PRODUCTION OF PURE TITANIUM OXIDE FROM ILMENITE

THE PRODUCTION of PURE TITANIUM OXIDE from ILMENITE.

Thesis submitted
by
C.R.Whittemore

In part requirement for the degree of Master of Science.

May 15th. 1924.

McGill University Montreal,Canada .

CONTENTS.

Part One.

Introduction.

Occurrence of titanium and the utilization of its oxide.

Physical and chemical properties of titanium oxide.

Resumé of the principal patented processes.

Part Two.

A study of the Mineralogical character of Ilmenite.

Theoretical considerations of reduction, leaching and electrolytic recovery of iron from ferrous chloride and ferrous sulphate solutions.

Part Three.

Experimental research.

General conclusions.

Part Four.

References.

Bibliography.

Sample calculations.

Part One.

INTRODUCTION.

Since[1] the discovery of titanium in 1791 the attention of the chemists and metallurgists has been directed towards the utilization of the metal and its compounds.

So far, although the metal has been little employed commercially, the use of alloys and compounds of titanium, as articles of commerce, has increased markedly in recent years. Even yet the amounts so used are comparatively small, and the use of titanium as an alloy or compound is confined to a few highly specialized lines of industry.

The advances in modern industrial chemistry and metallurgy have removed some of the economic handicaps under which the preparation of the compounds and alloys of titanium formerly laboured.

While the metal can be reduced from its ores only with great difficulty on account of the stability of its oxide, the advent of the electric furnace has made it possible to reduce the ores of titanium to a ferro-titanium alloy, which is used extensively in the purification of steel.

Titanium compounds have also found important application in the textile and leather industries for dyeing and bleaching; in the ceramic industries for making vitrified enamels; and in the manufacture of electrodes for electric arc lamps.

[*] The numbers in red refer to the references given in the appendix.

Researches during the past fifteen years by Norwegian and American chemists have shown that titanium oxide has remarkable properties as an opaque white pigment, and the more recent commercial development in Norway and the United States has been the result of this discovery.

The ores of titanium occur in massive formations of enormous size and also as sand deposits from which the most important titanium minerals, ilmenite and rutile, can be obtained by concentration.

In Canada ilmenite, or titanic iron, carrying 20 to 35 percent titanium oxide, occurs in two localities in Quebec, namely, at St. Urbain in Charlevoix county and at Ivry in Terrebonne county. Deposits of titanium minerals are also found in the province of Ontario.

The deposits in Quebec compare favourably as regards size, grade, and accessibility, with those of any other country. Conditions in Quebec appear to be eminently favourable to the establishment of a successful titanium industry but so far little notice has been taken of the possibilities by Canadian scientists and industrialists.

The recent introduction upon the market of titanium oxide, possessing very desirable properties as a white pigment, has caused the writer to investigate processes for the extraction of the titanium oxide from ilmenite ore, aiming so to cheapen the method of manufacture that the application of these properties may not be restricted to the present very limited field.

OCCURRENCE of TITANIUM and the UTILIZATION of its OXIDE.

In 1791[2] the Rev. William Gregor, a clergyman, published an analysis of a black sand found near the village of Menaccan in Cornwall. Approximately half of its weight consisted of a metallic oxide unknown to science. Almost simultaneously, Klaproth announced his discovery of a new element in a red schorl from Hungary and recognized it as identical with the substance isolated by Gregor. To this substance he gave the name titanium (from Titans, the first sons of the earth).

In 1824 Berzelius prepared the metal itself and showed it to be a dark grey substance somewhat resembling iron in appearance but different in properties and very infusible.

It is popularly classed as one of the rare elements but it is one of the ten most common elements in the earth's crust, titanium oxide making up 0.73 percent of the whole lithosphere. It is twice as adundant as carbon and exceeds chlorine, phosphorus and sulphur in abundance. The metal is never found in nature. As an oxide it is present in small amounts in almost all rocks. F.W. Clarke[3] says that out of 800 igneous rocks analyzed at the U.S. Geological Survey laboratory, 784 contained the element titanium. It forms the principal constitu ent of several minerals, such as rutile, anatase and brookite. It occurs most commonly with the oxide of iron as ilmenite ($FeTiO_3$).

The pure titanium oxide was not prepared until it was successfully purified by Rose in 1821.

According to Washburn[5] the first use of titanium oxide as a pigment seems to have been made by Dr. John Overton, of Louisville, U.S.A., about the year 1870. He describes a process for the manufacture of titanium paint as follows:- The rutile was pulverized, mixed with coal tar or other bituminous materials or compounds and used as a paint for ships bottoms. It was not affected by salt water or the heat of the sun. As was to be expected, the pigment did not prove satisfactory.

The fact that titanium oxide could be obtained as a white powder, possessing a high opacity which should render it a suitable pigment, has long been known but has only recently been exploited.

About twelve years ago the industrial production of TiO_2 was investigated in Norway and the United States. These researches were carried out almost simultaneously but independently of one another.

In the United States L. E. Barton and A. Rossi some nine years ago produced a pigment by extracting TiO_2 from ilmenite and combining it with calcium sulphate. Meanwhile, in Norway, Dr. Jebsen and Farup had been perfecting a process for the extraction of TiO_2 from ilmenite in order to utilize the ore as a source of iron, but they were unsuccessful, and started investigations with a view to utilizing the TiO_2 as a pigment. After six years of research a satisfactory process was finally elaborated and in 1914 a plant was established. After considerable modification in the process this plant, on an industrial scale, is now operating successfully, as is also a plant in the United States owned by the Titanium Pigment Co., Niagara Falls, New York.

PHYSICAL and CHEMICAL PROPERTIES of TITANIUM OXIDE.

Physical properties.[5] If the titanium oxide which is extracted from the ore ,is merely dried,an amorphous product is obtained.This cannot be used as a pigment as its opacity is not fully developed,and being a hydrate it is not perfectly stable in the presence of linseed oil.In order to develop a suitable physical condition,the oxide is calcined at a high temperature to convert it from the amorphous to the cryptocrystalline state.It is then finely pulverized.

The calcination is of great importance as the essential point is to change the internal structure of the particles without altering the size and shape in which they are precipitated. It was found difficult to control the reaction if pure TiO_2 was employed but by precipitating TiO_2 and barium sulphate together a physical combination of the two is formed which is more easily controlled on calcination.

The pigment is produced in two strengths,one containing 25 percent TiO_2 and 75 percent $BaSO_4$ and known as Titanox or Standard titanium white,the other containing a lower proportion of $BaSO_4$ and known as Extra-titanium white. The pigment has an opacity greater than any other known white pigment.

The opacity of a pigment is difficult to express but an instrument has been devised by Dr. Pfund,whereby the thickness of the paint film is measured,the opacities of the principal white pigments may be expressed as the relative weights required to produce equal obliteration of surface.

The following table gives the relative opacities of different pigments.

Extra-titanium white	130
Standard titanium white	100
Zinc oxide	70
Lithopone	65
White lead	65
Basic sulphate of lead	35

The opacity of any paint depends on the extent to which the light falling on it is reflected by the particles of the pigment. This is influenced by two things,namely,the size of the particle,and its refractive index. The smaller the size of the particles the more surfaces are presented for reflecting the light. This alone would be of little service unless each of the individual surfaces has a pronounced power of reflection,and the extent to which this is possessed depends particularly on the refractive power of the particle. The amount of light reflected by each particle depends upon the difference between the index of refraction of the particle and the index of refraction of the vehicle or medium in which the particle is suspended.The greater these differences become,the greater is the amount of light reflected on its passage through a separation surface,and the greater will be the opacity of the pigment. If the refractive index of linseed oil be taken as unity ,then that of zinc oxide is 1.34,of white lead 1.36, of amorphous TiO_2 1.48, and of crystalline TiO_2 1.8 . It is this high opacity of titanium oxide which is one of its most valuable properties and which gives it preeminence for special purposes.

The specific gravity is very low as shown by the following table.

Extra-titanium white	4.0
Barium sulphate	4.2
Standard titanium white	4.3
Lithopone	4.3
Zinc oxide	5.66
White lead	6.81

Chemical properties. As[6] would be expected from its composition titanium white is chemically stable and highly resistant to both acids and alkalies. Also it is not liable to discoloration by hydrogen sulphide as titanium does not readily form a colored sulphide. These properties render titanium oxide of value as a pigment, particularly for the preparation of protective paints. Being a fully oxidized substance it is not attacked by sea air or salt water. It is unaffected by the action of sunlight or gases and is inert toward other pigments, tinting materials and vehicles. This inertness is due to the fact that TiO_2 is quite neutral in character and for this reason is slow drying. Standard titanium white dries to an elastic film which is slightly too soft to resist the accumulation of dust particles. This condition is corrected by the addition of zinc oxide to the pigment formulae, thus hardening the film, and preventing discoloration from the accumulation of dust.

Titanium pigments may therefore be used with any of the grinding liquids, varnishes and oils without danger of chemical reactions which may result in hardening, cracking or granulation.

More important from the practical and economic point of view is the fact that on account of its chemical stability it is not readily absorbed into the system if accidently inhaled or otherwise taken into the body by the painter in the course of his work. It may be considered non-poisonous and harmless in use.

RESUMÉ of the PRINCIPAL PATENTS.[7]

The principal methods of ore treatment mentioned in various patents are as follows:-

1. Titaniferous ore is decomposed by sulphuric acid or potassium bisulphate and is then fused in the presence of a halogen salt at a temperature between 300°C.and 390°C. The titanium oxygen compounds are then recovered from the sintered mass.(U.S.Patent 14,289 and 1,348,843.)

2. Titaniferous ore and a reducing material are heated together in an atmosphere of nitrogen to form a titanium - nitrogen compound. The iron is reduced to the metallic state and dissolved in concentrated sulphuric acid.(U.S.Patent 1.343,441).

3. A charge consisting of titaniferous ore,carbon and the sulphate of a metal which is to accompany the titanium in the pigment,is smelted in a blast furnace. The resulting sulphide melt is dissolved in acid and the titanic oxide and accompanying metal precipitated. (U.S.Patent 1,396,924).

4. Finely ground titaniferous ore is heated with concentrated sulphuric acid under a pressure substantially above atmospheric pressure.(U.S.Patent 1,429,841).

The various methods for the production of pure titanic or composite titanic oxide ,suitable for pigments,are as follows.

1. To a titanic sulphate solution a compound such as calcium chloride or barium chloride is added which is capable of forming by reaction with the solution an insoluble sulphate. The mass is then digested at about 100° C. to precipitate titanic oxide .(U.S.Patent 1,155,462).

2. A base such as calcium hydroxide or barium hydroxide is added to a titanic sulphate solution.The reaction of the base with the sulphate in solution produces a precipitate of sulphate particles,and upon heating the solution a composite precipitate is produced which contains these particles and basic titanic sulphate. The precipitated pigment is calcined at 600°C.to 800° C.to decompose the basic titanic sulphate. (U.S.Patent 1,205,144).

3. Titanium oxides or complexes are precipitated at temperatures above 100°C. and under pressures substantially above atmospheric.(U.S.Patent 1,410.056).

4. The iron is removed from an iron -titanic sulphate solution by precipitating as a double cyanide.The carbonaceous matter is then removed and the titanic oxide precipitated from the solution by boiling.(U.S.Patent 1,354,940).

The experimental work of this research was not based on any one particular patent but certain ideas were obtained from the patents previously mentioned. U.S. patents, 1,343, 441 ; 1,429,841; 1,155,462 and 1,410,056 bear some relation to the experimental work and are therefore briefly outlined as follows:-

U.S. Patent 1,343,441, by P.Farup.

Process for producing titanium compounds.

Ilmenite ore is pulverized and mixed with pulverized carbon in sufficient amount to reduce the iron oxides to metallic iron and titanium oxide to metallic titanium The mixture is heated in an electric furnace supplied with nitrogen during the whole treatment. The temperature required ranges from 1200°C. to 1400°C.and is continued till the ilmenite is decomposed. The material is then crushed to the fineness of coarse sand and lixiviated with dilute acid. The iron dissolves leaving as residue the titanium-nitrogen compound,silica and other insoluble impurities. The residue is dried and mixed with concentrated sulphuric,in the proportion of two parts by weight of 90° H_2SO_4 to one by weight of the residue,and is placed in a cast iron vessel. The mixture is then heated till reaction takes place.The product is a solid mass of titanium sulphate and ammonium sulphate with small amounts of ferrous sulphate. The mass is then lixiviated with water,using four parts by weight of water to one of the solid mass. The residue,consisting principally of silica,is removed from the solution. The titanous oxide is then precipitated by boiling and the ammonium sulphate recovered by crystallization.

U.S.Patent 1,429,841, by H.H.Buckman.

Method of producing titanium complex.

Pulverized ilmenite is mixed with concentrated sulphuric acid,slightly in excess of the calculated amount,and introduced into an acid-proof container provided with means for sealing gas-tight and heating. The mixture is heated till the pressure generated is 200 pounds per square inch. Water equal to four times the volume of acid used is added to the hot container. If the pressure is lowered ,heat is applied till it is again raised to 200 pounds. The mixture is then allowed to cool and settle. A white precipitate settles out and the liquid contains iron,sulphuric acid and small amounts of titanium sulphate. The liquid is decanted off and the white precipitate is washed,dried and calcined.

U.S.Patent 1,155,462. by L.E.Barton.

The production of composite titanium oxide.

Titaniferous material is digested at 100°C. to 150°C. in a suitable vessel with 95 percent H_2SO_4 in the proportion of 2.5 to 2.6 parts by weight of H_2SO_4 to one part by weight of TiO_2. The mass is then dissolved in water,the volume of which is three times that of the sulphuric acid used. The resulting solution is filtered and calcium chloride added, equal in amount to the total sulphuric acid in the titanic sulphate solution. The mixed solution is diluted to three times its volume and digested at 100°C. for five to eight hours in a closed vessel. The composite precipitated product is washed,dried and calcined.

U.S.Patent 1,410,056. by H.H.Buckman.

Production of titanium oxide or titanium complex.

Concentrated solutions of titanium sulphate are heated above their atmospheric boiling points in closed gas-tight containers. The nature of the precipitate is modified at high temperatures and pressures. In addition to the new and useful properties of the material,the amount of yield from a given solution at these high temperatures and pressures is very nearly double that obtained at temperatures and atmospheric pressures previously used. A concentrated titanium sulphate solution containing free sulphuric acid is placed in a gas-tight container and heated to 185° C. and at a corresponding pressure for twenty minutes. The titanium oxide precipitates, forming a semi-solid mass too thick to pour. Water is added, the solution filtered and the precipitate washed, dried and calcined. Dissolved substances such as $BaCl_2$, $Ba(OH)_2$, $CaCl_2$ and $Ca(OH)_2$, designed to form precipitates with titanium, are introduced into the solution under pressure, while carrying out the operation.

