron, and the differences in decomposition temperatures caused by the presence of the clay. The per cent of the various gases in the kiln atmosphere would also affect the decomposition reactions of pyrite and marcasite.

The work of Thompson and Tilling (134) was carried out in atmospheres of dry air, moist air, carbon dioxide, carbon monoxide and hydrogen. Although these authors did not attempt to simulate the conditions existing in a ceramic kiln, the gases used are all found in the kiln atmosphere during the burning process.

In their first experiment, Thompson and Tilling (134) passed 17 liters of dry air over powdered pyrite containing 52.54 per cent sulfur at several temperatures. The pyrite residue was then analyzed for the per cent of sulfur remaining. Their results were as follows:

Table 1. Per cent Sulfur Remaining after Heating Pyrite at Various Temperatures in Dry Air

Temperature	Per cent sulfur in residue
<u>°C.</u>	
615	32.99
810	0.13
910	0.092

When air saturated with water vapor was passed over the five gram samples of ground pyrite, it was found that at temperatures below 650° C., moisture in the air had a tendency to remove the sulfur more rapidly than dry air, but at temperatures above 650° C., the removal of sulfur was less rapid than with dry air alone.

When steam alone was passed over the samples, the decomposition began in the range of 380° C. and increased rapidly as the temperature was raised to 500° C. From 500° C. to 680° C. the decomposition proceeded more gradually until at the temperature of 680° C. the presence of sulfur

in the residue was 35.69 per cent which corresponds favorably to the per cent of sulfur in FeS (36.36 per cent). It was assumed from the above results that FeS was formed according to the equation:



The hydrogen sulfide and sulfur dioxide from this reaction may react further to form sulfur and water:



At 680° C. the FeS begins to react with the water vapor according to the equation:



Carbon dioxide was not found to exert any oxidizing effect on pyrite at temperatures below 900° C. but at temperatures above 900° C. the CO<sub>2</sub> tends to dissociate, the oxygen then oxidizing the FeS.

Carbon monoxide caused pyrite to begin to lose sulfur at 350° C. and this decomposition continued up to 590° C. where the sulfur content of the residue indicated that FeS was formed. As FeS<sub>2</sub> does not dissociate below 575° C., the reason for the low initial temperature of the reaction with carbon monoxide was thought to be due to the formation of COS according to the equation:



The reaction between hydrogen and pyrite begins at 440° C. and at 530° C. the pyrite is converted completely to FeS according to the equation:  $\text{FeS}_2 + \text{H}_2 = \text{FeS} + \text{H}_2\text{S}$

At higher temperatures the  $\text{FeS}$  is reduced to metallic iron by the hydrogen:



Gallo (135) reported that the reduction of pyrite by hydrogen takes place in three steps:



He found that the first reaction begins in the range of 228° to 230° C., the second between 260° to 285° C., and the third between 370° and 375° C. In his experiments, it took 44 hours at a temperature of 900° C. to completely reduce  $\text{FeS}$  to  $\text{Fe}$ .

Bole and Jackson (136) and Jackson (137-138), in a series of papers on the oxidation of ceramic wares during firing, have found that the principal source of sulfur evolution is the oxidation of  $\text{FeS}_2$ , forming  $\text{SO}_2$  and  $\text{SO}$ , according to the following possible reactions:



The most common products of the various reactions of  $\text{FeS}_2$  with the different constituents of the kiln atmosphere

are the oxides of sulfur. These may combine with other basic materials in the clay to form the corresponding sulfates and sulfites. Under oxidizing conditions, sulfates would be formed almost exclusively.

#### B. The Decomposition and Reduction of Sulfates during the Burning of the Ware

The sulfates of iron, magnesium and calcium may be present in the natural clay or may be formed by reactions between the basic constituents of the clay and the products of oxidation of sulfides during the drying or burning of the ware. The extent of decomposition of these sulfates during the burning process will depend upon a number of factors: (a) the temperature and length of time of the burning process; (b) the presence of reducing materials, such as organic matter, in the clay; (c) the presence of certain inorganic compounds, such as  $\text{SiO}_2$ , which react with these sulfates at kiln temperatures; (d) the presence of certain metallic oxides which catalyze the oxidation of sulfur compounds; and (e) the chemical composition of the kiln atmosphere.

The thermal decomposition of ferrous sulfate in contact with various gases has been studied by a number of writers. Mellor (133, vol. 4, p. 256) has summarized the work done in this field up to 1935. Greulich (139) found that the

reaction in the absence of air proceeded according to the equation:



Keppler and d'Ans (140) believed that the reaction took place in two steps:



Mellor (133, vol. 14, p. 257) gives the following table showing the per cent of decomposition of ferrous sulfate when heated in a current of dry air for three hours at different temperatures according to the reaction:



Table 2. Decomposition of Ferrous Sulfate at Various Temperatures when Heated in Dry Air

Temperature	Per cent decomposition
<u>°C.</u>	
460	trace
475	3
500	12
510	20
520	40
530	80
550	100



Landis (141) heated anhydrous  $\text{FeSO}_4$  in a current of dry air and found that decomposition was first evident at  $550^\circ \text{C}$ . The rate of decomposition was slight between  $550^\circ \text{C}$ . and  $580^\circ \text{C}$ . but suddenly increased at  $600^\circ \text{C}$ . so that decomposition ceased in about two hours at this temperature. Very little more decomposition occurred until a temperature of  $960^\circ \text{C}$ . was reached. Saito (142) also reported  $550^\circ \text{C}$ . as the initial temperature of decomposition of  $\text{FeSO}_4$ .

Hoffman and Manjukow (143, p.903) found that  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is converted to  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_2$  at  $475^\circ \text{C}$ . when heated in a current of dry air and at  $492^\circ \text{C}$ . the  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_2$  begins to dissociate, the dissociation becoming rapid between  $550^\circ \text{C}$ . and  $568^\circ \text{C}$ .

The discrepancy in the values for the initial temperature of decomposition of ferrous sulfate as given by Mellor, Landis, Saito, Hoffman and Manjukow may be explained by the variations in the sensitivities of the methods used in detecting the start of the reaction. Hoffman and Manjukow used a method based upon the absorption of heat accompanying the decomposition of several metallic sulfates, rather than the detection of the presence of products of decomposition. The temperatures at which the various decomposition reactions took place were detected by variations in the heating curves. Their value of  $492^\circ \text{C}$ . is believed to be the most accurate for the temperature at which ferrous sulfate begins to decompose in the presence of air to form oxides of sulfur.

Considerable work has been done on the thermal decomposition of anhydrous calcium and magnesium sulfates from the viewpoint of ore roasting; the manufacture of sulfur dioxide; and quantitative separations of metals based upon the decomposition of anhydrous mixtures of the sulfates as well as studies of the soluble salt formation in ceramic wares. The presence of organic matter in clays may result in considerable reducing action on the sulfates due to incomplete oxidation of the carbon in the interior of the body.

Zawadzki and co-workers (144-147) found that calcium sulfate is reduced by carbon to calcium sulfide at temperatures in the range of 900° C. while at temperatures above 900° C., a reaction takes place between calcium sulfide and any undecomposed sulfate to form calcium oxide and sulfur dioxide.



The proportion of sulfate so converted into oxide increases with rise in temperature and with diminution of percentage of carbon in the original mixture. It is also increased by the addition of oxides of iron and aluminum. Mixtures of equal quantities of magnesium sulfate and carbon yielded magnesium sulfide and magnesium oxide. The gaseous products of this reaction were sulfur, sulfur dioxide, carbonyl sulfide, carbon monoxide and carbon dioxide.

Carbon monoxide was found to reduce calcium sulfate almost quantitatively to calcium sulfide between 700° C. and

900° C. and at temperatures above 900° C., the calcium sulfide decomposed.

Simon and Meier (148) found that the presence of kaolin causes a rapid dissociation of calcium sulfate between 750° C. and 900° C. while clays containing appreciable amounts of magnesium carbonate,  $\text{Fe}_2\text{O}_3$ , and the alkalies tend to retain the  $\text{SO}_2$ . The temperature range for maximum sulfate formation was found to be 600° C. to 800° C.

Bhatt and Watson (149) studied the behavior of  $\text{CaSO}_4$ ,  $\text{CaS}$  and  $\text{CaSO}_3$  on heating alone and in the presence of  $\text{SiO}_2$  at temperatures above 1100° C. The effect of adding reducing agents to the  $\text{CaSO}_4$ - $\text{SiO}_2$  mixture caused the  $\text{SO}_2$  to be evolved at a lower temperature but the temperature for complete decomposition was higher because of the formation of  $\text{CaS}$ . A quantitative decomposition of  $\text{CaSO}_4$  was obtained by heating  $\text{CaSO}_4$  with excess  $\text{SiO}_2$  for four hours at 1100° C. in a slow current of air.  $\text{SiO}_2$  was found to accelerate the decomposition of  $\text{MgSO}_4$  but to a less extent than  $\text{CaSO}_4$ .

Bischoff (150) heated equimolar mixtures of  $\text{CaSO}_4$  and  $\text{SiO}_2$  at a temperature of 1100° C. for four hours in air,  $\text{SO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , moist air and steam. He obtained a yield of 30 per cent  $\text{CaSiO}_3$  when nitrogen was used. The yield of  $\text{CaSiO}_3$  was slightly less when air was used and only a few per cent in the case of sulfur dioxide. Practically 100 per cent yields were obtained with steam.

Simon and Vetter (151) prepared a series of clay briquets containing known amounts of sulfate and chloride. These were burned for seven hours in an electric muffle. The sulfate and chloride remaining in the briquets were then determined to observe the temperatures at which these constituents reacted and were expelled. In brick clay, NaCl decomposes the sulfates of calcium, magnesium, sodium and potassium at temperatures above 750° C. even though above this temperature the chlorine has been almost completely expelled. The decomposition of sulfates was much less in kaolin than in brick clay and other impure clay masses. Magnesium silicate was also found to react with calcium sulfate to form magnesium sulfate.

Williams (39, p.271) mentions the removal of drier scum by maintaining reducing conditions in the kiln during the period of maximum burning temperature. He gives 1200° C. as the dissociation temperature of gypsum and states that in an atmosphere of carbon monoxide, this temperature is appreciably lowered.

Riesenfeld (152) studied the reduction of  $MgSO_4$  by carbon and found that two reactions may take place:



The products of the thermal decomposition of sulfates within the clay body consist of the corresponding oxides of the metals and the gaseous oxides of sulfur. When conditions

are such as to prevent the escape of these gaseous oxides, they may recombine with other metallic oxides forming the corresponding sulfates. In some cases the oxides of sulfur may be formed by decomposition of the more easily decomposed sulfates and recombine with other metallic oxides forming more stable sulfates. Calcium carbonate, for example, is said to begin to decompose at  $600^{\circ}$  C. (153) forming the oxide and carbon dioxide. If the calcium oxide formed from the decomposition of calcium carbonate combines with the  $SO_2$  from the decomposition of  $Fe_2O_3 \cdot 2SO_2$ , which takes place at  $492^{\circ}$  C. (143), the calcium sulfate thus formed may remain undecomposed throughout the remainder of the burning process.

#### C. Reactions of Clay Bodies with Sulfurous Gases during the Drying and Burning of the Ware

The atmosphere of the kiln may contain appreciable amounts of sulfurous gases which have originated from sulfides present in the clay, the thermal decomposition and reduction of sulfates in the clay, or from the fuel used in firing the kiln. Practically all fuels used in the ceramic industry contain some sulfur compounds which are oxidized to  $SO_2$  or  $SO_3$  when the fuel is burned. This is particularly true of coal which is the most common kiln fuel. Beyer (43, p.341) believed that the soluble sulfates in Iowa clay wares came from the absorption of sulfurous gases from the

combustion of coal. Olin (154) has published the analyses of two series of Iowa coals. The first series of 18 coals shows an average sulfur content of 4.2 per cent while the second series of 24 coals shows an average of 6.0 per cent sulfur. Both of these values are considered high for a kiln fuel. Rice (155) gives 1.0 per cent as the content of sulfur in an ideal coal for ceramic use.

When oil is used as a kiln fuel, the per cent of sulfur should be between 0.5 per cent and 0.75 per cent for first quality ware such as face brick and glazed units (156). The oil should have at least 0.5 per cent less sulfur than the corresponding coal which may be used in order that no scumming occur. One explanation of this theory is that in the burning of coal, part of the sulfur remains in the ash while in the case of oil, nearly all of the sulfur content would be released to the kiln atmosphere.

Lovejoy (157) mentions that during the early stages of the firing process, when water vapor is coming out of the ware, there is but shallow penetration of the kiln gases or of acid condensations from kiln gases. He found that the penetration below the surface of the ware is scarcely one-eighth inch and in the course of his investigations had never found the penetration to be greater than one-fourth inch.

Konarzewski and Krynski (158) found that clays fired in the presence of  $SO_2$  combine with small portions of it forming

the sulfates of Ca, Mg, Al and Fe. Simon and Schmider (159) reported that the amount of  $SO_2$  absorbed was directly proportional to its concentration in the kiln atmosphere when clays containing CaO and MgO were fired in atmospheres containing from 0.5 per cent to 2.0 per cent  $SO_2$ . For the same  $SO_2$  concentration, the quantity of  $SO_2$  absorbed and the sulfate formed increased with the temperature. The temperature interval  $300^\circ C.$  -  $600^\circ C.$  was found to be the most favorable for  $SO_2$  absorption, with maximum absorption probably occurring between  $400^\circ C.$  -  $500^\circ C.$  No absorption was reported at temperatures of  $750^\circ C.$  and above.

Simon and Meier (160) heated mixtures of calcium carbonate and clay in atmospheres containing  $SO_2$  and oxygen. The primary product of the reaction between  $CaCO_3$  and  $SO_2$  was calcium sulfite which was subsequently oxidized to calcium sulfate. Reduction of calcium sulfite to calcium sulfide will also take place in a reducing atmosphere but this later is oxidized to the sulfate.

Brady and Coleman (161) fired four clays over a temperature range of  $400^\circ C.$  -  $1000^\circ C.$  and "soaked" at  $600^\circ C.$ ,  $900^\circ C.$  and  $1000^\circ C.$  for periods up to six hours in air and in atmospheres containing 0.5 per cent, 1.5 per cent and 7.5 per cent  $SO_2$ . The highest soluble sulfate content was found in specimens fired at  $700^\circ C.$  "Soaking" temperatures of  $600^\circ C.$  and  $900^\circ C.$  in atmospheres containing  $SO_2$  increased the sulfate content, while at  $1100^\circ C.$  a decrease

in sulfate was noted. The clays high in the alkalis lost their sulfate content more readily than those high in calcium and magnesium during the prolonged heating.

#### D. Miscellaneous Sources of Soluble Salts

During the manufacture of ceramic products, considerable soluble salts may be introduced by the use of waters high in mineral content (162-168). Materials used to back up walls (38, p.583), particularly soils, may contain considerable soluble material which is carried to the surface of the wall by water and there deposited as efflorescence. Some four pounds extracted from the soil may react with materials in the brick or tile to produce soluble salts.

Fuel ash has been found to carry soluble salts to the ware (169-173). This may occur when the ware is stored in yards which are also used as dumping areas for ashes and cinders or when ashes are used instead of sand to separate the bricks in the kiln.

Among the earlier papers on the subject of efflorescence and soluble salts in clay products was that of Pemberton which was published in 1878 (174). One of the causes of efflorescence listed by Pemberton was the formation of magnesium sulfate in the mortar by reaction with sulfuric gases in the air. The presence of magnesium in the mortar was traced to the use of dolomitic lime. Since the



publication of Pemberton's paper a number of other writers have reported efflorescences of brick and tile which were traced to the mortar used as a binder (175-182).

Efflorescence has also been traced to the sand used in preparing the mortar (183). In the cases cited, the sand had been taken from stream beds which had become contaminated with soluble salts during a particularly dry year. The salts had become sufficiently concentrated in the sands of the stream bed to cause efflorescence on bricks in contact with mortar made from these sands.

Coloring materials which have been added to mortar have also contained sufficient soluble materials to produce efflorescence on the brick laid with this mortar (177-178). Orton (178) has traced the soluble salts to the iron oxide used to produce red mortar. This iron oxide was made by igniting ferrous sulfate and the decomposition of the ferrous sulfate had been incomplete, allowing some sulfate to remain in the product.

Zschokke (179-180) tested eleven binders and found that after setting, they all contained considerable soluble salts. He also placed a pile of brick beside a new building made of the same brick. After two years the walls of the building were effloresced while the bricks were not.

During the last decade of the nineteenth century, considerable difficulty arose in the city of Chicago over efflorescence. Many new buildings were covered with

efflorescences and a number of theories were given in attempts to explain its formation. Benfey (184) described it as an epidemic and it was common belief among the citizens that it had been caused by lightning. The difficulty was finally traced to accumulations of soot on the buildings. A heavy rain had washed the soluble material out of the soot and these soluble materials had reacted with the bricks to produce efflorescence.

Seger and Cramer (185) describe an instance where the inner brick walls of a building were dried by a fire burning a high sulfur coal. The sulfurous gases attacked the walls producing efflorescence. In order to eliminate the possibility of the efflorescence originating from soluble salts in brick, mortar and water, these were tested and found to be free from soluble salts.

#### IV. THE EFFECTS OF SOLUBLE SALTS ON CLAY WARES

##### A. Efflorescence

As stated in the introduction to this thesis, the term efflorescence, as generally used in the ceramic industry, refers to the formation of a deposit on the surface of the ware during its manufacture or after it has been built into a wall. The terms cryptoflorescence, efflorescence, inflorescence and scum have been proposed by some writers to identify the deposits formed during various stages in the life of the ware, either before or after it leaves the kiln. In this discussion of efflorescence, the interpretation of the term as given by Parmelee (186) will be followed. Parmelee defines the term as "the accumulation of salts upon the surface where they have been brought in solution and deposited upon evaporation of water. Scum is a term used interchangeably with efflorescence."

Certain types of efflorescence have little effect on the ware other than impairing its appearance by discoloration. This, however, is an important factor to the manufacturer of structural clay products as it affects the salability of his product. The builder is also interested in efflorescence, especially when it makes its first appearance after the brick or tile has been used in the construction of a wall or

building. Marschner (187) has raised the question whether salt efflorescences on brick are really injurious. In his discussion of the question he said that the question had not been answered conclusively. During a discussion which took place at the first meeting of the American Ceramic Society (22) it was brought out that scummed paving bricks are harder than adjacent ones in the kiln that are not scummed.

Many of the authors of papers on efflorescence have used the terms "markings", "staining", "perfect color", "spots", "discolorations", "white", "whitewash", "color appearances", and various colors such as brown, yellow and green in the titles of their papers (186-209). This would indicate that the problems of efflorescence in these cases were concerned with the appearance rather than mechanical failure or disintegration of the ware.

#### 1. Factors Affecting the Efflorescence of Ceramic Wares

In order for efflorescence or scum to form on a brick, three conditions must exist. These are (I) the presence of soluble salts in the brick; (II) the presence of moisture to carry the salts to the surface; (III) the ease of movement of the solution of soluble salts through the brick.

a. Humidity and moisture. It was noticed early in the study of efflorescence that efflorescences often follow seasons of wet weather (40). The efflorescence of basement walls also indicated to the earlier investigators that there

was some relationship between dampness and the formation of scum. Davis (21, p.53) stated in 1884 that "a degree of humidity about equal to that of garden earth is very favorable to the production of saltpeter". He also stated that a temperature of from 60° F. to 70° F. was most favorable, and at 32° F. it does not form. Elsom (177) pointed out in 1889 that buildings put up in wet weather usually effloresce badly.

Dawihl (210) devised a test to determine whether a brick will effloresce. The brick was immersed 3 cm. in water under a bell jar and air at 50 per cent and 70 per cent humidity passed over the brick at the rate of 50 liters per hour. He found that at the lower humidity efflorescences did not appear. Butterworth (211) pointed out that although  $\text{CaSO}_4$  is more difficult to eliminate when burning the ware, it caused failure only when the product is exposed to damp conditions.

b. Texture of the ware. Efflorescence depends not only on the quantity and composition of soluble salts but also on their accessibility, a factor determined by the texture of the brick. Butterworth (212) has devised tests for the liability of effloresce which make allowance for this factor.

c. Porosity of the ware. Machler (213) was one of the first to show that chemical analysis does not always indicate whether or not a brick will effloresce. He made a study of the relationship between the amount of soluble

salts in the brick, the amount of efflorescence that can be induced, and the size of the pores. The porosity of the brick was found to be an important factor in the formation of efflorescences.

d. Water absorption. Closely related to the porosity of the ware is the degree of water absorption. Dunn and Rands (214) found that a relationship between high liability to effloresce and water absorption seems to exist although cases were cited where pressed brick of high liability and low absorption did not conform.

e. Water permeability. Matejka (215) and Palmer (38, p. 582) have pointed out the importance of water permeability in the formation of efflorescence.

f. Capillary rise of water. Parmelee (186, p. 547) lists the capillary structure of the ware as one of the important factors influencing the appearance of efflorescence. Matejka (215) devised a method for determining the capillary rise of water or salt solutions in ceramic bodies and discussed the importance of this test in determining the liability to effloresce. Valisek (216) has discussed the physical reasons for the adherence of soluble materials to capillaries and to surfaces of ceramic bodies. He states that the infiltration of water into the capillaries of ceramic bodies is governed by the laws of solubility, absorption, diffusion and osmosis.

g. Colloidal matter in clays. Ashley (217-218) has shown

that the colloidal matter in a clay body opposes, to some extent, the flow of solutions through it. Even if chemical analysis should indicate a fairly high content of soluble salts, a brick from such a clay may not scum if the clay has sufficient colloidal matter in a suitable condition to prevent the appearance of the soluble matter at the surface.

