

THE UTILIZATION OF PAPER MILL WASTES
IN THE FLOTATION OF MANGANESE ORES

by

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in

CHEMICAL ENGINEERING

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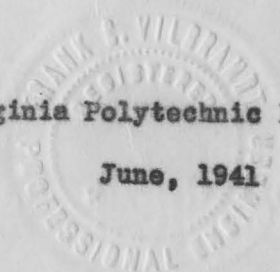


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I. INTRODUCTION

Today, the great majority of plants working non-ferrous minerals utilize the flotation process for the concentration of ores in at least one point in their operations. Chief among the reasons for the vigorous development of flotation in recent years has been the rapid depletion of available tonnages of direct smelting ore, and ores suitable to concentration by gravity methods. Particularly is this true of manganese ore deposits in the continental United States where there are vast ore-bodies of low-grade manganese ore waiting development. Ninety per cent of the manganese ore used in the United States is imported from foreign countries. Major foreign sources of manganese ore are Russia, Cuba, British India, Brazil, and South Africa, in order of magnitude of tonnage shipped.

In case of war, all of these supply sources with the exception of Cuba, and possibly Brazil, would either be cut off completely or rendered hazardous and uncertain. Thus, from the standpoint of national defense alone, it is important that methods of utilizing the internal deposits of American manganese in a more efficient manner be investigated.

Large deposits of low-grade manganese ore exist in Virginia which as yet have not been fully developed. At present, they are being wastefully exploited since only the larger, more easily recoverable sizes are extracted from the ore. The

tailings which are rejected still contain a very large proportion of the original manganese dioxide in the ore-body.

Located near the manganese deposits of Virginia are large Kraft paper mills which produce a waste product known as tallol. This waste product, known by various names such as, "tall oil", "liquid rosin", "tallol", is one of the paper industry's headaches as regards disposal. Its origin is in the digestors where the original fats and resins present in all wood are saponified by the alkaline cooking liquor during the digestion of the pulp. These saponified fats and resins, removed from the digestors as soluble soaps and combined with washings from the pulp, are sent to evaporators for concentration. During evaporation, the soaps are partially salted out and cause much trouble by excessive priming, foaming, and caking of the evaporator tubes. This necessitates frequent cleaning, and due to their corrosive properties, repair of damage or replacement of the tubes.

At one time, these soaps were considered worthless and were dumped into streams, or were burned for their fuel value. As a fuel, they were worth about six dollars per ton. Since 1907 research has been directed towards finding ways of recovering the valuable constituents found in the soap wastes. Acidification of the soaps with sulphuric acid yields the dark odiferous tallol. According to present practice, the separation and purification of the various constituents of tallol is accomplished by distillation, extraction, chemical treatment, or combinations

of these.

If it were shown possible to utilize this tallol as a flotation reagent for the concentration of manganese ores, two Virginia industries would be benefited. Not only tallol but also its derivatives are available for experimentation.

It was, therefore, proposed to try separately, crude oleic acid from tallol, sulphonated tallol, and the crude tallol itself, as collectors for the manganese dioxide in the ore. Other reagents such as frothers, activators, and depressors, were to be used in conjunction with the collecting agent and their effects observed.

II. LITERATURE REVIEW

Quantities of Tallol Available. There is no danger of a scarcity of tallol for carrying out large scale flotation operations, if it were proved feasible as a flotation reagent. The average amount of reagent required would be in the neighborhood of one pound per ton of ore treated. The available tallol according to Pollak⁽²⁹⁾ is potentially about 75,000 tons per year.

Yields of Tallol. The yields of tallol range from 2.2 per cent for mixed woods (7) (23) (43) to 5.2 per cent for 100 per cent pine wood. (6) These are only average values, however. The yields of tallol per ton of pulp are essentially a function of the wood type, age, variety, growth, climate, soil, season of cutting, the cooking process, and the method of separating the tallol. (43) (19) (37) (54)

Tallol Composition. Tallol is a mixture of many organic compounds, but the composition is usually reported in terms of three groups of components, as follows: (a) fatty acids, (b) rosin acids, and (c) unsaponifiables. The main constituents of the fatty acids (31) are oleic, linolenic, and linoleic acids, along with small amounts of related acids.