MINERALOGICAL CHARACTER of ILMENITE.

Ilmenite (titanic iron) has the following properties[8]:-

Composition	-Variable.
Hardness	- 5 to6.
Cleavage	- Undeveloped.
Fracture	- Conchoidal, brittle.
Lustre	- Submettalic to metallic.
Streak	- Black to brownish red.
Color	- Iron black.
	Opaque.

Ilmenite[9] has rather a wide variation in composition. In addition to oxide of titanium it usually contains both ferrous and ferric oxides, and sometimes also small percentages of manganese and magnesium oxides. Most analyses give the empirical formulae $FeTiO_3$ with, in addition, variable amounts of Fe_2O_3. The mineral was formerly regarded as a titaniferous hematite $(Fe.Ti.)_2O_3$, but this view is no longer held, since it fails to take account of the ferrous iron in the mineral. Also, the mineral is not strictly isomorphous with hematite. Although both are hexagonal, hematite (calcite class) has a higher symmetry than ilmenite (dioptase class).

When manganese or magnesium is present, it is always found replacing an equivalent amount of ferrous iron, that is, the ratio $(Fe.Mg.)O : TiO_2$ is invariably 1:1. On these grounds most authorities now regard ilmenite as a titanate essentially of iron, but grading by isomorphous replacement into magnesium or manganese titanate. According to this view ordinary ilmenite is $(Fe.Mg.Mn.)TiO_3$, an isomorphous mixture of $FeTiO_3$(pure ilmenite) with $MnTiO_3$ which occurs as the mineral pyrophanite,isomorphous with ilmenite,and $MgTiO_3$(not known as a mineral). It would thus be comparable with hypersthene (Fe.Mg.)SiO_3,bronzite(Mg.Fe.)SiO_3 and enstatite $MgSiO_3$, and it may be noted that these minerals are usually present in small amounts in the rock(anorthorsite) with which the ilmenite is assosiated.

If ilmenite is a titanate of ferrous iron,it becomes necessary to account for the fact that analysis of most specimens shows the presence of more or less ferric iron. This might be present as a molecular compound with the titanate or as a disseminated hematite as noted in the following investigation.

Previous Investigations.

Mosander[10] made the first analysis of 'titanic irons'and ascertained the presence of MgO. He concluded that they consisted of $FeO.TiO_2$ mixed with MnO.,MgO.,CaO.,TiO_2 and Fe_2O_3 and implied that these were isomorphous.

H.Rose emphasized the fact that no isomorphism is known to exist between two compounds of which the one is composed of two oxidized substances similar to their salts and the other of one simple oxide. Accordingly he assumed that titanium was really present as Ti_2O_3 and might be isomorphous with Fe_2O_3 and that the black color of titanium was due to Ti_2O_3 since a titanium acid salt would be brown.

Rammelsburg,as a result of many new analyses ,concluded that Mosander's formula was correct.He found MgO. always present and as high as 16.0 percent. It seemed necessary to assume the molecule $MgTiO_3$ present and isomorphous with $FeTiO_3$. When one compares the mixture of sesquioxide and metatitanate with the proportion in the pyroxene-amphibole group, the analogy of ilmenite to Tschermark's aluminum silicates, $Mg.Fe._2TiO_6$ will be apparent. Magnesium would be able to occur as $(Fe.Mg.)TiO_3$.

C. Frundel and Guerri artificially prepared Ti_2O_3 in rhombohedral crystals, isomorphous with hematite and concluded that $FeTiO_3$, $Fe.FeO_3$, and $Ti.TiO_3$ were isomorphous and the ilmenite occurred partly as the second compound and partly as a mixture of the first and second. They did not consider it as a mixture of Fe_2O_3 and Ti_2O_3 because the axial proportions do not lie between the two components.

Penfield and Foote came to the same conclusion regarding the correctness of the $RTiO_2$ formula, thereby supporting Mosander.

Groth considers Ti_2O_3 isomorphous with Fe_2O_3 in certain titaniferous hematites. He considers the 'Titanersenerz' to be partly represented by the formula $FeTiO_3$, but in part also containing Fe_2O_3, probably an isomorphous mixture, though he questions their isomorphism on account of their difference in formula and crystallization but prefers to consider them as molecular intergrowths.

W. O. Snelling[11] explains the variable composition as follows:- Both ferric oxide and titanium oxide unite with ferrous titanate (ilmenite) in all proportions, forming a series of compounds varying continuously in composition between the limits TiO_2 and $FeTiO_3$. Thus we have a light yellow rutile consisting of practically pure TiO_2; a darker colored TiO_2

containing a small quantity of $FeTiO_3$; then black rutile (nigrine) containing a relatively greater proportion of $FeTiO_3$ and so on, until ferrous titanate becomes the principal constituent and the proportion of TiO_2 less and less. But the series is extended still further, for the $FeTiO_3$, combining with the Fe_2O_3 produces compounds in which the ratio between the Ti_2 and Fe_2 becomes fractional, and which contains a greater quantity of Fe_2O_3 than $FeTiO_3$; and this continues till we have Fe_2O_3; containing a very small quantity of ferrous titanate, the compound now representing a slightly titaniferous hematite.

Chemical analyses, followed by microscopic studies, are of great value in determining the constitution of minerals. The following microscopic study was made of the equilibrium of the iron and the titanium oxides.

MICROSTRUCTURE of TITANIFEROUS HEMATITE.

Previous Investigations.

O. Mugge[12] in his paper on the regular intergrowths of minerals of different kinds, gives a summary of the earlier work relating to the parallel growths of ilmenite, hematite and spinels.

C.H. Warren[13] has described an intergrowth of hematite and ilmenite from St. Urbain, Quebec. His photomicrographs of polished specimens are identical with those obtained by the writer.

Metallographic Method of Investigation.

Polished surfaces of the ilmenite were prepared and etched with hydrochloric acid to bring out the structure which may then be observed by the metallographic microscope.

Metallographic apparatus N.L.A. 7-FSMT 9 of the Bausch and Lomb Optical Co.,Rochester N.Y. was used.

Preparation of the Specimen.

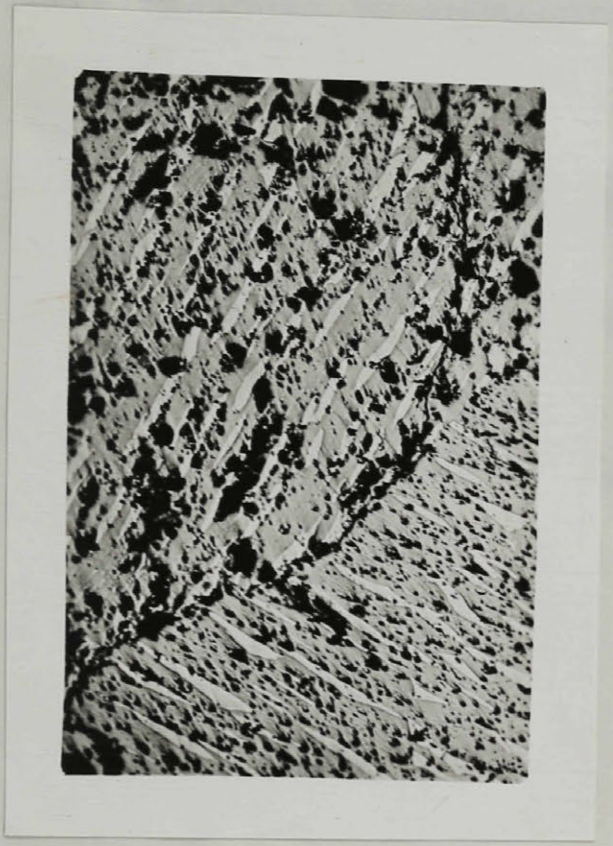
To prepare a polished section,a specimen about one-half inch square and one-quarter inch thick was chipped off a sample of ore. One face of the specimen was then ground,in the order given,on an emery wheel,coarse file,coarse,medium and fine emery paper.Care was observed in keeping an even pressure on the specimen to prevent any curvature of the surface which would prevent proper focusing of the microscope. The specimen after grinding on the fine emery paper was polished ,in succession,on an emery,tripoli and rouge wheel. The polished surface thus prepared was photographed,etched with strong hydrochloric acid for three minutes,and then re-photographed .

Three photomicrographs were made .Specimens No.1 and 2 were photographed without etching and photograph No.3 is sample No.2 photographed after etching.

Results of the Metallographic study.

The ore consists of an aggregate of medium sized ilmenite crystals containing a very small percentage of gangue consisting of spinel,plagioclase,biotite and hornblende. The character of the ilmenite is the same throughout .

Examination of the polished surface shows that the individual grains are not of homogenous composition but are similar to one another in character. Each crystal is made up of a very fine lamellae intergrowth (white portions in the photomicrographs) substantially parallel in arrangement for a given grain.



Photomicrograph No. 1.

Photomicrograph No. 2.

Photomicrographs numbers one and two (magnification 75 diameters) of the ore show the intimate crystallographic intergrowth of the ilmenite and hematite. The large dark line is the boundry line of two ilmenite grains and the large white spot at the top of photomicrograph No. 2 is an inclusion of pyrite. This shows up dark on etching. The black spots are holes.

Ilmenite crystals are frequently twinned on the basal plane and the lamellae are probably arranged along the twin plane. Many of them pinch out within the grain and some are flat lensiform bodies slightly curved in outline. According to C.H. Warren they vary in width from .036 m.m. to .09 m.m. Their length also varies but is many times their width. Between any two of the large lamellae a parallel series of still more minute lamellae may be seen. The photomicrographs show minute fault lines cutting across and slightly displacing these lensiform bodies. These lines are most likely caused by movements in the rock mass as a whole.

The whole intergrowth (light and grey areas) resembles the microperthic texture in feldspar. The chemical composition of the intergrowth, calculated from analysis is as follows÷ TiO_2 32.4%, Fe_2O_3 27.78%, FeO. 28.95%, SiO_2 3.9%, MgO. 1.59% and Al_2O_3 1.70%.

A micrometric estimation of the areas of the lamellae in one square inch of the photomicrograph gave about 28.5% .This is in fairly close agreement with the percentage of Fe_2O_3 in the chemical analysis.

Photomicrograph No. 3.

Photomicrograph No. 3 was etched with hydrochloric acid. The lamellae show up much darker on account of their deeping due to etching.

The polished surface was immersed in cold concentrated hydrochloric acid which soon showed the characteristic color of ferric chloride. The solution was tested for ferrous and ferric iron but reacted for ferric iron only. A polished specimen of pure magnetite was similarly treated and reacted for both ferrous and ferric iron. The lamellae(white) are deepened by the action of the acid ,indicating that the intergrowth is more readily dissolved than the ground mass (steel-grey) which is most likely of the composition $FeTiO_3$.

Photomicrograph No.3 shows that these lamellae have changed. The lamellae in the upper left-hand corner of the photo shows up dark as the light is not reflected back vertically. None of the lamellae are as distinct on account of the uneveness caused by etching.

These facts indicate quite clearly that these lamellae are hematite in intimate crystallographic growth with the ilmenite. Also the ilmenite grains are not attracted by an ordinary magnet but are slightly attracted by a strong electromagnet. Their weak magnetic property indicates quite clearly that there is no magnetite present.

This intergrowth[14] appears to be of some interest in connection with the composition of 'titanic iron ores' generally and the disputed question of isomorphism of hematite and ilmenite.

It is impossible to estimate the amount of ferric oxide present as such in the intergrowth but the approximate estimation given above agrees closely with the ferric oxide found by analysis. From this it appears that Fe_2O_3 mixed isomorphous with ilmenite must be small. The excess Fe_2O_3 in ilmenite analyses has generally been accorded to mean that ilmenite and hematite are isomorphous.

If[15] the ilmenite grains in the present instance possess the original structure assumed by them on crystallization from the magmatic condition, the Fe_2O_3 present in ilmenite may be always in large part, at least, present in the form of a fine intergrowth. It is by no means certain that the intergrowth is an original structure. The two molecules may have crystallized originally as an isomorphous mixture and subsequently under changed conditions of temperature , pressure, etc., being no longer stable in the isomorphous state separated.

This explanation given by C.H.Warren is in accordance with the intergrowth described.

The phenomena occurring on the solidification of the molten magma, under high temperature and high pressure may be analagous to the phenomena occurring on the solidification of an alloy. In this case when the molten magma, consisting of oxides of iron and titanium, solidified , the mineral ilmenite ($FeTiO_3$) was formed. The ilmenite may be considered analagous to the eutectic formed on the solidification of an alloy and the Fe_2O_3 over and above the eutectic ratio constitutes the excess substance which segregated out.

These two minerals Fe_2O_3 and $FeTiO_3$ have very nearly the same crystallographic constants but differ somewhat in symmetry and the accepted formulae for thetwo are not strictly analagous, ilmenite being $RTiO_3$ and hematite Fe_2O_3. The crystallographic and chemical analagoies of the two may not be sufficiently close to permit of isomorphous mixtures, but close enough to form an intimate and definite crystallographic intergrowth.

IMPORTANT THEORETICAL CONSIDERATIONS.

REDUCTION.

Carbon or carbon monoxide is most commonly used to effect the deoxidation of an oxide and in the following experiments carbon was used to deoxidize the iron oxides in the ilmenite.

The oxidation[16] of carbon begins at about 400°C. and the affinity of carbon for oxygen increases with increasing temperature. The reaction $2MO + C = M_2 + CO_2$ takes place at a low temperature or when carbon acts upon a readily reducible oxide. At a high temperature or acting upon an oxide difficult of reduction the reaction is $MO + C = M + CO$. The line of division between the two reactions is about 1000°C.

The formation of CO and CO_2 is not determined only by temperature, but also by the relative proportion of oxygen to be removed and the amount of carbon employed. An excess of oxygen favours the formation of CO_2 and an excess of carbon the formation of CO. As the reduction does not penetrate much into a particle of a metallic oxide of moderate size it is necessary to have both the oxide and the carbon finely divided and intimately mixed. Most of the reduction is probably accomplished by means of CO gas and not by the actual contact of the solid carbon with the ore.