## 2. Methods of Preventing and Controlling Efflorescence

a. Mechanical removal of pyrite from the raw clay. Because pyrite and the other sulfides of iron are recognized as being the most important sources of soluble salts in clays, it would seem feasible to remove these minerals before the clay is made into ceramic wares. This is done in some cases where the sulfides occur in sufficiently large pieces to be picked out by hand or by sieving. Often, however, the sulfides occur in extremely small grains and their removal involves the use of processes which are impractical in the ceramic industry. Mellor (219) mentions electromagnetic and electrostatic methods for the removal of certain sulfides from clay but like other mechanical methods, these have not been found to be practical in the average plant.

b. Destruction of pyrite by chemical agents. A number of chemical agents have been found which will decompose the sulfides of iron. Among these are solutions of hypochlorous acid (220-221), ferric chloride and iron alum (222-224), bromine water or bromine vapor (225-226), and solutions of

potassium permanganate or copper sulfate (227-228). Stokes (229-231) has studied the reactions of a large number of compounds on the sulfides of iron. Smith (232) has also studied the effect of passing an electrical current through a water suspension of pyrite.

Mellor (219) points out that the use of the above chemical agents is not practical on a manufacturing scale. Most of these chemical agents are too costly and in some cases they injure the clay by making it unfit for ceramic purposes. In any type of chemical treatment where a strong oxidizing agent is used to decompose the sulfides, the sulfur is oxidized to sulfate which must be removed by further treatment of the clay in order to eliminate the compounds responsible for the formation of efflorescences.

c. Weathering of clay. The chemical changes which accompany the weathering of pyritiferous clays involve the oxidation of the sulfides and leaching out of the soluble sulfates. For this reason a number of writers have advocated weathering or aging as one of the most practical methods of removing the sources of the soluble salts (167, 186, 215, 233-234).

Parmelee (186, p. 541) recommends either using the clay at once before any oxidation has taken place, or to allow the clay to weather until all of the pyrite is oxidized. If the clay is used after the pyrite has been oxidized to sulfates and before these sulfates have been leached out of the



clay, little will be accomplished by this treatment. It is possible, however, to control the firing conditions so that the pyrite is converted to the oxide of iron. This will result in the formation of sulfurous gases in the kiln atmosphere which may be absorbed by the ware forming soluble sulfates.

Matejka (215) found that after storing a clay for one year the per cent of soluble sulfates increased from 0.024 per cent to 0.076 per cent. Ralston and Stern (234) found that aging for six months doubled the soluble sulfate content of freshly milled ball clay.

d. Control of drying conditions. The condition under which the ware is dried has considerable influence on the formation of drier scum. The rate of evaporation from the surface of the body has been found to be an important factor. This may be controlled by varying the temperature and rate of flow of air through the drier. Bricks dried rapidly in a cold blast of air have been found to be free from scum while those dried by heat and using low velocity of air in the drier were found to be scummed (198). This may be explained by the fact that at lower temperatures with a high velocity of air in the drier, the humidity is lower than when higher temperatures and low velocities of air are used. It has already been pointed out that humidity is a factor to be considered in the formation of efflorescences on brick buildings. When the humidity is low, there is a tendency for the water

to evaporate immediately beneath the surface of the ware and deposit salts there, rather than carrying them to the surface.

The formation of scum on the ware while it is in the drier has been traced in some instances to reactions of the clay body with sulfurous gases in the atmosphere of the drier (205).

Several authors have called attention to the condensation of moisture on the ware while it is in the drier (170) and the difficulties arising from allowing it to remain in the drier for too long a time (235). Olshewsky (236) patented a process for treating the ware with calcium chloride solution and then drying in a closed room.

e. Control of firing conditions. The conditions of the atmosphere in the kiln during the firing of the ware have been found to have considerable influence on the formation of efflorescence. Water vapor in the kiln atmosphere was found by some of the earlier investigators to be one of the important factors (237). The use of peat as a kiln fuel causes difficulties because of the relatively high percentage of water as compared to coal (200).

As shown before in the discussion of the thermal decomposition of sulfides and sulfates, the materials present in the clay which form soluble salts can be decomposed if a sufficiently high temperature is used. Several have reported that wares fired at high temperatures effloresce less than those fired at low temperatures (177, 238). Matejka (239)

found that an increase in the firing temperature prevented efflorescences from forming on the ware. One manufacturer (240) was able to reduce the soluble salt content of his product from 0.4 per cent - 0.5 per cent to 0.001 per cent - 0.003 per cent by hard firing.

Crary (241) reported in 1890 that if a brick is heated too fast or made red hot on the surface before the water is out of the inside part of the brick, it will effloresce. He also stated that if the kiln is closed too quickly, or until the whitewash or drier scum is thoroughly burned off, the bricks will have a discolored motley appearance.

Although a high temperature in the kiln has been found to be a method of preventing efflorescence, one writer (242) has found that hard fired ware may contain more sulfate than soft fired ware. The higher sulfate content in this case, however, was probably due to kiln conditions other than temperature.

The choice of oxidizing or reducing conditions in the kiln would be determined by the mineral or chemical composition of the clay. Some authors (148) recommend a reducing atmosphere while others (243) found that reducing conditions caused scum. Cummer (244) recommended the use of a large volume of air in the kiln gases. From what has been said, concerning the oxidation of sulfides and the reduction of sulfates during the firing process, this discrepancy may be explained by the mineral contents of the two clays tested.

A clay containing a high percentage of sulfides would require an oxidizing condition to remove the sulfur while a clay containing a high percentage of sulfates would require a reducing condition.

f. The use of protective coatings while burning the ware. Among the earlier methods of preventing efflorescences from forming on the ware while drying or burning was to coat the ware with a thin layer of organic material before it was placed in the drier. The soluble salts were carried into this layer instead of depositing on the surface of the clay body. When the ware was burned, the organic material was consumed and the soluble salts fell from the surface with the ash.

Flour paste appears to have been the first of the organic materials which was used successfully (184, 245-246). Starch and glue were also recommended (247-248). Perkiewicz (249) has written a series of papers on various types of coatings. He proposed three types of mixtures for coating ceramic bodies. First, flour paste or dextrine; second, a mixture of glue and clay slip; and third, a mixture of farina and glue containing an antiseptic. Rodin (250) has recommended covering the ware with a film of fuel oil.

There are two reasons why these protective coatings prevent efflorescence. The first, as mentioned above, concerns the mechanical removal of the soluble salts which have deposited in the layer of organic material during the period

of drying and fall off when the coating burns in the kiln. The second concerns the chemical reduction of certain compounds due to the presence of carbon in the organic material. The treatment with an organic material such as oil or glue which will penetrate into the ware, would aid in the reduction of the sulfates in the outer layers of the ware. It has been shown before that the presence of organic material in the raw clay supplies carbon which acts as a reducing agent within the clay body.

g. The chemical treatment of the raw clay. Among the various methods of preventing efflorescence, the chemical treatment of the raw clay is most widely used. Because soluble sulfates are the usual cause of efflorescence, they may be rendered insoluble by the addition of certain compounds to the clay which will react chemically with the sulfates and convert the sulfur into an insoluble form. Magnesium sulfate, for example, would react with barium carbonate according to the following equation:



The solubilities of the compounds in this equation expressed in grams per ml. of water are shown in Table 3. These solubilities show that the sulfate which was originally present as soluble magnesium sulfate is converted into insoluble barium sulfate and because of the low solubility of this compound, it is no longer carried in solution to the surface of the ware where it would be deposited as scum or efflorescence.

Table 3. Solubilities of the Carbonates and Sulfates of Magnesium and Barium

Compound	Solubility in gms./ml.
BaCO <sub>3</sub>	0.0022
MgSO <sub>4</sub>	26.0
MgCO <sub>3</sub>	0.0106
BaSO <sub>4</sub>	0.00023

The use of barium carbonate was first recommended about 1884 and since then a number of manufacturers have found it to be the most satisfactory method of controlling efflorescence (7, 167, 168, 184, 192, 195, 246, 251-258).

Barium fluoride has been recommended for the prevention of drier scum (259-260). Staley (258) listed the following advantages of barium fluoride over barium carbonate: (I) It is less expensive. (II) It is more soluble than barium carbonate. (III) The amounts required are the same or less. (IV) It has no deleterious effect on the color of the ware. (V) An excess does not cause scum. (VI) It promotes vitrification.

Barium hydroxide has been recommended by Gates (260). The disadvantages of this compound have been discussed by Singer (132, p. 113). Barium chloride has been suggested by Searson and Jones (261). Motschmann (262) prefers both barium chloride and barium carbonate rather than only one compound.

In 1915 Staley (263) published the results of some experiments in which common salt and soda ash were mixed with the clay. Although both of these materials increased the amount of scum formed when drying the ware, they caused no scum on the fired ware. In one case, increasing the amounts of these salts progressively decreased the scum already present. It was assumed that these materials either fluxed or volatilized the sulfates.

Williams (206) found that ferric chloride, when mixed with the clay, helped to overcome scumming.

h. The chemical treatment of the burned ware. Bricks have been known to scum although the soluble salts in the clay were precipitated by the addition of barium compounds. Seger and Cramer (264) believe that this is caused by the formation of soluble salts during the burning of the ware and also by the formation of barium silicates, thus forming insoluble barium compounds which will not react with the sulfates. In order to prevent the formation of scum under these conditions, Seger and Cramer recommend dipping the burned brick in solutions of soluble barium compounds such as barium chloride or barium nitrate.

i. Proper construction and water-proofing of walls.

It was early recognized that moisture is an important factor in the formation of efflorescence (265) and methods of construction were adopted to prevent ground waters from penetrating the outer surfaces of walls. Butterworth (211) has

shown that efflorescing materials cause failure of brick only when they are exposed to damp conditions. Building tile have been designed which do not allow a continuous layer of mortar through which moisture may pass. Draining methods around the foundations of basement walls have been improved so that ground waters will be removed and not allowed to stand in contact with the wall.

It has also been found effective to cover the surface of the wall with some water-proofing material such as tar, paint or oil (267-268) thus sealing the surface against moisture. Unless precautions are taken to prevent moisture from coming in contact with the outer surface of the wall, efflorescence may develop under the paint causing it to peel off.

#### B. The Bloating of Clays during Burning

Austin, Nunes and Sullivan (268), in a study of the basic factors involved in the bloating of clays, concluded that the thermal expansion of entrapped gas is not sufficient to produce vesicular structure. There must be a gas liberated within the mass while it is in the pyroplastic condition. As shown before in this thesis, the thermal decomposition of several of the soluble salts in the clay produces gases which may not be evolved until the clay reaches a sufficiently high temperature to become pyroplastic, thus closing the pores and preventing the escape of this gas.



Orton and Staley (269) had previously stated that sulfur is the most important cause of bloating.

#### C. The Lowering of the Fusion Point of Clays

Stout (81, p. 506) ascribes the lowering of the fusion point of some clays to the presence of soluble salts.

#### D. Disintegration and Poor Durability of Brick

Dawihl (270) found that the alterations of magnesium sulfate and sodium sulfate due to changes in water of crystallization with fluctuations in temperature are important factors in the disintegration of brick. Blucher (271) reported in 1840 that magnesium sulfate absorbs the equivalent of seven molecules of water from the air. Visser (272) has described a case of disintegration of brick caused by magnesium sulfate. The anhydrous magnesium sulfate in the brick formed the hydrate  $MgSO_4 \cdot 7H_2O$  by reaction with water causing a corresponding increase in volume. This resulted in disintegration of the brick. On treating the new bricks with water, he found that they contained up to 2.88 per cent of magnesium sulfate.

Bisko (273) found that in a well preserved brick, containing 0.52 per cent of total sulfate, calcium sulfate was the predominating sulfate. In bricks showing the greatest amount of disintegration, the total sulfate was 18.29 per

cent, of which 7.78 per cent was magnesium sulfate. Butterworth (274) is of the opinion that because of the comparatively low solubility of calcium sulfate, it will not cause defects in brick. The magnesium content, however, should not be over 0.05 per cent or serious damage will occur. Phillips (275) attributes the durability of structural clay products to the low content of soluble salts.

In some cases, the disintegration of brick is believed to have been caused by the unequal expansion and contraction accompanying changes in temperature. The freezing and thawing of wet brick has also been thought to be the cause of disintegration. Hardesty's (276) results of freezing and thawing tests and microscopical examinations of disintegrating face brick only a few years old showed that the observed weathering was not due to frost action but to calcium sulfate crystals on and just underneath the exposed surface.

Siepp (277) observed the effects of soluble salts originating from the backfill on the red sandstone wall of a railway bridge. The sandstone was badly disintegrated. From his observations he concluded that disintegration and crumbling resulted from a chemical action of the salts in the water seeping through the backfill and mechanical effect of crystallization of these salts in the pores of the stone.

#### E. The Peeling of Glazes

When the soluble salts are deposited on the surface of

the ware while it is in the drier, this prevents the adherence of the engobe. As a result, the glaze on the finished ware may peel off (278-280).

#### F. Spitting-out of Glazes

"Spitting-out" is the term used to identify the minute bubbles which sometimes appear in the glaze while it is in the decorating kiln, providing the temperature is high enough to soften the glaze and allow the bubble to form. If the fire is continued long enough the bubble will burst, leaving the edges sharp. These holes do not heal, as the temperature reached is not sufficient to allow the glaze to flow. Cowan (281) has found that sulfur in the clay is one of the causes of "spitting-out".

#### G. Sulfuring and Feathering of Glazes

The terms "sulfuring", "starring", and "feathering" are used to denote the formation of a scum or film of undissolved sulfates on the glaze (282). The soluble sulfates are deposited on the surface of the ware during drying as a crystalline scum. When the piece is dipped and fired in the glaze kiln these sulfates may be dissolved by the glaze and cause "crawling", "rolling", or "creeping" of the glaze by preventing it from coming into sufficiently close contact with the bisque body.

Mellor (283) found that if conditions in the kiln be such that sulfates developed on the surface did not have time to diffuse into the rest of the glaze, a film of glaze saturated with sulfates is produced on the surface of the ware and this on cooling produces crystals of sulfates. The sulfates in the glaze may result from reactions with the kiln gases as well as from the bisque body.

#### H. Viscosity and Dispersion Problems in the Casting of Slips

Shell and Cartelyou (284) and Rieke (285) have found that the presence of soluble salts affects the viscosity of the clay slip.

#### I. Effect on Tensile Strength of Burned Wares

Grimsley and Grout (286) have compared the tensile strength of a number of clays with the per cent of soluble salts. Their data indicate that a direct relationship exists between the tensile strength and soluble salt content, within certain limits.

## V. THE CHEMICAL COMPOSITION OF THE SOLUBLE SALT FRACTION

In the discussion of the origin of soluble salts in natural clays and shales, it was brought out that the number of different minerals in a clay deposit is usually very large. All of these minerals are soluble to a certain degree but their solubilities will vary over a wide range. A qualitative analysis of the water soluble fraction of any clay would be expected to show the presence of all the elements present in the original clay and a qualitative analysis of a water soluble fraction from a piece of burned ware would show the presence of the elements in the original clay plus those elements introduced during the burning of the ware. A quantitative analysis of the water soluble fraction from either a natural clay or the burned ware made from it would be expected to show a preponderance of the materials having the greater solubilities.

### A. The Chemical Composition of Efflorescences

One of the first published statements on the chemical composition of efflorescences or scum was in an anonymous paper published in 1877 (208). The author stated that the analysis of a gray scum showed that it contained 42 per cent sodium sulfate. The following year Trautwine (287) published an account of his studies of incrustations on brick

walls. He found magnesium sulfate, calcium sulfate and ferrous sulfate in bricks fresh from the kiln. It was pointed out in 1892 (288) that efflorescences contain carbonates, sulfates, silicates, etc. Usually one acid radical predominates, but not always the same one.

A number of writers (132, 189, 199, 291-294) have reported the presence of alkali sulfates in efflorescences and some have found sodium sulfate to be the compound present in the larger amount. Seger (292) reported the analysis of a sample of effloresced salt containing 32.18 per cent potassium sulfate and 26.83 per cent sodium sulfate. A number of years later Mackler (213) stated that sodium sulfate would cause efflorescence but potassium sulfate would not. Wilson (293) published the analysis of a sample of scum but did not include the numerical value for the per cent of sodium sulfate. He stated that the sample contained a large amount of sodium.

McIntire (291) believes that sodium sulfate is the dominant constituent of the great bulk of efflorescences. He gives the following table showing the composition of eight samples of effloresced salts to support his statement. The totals of the per cents given in this table are those given by McIntire. The actual totals for Samples 3, 5 and 7 are 80.9 per cent, 96.0 per cent and 97.92 per cent, respectively.

Table 4. Composition of Effloresced Salts

Sample number	1	2	3	4
Calcium sulfate	1.24	0.68	10.95	---
Magnesium sulfate	0.38	---	1.69	54.04
Magnesium carbonate	---	---	---	---
Sodium sulfate	50.94	46.23	63.10	---
Sodium nitrate	---	---	---	---
Potassium sulfate	46.67	---	5.16	---
Water	0.86	53.12	---	45.72
Total	100.09	100.03	100.00	99.76

Sample number	5	6	7	8
Calcium sulfate	3.5	---	---	0.2
Magnesium sulfate	44.7	50.02	67.52	---
Magnesium carbonate	---	---	6.50	---
Sodium sulfate	3.0	---	3.58	31.1
Sodium nitrate	---	---	1.65	---
Potassium sulfate	---	---	1.17	28.4
Water	44.8	49.98	17.50	40.3
Total	100.0	100.0	99.99	100.0

McIntire observed considerable difference in the composition of the efflorescences from different parts of the same wall. The composition of the efflorescences on the outside of the wall was found to be different from those on the inside of the wall. He also found that the efflorescences from different bricks in the same wall showed considerable difference in composition.

A few writers (187, 217, 268) have reported calcium sulfate to be the dominant constituent in efflorescences, although Machler (213) states that calcium sulfate does not cause efflorescence. The majority of investigators have found either magnesium sulfate or a mixture of magnesium sulfate and calcium sulfate to be present in the larger amounts (43, 185, 188, 198, 211, 272, 273, 291, 294-295).

Cabot (266) stated that three substances cause "white" on bricks. Carbonate of soda was the most common constituent in the "white" on new brick work, silicate of soda is formed on wares made from salt clays and magnesium sulfate on wares from pyritiferous clays. Campredon (162) reported a case of efflorescence which was found to be practically pure sodium carbonate. This was traced to the water used in mixing the mortar.

Grimsley and Grout (286) reported the analysis of a sample of effloresced salts from the bricks of one of the West Virginia plants. This sample contained 5.7 per cent lime, 1.34 per cent magnesia and 1.34 per cent sulfur.



Although white efflorescences are the most common, yellow, green and brown efflorescences have also been reported. Colored efflorescences are sometimes due to a small amount of some colored material depositing with the white materials but in some cases the main constituent has been found to be a colored compound. Pellacini (166) has found that bricks made from marine deposits sometimes produce a yellowish efflorescence. This is explained by the action of sodium chloride on iron compounds in the clay. Green efflorescences have been found to be produced by vanadium compounds (26, p. 384), (188, 209, 296-297) although molybdenum (295), manganese (298-299) and iron (208) may also produce a green coloration. Brown efflorescences are caused by iron compounds (207, 301) due to the hydrolysis and oxidation of ferrous sulfate to form the hydrated oxide of iron.

Brown (301) has reported calcium carbonate as the main constituent in efflorescences and Orton (302) states that efflorescences are composed chiefly of lime.

Paterson (303) has called attention to the natural formation of alums in the shape of effloresced salts. These have been noted in certain volcanic districts where the sulfurous gases have reacted with the aluminous materials such as lava and trachite. Similar efflorescences of aluminous salts have been noted on bricks which form the inner wall of wool-bleaching chambers and are exposed to the sulfur dioxide used in bleaching.

