AN IMPROVED METHOD FOR THE ACID DECOMPOSITION OF CERTAIN SILICATES

By

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INTRODUCTION

The natural mineral resources of the United States are the source of our industrial strength and as high grade ore reserves are depleted, we must be prepared through an improved technology to utilize progressively lower grade raw materials. The United States was the only active combatant in the second World War whose continental territory, cities, and industrial plants were practically untouched by war. This nation not only paid dearly in blood and treasure, however, but has drawn heavily on its mineral resources in achieving final victory.

As a result we now face the disturbing fact that the country's reserves of high and medium grade metalliferous ores have been reduced to a point where our self-sufficiency is seriously threatened. Instead of having exportable surpluses, we are actually importing ores that were formerly supplied abundantly from domestic sources.

Undoubtedly conditions are still very abnormal, and mining development has not kept pace with actual mining operations; nevertheless, the fact remains that the demand for high grade ores of many metals is far greater than our present ability to produce them.1/

Many deposits of marginal and submarginal ore exist in the United States which have not previously been utilized because of processing difficulties and/or economic considerations. For example, the taconites of the Mesabi Range, the manganese nodules of the Dakotas, and the greensands of the east coast may be our future source of iron, manganese, and potash. Before such raw materials can be effectively absorbed in

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1/ Waggaman, W. H. and Gee, E. A., Titanium and Zirconium, Metals of Industrial Promise: Chem. and Eng. News, vol. 26, No. 6, 1948, pp. 377-381.

our industrial use pattern, however, great advancements in processing methods must be made. Not only will better equipment, improved materials of construction, and superior instrumentation be required, but also fundamental advances in the basic theories underlying mineralogical chemistry.

The silicates comprise the largest chemical group among minerals, although in general, industry has avoided their use as raw materials. Potentially silicates represent tremendous domestic reserves of vital commodities such as chromium, lithium, potash, aluminum, soda, zirconium, to mention but a few examples. One obvious reason for their restricted use has been general refractoriness to chemical decomposition. Advancements in equipment design and improvements in materials of construction, however, have resulted in a revaluation of their possibilities, especially in the last decade.

An important barrier to the more extensive use of silicates by alkaline decomposition has been the loss of soda or caustic ordinarily employed. This is particularly true when highly siliceous aluminiferous minerals are treated, operating costs in general being a direct function of the silica content of the raw material. The aluminum industry, for example, imports millions of pounds of bauxite annually from South American deposits although the very ground we walk upon contains substantial amounts of this metal. In an attempt to decrease this dependence on imports, an especially critical factor in time of national emergency, the Government constructed four demonstration scale plants during the last war to treat domestic aluminum bearing silicates. Although not economically competitive with foreign raw materials, the processes developed indicated the feasibility of producing this

essential metal from natural silicates.

Similarly, the formation of unfilterable silicic acid gels during acid decomposition has long been a primary barrier to commercial exploitation by this processing method. Separation of the gelatinous or colloidal hydrated silicic acid and metallic hydroxides from the leach solution represents the main difficulty.

Marginal copper, zinc, or vanadium ores, for example, may be leached with acid resulting in the formation of large quantities of silicic acid gel. Recovery of the metallic values from the leach liquor by electrolysis or precipitation necessitates elimination of the gel by filtration or sedimentation. The former alternative requires extremely large filtering areas at high capital expense and the latter excessive dilution with subsequent increases in both thickener capacity and final volume of filtrate for evaporation.

The investigation described in this report, dealing with the acid decomposition of silicates, was carried forward by the author through the facilities of the Bureau of Mines as part of that agency's broad war-time program to develop processes for the extraction of strategic metals from domestically abundant raw materials. As previously pointed out, the separation of silicic acid gel from leach solutions is an important, if not the most important barrier to the wider utilization of acid decomposition and this particular thesis is specifically concerned with the various factors influencing the separation.

After an examination of the basic theory underlying all silicate decomposition by acid and experimental studies on a typical mineral silicate, it was hoped that existing theory with regard to separation techniques could be extended to other minerals. The silicate

mineral olivine was selected because large domestic deposits are present in the mountains of western North Carolina, and in the Puget Sound region of Washington. Estimated reserves of these deposits, averaging 45 - 49 percent magnesia and carrying small amounts of chrome and nickel, are tremendous. The North Carolina deposit alone is reported to contain 230 million tons of ore.2/ In both regions the mineral is readily accessible and can be mined economically; one large Washington deposit is located at Tidewater.

Although the sea represents a virtually inexhaustable source of magnesium and its compounds, olivine has an attractive potential value. It contains magnesium in an extremely high percentage (28 - 30 percent); it contains chromite, nickel, and silica, all of which are possible by-products; it is free of calcium, a common contaminant of magnesium minerals, and boron, a detrimental factor in electrolytic cell operation; and it is, of course, readily attacked by acids with excessive gel formation.

2/ Hunter, C.E., Forsterite Olivine Deposits of North Carolina and Georgia: North Carolina Department of Conservation and Development, Bull. 41, 1941, 117 pp.

CHAPTER I

HISTORICAL

Silicon is second only to oxygen with regard to abundance in the earth's crust and past investigations have built up a tremendous background of knowledge concerning the element and its compounds. Little generalization can be made concerning the chemical and physical characteristics of silicates, however, and even after an exhaustive analysis of the literature, the conclusion is inevitably reached that immediate progress in their utilization must be based primarily on the prosaic technique of trial and error.

A. Chemistry of Silicates.

The silicates are mineralogically grouped as oxygen salts by Dana, and comprise the largest chemical group among minerals.3/ Their wide range of composition frequently results in complex compounds. X-ray studies revealed that the fundamental structural unit of all silicates has a tetrahedral shape with four oxygen atoms surrounding each atom of silicon and these SiO_4 groups may be linked together in various ways to form indefinitely extended series. In the orthosilicates, (R_2SiO_4) these SiO_4 groups are independent of the other elements present as is the case with ordinary chemical compounds such as carbonates, sulfates, etc. In other types of silicates, however, the SiO_4 groups are linked together through the sharing of one or more atoms of oxygen

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3/ Dana, E. S., A Textbook of Mineralogy, Revised by Ford, W. E.: New York, John Wiley and Sons, Inc., 1932, pp. 532.

with neighboring groups. When two adjacent silicate groups have one atom of oxygen in common, individual groups with such formulas as Si_2O_7, Si_3O_9, Si_4O_{12}, Si_6O_{18} may occur. Further, the SiO_4 groups may form chains in which oxygen atoms of adjacent groups are held in common. Single chains of this type corresponding to composition SiO_3 occur in pyroxene. In amphibole two such chains may be linked, giving a composition represented by Si_4O_{11}. Such chains on further linking give rise to the micas represented by a silicon-oxygen sheet, with a composition of Si_2O_5. Finally, linking of the silicon oxygen chains may take place to give a three dimensional network. This is characteristic of the different forms of silica such as quartz, and by allowing a partial replacement of silicon by atoms such as aluminum an extended acid network may be obtained into which basic atoms can be introduced. The latter structure may be considered characteristic of the zeolites, where metallic atoms may be artifically substituted for each other and the water content varied without disturbing the fundamental structure. In these various silicon oxygen structures, metallic atoms serve to bind the whole structure together. Wherever isomorphous replacement occurs the number of oxygen atoms remains constant for each unit cell of the structure. Variations may involve the substitution of Si by Al, of Al, Mg, and Fe by each other, etc. Bragg stated, "that a silicate may be regarded as a structure having a constant number of oxygen atoms in the unit, with a constant number of places for metal and silicon which can be filled by these elements in varying proportions consistant with a balance between valencies." 1/

1/ Bragg, W. L., The Structure of Silicates: Zeit. Krist., vol. 74, 1930, pp. 237-305.

Although Bragg postulated his theory in 1930, reclassification of silicates has lagged and the conventional classification employed by Dana is still almost universally utilized.

Silicates are in part strictly anhydrous, although a great many contain water of hydration or constitution. A large number of silicates yield more or less of their water content on ignition, and in many cases they are, therefore, regarded as basic or acid silicates. A line between the hydrous and anhydrous silicates cannot be sharply drawn, however, as many species that yield water upon ignition have an indefinite combination with hydrogen and oxygen.

The general mineralogical classification of silicates employed by Dana is described in outline form below.5/

Anhydrous Silicates

a. Disilicates, Polysilicates.

Disilicates, R Si_2O_5 are considered salts of disilicic acid, $H_2Si_2O_5$ with an oxygen ratio of silicon to bases of 4:1.

Polysilicates, $R_2Si_3O_8$, are salts of polysilicic acid, $H_4Si_3O_8$ with an oxygen ratio of 3:1.

b. Metasilicates.

Metasilicates, R SiO_3, are salts of metasilicic acid, H_2SiO_3, and have an oxygen ratio of 2:1.

c. Orthosilicates.

Orthosilicates, R_2SiO_4, are salts of orthosilicic acid, H_4SiO_4, and have an oxygen ration of 1:1.

5/ Dana, E. S., op. cit., pp. 534-640.

d. Subsilicates.

Subsilicates have an oxygen ratio of less than 1:1 and their true position is often in doubt; in most cases they are probably best regarded as basic salts belonging to one of the other groups.

It should be noted that the above classification is not strictly applicable and there are many species which do not exactly conform to any one of the groups named and often a true interpretation of the composition is impossible. Alternate classification schemes more recently developed and based completely on X-ray studies will probably replace the time worn mineralogical system.

Hydrous Silicates

The silicates of this second major subdivision include the true hydrous compounds with water of crystallization (zeolites); also hydrous amorphous species (clays). Other species such as micas, talcs, which yield water on ignition are no doubt structually related to the members of the preceding groups, orthosilicates, etc.

a. Zeolite Division.

Zeolites in general have an Al_2O_3: $CaO+Na_2O$ ratio of 1 and a Al+Si : O ratio of 1:2, for example, anorthite $CaO.Al_2O_3 \cdot 2SiO_2$.

b. Mica Division.

All species embraced under this division have the characteristic micaceous structure, that is they have highly perfect basial cleavage and yield easily thin laminae, for example, common mica, $2H_2O \cdot K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$.

c. Serpentine and Talc Division.

Principally composed of magnesium silicates similar in structure

to some members of the previous group, for example, serpentine, $3MgO.2SiO_2.2H_2O$.

d. Kaolin Division.

Usually composed of hydrous, clay-like masses; either compact, friable or brittle, for example kaolinite $2H_2O.Al_2O_3.2SiO_2$.

e. Miscellaneous.

Composed chiefly of silicates of the heavy metals such as iron, manganese; for example, chloropal, $2H_2O.Fe_2O_3.2SiO_2$.

A classification scheme based on Bragg's X-ray analyses was proposed by Berman and will ultimately replace that described above as it is a fundamental advance in mineralogical classification.6/

Starting with the basic relation that a silicon atom always occurs at the center of four oxygen atoms arranged as a tetrahedron about it the theory is systematically constructed. A universal rule is that two tetrahedra can only have one atom of oxygen in common between them and they can be shared at corners only, not sides or edges. Every oxygen atom of every tetrahedron may, however, be shared with another tetrahedra. If the tetrahedra are not combined with each other, the composition of the silicate is of the SiO_4 type; if all the corners are shared with other tetrahedra, the composition is that of the different forms of silica, SiO_2. Other relations yield intermediate types.

This concept, and the classification of silicates arising from it, is not simply another way of indicating a new group of silicic acids, because silicates cannot be regarded in this new theory, as acid radicals

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6/ Berman, H., Constitution and Classification of the Natural Silicates: The Amer. Mineralogist, vol. 22, 1937, pp. 342-408.

with the metallic elements. They must be considered as frameworks of silicon-oxygen tetrahedra indefinitely extended in the crystal. Acid compounds are made up of discrete radicals not joined together like silica tetrahedra.

Berman concludes that the following classification covers with few exceptions the total field.

I	Silica type	Z:O = 1:2
II	Disilicate type	Z:O = 2:5
III	Metasilicate type	
	Chains	Z:O = 3:8
		Z:O = 4:11
		Z:O = 1:3
	Rings	Z:O = n:3n
IV	Pyrosilicates	Z:O = 2:7
V	Orthosilicate	Z:O = 1:4

Z indicates the silicon-like atoms which include also Al in part; O refers to oxygen-type atoms such as OH and F.

Within each type the broadest division is families, the families in turn are divided into groups, the groups into isomorphous series and the series into species.

Silicate minerals that are decomposable by mineral acids such as hydrochloric or nitric fall into two broad categories: (1) Those minerals whose silica does not dissolve in acid but is left behind as residual separated silica when the mineral undergoes decomposition and (2) Those minerals that decompose completely in acid to yield a solution which is filtered with difficulty because of the silicic acid gel formed. The distinction between these two groups formed the

basis of an early classification scheme of minerals.7/ In very large excesses of acid the second group dissolves completely to yield a solution which sets to a firm silicic acid gel.

It should be noted that the majority of silicate minerals are unattacked or only slightly attacked by acid and are not included in the above grouping.

An interesting clue to the physical difference between the residual silica of the first group and the silicic acid gel of the second group is given by Brunauer. The former when dried has a surface area of about 80 square meters per gram while the latter has about 600 square meters per gram.8/

Murata has made extensive tests on the minerals of group 2 and correlated the gelatinizing behavior of silicates with internal structure.9/

Owing to the relatively large size of the oxygen atoms bonded to the silicon atoms, these silicon-oxygen structures dominate the internal structure of silicate minerals and largely determine their physical and chemical properties. Aluminum, as previously pointed out, freely substitutes for silicon, giving structures made up not only of SiO_4 tetrahedra but SiO_4 and AlO_4 tetrahedra linked together. Other bases such as calcium, magnesium, sodium and potassium are distributed

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7/ Brush, G. J. and Penfield, S. L., Manual of Determinative Mineralogy: New York, John Wiley and Sons, Inc., 1898, 312 pp.

8/ Brunauer, S., The Absorption of Bases and Vapors: Princeton Univ. Press, 1943, vol. 1, p. 298.

9/ Murata, K. J., Internal Structure of Silicate Minerals that Gelatinize with Acid: The Amer. Mineralogist, vol. 28, 1943, pp. 545-562.

variously and neutralize the excess negative charges of the silicon and aluminum oxygen structures.10/

When silicate minerals that gelatinize are classified according to their silicon oxygen structures, it becomes immediately apparent that they may be listed as follows:

1. Orthosilicates.

2. Pyrosilicates.

3. Possibly ring structures with three silicon atoms.

4. Possibly ring structures with six silicon atoms.

5. Sheet structures that contain considerable ferric iron substitution for silicon.

6. Three dimensional structures that contain sufficient aluminum substitutions for silicon to give an aluminum to silicon ratio of at least two aluminum atoms to three silicon atoms.

The gelatinization of orthosilicates is not surprising in view of the extensive literature on this phenomena. 11/ The gelatinization of pyrosilicates establishes the fact that a silicon-oxygen unit containing two silicon atoms also will form a silicic acid gel. Murata conclusively demonstrates that all elements exclusive to the silicon oxygen framework, like potassium, calcium, magnesium, zirconium, and fluorine, have negligible influence in determining whether a mineral gelatinizes or separates insoluble silicon. This assumption is justified by the fact that no correlation is apparent between these elements and silicate behavior toward acids. On the other hand, elements like

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10/ Murata, K. J., The Significance of Internal Structure in Gelatinizing Silicate Minerals: Geological Survey Bull. 950, 1946, pp. 25-33.

11/ Carman, P. C., Constitution of Colloidal Silica: Faraday Soc. Trans., vol. 36, 1940, pp. 964-973.

aluminum and iron, which occur within the silicon-oxygen framework as substitutes for silicon directly affect the behavior of these frameworks under acid attacks.12/

This conclusion is most important. In general we are primarily interested in the recovery of the elements outside the silicon-oxygen framework and if it can be successfully demonstrated that a particular silicate can be treated for economic recovery of its metallic value there is an excellent chance the results can be extrapolated to the entire second group, i.e. gelatinizing silicates.

Based on the work of Murata, we can, therefore, summarize that silicate minerals that dissolve in the usual mineral acids fall into two groups based on internal atomic structure.

1. Those minerals containing silicate radicals of low molecular weight, namely orthosilicates, pyrosilicates and possibly ring structures of three and six silicon atoms.

2. Those minerals of larger continuous silicon-oxygen frameworks that will disintegrate into units of low molecular weight under acid attack. This group contains disilicates, sheet structures, and three dimensional structures that contain aluminum in the ratio of two aluminum atoms to three silicon atoms.

Minerals that give insoluble silica instead of gelatinising are characterized by silicon-oxygen structures of large dimensions that do not disintegrate into small units under acid attack. These structures are SiO_3 chains, Si_4O_{11} double chains, Si_2O_5 sheets not containing large amounts of ferric iron replacing silicon, and three-dimensional frame-

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12/ Murata, K. J., The Significance of Internal Structure in Gelatinizing Silicate Minerals: Geological Survey Bull. 950, 1946, p. 28.

works having an aluminum content less than the ratio of two aluminum atoms to three silicon atoms.

B. Theories of Silicate Gelation.

With our present knowledge concerning gels and their general behavior any system resulting from the acid decomposition of a silicate containing, in addition to silicic acid, dissolved salts and metallic hydroxides, is necessarily a complex mixture. This complexity does not prohibit, however, the establishment of certain basic characteristics of silicic acid gels.

An excellent summary has been prepared by Hurd and the following data and discussion are largely taken from his results.13/ By definition a silicic acid gel is a semi-solid elastic mass which results when a "gel" sets. Frequently this term is erroneously applied to colloidal silicic acid which for the purpose of this discussion will be defined as a fluid mixture containing hydrated silica. Silica gel designates the harder, partially dehydrated product.

Silicic acid gels will result from almost any solution containing, as a sol, over 2 percent silica and the time of set will be a function of concentration of silica, temperature, pH and concentration of salts. The viscosity of any fluid of such a system is a direct function of the extent of gelation.

When initially formed, silicic acid seems to be composed of molecules of low molecular weight which, at first, will pass with

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13/ Hurd, C. B., Theories for the Mechanism of the Setting of Silicic Acid Gels: Chem. Reviews, vol. 22, 1938, pp. 403-422.

electrolytes through membranes, however, with lapse of sufficient time no silicic acid will pass. 14/

It is extremely difficult to remove last traces of electrolytes by washing and the pH of the silicic acid asymptotically approaches 7.15/ Silicic acid is charged positive in acid solution and negative in alkaline solution.16/ This may be due to adsorption of ions or to amphoteric ionization of the silicic acid which can leave the silicon in either a negative or positive ion.

One of the most striking properties of a sol of hydrated silica is its great insensitivity toward ions which ordinarily cause coagulation of colloids. Data available demonstrate conclusively the insensitivity of colloidal silicic acid toward electrolytes.17/

Three different theories of the structure of silicic acid gels exist.

a. The emulsion theory assumes that the gel consists of a liquid-liquid system with an emulsoid structure.18/ This theory is not well supported.

14/ Mylius, F. and Groschuff, E., (Studies on Solutions of Silicic Acid): Ber. 39, 1906, pp. 116-125.

15/ Kargin, V. A. and Rabinovitch, A. J., Some Electro-chemical Properties of Colloidal Silica: Faraday Soc. Trans., vol. 31, 1935, pp. 284-297.

16/ Losenbeck, O., (Electro-chemical Properties of Silicic Acid Sols): Kolloid.-Beihefte, vol. 16, 1922, pp. 27-46.

17/ Laskin, E., (The Electrolytic Coagulation of Colloids): Kolloid-Zeit., vol. 45, 1928, pp. 129-136.

18/ Ostwold, W., and Fischer, M. H., An Introduction to Theoretical and Applied Colloid Chemistry: New York, John Wiley & Sons, Inc., 1922, p. 102.

b. The cellular theory postulates that the liquid part of the gel is held in small droplets in a cellular structure made up of the solid phase.19/ This mechanism fails to explain syneresis or evaporation from silicic acid gels.

c. The fibrillar theory appears to have maximum support; it postulates both a continuous solid and continuous liquid phase, with the solid forming a fibrous structure containing the liquid in the pores.20/ It is further postulated that the interlaced fibrillar or brush heap structure consists of very large polysilicic acid molecules. To prepare these large molecules we assume that (1) silicon hydroxide is formed as the first step of the process (2) this hydroxide is amphoteric giving either hydrogen or hydroxyl ions. It is well established that particles of hydrated silica are positive in strongly acid solutions and negative in neutral and basic solutions.21/

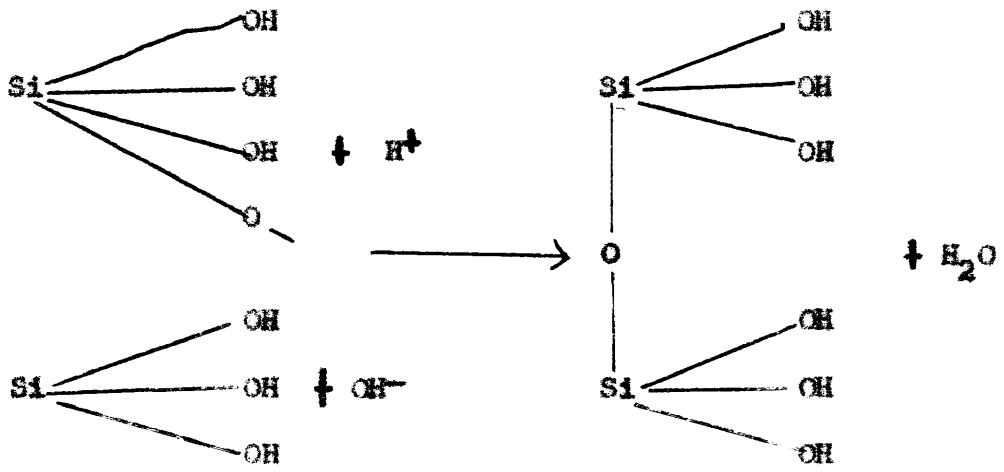
$$\underset{\text{(acid solutions)}}{OH^- + Si^{+}(OH)_3} \longleftarrow Si(OH)_4 \longrightarrow \underset{\text{(basic solutions)}}{SiO^-(OH)_3 + H^+}$$

(3) Condensation between positive and negative ions of the above type occurs and the time of set is a function of the frequency of collision which is in turn a function of temperature, concentration, and pH. Minimum set should occur when there are approximately equal numbers of acidic and basic ions, which would be the case near pH = 7. Condensation probably proceeds as follows:

19/ Buchner, E. H., Myricyl Alcohol Jellies: Rev. Trav. Chim., vol. 42, 1923, pp. 787-789.

20/ Hurd, C. B., loc. cit.

21/ Losenbeak, O., loc. cit.



(4) The water remains combined, or absorbed in the structure.

C. Previous Methods of Decomposition.

As previously outlined in the introduction, the separation of silicic acid gel and leach solutions resulting from the acid decomposition of silicates is one of the primary barriers to this method of attack. Numerous patents and literature references are available which supposedly improve the filtration characteristics of such slurries and, in general, they fall into four broad groups.

The first and largest group consists of various techniques whereby the effective acid concentration is maintained at a high value, thus minimizing gel formation through dehydrating action and the maintenance of low water-silica ratios. Koehler 22/ and Houston 23/, for example, advocated the use of gaseous hydrogen chloride to decompose silicates.

22/ Koehler, W., Process for the Reduction of Ores: U.S. Patent 824,663, June 26, 1906.

23/ Houston, E. C., and Rankin, H. S., Olivine as a Source of Magnesium Chloride: Am. Inst. Min. and Met. Eng., Tech. Pub. 1484, Min. Technol., 1942, 4 pp.

The latter states:

> A convenient method of treatment which prevents the formation of gelatinous silicic acid consists in treating crushed dry olivine with sufficient concentrated aqueous acid to wet the particles or passing anhydrous hydrogen chloride through moist olivine. Under these conditions, the reaction is rapid and considerable heat is evolved, which serves the double purpose of promoting the complete consumption of the acid and also the dehydration of the mixture.

After an extensive pilot plant campaign by the Tennessee Valley Authority and the University of Georgia, this method was abandoned because of prohibitive mechanical difficulties and excessive cost. Subsequent work by Houston followed the procedure which will be developed by this author although he failed to utilize the stage digestion technique.24/

Also in this group may be included the work of Chalmers, who used a rather ingenious capillarity process whereby sulfuric acid slowly rises through a bed of silicate and the exothermicity of the reaction together with the constant rate of acid consumption prevents gel formation.25/ Goldschmidt evaporates extract slurries obtained by conventional digestion to dryness, thus dehydrating the gel present and on subsequent leaching minimizes gelation of the silica.26/ Jourdan suspends the silicate in a cage having a perforated bottom and open top and encloses the entire mass in a cylinder provided with a

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24/ Houston, E. C., Magnesium Manufacture from Olivine: Amer. Inst. Min. and Met. Engr., Tech. Pub. 1828, Met. Technol., 1945, 14 pp.

25/ Chalmers, H. B., Method of Producing Magnesium Compounds: U.S. Patent 2,402,370, June 18, 1946.

26/ Aktieselskabet De norske Saltverker av Bergen, (Magnesium Sulfate from Rocks): Norwegian Patent 36,429, Jan. 2, 1923.

lower well of aqueous acid. By heating coils a wet saturated acid vapor is obtained which attacks the mineral silicate and the resulting soluble salts drip into the chamber below.27/ Peacock and Butt employ large excesses of ore to accentuate the effect of temperature on gel formation. 28/, 29/. Moxham avoids the use of dilute solutions by crystallizing, from strong acid, complex alums with recycling of the acid liquor.30/

The primary difficulties of all of the procedures outlined above result from mechanical complexity and the lack of satisfactory materials of construction. Metal and metal salts obtained from silicates are in general of low value, and it is not feasible to use high cost batch operations in gas tight autoclaves or similar reaction vessels. For this reason none of these procedures have ever achieved industrial utilization.

The second group advocates the use of dilution to permit settling or thickening of the extract slurries after completion of the decomposition cycle. Houston employed this technique in the second Tennessee Valley Authority pilot plant at Wilson Dam. This procedure requires large thickeners and decantation tanks because of the low concentration of salts in the final leach liquor.31/ In addition the evaporation

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27/ Jourdan, F., Process for the Treatment of Silicates with Acids in Order to Obtain Their Soluble Salts: U.S. Patent 1,976,564, Oct. 9, 1934.

28/ Peacock, S., Processing Producing Magnesium Compounds: U.S. Patent 1,205,659, Nov. 21, 1916.

29/ Butt, C. A., and Hallman, A. D., Process for Manufacturing Iron Free Magnesium Sulfate from Certain Minerals: U.S. Patent 2,375,749, 1945.

30/ Moxham, A. J., Process for Treating Siliceous Minerals: U.S. Patent 1,748,989, March 4, 1930.

31/Houston, E. C., loc. cit.

requirements are grossly increased if it is necessary to recover the metallic salts as solids or concentrated liquors. It is possible that such dilution aids in flocculating colloidal silicic acid.