Further information regarding the reduction of iron ores is to be found in the publications given in the references.

LEACHING.

The term 'leaching'[17] is defined as the dissolving of a constituent of a comminuted material and the separation of the resulting solution from the undissolved portion or residue

The problem involved is almost identical with that of dissolving any solid in a suitable liquid and is governed by the same physical and chemical laws if no chemical reaction is taking place other than that which dissolves the solid.

The velocity of dissolution is dependent upon the following factors:-

1. Physical condition or nature of the matter to be dissolved.
2. Velocity of diffusion.
3. The concentration of the solvent.
4. The rate of change of relative position between particles of solid and the adjacent liquid.
5. Temperature.
6. Solubility.
7. Pressure.

Effect of physical condition:- (1) When soluble material in a finely divided form is added to a saturated solution of the same it will often dissolve producing a supersaturated solution. This effect could never be obtained by contact with coarser particles. (2) The rate of dissolution for different faces of the same crystal usually varies.

These facts show the necessity when considering a leaching problem of making direct tests on the material to be treated.[1]

Effect of diffusion:- The process of dissolution appears to take place in two stages; first there is a reaction between the solid and the solvent in intimate contact which is followed by the diffusion of the products from the surface of the solid. It is assumed, that we have at all times in direct contact with the solid particles during the process of dissolution a thin film of saturated solution, and that the unsaturated solution never has contact with the solid but becomes concentrated by diffusion from this film .

Temperature:- The general effect of a rise in temperature is to aid the velocity of dissolution irrespective of the increase when the substance is more soluble in this hot solvent than when cold. This increase is usually small and in general it is of little use to heat the solutions employed.

One of the most common means of leaching is to agitate the material in the solvent till the dissolution is complete. This operation is followed by a separation of the solids from the solution.

Two main types of apparatus for leaching by agitation may be employed. The first keeps the particles and solution in motion relative to each other and the second merely holds the particles in suspension. The first type is more commonly employed.

THEORETICAL CONSIDERATIONS with respect to the ELECTRO-DEPOSITION of IRON.

The[18] purest iron is obtained from an aqueous solution of ferrous chloride or sulphate. The former solution is preferable as a greater concentration of iron can be obtained.

In the cathodic deposition of iron from a sulphate or chloride solution there are several points to be considered. Iron is much more electropositive than hydrogen and the hydrion concentration must therefore be carefully regulated. If the solution is neutral there may be danger of depositing oxide along with the iron. If strongly acid there may be a waste of current caused by the evolution of hydrogen and no deposition of iron can take place on account of the adhesion of hydrogen to the surface of the cathode, thereby causing the deposit to be pitted.

To obtain a satisfactory current efficiency the ratio $\frac{Fe^{++}}{H^{+}}$ must be as high as possible. This ratio is limited by the solubility of the iron salt employed and by the fact that at low H-ion concentration basic salts are liable to precipitate and adversely affect the quality of the cathodic deposit. This is particularly true of a ferrous sulphate solution.

The equilibrium potential Fe./n.$FeSO_4$ is about -0.46 volts, whilst in a neutral solution the potential of the hydrogen electrode is -0.41 volts. The reversible deposition of hydrogen from such a solution should therefore take place rather more easily than that of iron and the small hydrogen overvoltage at that metal barely equalizes matters.

Iron is a metal whose cathodic deposition encounters strong reaction resistances. These resistances may be offset by a rise in temperature which should increase the current efficiency. The same should result from an increase in current density which also increases the overvoltage effect and favours the production of metal as opposed to the production of hydrogen.

The following conditions are requisite for the best current efficency:- (a) high Fe.concentration.(b) H-ion concentration only high enough to prevent precipitation of basic salts.(c) high temperature.(d) high current density.

Faraday's law states that whenever 96540 coulombs of electricity pass from an electrode to a solution or vice versa,involving a chemical change,exactly one equivalent of the substance or substances taking part in the reaction must be affected by such a passage. (for calculation of e.m.f. required to effect electrolysis,see appendix.)

If only the cathodic deposition of iron is involved the passage of 96540 coulombs will deposit 1.041 grams of iron per ampere hour. What particular reaction will take place at the electrode depends on the voltage tendencies of the various possible reactions. Thus in a ferrous sulphate or chloride solution,containing a small amount of ferric iron three cathodic reactions occur.

1. $Fe^{++} = Fe.$(metal)$+ 2(+)$.
2. $2Fe^{++} = 2Fe. + 2(+)$.
3. $2H^{+} = H_2$(gas) $+ 2(+)$.

The last reaction may result from the fact that water is invariably dissociated into H and OH-ions. No.2 will take place first and will proceed spontaneously thus producing power. Therefore any ferric iron present tends to reduce to ferrous iron but will also tend to dissolve any metallic iron that is being deposited. This reaction is to be avoided. The next reaction that is likely to take place is No.3. Hydrogen gas is deposited at the cathode in preference to metallic iron. The equation for its formation in sulphate and chloride solutions is as follows:-

1. $Fe. + H_2SO_4 = Fe(SO)_4 + H_2.$

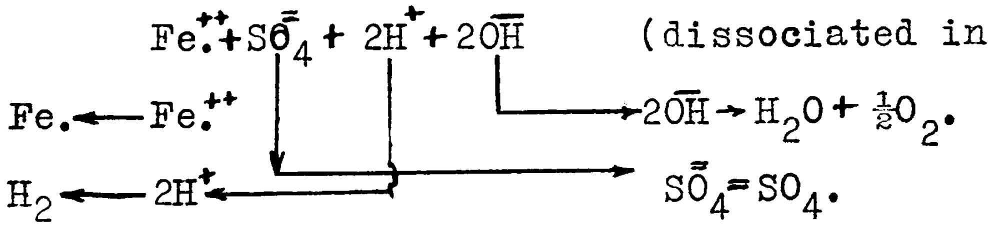
2. $Fe. + 2HCl = FeCl_2 + H_2.$

These reactions render electrolysis difficult. If the ferrous iron concentration could be enormously raised and that of the hydrogen reduced to a minimum the problem would be solved.

Experimental work by various investigators has shown that satisfactory deposits of iron can be obtained from both ferrous chloride and ferrous sulphate solutions which have a high iron concentration. The use of ferrous salts is limited, first by their low solubility in water and second by the fact that the H-ion concentration must be greater than in pure water to prevent the formation of basic salts and ferric hydroxide.

The following reactions occur when a current is passed through a ferrous sulphate solution, in which the anode and cathode are separated by a diaphragm.

Cathode (iron) $FeSO_4 + 2H_2O$ (in sol.) Insoluble anode.



$Fe^{++} + SO_4^{=} + 2H^{+} + 2OH^{-}$ (dissociated into ions)

$Fe. \leftarrow Fe^{++}$

$2OH^{-} \rightarrow H_2O + \frac{1}{2}O_2.$

$H_2 \leftarrow 2H^{+}$

$SO_4^{=} = SO_4.$

$SO_4 = SO_3 + \frac{1}{2}O_2.$

$SO_3 + H_2O = H_2SO_4.$

also

$4FeSO_4 + 2H_2SO_4 = 2Fe(SO_4)_3 + 2H_2O.$

Part Three.

EXPERIMENTAL RESEARCH.

A representative sample of ilmenite ore was obtained from the M^c^Arthur Irwin mine at Ivry, near St. Agathe, through the kindness of Mr. R. H. Monk.

The Ivry deposits[19] lie three miles west of the station of Ivry, on the St. Agathe branch of the Canadian Pacific Railway.

The ilmenite occurs as a segregated body in anorthosite. The anorthosite rarely presents a gneissic structure, some feldspars are cracked, or present strain shadows, but in the majority of specimens the rock appears to have crystallized quietly and to have been affected only by strains of minor importance.

For experimental purposes a fifty pound sample was cut out and crushed to minus one-eighth mesh. One-fifth of the sample was crushed to pass 80 mesh, for analysis and subsequent tests.

The analysis of the ore is as follows:-

Constituent	%
TiO_2	32.40
Fe.	41.818
SiO_2	3.92
Al_2O_3	1.70
CaO.	3.20
MgO.	1.01

The following analysis of the Ivry ore is taken from the report on Titanium by A.H.A. Robinson, Mines Branch, Ottawa. The two analyses agree very closely.

Constituent.	%
TiO_2	33.06
Fe.	42.98
P.	.076
S.	.144
V_2O_5	.04
Cr_2O_3	.08

This analysis was made by Mr. H.A. Leverin of the Mines Branch laboratory.

According to information derived from Dr. Carl Heintz's 'Handbuch der Mineralogie', volume 12, ilmenite is supposed to consist of $FeO.TiO_2$ mixed with MnO., MgO., CaO., TiO_2, and oxides of iron, FeO and Fe_2O_3.

The composition of the ore has been calculated on the assumption that it has the general formula $FeO.TiO_2.nFe_2O_3$.

Constituent	%	
TiO_2	32.40	Ilmenite $FeO.TiO_2$.
FeO.	28.95	
Fe_2O_3	27.778	
SiO_2	3.92	
Al_2O_3	1.70	
CaO.	3.20	
MgO.	1.01	
Total	98.958	

ELIMINATION of IRON by MAGNETIC SEPARATION.

Four experiments on magnetic separation were made. In the first it was attempted to separate the iron from the ore, under water ,by a hand magnet. The remaining tests were performed dry and the magnetic portion removed by an electromagnet.

The ore was crushed so that it would pass an 80 mesh screen.

The results of the experiments are as follows:-

Test.	Current.	Product.	Weight gms.	%Wt.	Remarks.
A.	Hand Mag. (5 in.)	Mag.Conc.	0.186	11.00	Under water.
		Tails	1.674	89.00	
B.	Electro-magnet 4-amps.	Mag.Conc.	0.251	12.55	Dry.
		Tails	1.749	87.45	
C.	6-amps.	Mag.Conc.	0.438	21.90	Dry.
		Tails	1.536	78.10	
D.	8-amps.	Mag.Conc.	0.573	28.65	Dry.
		Tails	1.472	71.45	

Test C was analyzed with the following results:-

				Total Products.		
Product	Wt.gms.	%Fe.	%TiO_2	%Wt.	Fe.	TiO_2.
Ore	1.974	41.818	32.4	100.0	0.824	0.640
Mag.Conc.	.438	43.50	31.75	21.9	0.191	0.137
Tails	1.536	40.79	33.1	78.1	0.626	0.510
Totals				100.0	0.817	0.647

These results show that the iron is practically all associated with the titanium in the ilmenite. The variation in the degree of separation with different strengths of current indicates that there is no sharp dividing line between the ilmenite ($FeTiO_3$) and iron oxide.

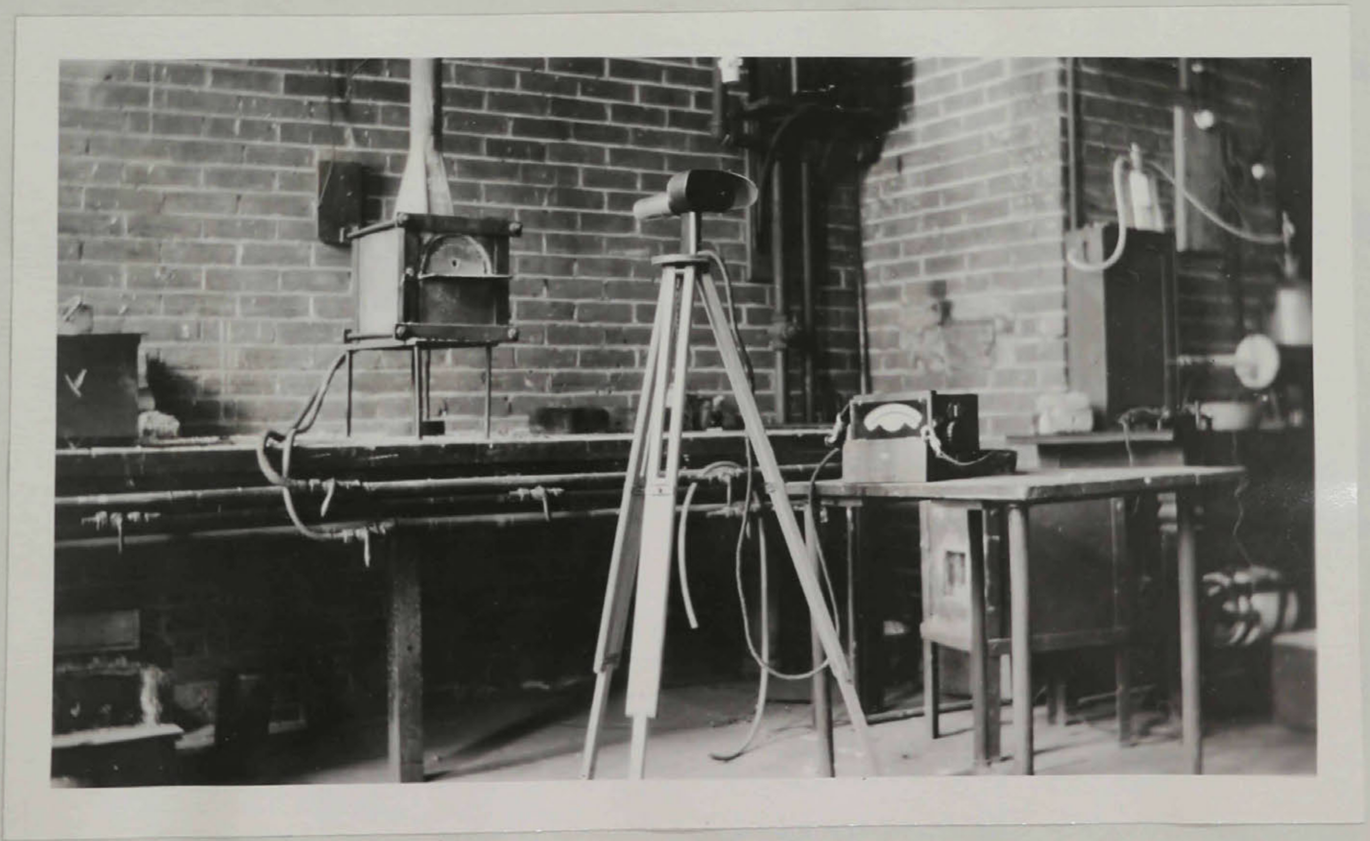
The chemical analysis of test C shows that no advantage is to be derived from the magnetic separation of the ore.

SEPARATION of IRON by REDUCTION followed by LEACHING.