McIntire and Schaffer (41, p. 364) give the following table of analyses of ten samples of efflorescences:

Table 5. Composition of Effloresced Salts

Sample number	1	2	3	4	5
Al <sub>2</sub> O <sub>3</sub>	1.70	---	---	---	---
FeO	2.26	---	---	---	---
CaO	3.53	---	---	0.75	---
MgO	11.70	25.56	16.26	16.06	---
Na <sub>2</sub> O	19.72	2.97	---	0.68	13.62
K <sub>2</sub> O	trace	0.62	---	---	14.06
SO <sub>3</sub>	60.89	48.70	32.52	34.09	29.58
CO <sub>2</sub>	trace	3.57	---	---	---
N <sub>2</sub> O <sub>5</sub>	---	1.10	---	---	---
Cl	---	---	---	---	---
H <sub>2</sub> O	---	17.51	51.22	48.42	42.40

Sample number	6	7	8	9	10
Al <sub>2</sub> O <sub>3</sub>	---	---	---	---	---
FeO	---	---	---	---	---
CaO	0.08	23.15	---	0.51	0.28
MgO	---	0.19	16.67	0.13	---
Na <sub>2</sub> O	13.52	2.92	---	22.22	20.18
K <sub>2</sub> O	15.36	19.98	---	25.21	---
SO <sub>3</sub>	30.73	25.23	33.35	51.16	26.45
CO <sub>2</sub>	---	17.65	---	---	---
N <sub>2</sub> O <sub>5</sub>	---	---	---	---	---
Cl	---	---	---	---	---
H <sub>2</sub> O	40.30	10.88	49.05	0.86	53.12

Seger (26, p. 380) gives the following analyses of two samples of effloresced salts from gray and black clays:

Table 6. Composition of Effloresced Salts

	From gray clay	From black clay
Sulfuric acid	55.13	55.05
Lime	11.24	trace
Magnesia	11.10	4.42
Ferric oxide with small quantities of ferrous oxide	6.22	32.15
Alumina	0.41	2.16
Alkalies	4.82	1.28
Organic matter	5.41	trace
Water, chlorine and constituents not determined	5.67	4.94
Total	100.00	100.00

The following per cents of the various compounds present were calculated from the above chemical analyses:

Table 7. Calculated Per Cents of Compounds Present in Effloresced Salts

	From gray clay	From black clay
Calcium sulfate	27.84	trace
Magnesium sulfate	33.30	13.26
Sulfate of iron	15.55	72.20
Aluminum sulfate	1.39	7.25
Alkaline sulfates	8.82	2.32
Organic matter	5.41	trace
Water, chlorine and constituents not determined	5.67	4.94
Total	100.00	100.00

The totals of the per cents given in Table 7 are those given by Seger. The actual totals for the per cents of the various compounds in salts from the gray clay is 97.98 per cent and from the black clay is 99.97 per cent.

Seger (26, p. 386) also gives the following analysis of the soluble materials obtained by extracting a powdered brick with water. This brick was made from the lignite clays of northern Germany and contained an unusual amount of vanadium.

Table 8. Composition of Soluble Salts from a Lignite Clay

---

Potash	19.82
Soda	3.17
Lime	3.24
Magnesia	3.34
Alumina and ferric oxide	0.77
Vanadic acid	29.43
Sulfuric acid	1.12
Molybdic acid	15.70
Silicic acid	2.07
Chlorine	2.63
Water	18.25
Insoluble residue	0.46
	<hr/>
Total	100.00

---

The following per cents of the various compounds present were calculated from the chemical analysis in Table 8:

Table 9. Calculated Per Cents of Compounds Present in Soluble Salts

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Potassium vanadate	44.38
Potassium sulfate	9.01
Calcium sulfate	7.97
Magnesium sulfate	10.02
Sodium molybdate	1.62
Sodium chloride	4.47
Soluble silicates	3.82
Water	18.25
Insoluble matter	.46
	<hr/>
Total	100.00

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#### B. The Classification of Soluble Salts

Lipinski (304) has classified the soluble constituents of raw clays into two groups. (I) Those which are soluble in water because of their chemical character, and (II) those which form colloidal solutions because of their fineness but are insoluble in their chemical nature. In the first group he includes the chlorides, nitrates and sulfates of sodium, potassium, calcium and magnesium. Seger (292) divides the

effloresced salts into three groupings. (I) Water soluble, (II) acid soluble, i.e. calcium carbonate and the oxides of iron aluminum, and (III) acid insoluble, i.e. sand or  $\text{SiO}_2$ .

### C. The Per Cent of Soluble Salts in Natural Clays

The per cent of soluble salts in natural clays varies over a rather wide range and will depend upon the chemical nature of the minerals making up the clay. The amount of soluble salts obtained from a clay sample will also depend upon the method used in making the soluble salt determination. A number of writers have reported values for the per cent of soluble salts in various clays but in most instances the methods used to obtain these values were not described. Mellor (305) reported that some ball clays released 0.4 per cent soluble salts while china clays gave only 0.015 per cent soluble matter. He was of the opinion that as high as 5 per cent soluble salts could be obtained from some clays by the proper treatment. Ries (306) reported that a series of New Jersey clays showed a variation between 0.00 per cent and 1.4 per cent and a series of Texas clays (307) showed values between 0.05 per cent and 1.21 per cent soluble salts. Grimsley and Grout (286, p. 18) examined seventy clays from West Virginia and found values ranging from a trace to 1.2 per cent. Palmer (38, p. 595) found values ranging from 0.02 per cent to 0.15 per cent from a series of ten clays.

Budnikov (308) gives a value of 0.073 per cent for a Volna clay, 0.015 per cent for an English clay and 0.04 per cent for a "fat" ball clay. Schlunz (309) reports 0.84 per cent for a marine concretion bearing clay and 0.21 per cent for a glacial diluvial clay.

A number of values have been given for the amount of soluble salts necessary to produce efflorescence. Butterworth (212, p. 274) believes that the value of 0.1 per cent soluble salts as given by the Syndicat des Fabricants de Produits Céramiques de France is too low and that higher percentages of soluble salts may not cause efflorescence. Ries (310) says that less than 0.1 per cent is often sufficient to cause scumming. Searle (311) states that as little as 0.01 per cent of the sulfates of lime, magnesia, the alkalies, ferrous iron and aluminum has been known to spoil face brick. Collin (312) states that as little as 0.1 per cent of calcium sulfate may give rise to the development of white coatings on burned wares. Butterworth (274, p. 273) states that the magnesium content should not be over 0.05 per cent or serious damage will result.

## VI. THE SOLUBLE SALT DETERMINATION

The methods which have been described in the literature for determining the per cent of soluble salts in a sample of raw clay or a piece of burned clay were usually consist of extracting a weighed portion of the material with water or some other solvent, filtering off the solution of salts and evaporating this solution to dryness. The weight of the residue so obtained is then called the weight of soluble salts and the per cent is calculated from this value.

All of these methods are purely empirical and the results obtained by one method will not be in agreement with those obtained by another. There is a need for the development of a standard method which will be acceptable to those analysts interested in clay research.

Most of the papers which have appeared in the literature giving values for the per cent of soluble salts, have included a description of the method used in obtaining these values. Others, however, have failed to include this information which makes it difficult for the researcher to give an accurate interpretation to their work.



## VII. SIGNIFICANCE OF THE VALUE FOR THE PER CENT OF SOLUBLE SALTS

In order that the value obtained in the soluble salt determination will be of maximum significance, it is necessary to consider the composition of the residue as weighed. In the examination of clays for ceramic use, the constituents in the soluble fraction which will affect the appearance, durability, or the adherence of glaze to the finished ware are the most important and in some cases, the analysis of the clay for the per cent of soluble sulfate, soluble magnesium, or soluble calcium may give values of greater significance than the value for the per cent of soluble salts.

In the mechanical analysis of sediments by elutriation methods, the particles of the sediment are classified according to size. These methods are usually based upon the differences in the rate of settling of particles of different sizes through a medium such as water. The amount of the finer fraction is often determined by evaporating to dryness the solution containing the finest particles and the soluble fraction of the sediment. The weight of the fine particles may then be determined by subtracting the weight of the soluble material. In this case, the value for the per cent of soluble salts in this mixture would be of more significance than the per cent of any one single constituent.

## VIII. FACTORS AFFECTING THE AMOUNT OF SOLUBLE SALTS EXTRACTED

### A. The Condition of the Sample

Schreiner and Failyer (313), in a discussion of methods of analysis of soils for soluble materials, state that the results from a moist soil are not comparable with those obtained from a dried soil, although both be stated in terms of dry soil. They found that dried soils gave somewhat greater concentrations of soluble salts in the soil extract.

Matejka (314) recommends drying the sample at 100° C. before weighing. Ashley (217, p. 793) recommends heating the sample at 300° C. for one hour, cooling and then crushing to pass a 60 mesh sieve before beginning the extraction.

### B. The Choice of Solvent

When a sample of clay is to be extracted with a solvent to remove the soluble constituents, a solvent should be chosen which will eliminate as many variables as possible. Distilled water or conductivity water are the most satisfactory for this purpose.

The addition of various electrolytes to the solution during the digestion of the sample, or to the turbid solution

before the final filtration, will affect the amount of salts extracted. Because of the difficulties arising during the filtration of clay suspensions, some investigators have added various electrolytes to coagulate the colloidal particles and to aid in clarifying the solution before filtering. Grimsley and Grout (286, p. 18) pointed out in 1905 that the addition of any substance to settle the clay particles altered the results.

Schlunz (309) used a 0.01 N solution of  $\text{NH}_3$  for the extraction of clay samples. Coats (315) agitated the clay sample in dilute  $\text{NaOH}$  solution in order to break up the particles of clay and to liberate the soluble salts. After settling, the clear liquid was tested for soluble salts.

The use of alkaline substances such as  $\text{NaOH}$ ,  $\text{NH}_3$  and  $\text{Na}_2\text{CO}_3$  as deflocculants is common practise in the mechanical analysis of sediments (316) but the presence of such materials in an extracting solution will cause certain reactions to occur which may increase or decrease the amount of soluble salts obtained in the extraction.

Any basic substance such as ammonia, sodium hydroxide, or sodium carbonate will increase the pH of the extracting solution. Iron and aluminum hydroxides precipitate in solutions having a pH range of 2 to 5 which is easily obtained with small amounts of these basic materials. Although the amount of iron or aluminum usually found in the soluble salt fraction is small, this amount of iron and aluminum would

remain in the clay and would carry with it a certain amount of sulfate by adsorption.

Basic substances are known to attack silicates. Basic solutions would, therefore, bring considerably more silica into solution than neutral solutions.

The presence of both a basic substance and carbonates, as would be found in solutions of  $\text{Na}_2\text{CO}_3$ , or in solutions of  $\text{NaOH}$  or  $\text{NH}_3$  in contact with the atmosphere, would precipitate insoluble carbonates. The amount of calcium found in the solution would be less than if water were used as the solvent.

Hirsch (317) suggested the use of aluminum chloride solutions in the determination of sulfates and soluble salts in clays. Aluminum salts are often used as clarifiers in industrial water treatment. Their action depends upon the hydrolysis of the salt producing the flocculant aluminum hydroxide. The second product of the hydrolysis reaction, however, is an acid. In the case of aluminum chloride, the acid would be hydrochloric acid. When a clay sample is extracted with a solution of aluminum chloride, the amount of soluble salts would be affected by the solvent action of the hydrochloric acid and by the adsorption of certain ions by the precipitated aluminum hydroxide.

Bleininger (318) recommends using distilled water containing a few drops of hydrochloric acid for the extraction of soluble salts.

Ashley (217, p. 793) recommends adding a measured volume

of standard magnesium sulfate solution to the turbid liquid after decanting from the bulk of the clay sample. This coagulates the clay particles and aids in filtration. The weight of the soluble salts obtained is then corrected for the amount of magnesium sulfate added. Magnesium sulfate hydrolyzes to give an acid solution which would be expected to have a solvent action on the clay sample. As calcium sulfate is rather insoluble, the presence of the excess sulfate ion in the solution before filtering, may precipitate some of the calcium which would otherwise appear in the evaporated residue.

Ashley ((217, p. 792) has found that when extractions are made with solutions of compounds such as sodium chloride or potassium nitrate, the clay gels are decomposed. He illustrates this type of decomposition with the following equation:



Extractions with salt solutions, therefore, are liable to give much more than the true water soluble materials in the clay.

### C. The Clay-Water Ratio

One of the principal difficulties in the soluble salt determination in which the sample is extracted with successive portions of the solvent, is to know when to stop the extraction. This also applies to the amount of solvent used for a single extraction. If sufficient solvent is used, one might assume that the entire soluble fraction could be removed by a single extraction.

When the determination of only one constituent, such as soluble sulfate, is to be made such an assumption may be correct but when the determination of the total soluble salts is to be made, it is found that there is considerable variation in the amount of soluble salts extracted with different amounts of water. Ashley (217, p. 792) calls attention to the fact that when such common salts as calcium, magnesium, and sodium sulfates have been extracted by successive extractions, then without a break (or rather with decided overlapping) alkaline silicates are removed.

Shell and Cortelyou (284) have recently made a study of the soluble sulfate content of pottery bodies during preparation. Although this study was confined to soluble sulfate determinations, some of their findings are applicable to the determination of soluble salts. They found that if considerable clay was present in the sample of slip to be filtered, the soluble sulfate found was an inverse function of the concentration of the clay. As the clay-water ratio was decreased, the sulfate was increased. A minimum clay-water ratio of 1:20 was found to extract the maximum sulfate content.

The methods given in both editions of Mellor's Treatise on Quantitative Inorganic Analysis (319, 72, p. 716) recommend treating a 5 gram sample of clay with 250 ml. of distilled water. Mellor's earlier method (320), however, called for 5 grams of clay with 150 ml. of water. Ashley (217, p. 793) recommends 100 grams of clay to 1000 ml. of distilled water.

Butterworth (294) treats a 5 gram sample of clay with 300 ml. of distilled water, decants off the liquid and extracts further with 100 to 150 ml. of distilled water. After filtering, the solution is made up to 500 ml. before aliquot portions are withdrawn for analysis. As the main solvent action occurs before filtering, we may say that the clay-water ratio in this case is 5 to 400 or 450. Bleininger (318) uses a ratio of 10 to 500 but in this case the water has been acidified with HCl.

Matejka (314) has studied a number of German methods for determining the soluble salts in clays. He recommends treating a 15 gram sample with 200 ml. of water, filtering and then washing with 300 ml. of water. After the clay has been sucked dry, 25 ml. of water are used to further wash the clay. The total volume of water coming in contact with the sample in this case is 525 ml., giving a clay-water ratio of 15 to 525.

McCartt (321) recommends using a 10 pound sample of clay and 25 pounds of water, or a clay-water ratio of 1 to 2.5.

In the preliminary experimental work on Iowa ceramic clays, a 5 gram sample of clay was boiled with distilled water for one hour and the suspension then filtered through a Gooch crucible containing a mat of asbestos fiber on which was formed a mat of macerated filter paper. The entire mat had a thickness of about one centimeter. After the filtration had been completed and the clay sample had been sucked dry,

the entire contents of the crucible including clay sample and filtering mat, were transferred to a flask, treated with a second 250 ml. portion of distilled water, boiled as before and filtered. The filtrates in both cases were evaporated to dryness in weighed Pyrex beakers and the weight of the residues determined. The following table shows the results of this experiment performed in duplicate.

Table 10. Weights of Residues from Two Successive Extractions

Weight of sample	Residue from first extraction	Residue from second extraction
5.0000	0.0232	0.0213
5.0000	0.0238	0.0215

There is a slight decrease in the amount of residue obtained in the second extraction but the amount of this decrease would indicate that several 250 ml. portions of water would be necessary to remove the more soluble constituents.

#### D. Time and Temperature of Digestion

In treating a clay sample with a definite volume of water for the extraction of soluble salts, conditions must be such as to allow equilibrium to become established between the sample and the solution. The action of the water should be limited to solvent action and it should not enter into any decomposition reactions with the silicates of the clay. The



silica content of the soluble salt residues indicates that some of the silicates have been brought into solution.

A number of authors recommend boiling the clay sample with water, while others prefer a longer treatment with water at room temperature with frequent stirring to dissolve the soluble constituents. The use of hot water has been criticized by some because of the tendency to break down the crystalline silicates.

Although the solubility of most compounds is increased with increase in temperature, calcium sulfate has a maximum solubility at about 38° C. Meller (133, vol. 3, p. 778) gives the solubility in grams of  $\text{CaSO}_4$  per 100 grams of water as 0.190 at 0° C., 0.215 at 38° C. and 0.175 at 99° C.

Meller's methods (72, p. 716; 319-320) for determining soluble salts recommend boiling the clay-water suspension for 30 minutes. Coats recommends boiling for two hours. Matejka (314) heats the sample with water on a water bath for 15 minutes. Kallauner (322) recommends boiling the sample, but does not state the time of boiling.

Shell and Cortelyou (284), in their method for soluble sulfates in clays, recommend shaking the clay-water suspension intermittently for 24 hours before filtering. Butterworth (294) leaves the clay sample in contact with the water for three hours with frequent stirring before decanting off the first part of the solution. He then extracts the residue with an additional 100 ml. of water, leaving this in

contact with the clay for one hour before filtering.

Bleininger (318) recommends shaking the sample with acidified water for an unspecified time and then boiling before adding aluminum chloride and ammonium nitrate to clarify the solution. He does not give the time of boiling nor the time the solution stands before filtering. Ashley (217) recommends shaking the sample with water for one hour at room temperature and allowing the solution to stand over night before filtering.

#### E. Method of Filtration

The filtration of the clay-water suspension is the most difficult part of the soluble salt determination. Filtration by suction is most commonly used although centrifugation (285) has proved satisfactory in some cases. Mellor (72, p. 716; 319) recommends a biscuit earthenware cone, or a porous ware filtering crucible (320). Shell and Cortelyou (284) used a Mandler diatomite filter. They found, however, that in some cases 1 to 2 mgm. of colloidal particles passed through the filter per 400 ml. of solution. As their method was for the determination of soluble sulfates, these colloidal particles were brought into solution by treatment with HCl.

Butterworth (294) found that a layer of filter paper pulp on a Buechner funnel gave a satisfactory filtration.

Bleininger (318) was able to get a satisfactory

filtration by means of a dense filter paper. His method, however, makes use of aluminum chloride and ammonium nitrate as clarifying agents. He also precipitates the aluminum with excess ammonia before filtering.

#### F. The Temperature of Drying the Residue

When weighing the residue from a soluble salt extraction, the usual practice is to dry the residue at some definite temperature until two successive weighings agree within the limits of experimental error (about 0.0002 gram). There is little agreement among the various writers on the soluble salt determination as to the temperature at which the residue should be dried. Mellor (320) originally recommended drying at 200° C. but his later methods (72, p. 716; 319) recommend 110° C. Shell and Cortelyou (284) recommend 100° C., and Matejka (314) recommends 110° C. Butterworth (294) heats the residue at 110° C. for one hour before cooling and weighing. Bleininger (318) heats the residue to a dark red heat. Kallauner (322) makes two weighings, the first after heating at 105-115° C. and the second after heating for 30 minutes at 400-450° C.

Because the soluble salt residue is composed chiefly of the hydrated sulfates of magnesium, calcium, sodium, iron and aluminum, it is necessary to know the temperatures of dehydration of these hydrates before drying and weighing the

residue. If the hydrates are weighed, the value obtained for the per cent of soluble salts will be considerably higher than if the anhydrous sulfates are weighed.

Hofman and Wanjukow (143, p. 940) have made a careful study of the decomposition temperatures of a number of hydrated sulfates and give the following table showing the temperatures at which various hydrates begin to lose water:

Table 11. Initial Temperatures of Dehydration of Various Hydrates

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$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	21	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	19
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	80	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	38
$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	406	$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$	112
$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	51	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	203
$\text{Al}_2(\text{SO}_4)_3 \cdot 13\text{H}_2\text{O}$	82	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	30
$\text{Al}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$	97	$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	80
$\text{Al}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$	109	$2\text{CaSO}_4 \cdot \text{H}_2\text{O}$	149
$\text{Al}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$	180		
$\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	316		

---

Rakuzin and Brodski (323) found that  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  lost  $10\text{H}_2\text{O}$  when heated for 2.5 hours on a water bath.

In the preliminary experimental work on the soluble salts in Iowa ceramic clays, it was noticed that considerable time was necessary to bring a soluble salt residue to constant

weight when it was heated at temperatures of from 105 to 110° C. In some cases a heating period of from weeks to months was necessary, and even then, the residues had not become constant in weight.

The following table illustrates the rate of drying of one of these residues when heated at 105-110° C. The data chosen for this illustration were taken from the weighing record of the first extraction of 5 Kg. of clay with 16 liters of conductivity water. The residue was obtained by evaporating 10 liters of the above solution on the steam plate and then placing in the drying oven.

Table 12. Loss in Weight of a Soluble Salt Residue at 105-110° C.

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	<u>gms.</u>
Weight when taken from steam plate	5.0531
After heating one day	5.0211
After heating six days	5.0145
After heating 11 days	5.0133
After heating 19 days	5.0049
After heating 44 days	4.9765
After heating 65 days	4.8979

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The loss in weight between the 44 and 65 day weighings indicates that this residue had not reached constant weight

even after heating at 105-110° C. for 65 days. It will be noticed that the weight of the residue used in this illustration is much larger than that usually obtained from a 5-gram sample. This weight usually falls in the range of from 0.005 to 0.03 gm.