The third group which might be considered a sub-group of the second advocates the use of very dilute acid with the prevention of temperature rise. Dilution as in the second group plays an important part but is not the primary consideration. Brandenberg utilized 2N hydrochloric acid and recycled through a series of layers of ore in such a fashion that the ratio of solid to solution was approximately 4 to 1.32/ The same worker states that sulfurous acid is the preferable leaching agent, and its use prevents the formation of excessive gelation.33/ Archibald and Hubler conducted extensive research on the acid decomposition of New Caledonia silicates by percolation leaching of coarse ore with 4-15 percent hydrochloric acid.34/ Blanc advocated passing extract slurry through a bed of previously leached residue to selectively absorb colloidal silica.35/ Jordis reports the greater the dilution the finer and more flocculent are precipitates of silicic acid obtained from water glass solutions.36/ As with the second

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32/ Brandenberg, H. R., Process for Recovering Magnesium Salts: U.S. Patent 2,384,009, September 4, 1945.

33/ Brandenberg, H. R., Method of Producing Magnesium Sulfate: U.S. Patent 2,384,010, June 8, 1943.

34/ Archibald, F. R., and Hubler, W. G., Private Communication: October 29, 1946.

35/ Blanc, A., Method for the Removal of Colloidal Silica from Mixed Solutions Obtained During the Treatment of Silicates with Acids: U.S. Patent 1,851,033, March 29, 1932.

36/ Jordis, E., (Silicic Acids or Colloidal Silica): Zeit. Anorg. Chem., vol. 44, 1905, pp. 200-208.

group the primary obstacles to industrial exploitation are the excessive costs of evaporation to produce solid or concentrated liquors and the accompanying increased capital cost for equipment.

The fourth and last group is concerned with various neutralization schemes to improve the filtration rate. Stevens et al, claim granular silica can be produced from a gelatinous phase suspended in a metal bearing solution by subjecting the slurry to a temperature of 50 to 65° C. in the presence of an excess of base such as magnesia in order to neutralize all free acid.37/ Deinbolt claimed similar results by using magnesium carbonate in large excess as the neutralizer to precipitate iron, nickel, and chromium hydroxides in oxidized form at about 70° C. He concludes the effect is due to the precipitated hydroxides.38/ This technique was utilized to some extent by the author and the behavior of silicic acid gels in solutions of various pH's was thoroughly investigated.

Titration curves show that silicic acid is an acidosol. The first addition of alkali quickly neutralizes the hydrogen ion of the colloidal acid and causes a coagulation of the silicic acid particles. Further addition of alkali peptizes the acid and produces a highly hydrated form.39/ Others report that strong acid may produce coagulation of colloidal silica but in general weaker acids stabilize the

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37/ Stevens, R. H., Norris, G. C., and Watson, W. N., Removal of Silica from Metal-Bearing Solutions: U.S. Patent 1,843,006, January 26, 1932.

38/ Aktieselskabet De norske Saltverker av Bergen, (Treatment of Magnesium Sulfate): Norwegian Patent 36,429, Jan. 2, 1923.

39/ Treadwell, W. D. and Konig, W., Colloidal Silicic Acid: Helv. Chim. Acta., vol. 16, 1933, pp. 468-478.

solution.40/ Weiser and Ray report that neutral or slightly acid mixtures coagulate most rapidly and with increasing concentration of acid the rate falls off then increases rapidly once more, possibly due to the dehydrating action of the acid.41/ 42/ Davis summarizes as follows: "On increasing the concentration of acid one finds four types of systems, stable alkaline negative silica sols, rapidly setting sols, stable acid positive silica sols and gels in concentrated acid systems."43/ Somewhat in contrast to the data of Weiser and Ray, Fleming reports that the velocity of gelation of silica gel is a minimum near the neutral point and becomes progressively greater in regions of high acidity or alkalinity and that other influences do not alter the characteristic shape of the curve.44/ Cole observed that granular silica may be obtained on precipitation from alkali silicates by the use of buffer salts such as NH_4Cl or NH_4NO_3. 45/

Although many of the references cited apply to the general case of stabilized sol vs. gel, it is apparent that coagulation of colloidal silicic acid is dependent upon the pH of the environment and neutral or slightly acid solutions at high temperature have a maximum coagulation velocity.

40/ Krestinskajo, V. N., and Natanson, N. E., The Action of Hydrochloric Acid on Colloidal Silicic Acid: U.R.S.S., Acta Physiochim., vol. 7, 1937, pp. 915-936.

41/ Weiser, H. B., Inorganic Colloid Chemistry: New York, John Wiley and Sons, Inc., vol. II, 1935, pp. 193-228.

42/ Ray, R. C. and Ganguly, P. B., The Optimum Conditions for the Formation of Silica Gels from Alkali Silicate Solutions: Jour. Phys. Chem., vol. 34, 1930, pp. 352-358.

43/ Davis, H. L. and Hay, K. D., Study of Setting Times of Silica Gels with various Acids: J. Am. Chem. Soc., vol. 61, 1939, pp. 1020-1023.

44/ Fleming, W., (On the Coagulation of Colloidal Silicic Acid): Zeit. Phys. Chem., vol. 41, 1902, pp. 427-457.

45/ Cole, E. K. and Evans, N. L., Manufacture of Precipitated Silicate: Brit. Patent 561,750, June 2, 1944.

CHAPTER II

STATEMENT AND ANALYSIS OF PROBLEM

A. Statement of the Problem.

The basic obstacle to the successful industrial utilization of many acid reactive silicates has been emphasized; in short it is the inherent difficulty in separating gelatinous solids from resulting leach solutions.

There are numerous methods utilized by the industry for the separation of solids and liquids although in general they usually fall into three broad groups: filtration, centrifugation and sedimentation. Equipment from all three groups had been utilized by previous workers with limited degrees of success and it appeared that the problem was logically one of changing the character of the gelatinous solids rather than devising new equipment and/or separation methods.

In general when the filtration properties of a slurry are improved one also finds improvement in centrifugation or sedimentation. Although frequently considered a simple operation, in reality filtration is one of the more difficult unit operations of chemical engineering. As any material will vary in its filterability with changing conditions, and as practically all materials differ under the same conditions, the complexity of filtration as a subject and the difficulty of applying any workable principles or formula is apparent.46/

46/ Dickey, G. D. and Bryden, C. L., Theory and Practice of Filtration: New York, Reinhold Publishing Corporation, 1946, p. 30.

B. Analysis of the Problem.

As pointed out by Genter:

> Pressure produces filtrate flow simultaneously with solid packing into the cake. . . . . In reality the various factors of these equations in some way measure the physical properties of the solids involved. If we understand these properties, we can maintain sludge and filter conditions which influence economic optimal yields providing the filter itself is properly constructed, installed and operated. 47/

He then lists ten general factors to be considered in any filtration operation.

1. Effective filter area.
2. Filtration pressure.
3. Solid - liquid ratio in slurry or sludge.
4. Rate of deposition of solids.
5. Resistance of filter cloth to liquid flow.
6. Time by which rate factors are measured.
7. Coefficient of viscosity of filtrate of sludge.
8. Temperature.
9. Nature of solids (density, particle size, compressibility).
10. Resistance of filter cake to liquid flow.

It is obvious that an increase in filter area will increase the overall rate of solid - liquid separation but this results in prohibitive equipment costs. In fact the large filter area required per volume of slurry handled prevented to a large degree previous exploitation of numerous silicates. Preliminary tests indicated rates as low as 1-2 gal./sq.ft.hr. are obtained which are not considered economical when

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47/ Genter, A. L., Principles and Factors Influencing Vacuum Filtration of Sludge; Sewage Works Journal, vol. 13, no. 6, 1941, pp. 1164-1204.

handling large tonnages of liquid.

Rates of filtration are dependent on the magnitude of the applied pressure although this dependence is not always a direct relation. With compressible sludges as are frequently encountered in the decomposition of silicates a point is reached beyond which increases in pressure actually result in a decrease in rate. Beyond this critical point the added driving force of increased pressure is more than offset by the increased resistance to liquid flow of the compressible cake.48/ Obviously, filter pressure for compressible sludges must be maintained at a value below the critical point and maximum practical pressures have negligible effect on the rate of filtration for the products of silicate decomposition.

In making separation studies there are obviously two methods of expressing the rate of filtration: (a) in units of filtrate per unit of time or (b) in units of solid per unit of time. The solid in this case is principally silicic acid gel and to express adequately the rate by method (b), the use of dry solid weight is necessary due to the variable hydration of the gel. Therefore, as the product of principal value is contained in the liquor and as the solid is of variable composition (a) is the preferable method of rate expression. It should be noted, however, that decreasing the solid-liquid ratio will result in an increase in the volumetric rate, possibly without any increase in the

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48/ Badger, W. L. and McCabe, W. L., Elements of Chemical Engineering: New York, McGraw-Hill Book Co., Inc., 1936, pp. 470 - 502.

gravimetric rate. Dilution of the decomposition mixture was employed by other investigators with the previously described difficulties, (Reference 24) and variation of the solid-liquid ratio was not considered further.

The rate of deposition of solids is especially important in the separation of gelatinous solids of colloidal size. In general the filter fabric is rarely the true filtering medium. The average particle of precipitate or crystal is usually much finer than the opening between cloth fibers and the real filtering medium is the layer of solid first deposited on the cloth. If the initial pressure is high this first layer is usually compacted into the pores of the cloth resulting in a low rate of filtration throughout the cycle. While low initial pressures may result in a cloudy discharge at the beginning of the cycle, the effect is more than offset by the more rapid overall filtration rate and consequently higher capacity.49/ Precoat filters have a coat of porous filter aid applied to the drum surface before initial solid deposition to prevent such clogging and the scraper blade removes on each revolution a small layer of the filter aid in addition to the solid deposited. The thickness of the cake and therefore its resistance to liquid penetration varies with the rate of deposition of solids. Neither of these variables have any appreciable effect on the filtration characteristics of the gelatinous slurries from silicate decomposition.

Resistance of filter cloth is usually of small significance as indicated in the preceding paragraph and utilization of this factor to

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49/ Badger, W. L. and McCabe, W. L., loc. cit.

achieve increased rates of filtration offered no promise.

The sixth factor, time by which rate factors are measured, is of only academic interest to this particular problem as long as all rates are measured under similar conditions and compared ultimately to industrially acceptable values.

The only practical methods for lowering the viscosity of filtrates encountered in this investigation are increased temperatures and dilution of the decomposition slurry. The disadvantages of the latter were previously discussed. Viscosity usually varies as an inverse function of temperature and the maximum attainable temperature is therefore desirable under atmospheric conditions; this value is limited only by the boiling point of the liquid which, wherever practical, is indicated. Higher temperatures are reached only in autoclaves which usually represent high cost batch operations with expensive equipment of special design.

The first eight factors theoretically capable of affecting filtration rates were eliminated without further consideration leaving only the nature of the solids and the resistance of the filter cake to liquid flow for evaluation. These two variables may well be jointly considered as they are obviously interdependent.

Thus, the problem, as previously suggested, narrows to a consideration of those factors affecting the physical structure of the gelatinous solids and the basic considerations may be outlined as follows:

First, in any investigation of a chemical reaction in a liquid system there are, in general, three variables to consider: time, temperature and concentration. By fixing any pair of variables desired data usually can be obtained as a function of the third. A thorough

analysis of silicate decomposition with regard to these three variables was necessary to determine their effect on the nature of the solids subsequently obtained.

Second, consideration must be given to artificial methods, for example, filter aids. Non-compressible porous solids such as diaspore, when added to difficulty filtering slurries, frequently effect marked improvement in rates. The possibility of similar results with the system under consideration may not be overlooked.

Third, it was noted during evaluation of previous investigations that improvement in rate was achieved by neutralization of the reaction mixture and such conclusions must be thoroughly evaluated.

Fourth, as physical state may vary from discrete crystals to highly hydrous gels by manipulation of external conditions, i.e. barium sulfate, a study of all factors affecting the gelation of silicic acid is indicated. Ideally there is desired a method of increasing the density of the fibrillar structure of the silicic acid to a point where its capacity for water absorption is minimized.

There are considerations in regard to gelation other than those of time, temperature and concentration outlined above although in the last analysis each may be considered an extension of one of these fundamental variables. For example, a routine experiment in chemical microscopy is the crystallization of salts with and without the addition of small quantities of starch or agar. In the first case there is obtained on cooling large well formed crystals while in the second their results a mush of finely divided solid. It is well known that nucleation and crystal growth are competing processes; at low supersaturation both are extremely low but the latter predominates. It is also known that

the former predominates with increasing supersaturation and with restricted movement of the precipitated or crystallized phase. While this phenomena is not based on gelation phenomena it is reported by Szper that coagulation and crystallization are analogous processes and the denaturation of albumin attains a maximum velocity at a certain minimum concentration of acid. The reaction is believed to be of the third order involving autocatalysis.50/

The author was particularly impressed in making the literature review of gelation theory by the similarity between this phenomena and that of polymerization in organic chemistry. Consider for example, the polycondensation of adipic acid and hexamethylene diamine. One pair of molecules react:

$$HO_2C(CH_2)_4COOH + H_2N(CH_2)_6NH_2 \rightarrow HOOC(CH_2)_4CO{\cdot}NH(CH_2)_6NH_2 + H_2O$$

The molecule produced has a carboxyl group at one end and an amino group at the other; the former can react with another hexamethylene diamine molecule and the latter with another adipic acid molecule. Two of these chains can also react together to condense out a molecule of water. The stepwise condensation continues until the reagents are consumed resulting in the familiar nylon. High molecular weights can be reached and no unique molecular weight can be assigned.

The discovery of the silicones represents another class of polycondensation products, linking silicon and carbon polymerization chemistry. Trimethyl chlorosilane on hydrolysis yields hexamethyl disiloxane as the corresponding silicol is incapable of existence.

50/ Szper, J. and Uzdanska S., Velocity of Coagulation of Colloids: Roczinki Chem., vol. 14, 1934, pp. 579-589.

$$2(CH_3)_3\ SiCl \rightarrow 2(CH_3)_3SiOH \rightarrow (CH_3)_3\ SiOSi(CH_3)_3 + H_2O.$$

When dimethyl dichlorosilane is hydrolyzed, a long chain molecule is built up by a repetition of the above type reaction, in which the repeating unit is the $\left[-OSi(CH_3)_2-\right]$ group.

Thus the necessary condition which reagents must satisfy in order to give a polycondensation product is that they contain two groups per molecule which can react to reject a smaller molecule, thus linking the parent compounds by covalent bonds while still retaining active end groups. Further, linear polymers, as far as their physical bulk properties are concerned, do not fit completely into any one of the three conventional categories of solid, liquid or gas, although they possess certain similarities to all three.51/

Contrasting the foregoing theory currently postulated for organic polymerization with the previously described theories of gelation, one cannot fail but conclude that there exist certain links between the two theories. The author is certain that in this analogy lies a fertile field for fundamental research of real significance. This concept was used only to a limited extent in solving the present problem although the technique of seeding the reaction mixture is based primarily on similar operations in organic chemistry.

C. Selection of a Particular Silicate.

Before undertaking experimental studies it was necessary to select a particular silicate for initial work. The mineral silicate

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51/ Fuoss, R. M., The Physical Chemistry of Polymers: Amer. Scientist, vol. 36, No. 1, 1948, pp. 75-101.

olivine had definite potentiality from both a national and economic point of view, and its possible value was discussed at some length in the introduction. Specifically it possessed some or all of the following advantages over alternate choices:

I. Economic

A. Potential source of magnesium, chromium and nickel.

B. Very abundant.

C. Easily mined.

D. Numerous investigators had evaluated its use with limited success.

E. Closely related structurally and chemically with other potentially valuable minerals.

II. Chemical

A. Readily attacked by mineral acids.

B. Forms excessive quantities of silicic acid gel on decomposition.

C. Almost unfilterable slurries result under normal decomposition.

D. Mineralogically it is a member of the orthosilicates, a very large group exhibiting without exception, gelation on decomposition.

Olivine is typical of the orthosilicates described by Berman and Murata with the general formula $(xMg.yFe)_2\ SiO_4$. X and y are mole fractions of Mg_2SiO_4 and Fe_2SiO_4, respectively, so that $x + y = 1$. As the principal value of this mineral is for the manufacture of magnesium chloride which in turn is used in Dow magnesium cells or to produce magnesia, hydrochloric acid was selected as the logical mineral acid

for initial work. Olivine reacts with hydrochloric acid according to the equation

$$(xMg.yFe)_2\ SiO_4 + 4\ HCl \rightarrow 2xMg\ Cl_2 + 2yFeCl_2 + H_2O{\cdot}SiO_2 + H_2O.$$

The possibilities of olivine as a raw material have been considered by numerous investigators both in this country and abroad, although processing difficulties have prevented appreciable commercial exploitation. 52 - 72/ A small plant for producing magnesium sulfate was operated for some time at Webster, North Carolina and is believed to be the only domestic installation.

Difficulty is frequently encountered in the commercial exploitation of techniques and processing methods derived from small scale laboratory tests. It was essential therefore that any hypothesis developed in the laboratory on the engineering aspects of the study be demonstrated in a process pilot plant where conventional materials of construction and industrial equipment could be utilized.

An evaluation and extension of any generalized hypothesis might then be made by actually decomposing a series of alternate silicates. Finally, the hypothesis if definitely proven could be postulated as a theory.

52/ Pawel, G. W., Olivine: Potential Source of Magnesia: Min. and Met., vol. 23, 1942, pp. 331-3.

53/ Hunter, R. M., The Electrochemistry of the Dow Magnesium Process: Trans. Electrochem. Soc., vol. 86, 1944, pp. 21-32.

54/ Brandenburg, H. R., Recovering Magnesium: U.S. Patent 2,210,892, August 13, 1940.

55/ Brandenburg, H. R., Serpentine as a Source of Magnesia: Min. Jour. (Ariz.), vol. 24, Oct. 15, 1940, pp. 2-3.

56/ Truman Committee, Report 10, part 17, 78th Cong., 2d Sess., March 13, 1944, pp. 51-53.

57/ Terpugov., S. V., Tiktina, A. M., Obtaining Magnesia Alba and Magnesia Usta from Serpentine: U.S.S.R., Jour. Chem. Ind., vol. 15, No. 9, 1938, pp. 9-11.

58/ Koehler, W., Recovery of Nickel from Oxide and Silicate Ores: Electrochem. and Met. Ind., vol. 6, 1908, pp. 145-147.

59/ Brown, C. E., Method of Obtaining Metallic Compounds from Silicates: U.S. Patent 1,492,016, April 29, 1924.

60/ Jackson, Louis L., Process of Extracting Metals from Silicates: U.S. Patent 1,305,969, June 3, 1919.

61/ Peacock, E., Process of Decomposing Natural Silicates: U.S. Patent 1,310,770, July 22, 1919.

62/ Peacock, S., Process of Extracting Magnesium Compounds from Magnesium Bearing Rocks: U.S. Patent 1,250,216, Dec. 18, 1917.

63/ Peacock, S., Process of Making Magnesium Compounds from Silicate Minerals: U.S. Patent 1,231,423, June 26, 1917.

64/ Aktieselskabet De norske Saltverker av Bergen, (Treatment of Silicates containing Magnesium): Norwegian Patent 37,109, April 9, 1923.

65/ Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry: Longmans Green & Co., New York, vol. 6, 1925, pp. 385 and 388.

66/ Oganesyau, M. A., (Treatment of Serpentine): Russian Patent 52,891, March 31, 1938.

67/ Magnesium Elektron Ltd., Magnesium: British Patent 508,647, July 4, 1939.

68/ Gire, G. and Fouquet, R., (Extracting Magnesium): French Patent 733,294, May 21, 1931. British Patent 382,899, Nov. 3, 1932.

69/ Belik, V. F., (Chlorination of Serpentines): U.S.S.R., Jour. Appl. Chem., vol. 12, 1939, pp. 1610-19.

70/ MacIntire, W. H., Producing Anhydrous Magnesium Sulfate: U.S. Patent 2,298,493, October 13, 1942.

71/ Gill, A. F., Thermal Decomposition of Certain Minerals and Salts: Canadian Jour. Research, vol. 10, 1934, pp. 703-712.

72/ Lloyd, R. R., Stoddard, C. K., Mattingly, K. L., Leidigh, E. T., and Knickerbocker, R. G., Pilot Plant Production of Electrolytic Magnesium from Magnesia: Am. Inst. Min. and Met. Eng., Tech. Pub. 1848, Metals Technol., 1945, 25 pp.

CHAPTER III

EXPERIMENTAL RESULTS

In order to fully evaluate the potentiality of olivine as a source of magnesium and valuable by-products it was necessary to determine the optimum conditions of operation on a laboratory scale and subsequently translate the findings to a process pilot plant. The results of these tests then provided the basis of a hypothesis for the achievement of improved filtration characteristics of slurries resulting from the acid decomposition of olivine and alternate silicates. The line of testing outlined in Chapter II was followed throughout.

A. Raw Materials and Apparatus

In Table 1 are listed all of the silicates tested together with their source, general formula and mineralogical group. Table 2 gives their chemical analyses and Table 3 their screen analyses.

TABLE 1. - General Data on Silicates Tested

Common Name	Source	General Formula	Classification
Olivine	Spruce Pine, N.C.	$(Mg,Fe)_2SiO_4$	Orthosilicate
Serpentine	Butte, Montana	$Mg_3Si_2O_7 \cdot 2H_2O$	Disilicate
Beryl	Beryl Mt., N. H.	$Be_3Al_2Si_6O_{18}$	Metasilicate
Kaolin	- , Ala.	$Al_4Si_4O_{10}(OH)_8$	Disilicate
Garnierite	Riddle, Oregon	$H_2(Ni,Mg)SiO_4 \cdot nH_2O$	Orthosilicate
Chlorite	Sheridan, Wyo.	$Mg_5Al_2Si_3O_{10}(OH)_8$	Disilicate
Chryostile	- , Va.	$(Mg,Fe)_6Si_4O_{11}(OH)_6 \cdot H_2O$	Metasilicate
Sodalite	Bancroft, Ont.	$Na_8Al_6Si_6O_{24} \cdot Cl_2$	Silica type
Talc	- , Ga.	$Mg_3Si_4O_{10}(OH)_2$	Disilicate
Wollastonite	Essex, N. Y.	$CaSiO_3$	Metasilicate
Heulandite	Crawfordsville, Oreg.	$H_4CaAl_2Si_6O_{18} \cdot 3H_2O$	Silica type

TABLE 2. - Chemical Analyses of Silicates Tested

Common Name	MgO %	SiO_2 %	FeO %	NiO %	BeO %	Al_2O_3 %	Ca %	Na_2O %	Cl %	Ignition
Olivine	47.2	42.5	7.5	0.35	-	-	-	-	-	2.3
Serpentine	42.0	46.3	5.4	0.25	-	-	-	-	-	6.9
Beryl	-	09.2	-	-	12.8	18.0	-	-	-	1.2
Kaolin	-	49.6	-	-	-	36.0	-	-	-	13.1
Garnierite	23.0	39.5	8.3	3.8	-	8.0	-	-	-	19.5
Chlorite	32.6	30.1	5.2	-	-	17.3	-	-	-	13.6
Chryostile	40.2	42.3	3.0	-	-	1.0	-	-	-	14.1
Sodalite	-	38.1	-	-	-	31.5	-	25.2	7.2	-
Talc	31.5	61.5	1.7	-	-	1.0	-	-	-	4.5
Wollastonite	1.0	49.2	-	-	-	-	46.7	-	-	4.0
Heulandite	-	58.1	-	-	-	16.5	7.5	-	-	16.0

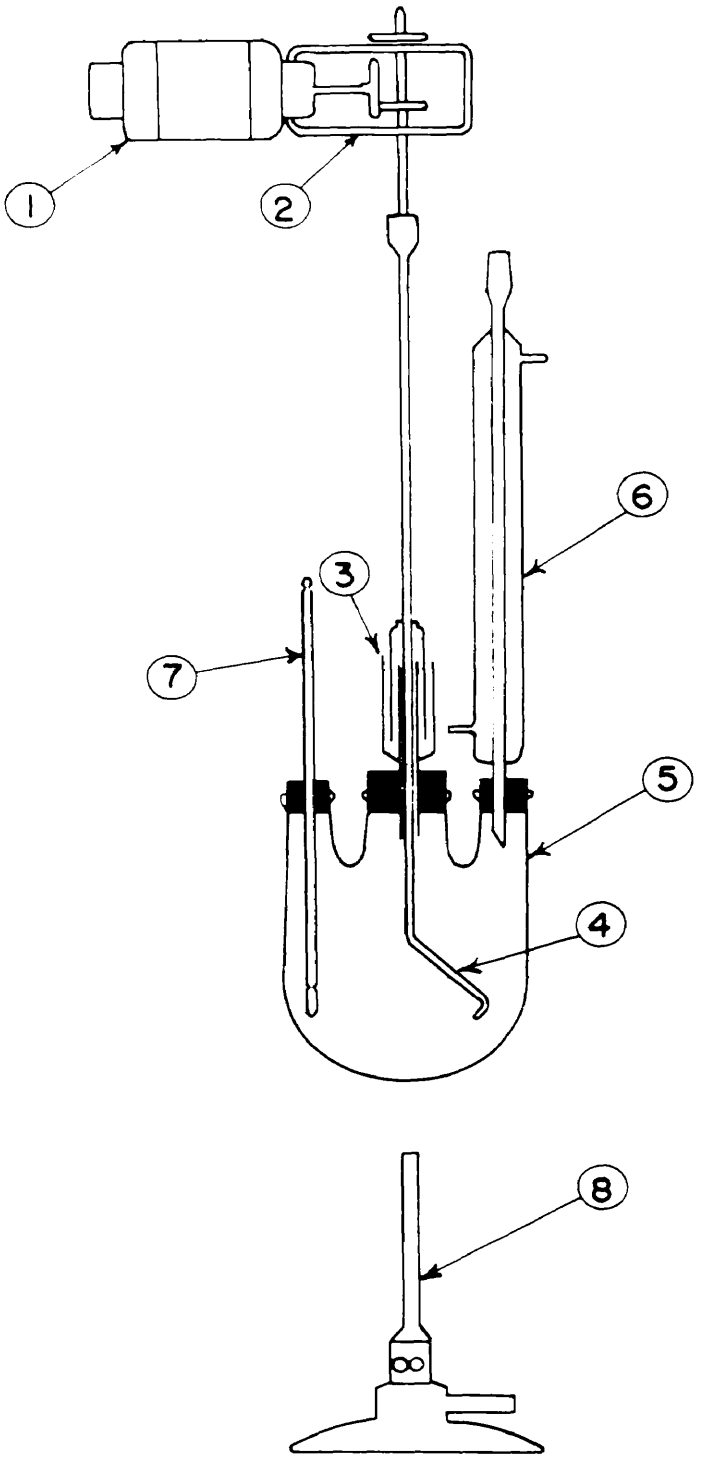
TABLE 3. - Screen Analyses of Silicates Tested

Common Name	(-20+48) %	(-48+65) %	(-65+100) %	(-100+200) %	(-200+325) %	(-325) %
Olivine	2.3	25.2	12.2	22.0	29.1	8.9
Serpentine	1.8	12.4	26.7	23.0	27.1	9.0
Beryl	1.0	13.8	15.5	35.1	30.2	6.4
Kaolin	2.8	20.0	21.0	26.4	20.5	20.5
Garnierite	3.5	18.0	30.8	25.9	20.5	2.1
Chlorite	A/					
Chryostile	A/					
Sodalite	A/					
Talc	A/					
Wollastonite	A/					
Heulandite	A/					

A/ Ground to approximately 100 mesh (average).