Experiments have shown that hematite and magnetite ores can be reduced to metallic iron by heating with carbon at temperatures of 800°C. to 900°C. It thus appeared possible that the iron in the ilmenite might be reduced in this manner to the metallic state, leaving the titanium oxide. The reduced iron might then be removed by some suitable reagent , leaving the titanium oxide behind.

The ore crushed to pass 80 or 200 mesh was mixed with minus 40 mesh charcoal, placed in a graphite crucible and heated at 1000°C. for one hour in a gas-fired muffle.

The accompanying photograph shows the arrangement of the apparatus and diagram No. 1 gives the details of the furnace.



Arrangement of apparatus for reduction.

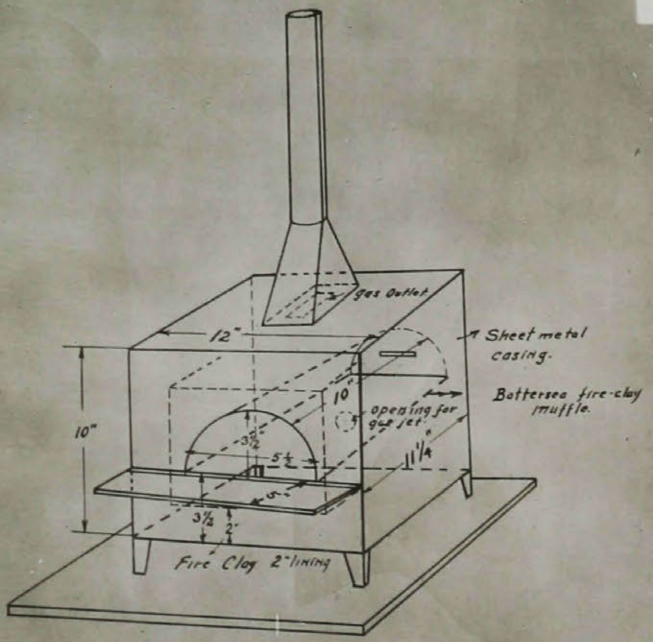


Fig I. Gas-fired Muffle.

Details of Gas-fired Muffle.

The crucibles were covered and sealed with viterex but a small opening was left to allow any gas to escape. The temperature was read every ten minutes by means of a Leeds-Northrup Optical pyrometer and was regulated by adjusting the flow of gas and air.

After reduction the charge was allowed to cool and the ore separated from the charcoal by an electromagnet, as the reduction had made it magnetic.

The following table gives the conditions of each reduction and the analysis of the reduced ore.

Red. No.	Ore gms.	Mesh.	Charcoal grams	Temp.°C.	Analysis.		
					%Fe.	%TiO_2	% Red.
1.	10	80	4	1004	47.99	35.2	69.5
2.	20	80	6	1010	44.29	37.2	----
3.	20	80	6	1010	47.38	39.0	89.5
4.	5	80	3	900	-----	----	----
5.	5	200	3	1110	43.26	34.4	----
6.	50	200	16.32	1030	43.57	34.5	----

Remarks. In the above tests more charcoal was used than is theoretically required to reduce the iron oxides in the ore. In reductions Nos. 2 and 5 the analysis of the reduced ore is low on account of the incomplete separation of the charcoal. Reduction No. 4 at 900° C. was carried out in a Hump Electric furnace as the temperature could be kept more uniform. The reduced ore was only slightly magnetic, showing that only partial reduction had taken place and in view of this no chemical analysis was made. Reduction No. 5 was seen to be practically complete as the reduced ore was readily separated from the gangue and charcoal by an electromagnet. The ore sintered and had to be recrushed.
The ore in Reduction No. 6 was reduced at 1030°C. for 1.5 hours.

Conclusions from tests 1 to 5.

It is evident that the best temperature for reduction lies between 900°C. and 1110°C. The reduction at 1000°C. for one hour gave satisfactory results in the subsequent leaching tests.

No reduction tests were made on the ore crushed to coarser sizes but as a rule the finer the ore the more complete is the reduction.

REDUCTION EXPERIMENTS with CARBON.

Reduction, as previously mentioned, is probably accomplished not by the actual contact of the carbon with the ore but by the CO gas which is formed by the oxidation of the carbon.

The reactions taking place may be represented by the following equations:-

(1) $3Fe_2O_3 + CO. = 2Fe_3O_4 + CO_2.$

(2) $Fe_3O_4 + CO. = 3FeO. + CO_2.$

(3) $FeO. + CO. = Fe. + CO_2.$

(4) $C + CO_2 = 2CO.$

(5) $4Fe_2O_3 + 9C = 3CO_2 + 6CO + 8Fe.$

(6) $FeO + C = CO + Fe.$

As an excess of carbon is generally required to force the reaction from left to right the following experiments were made to ascertain the amount of carbon required to reduce all the FeO and Fe_2O_3 according to equations five and six. These equations were chosen as they most likely represent the conditions under which the tests were made, namely, with increasing temperature till the desired temperature is reached. In equation No. 5 mostly CO_2 forms at low temperatures and only a small quantity of CO. As the temperature increases more CO forms and the final ratio of CO to CO_2 is substantially as given by the equation. This equation does not represent a definite chemical reaction but probably gives the proportion of CO to CO_2 that will come off. Equation No. 6 shows that no CO or CO_2 forms but this is probably not strictly true as at high temperatures the reduction of FeO by carbon results in nearly all CO and a little CO_2.

In test No.2 twice the theoretical amount of carbon was used and in test No.3 three times the theoretical amount was used.

The tests were carried out as follows:- The ore was crushed to minus 200 mesh and the charcoal to minus 40 mesh. The ore and charcoal for each test was mixed,placed in a crucible,and heated in a gas-fired muffle at 1010° C. for a period of one hour. The charcoal was carefully separated from the reduced ore by means of an electromagnet.

The results obtained are as follows:-

Red. test.	Ore grams.	Charcoal grams.	%Fe.	%TiO_2	% Reduction.
1.	5.0	0.477	48.45	37.4	86.00
2.	5.0	1.431	50.90	39.3	100.00
3.	5.0	2.385	51.10	39.6	100.00

Conclusions.

The experiments show that twice the theoretical amount of carbon is sufficient to give complete reduction of the iron oxides in one hour at 1010°C.

In test No.1 the charge sintered slightly but in numbers two and three there were no indications of sintering,there being sufficient charcoal between the ore particles to prevent their fusion.

LEACHING EXPERIMENTS.

Leaching tests were carried out simultaneously on raw and reduced ore from reduction No. 1 to ascertain the relative solubilities of iron and titanium oxide in dilute sulphuric acid. In all cases equal parts of chemically pure sulphuric (sp.gr. 1.84) and water were used as the leaching medium.

Series A. Leach No. 1.

One-half gram of reduced ore was digested one-half hour on a hot plate at 120°C. with 20 c.c. of 1:1 H_2SO_4 . The liquor was filtered off and the residue washed with hot water and again treated with 20 c.c. of 1:1 H_2SO_4 for one-half hour.

Results.

	Iron. % of reduced ore	TiO_2. % of reduced ore.
Total contents	47.988	35.2
Removed in first liquor	44.46	15.8
Removed in second liquor	3.60	5.0
Residue	Trace	14.5
Total	48.06	35.3

The above analysis shows that the iron is easily soluble, while the titanium oxide is less so but is not sufficiently insoluble for effective separation.

No test on the raw ore was made simultaneously with this test.

Leach No. 2

Leaching tests were carried out on raw and reduced ore. In each case one gram was leached for one hour with 20 c.c. of 1:1 H_2SO_4 at 120°C., the liquor filtered off and the residue treated for one hour with 20 c.c. of fresh 1:1 acid.

Results.

	Raw ore.		Reduced ore.	
	Fe. % of ore.	TiO_2 % of ore.	Fe. % of ore.	TiO_2 % of ore.
Total contents	41.818	32.4	47.988	35.2
Removed in first liquor.	19.22	13.4	44.46	18.1
Removed in second liquor	7.74	3.2	2.70	3.2
Residue	13.78	18.1	Trace	13.7
Total	40.74	34.7	47.16	35.0

These tests show that both the raw and reduced ore is soluble but the latter more readily so. At such high temperatures as in tests 1,2 and 3 there is most likely a concentration of acid. This would cause more TiO_2 to be dissolved than if the acid were dilute as TiO_2 is soluble in concentrated H_2SO_4 at fairly high temperatures.

These tests indicate that at a lower temperature the iron would still be readily soluble and the TiO_2 would be less so.

The following tests were made to ascertain this point.

Leach No.4

A one gram sample of the raw and reduced ore was leached for one hour with 20 c.c. of 1:1 H_2SO_4 at a temperature of 90° C. and maintained constant by means of a water bath. The residue from the first leach liquor was leached with 20 c.c. of fresh 1:1 H_2SO_4 for an additional hour.

Results.

	Raw ore.		Reduced ore.	
	Fe. % of ore.	TiO_2. % of ore.	Fe. % of ore.	TiO_2. % of ore.
Total contents	41.818	32.4	47.988	35.2
Removed in first liquor.	4.02	3.2	46.45	5.2
Removed in second leach.	2.57	2.5	2.06	1.6
Residue	34.50	30.0	Trace.	28.6
Total	41.09	35.7	48.51	35.4

These results show more clearly the advantage gained in first reducing the ore. Practically all the iron is removed in the first leach and only a small amount of TiO_2. A small amount of iron is left in the residue after the second leach.

Leach No. 5.

The leaching conditions are the same as in leach No. 4.

Results.

	Raw ore.		Reduced ore.	
	Fe. % of ore.	TiO_2. % of ore	Fe. % of ore.	TiO_2. % of ore.
Total contents	41.818	32.40	47.988	35.20
Removed in first leach	4.00	1.84	48.18	5.16
Removed in second leach	2.56	1.70	.75	2.55
Residue	35.19	29.60	Trace.	25.50?
Total	41.65	33.14	48.87	33.21

Weight of residue 0.378 grams.

$$\% \ TiO_2 = \frac{0.255}{0.378} = 68.50.$$

This test compares favourably with No. 4 but the analyses do not check as well due to some error in the assaying. The remaining constitutents in the residue have not been analyzed for.

Conclusions.

1. The reduction of the ore by heating with carbon renders the iron more soluble.

2. With a certain concentration of acid and at a certain temperature it may be possible to remove practically all the iron, leaving a concentrated titanium oxide product.

LEACHING with FERRIC CHLORIDE.

When iron is treated with a solution of ferric chloride, the iron reduces the ferric chloride to ferrous chloride according to the equation:-

$$Fe. + 2FeCl_3 = 3FeCl_2.$$

The leaching of ores in general, as previously mentioned, depends principally on the fineness to which the ore is ground, the temperature and concentration of the solvent.

When using ferric chloride the temperature must be below 100°C. as hydrolysis readily takes place at higher temperatures. The concentration must also be high to prevent hydrolysis.

Leaching tests on ore from Reduction No.2 Series B.

Conditions :-

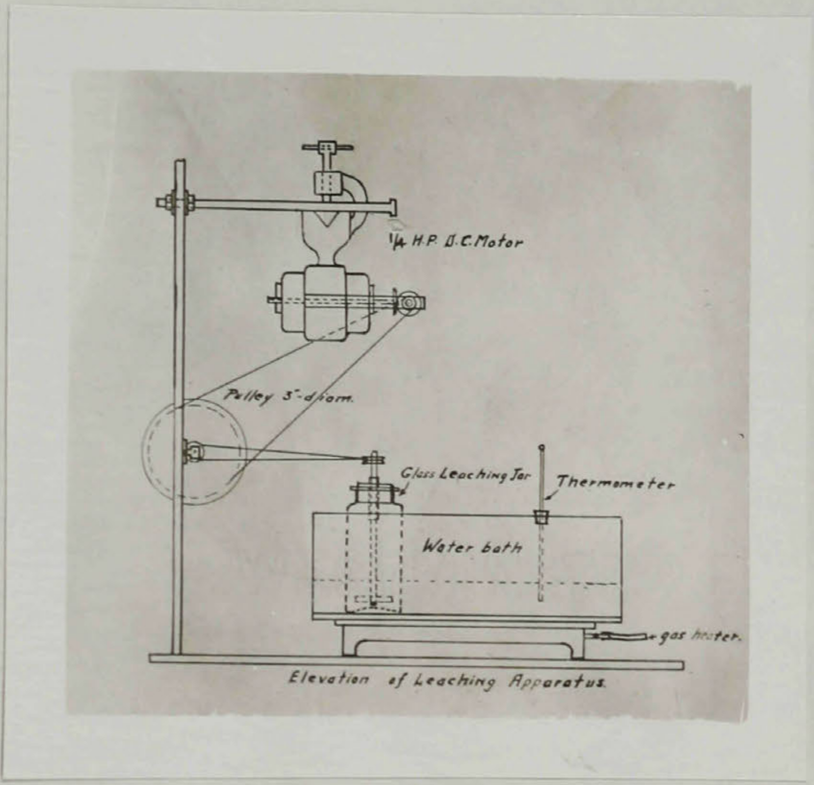
Volume of solution 100 c.c.

Temperature 90° C.

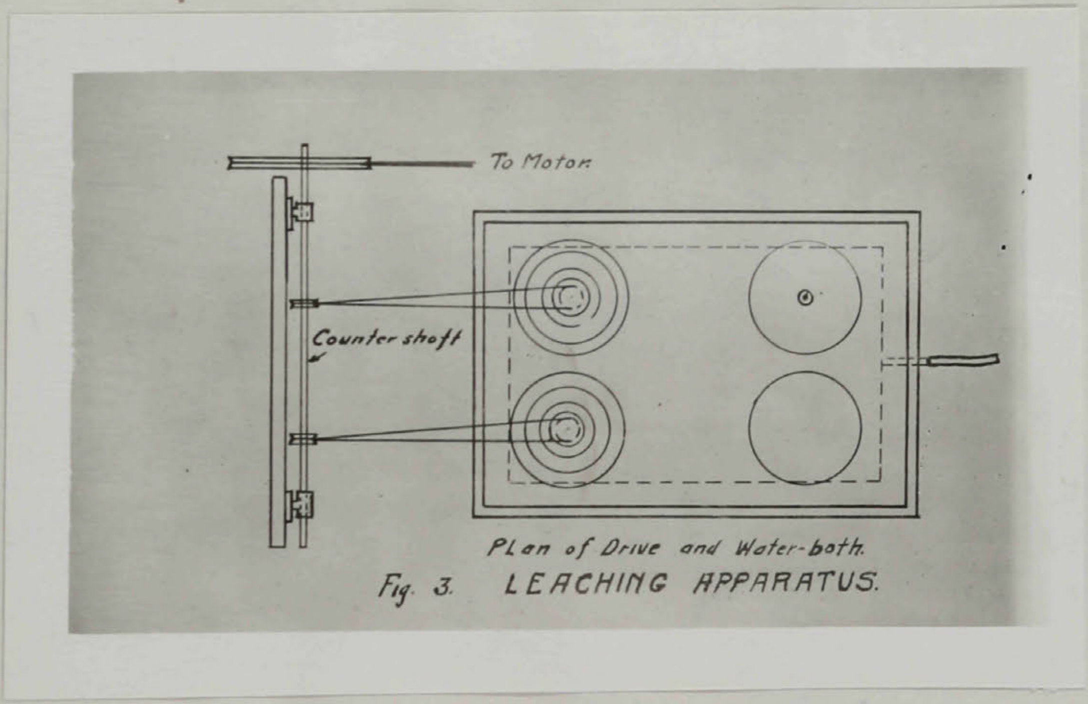
Analysis of reduced ore(No.2) Fe. 44.29% , TiO_2 37.20%.