The loss in weight of the above residue over a period of 65 days was 3 per cent. If this same per cent loss in weight is applied to a residue weighing 0.01 gram, the loss in weight is found to be 0.0003 gram which is close to the limit of experimental error in weighing.

In order to determine the rate of dehydration of some of the common hydrated sulfates found in soluble salt residues, stock samples of Epsom salt ( $MgSO_4 \cdot 7H_2O$ ), precipitated calcium sulfate ( $CaSO_4 \cdot 2H_2O$ ) and gypsum ( $CaSO_4 \cdot 2H_2O$ ) ground to pass a 100 mesh sieve, were heated in the electric oven at 105-110° C. for a period of 23 days. Several weighings of the residues were made during this period. After the last weight was obtained, the residues were analyzed for the per cent of  $SO_3$  and CaO or MgO and the amount of water remaining in the residue calculated by difference. Table 13 shows the gradual loss in weight of these samples when heated over a period of 23 days.

Table 13. Loss in Weight of Epsom Salt and Gypsum at 105-110° C.

	Epsom salt	Gypsum	Precipitated CaSO <sub>4</sub> ·2H <sub>2</sub> O
Weight of sample	1.0146	1.0399	1.0735
After heating 1 day	0.5805	0.8296	0.8622
Per cent loss	42.78	20.22	19.68
After heating 3 days	0.5757	0.8298	0.8616
Per cent loss	43.25	20.20	19.73
After heating 8 days	0.5734	0.8286	0.8617
Per cent loss	43.48	20.31	19.72
After heating 23 days	0.5739	0.8296	0.8600
Per cent loss	43.43	20.22	19.88

The following table gives the analyses of the residues after heating for 23 days:

Table 14. Composition of Residues from the Dehydration of Epsom Salt and Gypsum at 105-110° C.

Epsom salt		Gypsum		Precipitated CaSO <sub>4</sub> ·2H <sub>2</sub> O	
%		%		%	
MgO	29.61	CaO	41.21	CaO	41.19
SO <sub>3</sub>	57.43	SO <sub>3</sub>	58.12	SO <sub>3</sub>	57.81
H <sub>2</sub> O	12.96	H <sub>2</sub> O	0.67	H <sub>2</sub> O	1.00

The per cent of water obtained in the analysis of the Epsom salt residue (12.96%) corresponds favorably with the per cent of water in the mineral kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , 12.01%  $\text{H}_2\text{O}$ ). The sum of the per cent loss of the Epsom salt sample (43.43%) and the per cent of water in the residue ( $12.96\% \frac{100 - 43.43}{100} = 7.33\%$ ) gives 50.76% which corresponds favorably with the per cent of water in Epsom salt (51.16%).

The theoretical per cent of water in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is 20.92%. This corresponds favorably with the sum of the per cent of water remaining in the residue ( $0.67\% \frac{100 - 20.22}{100} = 0.53\%$ ) and the per cent loss (20.22%) or 20.75%. These values for the precipitated calcium sulfate were  $0.80\% + 19.88\% = 20.68\%$ .

This would indicate that at  $110^\circ \text{C}$ .  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  can be almost completely dehydrated if sufficient time is allowed. This is contrary to the findings of Hofman and Wanjukow (143) who report that the hydrate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  does not begin to lose water until a temperature of  $149^\circ \text{C}$ . is reached. Their value of  $112^\circ \text{C}$ . as the temperature at which the hydrate  $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$  begins to lose water is more closely in agreement with the above results obtained at  $110^\circ \text{C}$ .



## IX. OTHER METHODS OF DETERMINING SOLUBLE SALTS

The electrical conductivity of clays and clay suspensions has been investigated by Bleininger and Kinnison (324). They reported that the conductivity is not directly proportional to the amount of calcium sulfate added to the clay. Davis and Bryan (325) had previously designed an electrical bridge for the determination of soluble salts in soils. These methods are of value for the determination of the total electrolytes in clay or soil suspensions but do not give sufficient information concerning the nature of the electrolyte.

Cornille (326) measures the amount of soluble salts in the solution, after extracting a sample of clay or burned brick with water, by titration with a standard soap solution. This does not account for  $\text{Na}_2\text{SO}_4$ . The determination of hardness of water by the soap method roughly approximates the amount of calcium and magnesium in the water, although it actually measures the soap-consuming power of the water (327).

## X. THE EFFLORESCENCE TEST

Tests for liability to effloresce may be made on burned brick or other types of ceramic wares by the use of the so-called "wick test". In this test, the brick is placed in water to a definite depth. The water passes upward through the brick by capillary action, carrying with it the soluble salts in solution. These salts are then deposited on the upper surface of the brick as efflorescences. Methods of making the test have been described by Kallauner (322, p.69) and by McBurney and Parsons (328).

## XI. PRELIMINARY EXPERIMENTAL WORK

The following preliminary experimental work was carried out on a clay sample known to contain considerable soluble matter. The objects of this preliminary work were to (A) determine the effect of carbon dioxide in the water used in the extraction of soluble salts and (B) to determine the relative amounts of the various constituents extracted by successive extractions with water and solutions of carbon dioxide.

For these experiments, five kilogram samples of clay were placed in five gallon bottles. One sample was treated with 16 liters of conductivity water and the other was treated with 16 liters of conductivity water which had been saturated with carbon dioxide. Each sample was thoroughly shaken to disintegrate the clay and to allow the solvent to dissolve the soluble constituents. The bottles were then allowed to stand for 24 hours. At the end of this period the greater part of the clay had settled out, leaving a turbid solution.

Ten liters of this turbid solution were then siphoned off and filtered by suction through a Pasteur-Chamberland filter to remove the remaining suspended matter. The solutions obtained were clear and showed no turbidity.

The filtered solutions were partially evaporated in four liter Pyrex beakers and the evaporation completed by evaporating to dryness in weighed weighing bottles.

After the first ten liter portion of liquid had been siphoned off, a second ten liter portion of conductivity water (or conductivity water saturated with carbon dioxide) was added and the extraction, filtration and evaporation repeated. The extractions of each sample were continued until eleven samples of soluble salt residues were obtained.

The bottles used in the extraction of the clay samples were roughly calibrated by means of a 2 liter graduate. Marks were placed on the bottles to indicate the 6 liter and 16 liter points.

The residues obtained from the various extractions were heated in an electric oven at 110° C. As mentioned before in this thesis, the loss in weight of the various residues at this temperature was extremely slow and it is doubtful if the weights of residues used in the compilation of the data from this experiment represent anhydrous material. For this reason, the per cent of the various constituents in the residues should be taken only as approximations.

Values are not given for the five constituents in all the residues because of lack of sufficient samples. Sufficient data are given, however, to show the change in composition of the residues as the extractions proceeded. The analyses of the various residues are given in the following tables.

Table 15. Composition of Soluble Salt Residues. Successive Extractions with Conductivity Water

Extraction number	Wt. of residue	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	SO <sub>2</sub>
		<u>gms.</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
1	4.89	0.79	0.80	20.97	9.75	38.28
2	2.69	0.33	----	20.87	9.65	38.16
3	1.88	2.00	0.20	25.06	9.72	35.61
4	1.81	2.20	0.23	26.80	10.08	32.22
5	1.82	2.20	0.32	27.04	10.08	31.97
6	1.57	3.80	0.19	28.22	10.60	27.66
7	0.82	----	----	32.12	----	----
8	0.77	3.40	0.38	----	9.64	----
9	0.73	----	0.34	35.59	9.30	----
10	0.65	----	----	----	----	----
11	0.73	3.55	0.31	36.68	4.59	10.74

Table 16. Composition of Soluble Salt Residues. Successive Extractions with Carbonic Acid Solutions.

Extraction number	Wt. of residue	SiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>2</sub>
	<u>gms.</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
1	6.30	1.40	2.61	32.61	9.37	20.07
2	6.33	----	1.11	36.04	8.42	18.34
3	5.28	1.53	0.16	37.28	8.44	15.83
4	4.76	1.29	0.17	38.45	8.97	10.71
5	3.91	1.56	----	39.19	9.17	9.91
6	3.70	----	----	40.71	----	5.99
7	3.88	1.60	----	----	9.42	5.21
8	2.83	1.43	0.21	40.14	9.53	4.03
9	3.78	----	0.25	40.00	10.19	2.50
10	2.85	1.68	0.11	40.54	----	2.19
11	3.44	1.63	0.13	----	11.13	1.94

It will be noted that the amount of soluble material extracted by solutions of carbon dioxide is appreciably larger than with conductivity water. This would be expected because of the formation of bicarbonates.

The per cent of  $\text{SiO}_2$  in the residues showed a gradual increase when conductivity water was used. The first two extractions gave residues rather low in  $\text{SiO}_2$ , but the  $\text{SiO}_2$  content of the third residue was considerably higher and the values were found to increase as the extractions proceeded. The values for the per cent of  $\text{SiO}_2$  in the residues from the carbonic acid extractions are all within the same range and the variations are not significant.

This difference in the general trend of the  $\text{SiO}_2$  content of the residues from the conductivity water extractions may be explained in terms of change in pH of the solutions during repeated extractions with conductivity water. The first two extractions were necessary to remove the soluble materials which produced a low pH. After the concentrations of these substances had been lowered, the pH increased to a point where the action of the solution on the silicates was more pronounced. When the extracting solution was saturated with  $\text{CO}_2$ , the pH of the solutions remained about the same throughout the successive extractions, and was not high enough to allow the solution to attack the silicates in any great amount.

The per cent of  $\text{R}_2\text{O}_3$  in the residues did not show any

great variation when the clay was extracted with conductivity water. The first sample showed the largest per cent of  $R_2O_3$ , probably due to the relatively low pH of this extracting solution. It will be noted that the lowest values of  $SiO_2$  were obtained in the first extractions while the highest value for  $R_2O_3$  was obtained in the first extraction.

The greater part of the iron and aluminum present in a soluble form in the original clay were probably present in the form of sulfates. These were soluble in the extracting solutions having low pH and were extracted almost completely by these low pH solutions. The low values for  $R_2O_3$  in the later extractions may have been caused by the hydrolysis of the remaining iron and aluminum compounds as the pH of the solutions increased. This would precipitate the iron and aluminum and cause them to remain with the solid portion of the sample. The fairly constant values for the  $R_2O_3$  in the residues from the last few extractions indicate that the iron and aluminum have been brought into solution due to the slight solubility of the various silicates containing these elements, or by slight decomposition of these silicates by the extracting solution.

The per cent of  $CaO$  in the residues was found to increase as the extractions proceeded when either conductivity water or carbon dioxide solutions were used. The increase was greater during the conductivity water extractions.

The residues from the extractions of this clay sample



showed the highest per cents of CaO and SO<sub>3</sub>. The per cent of MgO was also found to be quite high. As the sulfate was removed from the clay by successive extractions, the per cent of SO<sub>3</sub> in the residue decreased causing a corresponding increase in the per cent of CaO.

## XII. EXPERIMENTAL PART

### A. Description of Samples

The Iowa ceramic clays used in this work were obtained from several brick and tile manufacturers over the state. The following descriptions of the clays were given by these manufacturers. The deposits from which the samples were taken have been described by Gwynne (45).

Sample A. Rockford Brick and Tile Company, Rockford, Iowa. This sample had been ground to about one-eighth mesh. It is the product which this company sells under the name of "mortar mix".

Sample B. Adel Clay Products Company, one mile east of Redfield, Iowa. This sample is described as being a mixture from a 45 foot face. It contains 20 per cent fire clay and 80 per cent coal measure shale.

Sample C. United Brick and Tile, Adel, Iowa. This sample contains 30 per cent fire clay and 70 per cent coal measure shale.

Sample D. Lehigh Sewer Pipe and Tile Company, Lehigh, Iowa. This sample represents a mixture from a 40 foot face.

Sample E. Redfield Brick and Tile Company, Redfield, Iowa. This sample represents a mixture from a 40 foot face.

Sample F. Vincent Clay Products Company, Fort Dodge, Iowa. A white burning shale.

Sample G. Vincent Clay Products Company, Fort Dodge, Iowa. A red burning shale.

Sample H. Vincent Clay Products Company, Fort Dodge, Iowa. A high iron fire clay. This sample contains considerable pyrite.

A sample of this material was stored over a period of two years in a closed bottle. At the end of this time it was noticed that considerable white crystalline material had formed on some of the pieces. When examined with a hand lens, the white material was found to be a white silky fibrous crystalline mass growing from fragments of marcasite or pyrite in the sample.

A chemical examination of the material showed that it was easily soluble in water; the water solution gave a deep blue precipitate with potassium ferricyanide solution and a light blue precipitate with potassium ferrocyanide solution. The water solution also gave a heavy white precipitate with barium chloride solution in the presence of hydrochloric acid.

From the above tests, it was concluded that the white material was the mineral melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) which had been formed by the partial oxidation of the pyrite or marcasite in the sample.

Sample I. Iowa Pipe and Tile Company, Des Moines, Iowa. This sample is from a 40 foot face and contains fourteen

different colors of clay.

Sample J. Mason City Brick and Tile Company, Mason City, Iowa. A sandy, yellow clay containing some dirt from the surface and some yellow rock.

#### B. Experimental Procedure

The clay samples were first analyzed for the usual constituents determined in rock analysis. The methods used in analyzing the clays and the soluble salt residues are described under "Methods of Analysis" later in this thesis.

In order to determine the effect of the clay-water ratio on the per cent of soluble salts extracted, a modification of Mellor's (72, p. 716) method for determining soluble salts was used.

The clay samples were placed in 500 ml. Pyrex Erlenmeyer flasks and treated with 250 ml. of distilled water. One No. 42 Whatman 9 cm. filter paper was macerated by shaking with hydrochloric acid in an Erlenmeyer flask. It was then filtered and washed free from chlorides and added to the flask containing the sample and water. A six inch Hopkins reflux condenser was fitted to each flask and the samples boiled for 30 minutes. They were then allowed to stand over night at room temperature before filtering.

A Gooch crucible containing a mat of filter paper pulp was used for the filtration. The paper pulp was prepared by macerating one Whatman No. 42, 9 cm. filter paper with hydro-

chloric acid, filtering and washing free from chlorides. The pulp was then suspended in 50 ml. of distilled water and poured into the Gooch crucible which had a disk of common white blotting paper in the bottom to prevent any filter paper fibers from passing through during the filtration. Small disks of filter paper were tried for this purpose but it was found that the blotting paper gave more rapid filtration.

A small disk of filter paper was placed on the top of the paper mat to prevent its being churned up when the solution was poured into the crucible. The entire filter mat was about one centimeter thick.

This filtering crucible was found to give more satisfactory filtrations than alundum crucibles or Sela Micro-Porous filter crucibles. The colloidal clay particles filled up the pores of these crucibles and slowed down the filtration to about eight or ten hours for 250 ml. of solution.

The Gooch crucible with paper mat filtered much more rapidly but it was sometimes necessary to filter the solutions two or three times in order to completely remove the turbidity. When this was necessary, more macerated filter paper was added to the solution and it was filtered through a fresh crucible.

After the solutions had been filtered, they were evaporated to dryness on the steam plate in weighed 50 ml. Pyrex beakers and then placed in the electric oven at 110° C. until the weights had become constant, or until the loss in weight between two successive weighings was within the usual limit of

experimental error (0.0002 gm.). This usually required from seven to ten days. As shown in the discussion of the preliminary experimental work, the residues had probably not reached constant weight during this time but the magnitude of the loss in weight is small with the amount of residue usually obtained from a 5 gram sample. As an illustration, the residue from a 7 gram sample of clay weighed 0.0400 gram after one day in the oven. This residue lost 0.0007 gram after three days in the oven and an additional 0.0001 gram the next six days.

The variations in the clay-water ratio were produced by varying the weight of the clay used in each extraction and using 250 ml. of water for each extraction. The per cents of soluble salts obtained from each clay when the clay-water ratio was varied are given in the experimental data.

In order to determine the amounts of the various constituents removed by successive extractions of a sample of clay, a second modification of Meller's (72, p. 716) method was used. In order to obtain larger amounts of the soluble salt residues, 125 gram samples of each clay were used. These were treated with 6 liters of distilled water and boiled for 30 minutes in six liter Pyrex Erlenmeyer flasks. The samples were then allowed to stand for 72 hours to allow the bulk of the solids to settle out, and then 5 liters of the turbid solution were siphoned off. The volume of this solution was measured accurately by means of volumetric

flasks and then transferred to five liter Pyrex flasks. Macerated filter paper was then added to aid in clarifying the solution during filtration.

The macerated filter paper was prepared by disintegrating one 20" x 20" sheet of medium grade filter paper with hydrochloric acid, filtering and washing free from chlorides.

The solutions were filtered by suction through a 1 cm. mat of filter paper pulp in a 10 cm. Buechner funnel. A disk of white blotting paper was placed on the bottom of the Buechner funnel to prevent any paper fibers from passing into the filtrate, and a disk of common filter paper was placed on the top of the mat to prevent the filter mat from churning up while the solution was being poured into the funnel.

All solutions were filtered twice and in some cases three filtrations were necessary. Each filtration was made through a fresh mat of paper pulp and additional macerated filter paper was added to the solution.

After filtration, the solutions were evaporated to dryness in weighed 250 ml. Pyrex beakers. The beakers were then placed in an electric oven where they were dried at 110° C. The dried residues were then analyzed for  $\text{SiO}_2$ ,  $\text{R}_2\text{O}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SO}_2$ .

#### C. Method of Tabulation of Experimental Data

The data obtained from the analyses of the original clay samples; the variation in the per cent of soluble salts

obtained by varying the clay-water ratio; and the analyses of the residues obtained by successive extractions of each sample have been given separately for each clay examined.

In order to determine the amount of residue, and also the amount of the various constituents that would have been extracted by 6 liter portions of water, it was necessary to apply a correction to the weights of residues and constituents obtained by evaporating each 5 liter portion. This was necessary because one liter of the extracting solution remained in the flask each time a 5 liter portion was withdrawn. This correction was not necessary for the first extraction.

After the corrected weights from 5 liter extractions had been obtained, the weights of residues and constituents which would have been extracted if 6 liter portions of water had been used for each extraction were calculated. These values may then be used to estimate the weight of each constituent extracted with 6, 12 or 18 liters of water. This would correspond approximately to a clay-water ratio of 1:40, 1:80 or 1:120.

The following sample calculation illustrates the method of obtaining these values. The total residues obtained in extracting sample "A" are used in this illustration:



	Wt. of residue from 5 L. <u>gm.</u>	Corrected wt. of residue from 5 L. <u>gm.</u>	Wt. of residue calculated to 6 L. <u>gm.</u>
First extraction	0.6165	0.6165	0.7398
Second extraction	0.2767	0.1740	0.2088
Third extraction	0.2435	0.2145	0.2574

First extraction:

Wt. of residue calculated to 6 L. =  $(.6165)6/5 = .7398$

Wt. of residue remaining in one liter of

solution not siphoned off =  $(.7398)1/6 = .1233$

Second extraction:

Wt. of residue obtained in second 5 L. extraction .2767

Wt. of residue carried over from first

extraction to 5 L. of solution =  $(.1233)5/6 = .1027$

Corrected wt. of residue obtained in second

extraction =  $(.2767 - .1027) = .1740$

Calculated to 6 L. =  $(.1740)6/5 = .2088$

Wt. of residue remaining in the one liter of

solution not siphoned off =  $(.2088)1/6 = .0348$

Third extraction:

Wt. of residue obtained in third 5 L. extraction .2435

Wt. of residue carried over from second

extraction to 5 L. of solution =  $(.0348)5/6 = .0290$

Corrected wt. of residue obtained in third

extraction =  $(.2435 - .0290) = .2145$

Calculated to 6 L. =  $(.2145)6/5 = .2574$

In addition to the weights of the various constituents removed in each extraction, the milligrams of each constituent per liter of extracting solution are given in the data on the analysis of the salt residues. Values for the percent of each constituent in the residues have been included but due to the uncertainty of the degree of dehydration of the residues, these values should be considered as only approximations.

### XIII. METHODS OF ANALYSIS

#### A. Analysis of Clay Samples

The clay samples were analyzed according to the methods of Washington (329) with the following exceptions.

##### 1. Ignition Loss

One gram samples of clay were ignited to constant weight in open platinum crucibles. In order to avoid losses due to decrepitation, the covers were left on the crucibles for the first fifteen minutes of the ignition period. The temperature of the sample during the final ignition period was found to be between 1050° C. and 1100° C. when measured with an optical pyrometer.