Chemically pure hydrochloric, nitric and sulfuric acids for small-scale tests were obtained from the J. T. Baker Chemical Company.

The digestion of various silicates in acid was carried out in a one liter, three necked flask fitted with mercury seal and stirrer, reflux condenser and thermometer. See Figure 1. Subsequent neutralization was carried out in a duplicate of the digestion vessel provided with an air bubbler for oxidation.



1. Motor - 1/12 HP
2. Variable-Speed Drive
3. Mercury Seal
4. Stirrer
5. One-liter flask
6. Reflux Condensor
7. Thermometer
8. Tirrel Burner

FIG. 1.-DIGESTION APPARATUS.

Solid-liquid separation was effected with a 6-inch Buchner funnel under approximately 26 inches of vacuum, a small 5-inch basket centrifuge operated at 600-800 times gravity, and a conventional Oliver test leaf filter.

B. Evaluation of the Basic Variables.

As pointed out, in any investigation of a chemical reaction there are, in general, three variables to consider: time, temperature, and concentration. By fixing any pair of variables desired data can be usually obtained as a function of the third.

The initial investigation consisted of fixing time and temperature and varying concentration. The desired data included magnesia recovery, residual acidity, hydrogen chloride loss, and filtration rate. To expedite the work it was arbitrarily stipulated that olivine particle size would be fixed until the major variables had been explored. All experiments were conducted at a constant agitation rate shown by test to be above any possible critical value.

To facilitate the study, use was made of the triangular diagram shown in Figure 2 of the system: olivine - hydrogen chloride - water. With this as a research tool, it was a relatively simple matter to rule out a considerable amount of possible experimental work on either theoretical or empirical grounds. For instance, as it was not contemplated that the reaction would be carried out under pressure, the area ACD could be eliminated immediately. Compositions in this area correspond to greater hydrogen chloride:water ratios than are found for hydrochloric acid solutions stable under ordinary conditions.73/

73/ Hunter, F. L., Absorption of Hydrogen Chloride: Trans. Am. Inst. Chem. Eng., vol. 37, 1941, pp. 741-762.

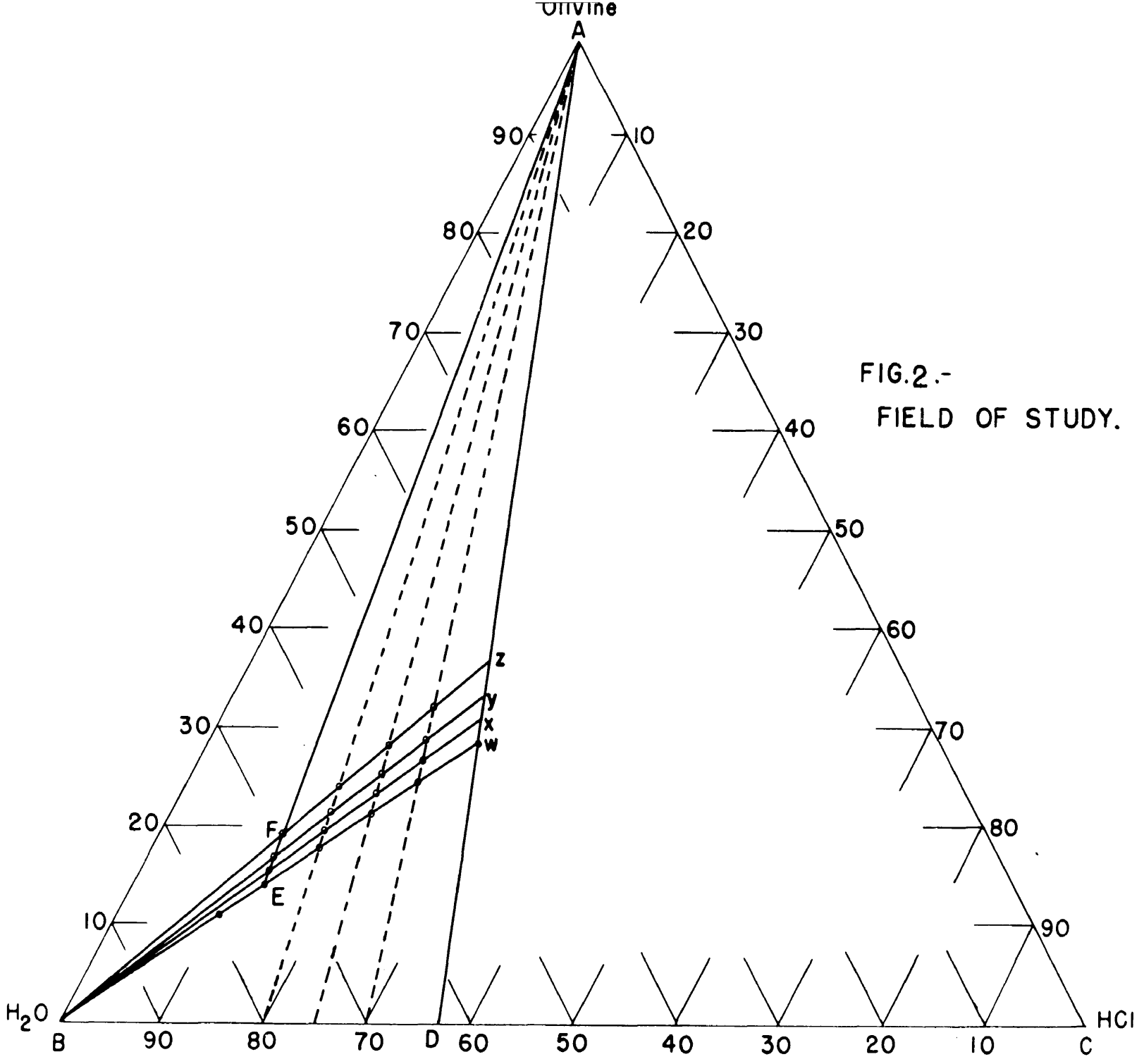


FIG.2.-
FIELD OF STUDY.

Practical considerations dictated the elimination of area WED, as all compositions in this triangle represent a stoichiometric excess of hydrochloric acid. Were the digestion to be carried out in this manner, an excessive amount of neutralizer would be needed to eliminate metallic impurities and excess acid.

Area ABW remained for consideration. All compositions along line BW correspond to hydrogen chloride-olivine ratios equivalent to one hundred percent decomposition of the ore. A series of experiments was conducted to determine the effect of aqueous acid concentration at acid-olivine ratios corresponding to points on this line. One hundred-gram portions of olivine were added to the theoretically required quantity of hydrochloric acid to react with the magnesia and iron present. The mixture was heated to and maintained at boiling in the previously described reaction vessel for varying periods of time after which the slurry was filtered hot on a 6-inch Buchner funnel and the residue then washed with 500 ml. of water. The data are summarized in Table 4.

TABLE 4. - Effect of Time and Aqueous Acid Concentration

HCl, weight percent	Time, minutes	MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
37	30	67.2	8.9	36.0	2.2
30	30	84.0	9.6	14.3	10.7
25	30	80.2	18.2	6.0	6.7
20	30	80.6	22.0	3.3	3.9
15	30	75.6	26.4	2.6	0.8
10	30	55.3	28.6	27.4	-
30	60	79.6	13.3	23.3	4.7
30	60	80.0	13.3	23.3	3.3
25	60	81.7	20.0	9.0	-
25	60	86.1	18.6	9.7	2.3
20	60	83.8	21.1	6.2	1.5
20	60	86.5	20.1	4.4	1.5
15	60	83.2	22.2	4.8	-

TABIE 4. - Effect of Time and Aqueous Acid Concentration (Contd.)

HCl, weight percent	Time, minutes	MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
15	60	84.0	21.9	3.9	1.0
30	15	76.5	14.7	26.3	4.5
25	15	75.4	20.8	14.1	-
20	15	78.4	24.1	6.0	2.5
15	15	74.4	27.6	3.0	0.6

The various table headings encountered in this and following tables have been standardized to facilitate comparisons. HCl, weight percent, refers to the aqueous acid concentration on a gravimetric basis. Magnesia recovery refers to that percent of the magnesia in the olivine obtained as magnesium chloride in the leach solution and washings. Excess acidity provides an indication of the extent of reaction as all of the hydrogen chloride which does not combine directly with the magnesia of the olivine must be subsequently eliminated by metathesis. In addition, ferrous and ferric chlorides are hydrolyzed by regulation of pH and the hydrogen chloride released as well as free hydrochloric acid must be neutralized to precipitate the iron hydroxides. Excess acidity refers to the residual quantity of hydrogen chloride not directly in combination with magnesium and by definition is as follows:

$$\text{Excess Acidity} = \frac{\text{HCl} + \text{FeCl}_2 + \text{FeCl}_3 \text{ (In HCl Equivalents)}}{\text{HCl} + \text{FeCl}_2 + \text{FeCl}_3 + \text{MgCl}_2 \text{ (In HCl Equivalents)}} \times 100$$

A description of this and other analytical methods will be found in Appendix A.

A large hydrogen chloride loss occurred at the higher acid concentrations. This was expected as hydrochloric acid solutions stronger than 20 percent by weight volatilize more hydrogen chloride than can be

absorbed in the evaporated water. In addition, the high salt concentration of the leach solution increases the hydrogen chloride concentration in the gaseous phase.

Fifteen percent aqueous acid gave a product which filtered with difficulty and ten percent gave an impermeable mass due to the large quantities of hydrated silicic acid gel formed.

It was evident that a reaction time of thirty minutes was optimum for the three intervals tested. Fifteen minutes was definitely too short; sixty minutes produced little variation from the thirty-minute reaction time except at low acid concentrations. The field of investigation was further limited by the elimination of area ABE corresponding to acid concentrations below fifteen percent for digestions at boiling temperatures. This was possible due to the prohibitively low filtration rates.

In an effort to reduce the excess acidity and to cover the field of investigation further, digestions were run at attempted decompositions of 90, 80, and 70 percent of theoretical by varying the quantity of acid used. The acid concentration was varied from 30 to 15 percent with a reaction time of thirty minutes. These three series corresponded to lines BX, BY, BZ on the triangular coordinate diagram. The data are given in Table 5.

After these two series of initial tests were run several conclusions were drawn:

1. For boiling reaction temperatures thirty minutes appears to be the optimum reaction time.

2. Aqueous acid concentrations below fifteen percent give slurries which are difficult to filter.

3. Attempted decomposition below 80 percent does not appear warranted because the excess acidity is not substantially reduced at lower attempted decomposition.

4. The range of optimum digestion with respect to yield of magnesium chloride lies between 80 to 90 percent decomposition.

5. Increased final acidity indicating the necessity of increased digestion time is obtained at acid concentrations below 20 percent.

6. Large hydrogen chloride losses occur at aqueous acid concentrations above 25 percent.

Based on these conclusions, the field of investigation was limited to aqueous acid concentrations of 20 to 25 percent and attempted decompositions approximating 80 to 90 percent.

TABLE 5. - Effect of Aqueous Acid Concentration

HCl, weight percent	MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
		90 percent stoichiometric HCl		
30	74.8	9.7	20.9	1.4
25	88.3	11.4	6.2	1.3
20	86.8	17.9	0.0	1.6
15	83.8	19.3	0.0	1.4
		80 percent stoichiometric HCl		
30	73.1	11.2	24.6	1.3
25	82.6A/	11.0	6.7	1.1
20	83.7A/	11.0	1.3	0.9
15	78.6	16.4	2.5	1.0
		70 percent stoichiometric HCl		
30	62.2	10.5	20.6	1.9
25	68.6	11.8	4.5	0.7
20	70.2A/	11.7	4.0	0.8
15	73.2A/	12.0	1.0	0.7

A/ These figures exceed the theoretical decomposition value. This was attributable to two factors. First, additional hydrochloric acid above the stoichiometric magnesium oxide-hydrogen chloride ratio was added to react with the iron present. Second, there was an experimental deviation of one to two percent in the measurement of the hydrochloric acid used and an additional deviation of one to two percent in the final analyses.

A series of experiments was then conducted at attempted decompositions of olivine from 83 to 93 percent of theoretical by varying the quantity of acid used. Data are summarized in Table 6.

TABLE 6. - Effect of Varying Attempted Decomposition

Attempted decomposition, percent	HCl, weight percent	MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
83	20	81.0	13.1	1.7	1.6
85	20	81.1	16.3	2.6	2.4
87	20	82.6	17.5	2.1	2.5
89	20	82.8	18.5	1.5	2.8
91	20	83.1	18.5	2.6	2.5
93	20	85.2	21.4	0.7	2.4
83	25	74.9	13.0	12.6	2.2
85	25	77.4	12.0	9.7	2.2
87	25	80.5	13.3	8.9	1.6
89	25	81.0	13.9	8.8	1.9
91	25	82.8	14.4	9.7	2.6
93	25	81.2	18.2	9.3	2.5

A significant loss of hydrogen chloride occurred when 25 percent aqueous acid was utilized. The lowest residual acidities occurred at attempted decompositions of 83-87 percent although the magnesia recovery was fairly independent of the acid-olivine ratio, varying between 81-85 percent with 20 percent hydrochloric acid.

Tentative conditions of operation were now established and additional studies were made to substantiate them.

An experiment was run to determine the variation in excess acidity as a function of time using boiling twenty percent hydrochloric acid at an 85 percent attempted decomposition. Samples of the digestion slurry were periodically analyzed and the results are tabulated in Table 7.

Extending the time of reaction results in slightly decreased final acidities; however, this impairs the rate of subsequent filtration.

The field of reactant concentration at boiling temperatures was

thus surveyed from a preliminary standpoint and definite conditions were established for subsequent tests. The hydrogen chloride loss from 25 percent aqueous acid eliminated this concentration from future consideration.

TABLE 7. - Rate of Change of Excess Acidity With Time

Time, hours	Excess Acidity, percent
0.00	55.0
.08	43.0
.17	27.0
.25	15.8
.33	14.8
.42	13.6
.50	12.4
.75	11.9
1.75	10.0
2.75	9.7

The preceding tests were all conducted at boiling temperatures as it was felt that a faster rate of reaction would be obtained at this rather than lower temperatures. This was substantiated by the following data in Table 8 at a thirty-minute reaction period and an attempted decomposition of 85 percent of theoretical.

TABLE 8. - Effect of Temperature

Temperature of reaction, °C	HCl, weight percent	MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
114	30	84.0	9.6	14.3	10.7
112	25	80.2	18.2	6.0	6.7
109	20	80.6	22.0	3.3	3.9
106	15	75.6	26.4	2.6	0.8
100	30	78.3	12.9	8.4	-
100	25	76.1	20.3	4.2	-
100	20	75.8	26.4	1.6	4.1
100	15	70.5	32.8	0.8	2.3
70	30	50.8	48.9	3.2	18.6
70	25	46.4	52.1	2.8	11.2
70	20	41.2	50.7	2.0	7.2
70	15	39.1	62.1	1.7	9.3

Conditions were then fixed at an acid-olivine ratio corresponding to 85 percent attempted decomposition with 20 percent aqueous acid and a reaction time of thirty minutes at boiling temperature.

The reaction with olivine was believed to be primarily a surface phenomenon and should, therefore, be influenced by particle size. Three grinds of material were prepared which were designated A, B, and C. The screen analyses are given in Table 9. The preceding preliminary tests were made with material corresponding to "C" composition.

TABLE 9. - Screen Analyses of Olivine

Particle size, (mesh)	A	B	C
+20	0.0	0.0	0.0
-20 + 48	33.8	19.8	2.3
-48 + 65	29.6	30.1	25.5
-65 + 100	13.7	17.1	12.2
-100+ 200	6.9	9.4	22.0
-200+ 325	9.1	14.1	29.1
-325	6.9	9.5	8.9

A series of experiments was conducted at the established optimum to determine the effect of particle size; data are summarized in Table 10.

TABLE 10. - Effect of Particle Size

Particle size	MgO recovery, percent	Excess Acidity, percent	Filtration rate
A	75.1	19.3	3.8
A	77.4	19.3	4.0
B	81.0	19.7	5.9
B	82.0	19.2	7.7
C	85.0	13.8	2.3
C	83.5	14.1	2.0
-100 + 200 (mesh)	81.4	11.3	2.5
-200 + 325 (mesh)	80.3	9.5	1.1
-325 (mesh)	(A)	9.2	0.4

(A) Cake could not be washed due to gelatinous structure.

The smaller the particle size the greater was the extent and speed

of the reaction, however, the smaller particle sizes resulted in slow filtration rates. For example, with the coarser grinds, A and B, the final slurries had better filtering characteristics but also excessive residual acid. The finer grinds, -100 + 200, —200 + 325, -325, had low residual acidities but only at the expense of the filtration rates.

The possibility that by increasing the reaction time of the coarser olivine a comparable degree of reaction might be obtained was considered and tested. The final acidity was lowered by increased time of reaction, although a marked decrease of filtration rate occurred which defeated the purpose of utilizing coarser material.

There is present in the olivine used in this work approximately 47 percent magnesia and 7.5 percent ferrous oxide corresponding to a FeO/MgO ratio of 0.16. The same ratio was determined experimentally in 85 filtrates obtained from the digestion step. Under widely varying conditions an average value of 0.155 was obtained. It is apparent that iron is extracted in the same relative proportion as magnesium which could be predicted on the basis of structure.

Digestion slurries obtained under the established conditions of operation previously described were washed with water to determine the quantity of wash necessary to completely remove the retained mother liquor. The first series of experiments was made under vacuum on a Buchner funnel, with the wash water divided into 50 ml. increments; 500 to 750 ml. were used. The filtrate and wash increments were collected and analyzed for chloride ion. The apparent wash liquor retention was then calculated by drying the cake for twenty-four hours at 110°C. Percent chloride ion remaining in the dry cake was determined by analysis. A second series of tests was made on a small basket centrifuge

using similar operating technique and both groups of data collected are given in Tables 11 and 12.

TABLE 11. - Washing Data on Buchner Funnel

Temperature, °C. slurry	wash	Total Wash ml.	Wash Water to remove 99.9 percent of Cl ion, ml./g.	Cl, dry washed cake, percent	Filtration rate	Wash liquor retention, percent
100	25	500	9.5	0.03	2.3	-
100	25	500	8.9	.04	1.5	-
100	100	750	9.2	.04	3.1	76.4
100	100	750	9.0	.08	2.5	77.8
25	25	500	9.1	.05	0.8	-

TABLE 12. - Washing Data on Centrifuge

Temperature, °C. slurry	wash	Total Wash ml.	Wash Water to remove 99.9 percent of Cl ion, ml./g.	Cl, dry washed cake, percent	Filtration rate	Wash liquor retention, percent
100	25	500	8.2	0.04	2.8	57.6
100	25	500	7.6	.04	2.8	61.0
100	100	750	7.8	.02	4.5	-
100	100	750	8.1	.07	4.9	-
25	25	500	8.0	.05	4.8	-

Analysis showed it is possible to remove 99.9 percent of the residual chloride ion in the cake by eight milliliters of wash water per gram of dry cake on the centrifuge and the same percentage removal can be effected on a Buchner funnel using nine milliliters of water per gram of dry cake. An approximate rate of two gallons per square foot per hour was obtained with the Buchner funnel and four gallons per square foot per hour on the centrifuge. These rates are not strictly comparable as the centrifuge has an operating area of 25.5 square inches while the Buchner funnel has only 16 square inches and the cake thickness, therefore, varies. A lower wash liquor retention was obtained on the centrifuge, the centrifuge giving 55-60 percent and the funnel 70-78 percent retention. The cake cracked in the centrifuge

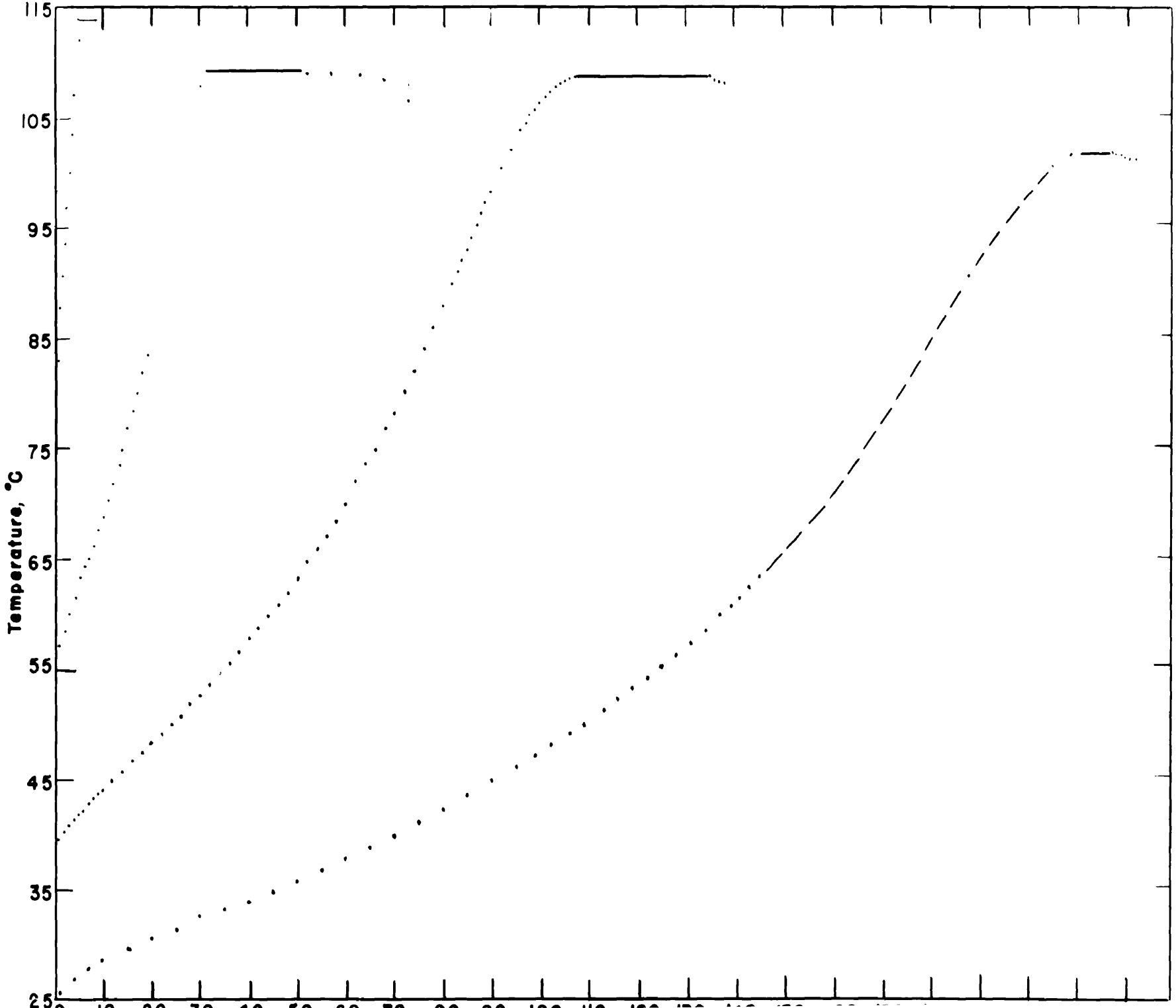
but little or no channeling resulted as the cracking localized at the surface of the cake.

Filtration rates were determined for both the residual mother liquor and the wash water; after initial establishment of the cake no difference in rate was observed.

Simple thermal measurements were made to provide an index of the heat requirements of the reaction by adding olivine corresponding to grind "C" to aqueous 20 percent hydrochloric acid at various temperatures in a calorimeter. The acid-olivine ratio corresponded to 85 percent attempted decomposition. Time-temperature measurements were taken and the data plotted in Figure 3. It can be seen that the reaction is highly exothermic and sufficient heat is liberated to maintain the slurry at boiling throughout the digestion period. With initial acid temperatures of 75°C and above, the reaction reached boiling temperature in a very few minutes. The experimental heat of reaction (ΔH_{298}) was found to be -49,300 calories. It was necessary to base this value on a series of determinations at 100°C and subsequently correct to the lower temperature by the usual thermochemical equation equating heats of reaction and ΔCp. Several assumptions were necessarily made in calculating ΔCp and this represents an approximation.

It is interesting to contrast this value with the calculated heat of reaction obtained from reported thermochemical data. The basic reaction may be expressed as

$$(x\text{Mg}\cdot y\text{Fe})_2SiO_4 + 4HCl(aq) = 2xMgCl_2(aq) + 2yFeCl_2(aq) + H_2O(l) + H_2SiO_3(ppt),$$


115
105
95
85
75
65
55
45
35
25
Temperature, °C

in which x and y are mole fractions of Mg_2SiO_4 and Fe_2SiO_4, respectively, in olivine, so that x + y = 1. This reaction may be considered thermochemically as the sum of the following six reactions:

(1) $(xMg \cdot yFe)_2SiO_4 = xMg_2SiO_4 + yFe_2SiO_4$; $H_{298} = 0$

(2) $xMg_2SiO_4 = 2xMgO + xSiO_2$; $H_{298} = 15,120x$

(3) $yFe_2SiO_4 = 2yFeO + ySiO_2$; $H_{298} = 11,300y$

(4) $2xMgO + 4xHCl\ (aq) = 2xMgCl_2(aq) + 2xH_2O(l)$; $H_{298} = -72,800x$

(5) $2yFeO + 4yHCl(aq) = 2yFeCl_2(aq) + 2yH_2O(l)$; $H_{298} = -54,200y$

(6) $SiO_2 + H_2O(l) = H_2SiO_3(ppt)$; $H_{298} = 2,900$

Therefore, for the desired reaction,

$$H_{298} = 2,900 - 57,700x - 42,900y.$$

The heat of reaction (1) involves no assumption. Sahama and Torgeson found it to be zero within their limits of error of measurement.74/

The heat of reaction (2) was measured by Torgeson and Sahama.75/

The heat of reaction (3) was measured by Troitzsch.76/

The heat of reaction (4) was measured by Shomate and Huffman as $H_{298} = -35,800$ cal. per mole of MgO, under conditions in which a small amount of MgO was dissolved in a relatively large amount of 1.000 N - HCl.77/ Their value was corrected to match approximately the

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74/ Sahama, T. G. and Torgeson, D. R., Unpublished Report, Bureau of Mines.

75/ Torgeson, D. R., and Sahama, T. G., A Hydrofluoric Acid Solution Colorimeter and the Determination of the Heats or Formation of Mg_2SiO_4, $MgSiO_3$, and $CaSiO_3$: Pending Publication, Jour. Am. Chem. Soc.

76/ Troitzsch, H., (Thesis on the Thermochemistry of Silicates): Dissertation, (Braunscheweig), 1935.