The ore was agitated in the solution for five hours by a mechanical stirrer running at approximately

200 r.p.m.. The general arrangement of the leaching apparatus is shown in figures 2 and 3.



Elevation of Leaching Apparatus.



Plan of Leaching Apparatus.

Results of Tests.

Test	Wt. of ore. grams	Conc. $FeCl_3$ g/100c.c	HCl. c.c.	Residue. Wt.	Residue. %Fe.	Residue. $\%TiO_2$	Extraction. %Fe.	Extraction. $\%TiO_2$
1.	2	5.25	---	1.215	14.42	56.0	83.9	8.0
2.	3	7.86	---	1.477	14.31	56.5	88.0	25.0
3.	4	11.04	10	2.024	8.75	68.0	90.5	9.0

Conclusions:-

In tests one and two a considerable percentage of the iron has been extracted thus increasing the percentage of TiO_2 in the residue. Neither of these tests proved satisfactory as considerable hydrolysis took place thus contaminating the residue with iron oxide which had to be washed out with dilute acid.

Test No.3 contained 10.0% HCl which entirely prevented hydrolysis and improved the extraction of the iron.

Only a small amount of titanium has gone into solution as is shown by tests one and three. The percentage of TiO_2 extracted in test No.2 is probably incorrect owing to an error in chemical analysis or to mechanical loss.

Leaching test No.4 on Reduction No.3.

Conditions:-

Volume 100 c.c.

Temperature 90° C.

Concentration of $FeCl_3$, 11.04 grams per 100c.c.

Hydrochloric acid 10.0%.

Analysis of reduced ore Fe. 47.38%, TiO_2 39.0%

The reduced ore was leached for five hours, the liquor then filtered off and the residue leached for an additional five hours with fresh solution.

Leach	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	%TiO$_2$.	Wt.	%Fe.	%TiO$_2$.	%Fe.	%TiO$_2$.
First	4.00	47.38	39.0	2.005	8.75	77.9	90.75	----
Second	2.005	8.75	77.9	1.426	7.70	82.0	3.65	25.0
Total							94.40	25.0

An 0.2 gram sample was removed from the first residue, in this and subsequent tests, and used for analysis.

The extraction of the iron was increased considerably, but some titanium had also gone into solution. Practically no titanium was extracted in the first leach as shown by a qualitative test of the resulting leach liquor.

Leaching test No.5 on Reduction No.3.

Conditions were the same as in test No.4 except that 5.0% hydrochloric acid was used.

Leach	Material treated			Residue.			Extraction.	
	Wt.gms.	%Fe.	%TiO$_2$	Wt.	%Fe.	%TiO$_2$.	%Fe.	%TiO$_2$.
First	4.000	47.38	39.0	2.034	15.96	77.5	82.8	----
Second	2.034	15.96	77.5	1.475	8.24	79.5	10.8	525.0
Total							93.6	25.0

No hydrolysis took place in this test and no doubt a smaller percentage of HCl could be used.

There is practically no difference in the percentage of iron extracted so that the addition of acid is of little benefit except in so far as to prevent hydrolysis.

Conclusions:-

1. Ferric chloride is a suitable solvent for the extraction of iron from reduced titaniferous ores.

2. The last 10 to 15 percent of the total iron seems difficult to remove. This iron may be decreased by finer

grinding and a longer period of reduction.

3. Hydrolysis is prevented by the addition of hydrochloric acid and the residue is not contaminated with insoluble ferric hydroxide.

Leaching with dilute sulphuric acid.

Test No.1 Series C.

Conditions:-

Temperature 90° C.

Volume 100 c.c.,10.0% H_2SO_4.

Time. First leach one hour,second leach one and one-half hours.

Ore- Reduction No.3.

Leach.	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	%TiO_2.	Wt.	%Fe.	%TiO_2	%Fe.	%TiO_2.
First	4.000	47.38	39.0	1.955	5.15	79.6	94.68	---
Second	1.955	5.15	79.6	1.705	4.12	83.4	1.59	14.7
Total							96.27	14.7

First leach liquor 1.75 grams of iron per 100 c.c. of solution

Second " " .103 " " " " " " " "

Conclusions:-

Dilute sulphuric acid gives a ferrous sulphate solution and no hydrolysis takes place. This insures a residue free from iron.

The extraction of iron is slightly higher than was obtained when leaching with ferric chloride.

Test No.2 Series C.

Conditions:-

Temperature 90° C.

Volume 100 c.c.

Time .First leach one hour,second leach
1.5 hours.

Ore- Reduction No.3.

Leach.	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	$\%TiO_2$.	Wt.	%Fe.	$\%TiO_2$.	%Fe.	$\%TiO_2$.
First	4.000	47.38	39.0	1.925	4.63	81.0	95.3	---
Second	1.925	4.63	81.0	1.597	4.12	83.5	1.21	14.8
Total							96.51	14.8

Conclusions.

Nearly all the iron is extracted in the first leach and the increase in extraction is not sufficiently great to warrant the additional increase of acid.

The same amount of titanium has been extracted in each case but only on the addition of fresh acid.

Test No.3 Series C.

Conditions:-

Temperature 18°C.

Time -2 hours for each leaching operation.

Volume 100 c.c.,10.0% H_2SO_4.

Ore- Reduction No.3.

Leach.	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	$\%TiO_2$.	Wt.	%Fe.	$\%TiO_2$.	%Fe.	$\%TiO_2$.
First	4.000	47.38	39.0	2.176	10.4	---	88.1	---
Second	2.176	10.4	----	1.861	9.27	---	2.8	10.4
Total							90.9	10.4

First leach liquor 1.75 grams of iron per 100 c.c.
Second '' '' .077 '' '' '' '' '' ''.

Conclusions:-

The extraction of the iron at room temperature is considerably lower than in the previous test and therefore heating the solution is necessary to obtain the maximum extraction. To what temperature the solution must be heated can be determined by running a series of tests at various temperatures, keeping all other conditions constant.

Test No.4 Series C.

Conditions in this test are the same as in test No.3 except that the leaching solution contains 20.0% H_2SO_4.

Leach	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	%TiO_2.	Wt.	%Fe.	%TiO_2	%Fe.	%TiO_2.
First	4.00	47.38	39.0	2.07	7.72	---	91.60	---
Second	2.07	7.72	----	1.78	7.21	77.5	1.64	11.5
Total							93.24	11.5

First leach liquor 1.67 grams of iron per 100 c.c.
Second " " .18 " " " " " ".

Conclusions:-

With an increase in acid concentration a better extraction of iron has been obtained but the percentage of titanium going into solution in the second leach has also increased.

By slightly heating the leaching solution and keeping the acid concentration about 10.0% a satisfactory extraction of iron can be made.

General conclusions from leaching tests.

In all leaching tests, either with ferric chloride or dilute sulphuric acid a complete extraction of the iron is impossible. About 90.0% of the iron is removed without dissolving any of the titanium but above this a fairly large proportion of the titanium is dissolved when attempts are made to remove the remaining iron. The percentage of iron that is removed is greater than that present as Fe_2O_3 so a large part of the iron in the $FeO.TiO_2$ must be soluble. It is probable that the iron in the $FeO.TiO_2$ is molecularly combined and therefore difficult to separate completely without dissolving some of the titanium.

The residue can be dissolved in concentrated sulphuric acid but it may then be difficult to separate the iron from the iron-titanic sulphate solution.

TREATMENT of the RESIDUE.

The combined residues after leaching the reduced ore with dilute sulphuric acid, were treated with concentrated sulphuric in a porcelain dish on a hot plate for a considerable time. The product was diluted by adding water, and then filtered. A greyish white residue remained which consisted mostly of titanic sulphate and some iron and silica. It was given a second treatment with acid.

As the solution from the first treatment was thought to contain too much acid it was not hydrolyzed.

The product from the second acid treatment was diluted and filtered. The solution was hydrolyzed by boiling, thus precipitating the titanic acid. The residue remaining on the filter was not given any further treatment.

Two experiments were made and the conditions for each were as follows:-

In No. 1 Barium chloride was added, thus precipitating barium sulphate at the same time as the solution was being hydrolyzed.

In No.2 titanic acid alone was precipitated.

The analysis of the material treated (the solution from the dilute acid leach) is as follows:- Fe. 11.54 percent and TiO_2 69.6 percent.

In each experiment 4 grams of this residue was digested at 135°C. in 100 c.c. of 50.0% sulphuric acid for 2 hours. Nearly all the iron and about 30.0% of the titanium was extracted by the first treatment.

The following results were obtained:-

	Test No.1			Test No.2.		
	Wt.gms.	%Fe.	%TiO_2.	Wt.gms.	%Fe.	%TiO_2.
Material treated	4.00	11.54	69.6	4.00	11.54	69.6
Final residue	.55	1.80	38.0	2.66	2.00	28.0

As previously mentioned the solution from the first acid treatment was set aside. The solution from the second acid treatment was diluted to 400 c.c. by the addition of water and was hydrolyzed by heating at about 90° C. for 2.0 hours.

In test No.1 30 c.c. of a 25.0% barium chloride solution was added during hydrolysis.

The product of hydrolysis was washed several times with water, dried and calcined at a dull red heat for one-half hour.

The precipitate $BaSO_4+TiO_2$ in test No.1 and TiO_2 in test No.2 appeared quite white but on calcining at a dull red heat for one-half hour they both became yellowish brown in color but the composite pigment ($BaSO_4+TiO_2$) was less discolored than the simple TiO_2 pigment.

<u>Conclusions</u>:-

These two tests are of a preliminary nature and indicate that the residue can be converted to sulphate of titanium and subsequently hydrolyzed. It appears that a large volume is necessary to hydrolyze the titanic acid. This may not be the case if care is taken to avoid a large excess of acid in the solution.

The best way of making a sulphate solution is to heat the pasty mass so as to form sulphates and drive off any excess acid by heating. The acid concentration would then be low and it would not be necessary to dilute so largely to effect hydrolysis.

The two following tests were made to ascertain these points.

Leaching Tests.

Two leaches (No.8 and 9) were made on the reduced ore, from Reduction No.6, in order to obtain the residues for subsequent treatment.

Conditions for leaches No.8 and 9.

Volume -200 c.c. ,20.0% H_2SO_4.

Temperature 90°C.

Time 2.0 hours.

Mechanical agitation.

Ore - Reduction No.6 -10 grams for each test.

Leach.	Material treated.			Residue.			Extraction.	
	Wt.gms.	%Fe.	%TiO_2.	Wt.gms.	%Fe.	%TiO_2	%Fe.	%TiO_2
No.8	10.0	43.57	34.5	5.10	9.36	64.0	89.0	5.00
No.9	10.0	43.57	34.5	5.02	9.57	65.1	88.6	4.25

The residues were combined and again heated with carbon to see if any further reduction would take place and make the residue more soluble in concentrated sulphuric acid. The object being to reduce the TiO_2 to a lower state of oxidation.which would then be more soluble.

The conditions of the reduction are as follows:-

Temperature 1100°C. to 1150°C.

Time- 1 hour 20 minutes.

Weight of residue -6.3 grams (after taking a sample for analysis).

Charcoal -20 grams,minus 200 mesh.

Analysis of residue,Fe. 9.40%,TiO_2 64.7%.

The reduction was effected in a closed crucible,heated in a gas-fired muffle.

The ore after reduction was not magnetic and so it could not be separated from the charcoal by means of a magnet. The charcoal was separated by shaking the ore which brought the charcoal to the top. The charcoal was then blown off,leaving a fairly clean product.

Treatment of the residue from the dilute acid leach.

The residue (5.33 grams) after reduction was treated with 35 c.c. of concentrated sulphuric acid for 2.5 hours and any excess acid was driven off. The product (12.75 grams after treatment with acid) now consisting mostly of iron and titanium sulphates was leached for 3.0 hours with 100 c.c. of water. The solution was decanted and the residue washed with water and weighed. The residue weighed 2.795 grams and contained 2.22% Fe. and 48.30% TiO_2. Thus 78.0% of the sulphates were water soluble. 46.40% of the TiO_2 and 83.50% of the iron dissolved in this leach. The solution was diluted to 130 c.c. by the washings from the residue and hydrolyzed at atmospheric pressure and at a temperature of 97°C. for 3 hours. Only 15.7 % of the TiO_2 in solution precipitated.

The product from the water leach was again heated to dryness with 5 c.c. of concentrated H_2SO_4 for 1.5 hours and leached with 200 c.c. of water at a temperature of 60°C. for 3.5 hours. Nearly all the remaining iron and some of the titanium went into solution. The solution was filtered off and hydrolyzed as in the previous case. (.115 grams of TiO_2 precipitated)·

The residue from the second leach with water was calcined at a dull red heat and weighed. It weighed 1.725 grams and contained about 28.0% of the TiO_2 present in the residue from the dilute acid leach.

The calcined products were not discolored as much as those obtained in the previous test.

Conclusions:-

A solution containing considerable amounts of iron and titanium sulphates seems to hydrolyze less readily than one containing a large proportion of titanium sulphate and in which the amount of ferrous sulphate is small.

The effect of Reduction on the Residue after Leaching with dilute sulphuric.

The following experiment was made to determine if more of the iron could be dissolved, without dissolving much of the titanium, after the residue from the first dilute acid leach is reduced with carbon at a higher temperature.