Several authors (137, p. 223) (269, 290, 330-331) have stated that sulfur is not completely removed from clays during the firing process. Ogan (331), after making a study of the cause of permanent expansion of fire brick, reported that 38 per cent of the total soluble salts contained in the unburned clays were "fixed" by the firing of the clay. Jackson (137, p. 223) found that the sulfur remaining in a clay body after firing was practically insoluble in water or aqua regia, but was rendered soluble by hydrofluoric acid. Hillebrand and Lundell (332), however, state that at the

temperature of a moderate blast (1100° C.), with the crucible covered, sulfides are oxidized to sulfates and all the sulfur is retained by the calcium. With a powerful blast (1200° C.-1300° C.) the sulfate is decomposed gradually, with eventual loss of the entire sulfur content. Mellor and Thompson (72, p. 136) also mention the expulsion of sulfurous gases from sulfates and the oxidation of sulfides during the ignition loss determination. O'Sullivan (333) and Ratcliff (334) have called attention to the errors introduced in an analysis of vinegar and beer for sulfur by first washing the sample. Fresenius (335) found that magnesium sulfate could be completely decomposed by means of heat. After heating the sample in a platinum crucible, he was unable to detect the presence of sulfate in the residue.

Because the per cent of sulfur is one of the most significant values in the study of the soluble salts in clays, it was necessary to determine whether or not any sulfur was retained in the sample after it had been ignited for the determination of ignition loss. This was done by treating the ignited residue in the platinum crucible with  $H_2F_2$  and  $HNO_3$  to insure the decomposition of any sulfate containing silicates and to oxidize any sulfide to sulfate. The crucible was then placed on the steam plate and the contents evaporated to dryness. More  $HNO_3$  and  $H_2F_2$  were added and the evaporation repeated. After the second evaporation, the crucible was heated to 350° C. for two hours, cooled and HCl

added to decompose any nitrates. The crucible was then placed on the steam plate and the contents evaporated to dryness. The ignition at 350° C., treatment with HCl and evaporation to dryness was repeated in order to decompose any nitrates or fluorides which would be adsorbed by the BaSO<sub>4</sub> precipitate.

The samples were then transferred to 600 ml. Pyrex beakers, treated with HCl and warmed to dissolve the soluble oxides. The solutions were diluted to 400 ml. and the iron, aluminum, etc. precipitated with NH<sub>4</sub>OH. The ammonia precipitate was filtered, dissolved in HCl and the solution diluted to 400 ml. The iron, aluminum, etc. were again precipitated with NH<sub>4</sub>OH. This precipitate was dissolved and reprecipitated to insure complete removal of any sulfate which may have adsorbed on the precipitated hydroxides. The filtrates and washings from the three precipitations were combined and evaporated to 400 ml., the acidity adjusted to 0.05N, heated to boiling and 10 ml. of 5 per cent barium chloride solution added. An extremely small amount of BaSO<sub>4</sub> precipitate was noted in some beakers, while in others no precipitate could be seen. The weights of the BaSO<sub>4</sub> precipitates varied between 0.0000 and 0.0005 gm. from 2.0000 gram samples. This would correspond to a maximum of 0.003 per cent of sulfur in the residues after ignition to constant weight. This value is negligible and was disregarded in the calculation of per cent ignition loss.

Sulfur was the only constituent determined in the analysis of the clays which was driven off during the ignition of the sample. The per cent of sulfur (S) and of sulfur trioxide (SO<sub>2</sub>) should then be subtracted from the values obtained in the ignition loss determination.

In the analysis of the original clay samples, the per cent of sulfate sulfur and of sulfide sulfur were estimated only for those samples showing a total sulfur content of over 1.00 per cent (as SO<sub>2</sub>). The ignition loss correction does not appear in the tables of analyses of those samples showing a total per cent of sulfur below 1.00 per cent (as SO<sub>2</sub>). The corrected per cent of loss on ignition was calculated as follows:

$$\text{Corrected \% ignition loss} = (\% \text{ ignition loss obtained}) - (\% \text{ SO}_2 + \% \text{ S}) + (\% \text{ FeO} \frac{\text{Fe}_2\text{O}_3}{2\text{FeO}} - \% \text{ FeO})$$

## 2. Magnesium

Magnesium was determined in the filtrate from the calcium precipitation according to the method of Fales and Kenny (336). Fifty ml. of concentrated HNO<sub>3</sub> were added to the combined filtrates and washings from the calcium precipitation and the solution evaporated to dryness on the steam plate to decompose the ammonium salts. The residue was dissolved in HCl and distilled water and Na<sub>2</sub>HPO<sub>4</sub> solution added. Sufficient NH<sub>4</sub>OH was then added to make the NH<sub>4</sub>Cl concentration 0.4 molar and the NH<sub>4</sub>OH concentration 1.5 molar. After

standing over night, the  $MgNH_4PO_4 \cdot 6H_2O$  was filtered and ignited to  $Mg_2P_2O_7$ , before weighing.

### 3. Total Sulfur

Total sulfur was determined by a modification of the method of Allen and Bishop (337). The original method is designed for the determination of sulfur in pyrite by oxidation with bromine. The iron is reduced to the ferrous condition and the sulfur precipitated as  $BaSO_4$  in the presence of the reduced iron. Because clays contain considerable insoluble material, this must be removed before precipitating the  $BaSO_4$ . This insoluble material was filtered off with the insoluble hydroxides after addition of ammonia.

Two grams of clay were treated with 30 ml. of a solution of bromine in carbon tetrachloride (2:3 by volume) and allowed to stand over night at room temperature. Thirty ml. of concentrated  $HNO_3$  were then added and the solution evaporated to dryness on the steam plate. The residue was then treated with 30 ml. of concentrated  $HCl$  and again evaporated to dryness. Two more 30 ml. portions of concentrated  $HCl$  were added and the solution evaporated to dryness after each addition in order to decompose nitrates.

The final residue was taken up in 15 ml. of concentrated  $HCl$  and 250 ml. of distilled water. The solution was heated to boiling and ammonium hydroxide added to precipitate the iron, aluminum, etc. This ammonia precipitate also carried

down with it any suspended clay material remaining after the above acid treatment and served to clarify the solution.

The ammonia precipitate was then filtered, washed with dilute ammonium hydroxide (1 per cent) and then reprecipitated twice. The combined filtrates were evaporated to 400 ml. and the sulfur precipitated from the boiling solution as  $\text{BaSO}_4$  by slow addition of 5 per cent  $\text{BaCl}_2$  solution. The acidity of the solution was adjusted to 0.05M with HCl before addition of barium chloride as recommended by Kolthoff and Sandell (338).

#### 4. Soluble Sulfate

Several methods have been suggested for the determination of soluble sulfates in clays. Mellor and Thompson (72, p. 716) extract the sample with boiling water, filter and precipitate the sulfate from the filtrate. Hillebrand and Lundell (322, p. 812) and Hillebrand (339) extract the sample with dilute hydrochloric acid and precipitate the sulfate from the resulting solution. These methods assume the absence of certain ions in the filtrate which adsorb on the  $\text{BaSO}_4$  precipitate.

In the analysis of the clay samples, a modification of Hillebrand and Lundell's method was used. The total soluble sulfur was calculated as  $\text{SO}_4$  and reported as soluble sulfate.

Five gram samples of clay were treated with 450 ml. of boiled distilled water and 2 ml. of 0.14 N HCl. The solutions



were digested on the steam plate for two hours and then allowed to stand at room temperature over night.

The slightly turbid solution was carefully drawn off by means of a large pipet and transferred to a large beaker. This digestion of the samples with boiled distilled water and dilute HCl was repeated three times. The solutions were combined, treated with 5 ml. of saturated bromine water and then evaporated to about 400 ml.

Although the greater part of the clay had settled out before the solutions were drawn off, there was still considerable material remaining in suspension. In order to clarify the solutions before precipitating the  $\text{BaSO}_4$ , 20 drops of 10 per cent ferric chloride solution were added, the solution heated to boiling and the iron then precipitated with  $\text{NH}_4\text{OH}$ . The  $\text{Fe}(\text{OH})_3$  removed the suspended colloids during its precipitation.

The materials precipitated by the  $\text{NH}_4\text{OH}$  were filtered, dissolved in hydrochloric acid and reprecipitated from a volume of 450 ml. The reprecipitation of the hydroxides was done a third time, the filtrates and washings combined and evaporated to 400 ml. The  $\text{BaSO}_4$  was precipitated as described in the method for total sulfur.

##### 5. Sulfide Sulfur

In calculating the per cent of sulfide sulfur present as  $\text{FeS}_2$ , the following assumptions were made: (1) The sample

contained no soluble sulfur compounds other than sulfates.

(2) The treatment of the sample with boiled distilled water and dilute HCl did not dissolve any of the  $\text{FeS}_2$ . Pyrrhotite is known to be partially soluble in hydrochloric acid but both marcasite and pyrite are insoluble, provided oxidizing agents are absent.

The per cent of soluble sulfate (as  $\text{SO}_4$ ) was subtracted from the per cent of total sulfur (as  $\text{SO}_2$ ) and the resulting value converted to the per cent of sulfide sulfur by multiplying by the factor 0.4004 and reported as per cent S.

#### 6. Ferrous Iron

Hillebrand and Lundell (332, p. 778) state that the presence of organic matter in a sample renders the determination of ferrous iron impossible. The oxidizing effect of ferric salts on pyrite and marcasite has also been found to introduce considerable error in this determination (229,340). Pyrite, in the quantities usually found in igneous rocks (usually only a few tenths of one per cent) is probably without serious effect on the ferrous iron determination. The amount of  $\text{FeS}_2$  present in some of the clays examined would produce considerable error in the ferrous iron determination.

In estimating the per cent of ferrous iron, it was assumed that the only source of ferrous iron was from pyrite or marcasite and that there were no silicates containing ferrous iron in the samples. It was also assumed that there

was no ferrous iron present as ferrous sulfate.

The per cent of ferrous iron was calculated by converting the per cent of sulfide sulfur to per cent of ferrous iron by multiplying by the factor  $\frac{\text{FeO}}{2\text{S}}$  or 1.1204 and reporting as per cent FeO.

As the per cent of sulfide sulfur was calculated for only those samples containing over 1.00 per cent of total sulfur (as  $\text{SO}_2$ ), the values for per cent FeO do not appear in the tables of analyses of those samples containing less than 1.00 per cent of total sulfure (as  $\text{SO}_2$ ).

#### 7. Ferric Iron

The per cent of ferric iron was estimated from the value for the per cent of total iron (as  $\text{Fe}_2\text{O}_3$ ) and the per cent of ferrous iron (as FeO). The per cent of FeO was converted to per cent  $\text{Fe}_2\text{O}_3$  by multiplying by the factor  $\frac{\text{Fe}_2\text{O}_3}{2\text{FeO}}$  or 1.1114. This value was then subtracted from the per cent of total iron as  $\text{Fe}_2\text{O}_3$  and the resulting value recorded as per cent of  $\text{Fe}_2\text{O}_3$ .

#### B. Analysis of Soluble Salt Residues

After the soluble salt residues had been dried, they were treated with 25 ml. of 6 N HCl and evaporated to dryness on the steam plate in order to dehydrate the silica. The residue was then taken up in 10 ml. of 6 N HCl and 100 ml. of

distilled water and the solution filtered. The insoluble material was washed in the filter paper until free from chlorides, transferred to a platinum crucible and ignited to constant weight. The impure  $\text{SiO}_2$  was then treated with  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$ , evaporated to dryness on the steam plate and again ignited to constant weight. The loss in weight of the residue was taken as the weight of  $\text{SiO}_2$  in the residue.

The  $\text{R}_2\text{O}_3$  was precipitated from the filtrate from the  $\text{SiO}_2$  filtration. The filtrate and washings from the  $\text{R}_2\text{O}_3$  determination were made acid with  $\text{HCl}$  and then evaporated to about 200 ml. The solution was then transferred to a 250 ml. volumetric flask and made up to the mark with distilled water. A 100 ml. aliquot of this solution was used for the sulfate determination, and a 225 ml. aliquot for the calcium and magnesium determination.

XIV. EXPERIMENTAL DATA

Table 17. Analysis of Original Clay Sample A

	%	%
Ignition loss	14.20	
Corrected ignition loss		13.82
SiO <sub>2</sub>		49.91
R <sub>2</sub> O <sub>3</sub>	19.34	
Al <sub>2</sub> O <sub>3</sub> (by difference)		14.44
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )	4.87	
Fe <sub>2</sub> O <sub>3</sub>		4.35
FeO		0.47
MgO		4.53
CaO		7.01
K <sub>2</sub> O		4.58
Na <sub>2</sub> O		0.67
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>3</sub> )	1.27	
Sulfide S		0.42
Soluble sulfate (as SO <sub>3</sub> )		0.24
		<u>100.47</u>

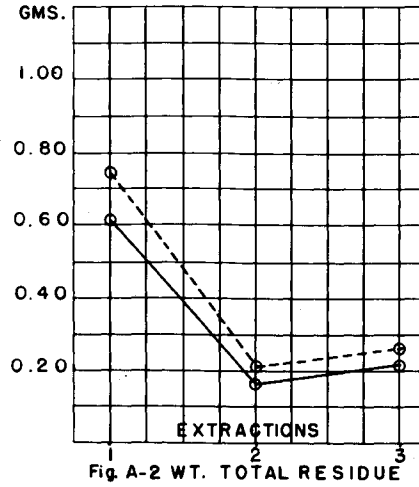
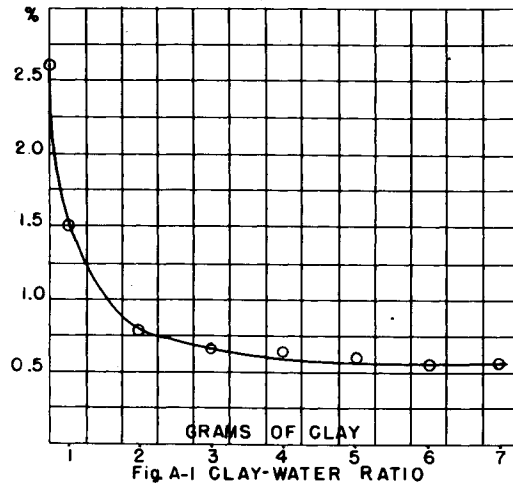
Table 18. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample A

Grams of clay	Clay-water ratio	Per cent soluble salts
7.0	1:37.5	0.57
6.0	1:41.7	0.55
5.0	1:50	0.60
4.0	1:62.5	0.66
3.0	1:83.3	0.69
2.0	1:125	0.82
1.0	1:250	1.50
0.5	1:500	2.66

Table 19. Analysis of Salt Residues - Sample A

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.6165	.7398	.2767	.1740	.2088	.2435	.2145	.2574
Wt. SiO <sub>2</sub>	.9562	.0674	.0329	.0236	.0283	.0430	.0391	.0469
Mgn. SiO <sub>2</sub> per L.	11.2		6.5			8.6		
% SiO <sub>2</sub> in residue	9.11		11.88			17.65		
Wt. R <sub>2</sub> O <sub>3</sub>	.0037	.0044	.0023	.0017	.0020	.0026	.0024	.0029
Mgn. R <sub>2</sub> O <sub>3</sub> per L.	0.72		0.46			0.52		
% R <sub>2</sub> O <sub>3</sub> in residue	0.60		0.83			1.05		
Wt. CaO	.1836	.2203	.0912	.0619	.0743	.0846	.0743	.0891
Mgn. CaO per L.	36.7		18.2			16.9		
% CaO in residue	29.78		32.95			34.74		
Wt. MgO	.0336	.0403	.0158	.0102	.0122	.0198	.0181	.0217
Mgn. MgO per L.	6.7		3.1			3.9		
% MgO in residue	5.45		5.71			8.13		
Wt. SO <sub>3</sub>	.2438	.2926	.0512	.0105	.0126	.0235	.0218	.0262
Mgn. SO <sub>3</sub> per L.	48.7		10.2			4.7		
% SO <sub>3</sub> in residue	39.54		18.50			9.65		

SAMPLE A



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - - -

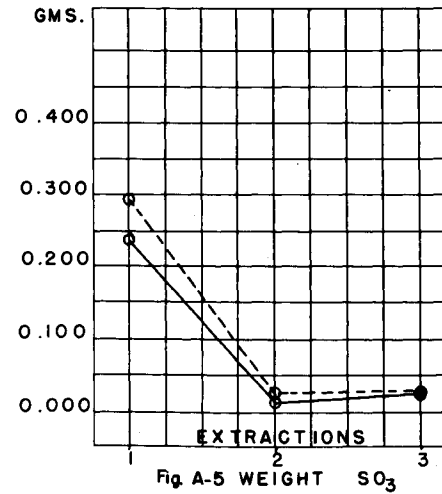
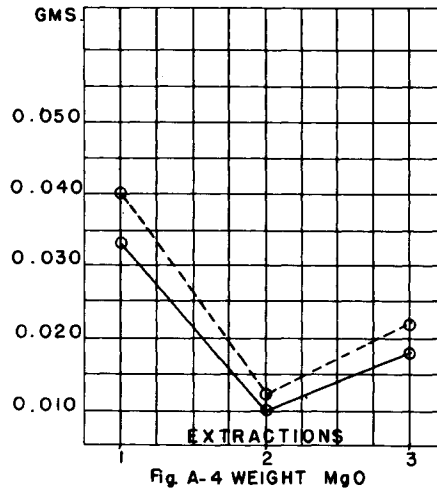
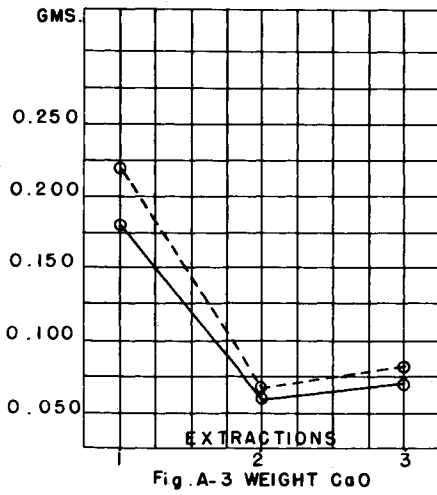


Table 20. Analysis of Original Clay Sample B

	<u>%</u>	<u>%</u>
Ignition loss		7.26
SiO <sub>2</sub>		63.28
R <sub>2</sub> O <sub>3</sub>	23.78	
Al <sub>2</sub> O <sub>3</sub> (by difference)		17.20
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		6.55
MgO		1.41
CaO		1.20
K <sub>2</sub> O		2.69
Na <sub>2</sub> O		0.91
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>2</sub> )		<u>0.06</u>
	Total	100.59

Table 21. Variation in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample B.