Rosin Acids in Tallol. The term, "rosin acids", is applied to those acids present in tallol which do not form esters with methanol when boiled in the presence of sulphuric acid.

Probably 60 to 90 per cent of these acids are abietic acid. (10)
However, Shipp (44) states that abietic acid is known to be the only rosin acid present.

Unsaponifiabiles in Tallol. That portion of tallol which is unsaponifiable is known to contain around two to three per cent of phytosterin. (10) The remainder appears to contain higher alcohols, such as the sterols, and miscellaneous hydrocarbons.

Fatty Acids in Tallol. The fatty acids in tallol are oleic, linolenic, and linoleic acids. They are all unsaturated fatty acids with one, three and two ethylenic linkages, respectively. Each is known to have several isomers with respect to linkage position. (36) The 9-10 oleic acid is also said to exist (27) in the cis- and trans- forms. Of these, the trans-form is the most stable. The presence of oleic acid is particularly important, for it has been extensively used as a flocculation reagent. Its use is especially notable in the non-metallic field.

Flotation Research in the Past. As regards the flotation end of the problem, it is evident that research along this line has been poorly conducted in the past. (26) This is true in particular of the non-metallic minerals such as the manganese ore under consideration. They have been regarded as cheap products and not worth much beneficiation. Consequently (42), only high-

grade natural deposits suitable for direct mining and sale have been utilized. Ralston (42) states further, "The mining of these minerals has too frequently been in the hands of super-practical men, men of no technical or other training, who are willing to work for a very low wage. From the social standpoint, non-metallies has been the field for small untrained enterprisers with little money to spend on plant or equipment. But times have been changing. The impact of technically trained men on the little industry has revealed appalling losses and inefficiencies, and proved the value of processing materials discarded or avoided by the old regime."

The advent of the technical men is comparatively recent. Only 15 years ago, in 1925, Ernest Heisam (26) had this to say on the status of research, "While companies or firms are adequately taking care of routine tests and the mechanical features involved in their operations, no comprehensive study of the fundamental principles of ore reduction is now in process or is contemplated. Many industries are interested in the preparation of material for final treatment. This class of fundamental research is neglected by industry, unless there is some agency which can bring together at least a majority of those interested in co-operative effort."

Present Status of Research. The research being carried on at present to determine conditions best for concentration by flotation is, in most cases, specific. It is directed to some

immediate working problem which offers only minor information when transferred to new conditions. This lack of fundamental knowledge retards improvement, and the unknown factors compel the continuance of the cut-and-try methods. The mining industry has become so accustomed to judging flotation by results under particular treatment, that there has been neglect of the more thorough and scientific understanding of the process.

Nonmetallic Flotation: First Stage. As far as non-metallic minerals are concerned, the development of suitable reagents for "collection", "selective filming", "activation", or "selective greasing", all meaning the same operation, has come through five main stages. Originally, there was known a method called "Oil Flotation" or "Bulk Oil Flotation", which was first described (24) by William Haynes in 1860. His process consisted in triturating finely ground sulphide ores with one-ninth to one-fifth their weight of fats and oils with subsequent agitation and flotation on water to separate the sulphides from the gangue. This was the signal for the start of chemical and mechanical improvements (2) to flotation technique. No one tried to recover nonmetallics in those days (42), and if graphite, sulphur, talcose, or sericitic materials were present and tended to pass into the froth, they were lost.

Second Stage. The second stage involved the use of soluble anionic collectors, such as the exanthates or phospho-

cresylates. However, these were better adapted (42) to collection of the basic sulphides and rejection of gangue material. The non-metallic minerals were still concentrated into the tailings.

Third Stage. The third stage was marked by deliberate attempts to recover the nonmetallic minerals. Among the first of these successfully floated was limestone, with the use of such filming agents as calcium oleates, stearates, or palmitates (42). The collection agents were either soaps or fatty acids. Other important nonmetallics which yielded to such treatment were calcite, dolomite, magnesite, barite, fluorite, apatite, and similar minerals whose basic portions could form insoluble soap films.