77/ Shomate, C. H., and Huffman, E. H., Heats of Formation of MgO, $MgCl_2$, $MgCl_2 \cdot H_2O$, $MgCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$: Jour. Am. Chem. Soc., vol. 65, 1943, p. 1625.

conditions by use of heat of dilution data for HCl 78/ and heat of dilution data for $MgCl_2$(aq).79/ This correction brings the heat value to ΔH_{298} =-96,400 cal. per mole of MgO.

The heats of reaction (5) and (6) were compiled from data given by Bichowsky and Rossini.80/ It is not possible, because of incomplete data to correct the heat of reaction (5) to match actual conditions.

Substituting the mole fraction values for Mg and Fe in the equation

$$\Delta H_{298} = 2,900 - 57,700\ x - 42,900\ y$$

A value of - 53,400 calories per g. mole is obtained. This represents a deviation of 4,100 calories from the experimentally determined value of -49,300. Considering the assumptions made in the foregoing development, especially with regard to the silica hydration, the experimental error of ± 3 percent in the actual measurement, and the assumption made in calculation of ΔCp, this variation is not excessive; representing a deviation of less than 9 percent. In fact, it is probable that the assumptions made in calculating ΔH_{298} and ΔCp were of a compensating nature.

Numerous other tests were performed on the digestion reaction but their importance to this analysis is negligible. The experimental results on the basic variables of time, temperature and concentration described in the body of this section are briefly summarized below:

78/ Selected Values of Chemical Thermodynamic Properties: National Bureau of Standards.

79/ Bichowsky, F. R., and Rossini, F. D., Thermochemistry of the Chemical Substances: New York, Reinhold Publishing Corp., 1936, pp. 113-114.

80/ Bichowsky, F.R. and Rossini, F. D., ibid., pp. 23, 54, 89-90.

1. The hydrogen chloride loss increases rapidly when acid concentrations above 20 percent by weight are used. It varies from about 2.5 to 36.0 percent for an acid-concentration range of 15 to 37 percent. Although the loss using the azeotropic mixture was about 1.0 percent higher than the minimum, the reaction product using 15 percent acid was practically unfilterable.

2. The maximum reaction rate under the conditions examined occurs at the boiling point. Although it was possible to reduce hydrogen chloride losses by operating below this temperature, in no case was the gain adequate to compensate either for the necessary increase in reaction time or the harmful effect on the slurry filtration rate.

3. The optimum total reaction period at boiling is approximately 30 minutes. This period may be divided into a heating time for the reaction mass of 15 minutes and an equal holding time.

4. The lowest residual acidities are obtained using 83 to 87 percent of the stoichiometric hydrogen chloride:olivine ratio.

5. While it is true that the reaction rate is a function of surface, the use of olivine in particle-size ranges finer than (-48 + 100) results in marked lowering of the filtration rate.

6. Magnesium chloride loss in the filter cake from the digestion reaction could be reduced to less than 0.2 percent by using about 8 pounds of water per pound of dry cake.

7. The digestion reaction is highly exothermic. Providing the reacting mass is initially heated above 70° to 75°C, the heat of reaction, excluding losses, is more than adequate to raise the system to the boiling point and maintain it for the 30-minute reaction period.

8. In filtration tests using a Buchner funnel with vacuum, an average filtration rate of 2 gallons per square foot per hour was obtained for digestions made under optimum conditions. Using the centrifuge, this rate doubled although conditions were not strictly comparable.

9. The filtration rates described above are not considered commercially practical and alternate methods of effecting higher values must be considered.81/

C. Filter Aids

Non compressible solids such as diaspore frequently improve the filtering characteristics of many slurries. A series of tests was made to test this possibility and the data are described in Table 13.

TABLE 13. - Effect of Filter Aids on Filtration

Filter aid	Filter aid added, weight-percent	Filtration rate
None	-	2.9
Celite 503	0.5	3.5
Celite 503	1.0	3.8
Celite 503	2.0	5.1
Celite 503	5.0	8.2
Celite 503	10.0	15.1
Celite 501	2.0	5.0
Hyflo	2.0	4.4
Kaolin	2.0	1.9
Olivine B	5.0	3.1
Olivine C	5.0	3.2

As the cost of utilizing filter aids in quantities of more than 1 - 2 percent is prohibitive when producing relatively cheap inorganic chemicals, these results were definitely discouraging and this line of

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81/ Perry, J. H., Chemical Engineers Handbook, 2nd Ed.: New York, McGraw Hill Book Company, 1941, p. 1687.

attack was recessed in favor of more promising possibilities.

D. Neutralization

The work of Stevens and Deinbolt indicated that gelatinous slurries from the acid decomposition of silicates filtered better when neutralized to a pH of about 7.82, 83/ Again the results were not promising although some increase was noted by neutralizing the digestion slurry, before filtering, with the stoichiometric quantity of magnesia as calculated from the excess residual acidity.

TABLE 14. - Effect of Neutralization

Run	Not neutralized	Neutralized
1	1.8	2.9
2	2.3	3.1
3	1.9	3.2
4	2.6	3.0
Average	2.2	3.1

E. Development of Increment Digestion

After evaluating all of the conventional techniques for improving the filtration characteristics of the digestion slurry with discouraging results, the fourth alternative, that of attempting to produce a more dense silicic acid structure, was attempted.

As an extension of the work on neutralization, the olivine was divided into two portions; the first containing the bulk of the charge as relatively coarse material and the latter consisting of fines.

82/ Stevens, R. H., Norris, G. C., and Watson, W. N., loc. cit.

83/ Aktieselskabet De norske Saltverker av Bergen, (Treatment of Magnesium Sulfate): Norwegian Patent 36,429, Jan. 2, 1923.

Eighty-five percent of the olivine charge corresponding to coarse grind B (see Table 9) was reacted with the total stoichiometric quantity of 20 percent hydrochloric acid for twenty minutes. The remaining 15 percent was added in a smaller mesh size, e.g., -100 or -200 mesh and the final mixture digested for ten minutes to complete the usual overall digestion period of thirty minutes. This procedure presented to the reaction mixture a large fresh surface area of olivine at the lower hydrochloric acid concentrations and thus favored a more rapid reaction. In addition, the finer material had a shorter period of contact with the solution which, it was thought, might minimize gel formation. The data collected are given in Table 15.

TABLE 15. - Increment Olivine Addition, 85-15 Increments

MgO recovery, percent	Excess Acidity, percent	HCl loss, percent	Filtration rate
83.4	14.0	0.7	4.5
81.6	13.8	0.9	6.1
82.1	15.0	1.0	8.4
82.8	13.1	1.2	6.6
Average 82.5	14.0	1.0	6.4

A significant increase in filtration rate of the slurry occurred with the innovation of increment addition. This series of tests was the first reported observation of improvement through the utilization of such a technique and intensive small scale tests were undertaken to determine its significance.

As a consequence of results obtained during the exploratory work on neutralization and the studies by earlier workers, it was considered that partial neutralization of the reacted slurry had worthwhile aspects from both a process-cost standpoint because of the saving that might

be made in the quantity of recycled neutralizer and that of improved filtration. In a series of experiments in which the effect of variation in size of increment was studied, neutralization with the stoichiometric quantity of magnesia determined from the excess acidity was carried on by boiling for an additional 15 minutes beyond the previously established reaction period. The data are given in Table 16. Two series of tests were conducted, designated as A and B, mainly to test reproducibility of results.

TABLE 16. - Effect of Increment Ratio Variation

Grams olivine added at			Filtration and Washing Rates -		
0 min.	10 min.	20 min.	Series A	Series B	Difference
100	0	0	2.0	2.9	+ 0.9
60	20	20	6.5	5.8	- 0.7
20	20	60	0.4	.5	+ 0.5
20	60	20	21.2	20.0	- 1.2
30	60	10	15.2	14.6	- 0.6
20	70	10	22.7	24.4	+ 1.7
15	75	10	15.2	12.2	- 3.0
20	80	0	17.1	19.1	+ 2.0
25	75	0	18.1	19.3	+ 2.2
40	60	0	9.3	10.4	+ 1.1
50	50	0	5.4	6.8	+ 1.6

Attention is again directed to the marked increase in filtration rates. Utilization of increment digestion coupled with neutralization gave an almost 10-fold increase in rate on a volumetric basis. The correlation of rate with the magnitude of the first increment indicated the possibility of a seeding effect such as that previously described in Chapter II. This great improvement brought with it, however, an attendant serious problem. Increment addition of dry, rather finely divided olivine to the boiling reaction mass gave rise to caking and excessive foaming in the digestion vessel. When the second increment

constituted a large percentage of the charge, which appeared optimum, the violence of the reaction was sometimes sufficient to eject the vessel contents from the system through the reflux condenser. It was appreciated that such violence would impose considerable difficulty in the design and operation of a possible plant.

To test a proposed solution of the problem, the charge of acid (350 ml.) was divided into 250- and 100-ml. portions. The first increment of ore was mixed with the 250-ml. of acid, brought to the boiling point, and held for the specified period. At the proper time, the second olivine increment was added to the reaction vessel as a cold slurry in the remaining acid and the reaction carried to completion. To a large degree, the use of this procedure solved the caking and foaming problems. A filtration-rate comparison of the two techniques is given in Table 17, and it is noted that a sacrifice in overall rate must be made if this method is utilized.

TABLE 17. - Comparison of Filtration Rates

	Slurry Addition	Dry Addition
	9.4	17.5
	9.9	17.6
	11.1	18.1
	11.9	19.1
	12.2	20.3
Average	10.9	18.5

The importance of stage addition must be emphasized. Of the hundreds of tests conducted on olivine to improve the filtration characteristics of its acid slurries, this technique was the first to offer definite promise. Not only were substantial savings in capital investment indicated, but concomitant reductions in labor and processing costs were

immediately apparent.

F. Determination of Optimum Conditions for Increment Digestion

As a consequence of the potential decrease in operating and capital costs that might result from use of the increment digestion technique, it was considered worthwhile to define the optimum operating conditions.

To determine the possible effect of variation in the amount of acid used in the slurry technique of olivine incremental addition, a series of tests was run in which the incremental quantity of hydrochloric acid used for this purpose ranged from 25 to 200 ml. of a total of 350 ml: twenty-five grams of olivine were added to a quantity of hydrochloric acid ranging from 325 to 150 ml. and reacted for 10 minutes at the boiling point. At the end of this period, a cold slurry made up of the remaining 75 grams of olivine and acid was added to the reaction mixture. As the addition caused a decrease in temperature, the zero time for the second increment reaction was arbitrarily taken at the instant the boiling point was regained. The digestion was then continued for 40 minutes, after which neutralization was carried out in a standard manner. Data are given in Table 18.

It is evident from the data in Table 18 that there is little, if any, detrimental effect on filtration rate by using the acid-slurry addition technique for the second olivine increment when not more than 15 percent of the total acid is employed for this purpose.

TABLE 18. - Variation of Excess Acidity and Filter Rate with Amount of HCl in Second Increment

20 percent HCl in 2d increment, ml. A/		Excess Acidity, percent (40 minutes)	Filter rate (neut. slurry)
25		10.0	15.3
		9.6	14.6
		10.0	15.9
		10.5	14.0
	Average	10.0	15.0
50		8.3	18.9
		8.5	17.8
		8.9	21.6
		9.3	21.5
	Average	8.7	20.0
75		9.4	12.4
		10.0	17.6
		9.0	16.8
		9.6	14.2
	Average	9.5	15.8
100		9.2	11.9
		9.8	12.2
		9.0	16.3
	Average	9.3	13.1
150		10.0	11.5
		10.0	11.3
		8.6	15.3
		8.3	13.5
	Average	9.5	12.9
200		11.9	5.5
		12.2	5.9
		10.5	10.5
		10.5	12.0
	Average	11.3	8.2

A/ Total acid = 350 ml.

It will be recalled from Table 16 that filtration rates of 20.0, 24.4, 19.1, and 19.3 gallons per square foot per hour were obtained at

incremental addition ratios of 20:60:20, 20:70:10, 20:80, and 25:75, respectively. Considering these results from the viewpoint of projected plant operation, it seemed that the relative simplicity of the two-increment procedure would outweigh any filtration rate advantage of the three-stage technique.

In making confirmatory tests on the selected procedure it was necessary to use a light magnesia (basicity, 76 percent), supplied by the J. T. Baker Co., as the stock of previously used material was exhausted. It is this light magnesia to which reference is made when "standard magnesia" is designated in the text hereafter. These experiments were carried out under the conditions outlined in the previous section and the data are given in Table 19.

TABLE 19. - Definition of Optimum Increment Ratio

Increment ratio	Excess Acidity, percent	Filter rate
20:80	8.9	10.2
	8.9	12.5
	8.6	15.9
	9.1	16.1
	8.9 (Average)	13.7 (Average)
25:75	9.1	15.5
	9.0	14.6
	9.0	15.4
	8.7	13.4
	9.0 (Average)	14.7 (Average)
30:70	9.1	14.5
	8.6	13.9
	9.0	10.5
	9.2	10.5
	9.0 (Average)	12.4 (Average)

In view of the spread in the filtration rate values shown for the 20:80 and 30:70 ratios, the 25:75 might be preferred on the basis of

consistency alone. It was realized, however, that the smallness of the operational scale might preclude the definition of the optimum within the degree of precision attempted. On this basis it was stipulated that either the 20:80 or 25:75 could be considered as optima in view of the data reported.

It is possible that the difference of about 5 gallons per square foot per hour in the filtration rate for similar tests reported in Tables 18 and 19 may be attributable in part to a variation in physical or chemical properties of the magnesia used in each instance.

In the tests for determination of optimum particle-size range, the technique of adding the second olivine increment as a slurry was not followed. In each instance the acid and 20 percent of the total olivine were added to the 1-liter flask and boiled under reflux for 10 minutes before the remaining olivine was introduced. The reaction was carried on for 60 minutes after the second olivine portion was added. The course of the reaction was charted by acidity determinations made every 5 minutes during the second-increment digestion.

Before use, a quantity of olivine was separated into the following size ranges, using U. S. Standard screens: -8 + 20; -20 + 40; -40 + 70; -70 + 100; -100 + 200; and -200.

Analysis showed a variation in MgO content with the screen fractions as shown in Table 20.

The minus 100 plus 200 "A" and minus 200 "A" curves of Figure 4 were made using these analyses of the olivine fractions.

To obtain a more nearly correct picture of the effect of particle size with elimination of the composition variable, the minus 40-plus 70-mesh material, analyzing 49.3 percent MgO, was ground to minus

100-mesh. Minus 100-mesh plus 200-mesh and minus 200-mesh samples were prepared from this material. The "B" curves in Figure 4 were obtained with these materials. The MgO analysis of these fractions was 47.4 percent for the minus 100 plus 200 and 47.1 percent for the minus 200-mesh fraction.

TABLE 20. - MgO Content of Screened Fractions

Mesh	MgO percent
-8 + 20	45.5
-20 + 40	48.8
-40 + 70	49.3
-70 + 100	49.1
-100 + 200	47.8
-200	44.7

The plotted average data shown in Figure 4 confirm the previous results that the rate of reaction is a direct function of olivine surface area.

To outline more exactly the optimum screen analysis, a series of tests was run using a 1:1 mixture of the minus 40- plus 70- and the minus 70- plus 100-mesh fractions blended in various proportions with the minus 100- plus 200- and minus 200-mesh sizes of the composition given in Table 20. In the tests the excess acidity was measured at the end of 30, 40, and 60 minutes digestion time for the second increment. The data obtained are given in Table 21.

The significance of the data given in Table 21 is masked to some extent because of the use of the minus 200-mesh material that had an MgO content of but 44.7 percent. As it was shown in Figure 4 that this material attained its equilibrium acidity within 25 to 30 minutes (A-200 curve), it is considered permissible to correct for the effect

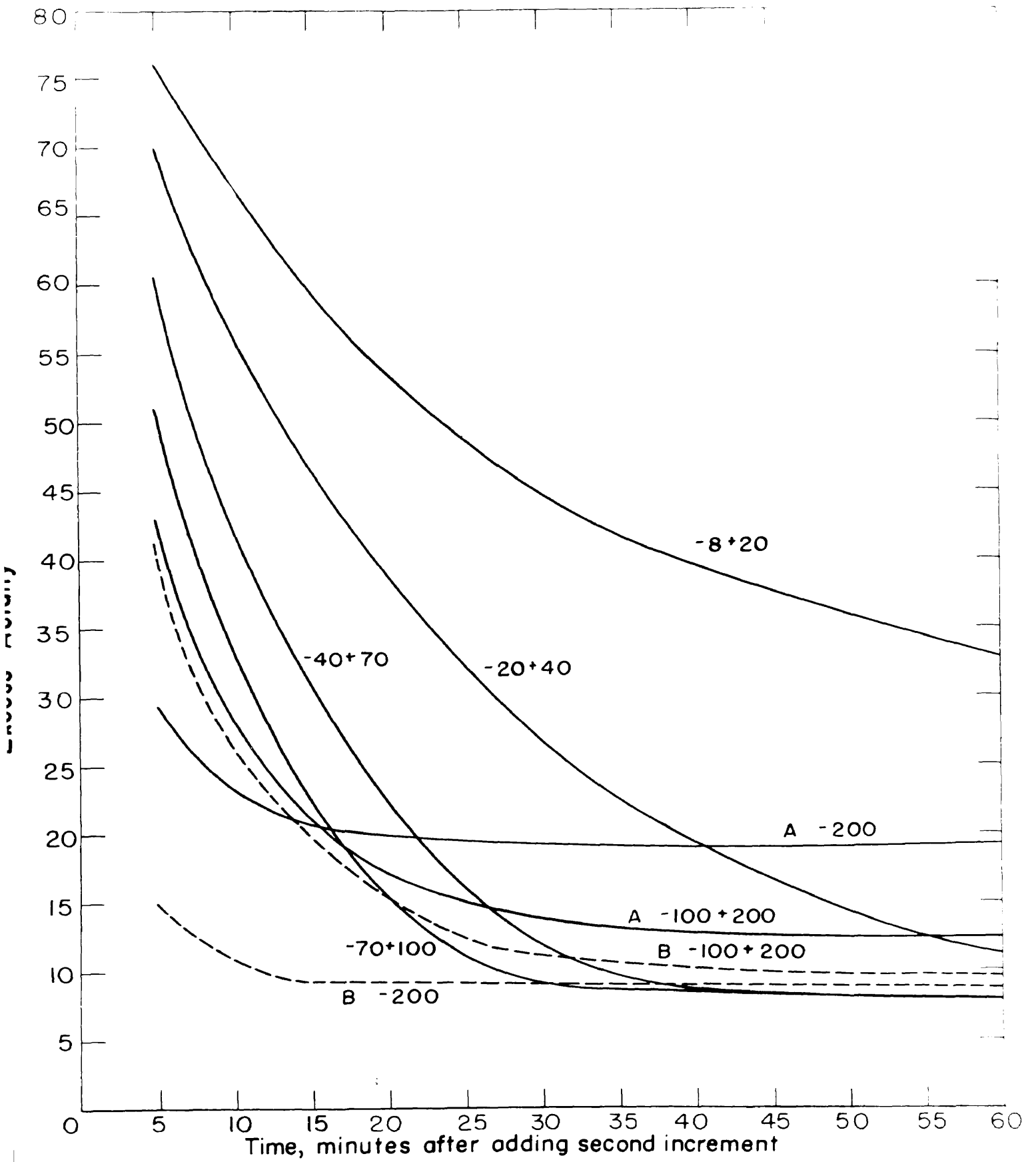


FIG. 4 - VARIATION OF EXCESS ACIDITY WITH TIME FOR DIFFERENT PARTICLE SIZES

of the difference of magnesia content on the actual residual acidity obtained with this material present. Making the proper calculation, it can be shown that at 30 minutes, acidity of about 10.0 units would be obtained for the 35-35-15-15 blend shown in Table 21. Actually there would be but a small practical difference in reaction rate among the three blends containing minus 200-mesh material. Any of these or others intermediate in character should be considered optimum for the process, as they can be readily obtained in commercial practice.

TABLE 21. - Effect of Particle-Size Range on Digestion Reaction

Screen analyses of blends		Digestion time, minutes		
		30	40	60
Percent	Mesh	Excess Acidity, percent		
50	-40 + 70			
50	-70 + 100	13.4	10.0	8.5
40	-40 + 70			
40	-70 + 100			
10	-100 + 200			
10	-200	14.7	11.6	10.0
35	-40 + 70			
35	-70 + 100			
15	-100 + 200			
15	-200	14.4	11.6	8.7
30	-40 + 70			
30	-70 + 100			
20	-100 + 200			
20	-200	16.2	12.4	10.6
40	-40 + 70			
40	-70 + 100			
20	-100 + 200	11.6	10.0	8.4

To circumscribe more closely the effect of reaction time for each increment, a series of tests was run using the optimum acid-slurry-addition technique for the second increment. All tests were made under identical conditions with a 20:80 olivine incremental ratio. The

filtration rates are given in Table 22.

TABLE 22. - Optimum Reaction Time for Incremental Digestion

Elapsed time of digestion, min. Increment		Filtration rate
First	Second	
5	20	7.8
5	30	7.5
5	40	7.4
5	50	7.6
7	40	12.5
7	50	11.5
9	30	12.1
9	40	12.0
9	50	11.0
10	20	15.6
10	30	15.5
10	40	13.9
10	50	12.0
11	30	15.0
11	40	13.0
11	50	12.0

It is apparent from the data in Table 22 that the optimum digestion times for the first and second increment have been demonstrated as 10 and 20 minutes, respectively.

Neutralization of itself fails completely to account for the rate phenomena observed with increment or stage digestion. It is, however, an important step in the production of the overall phenomena as can be seen from Table 23 wherein slurries obtained by stage digestion were neutralized with various amounts of magnesia leaving solutions of varying residual acidity.

The marked difference in the physical characteristics of the residues

obtained by increment and non increment digestion is well illustrated by Figure 5. The former technique gives a relatively dry, granular structure while the latter results in a gelatinous cake quite resistant to fluid flow. Measurement of residue volumes discloses that the non increment residue is approximately 30 percent larger, attributable to increased hydration.

TABLE 23. - Effect of Neutralization

Gms. MgO added	Initial Excess Acidity, percent	Final Excess Acidity, percent	Filtration rate
0	9.0	9.0	2.0
0	11.3	11.3	1.2
1	9.7	7.0	1.6
1	8.9	7.7	2.0
2	10.3	6.9	7.4
2	10.1	7.0	9.3
3	9.0	6.0	12.9
3	8.7	5.3	13.6
4	10.8	4.0	16.3
4	8.6	3.2	21.2
5	9.6	2.5	17.1
5	10.0	2.7	18.5

G. Pilot Plant Testing

Difficulty is frequently encountered in the commercial exploitation of techniques and processing methods developed from small scale laboratory tests. Surface volume relationships, to give but a single example, frequently result in completely different results. It was essential, therefore, that the technique of increment or stage digestion be demonstrated in a process pilot plant where conventional materials of construction and industrial equipment could be utilized. In addition, operation of a pilot plant was necessary to obtain information for the design of a larger industrial unit.

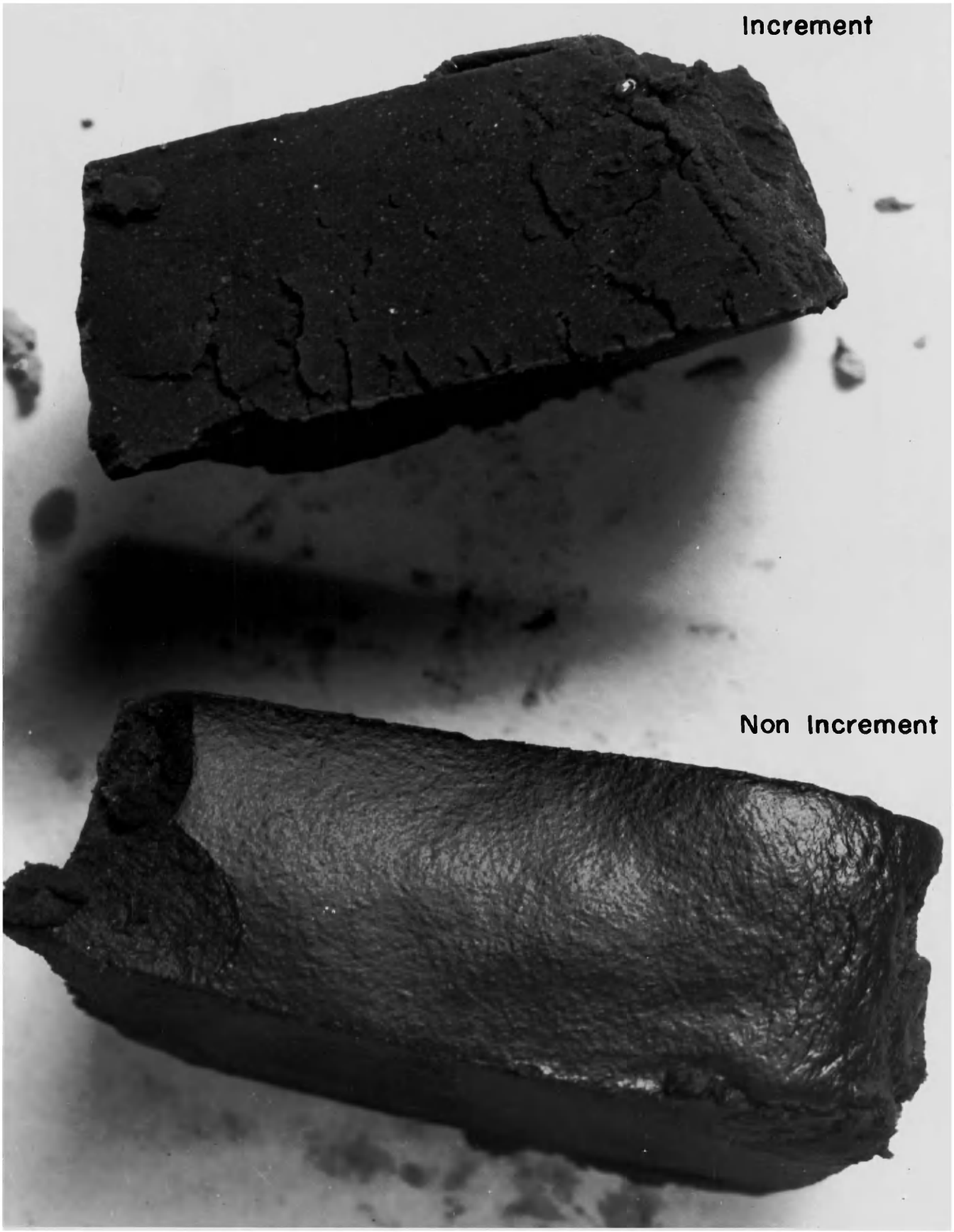


FIG. 5. - COMPARISON RESIDUES

In order to test the various conclusions of the preceding laboratory study preparatory to construction of the pilot plant, a series of complete runs was made from the initial digestion to the final purification. The initial charge of 20 gm. of olivine and 250 ml. of 20 percent acid was added to the reaction vessel cold, raised to boiling and boiled for ten minutes. The second increment containing 80 gm. of olivine and 100 ml. of acid was then added as a cold slurry and boiled for an additional 30 minutes. After digestion, the slurry was neutralized with the theoretical quantity of magnesia, as determined by the excess acidity, at boiling for 3 minutes and filtered hot. The cake was washed with 150 ml. of water which was combined with the filtrate. The combined filtrate and wash was neutralized with the theoretical quantity of magnesia and aerated at 40° C. for ten minutes before filtration. The data collected are summarized in Tables 24 - 25 and provided the basis for the flow sheet and material balance illustrated in Figures 6 and 7. Operations enclosed by broken lines are not deemed part of this thesis and are based on analogous industrial operations.