Grams of clay	Clay-water ratio	Per cent soluble salts
6.0	1:41.7	0.40
5.0	1:50	0.38
4.0	1:62.5	0.36
3.0	1:83.3	0.58
2.0	1:125	0.46
1.0	1:250	0.77
0.5	1:500	1.20



Table 22. Analysis of Salt Residues - Sample B

	First extraction		Second extraction		Third extraction	
	Wt. from Calc. to 5 L.	Wt. from Calc. to 6 L.	Wt. from Corrected Calc. to 5 L.	Wt. from Corrected Calc. to 6 L.	Wt. from Corrected Calc. to 5 L.	Wt. from Corrected Calc. to 6 L.
Total residue	.2304	.2765	.2060	.1617	.2011	.1996
Wt. SiO <sub>2</sub>	.0505	.0607	.0235	.0151	.0181	.0212
Wt. SO <sub>2</sub>	10.1		4.7			4.8
Wt. SO <sub>3</sub> in residue	21.96		11.40			12.12
Wt. R <sub>2</sub> O <sub>3</sub>	.0036	.0013	.0017	.0011	.0019	.0028
Wt. R <sub>2</sub> O <sub>3</sub> per L.	0.7		0.9			0.6
Wt. R <sub>2</sub> O <sub>3</sub> in residue	1.12		2.28			1.40
Wt. CaO	.0602	.0722	.0690	.0590	.0708	.0778
Wt. CaO per L.	12.0		13.8			15.6
Wt. CaO in residue	26.04		33.48			38.97
Wt. MgO	.0062	.0074	.0013	.0033	.0039	.0071
Wt. MgO per L.	1.2		0.8			1.4
Wt. MgO in residue	2.69		2.06			3.55
Wt. SO <sub>3</sub>	.0155	.0138	.0076	.0057	.0068	.0018
Wt. SO <sub>3</sub> per L.	2.3		1.5			0.9
Wt. SO <sub>3</sub> in residue	4.99		3.63			2.40

SAMPLE B

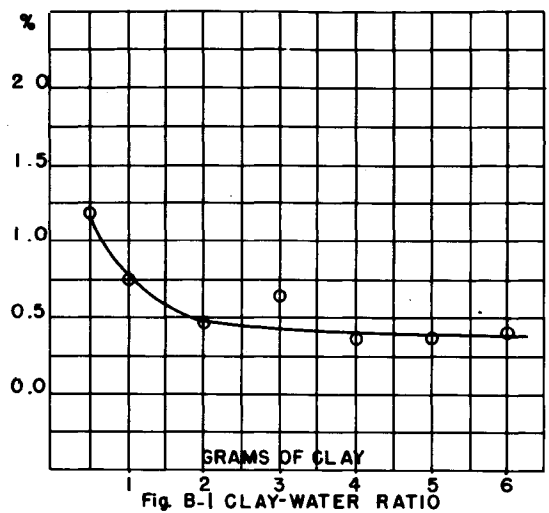


Fig. B-1 CLAY-WATER RATIO

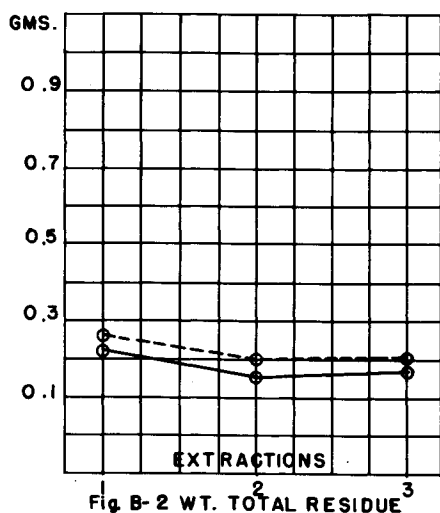


Fig. B-2 WT. TOTAL RESIDUE

Legend:  
Corrected wt. 5 L ———  
Calculated to 6 L - - - -

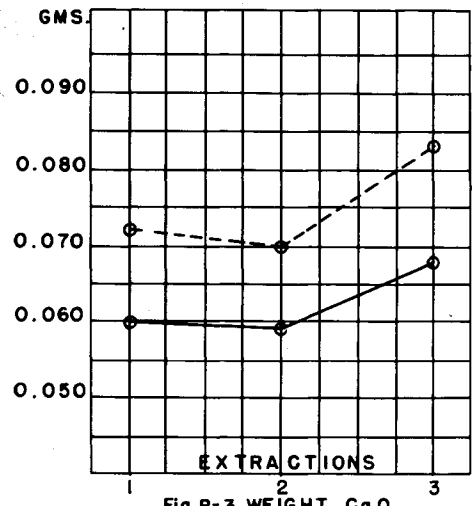


Fig. B-3 WEIGHT CaO

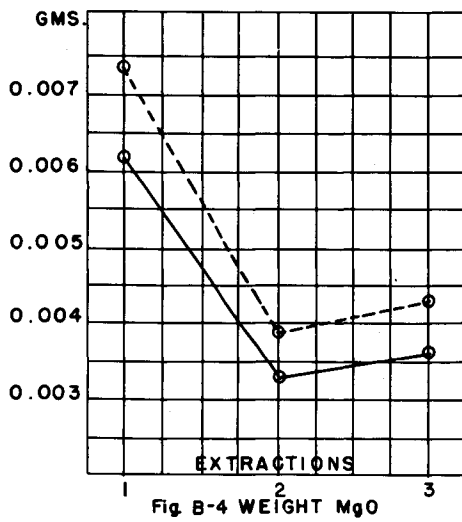


Fig. B-4 WEIGHT MgO

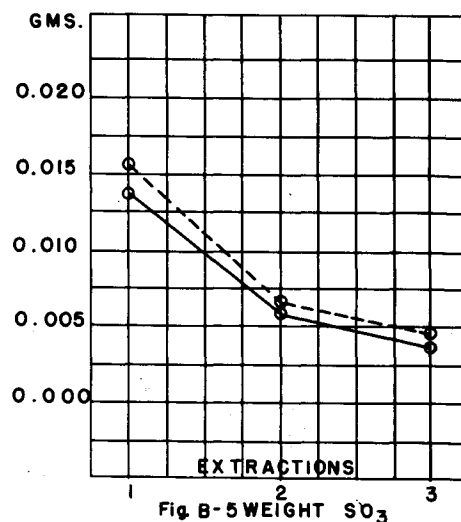


Fig. B-5 WEIGHT SO3

Table 23. Analysis of Original Clay Sample C

	%	%
Ignition loss		7.73
SiO <sub>2</sub>		61.33
R <sub>2</sub> O <sub>3</sub>	25.67	
Al <sub>2</sub> O <sub>3</sub> (by difference)		19.26
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		6.25
MgO		1.66
CaO		0.44
K <sub>2</sub> O		3.11
Na <sub>2</sub> O		0.99
P <sub>2</sub> O <sub>5</sub>		0.16
Total S (as SO <sub>2</sub> )		0.04
	Total	100.97

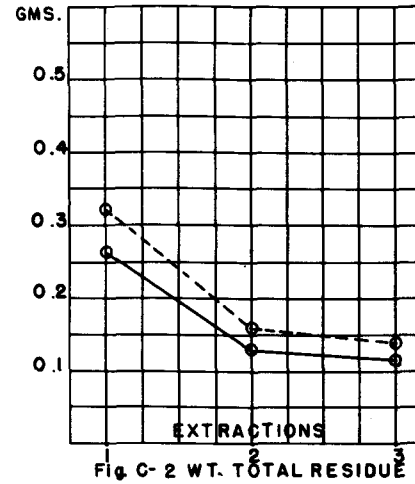
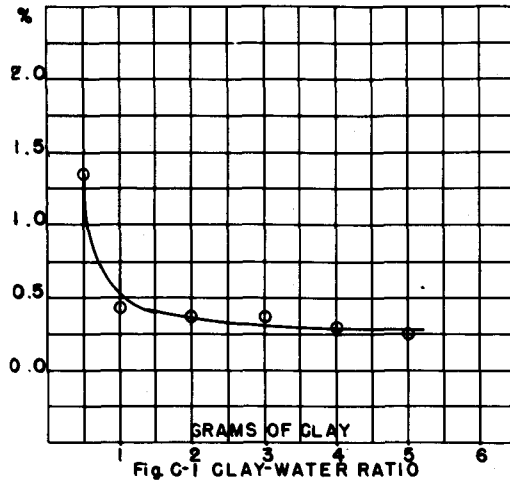
Table 24. Variation in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample C.

Grams of clay	Clay-water ratio	Per cent soluble salts
5.00	1:50	0.25
4.00	1:62.5	0.33
3.00	1:83.3	0.37
2.00	1:125	0.37
1.00	1:250	0.44
0.5	1:500	1.34

Table 25. Analysis of Salt Residues - Sample C

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.2669	.3203	.1753	.1306	.1567	.1395	.1178	.1413
Wt. SiO <sub>2</sub>	.0425	.0510	.0336	.0265	.0318	.0304	.0258	.1310
Mgm. SiO <sub>2</sub> per L.	8.5		6.7			6.1		
% SiO <sub>2</sub> in residue	15.74		19.17			21.79		
Wt. R <sub>2</sub> O <sub>3</sub>	.0045	.0054	.0033	.0026	.0031	.0024	.0023	.0028
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	0.9		0.6			0.5		
% R <sub>2</sub> O <sub>3</sub> in residue	1.66		1.88			1.79		
Wt. CaO	.0620	.0744	.0452	.0326	.0391	.0394	.0331	.0397
Mgm. CaO per L.	12.4		9.0			7.9		
% CaO in residue	22.97		25.79			28.24		
Wt. MgO	.0107	.0128	.0106	.0089	.0107	.0091	.0076	.0091
Mgm. MgO per L.	2.1		2.1			1.8		
% MgO in residue	3.95		6.04			6.52		
Wt. SO <sub>3</sub>	.0304	.0365	.0098	.0047	.0056	.0074	.0067	.0080
Mgm. SO <sub>3</sub> per L.	6.1		2.0			1.5		
% SO <sub>3</sub> in residue	11.26		5.59			5.30		

SAMPLE C



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - - -

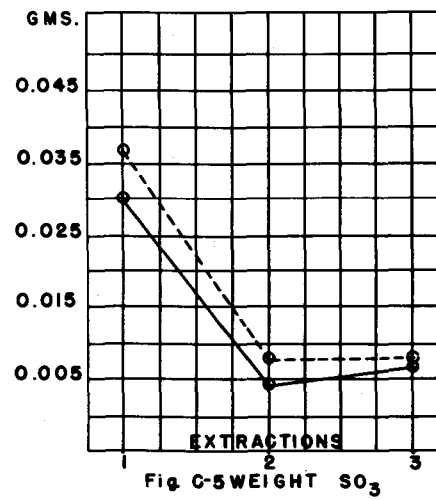
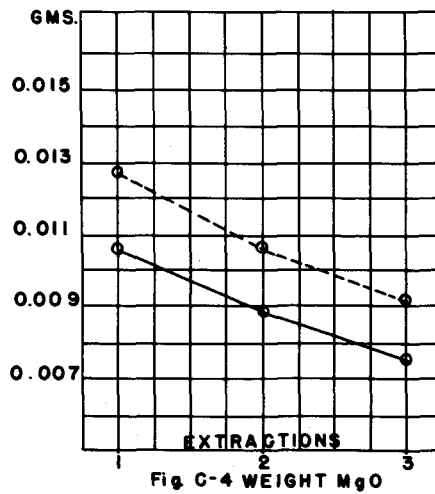
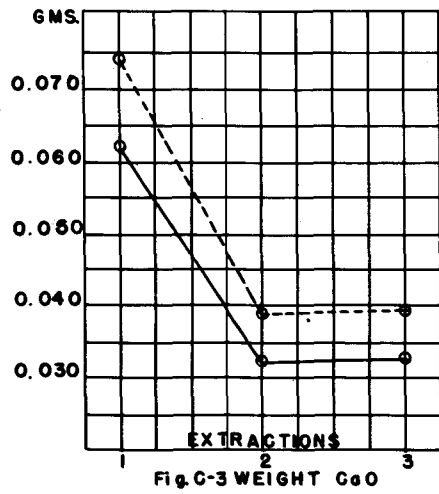


Table 26. Analysis of Original Clay Sample D

	%	%
Ignition loss		9.36
SiO <sub>2</sub>		58.33
R <sub>2</sub> O <sub>3</sub>	28.06	
Al <sub>2</sub> O <sub>3</sub> (by difference)		20.68
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		7.22
MgO		0.66
CaO		0.82
K <sub>2</sub> O		2.13
Na <sub>2</sub> O		0.45
P <sub>2</sub> O <sub>5</sub>		0.41
Total S (as SO <sub>2</sub> )		0.12
	Total	100.18

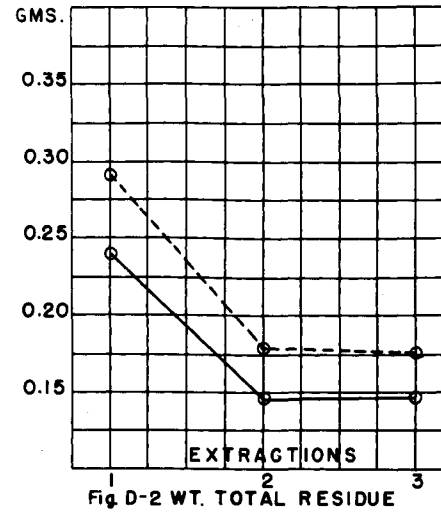
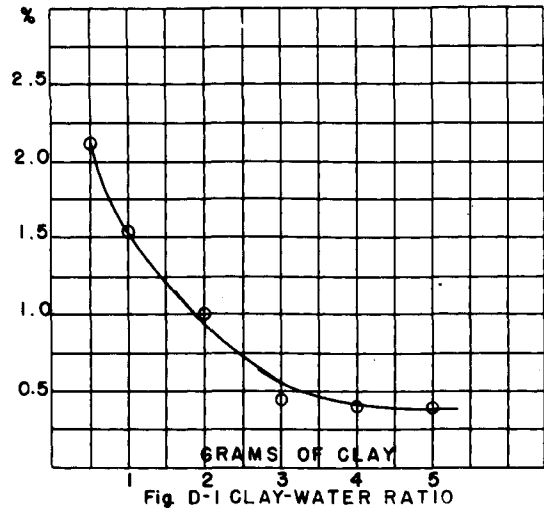
Table 27. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample D.

Grams of clay	Clay-water ratio	Per cent soluble salts
5.00	1:50.5	0.37
4.00	1:62.5	0.45
3.00	1:83.3	0.47
2.00	1:125	1.01
1.00	1:250	1.52
0.50	1:500	2.10

Table 28. Analysis of Salt Residues - Sample D

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.2439	.2927	.1905	.1497	.1796	.1742	.1493	.1792
Wt. SiO <sub>2</sub>	.0414	.0497	.0258	.0189	.0227	.0300	.0269	.0323
Mgm. SiO <sub>2</sub> per L.	8.3		5.1	3.8		6.0	5.4	
% SiO <sub>2</sub> in residue	16.97		13.54			17.22		
Wt. R <sub>2</sub> O <sub>3</sub>	.0045	.0054	.0051	.0043	.0051	.0024	.0017	.0020
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	0.9		1.0	0.9		0.5	0.3	
% R <sub>2</sub> O <sub>3</sub> in residue	1.84		2.67			1.38		
Wt. CaO	.0680	.0816	.0606	.0493	.0591	.0616	.0534	.0641
Mgm. CaO per L.	13.6		12.1	9.9		12.3	10.7	
% CaO in residue	27.88		31.81			35.57		
Wt. MgO	.0084	.0101	.0058	.0044	.0053	.0058	.0051	.0061
Mgm. MgO per L.	1.7		1.2	0.9		1.1	1.0	
% MgO in residue	3.44		3.04			3.32		
Wt. SO <sub>3</sub>	.0208	.0249	.0076	.0042	.0050	.0120	.0113	.0136
Mgm. SO <sub>3</sub> per L.	4.2		1.5	0.8		2.4	2.3	
% SO <sub>3</sub> in residue	8.52		3.98			6.88		

SAMPLE D



Legend:  
 Corrected wt. 5L. ———  
 Calculated to 6L. - - -

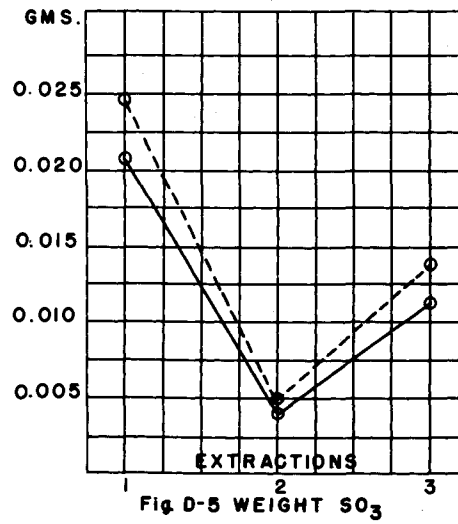
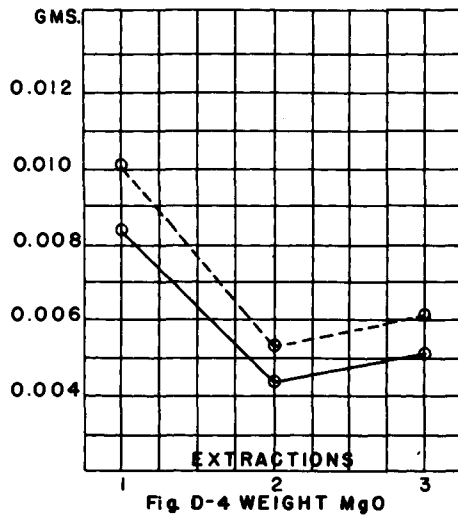
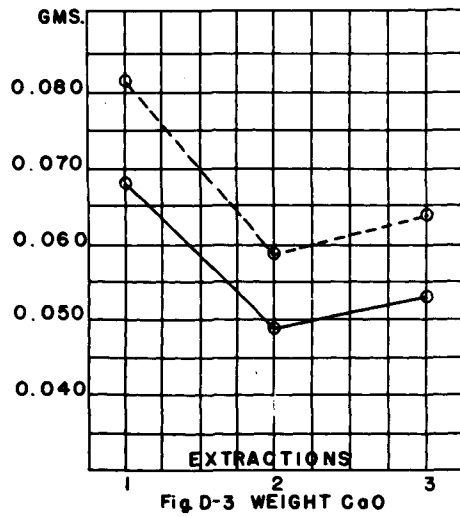




Table 29. Analysis of Original Clay Sample E

	%	%
Ignition loss		8.48
SiO <sub>2</sub>		58.22
R <sub>2</sub> O <sub>3</sub>	26.98	
Al <sub>2</sub> O <sub>3</sub> (by difference)		19.37
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		7.56
MgO		1.42
CaO		0.70
K <sub>2</sub> O		3.17
Na <sub>2</sub> O		0.70
P <sub>2</sub> O <sub>5</sub>		0.05
Total S (as SO <sub>2</sub> )		0.52
	Total	99.99

Table 30. Variation in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample E.

Grams of clay	Clay-water ratio	Per cent soluble salts
5.0	1:50	0.29
4.0	1:62.5	0.32
3.0	1:83.3	0.72
2.0	1:125	0.86
1.0	1:250	0.93
0.5	1:500	2.04

Table 31. Analysis of Salt Residues - Sample E.

	First extraction		Second extraction		Third extraction	
	Wt. from Calc. to 5 L.	Wt. from Calc. to 6 L.	Wt. from Calc. to 5 L.	Wt. from Calc. to 6 L.	Wt. from Calc. to 5 L.	Wt. from Calc. to 6 L.
Total residue	.2299	.2759	.2336	.1953	.1325	.0999
Wt. SiO <sub>2</sub>	.0522	.0626	.0302	.0215	.0280	.0244
Mgm. SiO <sub>2</sub> per L.	10.4	6.0	4.3	5.6	4.9	
% SiO <sub>2</sub> in residue	22.70	12.92		21.13		
Wt. R <sub>2</sub> O <sub>3</sub>	.0045	.0054	.0020	.0013	.0024	.0021
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	0.9	0.4	0.2	0.5	0.4	
% R <sub>2</sub> O <sub>3</sub> in residue	1.96	0.85		1.81		
Wt. CaO	.0480	.0576	.0740	.0660	.0434	.0324
Mgm. CaO per L.	9.6	14.8	13.2	8.7	6.5	
% CaO in residue	20.87	31.68		32.75		
Wt. MgO	.0060	.0072	.0077	.0067	.0064	.0053
Mgm. MgO per L.	1.2	1.5	1.4	1.3	1.1	
% MgO in residue	2.61	3.29		4.82		
Wt. SO <sub>3</sub>	.0141	.0169	.0331	.0308	.0038	
Mgm. SO <sub>3</sub> per L.	2.8	6.6	6.1	0.7		
% SO <sub>3</sub> in residue	6.13	14.17		2.86		

SAMPLE E

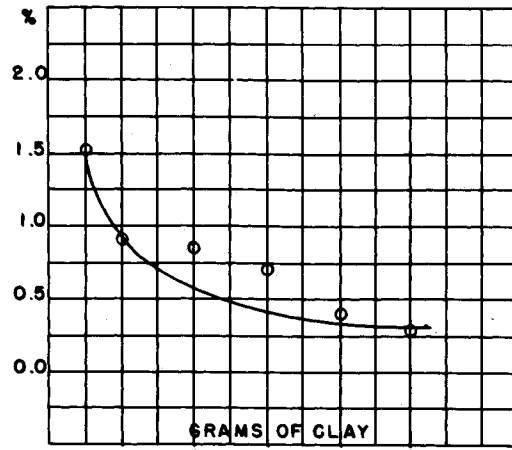


Fig E-1 CLAY-WATER RATIO

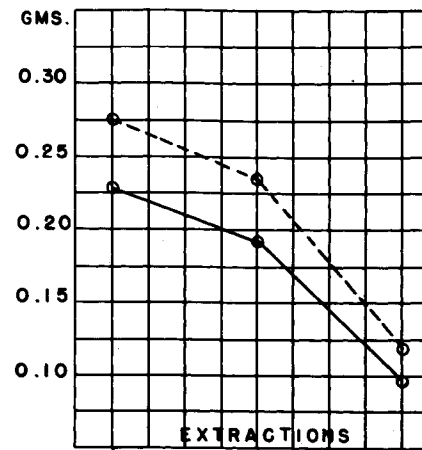


Fig E-2 WT. TOTAL RESIDUE

Legend:  
 Corrected wt. 5L ———  
 Calculated to 6L - - -

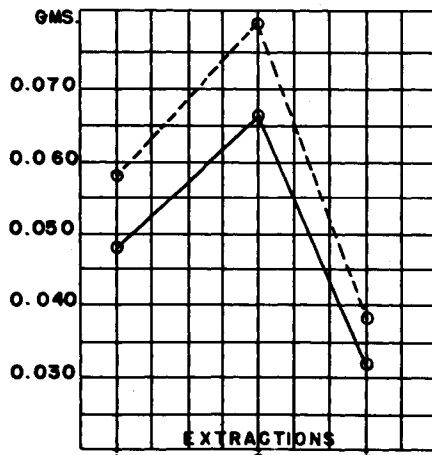


Fig E-3 WEIGHT CoO

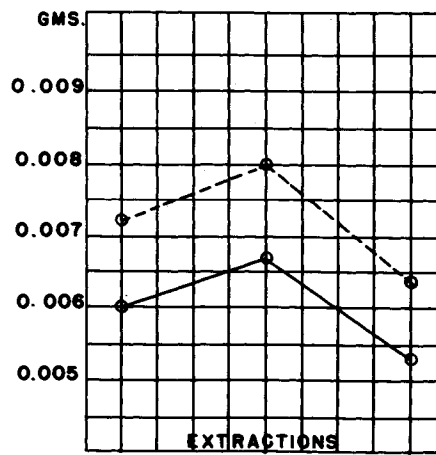


Fig E-4 WEIGHT MgO

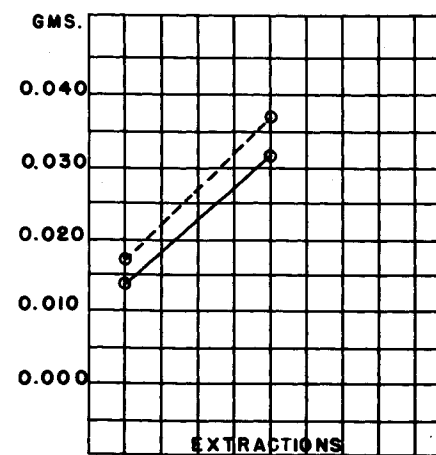


Fig E-5 WEIGHT SO3

Table 32. Analysis of Original Clay Sample F

	%	%
Ignition loss	10.90	
Corrected ignition loss		10.01
SiO <sub>2</sub>		57.42
R <sub>2</sub> O <sub>3</sub>	27.53	
Al <sub>2</sub> O <sub>3</sub> (by difference)		23.12
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )	4.38	
Fe <sub>2</sub> O <sub>3</sub>		3.30
FeO		0.98
MgO		0.69
CaO		0.43
K <sub>2</sub> O		1.85
Na <sub>2</sub> O		0.62
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>3</sub> )	2.31	
Sulfide S		0.88
Soluble sulfate (as SO <sub>3</sub> )		0.11
	Total	99.44