Fourth Stage. Ushering in the fourth stage was the discovery that wetting agents were applicable to the same series of minerals and also to a larger series. Long chain anionic reagents (32) (45) were tried, in which the complex anion did not form insoluble soaps with the basic mineral. Nevertheless, these basic minerals could be filmed, floated, and if desired, deactivated and sunk.

Present Stage. The forward strides in the chemistry and metallurgy involved in flotation which gave the process its greatest impetus toward present day perfection were made between 1900 and 1925. It was in 1900 that Sulman, Picard, and Ballot (45) described a flotation process which used the fats and oils in quantities less than one-hundredth the weight of the ore treated.

They definitely proved that such small quantities greatly improved results, and that Haynes proportion (24) of one-ninth to one-fifth the weight of the ore treated actually lowered recoveries.

Skin Flotation. During the next decade, various inorganic chemicals were tried in flotation processes for activating or depressing certain minerals. One group of experimentors found that a water surface shows a marked preference for sulphide minerals over earthy gangue minerals, and would select the sulphides from among dry, or nearly dry mineral particles cast on the water surface. This was the so-called Skin Flotation Process. (46) Plants were built for its application (2) in Nevada and Idaho, but the method did not prove to be a lasting success.

Advent of the Organic Collector. The big forward stride in flotation came in 1921. In that year, Perkins demonstrated (40) that various slightly soluble, non-oleaginous, organic compounds used in flotation did effectively "collect" the mineral particles. This marked the entrance of the organic collector into flotation history. From this time on, and for several years to come, the trend in flotation reagents was away from the use of oils.

Advent of Xanthates. Perhaps even more significant to commercial flotation practice than the foregoing was Keller's discovery (28) in 1925 of the efficiency of soluble xanthates in

in the flotation of sulphide minerals. Selective flotation now became known, perfected, and widely applied in North America. The process is rumored⁽²⁾ to have been attempted in Australia some years earlier, however. The xanthates, even today, rank highest among the flotation reagents due to their combination of great collecting power with a highly selective action.

Mechanical Improvements. While flotation chemistry and metallurgy advanced between 1900 and 1925, mechanical improvements were equally noteworthy. Until 1905, oil had been the buoyant medium, at which time the use of gas bubbles was introduced for this purpose. Originally, the bubbles were formed by acidulation of the pulp containing carbonates, either naturally present or added for the purpose. Another method was the use of a partial vacuum ⁽²¹⁾ to generate the bubbles from the dissolved gases in the pulp. Neither of these found commercial application in the United States ⁽⁴²⁾.

In 1909, the greatest mechanical improvement was the generation ⁽²⁾ of gas bubbles in the pulp by means of a rapidly revolving impellor. Bubbles ⁽¹⁸⁾ have ever since been the bearers of the vast tonnages of heavy metal-bearing ores recovered by flotation.

Froth Flotation. With the increasing use of bubbles as mineral particle carriers, froth flotation came to be applied commercially with great success, not only in North America, but also throughout the world. The method was called "Bulk Flotation"

as well as "Froth Flotation" because all the ore particles present in the pulp at the time of flotation were floated off together.

pH of Flotation Circuits. In general, the circuits were originally all acidified either by sulphuric acid or inorganic activators containing sulphuric acid. However, since Perkins and Keller's discoveries (40) (28) of 1921 and 1925, acid circuits rapidly gave way (2) to alkaline circuits. Few, if any, acid circuits are used today since the alkaline circuits do not corrode equipment as rapidly and tend to reduce reagent consumption.

Recent Advances. The most recent advances in the chemical technology of flotation have been the cationic reagents (12) (49) (8) (29) (30) (33) (35) (47) such as tetra-substituted ammonium salts. These are long chain amine salts in which a large complex, "greasy" cation is united with a simple soluble anion such as a chloride or sulphate. They have the tendency to reject basic minerals and to float acid minerals such as quartz, feldspar, mica, kaolinite, and other clay materials, even to the extent of making them water repellent.