The conditions of the first leach were as follows:-

Twenty grams of reduced ore (Reductio No.7) were leached with 400 c.c. of 20.0% H_2SO_4 at 85° C. for three hours. The pulp was then filtered by a suction filter and the residue washed, dried and weighed. The residue weighed 9.65 grams and contained 6.51% iron and 58.0% titanium oxide. This gives an extraction of 19.0% of the titanium oxide.

This residue was mixed with 2.5 grams of minus 40 mesh charcoal and reduced in a gas-fired muffle for one hour at 1120° C. The charcoal was then separated from the reduced ore by blowing it away as the ore was not readily separated by a magnet.

The reduced ore was leached with 100 c.c. of 10.0% H_2SO_4 at 75° C. for two hours. The pulp was then filtered and the residue washed, weighed and analyzed. The residue weighed 5.17 grams and contained 2.44% iron and 58.1% titanium oxide.

The two leaches extracted 98.0% of the total iron and 32.48 % of the titanium oxide.

The second reduction is therefore of no advantage as too much of the titanium is lost in the solution and a complete separation of the iron is not effected.

REDUCTION with SULPHUR.

As sulphur acts as a reducing agent and has a great affinity for iron, experiments were made to ascertain if an iron sulphide would be formed in preference to a titanium sulphide. If the iron could be made to combine with the sulphur,the sulphide formed could then be leached with sulphuric acid,hydrochloric acid or ferric chloride,preferably the latter,as the sulphur could be recovered as a by-product .

Titanium forms sulphides corresponding to its oxides but in all probability they are unstable as there are no naturally occurring titanium sulphides.

In each case 10 grams of raw ore,crushed to minus 100 mesh,was mixed with its own weight of sulphur,placed in a crucible,sealed and heated in a gas-fired muffle. The operation,in most cases,was not continued longer than for one-half hour as it was feared that prolonged heating would drive off any combined sulphur and the ore would become oxidized.

Temperatures from 500°C. to 900°C. were recorded by a Hoskins thermocouple and above 900° C. by a Leeds Northrup Optical pyrometer.

The ore after reduction was leached with dilute sulphuric acid.

The analysis of the raw ore is as follows:-

Fe. 41.81% and TiO_2 32.4% .

REDUCTION TESTS.

Red. No.	Temp. C.	Time Hrs.	Analysis of Product.		
			% Fe.	%TiO_2	%S.
1.	500-550	1.5	41.95	33.0	1.40
2.	700-750	.5	41.53	33.0	3.76
3.	900-940	.5	40.79	32.4	5.74
4.	1050-1100	.5	43.57	33.2	6.22

Remarks. In reduction No.1 the reduced ore had a reddish tinge, showing that some iron oxide had been formed. In reductions 2 and 3 the reduced ore was black and slightly agglomerated. In reduction No.4 the reduced ore was slightly fused and quite difficult to crush.

The analysis shows that the sulphur content has increased with the temperature.

LEACHING.

A leaching test was made on each of the above reductions.

The conditions for each test were as follows:-

Charge -10 grams of reduced ore.

Leaching solution -200 c.c. of 20.0% H_2SO_4.

Temperature -90° C.

Time - 2 hours.

The results of the leaches are given in the following table:-

Leach	Material treated.				Residue			Extraction.	
No.	Wt. gms.	%Fe.	%TiO_2.	%S.	Wt. gms.	%Fe.	%TiO_2	%Fe.	%TiO_2.
1.	10	41.95	33.00	1.4	7.60	39.70	40.5	27.98	6.60
2.	10	41.53	34.20	3.76	7.11	32.57	42.2	44.00	11.60
3.	10	40.79	32.40	5.74	6.37	31.33	44.4	50.00	13.00
4.	10	43.57	33.20	6.22	5.60	29.51	49.2	63.50	17.40

Conclusions.

The extraction of iron after reduction by sulphur is in all cases less complete than after reduction by carbon, and the loss of titanium is relatively greater. It appears therefore that the sulphur process offers no advantages in comparison with the carbon reduction.

ELECTROLYSIS of FERROUS SULPHATE SOLUTIONS.

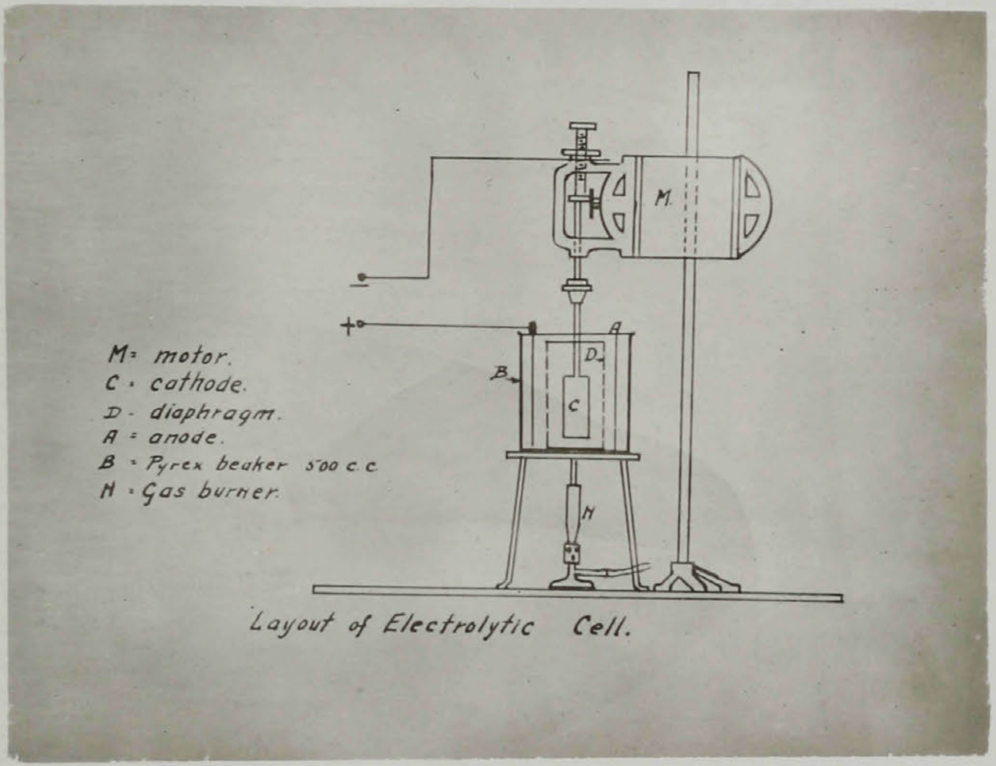
The following experiments in electrolysis were made on solutions of ferrous sulphate to ascertain some of the conditions necessary for the recovery of the iron. Electrolytic experiments were then carried out on iron - titanic sulphate solutions containing small quantities of iron to determine if a complete separation of the iron could be made.

Experiments Performed.

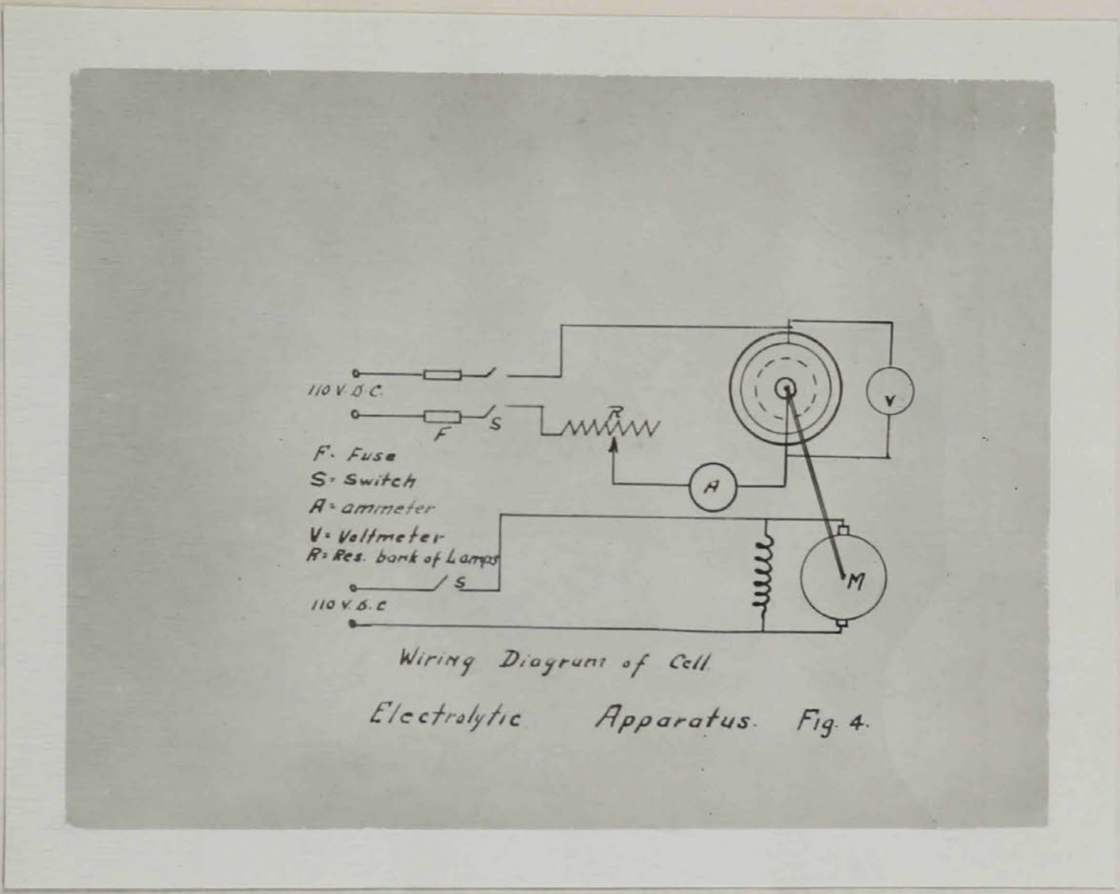
Apparatus. The cell consistedof a 500 c.c. pyrex beaker,divided into two compartments by a cylind rical asbestos diaphragm or porous clay pot. The asbestos diaphragm was 5 in. high and 2 in. in diameter. It was made of two layers of asbestos cloth fitted around a 2 inch wooden block and a wire frame at the top to support it in the cell. The porous clay pot was 4.12 inches high and 1.12 inches in diameter. A revolving cathode was used consisting of a steel rod machined to $\frac{3}{4}$ in. diameter and having an effective surface of 4.71 sq.in.(.0327 sq.ft.,.0968 sq.dcm.). The cathode was directly connected to a variable speed D.C. motor connected electrically to a 110 volt lighting circuit. Both graphite and lead anodes were used. The graphite anodes were 4.88 in.long,1 in. wide, and $\frac{1}{4}$ in. thick, supported in wooden frames and having screw connections at the top. The lead anode was cylind rical,being 4.5 in. high and 3 in. in diameter. Electrical connections were made by welding a copper wire to the lead lugs. The electrical supply was obtained from a 110 volt D.C. lighting circuit and the current regulated by a bank of lamps connected in parallel. The voltage was read at intervals by a five volt range Weston ammeter.

The electrolyte was heated by a gas burner placed under the cell.

The accompanying diagrams show the arrangement of the cell and electrical connections.



Layout of the Electrolytic Cell.



Wiring diagram of Electrolytic Cell.

The following tests (1 to 4 inclusive) are of a preliminary nature and were made to determine some of the conditions under which iron can be deposited from a ferrous sulphate solution.

RESULTS.

Test No.	Fe.gms. /100c.c.	Temp.°C.	Vol. c.c.	C.D.amps. /sq.ft.	e.m.f. volts.	Time min.	Current eff.%	R.P.M.
1.	6.59	62.5	400	45.8	2.25	60	----	500
2.	6.90	52.0	400	36.6	1.40	60	72.0	500
3.	9.49	50.0	450	42.8	1.40	40	90.0	800
4.	6.90	55.0	450	70.0	1.20	45	64.0	500

Remarks. The deposit in test No.1 was non-coherent and scaly but in No.2 it was fairly coherent. In each test an asbestos diaphragm was used and graphite anodes. In test No.

3 no diaphragm was used and the anodes were iron. The deposit in this case was smooth and coherent. In test No.4 an asbestos diaphragm was used and the anode was lead. The deposit was a little scaly and very brittle. Tests were also run in which no diaphragm was used and with an insoluble anode. The results were unsatisfactory.

Conclusions.

The concentration of the electrolyte must be high, so that the available iron ions at the cathode surface may be large.

A diaphragm is necessary to separate the ferrous and ferric iron. The catholyte must be completely ferrous to obtain the maximum current efficiency.

Hydrolysis occurs to some extent in any case but with an increase of temperature it takes place more readily.

The speed of the mandrel affects the deposit. To what extent was not determined, but the greater the speed the more coherent the deposit as there is less chance for the adhesion of the hydrogen bubbles. In[20] the deposition of iron from a ferrous chloride solution a speed of about 1200 r.p.m. gives the best results.

Experiments Series 2.

To deposit iron from solutions of low iron concentration (3 to 4 grams per 100 c.c.) it is necessary to have a low H-ion concentration. To obtain this condition potassium hydroxide was added to the electrolyte. In the first test no diaphragm was used and the anode was lead. In the second a porous clay pot was used and the potassium hydroxide added to the anolyte.

The results were unsatisfactory as iron hydroxide was formed in both cases and in the second case the catholyte became alkaline.

The next experiment was made on an iron-titanic sulphate solution obtained from the treatment of the residue of leach No.12. The solution contained 3.65 grams of TiO_2 and 0.616 grams of Fe. per 100 c.c. A porous clay pot was used as diaphragm. The cathode was the same as in the previous tests and the anode was lead.

The conditions of the test were as follows:-

Time.	Current density.	Volts.	Temp.°C.
50 mi.	22.8 amps./sq.ft.	4.5	20.0

After twenty minutes a five c.c. sample of the catholyte was analyzed for iron and the iron was found to have increased, the increase being due to the dissolving of the cathode by free acid or ferric sulphate. After forty minutes the catholyte showed a purplish tinge and at the end of the test it was a deep purple.

This[21] is due to the reduction of tetravalent titanium (titanic sulphate) to trivalent titanium (titanous sulphate) and it is probable that in electrolytic reduction in which there is a change of valency in the metal, the active agent is either the hydrogen which has been discharged on the surface of the metal or the metal of the electrode which is reprecipitated by the current. In this case the change of valency is most likely due to the hydrogen.

Conclusions.