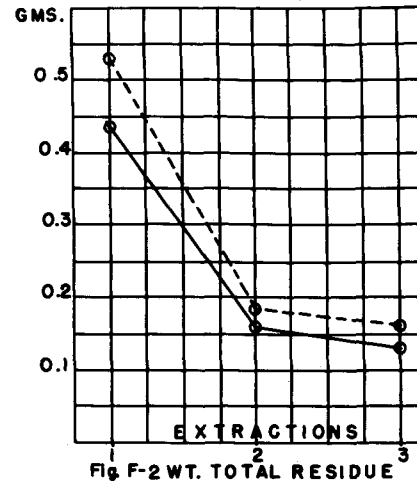
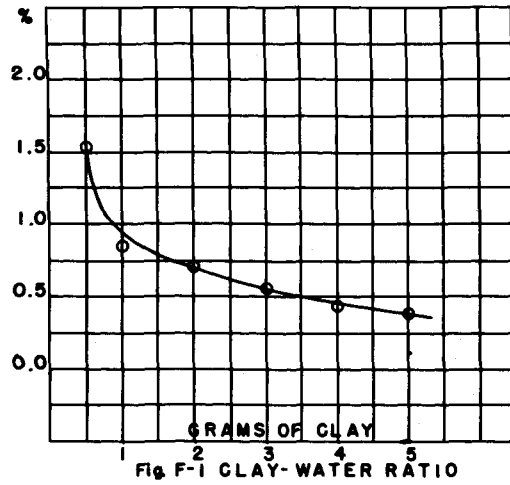
Table 33. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample F.

Grams of clay	Clay-water ratio	Per cent soluble salts
5.0	1:50	0.38
4.0	1:62.5	0.45
3.0	1:83.3	0.54
2.0	1:125	0.73
1.0	1:250	0.85
0.5	1:500	1.52

Table 34. Analysis of Salt Residues - Sample F

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.4423	.5308	.2299	.1562	.1874	.1620	.1360	.1632
Wt. SiO <sub>2</sub>	.0527	.0632	.0294	.0207	.0041	.0120	.0086	.0103
Mgm. SiO <sub>2</sub> per L.	10.5		5.9	4.1		2.4	1.7	
% SiO <sub>2</sub> in residue	11.89		12.78			7.40		
Wt. R <sub>2</sub> O <sub>3</sub>	.0043	.0052	.0050	.0043	.0051	.0051	.0045	.0054
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	0.9		1.0	0.9		1.0	0.9	
% R <sub>2</sub> O <sub>3</sub> in residue	0.97		2.18		3.14			
Wt. CaO	.1250	.1500	.0694	.0486	.0583	.0432	.0351	.0421
Mgm. CaO per L.	25.0		13.9	9.7		8.6	7.0	
% CaO in residue	28.26		30.18			26.66		
Wt. MgO	.0278	.0334	.0161	.0112	.0134	.0126	.0108	.0129
Mgm. MgO per L.	5.6		3.2	2.2		2.5	2.1	
% MgO in residue	6.28		7.00			7.77		
Wt. SO <sub>3</sub>	.1577	.1892	.0776	.0513	.0616	.0580	.0494	.0593
Mgm SO <sub>3</sub> per L.	31.6		15.5	10.2		11.6	9.9	
% SO <sub>3</sub> in residue	35.65		33.75			38.02		

SAMPLE F



Legend:  
 Corrected wt. 5 L —  
 Calculated to 6 L - - -

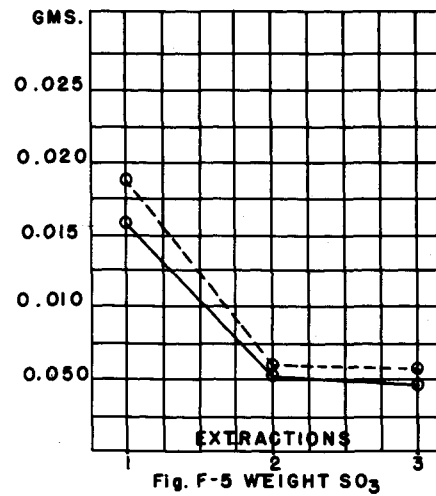
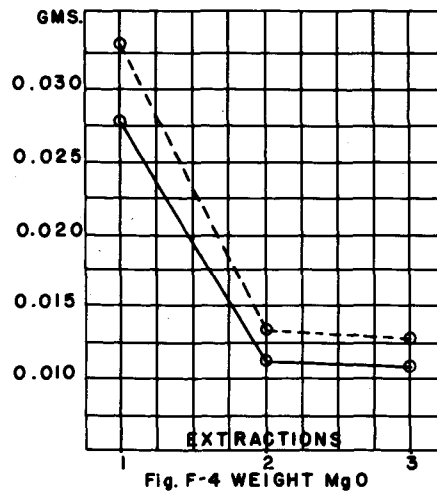
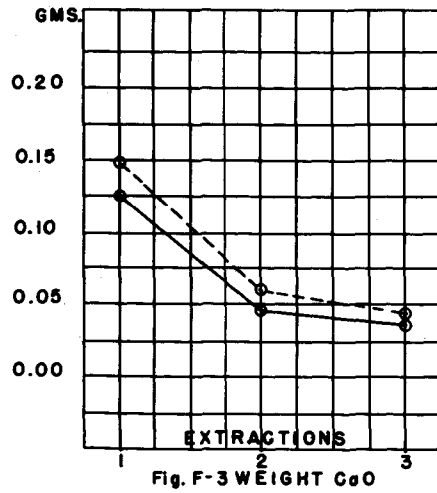


Table 35. Analysis of Original Clay Sample G

	$\frac{1}{2}$	$\frac{1}{2}$
Ignition loss		7.79
SiO <sub>2</sub>		62.91
R <sub>2</sub> O <sub>3</sub>	25.58	
Al <sub>2</sub> O <sub>3</sub> (by difference)		16.88
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		8.67
MgO		0.58
CaO		0.49
K <sub>2</sub> O		1.71
Na <sub>2</sub> O		0.45
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>2</sub> )		0.45
	<b>Total</b>	<b>99.96</b>

Table 36. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample G.

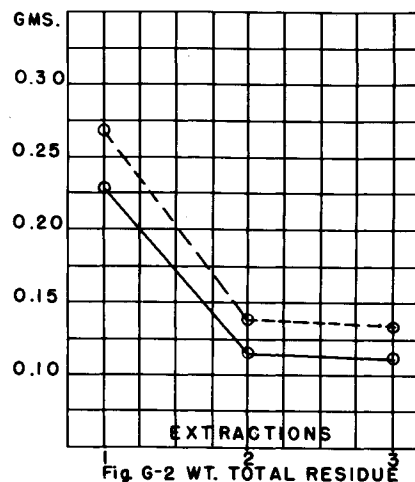
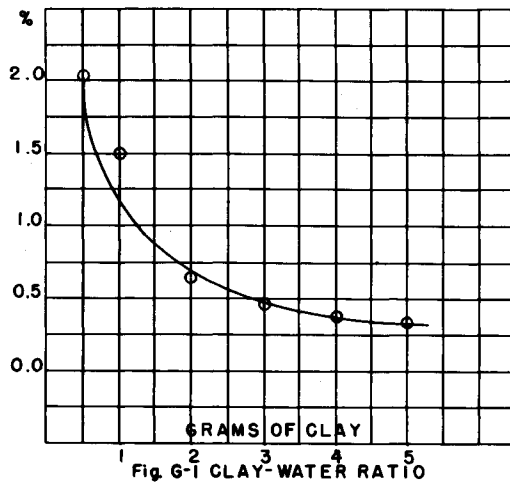
Grams of clay	Clay-water ratio	Per cent soluble salts
5.0	1:50	0.33
4.0	1:62.5	0.38
3.0	1:83.3	0.47
2.0	1:125	0.67
1.0	1:250	1.50
0.5	1:500	2.04

Table 37. Analysis of Salt Residues - Sample G

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.2264	.2717	.1540	.1163	.1396	.1355	.1122	.1346
Wt. SiO <sub>2</sub>	.0480	.0576	.0276	.0196	.0235	.0146	.0113	.0136
Mgm. SiO <sub>2</sub> per L.	9.6		5.5	3.9		2.9	2.3	
% SiO <sub>2</sub> in residue	21.20		17.92			10.77		
Wt. R <sub>2</sub> O <sub>3</sub>	.0135	.0162	.0119	.0096	.0115	.0094	.0078	.0094
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	2.7		2.4	1.9		1.9	1.6	
% R <sub>2</sub> O <sub>3</sub> in residue	5.96		7.72			6.89		
Wt. CaO	.0498	.0598	.0386	.0303	.0363	.0372	.0322	.0386
Mgm. CaO per L.	9.9		7.7	6.1		7.4	6.4	
% CaO in residue	21.99		25.06			27.45		
Wt. MgO	.0064	.0077	.0053	.0042	.0050	.0048	.0041	.0049
Mgm. MgO per L.	1.3		1.1	0.8		0.9	0.8	
% MgO in residue	2.82		3.44			3.54		
Wt. SO <sub>3</sub>	.0935	.1122	.0847	.0691	.0829	.0695	.0580	.0696
Mgm. SO <sub>3</sub> per L.	18.7		16.9	13.8		13.9	11.6	
% SO <sub>3</sub> in residue	41.29		55.00			51.29		



SAMPLE G



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - - -

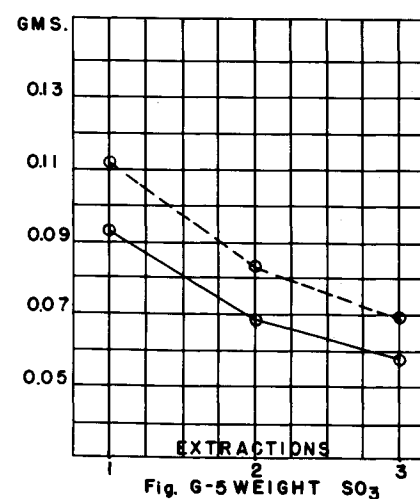
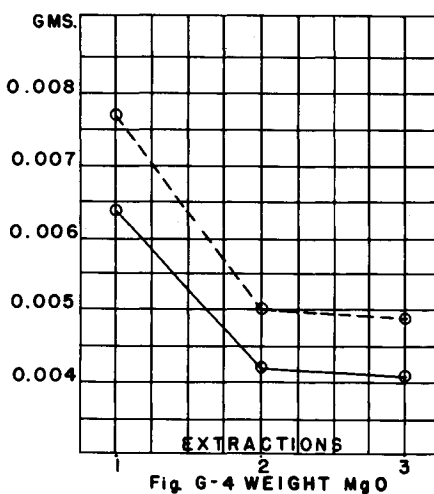
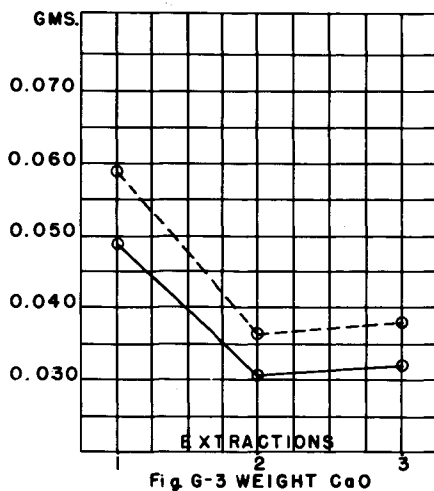


Table 38. Analysis of Original Clay Sample H

	<u>%</u>	<u>%</u>
Ignition loss	18.34	
Corrected ignition loss		14.19
SiO <sub>2</sub>		44.11
R <sub>2</sub> O <sub>3</sub>	34.64	
Al <sub>2</sub> O <sub>3</sub> (by difference)		27.17
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )	7.44	
Fe <sub>2</sub> O <sub>3</sub>		3.91
FeO		3.18
MgO		0.71
CaO		0.38
K <sub>2</sub> O		1.33
Na <sub>2</sub> O		0.34
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>2</sub> )	8.76	
Sulfide S		2.84
Soluble sulfate (as SO <sub>2</sub> )		1.66
	Total	99.85

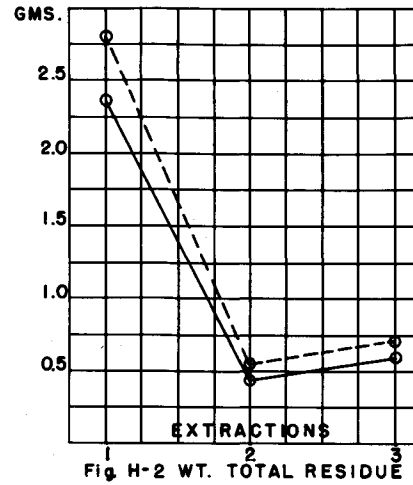
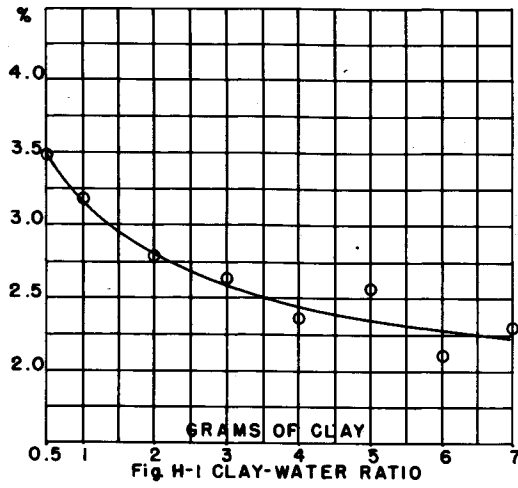
Table 39. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample H.

Grams of clay	Clay-water ratio	Per cent soluble salts
7.0	1:37.5	2.28
6.0	1:41.7	2.11
5.0	1:50	2.57
4.0	1:62.5	2.36
3.0	1:83.3	2.65
2.0	1:125	2.79
1.0	1:250	3.21
0.5	1:500	3.50

Table 40. Analysis of Salt Residues - Sample H

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	2.3357	2.8028	.8438	.4546	.5455	.6753	.5996	.7175
Wt. SiO <sub>2</sub>	.1469	.1763	.0899	.0654	.0785	.0688	.0579	.0695
Mgm. SiO <sub>2</sub> per L.	29.4		18.0	13.1		13.8	11.6	
% SiO <sub>2</sub> in residue	6.28		10.65			10.18		
Wt. R <sub>2</sub> O <sub>3</sub>	.3964	.4754	.1769	.1109	.1331	.1612	.1427	.1712
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	79.3		35.4	22.1		32.2	28.5	
% R <sub>2</sub> O <sub>3</sub> in residue	16.96		20.96			23.87		
Wt. CaO	.2986	.3583	.0614	.0117	.0140	.0326	.0307	.0368
Mgm. CaO per L.	59.7		12.3	2.3		6.5	6.1	
% CaO in residue	12.78		7.27			4.67		
Wt. MgO	.0722	.0866	.0171	.0051	.0061	.0099	.0091	.0109
Mgm. MgO per L.	14.4		3.4	1.0		2.0	1.8	
% MgO in residue	3.09		2.02			1.46		
Wt. SO <sub>3</sub>	.8216	.9859	.3761	.2392	.2870	.2958	.2560	.3072
Mgm. SO <sub>3</sub> per L.	164.3		75.2	47.8		59.1	51.2	
% SO <sub>3</sub> in residue	35.17		44.57			43.78		

SAMPLE H



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - -

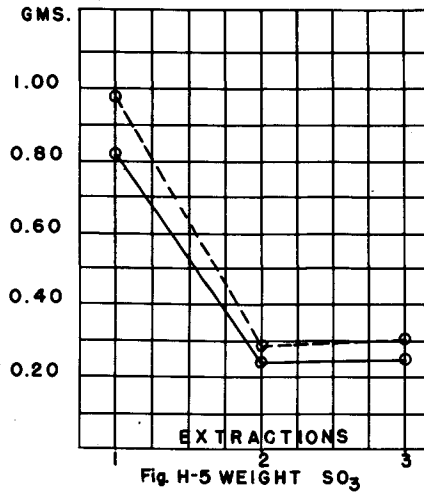
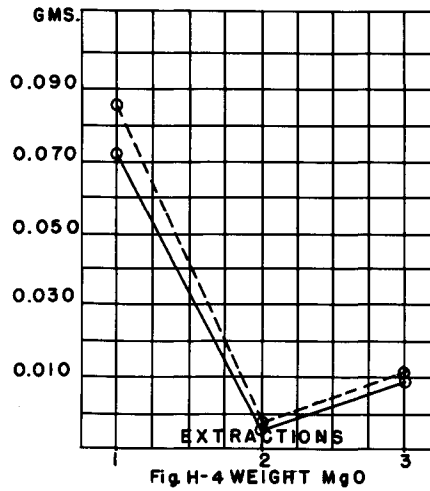
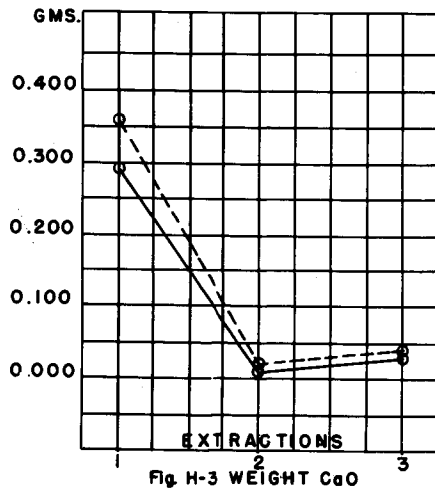


Table 41. Analysis of Original Clay Sample I

	%	%
Ignition loss		9.41
SiO <sub>2</sub>		54.79
R <sub>2</sub> O <sub>3</sub>	29.02	
Al <sub>2</sub> O <sub>3</sub> (by difference)		20.58
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		8.41
MgO		2.30
CaO		0.84
K <sub>2</sub> O		3.36
Na <sub>2</sub> O		0.48
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>2</sub> )		0.01
	Total	100.21

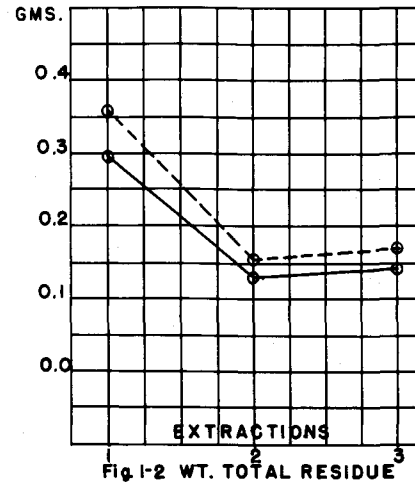
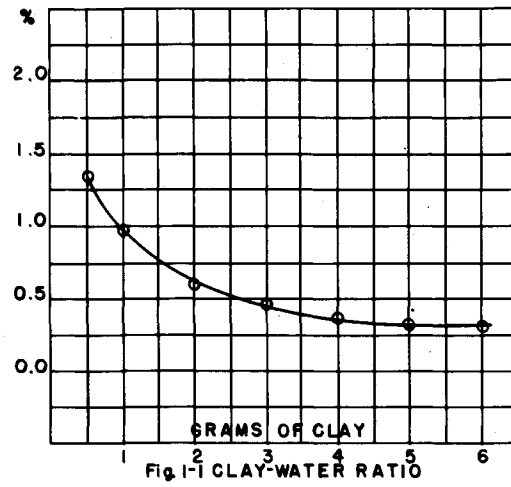
Table 42. Variation in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample I