The material balance was constructed on the following assumptions:

Temperature

(a) Digestion-first neutralization - 109° C. (atmospheric boiling point)

(b) Second neutralization - 40° C. with aeration.

Time

(a) Digestion-first neutralization

First-increment digestion - 10 minutes

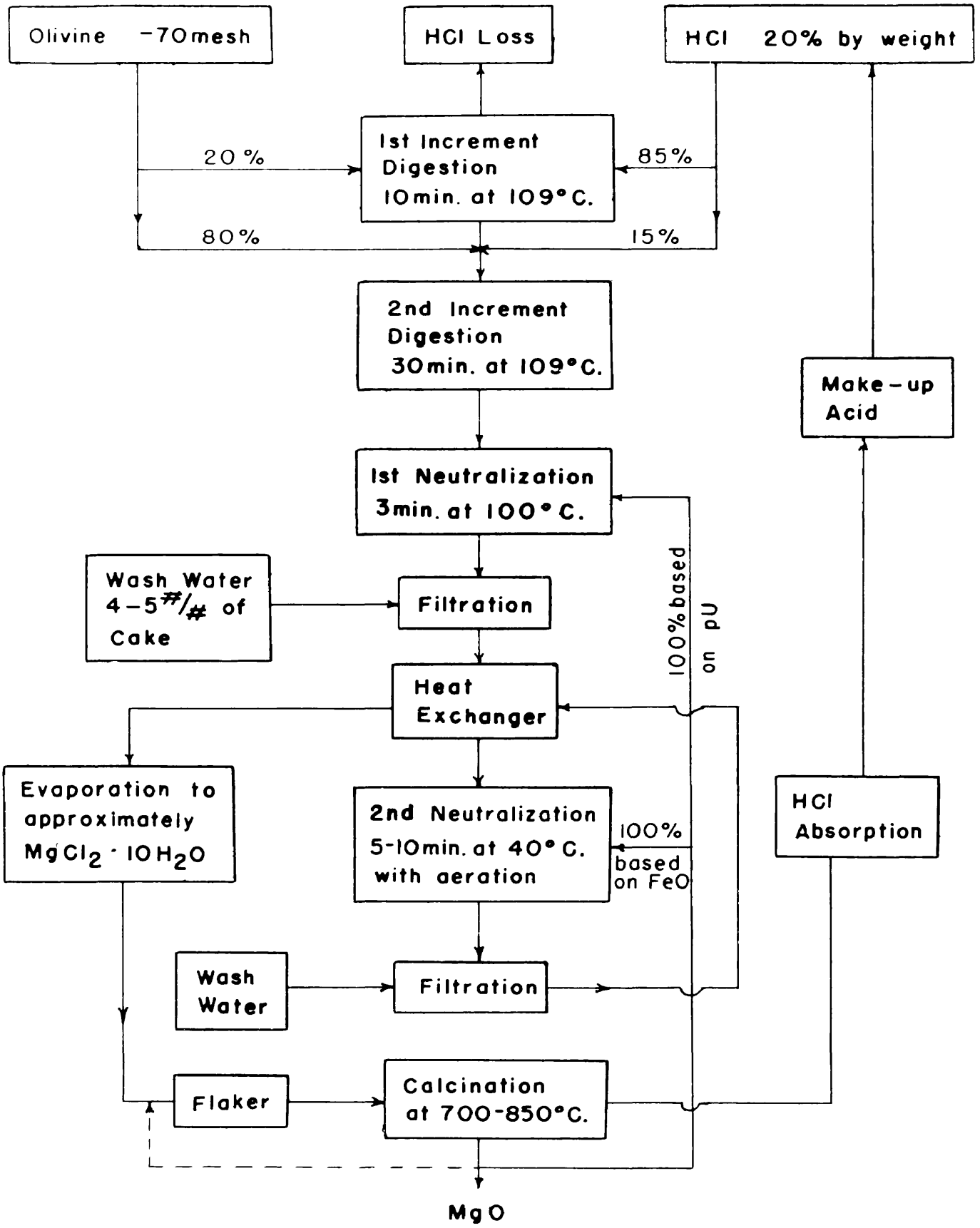
Second -increment digestion - 30 minutes to excess

TABLE 24. - Data on Complete Flow Sheet: Digestion, First Neutralization and Filtration

1st Neutralization Excess Acidity initial	final	Utilization MgO percent	Filtration rate	$MgCl_2$ gm./l.	FeO gm./l.	Wet cake, grams	Dry cake, grams	Wash liquor retention percent	Filtrate ml.
10.2	1.1	76	9.4	230.7	1.2	186.1	65.0	65.0	355
10.1	1.1	75	11.9	227.7	1.3	200.0	71.5	64.3	360
10.6	1.3	84	12.2	227.7	1.5	195.0	69.7	64.3	370
10.9	1.5	86	9.9	226.2	1.3	199.0	71.4	64.1	375
11.4	1.5	90	11.1	216.8	1.7	193.0	69.8	63.9	377
10.9	1.5	85	7.9	233.6	1.4	180.4	63.0	65.0	360
11.2	2.1	83	7.6	236.8	1.4	178.3	57.0	67.9	345
10.6	2.2	76	12.6	-	-	175.6	67.0	61.8	365
10.9	2.1	80	12.4	256.0	2.6	174.7	64.0	63.3	365
10.4	-	-	11.6	234.6	1.6	181.8	64.0	64.7	385

TABLE 25. - Data on Complete Flow Sheet: Second Neutralization and Purification

2nd Neutralization Excess Acidity initial	final	Utilization MgO, percent	$MgCl_2$ gm./l.	FeO gm./l.	NiO gm./l.	SiO gm./l.	MnO gm./l.	Wet cake, grams	Dry cake, grams	Filtrate ml.
1.1	Alk.	92	241.1	<0.001	<0.001	0.008	0.13	3.2	1.7	322
1.1	Alk.	92	235.3	<0.001	<0.001	0.011	0.13	2.8	1.6	330
1.3	Alk.	93	230.7	0.003	<0.001	0.044	0.14	3.0	1.1	345
1.5	Alk.	94	236.7	<0.001	<0.001	0.002	0.13	3.2	1.1	335
1.5	Alk.	94	224.2	<0.001	<0.001	0.012	0.13	2.9	1.2	350
1.5	Alk.	94	233.8	0.004	<0.001	0.005	0.13	8.5	3.9	335
2.1	Alk.	95	230.6	0.003	<0.001	0.002	0.10	8.2	3.8	330
2.2	Alk.	96	252.2	0.002	<0.001	0.022	0.14	9.0	4.1	350
2.1	Alk.	95	256.8	0.003	<0.001	0.029	0.16	11.1	5.0	360
-	Alk.	-	244.1	<0.001	<0.001	0.003	0.14	9.2	4.1	360



IG.6. MAGNESIA FROM OLIVINE- SCHEMATIC FLOW SHEET

MAGNESIA FROM OLIVINE AND HYDROCHLORIC ACID

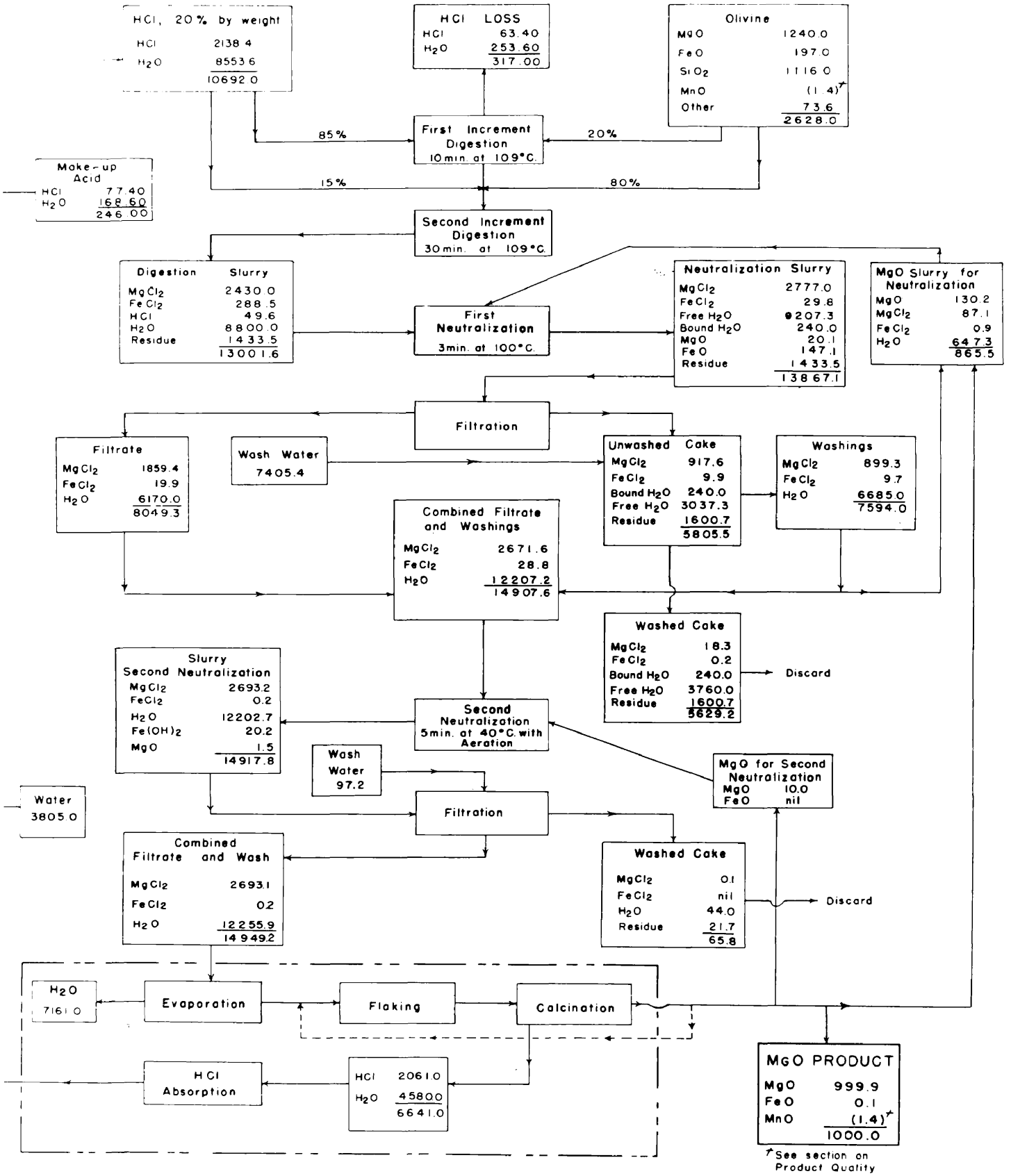


FIG.7.- MATERIALS BALANCE.

acidity of 10.4

First neutralization - 3 minutes to excess residual acidity of 1.5

(b) Second neutralization - 5 minutes to FeO/MgO ratio of 0.0002.

Concentration

(a) Olivine - 100 units

(b) Hydrochloric acid, 20 percent by weight - 85 percent of the stoichiometric requirement for reaction with MgO and FeO content of olivine.

(c) MgO for first neutralization - 100 percent of theoretical (acid-soluble MgO basis) determined by the excess residual acidity at end of digestion reaction. MgO for final purification - 100 percent of stoichiometric requirement based on FeO content of solution.

(d) Olivine to be added in 20:80 and hydrochloric acid in 85:15 increment ratios.

Particle Size

(a) Olivine used should be in the size range

(-40 + 70)	40-30 percent
(-70 + 100)	30-40 percent
(-100 + 200)	10-20 percent
(-200)	20-10 percent

(b) The MgO used for neutralization should be minus 300-mesh.

Agitation during digestion - first neutralization

It was impossible to obtain significant data for the effect of this variable on the operational scale used in these tests.

FeO/MgO weight ratio in solution

At end of digestion 0.1590

After first neutralization . .0150

After second neutralization. .0002

Recoveries	Percent
MgO and FeO from olivine (digestion - first-neutralization process) Note: MgO is discarded in the undecomposed olivine of the residue.	83
Hydrochloric acid (digestion - first-neutralization process)	97
Solubles in residue (digestion - first-neutralization process)	98
Solubles in residue (second-neutralization process)	98
Magnesia for neutralization (total input basis)	85+
Over-all magnesia from olivine	80+

Mother liquor and wash-water data

Mother-liquor retention of residue

(a) Digestion - first-neutralization - 33 percent of solution produced on digestion

(b) Second neutralization - arbitrarily the same, in the weight ratio of the two residues.

Wash-water requirements

(a) Digestion-first neutralization - 4-5 pounds H_2O per pound of residue dried at 800° C.

(b) Second neutralization - arbitrarily the same.

Permissible $MgCl_2$ concentration of 20-percent hydrochloric acid

25 to 30 grams per liter (for batch operation only).

A pilot plant was designed on the foregoing laboratory data and subsequently erected. Numerous batch operations were made and the data obtained are summarized in the latter half of this section. Unfortunately, it became necessary to cease the investigation before any continuous testing and as a result, it was not possible to obtain performance characteristics of equipment essentially continuous in nature. The plant arrangement was not such that batches could be made and stored prior to test runs of the equipment, thus only qualitative estimations of equipment performance were possible. Description of the pilot plant equipment follows:

Olivine Storage: Ground olivine was stored in the steel hopper shown in Figure 8. Ore was dumped out the bottom into ore boxes and these taken to the scales, where the desired amounts were weighed.

Acid Storage: The acid storage tanks, Figure 8, were obtained from another pilot plant project. They were 5 feet diameter by 5 feet high with a capacity of 700 gallons. Their construction was of welded steel, fitted with a steel cover. The first lining applied was "Lastiglas," a plastic covering applied by the Bishropic Products Company, Cincinnati, Ohio. Although this material is unaffected by 20% HCl, it has the disadvantage of being fragile, requiring extreme care in handling the tanks in order to prevent chipping. The Lastiglas lining proved inadequate, either because of rough handling of the tanks or the nature of the tank surfaces making the requisite bond of lining to steel impossible to attain.

The Lastiglas was subsequently removed by sand-blasting and the

Fig. 8— Raw Material Storage

tanks lined with Nukem Sealtex, an asphaltic type coating made by Nukem Products Inc., Buffalo, New York. This was acidproof, but required extreme care in its application so as to prevent pin holes. As finally used, the tanks held acid for several weeks; however, occasional bubbles were noted in the acid, showing that one or two pin holes were present. These caused rapid deterioration of the lining.

Acid heater: The acid heater, Figure 9, was a Karbate kettle made from a section of a Karbate absorbing tower, 33 inches diameter by 36 inches high, holding 110 gallons. The top and bottom sections were Karbate also, the bottom being cemented to the shell, and the top held in place by bolting a flat ring to the steel base on which the kettle rested.

The kettle was heated by 60 p.s.i. steam using 4 bayonet-type tantalum heaters inserted through nozzles in the cover. The heaters were 2 inches diameter by 39 inches long; they were adapted for the kettle with home-made graphite adaptors, lined with Karbate cement. Karbate heaters 3 inches diameter by 36 inches long were also used; they had approximately one-half the rate of heat transfer of the tantalum heaters, but cost only one-twelfth as much. In a commercial installation the Karbate heaters would be preferred on an economic basis.

Agitation was provided by a 12-inch diameter, 4-blade, 45° Haveg turbine-type agitator, rotated at 230 r.p.m. by a gear head motor. Originally, a 12-inch 6-blade, 45° turbine-type agitator fabricated from Hastelloy B was installed. The impeller, a casting, was soon sufficiently corroded so that agitation was poor, although the shaft was not noticeably attacked.

A thermometer well and a reflux condenser completed the accessories

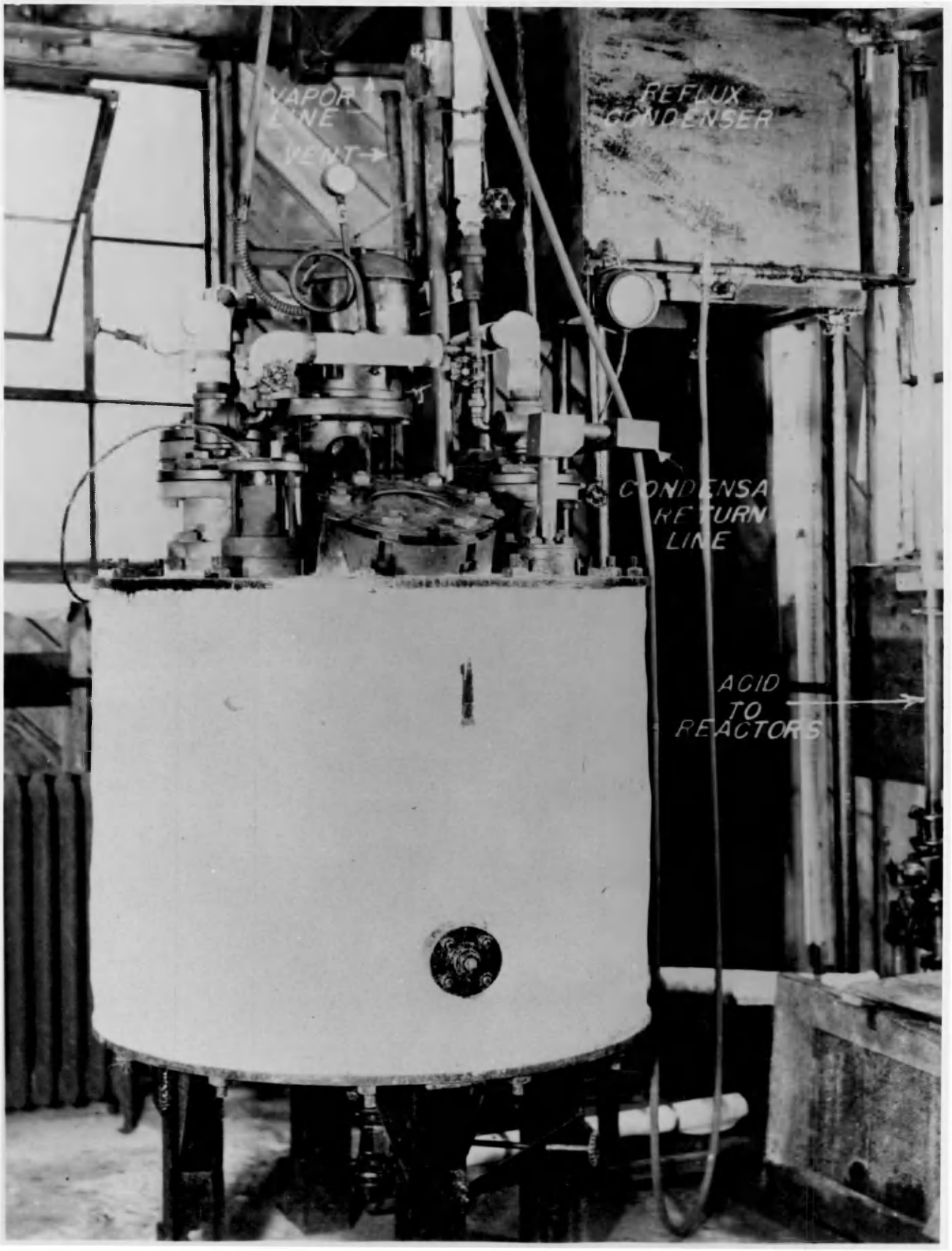


Fig. 9 — Acid Heater

of the acid heater.

Using 60 p.s.i. steam and the tantalum heaters, 100 gallons of 20 percent HCl could be heated from 20° to 105°C. in 30 minutes.

Reactors: The reactors, Figures 10 and 11, were made of Haveg. Each had a capacity of 68 gallons.

Each reactor was connected to a reflux condenser and was equipped with a thermometer well and electrical level controls. Acid was piped from the heater to the reactors in 1-inch Pyrex glass lines, the valve at the reactor being a 1-inch Pyrex plug cock. Illumination was provided by a 25-watt bulb through a sight glass affixed to a 1-inch nozzle; a 7-inch sight glass permitted observation of the tank contents during reaction.

The agitators were 4-blade, 45° Haveg turbines, either 12 inches or 7 inches diameter, driven by gear head motors. The 12-inch diameter impellers rotated at 230 r.p.m., the 7-inch impellers at 420 r.p.m. The thermometer well and electrical level controls served as baffles.

Reflux condensers: The reflux condensers were 1-inch Karbate pipe immersed in a steel shell using Flexlock connections. The cooling water inlet was at the shell bottom, and the overflow was from the top. Each condenser had 24 feet of pipe, equivalent to 9.5 sq. ft. area.

The condensers were connected to the heater and the reactors by Karbate pipe; the return was through a liquid seal. Spool pieces of Pyrex pipe were inserted in the return line to allow observation of the condensate flow.

Slurry mixing tank: The slurry mixing tank, Figure 10, was of mild steel and welded construction. It was a cone-bottom tank, 20 inches diameter by 15 inches high on the straight side. The cone was

Fig. 10— Reactor For Digestion And First Neutralization

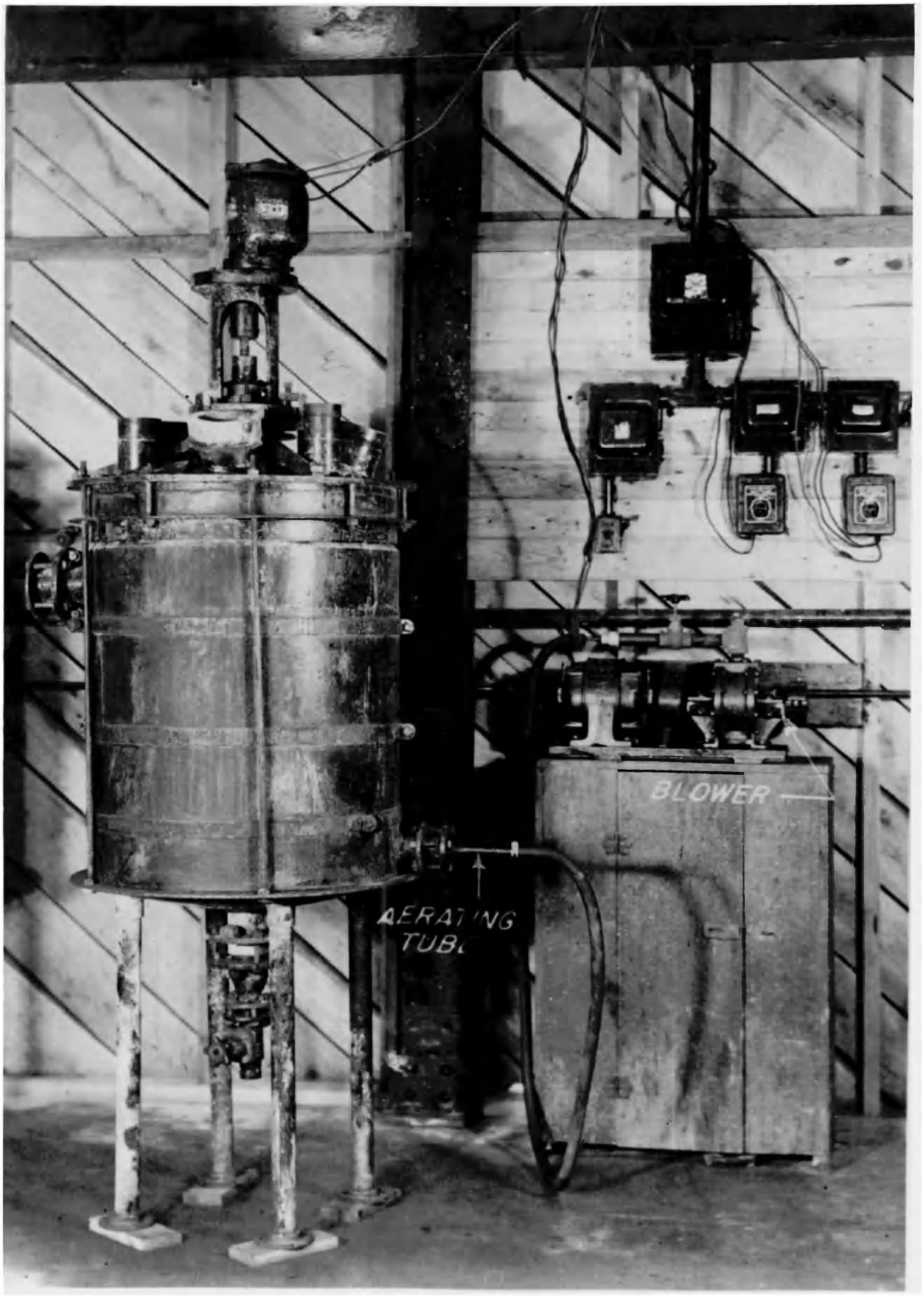


Fig. II – Reactor For Second Neutralization

7 inches high. The shell was lined with Tygon paint, the cone with Nukem Sealtex. No trouble was encountered with these linings.

Vacuum filter: The vacuum filter, Figure 12, was a combination precoat or conventional, high or low submergence type. It was fabricated from Monel metal. The 24 section drum was 3 feet in diameter with a 1-foot wide face, equipped with Monel screen as the filtering medium.

In addition to a dry vacuum pump and receivers, a condenser was supplied to eliminate any flashing of filtrate with possible carry over of acid vapors to the filtrate pump.

Pressure filter: The pressure filter, Figure 13, was the Sweetland type, also made of Monel. It had 11 leaves 8-inches in diameter; 6 were of Monel screen, the remainder being covered with canvas duck.

Bird centrifuge: The Bird centrifuge, Figure 14, was the standard 18-inch bowl size, made of #304 stainless steel. It rotated at 2000 r.p.m. with filtrate discharge by a lead diaphragm pump.

Pumps: Acid was pumped by a Pyrex pump, 3/4 by 1-inch size, rotating at 3600 r.p.m. The slurries were handled in pumps made of Hastelloy B, size 1-1/2 inch by 1-inch, rotating at 1750 r.p.m. The Hastelloy pumps were of both open and closed impeller types. Erosion and corrosion on these pumps over a series of 250 runs was insignificant.

Electrical level controls: The controls were made by attaching platinum contacts to bell wire through a glass seal, and encasing the wires in glass tubes, the whole assembly fitting in a 1-inch Haveg pipe in which 1/2-inch holes had been drilled. The system had 3 electrodes giving 2 contacts; the first gave a warning and the second indicated the desired level of acid in the reactors.