Research on Manganese Ores. As regards manganese ores specifically, several commercial operations have shown that by soap flotation of the manganese carbonate and oxide ores, including rhodochrosite, manganite, and pyrolusite, it is possible to separate out the siliceous gangue. Some of the oxide ores, however, are too intimately mixed with iron ores (42) (13) to

permit of good flotation separation, but others are very easily treated. An outstanding example of successful treatment of oxide ores is that of the Cuban-American Manganese Corporation mine⁽⁹⁾ at Cristo, Cuba. This company has improved their treatment from time to time. At one time, the manganese ores were calcined, preferably by roasting the dry crushed ore at about 600° F. for approximately 15 minutes prior to flotation, or gravity concentration. A mixture (1) of fish oil soap and a hydro-carbon, preferable sulphurized dipentene was used as the flotation reagents. Later modifications of the treatment used by Weinig⁽⁵²⁾ consisted in using a cruder form of soap, fish oil soap with tannin, as a further reagent for dispersion of the gangue. In collaborating with Cuthbertson, however⁽⁵³⁾, he dispensed with the tannin. Lenker and Gillsons⁽⁵⁴⁾, working on the same type of Cuban ore, prescribed agitation and aeration of the ore in the presence of a pre-emulsified mineral oil agent, and a water soluble compound such as sodium alkyl sulphate esters. These esters have the general formula, $ROSO_3Y$, in which R represents the residue of a normal primary alcohol containing from eight to eighteen carbon atoms, and Y represents the residue of a salt-forming compound.

In the Cuyuna district of Minnesota, successful flotation of oxide ores was obtained⁽¹⁵⁾ with a mixture of oleic acid with pine oil, modified by sodium silicate with sodium carbonate as its protector. The same reagents were also used by DeVaney and Coghill⁽¹⁷⁾ on rhodochrosite manganese ore. Manganese oxide

ores were also successfully treated with these reagents by DeVaney and Clemmer (16). Of the manganese in the oxide ores, 96 per cent was recovered in the concentrate and 97 per cent of the insoluble gangue material was rejected. They also found that heating the pulp to a temperature above the melting point of the fatty acid not only decreased the amount of reagents required, but also materially speeded up the flotation process. In this connection, Hegemann (25) advocates heating oxidic manganese ores above 100° C., and preferably to 470° C., if this latter temperature remains below the decomposition temperature of the ore. Weed (50) has used oleic acid along with kerosene which is dispersed into an emulsion with triethanolamine. He and Ellis also used oleic acid colloiddally dispersed in an alkylamine soap solution to form a froth capable of bearing the oxidized mineral particles. (51)

Use of Xanthates. DeVaney and Clemmer (15) (14) have used crude sodium oleate with a frothing agent containing copper sulphate, sodium ethyl xanthate, and pine oil. Orelli (39) conditions an oxidized manganese ore with sodium silicate and sodium vanadate, following which quebracho bark is added as a depressor for the gangue. The flotation is then effected at 35° C., with stearic acid and ammonium xanthate as collectors and terpineol as a frother.

Effect of Varying Reagents. In a study of Philipsburg, Montana manganese dioxide ores with a gangue containing quartz, silicates, calcium carbonate, dolomite and magnesite, Gaudin and

Behrens (22) tried various reagents with varying degrees of success. Oleic acid was found to be most adaptable, but a higher selection in floating carbonates away was obtained with stearic acid, palmitic acid, and undecylenic acid. It was also noted that fuel oil, when added to the collector, seemed to assist materially the flotation of the manganese dioxide minerals, and to aid the rejection of the silicate gangues. This fact is verified by Dean (11) who states that an emulsion of Avirol 100 with Louisiana crude oil is a very powerful collector of pyrolusite and manganite. Sodium silicate seemed to be the best depressant for the silicates present in the Montana ores.