The removal by electrolysis of small quantities of iron from ferrous sulphate solutions to which an alkali is added, during electrolysis, to lower the H-ion concentration does not appear promising and would not be a satisfactory method on a commercial scale as suitable conditions would be difficult to maintain.

Iron cannot be deposited from an iron - titanic sulphate solution and the change in valency of the titanium renders such a method impossible.

EXPERIMENTS in HYDROLYSIS.

The previous experiments have shown that iron could not be separated electrolytically from an iron-titanic sulphate solution.

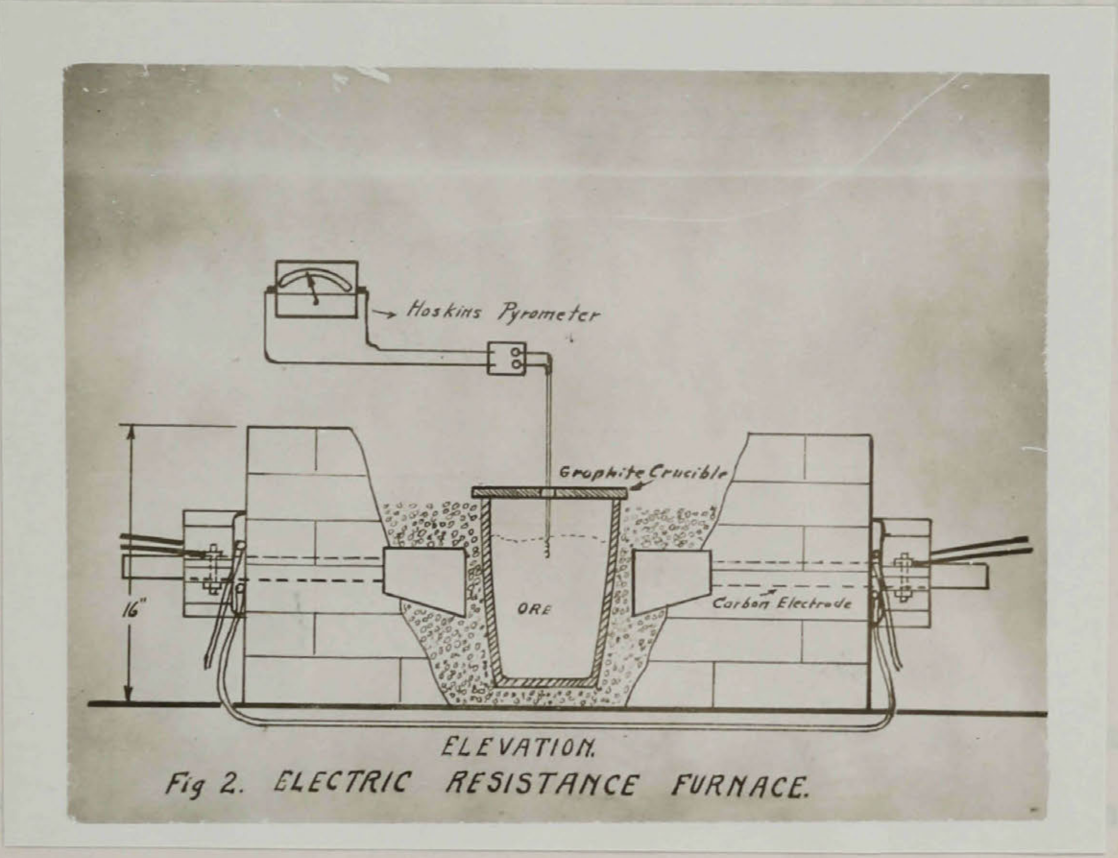
As the ratio of titanium to iron is high in the iron-titanic sulphate solution, obtained by treating the residue from the dilute acid leach with concentrated sulphuric acid, and dissolving the sulphate in water, experiments were made on precipitating the TiO_2 by boiling.

Experiments.

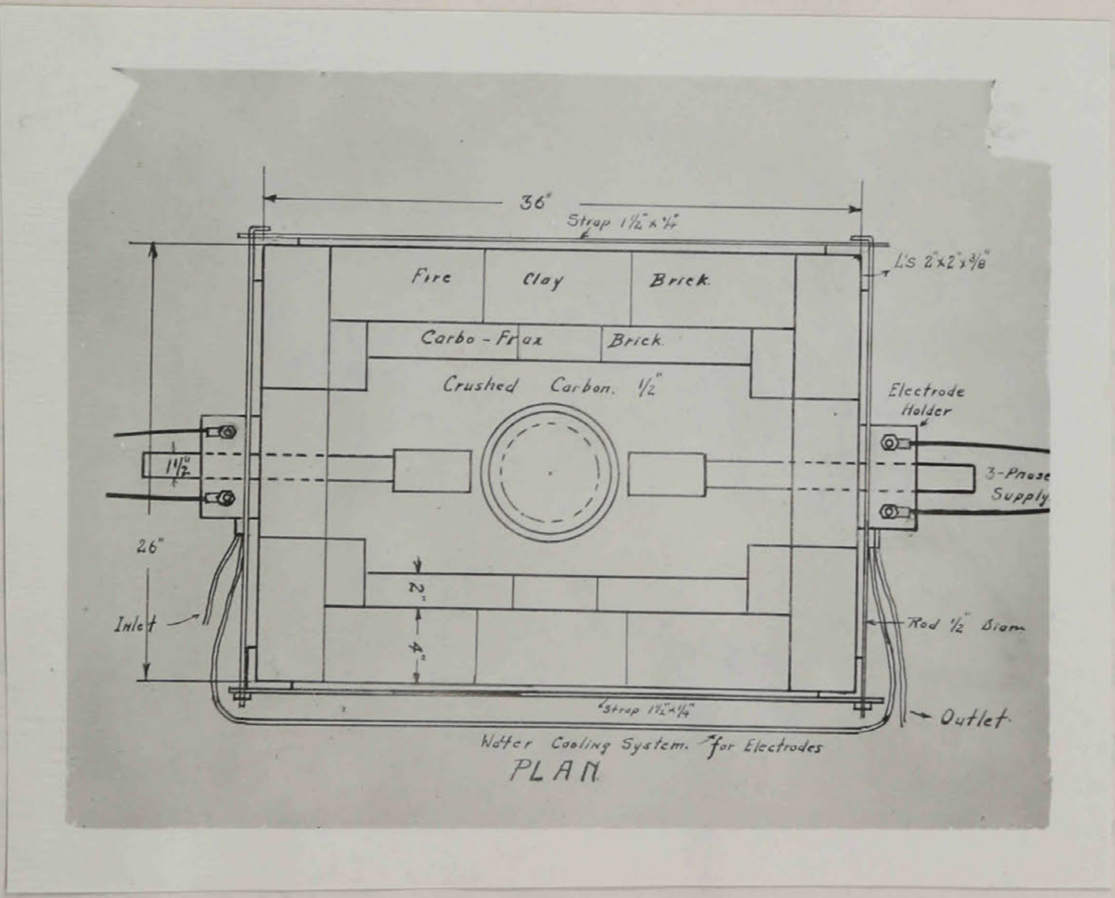
Reduction. Three pounds of minus 100 mesh ore was mixed with one pound of minus $\frac{1}{4}$ inch charcoal, placed in a graphite crucible and heated in an electric resistance furnace for one hour at a temperature of 1130° C. Temperatures were read every ten minutes by means of a Hoskins pyrometer.

The ore after reduction was crushed and separated from the charcoal by a Wetherill magnetic separator.

Elevation and plan of the electric resistance furnace used for reduction.



ELEVATION.
Fig 2. ELECTRIC RESISTANCE FURNACE.



PLAN

The analysis of the reduced ore is as follows:-

Fe. 44.68 % and TiO_2 34.8 % .

Leaching. For each test 25 grams of reduced ore was leached at 80° C. with 400 c.c. of 20.0% H_2SO_4 for 2 hours. The pulp was then filtered by a suction filter and the residue washed several times with hot water. The results of each leach are given in the following table.

Leach. No.	Residue. Wt. gms.	%Fe.	$\%TiO_2$	Extraction. %Fe.	$\%TiO_2$.
11	12.23	7.53	68.4	91.4	3.6
12	12.52	8.55	69.2	88.6	trace.
13	12.14	8.35	71.4	91.5	0.9
14	13.43	11.40	70.8	86.4	1.61

The percentage of iron and titanium extracted in leaches 11 and 12 is low. This is on account of the residue not being washed thoroughly.

These results show that only about 1.5% of the titanium is lost and that 90.0% of the iron is eliminated . This gives a very satisfactory product for future treatment.

Treatment of the Residues.

The residue from each test was digested with concentrated sulphuric acid(1.84 sp.gr.) on a hot plate at 135°C. The excess H_2SO_4 was then driven off and the sulphated mass lixiviated with 100 c.c. of cold water for two hours. The pulp was then filtered by suction and the residue on the filter washed with water. The washings were kept separate and used for the dilution of the solution to be hydrolyzed.

The conditions of each treatment are given in the following table.

No.	Residue grams	H_2SO_4 c.c.	Time hrs.	Wt. gms.	Final Residue. %Fe.	%TiO2	$\%SiO_2$	Ext. $\%TiO_2$.
11A	11.26	20	2.0	2.03	---	-----	----	----
12A	10.09	15	2.0	2.66	.02	61.0	27.0	77.1
13A	10.64	15	2.0	3.98	.81	67.4	22.0	64.5
14A	11.40	10	0.75	6.04	1.12	75.4	14.8	56.4

The weight of the residue treated does not correspond to that given above as samples were removed for analysis.

To ascertain how much of the residue from the first treatment with concentrated H_2SO_4 would be water soluble if treated the second time with concentrated H_2SO_4 the following experiment was made.

The residues ,13A and 14A were combined (8 grams) and treated with 8 c.c. of concentrated H_2SO_4 for one hour at 135° C. The sulphated mass was leached with cold water for one hour, filtered by suction and the residues analyzed with the following results:- TiO_2 52.4 % , SiO_2 46.4 % .

The total loss of titanium is about 16.0 % of the original ore.

HYDROLYSIS.

Hydrolysis[22] is the dissociation of a salt dissolved in water into the acid and the base from which it is supposed to be derived. Salts of weak acids and weak bases are the most easily hydrolyzed. The magnitude of hydrolysis depends on the actual strengths of the acid and the base which forms the salt in question. Dissociation is favoured by an increase in the quantity of water present and by a rise in temperature.

The following experiments were made on solutions resulting from the treatment of the residues. The conditions of each test and the percent extraction of TiO_2 are given in the following table.

Before dilution the original solution was boiled for 15 minutes, during which time considerable titanium precipitated. The solution was then diluted by using the washings previously mentioned and was boiled again.

Results.

Solution.							
Test No.	c.c orig. soln.	c.c final.	Temp. °C.	Time min.	TiO_2in orig.sol.	TiO_2 ppt'd.	%TiO_2 Ext.
11B	90	250	Boiling.	25	3.55	2.11	59.6
12B	130	200	''	20	5.50	1.72	31.2
13B	84	170	''	30	4.92	2.29	46.5
14B	92	250	''	45	3.44	1.88	54.6

Remarks. The precipitated TiO_2 was filtered by a suction filter and washed several times with hot water. The TiO_2 was then dried in an electric drying oven for several hours at 100° C. Numbers 11 and 12 were discolored slightly as the iron was not thoroughly washed out. No. 13 was chalk white and shows that a white pigment can be obtained in this way if sufficient care be taken in washing. In No. 14 sodium carbonate was added during electrolysis. The amount added was not sufficient to make the solution alkaline. As soon as a small quantity was added, iron hydroxide formed and then redissolved, but not completely, as the solution had a yellowish tinge. The precipitated TiO_2 after being thoroughly washed and calcined was distinctly yellow in color from the iron hydroxide.

Conclusions:-

These experiments indicate that the separation of TiO_2 by hydrolysis can be satisfactorily carried out if the conditions of acidity, temperature and dilution are carefully regulated.

No hydroxides of iron would be precipitated under suitable conditions.

The precipitated TiO_2 can be thoroughly washed with water by the counter-current system of decantation .

At a higher temperature and at the corresponding pressure the yield of TiO_2 would be increased considerably.

General Summary.

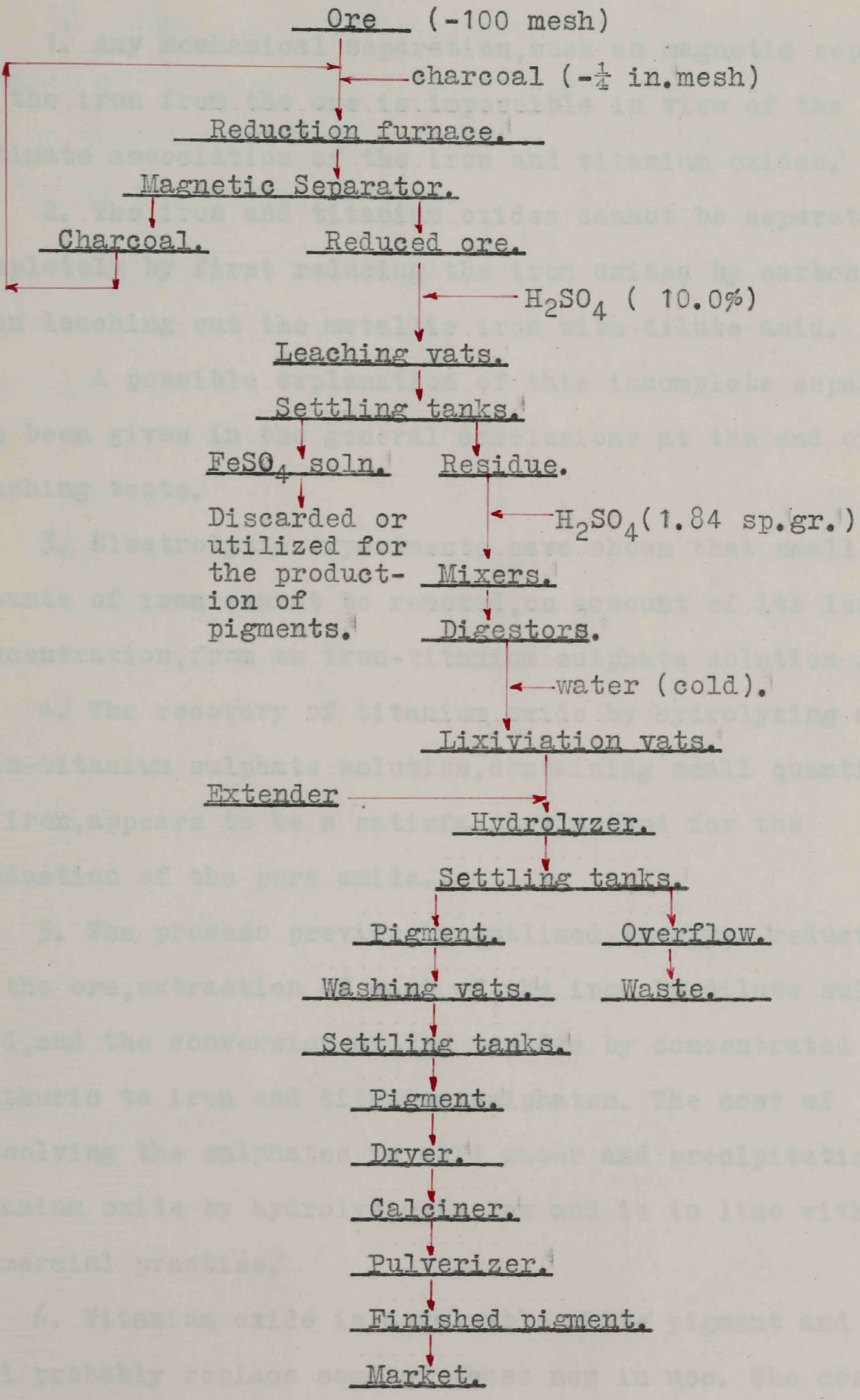
Unfortunately time did not permit further investigation of the separation of pure titanium oxide from ilmenite. The results obtained have indicated that a very simple and economical process for the production of pure TiO_2 from ilmenite can be worked out.