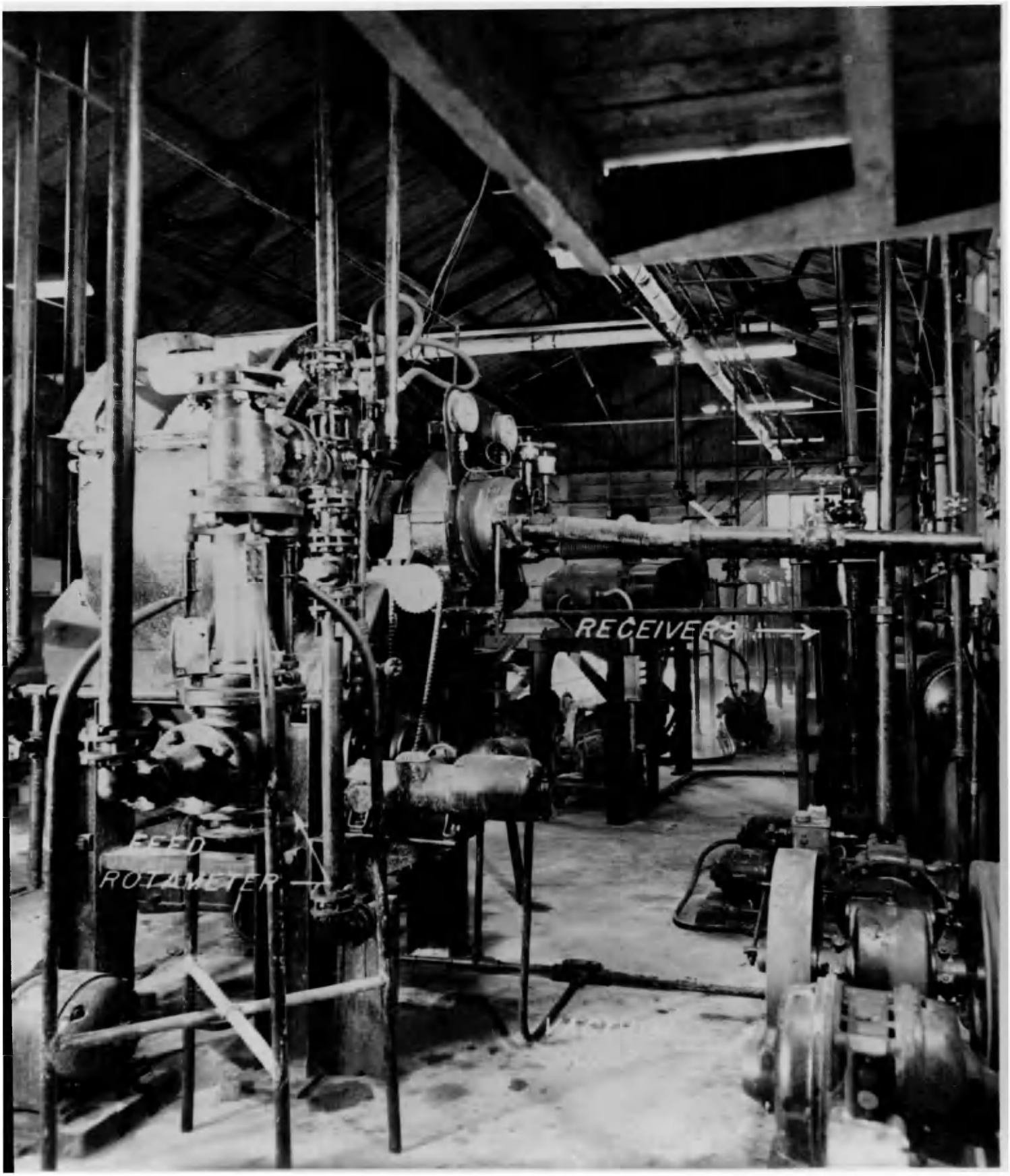


Fig. 12— Continuous Vacuum Filter

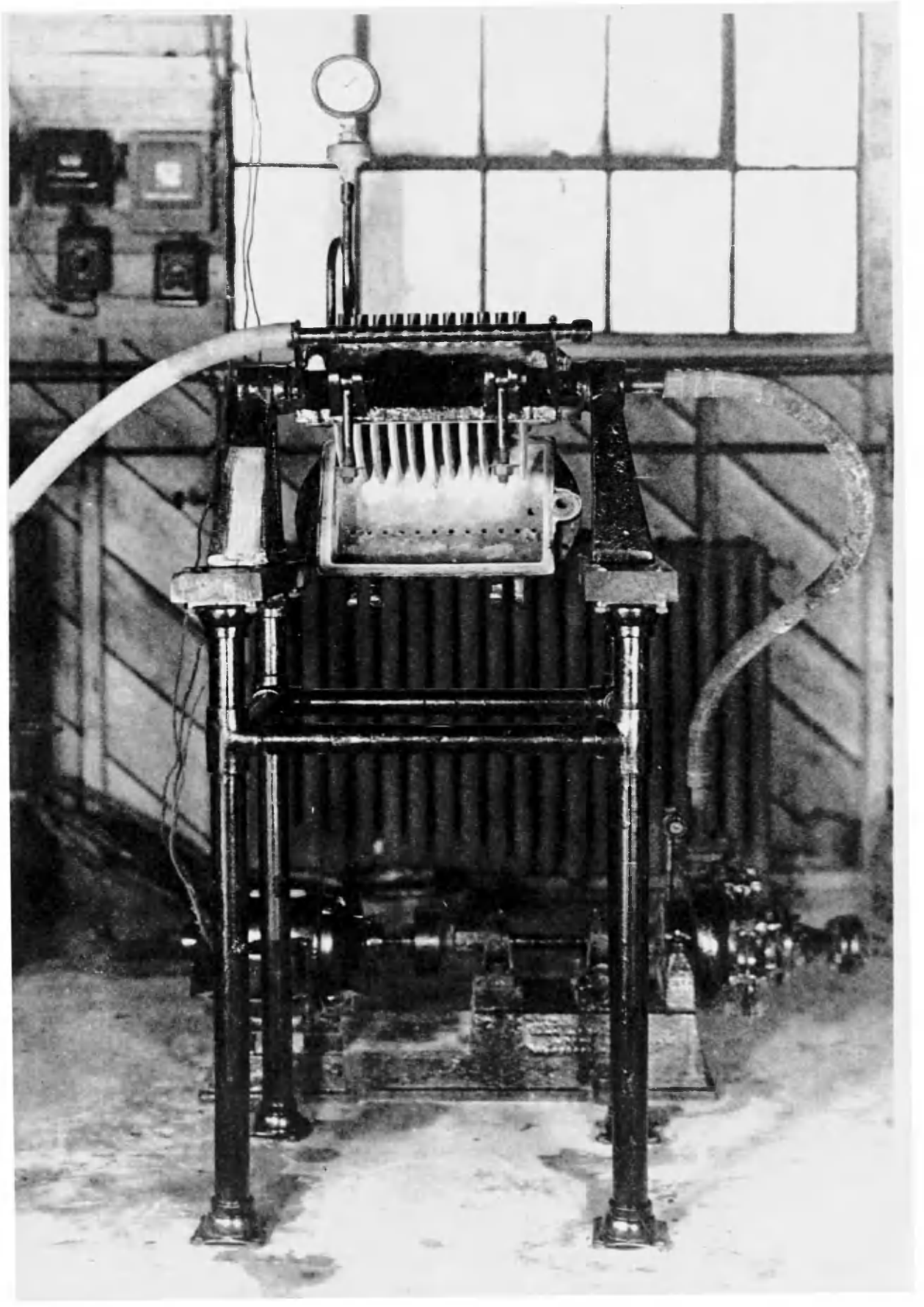


Fig.13—Pressure Filter

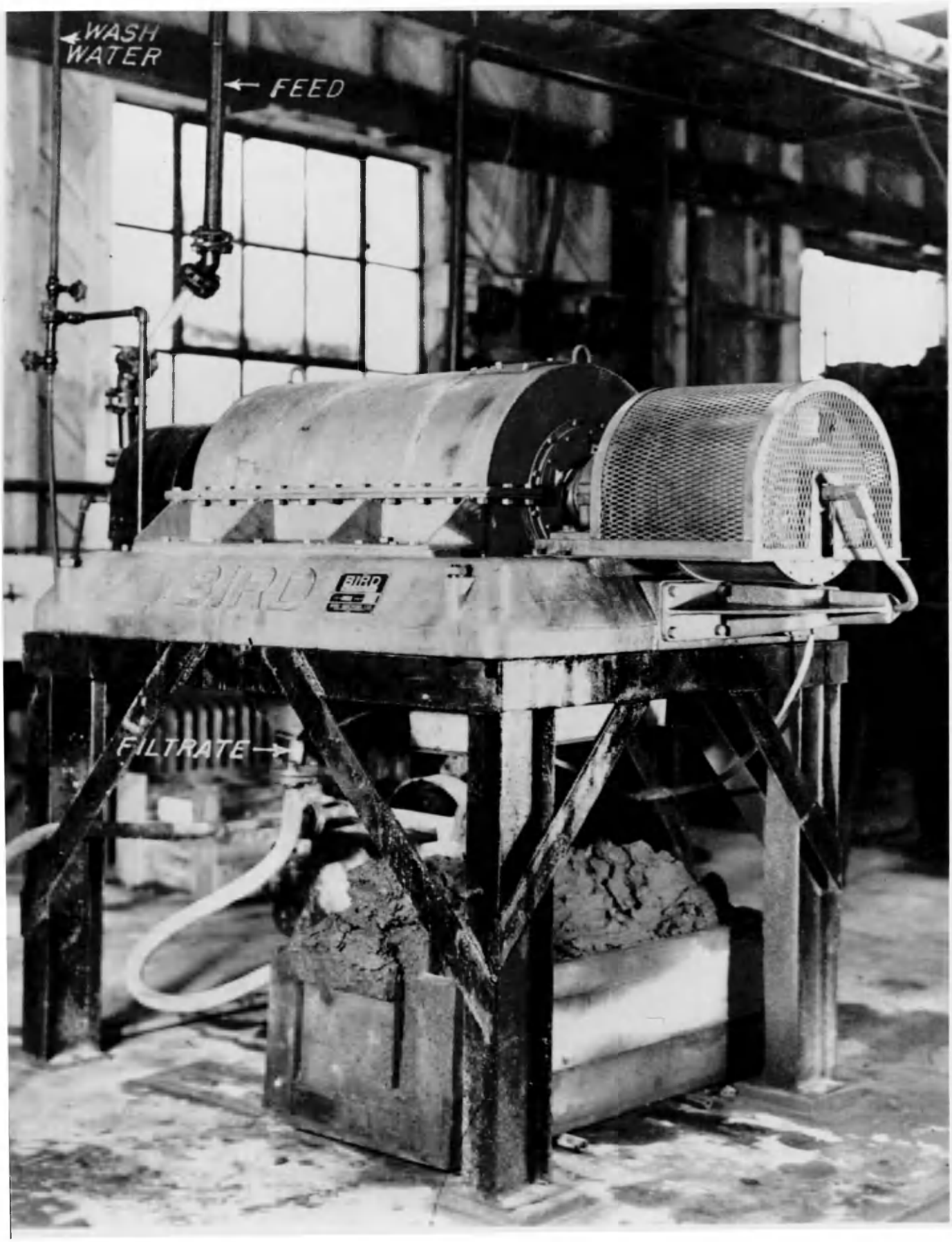


Fig. 14 – Continuous Centrifuge

Processing piping: Other than the Pyrex acid lines, all process piping was 1-inch Haveg pipe. Gaskets were of Koroseal #117.

The method of operation of the pilot plant finally used was the outcome of numerous experiments with different techniques. The original design had tantalum heaters in each reactor to bring the acid-olivine charge to temperature; the heaters soon became coated with a dense silica scale reducing the heat transfer rate. It was then decided to heat the acid outside the reactors, resulting in the acid heater being assembled and used. Similar changes were made in various other phases of the plant operation. The final procedure was as follows:

Acid was heated to 105-108° C. in the heater and pumped to the reactor. The first olivine increment was added through the charging nozzle and the agitator started. Five minutes after reaching the maximum temperature, the second increment slurry was pumped from the slurry tank into the reactor. This was usually done in 5 minutes, as more rapid addition results in foaming out the condenser vent.

The digestion slurry was reacted for the desired time after which samples for excess acidity were obtained. From this, the desired MgO was computed which was slurried with water or $MgCl_2$ solution and added to the digestion slurry. Samples were taken as desired.

The partially neutralized mass was then either centrifuged or filtered. The filtrate was analyzed for FeO, and the amount of MgO needed for a given volume of liquor calculated from this analysis. The MgO was again slurried and added to the liquor, and the mass was reacted and aerated. This final slurry was filtered through the Sweetland filter, using filter aid to precoat the leaves. The final water-white liquor was sampled and analyzed.

The pilot plant digestions used 57 lb. olivine and 25 gal. HCl per batch; this was 300 times the laboratory scale.

The equipment described was used for batchwise operation. Additional equipment purchased for continuous operation but never used included two belt feeders, two disc feeders and four rotometers.

(1) Plant Procedure

As preliminary experiments showed that internal heating of the acid-ore slurry resulted in rapid fouling of the heat transfer surfaces with a dense silica scale, the acid was brought to approximately 105° C. in the heater, Figure 9. The reactors were preheated with live steam to prevent excessive cooling of the acid when it was finally transferred from the acid heater.

For an attempted 85-percent decomposition of the olivine, 21.4 gallons of 20-percent HCl, measured at 105° C., were pumped from the heater into the reactor. The first ore increment, 11 pounds, was then added through the charging nozzle, the cover fastened, the agitator started and the mass reacted for the desired time. When the acid in the reactor was above 95° C., the heat of the reaction was sufficient to maintain the required temperature.

Five gallons of cold, 20-percent acid were slurried with 46 pounds of olivine in the slurry tank, Figure 10, and added to the reactor as the second increment. After this had been added, samples were taken, usually at five-minute intervals, until the total reaction time was 60 to 90 minutes.

(2) Particle Size

The first pilot-plant digestions were run using minus 200-mesh olivine. While no trouble in the first increment was encountered, it

was unsuitable for the second increment. If the second increment in slurry was added too rapidly, reaction was so fast that the condenser flooded and material surged out the vent. In attempting to reduce the rate of the second increment addition, it was found that in a very short time the components reacted in the slurry tank forming a stiff paste which could not be pumped. The operating conditions were so critical that use of such fine ore was impractical and a new batch of ore was ball-milled to the screen analysis given in Table 26.

TABLE 26. - Screen Analysis of Olivine

Mesh size	Weight, percent
-70 + 100	10
-100 + 200	50
-200 + 300	25
-300	15
	100

Using this material, the second increment could be added in four or five minutes without untoward surging and no trouble was experienced in the slurry tank. The reaction was slower than with the minus 200-mesh olivine, so that some runs were made using the fine material in the first increment, the coarser ore in the second.

(3) Time of Addition of Second Increment

In the laboratory, the first increment was reacted for 10 minutes at 108° C. In the pilot plant using the filtration rate as the criterion, it was found that the preferred time was five minutes after the first increment had attained its maximum temperature, ±1° C. Usually, the maximum temperature during the first increment reaction was 104-106° C. This procedure gave a filtration rate of 20 gal./hr./sq.ft., compared

to a maximum of 11 gal./hr./sq.ft., obtained by adding the second increment at a fixed time after the initiation of the reaction. The results are in excellent agreement with the rates obtained with small scale testing. Non increment digestion in the pilot plant gave a relatively unfilterable mass.

(4) Acid-Ore Ratio

The first variable investigated was the ratio of acid to olivine. Runs were made in the range of 80 - 95.4 percent of the stoichiometrically required acid (calculated on the basis of the MgO and FeO content of the olivine). Data given in Table 27 indicate that the actual MgO yield deviates from the theoretical by an increasing amount as the attempted percent decomposition increases.

TABLE 27. - Determination of Optimum Acid: Ore Ratio

Attempted decomposition, percent total required acid	Recovery, percent of original material in olivine		Filtration rate	Excess Acidity, percent	Time to reach equil., min. [1]
	MgO	FeO			
80	80.7	79.8	17.6	——	20
81.2	81.3	77.1	11.0	10.3	20
85	83.6	80.9	16.2	——	30
86.2	83.6	82.2	14.0	10.1	30
89.2	85.0	83.8	18.6	12.0	30
90	87.2	84.2	17.2	——	30
91.2	87.4	88.1	15.0	14.3	30
93.6	86.7	87.8	18.9	15.9	40
95.4	87.9	82.5	18.8	17.3	40

[1] Time is given to the nearest five minutes when for this period $\frac{\triangle (E.A.)}{\triangle t} = 0$.

The optimum acid-ore ratio was determined by an economic appraisal. All digestion slurries were assumed to be neutralized by the same procedure, and the efficiency of MgO utilization in the neutralizing

reaction was taken as constant. A comparison of equipment and MgO costs showed that the cost per lb. of MgO was essentially constant in the range of 85 to 89 percent attempted decomposition. Inasmuch as all preliminary laboratory work had been done with a ratio of 85 percent, it was deemed desirable to continue this in the pilot plant so that laboratory and pilot plant work could be more readily compared.

(5) Increment Proportions

Laboratory work had indicated the use of 20 percent of the olivine in the first increment and 80 percent in the second. Several incremental splits were checked in the pilot plant, the results confirming the laboratory findings. Filtration rates were employed as the criterion, no significant difference being detected in the MgO yields. The 10-90 olivine split was inoperable as the first increment could not maintain the desired temperature, while the second increment then had an appreciable induction period before reacting. When it did react, the mass could not be contained in the reaction vessel, resulting in considerable loss through the vent.

The data from pilot-plant runs are given in Table 28.

The improvement in filtration rate was very marked as the first increment was lowered from 40 to 20 percent, the data being quite consistent. From the standpoint of rapid filtering material, the 20-80 incremental split is much to be preferred to the others.

The check series, the 30-70 split with minus 200-mesh ore in the first increment, showed plainly that the use of finely divided ore lowered the filtration rate. This had been anticipated from previous laboratory work.

As there was no difference in yields or residual acidities, the

higher filtration rates pointed to the use of minus 70-mesh material in both increments.

TABLE 28. - Effect of Variation in Increment Ratio A/

Run No.	Increment Ratio	Recovery, percent of original material in olivine		Filtration Rate	Excess Acidity, percent
		MgO, percent	FeO, percent		
First increment minus 200-mesh, second increment minus 70-mesh olivine					
172	30- 70	83.5	80.8	5.5	10.0
176		85.2	85.1	7.0	11.2
Average		84.3	83.0	6.3	10.6
Both increments minus 70-mesh olivine					
184	40- 60	78.5	71.2	8.4	12.5
186		80.5	73.2	5.8	10.7
188		84.0	77.6	8.5	10.5
Average		81.0	74.0	7.6	11.2
177	30- 70	83.5	81.7	12.1	12.5
178		82.0	79.1	12.9	11.4
179		86.8	84.7	12.2	10.9
Average		84.1	81.8	12.4	11.6
181	20- 80	80.6	75.0	20.0	11.3
187		83.2	76.5	19.5	13.7
189		80.6	76.3	19.5	11.1
Average		81.5	75.9	19.6	12.0

A/ Attempted decomposition - 85.2 percent

(6) Reaction Rate

The reaction rate in the pilot plant for 80-percent attempted decomposition was checked by residual acidity determinations. These excess acidity values became essentially constant 30 minutes after the second increment had been added to the reactor. Figure 15 shows the

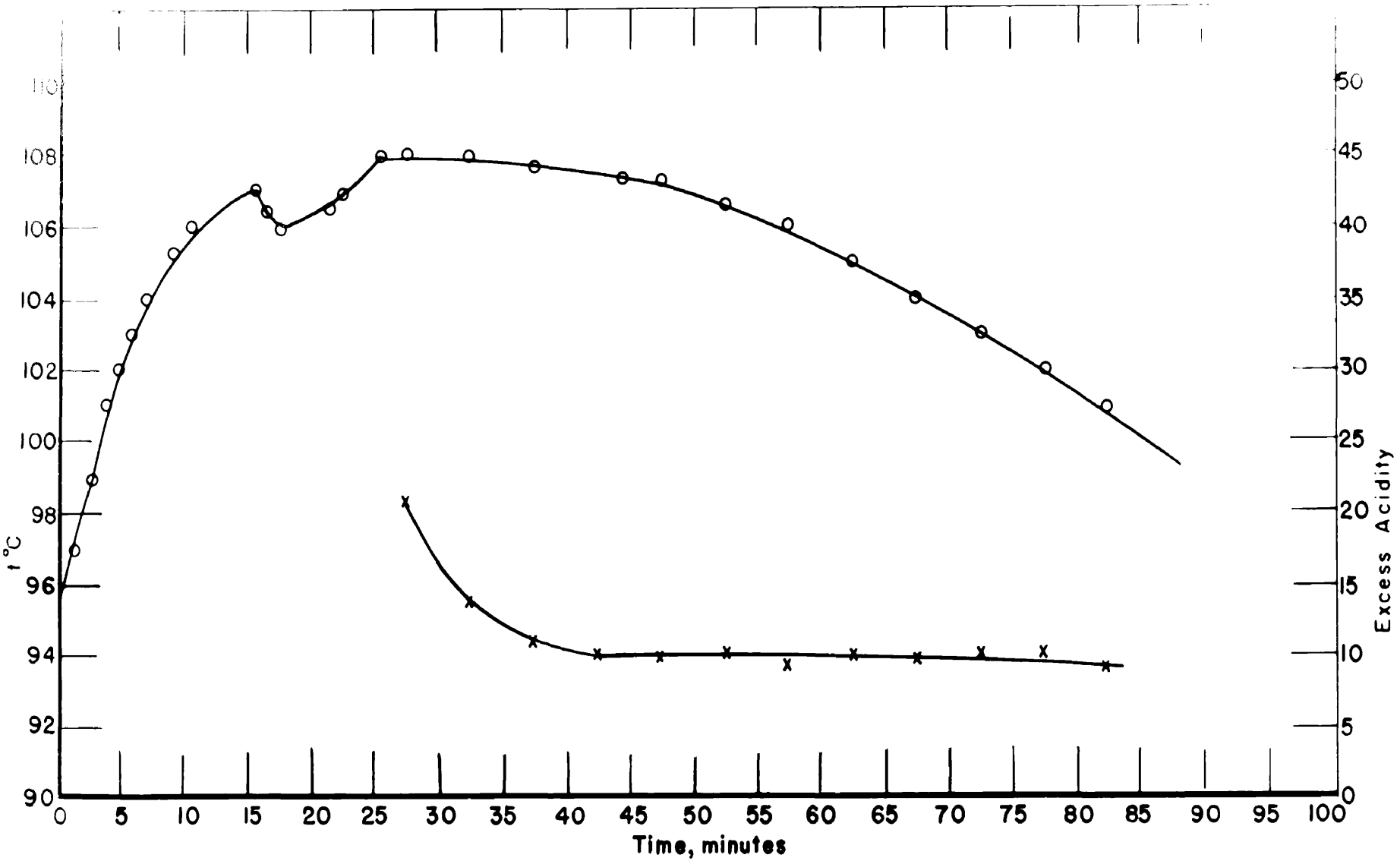


Fig. 15 Rate of Reaction

Filtration Rate: 21.7 gal./sq. ft. hr.

course of the reaction during a run. The lower curve represents excess acidity and the upper, temperature, both as a function of time. The fundamental kinetics of the decomposition will be subsequently treated in detail.

(7) Acid Losses

Ideally, the only source of HCl loss is through the condenser vent. An absorption train was connected to the vent, and any HCl given off collected and analyzed. Over several pilot plant runs, the average was 1 gm. HCl per run, a negligible amount.

(8) Optional Procedures

During the course of the pilot-plant experiments, it was observed that the reflux was heavy after the second increment had been added and ceased an appreciable period of time before the reaction had reached equilibrium.

It was postulated that if the condensate were collected in an outside container instead of being refluxed, the reaction time might be shortened. If the majority of the reaction took place in the first few minutes after the second increment had been added, only a small increase in MgO yield could be obtained with the evaporated and refluxed HCl in the additional reaction time. The excess acidity versus time curves show that the rate of change of acidity with time is high initially, but decreases rapidly and approaches zero. Also, any water vaporized would lower the amount of subsequent evaporation.

Pilot-plant runs were made to check the former possibility. The condensate averaged 3.5 to 4.0 percent of the HCl utilized and flow ceased 20 minutes after addition of the second increment. Five and five tenths percent of the water added with the acid was contained in the

condensate and MgO recovery approximated 82 percent.

From this, it would seem desirable, on a commercial scale, to eliminate the reflux condensers, passing the vapors from the reactors into the HCl-absorption system along with the gases produced by the calcination of $MgCl_2.6H_2O$. This would reduce capital expenditure by the difference in the cost of the condensers and the slight cost of enlarging the HCl absorbers to handle the extra load. This reduction in capital cost, coupled with the reduction in processing time, makes this scheme attractive for an industrial installation.

The preceding pilot plant tests clearly substantiated the results of the laboratory development and it was concluded that the basic technique of increment or stage addition had definite industrial value.

CHAPTER IV

STATEMENT AND ANALYSIS OF THE THEORY

The foregoing results in both the laboratory and pilot plant demonstrated beyond question the validity of the phenomena of increased filtration rates with increment digestion. Remaining was the problem of developing a logical hypothesis of explanation and extending the technique to other silicates.

A. Hypotheses of Explanation

Based upon the general theory of gelation previously discussed (Chapter I), three possible hypotheses for the phenomena of increased filtration rate with stage digestion may be given:

(1) Solution properties such as dissolved salts, acidity, or water content could be the principal factor.

(2) Solid properties such as electrical charge, degree of hydration, or nucleation could be the principal factor.

(3) The increased rate might result from a combination (1) and (2).

Experimental results and the data of previous investigations clearly indicated that solution properties are a factor of considerable importance. The influence of acid concentration and/or small water-solid ratios was discussed (Chapter I) for the data of earlier workers and the author's results are given in Tables 4 and 5. In short, higher acid concentrations give improved filtration characteristics with a concomitant increase in structural density of the gel. This effect per se, however, cannot account for the phenomena of increased rate with increment digestion as the over-all acid concentration is identical with that for

which prohibitively slow filtration rates are usually obtained. Similar reasoning eliminates any possible effect attributable to variation of the liquid-solid ratio.

In connection with their work on gaseous decomposition of olivine, Houston and Rankin state, "It is our hypothesis that the formation of gelatinous silicic acid is avoided by the dehydrating action of magnesium chloride, which takes up water to form a series of hydrates and leaves the silicic acid in a granular condition." 84/ To evaluate this hypothesis, a series of digestions was performed in which 5, 10, 20, and 30 percent by weight of magnesium chloride was added to the raw acid. Ore and acid were mixed in conventional fashion and reacted at boiling. The only observable effect was excessive loss in hydrogen chloride because of its increased vapor pressure.

Subsequent digestions were carried out in a similar fashion with excess quantities of all of the various reactants and products added one at a time to the raw acid.