Addition of oxidizing agents such as potassium chlorate and calcium chloride tended to depress the manganese dioxide while, on the other hand, reducing agents such as citric acid, citrates, and tartrates, did not promote manganese flotation. Dextrin absolutely prevented flotation. Gaudin and Behrens (22) advanced the hypothesis that, "reducing agents may be needed, due to the fact that manganese soaps are manganous and not manganic. Hence, prior surface reduction would appear to be necessary for chemical filming". Arnold (3) has claimed that his heteropoly acids such as phosphomolybdic acid, are good activators for manganese ores.

Sliming Difficulties. The chief problem, as in other nonmetallic ore treatments, has been the extreme sliming encountered. In the U. S. S. R., a plant in the Chiaturi district engaged in washing manganese ores, grades up a 40 per cent ore to a 52 per cent manganese concentrate with an 80 per cent extrac-

tion. The losses due to sliming average 40 per cent in the Chiaturi district, but Basmanov (5) and Gamelaini (20) claim to have solved the problem. Both methods were similar and differed only in slight details. Basmanov's treatment involved preliminary agitation of the slimes with sulphuric acid for ten to fifteen minutes, with subsequent additions of sodium oleate, water glass, and pine oil. He claims that the use of 0.2 to 0.5 pounds of sulphuric acid and 1.0 pounds of sodium oleate per ton of slime resulted in a 96 per cent extraction of the manganese in the form of a concentrate analysing 48 per cent as metallic manganese. These values are based on a classified material of minus 100 to plus 250 mesh, but no figures are given on the amount of true slime. Gamelaini claimed total yield of concentrate of 38 per cent with a total extraction of 68 per cent. On a large scale, it was expected to be able to obtain a 40 per cent concentrate and an extraction of 75 per cent of the manganese.

III. EXPERIMENTAL.

General Statement of Problem. Large deposits of low-grade manganese ore exist in Virginia which as yet have not been fully developed. Manganese ores of much greater purity and value are now imported into the United States from foreign lands. Since this supply will not last indefinitely, or may be subject to various restrictions at any time, the utilization of native ores should be investigated. Much of the research to date on the beneficiation of oxide minerals has yielded little information capable of general application. The work was done on a specific ore with the sole purpose of finding a commercial means of recovery.

Also in Virginia are located large paper mills which produce a waste product known as tallol. If it were possible to use this tallol as a flotation reagent for concentration of manganese ores, two Virginia industries would be benefited. Not only tallol, but also its derivatives are available for experimentation.

Purpose of Study. It was proposed to try separately, crude oleic acid from tallol, sulfonated tallol, and the crude tallol itself, as collectors for manganese dioxide in the ore. Other reagents, such as, frothers, activators, and depressors were to be used as an aid to the action of the collector, and their effects observed and recorded.

Plan of Investigation. The general plan of attack was to try each of the three collecting agents, crude oleic acid, crude tallol, and sulfonated tallol, under varied conditions in the flotation cell. With each, it was proposed to make runs varying the following elements:

1. Hydrogen ion concentration.
2. Amount of collector.
3. Amount of depressor.
4. Amount of frother.

There would be three constituents with each run, the head or feed, the concentrate, and the tailings. On each of these, the per cent manganese would be determined, and their respective weights observed and recorded.

Materials

Manganese Ore. The manganese ore to be used in the investigation was supplied by the operators of the Paint Bank deposits, near Paint Bank, Virginia. The source of the samples was from the screening operations following the log-washers. The practice of the mine was to reject this screen undersize, saving only the larger sizes. A typical analysis of the ore as received was approximately 25 per cent manganese, or 38 per cent manganese dioxide.

Crude Oleic Acid. The crude oleic acid was supplied by the West Virginia Pulp and Paper Company. It is refined grade of tallol, and is usually sold under the trade name, Liqro.

Crude Tallol. The crude tallol was also supplied by the West Virginia Pulp and Paper Company. It is a very viscous material, grading in color from black to brown in color, and is the concentrated product of the evaporators, which remove most of the water from the digester liquors.