Grams of clay	Clay-water ratio	Per cent soluble salts
6.0	1:41.7	0.29
5.0	1:50	0.32
4.0	1:62.5	0.38
3.0	1:83.3	0.48
2.0	1:125	0.57
1.0	1:250	0.99
0.5	1:500	1.32

Table 43. Analysis of Salt Residues - Sample I

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.2994	.3593	.1786	.1287	.1544	.1646	.1432	.1718
Wt. SiO <sub>2</sub>	.0730	.0876	.0401	.0279	.0335	.0335	.0288	.0346
Mgm. SiO <sub>2</sub> per L.	14.6		8.0	5.6		6.7	5.7	
% SiO <sub>2</sub> in residue	24.38		22.45			20.35		
Wt. R <sub>2</sub> O <sub>3</sub>	.0039	.0047	.0031	.0024	.0029	.0019	.0015	.0018
Mgm. R <sub>2</sub> O <sub>3</sub> per L.	0.8		0.6	0.5		0.4	0.3	
% R <sub>2</sub> O <sub>3</sub> in residue	1.30		1.73			1.15		
Wt. CaO	.0328	.0394	.0376	.0321	.0385	.0486	.0433	.0519
Mgm. CaO per L.	6.6		7.5	6.4		8.7	8.7	
% CaO in residue	10.95		21.05			29.52		
Wt. MgO	.0077	.0092	.0133	.0120	.0144	.0165	.0145	.0174
Mgm. MgO per L.	1.5		2.7	2.4		5.5	2.9	
% MgO in residue	2.56		7.45			10.02		
Wt. SO <sub>3</sub>	.0226	.0271	.0053	.0016	.0019	.0086	.0083	.0099
Mgm. SO <sub>3</sub> per L.	4.5		1.1	0.3		1.7	1.6	
% SO <sub>3</sub> in residue	7.54		2.97			5.22		

SAMPLE I



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - -

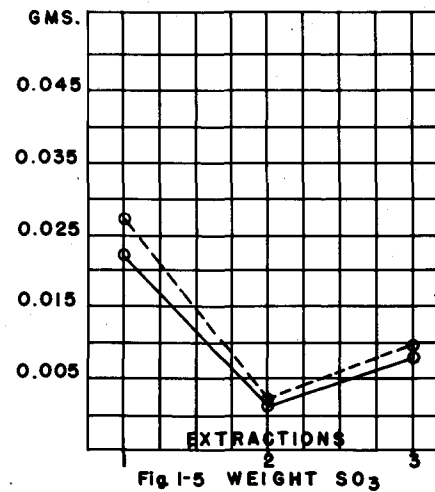
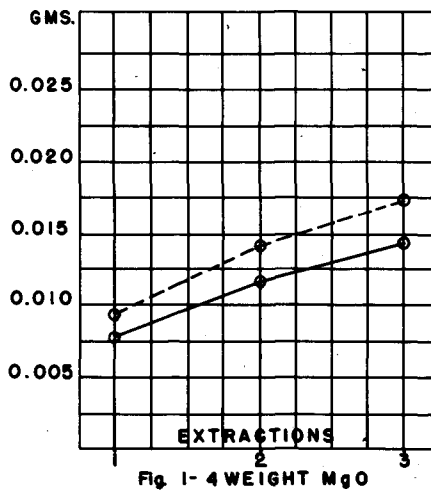
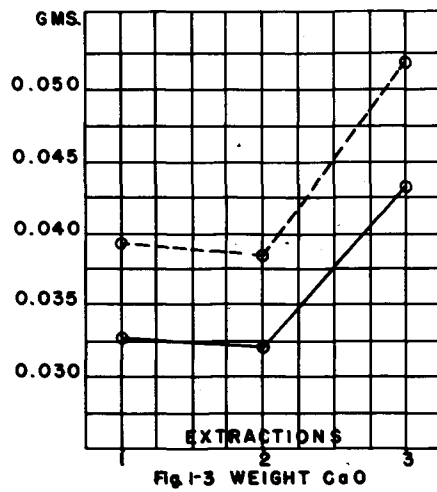


Table 44. Analysis of Original Clay Sample J

	%	%
Ignition loss		27.92
SiO <sub>2</sub>		31.24
R <sub>2</sub> O <sub>3</sub>	12.71	
Al <sub>2</sub> O <sub>3</sub> (by difference)		9.21
Total Fe (as Fe <sub>2</sub> O <sub>3</sub> )		3.47
MgO		9.18
CaO		16.61
K <sub>2</sub> O		2.02
Na <sub>2</sub> O		0.34
P <sub>2</sub> O <sub>5</sub>		0.03
Total S (as SO <sub>2</sub> )		0.03
	Total	100.05

Table 45. Variations in the per cent of soluble salts produced by varying the clay-water ratio. Each sample treated with 250 ml. of distilled water - Sample J.

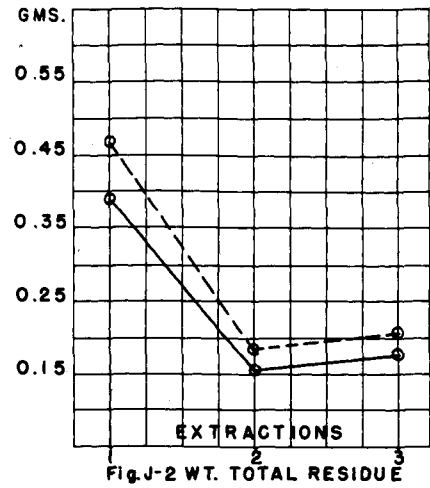
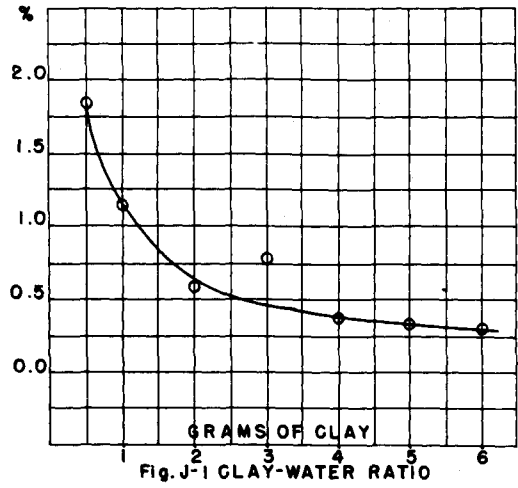
Grams of clay	Clay-water ratio	Per cent soluble salts
6.0	1:41.7	0.29
5.0	1:50	0.32
4.0	1:62.5	0.38
3.0	1:83.3	0.76
2.0	1:125	0.56
1.0	1:250	1.17
0.5	1:500	1.84



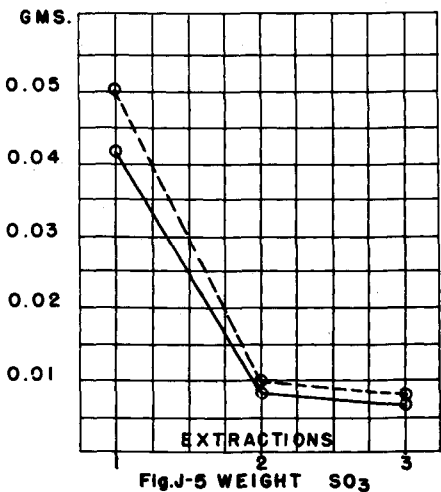
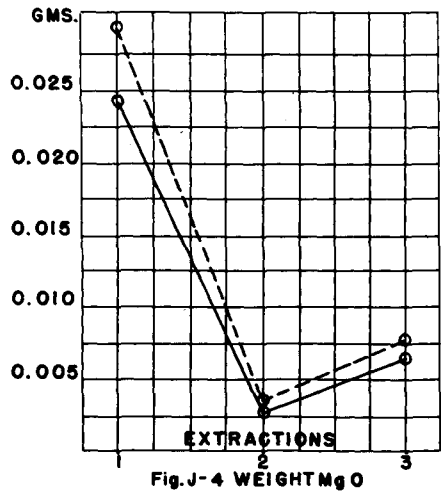
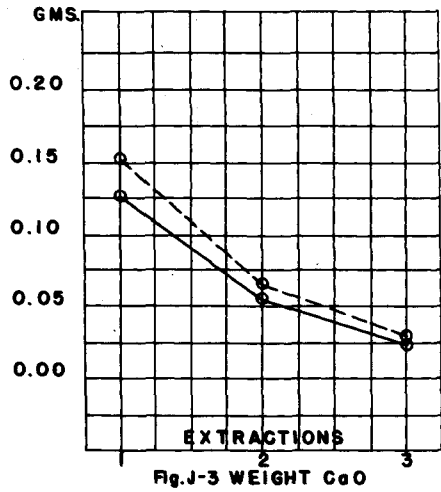
Table 46. Analysis of Salt Residues - Sample J

	First extraction		Second extraction		Third extraction			
	Wt. from 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.	Wt. from 5 L.	Corrected wt. 5 L.	Calc. to 6 L.
Total residue	.3902	.4682	.2198	.1548	.1858	.1986	.1727	.2072
Wt. SiO <sub>2</sub>	.9585	.0702	.0282	.0184	.0221	.0395	.0364	.0437
Mgn. SiO <sub>2</sub> per L.	11.7		5.6	3.7		7.9	7.3	
% SiO <sub>2</sub> in residue	14.99		12.82			19.88		
Wt. R <sub>2</sub> O <sub>3</sub>	.0018	.0022	.0036	.0033	.0040	.0031	.0025	.0030
Mgn. R <sub>2</sub> O <sub>3</sub> per L.	0.4		0.7	0.7		0.6	0.5	
% R <sub>2</sub> O <sub>3</sub> in residue	0.46		1.63			1.56		
Wt. CaO	.1268	.1522	.0760	.0548	.0658	.0336	.0244	.0293
Mgn. CaO per L.	25.4		15.2	11.0		6.7	4.9	
% CaO in residue	32.49		34.57			16.91		
Wt. MgO	.0243	.0292	.0069	.0028	.0034	.0071	.0066	.0079
Mgn. MgO per L.	4.9		1.4	0.5		1.4	1.3	
% MgO in residue	6.22		3.14			3.57		
Wt. SO <sub>3</sub>	.0418	.0502	.0153	.0083	.0100	.0083	.0069	.0083
Mgn. SO <sub>3</sub> per L.	8.4		3.1	1.7		1.7	1.4	
% SO <sub>3</sub> in residue	10.71		6.96			4.17		

SAMPLE J



Legend:  
 Corrected wt. 5 L ———  
 Calculated to 6 L - - - -



## XV. CONCLUSIONS

Of the several factors which influence the formation of efflorescence or scum on burned wares, the presence of soluble salts is of greatest importance. Without sufficient soluble salts in the ware, efflorescence will not form. The chemical composition of the soluble salt fraction of raw clays and burned wares as well as the composition of the effloresced salts from the surfaces of walls, have been found to vary over wide limits. The examination of a large number of clays and samples of effloresced salts have led the majority of writers on the subject of efflorescence to conclude that sulfur in the form of pyrite or sulfates in the raw clay is the most common cause of efflorescence.

All of the Iowa ceramic clays examined in this work contained sulfur, the per cents varying between 0.01 per cent and 8.76 per cent as  $SO_2$ . When these clays were extracted with boiling water and the resulting solution evaporated to dryness, it was found that there was considerable variation in the amounts of residues obtained. It was also found that there was little relationship between the chemical composition of the soluble salt residues and the chemical composition of the original clays.

The following table arranged in the order of increasing per cents of  $SO_2$  in the raw clays, shows the comparison of

the sulfur contents of the clays and the soluble salts extracted from them. The values for the per cent of SO<sub>2</sub> in the residues were obtained from the first extraction of the clays with 5 liter portions of distilled water.

Table 47. Per Cents of Sulfur in Original Clays and Their Soluble Salt Residues

Sample	SO <sub>2</sub> in clay %	SO <sub>2</sub> in residue %
I	0.01	7.54
J	0.03	10.71
C	0.04	11.26
B	0.06	4.99
D	0.12	8.52
E	0.32	6.13
G	0.45	41.29
A	1.27	39.54
F	2.31	35.65
H	8.76	35.17

The amounts of sulfur found in both the original clays and their soluble salt fractions would indicate that there is sufficient sulfur present to cause efflorescence on wares made from these clays. This is contrary to the opinion of Beyer (43, p. 341) that efflorescence of Iowa clay wares is caused by the introduction of sulfur into the ware from the fuel.

According to the majority of writers, the magnesium content of a clay ranks second in importance to sulfur as a cause of efflorescence. Butterworth (274, p. 273) believes that the magnesium content should not be over 0.05 per cent (0.08 per

cent MgO) or serious damage will occur. All of the Iowa clays examined contained considerably more than this amount. As in the case of sulfur, there was no relationship between the amounts of magnesium found in the original clays and the soluble salt residues.

Table 48. Per Cents of Magnesium in Original Clays and Their Soluble Salt Residues

Sample	MgO in clay %	MgO in residue %
G	0.58	2.82
D	0.66	3.44
F	0.69	6.28
H	0.71	3.09
B	1.41	2.69
E	1.42	2.61
C	1.66	3.95
I	2.30	2.56
A	4.53	5.45
J	9.18	6.22

Although calcium is not considered to be as important as magnesium in the formation of efflorescence, the analyses of the soluble salt residues indicate that it is one of the more abundant constituents in these residues. There was no relationship between the amounts of calcium found in the raw clays and the amounts in the soluble salt residues.

Although the silica and  $R_2O_3$  content of soluble salt residues are of minor importance from the viewpoint of scum formation, the amounts of these constituents found in the soluble fractions of the Iowa clays examined indicate that

Table 49. Per Cents of Calcium in Original Clays and Their Soluble Salt Residues

Sample	CaO in clay %	CaO in residue %
H	0.38	12.78
F	0.43	28.26
C	0.44	22.97
G	0.49	21.99
E	0.70	20.87
D	0.82	27.88
I	0.84	10.95
B	1.20	26.04
A	7.01	29.78
J	16.61	32.49

they should be taken into account when drying or igniting the residues. The maximum weight of  $\text{SiO}_2$  was obtained from the first extraction of sample H (0.1469 gm.) which on the per cent basis corresponds to approximately 6.82 per cent of the total residue. The first extraction of sample I gave 0.0730 gm. but because of the relatively small amount of total residue obtained in this extraction, the per cent of  $\text{SiO}_2$  amounted to 24.39 per cent of the total residue.

With the exception of the residue from the first extraction of sample H which contained 0.3964 gm. of  $\text{R}_2\text{O}_3$ , the majority of the residues contained from 0.0018 to 0.0135 gm. of  $\text{R}_2\text{O}_3$ .

When determining the per cent of soluble salts in a clay by extraction methods, it has been shown that the amount of soluble material extracted will depend upon the volume of water

used with a given sample of clay. The amount of  $R_2O_3$  in the residues shows the least variation when the clay samples are extracted with successive portions of water while the amounts of  $CaO$ ,  $MgO$  and  $SO_2$  are found to vary over wider limits.

Although chlorides, nitrates and carbonates have been reported in the soluble salt residues, sulfates are the most common acid ions and for this reason, sulfate may be considered as the principal "carrier" for calcium, magnesium, iron, aluminum and other metals.

In determining the per cent of soluble salts in a clay, it is believed that the value obtained should include all of the soluble sulfate in the clay sample plus the equivalent amounts of the various metals. In addition to these values, the per cent soluble salts will include a certain amount of silicates which are invariably present. In order to obtain such a value, a clay-water ratio should be used which will extract all of the soluble sulfate. The total residue extracted by this amount of water would then represent the soluble fraction of the clay based on the soluble sulfate content.

Such a determination involves a separate determination of the per cent of soluble sulfate. It also involves the determination of the amount of total residue obtained by several clay-water ratios. The clay-water ratio which will extract the total of the soluble sulfates may then be calculated from this data.

Shell and Cortelyou (284, p. 180) have published data showing the per cent of  $SO_2$  extracted in a slip by varying the concentration of dry clay from 0 to 1000 grams in 1000 ml. of water. Their data indicate that within certain ranges of concentration of the clay-water suspensions, the amount of soluble sulfate extracted is proportional to the clay-water ratio.

In calculating the per cent of soluble salts in the clays used in the following illustrations, it was assumed that the weight of soluble sulfate extracted was proportional to the clay-water ratio. It was also assumed that the weight of total residue extracted was proportional to the clay-water ratio. The accuracy of these assumptions will increase as more extractions of the clay sample are made.

In the following tables, three illustrations are given showing the application of this method of calculating the per cent of soluble salts. The clays used in these illustrations showed considerable variation in soluble sulfate content.

Table 50. Sulfur Content of Original Clay - Sample A

	%	Gms. in 125 gms. of clay
Total sulfur as $SO_2$	1.27	1.5875
Sulfide sulfur	0.42	0.5250
Soluble sulfate as $SO_2$	0.24	0.3000



Table 50 (cont'd). Sulfur Content of Original Clay - Sample A

Clay-water ratio	Gms. SO <sub>2</sub> extracted
1:140	0.2926
1:80	0.3052
1:120	0.3314

Calculated Values

Clay-water ratio to extract 0.3000 gm. soluble SO<sub>2</sub> = 1:78.6

Weight of total residue extracted by above clay-water ratio = 0.7268

(calculated from a total residue of 0.7398 gm. extracted with a clay-water ratio of 1:80)

Per cent of soluble salts on the basis of 125 gram of clay and 0.7268 gm. of total residue = 0.58%.

Table 51. Sulfur Content of Original Clay - Sample F

	%	Gms. in 125 gms. of clay
Total sulfur as SO <sub>2</sub>	2.31	2.8875
Sulfide sulfur	0.88	1.1000
Soluble sulfate as SO <sub>2</sub>	0.11	0.1375

Clay-water ratio	Gms. SO <sub>2</sub> extracted
1:40	0.1892
1:80	0.2508
1:120	0.3101

Calculated Values

Clay-water ratio to extract 0.1375 gm. soluble SO<sub>2</sub> = 1:29

Weight of total residue extracted by above clay-water

ratio = 0.3848

(calculated from a total residue of 0.5308 gm.

extracted with a clay-water ratio of 1:40)

Per cent of soluble salts on the basis of 125 gms. of clay and

0.3848 gm. of total residue = 0.307%

Table 52. Sulfur Content of Original Clay - Sample H

	%	Gms. in 125 gms. of clay
Total sulfur as SO <sub>2</sub>	8.76	10.9500
Sulfide sulfur	2.84	3.5500
Soluble sulfate as SO <sub>2</sub>	1.66	2.0750

Clay-water ratio	Gms. SO <sub>2</sub> extracted
1:40	0.9859
1:80	1.2729
1:120	1.5801

Calculated Values

Clay-water ratio to extract 2.0750 gm. soluble SO<sub>2</sub> = 1:157.6

Weight of total residue extracted by above clay-water

ratio = 2.0752

Per cent of soluble salts on the basis of 125 gms. of clay and

2.0752 g. of total residue = 1.66%

The above calculated values for the per cent of soluble salts in these clays are somewhat lower than those obtained by Mellor's method:

Table 53. Comparison of Soluble Salt Values Obtained by Mellor's Single Extraction Method and by Calculation Based upon Soluble Sulfate Content

Sample	Soluble salts Mellor's method $\frac{\%}{2}$	Soluble salts above method $\frac{\%}{2}$
A	0.60	0.58
F	0.38	0.307
H	2.57	1.66

The above method of calculating the per cent of soluble salts in clays eliminates the uncertainty of the correct clay-water ratio to be used in the extraction of each clay. It is evident that no single clay-water ratio will be suitable for all clays. The method is based upon the per cent of soluble sulfate as this is a constant value for each clay.

When the residues from the successive extractions of 125 gram samples of clay were weighed, it was noticed that in most cases the second residue weighed less than the first while the third residue was heavier than the second. This same variation was also found in the weights of CaO, MgO and SO<sub>2</sub> in these residues.

The variation in the weights of these residues would be expected to show a gradual decrease from the second to the third, as well as from the first to the second.

The reason for this apparent abnormal variation is not known. The following explanation is suggested and is being

investigated by further experimental work.

After each 5 liter portion of solution had been siphoned from the clay samples, the flask containing the clay and the remaining 1 liter of solution was stoppered and left in this condition until the extraction solution had been filtered and evaporated. During this period, the wet clay samples were left exposed to approximately 5 liters of air in the flasks.

Under the above conditions, the pyrite or marcasite present in the clay would become oxidized forming sulfates. The amount of sulfates formed would depend upon the length of time the wet clay remained in contact with the air.

Although a record was not kept of the length of time the wet clay remained in contact with the air in the flasks, it is believed that this period was longer between the siphoning of the third extraction than that of the second extraction. This would account for an increase in weight of the residues from the third extraction over that of the second extraction.

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