TABLE 29. - Effect of Excess Reactants

Substance Added	Weight, grams	Filtration Rate
$MgCl_2$	10	1.2
$FeCl_3$	10	0.7
$NiCl_2$	10	1.0
Olivine	10	1.0
$MnCl_2$	10	1.6
H_2O	10	2.0

84/ Houston, E. C., loc. cit.

No filtration improvement to any measurable extent was obtained and when this series was repeated using increment or stage addition, the final filtration rate was substantially lowered. This effect was particularly marked when magnesium chloride was added to the mixture. The conclusion was reached that the effect of salt concentration is not an important factor in the improvement of rate through stage addition.

The first hypothesis was further invalidated in the following manner: A digestion of olivine in aqueous hydrochloric acid was carried out using the standard first stage addition of 20 grams of olivine to 358 ml. of 20 percent acid; but after the initial reaction time of ten minutes, the silicic acid resulting was filtered off. The filtrate was identical in every respect to the environment into which the second increment of olivine is usually added except of course for the absence of the solid phase. Using this filtrate, digestion of the second 80 gram increment was carried out, resulting in prohibitively low rates of 1.9, 2.3, and 2.0 gal./sq.ft., hour even though twenty percent less residual solid was present. This conclusion could be reached from previous data but the foregoing results are perhaps more direct experimental evidence.

The third possibility involving a combination of solution and solid properties was invalidated by similar experimentation. Silicic acid gel formed by digestion of the first increment was separated from the filtrate as in the preceding case. This freshly precipitated solid was washed and repulped five to eight hours with water until no chloride ion was present in the washings as shown by silver nitrate tests. It was assumed at this point that for all practical purposes, the silica gel was free of electrolytes. The solid was then washed

with 20 percent hydrochloric acid for two hours to replace as nearly as possible all absorbed and adsorbed water. This solid was subsequently added to a normal digestion of olivine and acid in which the total charge of ore was added directly to the acid. Filtration rates of 15.3, 22.4 and 10.3 gal./sq.ft., hour were obtained indicating that the increased rate is a function of the residual solid or silicic acid alone.

This experiment, while substantiating the above conclusion, did not completely eliminate the possibility of a solution-solid effect at the time of initial mixing, previous conditioning of the gel, nor the possibility of adsorbed, non-removable ions. It will be subsequently shown, however, that increased rates can be obtained with mineral acids other than hydrochloric acid and for a variety of silicates, widely differing in structure and chemical composition. These latter results eliminated from consideration the effect of particular ions, specific water-solid ratios, etc., characteristic of the olivine-hydrochloric acid system and further minimized the possibility of any dual role by the solid-liquid system in accounting for the phenomena. It was therefore concluded that the primary factor responsible for increased filtration rates with increment digestion was the residual solid and/or silicic acid of the first increment.

B. Experimental Basis of the Theory

The particular manner in which the solid effected the increased rate remained to be determined. It was known that less hydration of the silicic acid resulted from stage addition as can be seen from the contrasting microphotographs in Figure 5, and the data in Table 30 wherein

relative filtrate volumes from stage and normal digestions are contrasted. The same total volume of solution was employed during each series.

TABLE 30. - Relative Filtrate Volume

	Stage additions, ml.	Normal addition, ml.
	230	182
	250	178
	240	170
	235	170
	225	165
	245	160
	210	155
Average	234	169

It should be noted that the increase in filtrate volume exceeds 38 percent. This relatively large increase with stage addition definitely proves that the gel produced by this technique is less hydrous than that ordinarily obtained, probably representing the fundamental reason for increased rates. In addition to the obvious advantages with regard to filtration of the final slurry this decrease in volume of residual solid minimizes wash water requirements.

To eliminate possible effects of unreacted ore in the silica gel and the effects of gel conditioning by the solution environment during its formation, a "synthetic" gel was produced. Baker's analyzed sodium silicate containing nine molecules of water was treated with a large excess of twenty percent hydrochloric acid to produce a gel whose history could in no way be related to the impurities such as iron, nickel, manganese, chromium, present in olivine. The addition of this gel to a normal digestion of olivine and acid gave rates of 8.8, 10.3, and 11.2 gal./sq.ft., hour. Although these are not as high as those obtained with multistage digestion, they represent more than a five-fold increase

in the average rate obtained with normal digestion.

The foregoing experiment is of great significance. It shows that the phenomena is not dependent upon silicic acid gel obtained from olivine nor is it a function of any particular solution conditioning during the gel formation.

Before evolving a hypothesis which is believed to best describe the observed phenomena, a survey of certain facts, many of which have been already discussed, will be useful.

(1) The volume of filter cake is decreased by about 50 percent when increment digestion is employed.

(2) The volume of filtrate is increased by about 40 percent when increment digestion is employed.

(3) Microscopic examination of the filter cakes by the two procedures discloses the increment residue to be much drier and apparently more granular.

(4) Use of large excesses of 20 percent hydrochloric acid as exists in the environment of the first increment causes prohibitively low rates.

(5) Use of weaker concentrations of hydrochloric acid causes gelation.

(6) Stronger concentrations of hydrochloric acid give increased filtration rates.

(7) The increased rate with multistage digestion is apparently a function of the solid phase alone, i.e. the silicic acid gel produced from the first increment of ore.

(8) The increased rate with multistage digestion is not a function of solution properties of the reaction slurry.

(9) "Synthetic" gels produced from silicate salts also give

increased filtration rates.

(10) X-ray studies show no difference in structure between residue obtained by multistage and normal digestion.

(11) The final reaction slurry obtained by any procedure must be neutralized to obtain the maximum increased rate.

(12) Multistage digestions yield slurries which possess good filtration characteristics even at low temperatures which is in direct contrast to slurries obtained from conventional decomposition techniques.

C. Statement of the Theory

Based upon the above facts, the following theory was developed: The first increment of ore added to the strong acid reacts to form a gelatinous finely divided silicic acid gel which rapidly adsorbs hydrogen ions from the large excess of acid present; this agrees with the results of Iosenbeck. 85/ Particles of the much larger second increment added to an overall acid concentration which, under ordinary conditions, would produce excessive gelation, are immediately coated with very finely divided gel of the first increment. Adsorbed hydrogen ions on the surface of the initial gel are in preferred state for reaction, however, and their effective concentration is therefore much higher than indicated by the overall acid concentration. Surface phenomena of this type, especially catalytic reactions, are not uncommon and the increased temperature at the phase boundry of gel and olivine minimizes hydration of the silicic acid colloid produced. The general conclusion is substantiated by the fact that higher concentrations of acid, reacting at

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85/ Iosenbeck, O., loc. cit.

higher temperatures, produce less highly hydrated residues (Tables 4 and 5).

Silicic acid gel formed by this reaction is then in an ideal condition for aggregating and condensing with the gel of the first increment which results in minimum entrainment and absorption of water. Aggregatized silicic acid and free colloid present in the slurry after digestion, however, are in a highly charged condition which prevents complete flocculation and immediate filtration fails to achieve maximum rates. After neutralization the charge on the particles is removed permitting condensation of the colloid and giving a relatively coarse, quickly filtering, slightly hydrated residue.

D. Analysis of the Theory

The author has postulated that the reaction between olivine or any alternate gelatinizing silicate in the presence of silicic acid gel is essentially catalytic in nature and a brief consideration of the fundamental bases of such mechanisms is in order.

In the majority of positive catalytic reactions, the catalyst causes chemical reactions to take place at an energy level lower than that at which they would occur without the catalyst. Many colloidal substances are recognized for their catalytic effect on chemical reactions, e.g., colloidal aluminum silicates, hydrous alumina, hydrous iron oxide, and as postulated for this reaction, silicic acid gel.86/

It may be considered probable that any chemical compound can act

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86/ Lohse, H. W., Catalytic Chemistry: New York, Chemical Publishing Co., Inc., 1945, p. 2.

catalytically under one particular set of conditions or another. Consequently a discussion of the subject requires definition and limitation. Catalytically active substances can be divided into two broad groups:

1. Well defined chemical compounds which react according to well defined catalytic reaction schemes, their special action mostly being the formation of a labile intermediary compound. This type is commonly encountered in homogeneous catalysis, examples being the halogens, acids, bases and salts.

2. Contact masses, such as are encountered in heterogeneous catalytic reactions where the reacting and resulting substances are in different phases. As heterogeneous reactions take place on phase boundaries, the term phase-boundary catalyst is frequently used. This latter type, with which we are solely concerned, has no completely satisfactory interpretation by theory. It appears, that a labile compound of very short existance is formed between unsaturated surface atoms and those of one or both of the reactants. The contact surface may react with one reactant forming a labile compound which is reactive with the other reactant; or both reactants may form a labile compound with the contact surface, the adjacent surface compounds reacting with each other forming a compound of less affinity to the surface.87/

In general it is assumed that catalytic reactions and possibly all reactions, proceed by the formation of a critical complex, which decomposes into the substances resulting from the reaction,

$$A + B \longrightarrow X \longrightarrow C + D.$$

87/ Lohse, H. W., Ibid, p. 115.

The formation of this critical complex is slow and frequently determines the velocity of the reaction. The formation of X depends upon the activities of A and B, and the reaction velocity is expressed by

$$V = k\, a_A\, a_B \cdot \frac{1}{f_X}$$

where a_A and a_B are the activities of A and B, f_X is the activity coefficient of X and k is a constant. 88/ For the system at hand it appears that the formation of the hydrogen ion-silicic acid-olivine complex corresponds to the labile compound or critical complex.

Taylor conceives the catalyst surface as consisting of unsaturated atoms, more or less loosely held to the underlying lattice structure, such peak atoms being haphazardly distributed on the surface and having a varied number of free valances. Such peak atoms, with unsaturated valance forces, are considered to be the seat of catalytic activity of the surface, being termed active centers. Silica gel and silicic acid colloids are known to exhibit these characteristics. With such solids the rigidity of surface atoms prevents the formation of surface tension effects, although the surface of the solid still tends to reduce itself, this being accomplished by adsorption onto the surface of molecules or atoms from the liquid phase with which the solid surface is in contact.89/ For the system at hand this is accomplished by the adsorption of hydrogen ions.

88/ Bronsted, J. N., (Theory of Chemical Reaction Velocity): Zeit. Phys. Chem., vol. 102, 1922, pp. 169 - 207.

89/ Burk, R. E., Twelfth Report of the Committee on Catalysis, National Research Council: New York, John Wiley & Sons, Inc., 1940, pp. 41. (Section by H. S. Taylor.)

The catalytic nature of the olivine-hydrochloric acid reaction will be subsequently substantiated by an examination of the reaction kinetics and a general discussion of the controlling variables is indicated. As is common with complex heterogeneous systems of this type, especially where catalysis is concerned, the reaction does not fit a particular order based on collision mechanism. Empirically it can be deduced that the rate is a function of temperature, hydrogen ion concentration, surface area and the diffusion resistance of the gelatinous film adhering to each particle of silicate. The overall rate is, however, a function primarily of the slowest variable, which in this case is the diffusion resistance of the gelatinous film which serves as a barrier both to the transfer of hydrogen ion to the contact surface and the removal of the products of reaction.

There had been observed a certain critical agitation rate below which the rate of reaction became a function of the stirring velocity. Apparently with agitation characteristics above the critical, the mutual affinity of the components of the contact surface prevents further decrease in film thickness by slurry abrasion, while below this point, there is an increase in the linear thickness with an accompanying increase in resistance to ion diffusion.

There is some indication that the diffusion rate of magnesium and chloride ions from the surface is the controlling variable. Very low filtration rates were obtained with increment digestion when large amounts of the salt were added to the reaction slurry. This was also accompanied by a decrease in the rate of reaction.

It is possible to develop an equation for reactions of this type

based on established theory for the rate of dissolution of solid crystals.90/

$$\frac{dx}{dt} = KA(C-x)$$

K is the dissolution constant and for the system under consideration is dependent upon the coefficient of diffusion (D) of the reactants and products through the gel film and the thickness of the film (l). Let (A) be the area of the contact surface, (C) the saturation concentration of the dissolved substances at the phase boundary and (x) the concentration in the liquid phase. Also to be considered are the mutual affinity of contact surface and the resultants (h) and the heat of formation (H). Substituting in the above equation a general equation for the reaction would approximate:

$$\frac{dx}{dt} = \frac{D}{\ell}\,\frac{HA}{h}(C-x)$$

For a given temperature and given agitation rate, D/l will be constant and as pointed out earlier in this section there was a certain critical agitation rate below which the rate decreased, other conditions being equal. This is in agreement with the above equation, for as agitation is increased, a point is reached beyond which the affinity of the gel for the particle surface exceeds the abrasive action of the slurry. There is encountered at this point a problem which frequently results on analyzing analogous systems for the rate of solution of solid crystals and the following approach is believed unique:

90/ Brunner, E. I., (Reaction Velocity in Heterogeneous Systems): Zeit. Phys. Chem., vol. 47, 1904, p. 56.

As reaction proceeds, the solid surface A varies and the above equation therefore represents a maximum rate. This fact can be incorporated as follows:

Let g = moles of olivine taken for test

ρ = density of particles

D = original average diameter of particle assuming them to be spheres (surface of one particle = πD^2 volume of one particle = $\frac{\pi D^3}{6}$)

m = molecular weight

V = volume of liquid system

The number of particles charged N, is given by

$$N = \frac{gm}{\rho} \cdot \frac{6}{\pi D^3} = \frac{6gm}{\pi \rho D^3}$$

The mass of one particle is $\frac{\pi D^3 \rho}{6}$. Now, if at time t, Vx moles of olivine have reacted, the decrease in mass per particle is given by

$$\frac{Vx\,m}{N} = Vx \frac{\pi \rho D^3}{6gm} = \frac{\pi \rho D^3 Vx}{6g}$$

the variable mass of one particle is then

$$\frac{\pi D^3 \rho}{6} - \frac{\pi \rho D^3 Vx}{6g} = \frac{\pi \rho D^3}{6}\left[1 - \frac{Vx}{g}\right] = \frac{\pi \rho D^3}{6g}(g - Vx)$$

The volume of the variable particle is

$$\frac{1}{\rho} \cdot \frac{\pi \rho D^3}{6g}(g - Vx) = \frac{\pi D^3}{6g}(g - Vx)$$

Let d = variable diameter of the particle, so

$$\frac{\pi d^3}{6} = \frac{\pi D^3}{6g}(g - Vx) \quad \text{or} \quad d = D\left(\frac{g - Vx}{g}\right)^{1/3}$$

The variable surface per particle is $\pi d^2 = \pi D^2 \left(\frac{g - Vx}{g}\right)^{2/3}$

So that the total variable surface on which reaction can occur is given by

$$A = (\pi d^2) N = \frac{6gm}{\pi \rho D^3} \cdot \pi D^2 \left(\frac{g - Vx}{g}\right)^{2/3} = \frac{6gm}{\rho D}\left(\frac{g - Vx}{g}\right)^{2/3} = \frac{6m}{\rho D}(g)^{1/3}(g - Vx)^{2/3}$$

Accordingly, the differential equation may be expressed by

$$\frac{dx}{dt} = \frac{D}{\ell}\,\frac{H}{h}\,\frac{6m}{\rho D}\,(g)^{1/3}(g - Vx)^{2/3}\,(C - x)$$

As at a given temperature and agitation rate, $\frac{D}{\ell}$ is constant, we can unite

$$\frac{dx}{dt} = k\,\frac{H}{h}\,\frac{6m}{\rho D}\,(g)^{1/3}\,(g - Vx)^{2/3}\,(C - x)$$

It was not possible to integrate the above equation because of the unknown concentration of salts at the contact surface. Similar equations may be integrated, however, in slightly different form for the general problem of dissolution of solid crystals, where to the best of the author's knowledge, no such correction for variation in particle size has been made. For such cases the concentration at the interface can be assumed equal to the saturation solubility value of the salt and the equation thus becomes integrable.

Qualitatively the results of actual kinetic measurements are in agreement with the above equation. A series of digestions of olivine and hydrochloric acid were carried out for various periods of time followed by quenching in a large excess of water to minimize further reaction and the results are tabulated in Table 31 and plotted in Figure 16. Two series are tabulated, the first corresponds to a conventional digestion in which the total quantity of olivine is added directly to the acid and the second corresponds to increment or stage addition. In order to obtain a continuous series of data, it was necessary to simulate increment digestion by adding washed silica gel to the normal reaction mixture. The validity of this method of operation was previously discussed.

There is a striking increase in the initial rate when conditions

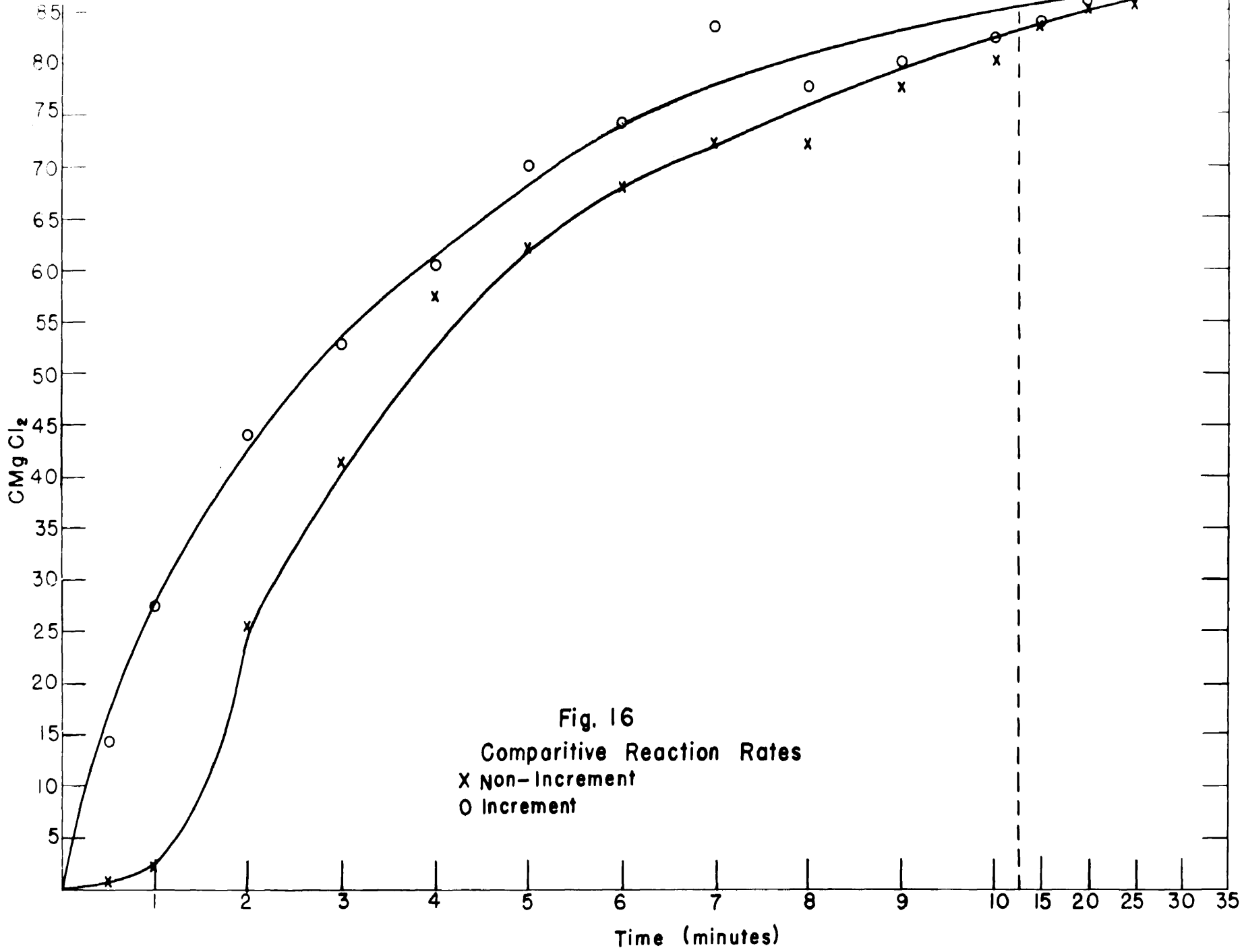

Fig. 16

Comparitive Reaction Rates

X Non-Increment

O Increment

approximating increment digestion are simulated. Therefore, it appears logical to assume that the reaction is catalytic in nature as by definition catalytic reactions are those wherein either an increase or decrease in rate occurs through the addition of a material which is recovered unchanged at the conclusion of the reaction. The silicic acid gel initially formed is the catalytic substance which functions through the adsorption of hydrogen ions probably on the peak atoms of the gel surface with unsatisfied valance forces.

TABLE 31. - Rate of Reaction

Time, Minutes	Non-Increment Concentration $MgCl_2$, grams	Increment Concentration $MgCl_2$, grams
0.5	1.0	14.5
1	2.1	27.8
2	25.3	44.1
3	41.8	53.0
4	57.5	60.5
5	62.0	70.1
6	67.3	74.1
7	72.0	83.5
8	71.8	77.8
9	77.5	80.0
10	80.0	82.5
15	83.4	84.2
20	85.0	86.0
25	85.6	86.6
30	87.0	87.3
35	88.1	88.1
40	88.2	87.9
45	88.5	88.2
50	88.7	88.8
55	89.0	88.6
60	88.9	89.0

Although the particular mechanism by which heterogeneous catalysis occurs is still relatively unknown, some investigators feel that the contact surface causes a diminution of the required heat of activation

due to disruption of the reacting molecules by a strain action, which is developed by attachment of neighboring atoms to two adjacent atoms on the surface of the catalyst.91/ In contrast to the simpler case involving diffusion of gaseous reactants to metallic surfaces, catalytic contact between hydrogen ions and olivine particles is believed to result only through actual coating of the particles whereby strain action can develop. The hydrogen ion-silicic acid-olivine complex is believed to correspond to the labile compound postulated by the present theory.

Chemical-physical action on a catalytic contact surface is much enhanced by the very large amount of heat envolved during the chemical change on the surface. In other words, the chemical reaction sphere, on contact surfaces, is probably a zone of higher temperatures than the surroundings.92/ This effect accounts at least in part for the lowering of the hydration of the silicic acid colloid produced on reaction of the second increment. It has been established that increased temperatures decrease the extent of gel hydration, this conclusion extending even into the range of autoclaving, and as indicated, temperatures greater than those of surroundings are probably encountered at the contact surface. It must be emphasized that the usual heat of chemical reaction starts and maintains the overall reaction and it is the resistance of the diffusion barrier to heat transfer which permits increased surface temperatures.

91/ Burk, R. E. V., Possible Mechanisms for the Lowering of the Heat of Activation of a Reaction by a Catalytic Surface: Jour. Phys. Chem., vol. 30, 1926, p. 1134.

92/ Lohse, H. W., op. cit., pp. 18 - 19.

An examination of Figure 16 discloses that non-increment digestions have a relatively low initial rate of reaction which rapidly increases after a few minutes, gradually approaching the increment rate as a limit. This is believed to be a direct result of the formation of silicic acid which provides a catalytic reaction surface similar to that obtained by the initial addition of gel. There is some indication that the adsorption of hydrogen ions by the colloid and gel is not instantaneous, the result of which would be to emphasize the difference in velocity rate between the two procedures of decomposition. The manner in which reaction rates for both increment and non-increment decompositions converge after widely differing initial velocities is attributable to the gradual increase in silicic acid gel, present in the latter case, to a certain required minimum concentration. The second situation may be compared to the usual case of autocatalysis where a reaction product acts as a catalyst, there being no catalyst present at the beginning of the reaction. The slow initial velocity encountered with non-increment digestion may be thus interpreted as an induction period due to the lack of sufficient intermediary silicic acid from the reaction to initiate autocatalysis.

At the conclusion of the reaction under normal procedures of operation there remains an excess of both olivine and a small amount of free acid. Reversible conditions are therefore assumed, although in this system the reversibility may be a function of the diffusion barrier resistance. In ordinary reversible processes, a catalyst acts in bringing about equilibrium more rapidly than without a catalyst, but the catalyst does not change the equilibrium point. Consequently the two opposing reactions are accelerated to the same extent by the

catalyst, which is possibly the case with the system at hand.93/ As previously pointed out the convergence of the two velocity rates near the equilibrium concentration is probably a function of the auto-catalytic nature of the silicic acid produced.

As the reaction proceeds silicic acid colloid is constantly being produced and subsequently removed from the surface of olivine particles by slurry attrition. This colloid is in a preferred condition for aggregating and condensing with gel of the first increment, from the point of view of final filtration rate, as it is less hydrated than that obtained under normal conditions.

The electrical charge on the colloid prevents immediate and complete condensation to a relatively dense silicic acid structure, however, and neutralization of the acid and acidic salts present in the system is necessary to achieve maximum filtration rates. The maximum aggregation or condensation velocity of silicic acid colloid occurs near pH - 7 as at this point there are equal numbers of positive and negative particles of colloid which on impact can condense through the elimination of a molecule of water. The reaction collision frequency for a given quantity of colloid is obviously a maximum when there are equivalent numbers of positive and negative particles. Formation of the final, relatively dense fibrillar or brush heap structure of silicic acid is believed to follow the previously described condensation mechanism.

The theory advanced in the preceding section is believed to be

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93/ Bronsted, J. N., Physical Chemistry: London, William Heineman Ltd., 1937, p. 247.

consistent with the accepted mechanism of gelation previously outlined and observed experimental results; only one alternate hypothesis was given serious consideration. At one stage of the study it had been the tentative conclusion of the author that the preliminary increment, reacted in a relatively fluid solution with freedom of movement, formed nuclei with which subsequently precipitated silicic acid of the second increment could condense before excessive hydration occurred. A brief analysis of this hypothesis is of value and some theoretical support is available.

Nucleation and crystal growth for example are competing processes; at low supersaturation both are extremely slow but the latter predominates. It is also well known that the former predominates with increasing supersaturation and with restricted movement of the precipitated or crystallized phase. While this concept was not based on gelation phenomena, it was reported that coagulation of colloids and crystallization are analogous processes, and the extrapolation does not appear unreasonable (See Chapter II). The example of $BaSO_4$ may be cited in which its state varies from discrete crystals to a clear jelly simply by changes in concentration. In short, this alternate hypothesis postulated simple nucleation as the proper mechanism wherein relatively dense gelatinous silicic acid filaments build up on the residue of the first increment.

Two fundamental experiments indicated this mechanism alone would not adequately explain the phenomena. On first attempting to achieve an increased rate by utilizing filtered and washed silicic acid gel from the first increment, negative results were continually obtained. When the filtered solid was washed with hydrochloric acid prior to its use,

however, the increased rate phenomena was again immediately apparent. It was concluded that one of two possibilities existed. Either the gel contained sufficient water to effectively lower the overall acid concentration during the above initial attempts, or the gel absorbed hydrogen ions, chlorine ions, or both, which were essential to the phenomena of increased rate.