Sulphonated Tallol: The sulphonated tallol was prepared from the refined tallol by Mr. J. M. Crockin of the Chemical Engineering Department, Virginia Polytechnic Institute. It is a water soluble compound and was prepared by direct sulphonation of tallol dissolved in gasoline with 95 per cent sulphuric acid.

Bureau of Standards Ore. The Bureau of Standards manganese ore was obtained from the Department of Commerce, Washington, D.C. It is known as Standard Sample No. 25b Manganese Ore, and the accompanying certificate of analysis stated that it contained 58.35 per cent metallic manganese. This analysis was an average determinations made by Hoffman, J. I., Bureau of Standards, Cunningham, T. R. and Price, R. J., Electro Metallurgical Co., and Fry, H. M., also of the Electro Metallurgical Co.

Pine Oil. The pine oil used as a frothing agent was a clear, slightly yellow grade manufactured by the Hercules Powder Company. It is sold under the trade name, Yarmor F Pine Oil.

Sodium Silicate. The sodium silicate used as a depressing agent was a standard concentrated solution of water glass with a specific gravity of 1.30. It was obtained from the Phipps and Bird Company, Richmond, Virginia.

Lime. The lime used to regulate pH was a very pure grade manufactured by the American Cyanamid Company.

Sulphuric Acid. The sulphuric acid used as a pH regulator was C.P. acid, specific gravity 1.84, obtained from the General Chemical Company through the Chemistry Store Room, Virginia Polytechnic Institute.

Miscellaneous Chemicals. Other test chemicals used for analytical procedures were the following: hydrochloric acid, sodium carbonate, mercuric chloride, stannous chloride, phosphoric acid, zinc sulphate, zinc oxide, potassium permanganate, potassium dichromate, sodium oxalate, ferrous ammonium sulphate, and diphenylamine indicator.

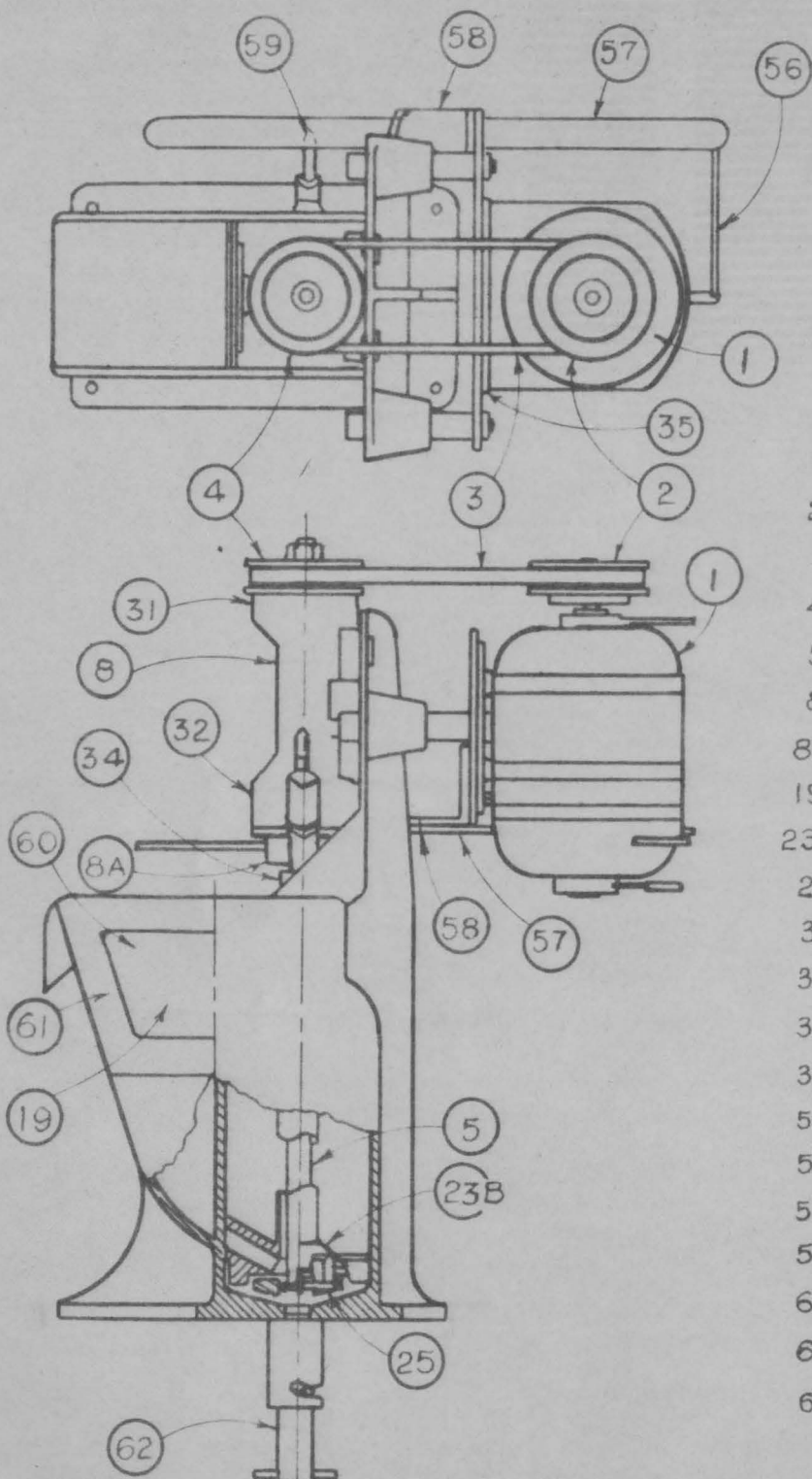
Apparatus. The apparatus used in this investigation is shown in Figure 1, (A-2252), 2. (A-2249), 3.(A-2250) and 4. (A-102).