The process would involve grinding the ore to minus 100 mesh, reducing the iron oxides to metallic iron, by means of charcoal at a temperature of 1000° C., followed by magnetic separation to remove the reduced ore from the charcoal. The reduced ore is then leached with dilute sulphuric acid to remove most of the iron and the residue treated with sufficient concentrated H_2SO_4 (1.84 sp.gr.) to convert all titanium and iron to sulphates which are soluble in water. The solution obtained would then be hydrolyzed, diluted by the washings from the residue and hydrolyzed again. The residue would be retreated and the precipitated TiO_2 thoroughly washed by some suitable method such as the counter-current system . As TiO_2 is not used alone as a pigment but is mixed with some substance ,known as an extender, such as barium sulphate or calcium sulphate,it is advisable to add the extender during the precipitation of the TiO_2.

The ferrous sulphate liquor could be utilized for the production of pigments such as Prussian blue,Venetian red, yellow and red ochres.

The accompanying flow-sheet indicates the steps involved in the production of pure TiO_2 from ilmenite.

FLOW SHEET.


Ore (-100 mesh)
charcoal (-$\frac{1}{4}$ in.mesh)
Reduction furnace.
Magnetic Separator.
Charcoal.
Reduced ore.
H_2SO_4 (10.0%)
Leaching vats.
Settling tanks.
$FeSO_4$ soln.
Residue.
Discarded or utilized for the production of pigments.
H_2SO_4(1.84 sp.gr.)
Mixers.
Digestors.
water (cold).
Lixiviation vats.
Extender
Hydrolyzer.
Settling tanks.
Pigment.
Overflow.
Washing vats.
Waste.
Settling tanks.
Pigment.
Dryer.
Calciner.
Pulverizer.
Finished pigment.
Market.

GENERAL CONCLUSIONS.

1. Any mechanical separation, such as magnetic separation, of the iron from the ore is impossible in view of the intimate association of the iron and titanium oxides.

2. The iron and titanium oxides cannot be separated completely by first reducing the iron oxides by carbon and then leaching out the metallic iron with dilute acid.

A possible explanation of this incomplete separation has been given in the general conclusions at the end of the leaching tests.

3. Electrolytic experiments have shown that small amounts of iron cannot be removed, on account of its low concentration, from an iron-titanium sulphate solution.

4. The recovery of titanium oxide by hydrolyzing an iron-titanium sulphate solution, containing small quantities of iron, appears to be a satisfactory method for the production of the pure oxide.

5. The process previously outlined, involves reduction of the ore, extraction of most of the iron by dilute sulphuric acid, and the conversion of the residue by concentrated sulphuric to iron and titanium sulphates. The cost of dissolving the sulphates in cold water and precipitating the titanium oxide by hydrolysis is low and is in line with good commercial practise.

6. Titanium oxide is a valuable white pigment and it will probably replace some of those now in use. The cost of production must necessarily be such as to enable it to compete with the better known pigments, andthe trade must be

educated in the advantages obtained from its use.

7. Large quantities of ilmenite are available in Canada and an important titanium industry can be established if an economic process is worked out for the recovery of titanium oxide from these ores.

In concluding the writer wishes to express his appreciation to the following who rendered assistance in carrying out this investigation.

Dr. A. Stansfield	Prof. of Metallurgy.
R.H.Monk	Vice-Pres. M^{c}Arthur Irwin Paint Co
Dr.Otto Maass	Associate Prof. of Chemistry.
Dr. F.M.G.Johnson	Prof. of Inorganic Chemistry.
R.P.D. Graham	Assoc.Prof. of Mineralogy.

Part Four.

APPENDIX.

References.

1. Robinson H.H. ,Titanium,Mines Branch ,Ottawa.

2. Hopkins B.B. ,Chemistry of the Rarer Elements.

3. Bulletin 616,U.S. Geological Survey.page 21.

4. Proceedings of the Paint and Varnish Society,page21.

5-6. Heaton Noel, Production of Titanium Oxide and its use as a paint material, Royal Society of Arts,May3rd. 1922.

7. Patent papers from U.S. patent office.

8. Robinson H.H., Titanium.Mines Branch Ottawa.

9. Iddings, Rock Minerals.

10. Iddings, Igneous Rocks,Volume One.

Miers Henry A. ,Mineralogy.

10. Heinze's Carl Dr. ,Handbuch der Mineralogie,vol.12,

11. Snelling W.O. ,Titaniferous ores,U.S.Geological Survey, Mineral Resources,1901.p.p. 271-278.

12. Bulletin 64. Titaniferous Iron ores in U.S.

13-14-15. Warren C.H. ,Economic Geology,vol.13,1918,pp.419.

16. Hoffman H.O. ,General Metallurgy.

Stansfield A. ,"The reduction of iron ores at moderate temperatures",Report to the Advisory Research Council, May, 1921.

Stansfield A. and Harrison D.R. , Reduction of Iron ores by CO. ,Royal Society of Canada,May 1922.

Matsubara A. Chemical Equilibrium between Fe. ,C. , and CO. Trans. Amer.Inst. of Min.andMet. Vol.lxv11 ,p.3,1922.

17. Liddell D.M. Handbook of Chemical Engineering ,Vol.1.

18. Allamand,Applied Electrochemistry.
    Evans W., Metals and Metallic Compounds.Vol.1.

19. Dulieux E.,Iron ore Resources,Que.,Can.Inst.Min.andMet.
    pages 381-7.Vol.16-1913.

20. Experimental work,Metallurgical Depart.M^{c}Gill University.

21. Duthlem D.and ForrestenF.,Z.physik.Chem.,62 -1908.

22. Evans,Metals and Metallic Compounds. Vol.1.
    Jones, Theory of Solutions.

23. Richards, Metallurgical Calculations,Vol.1.

24. Hoffman H.O., General Metallurgy.

Bibliography of Titanium.

'Titanium oxide',Electrochemical and Met. Industry,1907, vol. 7,page 285.

Barnes J. 'Use of titanium compounds as Mordants and Pigments',Jour. of Soc. Chem.Ind.,1899.vol.18,pp.15-16.

Langier,'Experiences sur la Purification et la Reduction des Oxides de Titans et de Cerum' Ann.de Chemie, 1824,vol.lxxxix, pp. 306-324.

Singewald J.T. Jr. Titaniferous Iron ores of U.S.,Bull.64, U.S. Bureau of Mines,1913.

Robinson H.H.,Titanium, Mines Branch,Ottawa.

Washburn W. Proceedings of the Paint and Varnish Society, March,1922.

Heaton Noel,Production of Titanium Oxide and its use as a paint material,Royal Society of Arts, May 3,1922.

Barton L.E. Titanium Oxide,Met.and Chem. Feb.1st.1917. pp. 164-439.

'Titanium Paint Industry in Norway', Met.and Chem. p.845,1920

Carteret G., Process for treating titanium ores containing iron, Chemical Age,Sept. 30th. 1922.

'Titanox' booklet by the Titanium Pigment Co. Niagara Falls, New York.

Calculations.

Reduction. Calculations showing the theoretical amount of carbon required to reduce the iron oxides in the ilmenite ($FeO.TiO_2,n.Fe_2O_3$) to metallic iron are as follows:-

From the equations.

(1) $FeO + C = Fe. + CO.$
$71.85 + 12$

One gram of FeO requires $\frac{12}{71.85} = .167$ grams of carbon.

(2) $4Fe_2O_3 + 9C = 3CO_2 + 6CO + 4Fe_2.$
$638.8 + 108$

One gram of Fe_2O_3 requires $\frac{108}{638.80} = .170$ grams of C.

Analysis of ore, 28.95% FeO.,27.78% Fe_2O_3.

In 5 grams of ore FeO. equals 1.44, Fe_2O_3 equals 1.39 grams.

Theoretical carbon required:-

(1) 1.44 x .167 = .241 grams of C.

(2) 1.39 x .170 = .236 " " " ".

Total .477 grams of C.

Calculations showing the method of arriving at the percentage of Reduction.

In calculating the percent reduction of the ore only the iron oxides FeO and Fe_2O_3 were considered to be reduced. It was also assumed that the ratio of iron plus titanium oxide to insoluble would be the same in the original and the reduced ore.

100 grams of the original ore contains,

TiO_2	32.4	grams.
Fe.	41.818	'' .
SiO_2	3.92	'' .
Al_2O_3	1.70	'' .
O_2	15.50	'' .
Total	94.838	grams.

The oxygen is the amount combined with the iron to form the amount of FeO theoretically present in the ilmenite plus the oxygen combined with the remaining iron, which is assumed to be in the form of Fe_2O_3.

100 grams of reduced ore contains,

TiO_2	39.00	grams.	85.856 grams.
Fe.	47.38	'' .	
$Al_2O_3+SiO_2$	6.55	'' .	$= 5.62 \times \frac{39.0+47.38}{32.4+41.80}$
O_2	1.908	by diff.	
Total	94.838		

The oxygen found by difference, 1.908 grams, is reduced to the equivalent amount in the original ore as follows:-

$$1.98 \times \frac{32.4 \quad 41.80}{39.0 \quad 47.40} = 1.65.$$

The percentage reduction is then, $\frac{15.5 - 1.65}{15.5} \times 100 = 89.5$

Leaching with ferric chloride.

To determine the amount of standard ferric chloride required for a given concentration of solution.

The equation of reaction is as follows:-

$$2FeCl_3 + Fe. = 3FeCl_2.$$

Molecular wts.324.4+55.84

$FeCl_2$ to dissolve one gram of iron= $\frac{324.44}{55.84}$ =5.81 grams.

Say iron in the ore 44.29%.

No. of grams of ore required to give 1 gram of iron=

$$\frac{1}{.4429} = 2.22$$

Therefore one gram of ore requires $\frac{5.81}{2.22}$ =2.62 grams of ferric chloride.

Ratio of ore to $FeCl_3$ equals 1: 2.62.

Concentrations are taken as grams of ferric chloride per litre.

If 20 grams of ore are used, 20 x2.62 =52.4 grams $FeCl_3$ per litre are required.

There are 162.22 grams $FeCl_3$ in 1000 c.c.

" is 1 gram " " $\frac{1000}{162.22}$ = 6.8 c.c.

The amount of standard solution required = 52.4 x 6.8= 366 c.c. To make up to 1 litre add 644 c.c. of water.

This gives a solution having a concentration of 52.4 grams of $FeCl_3$ per litre.

Calculation of e.m.f. required for the decomposition of ferrous sulphate.

The e.m.f.[23] required to decompose a compound may be calculated, approximately from its heat of formation.

From Richard's tables of thermo-chemical constants of bases to dilute solution per chemical equivalent of base and acid radical.

$$FeSO_4 = Fe^{++} + SO_4^{=}.$$

$$\tfrac{1}{2}Fe^{++} = 10900 \text{ cal.}$$

$$\tfrac{1}{2}SO_4^{=} = 107.000 \text{ cal.}$$

The heat of formation of $FeSO_4$ = 2(10,900) + 2(107,000) 235.800)calories.

The heat of formation of water = 69,000 calories.

As sulphuric acid is formed and heat is therefore generated; its heat of formation, 210,200 calories must be deducted from the sum of the above as shown by the equation.

$$\begin{array}{ccccc} FeSO_4 & + & H_2O & = & Fe. + H_2SO_4 + \tfrac{1}{2}O_2. \\ 234,900 & + & 69,000 & & 210,200 \end{array}$$

The final heat of combination = 304,800-210200 = 94,600

Decomposition voltage x number of coulombs = heat of formation x 4.2 (mechanical equivalent of heat).

To liberate one gram equivalent of any element it requires 2 x 96540 coulombs.

$$\text{Decomposition voltage} = \frac{94600 \times 4.2}{96540 \times 2} = 2.06 \text{ volts.}$$

2.06 volts is the voltage required for the decomposition of ferrous sulphate if insoluble anodes are used.

Calculation[24] for the quantity of iron deposited per ampere hour.

One coulomb (1 ampere per second) liberates .000010384 grams of hydrogen, which is the electro-chemical equivalent (e.c.e.) of hydrogen. To find the e.c.e. of any other element multiply its chemical equivalent, that is, atomic weight divided by its valency, by .000010384.

$$\text{e.c.e. for iron} = \frac{55.84}{2} \times .000010384 = .0002899 \text{ grams.}$$

To find the weight of an element deposited by electrolysis, multiply the e.c.e. by the strength of the current (amperes) and the time (seconds) during which it flows.

A current of one ampere flowing for one hour through a vat containing divalent iron will deposit iron equal to

$$\underset{(\text{e.c.e.})}{.0002899} \times 1 \times \underset{(\text{sec.})}{(60 \times 60)} \quad 1.042 \text{ grams of iron.}$$

$$\text{The current efficiency} = \frac{\text{Actual iron deposited}}{\text{Theoretical}} \times 100 =$$

x percent.