By calculation, the amount of water in the gel was easily determined and sufficient hydrochloric acid was added, not to the gel, but to the reaction mixture of gel and olivine to offset this effect. Low rates of 1.6, 0.8, 1.8 gal./sq.ft., hour were obtained which apparently eliminates this possibility. This result may be explained in the light of the present theory. It appears that the absorption of hydrogen ions on the colloid, at least in regard to operation for catalytic reaction, is not instantaneous and there is an appreciable lag before the gel can initially function catalytically. Therefore, reaction in the presence of thoroughly washed silica gel results in the usual film on the solid particles which in this instance functions as a barrier to the diffusion of hydrogen ions to the catalytic surface. Simple mixing of gel with the reaction mixture should thus be avoided. A large number of reactions start with induction periods, the rate of change of which may be quite small, but at the end of the induction period, measurable reaction occurs.94/

A second series of experiments was performed in which gel of the first increment was washed and dried at 130° C. for twenty-four hours.

94/ Hinshelwood, C. N., The Kinetics of Chemical Change in Gaseous Systems: Oxford, Clarenden Press, 1933, p. 299.

The gel deteriorated, of course, to a fine powder and additions of this powder to normal reaction systems had no observable effect on filtration rate. This result is not unpredictable as the literature describes silica gel as being, in contrast to gelatin, of the non-elastic or rigid type which is not reversible after dehydration.95/

An effort was made to obtain direct experimental evidence regarding the charge on the gel. Numerous references previously quoted established the charge on silicic acid as positive in strongly acid solutions due to adsorbed hydrogen ions. Considering the complexity of the system, however, it was desirable to substantiate, if possible, this conclusion. Using migration methods in solution no observable effect was produced which is frequently the case with gelatinous systems of this type. A sample of thoroughly washed gel (8 hours of washing with repulping) was then added to a carefully standardized solution of 0.01 N sodium hydroxide. There was a definite change in the titre of the alkali solution toward the acid side suggesting that the gel was charged with adsorbed hydrogen ions.

Apparently it is possible to remove a sufficient number of surface oriented ions by washing to render the surface unsuitable for catalytic behavior as thoroughly washed gel will not give rise either to increased reaction velocity or filtration rate. This result was previously discussed.

Neutralization was established as one requirement for the attainment of maximum filtration rates and this requirement is a direct consequence

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95/ Glasstone, S., Textbook of Physical Chemistry; New York, D. Van Nostrand Co., Inc., 1940, p. 1233.

of the electrical charge on masses of aggregatized and condensed colloid. No noticeable effect on filtration rate was produced, however, through the addition of excess quantities of reactants and products to the reaction mixture, Table 29. In this connection Werner states that electrolytes have negligible effect on the coagulation of silicic acid colloid in acid media but have marked effect in alkaline solution.96/ Various electrolytes containing multivalent cations and anions were added, however, to digestions in which normal and multistage digestion was employed to determine if these additions would affect the electrical properties of the gel, a measure of which could be obtained from the final filtration rate. Potassium ferricyanide, aluminum chloride, potassium oxalate, potassium sulfate, zinc chloride and barium chloride were tested, all with negative results.

An attempt was made to demonstrate that the gel of the first increment actually coats the particles of olivine of the second increment. After normal reaction of the first increment, the second increment was added and a sample immediately taken for petrographic examination. The hot material fogged the objective of the microscope but by chilling good observations could be made. The majority of particles of olivine were covered by a film of gel and while the possibility of initial reaction on the fresh surfaces must be admitted, the results are substantiating.

"Synthetic" gel produced by reaction of sodium silicate and hydrochloric acid did not give rise to the maximum filtration rates obtained with gel of the first increment decomposition. This result

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96/ Werner, J. F., The Effect of Various Ionogens on the Time Required for the Gelation of Colloidal Silicic Acid; Jour. Pharm. Assoc., vol. 9, 1920, pp. 501-508.

is undoubtedly due to the mode of gel preparation. It is generally agreed that the mere physical adsorption of gases, vapor or liquids on ordinary contact surfaces such as silica gel is not sufficient inducement for chemical activity. In order to become chemically active the contact surface must possess those specific properties which are called the activity of the catalyst, such properties being a direct function of the preparation technique.

In summarizing a brief discussion of the kinetic equation will be of value. As stated,

$$\frac{dx}{dt} = k \frac{\alpha H}{h} \frac{6m}{\rho D} (g)^{1/3} (g - Vx)^{2/3} (C - x)$$

the velocity rate is a direct function of temperature for $k \propto D \propto T$. This is in agreement with fact as the reaction rate for both increment and non-increment decompositions increases with temperature. Generally speaking, diffusion coefficients likewise increase with temperature and the resistance of the colloidal barrier is thus reduced.

Agitation was also found to affect adversely the rate of reaction, although only below a certain critical minimum. From the equation we can see $k \propto \frac{1}{\ell}$ and decreasing rates of agitation result in increasing thicknesses of the diffusion barrier. Above the critical, mutual affinity of the components of the contact surface exceeds abrasive action by the slurry. The mutual affinity between the contact surface and the resultants functions to decrease the overall rate and this variable is included as h .

Surface area decreases as the olivine reacts and correction terms for this are included as $\frac{6m}{\rho D} (g)^{1/3} (g - Vx)^{2/3}$.

As catalysis does not usually occur if the entire contact surface is covered by resultant a certain correction factor for the area must be introduced. This is designated as α and it is assumed that the fraction of the surface covered is a constant independent of total area.

Heat of reaction is important in catalytic reactions as it increases the temperature of the contact surface, thus aiding diffusion and increasing the overall velocity. In the decomposition of silicates with acid it is of special importance in decreasing the extent of colloid hydration.

At first glance the above equation does not appear in agreement with the poor filtration characteristics of finer particle sizes of olivine. (Tables 10, 21). More rapid reaction results with finer material (Figure 4) and if the proposed higher temperature at the contact surface actually exists, less hydration should result. It must be remembered, however, that the second phase of the proposed mechanism is a condensation of colloid to a relatively dense fibrillar structure. When decomposition occurs at the high rates characteristic of fine ore, silicic acid colloid is produced at a proportionately increased rate. Such colloid apparently cannot condense into larger molecules as fast as it is formed and there results a mass of small colloidal nuclei each unable to condense with its neighbors probably because of the high surface energy possessed.

The larger polysilicic acid condensation products are still charged by ion adsorption and as characteristic of charged particles, they tend to oppose coagulation. Relatively large amounts of water are probably held in their fields of electrical influence which is released upon neutralization, and permits further condensation. The final

product as illustrated in Figure 5 is a relatively dense, granular product.

CHAPTER V

EXTENSION OF THE THEORY

Tremendous tonnages of numerous silicates exist in nature as pointed out in the introduction. Many, however, are unreactive in 20 percent hydrochloric acid and still others have no commercial significance. A group of ten additional silicates was selected, Table 32, which met or had possibility of meeting both of the foregoing objections to some degree and which were typical of the entire group.

TABLE 32. - Silicates Tested

Silicates	Economic Importance
Olivine	Source of magnesium, chromium and nickel
Serpentine	Source of magnesium, chromium and nickel
Beryl	Source of beryllium.
Kaolin	Source of alumina, ceramics.
Garnierite (Siliceous Nickel)	Source of nickel and magnesium.
Chlorite	-
Chryostile	Non-flammable electrical and heat insulation.
Sodalite	-
Talc	High temperature insulation, cosmetics, filler.
Wollastonite	Filler, ceramic bodies, welding flux.
Heulandite	-

A. Extension to Alternate Silicates

As the theory established for the olivine-hydrochloric acid reaction required for its basic mechanism only silicic acid gel and hydrogen ions it was felt that all gelatinizing silicates should be benefited by the technique of stage addition. This view was supported by the results of tests using "synthetic" gel from reactions of sodium silicate and hydrochloric acid. According to the data of Murata it could be therefore

predicted that olivine, serpentine, sodalite and possibly wollastonite would have better filtering characteristics with stage addition than garnierite, kaolin, chlorite, chryostile, talc, and heulandite. 97, 98/

The former group is characteristic of those minerals of low molecular weight such as orthosilicates and those of larger molecular weight such as disilicates that decompose on acid attack, both of which gelatinize on decomposition. In contrast the second group is composed completely of non-gelatinizing minerals.

Using normal digestion techniques in which the mineral was reacted with 85 percent of the stoichiometric quantity of 20 percent hydrochloric acid, filtration rates given in the following tables were obtained which are contrasted with those resulting from the application of increment or stage digestion. In several cases the reaction was incomplete and prohibitive quantities of magnesia were required to neutralize the resulting slurry. Because of difficulties with deterioration of filter paper in high residual acidities, a four-inch fritted glass filter was sometimes used.

TABLE 33. - Digestion of Serpentine

Run	Normal Filter Rate	Stage or Increment Filter Rate
1	3.6	6.3
2	2.5	7.4
3	4.3	8.0
4	2.1	6.6
Average	3.1	7.1

97/ Murata, K. J., Internal Structure of Silicate Minerals that Gelatinize with Acid: The Amer. Mineralogist, vol. 28, 1943, pp. 545 - 562.

98/ Murata, K. J., The Significance of Internal Structure in Gelatinizing Silicate Minerals: Geological Survey Bu.. 950, 1946, pp. 25-33.

Serpentine was calcined at 650° C. before digestion to obtain a comparable degree of reaction with hydrochloric acid. The slurry was filtered on the 6-inch Buchner funnel and, although the rate with normal digestion is superior to olivine, probably due to an insensitization of the silica by calcination, definite improvement in rate was obtained with increment digestion.

TABLE 34. - Digestion of Siliceous Nickel (Garnierite)

Run	Normal Filter Rate	Stage or Increment Digestion
1	5.3	10.0
2	6.4	9.6
3	5.1	12.4
4	5.9	10.3
Average	5.8	10.6

The siliceous nickel ore was calcined at 600° C. before digestion for the same reason as the serpentine. Slurry was filtered on the 6-inch Buchner funnel and again the initial rate was markedly superior to olivine under similar digestion conditions. Definite improvement resulted, however, when increment or stage digestion was employed.

Beryl was calcined at 1500° C. followed by a quick water quench to break the $Al_2O_3 \cdot SiO_2$-BeO structural link which is necessary to achieve any appreciable solubility in acid. Unfortunately no definite reaction with 20 percent hydrochloric acid resulted and only in sulfuric acid concentrations above 50 percent did any noticeable decomposition occur. There was no difference in rate between normal and stage digestion, but this is not unexpected considering the extremely low water-solid ratio which probably obscured other effects.

Sodalite was reacted under the same conditions as the serpentine

and garnierite although without calcination.

TABLE 35. - Digestion of Sodalite

Normal Filter Rate	Stage or Increment Filter Rate
8.2	10.1
6.7	11.0
7.3	11.3
7.1	11.2
7.4	10.9

Although improvement in filtration rate is not as marked as in the preceding cases definite increases were observed. The remaining gelatinizing silicate, wollastonite, was then tested in a similar fashion and the data are given in Table 36.

TABLE 36. - Digestion of Wollastonite

Normal Filter Rate	Stage or Increment Filter Rate
5.8	10.4
6.3	11.3
5.7	11.0
6.0	10.7
5.8	10.9

Once again the marked improvement in rate characteristic of gelatinizing silicates was obtained.

Digestions of kaolin, chlorite, chryostile, talc and heulandite were next carried out and the results are summarized in Table 37. Twenty percent hydrochloric acid equivalent to 85 percent of the stoichiometric requirement was utilized.

Kaolin failed to react to any appreciable extent with twenty percent hydrochloric acid although the remaining four minerals gave relatively complete reactions as measured from the excess residual acidity. It was

concluded that no improvement in filtration characteristics is obtained with minerals of this type.

TABLE 37. - Digestion of Non-Gelatinizing Silicates

Silicate	Normal Filter Rate	Stage or Increment Filter Rate
Kaolin	10.1	8.2
Chlorite	16.2	16.8
Chryostile	5.0	4.2
Talc	15.8	12.6
Heulandite	11.9	13.0

A definite correlation can be made between those minerals which gave improved filtration rates with increment or stage addition and those which did not. With the exception of garnierite all minerals listed by Murata as non-gelatinizing in acid were unaffected by the application of increment digestion. In this case (garnierite) it is possible that the increased rate can be attributed to the presence of substantial amounts of olivine which petrographic analysis showed to be present. It should be emphasized that commercial high grade concentrates of each mineral were utilized with no special mineralogical separation.

Olivine, serpentine, sodalite, wollastonite and garnierite gave improved filtration rates with increment digestion and, with the exception of wollastonite which is a borderline case, these same minerals are considered by Murata to be gelatinizers in mineral acids.99/ These conclusions are summarized in Table 38. In short, for gelation to occur on decomposition of a mineral with acid, its siliceous structure

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99/ Murata, K. J., Private Communication, January, 1948.

must be of such a nature as to break down into soluble units of small molecular weight containing not more than a certain maximum number of silicon atoms. We can therefore conclude that the technique of increment digestion has definite application to the general group of gelatinizing silicates.

It is extremely interesting in this connection, to note in addition the relationship between the structure of minerals containing silica and the danger of silicosis. The damaging power is largely dependent on the SiO_2 lattice and its partial possible replacement with alumina. The gelatinizing and non-gelatinizing groups described by Murata correlate very well with the "less" and "more" dangerous mineral grouping by Hellmers.100/

TABLE 38. - Correlation of Filtration Characteristics

Silicate	Filtration Improvement	Gelatinizer
Olivine	Yes	Yes
Serpentine	Yes	Yes
Sodalite	Yes	Yes
Wollastonite	Yes	Yes (?)
Garnierite	Yes	No
. . . . .	. . . . .	. . . . .
Kaolin	No	No
Chlorite	No	No
Chryostile	No	No
Talc	No	No
Heulandite	No	No

B. Extension to Alternate Acids

The phenomena of improved filtration rates with stage or increment digestion was subsequently extrapolated to mineral acids other than

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100/ Hellmers, J. H., (The Various Forms of Silicic Acid and its Linkage in Minerals); Chem. Zentr., vol. 47, 1944.

hydrochloric with complete agreement with the postulated theory. Most of the previously reported and immediate data were based upon hydrochloric acid. In order to achieve any degree of generalization of the basic procedure it was necessary to evaluate alternate acids and for this purpose nitric and sulfuric acids were believed indicative of the entire group. Comparable extent of reaction could not be obtained between olivine and 20 percent concentrations of these acids and it was necessary to utilize solutions equivalent in hydrogen ion concentration to 40 percent hydrochloric. With even higher concentrations of these acids, i.e., about 50 percent, the phenomena of increased rate on increment digestion disappeared, probably due to the low liquid-solid ratio and the higher temperature of reaction. Previous investigators found filtration rates markedly improved under such conditions. Economic considerations would probably dictate the utilization of these alternate acids in concentrations above 40 percent but to demonstrate the general utility of stage addition a series was run at the lower concentration. Data are summarized in Table 39.

TABLE 39. - Effect of Mineral Acid on Filter Rates

Hydrochloric Acid		Nitric Acid		Sulfuric Acid	
(Non-increment)	(Increment)	(Non-Increment)	(Increment)	(Non-increment)	(Increment)
2.9	10.4	4.8	10.2	5.0	11.3
3.1	11.9	4.5	10.8	5.8	11.0
3.2	12.9	5.1	11.1	5.8	12.1
3.0	9.9	4.5	10.5	6.0	10.9
3.1	11.3	4.7	10.6	5.7	11.4

Although the percentage increase in filtration rate was not as great with nitric and sulfuric as with hydrochloric acid, it is seen that in all cases a definite improvement was obtained. The former two gave a

twofold increase in comparison with a threefold increase by the latter.

It has thus been demonstrated that the phenomena of improved filtration rates with increment or stage digestion is applicable to a variety of gelatinizing silicates and the results are reproducible utilizing mineral acids other than hydrochloric. These conclusions further substantiate the theory developed in the preceding section and greatly extend both the engineering and theoretical significance of the development.

CHAPTER VI

SIGNIFICANCE OF THIS STUDY

The fundamental engineering significance of this development is the establishment of a general method for treating gelatinizing silicates which greatly reduces past difficulties in solid-liquid separation. This problem had long been a barrier to more extensive utilization of many silicates and at least two commercial organizations are now considering the utilization of the author's decomposition technique developed in connection with this study. One organization expects to construct plant facilities for treating about a hundred tons of ore per day for recovery of magnesium chloride as cell feed.

A. Theoretical Significance

It has been shown that hydration of the residual silicic acid gel remaining after decomposition of gelatinizing silicates can be controlled to a considerable degree by the inovation of increment or stage digestion. Through this mechanism, which is believed catalytic in nature, the increased temperatures at the contact surface between gel and olivine minimize hydration of subsequently formed colloid. The increased initial rate of reaction in the presence of silicic acid colloid, the adverse effect of magnesium chloride on the reaction rate and filtration characteristics, the charge on the gel, the use of "synthetic" gels and finally, the extension of the phenomena to alternate mineral acids and silicates, widely differing in analysis and constitution, are all direct experimental support for this theory.

The technique of improving the filtration rates of slurries from

silicate decompositions is thus based on a catalytic mechanism which is of fundamental significance. Establishment of the previously postulated theory provides an explanation for the observed experimental results with olivine and permits a logical extension of the phenomena to alternate minerals and acids.

Silicic acid colloid thus produced is of a relatively low degree of hydration and its polymerization into larger polysilicic acid molecules results in a relatively dense structure. Because of the charged condition of these latter particles and uncondensed colloid it is necessary to neutralize the reaction mixture in order to obtain maximum improvement of the filtration characteristics.

The study supplies additional evidence to Murata's classification of silicates, as in no case did a gelatinizing silicate fail to give an increased rate with increment digestion and in general all non-gelatinizing silicates exhibited converse behavior. Therefore, it is concluded that minerals which give insoluble silica in lieu of gelatinizing, i.e., SiO_3 chains, Si_4O_{11} double chains, Si_2O_5 sheets, will not be affected by stage addition. Conversely minerals of low molecular weight, namely orthosilicates, pyrosilicates, ring structures of three and six silicon atoms and those capable of disintegrating into units of low molecular weight on acid attack, will give more dense, less hydrous gels with this technique.

B. Economic Significance

A cost estimate prepared for the production of magnesia based on the mineral silicate olivine is briefly summarized below. The costs given were obtained directly from identical operations or from reported

data for the pilot plant. The values are on a ton-of-MgO product per day basis and taken into account are: power, operating labor, supervision and overhead, maintenance, depreciation, supplies, insurance, and social security. Plant location was not considered. All figures have been rounded off to the nearest tenth of a dollar.

Heat Requirements

Digestion-first neutralization - none

Radiation loss and solution temperature control - approximately 0.5×10^6 B.t.u.

Evaporation to $MgCl_2 \cdot 10H_2O$ - approximately 5.0×10^6 B.t.u.

Calcination to MgO and HCl - approximately 15.5×10^6 B.t.u.

Total heat requirements 21.0×10^6 B.t.u.

Cost at \$0.38 per 10^6 B.t.u. \$8.00

Operating cost

Olivine mining, handling, storage, and reclaiming	\$3.40
Crushing and grinding	1.00
Digestion-first neutralization, including filtration	7.00
Final purification, including filtration	1.00
Evaporation	2.30
Calcination	3.00
HCl absorption	2.00
Total MgO for neutralization at \$80 per ton	11.30
Make-up HCl at \$20 per ton of 20° B	5.00
Cooling water at \$0.04 per M gal.	1.00
Fuel at \$0.38 per 10^6 B.t.u.	8.00
Total cost per ton MgO per day	45.00

From the same sources mentioned above, it is estimated that the

plant investment, including working capital, would be $50,000 to $60,000 per ton of MgO per day. At a probable selling price of at least $70 per ton (MgO of the grade produced is quoted at $80 per ton), the investment can potentially be returned in less than 10 years. For the production of $MgCl_2 \cdot (1-2)H_2O$, it can be shown that similar potentialities exist.

Although the details of the process developed and pilot planted by the Tennessee Valley Authority are not available for publication, two outstanding advantages are gained through the utilization of increment or stage addition.

First, the evaporation cost of $8.00 utilizing steam at $0.38 per 1,000,000 B.T.U., represents a savings of $6.00 in this item alone. Stage addition permits the direct utilization of filtration equipment without the dilution necessary for countercurrent decantation. Savings in heat represents over 13 percent of the total operating cost.

Second, similar savings in capital investment can be effected. Plant investment for the process proposed by the author will vary between $50,000 to $60,000 per ton of MgO per day for plants producing over 100 tons of magnesia per day. Evaluating the increased evaporator capacity and additional building space required, the cost would approximate $65,000 to $75,000 per ton of MgO per day for a plant utilizing the basic T.V.A. process.

Although estimates for other potentially important silicates have not been made it can be seen that similar savings may be effected.

CHAPTER VII

CONCLUSIONS

1. A novel method for the treatment of gelatinizing silicates was tested on a laboratory and pilot plant scale using olivine as the raw material.

2. Addition of the ore charge in increments effected approximately a tenfold increase in the filtration rate.

3. This technique can be extended to other gelatinizing silicates such as serpentine and sodalite with corresponding improvement in filtration rates.

4. Similar extrapolation can be made to alternate mineral acids such as nitric and sulfuric.

5. It was demonstrated that the increased filtration rate with gelatinizing silicates is a function of the silicic acid gel first formed. It is believed that adsorption enhances the activity of the (H_4) ion with regard to the olivine and subsequent increments are reacted in a media of effectively increased acid concentration. It is possible that lower hydration of the silicic acid colloid produced results from an increased temperature of the contact surface. It is further suggested that this less hydrous colloid is in a preferred condition to aggregate or polymerize to a fibrillar structure.

6. The reaction is therefore essentially catalytic in nature and some experimental evidence for this hypothesis was developed.

7. The technique of increment digestion permits substantial

lowering of operating and capital costs for the processing of gelatinizing silicates.

8. Because of the high purity of the product and the competitive operating costs indicated by this study, two commercial companies are now evaluating the results. It is expected that a commercial plant will be constructed in Idaho to treat olivine rejects from a chromite beneficiation mill.

APPENDIX

Analytical Methods

The analytical methods used in this investigation were as follows:

Excess acidity: The sample for this determination was customarily prepared by diluting one part of digestion or first neutralization slurry with ten parts water. A portion of this material was then diluted and treated with hydrogen peroxide in order to oxidize all iron to the ferric state, and titrated with 0.05 N NaOH to a phenolphthalein end point. The end color was discharged with one or two drops of H_2SO_4, and the total chlorides determined by the Volhard method.

MgO: The magnesia content of leach solutions was determined by the potentiometric method. 101/ The sample, containing preferably about 400 mg. of MgO, was acidified slightly with HCl to insure solution of all MgO. The solution was made up to 80 ml. with H_2O, and an excess of about 1 g. C.P. $CaCO_3$ added. This precipitated the weak bases such as Fe, Al, Ti, etc., and adjusted the acidity to a pH of 7.0 to 7.5. The mixture was boiled for four to six minutes to remove CO_2 and complete the precipitation of the weak bases. Ninety ml. of 195-proof C_2H_5OH were now added, and the sample kept at boiling in a water bath. The boiling solution was titrated with NaOH (1 ml. = 10 mg. MgO) to the point of maximum change in potential. The potential was determined by a Beckmann pH meter, using a calomel and a glass electrode, both internally shielded and adapted for use at 90° C.

101/ Boyle, A. J., Costo, C.C., and Haney, R. M., Determination of Magnesia in Magnesite and Dolomite — A Potentiometric Method: Ind. Eng. Chem. Anal. Ed., vol. 16, No. 5, 1944, pp. 313-314.

In actual practice, the end point of the titration was determined by use of a standard $MgCl_2$ solution before and after a series of determinations. This was considered as accurate as plotting points for each determination, and saved time.

Determinations were made occasionally by the standard pyrophosphate method or variations thereof.

FeO: As no interfering elements were present in the $MgCl_2$ leach solutions in any quantity, the determination of large quantities of FeO, in excess of 1 g./l/ was made by the standard $SnCl_2$ - $K_2Cr_2O_7$ method.102, 103/

Smaller quantities of FeO were determined colorimetrically with O-phenanthroline. 104, 105, 106/ A sample of leach solution, containing not more than 0.5 mg. FeO, but of sufficient volume to give results within the desired accuracy, was pipetted into a 100 ml. volumetric flask. If cloudy, it was cleared with a few drops of HCl. One ml. of 10% hydroxylamine hydrochloride was added to reduce the iron, after which 10 ml. of 0.1% O-phenanthroline and 10 ml. of buffer solution (30 g.

102/ Furman, N. H., Scott's Standard Methods of Chemical Analysis: D. Van Nostrand Company, 1939, 1234 pages.

103/ Hillebrand, W. F., and Lundell, G. E. F., Applied Inorganic Analysis: New York, John Wiley & Sons, 1929, p. 315.

104/ Fortune, W. B., and Mellon, M. G., Determination of Iron with O-phenanthroline--A Spectrophotometric Study: Ind. Eng. Chem., Anal. Ed., vol. 10, No. 2, 1938, pp. 60-64.

105/ Bandemer, S. L., and Schaible, P. L., Determination of Iron--A Study of the O-phenanthroline Method: Ind. Eng. Chem., Anal. Ed., vol. 16, No. 5, 1944, pp. 317-319.

106/ Sandell, E. B., Colorimetric Determination of Traces of Metals: Interscience Publishers, Inc., New York, vol. III, 1944, 487 pp.

ammonium acetate plus 2 g. tartaric acid per 100 ml. solution) were added. The volume was made to 100 ml. with water. The percent transmission was obtained at 508 mμ using a Coleman photoelectric spectrophotometer. The iron present in the sample was read from a calibration curve made by using standard samples prepared from pure iron wire.

SiO_2: SiO_2, present in solution or as a colloid, was determined by the gravimetric method using perchloric acid as the dehydrating agent. 107, 108/

NiO: NiO was determined using the common dimethylglcxime method.109/

MnO: MnO was determined colorimetrically after oxidation of Mn to MnO_4 with KIO_4. A spectrophotometer was used to evaluate the colors at 535 mμ using the method of Willard and Greathouse. 110, 111/

107/ Walthall, J. H., and Bridger, G. L., Fertilizer by Fusion of Rock Phosphate with Olivine: Ind. & Eng. Chem., vol. 35, 1943, p. 774.

108/ Seaton, M. Y., Production and Properties of the Commercial Magnesias: A.I.M.E. Mining Technology, Tech. Pub. 1496, vol. 6, No. 4, 1942, pp. 1-21.

109/ Diehl, Harvey, The Applications of the Dioximes to Analytical Chemistry: Columbus, Ohio, G. Frederick Smith Chemical Co., 1940, 54 pp.

110/ Smith, G. Frederick, Perchloric Acid: Columbus, Ohio, G. Frederick Smith Chemical Company, 4th Ed., 1940.

111/ Willard, H. H., and Cake, W. E., Perchloric Acid as a Dehydrating Agent in the Determination of Silica: Jour. Amer. Chem. Soc., vol. 42, 1920, pp. 2208-2212.

Percent basicity of neutralizing MgO: A 0.5-1.0 sample of MgO was boiled with excess 0.5 N H_2SO_4 until all solid material had dissolved, or in case some acid insoluble residue was left, for one-half hour. The excess H_2SO_4 was titrated with NaOH to pH 5.5-6.5. Percent basicity was the ratio (x100) of the dissolved MgO to the sample weight.