Figure 1. (A-2252) is a plan and elevation of the Denver Equipment Company's Laboratory Flotation Cell, giving a list of the parts and showing their location. The particular cell used was the 500 grams capacity with reference to the maximum amount of ore it can efficiently handle.

Figure 2. (A-2249) is a plan, front elevation and side elevation of the same flotation cell. The general arrangement and dimensions of the cell are also shown.

Figure 3. (A-2250) is an elevation of the flotation cell shaft assembly with a cut-a-way portion showing the internal features. This is the most important feature of the cell as it drives the disk type impellor which is the means of dispersing the ore pulp and mixing it with air in the form of many small bubbles.

Referring to Figure 1. (A-2252), the mechanism of operation of the flotation cell is as follows. It is powered by a variable speed electric motor (1), the speed being varied by means of the shifter lever (57). The power of the motor is transmitted by a leather V-belt (3) to the impellor sheave (4) which in turn causes the impellor shaft (5) to rotate on its spindle bearing (8). The lower end of the shaft rotates on bearings (31) (32). The shaft drives the recessed disk impellor (25) which is equipped with a diffuser and hood (23-B), dispersing the ore particles throughout the flotation pulp. Air is drawn through the standpipe and valve (34) and introduced just above the impellor which dispersed the air in the form of many small bubbles throughout the flotation pulp. The bubbles rise to the surface of the cell, carrying the particles of ore with them. The circulation caused by the impellor carries the froth thus formed to the lip of the cell where it overflows and is caught



PARTS LIST

- 1 MOTOR VARIABLE SPEED
- 2 MOTOR SHEAVE
- 3 V BELT
- 4 IMPELLER SHEAVE
- 5 IMPELLER SHAFT
- 8 SPINDLE BEARING
- 8A GREASE SEAL
- 19 TANK GLASS SIDE
- 23B DIFFUSER AND HOOD
- 25 BRONZE IMPELLER
- 31 UPPER BALL BEARING
- 32 LOWER BALL BEARING
- 34 STANDPIPE AND VALVE
- 35 MOTOR BRACKET
- 56 SHIFTER LEVER LINK
- 57 SHIFTER LEVER
- 58 SHIFTER LEVER BRACKET
- 59 SAMPLE SPIGOT
- 60 GLASS SIDE
- 61 GLASS SIDE FRAME & GASKET
- 62 DRAIN PLUG

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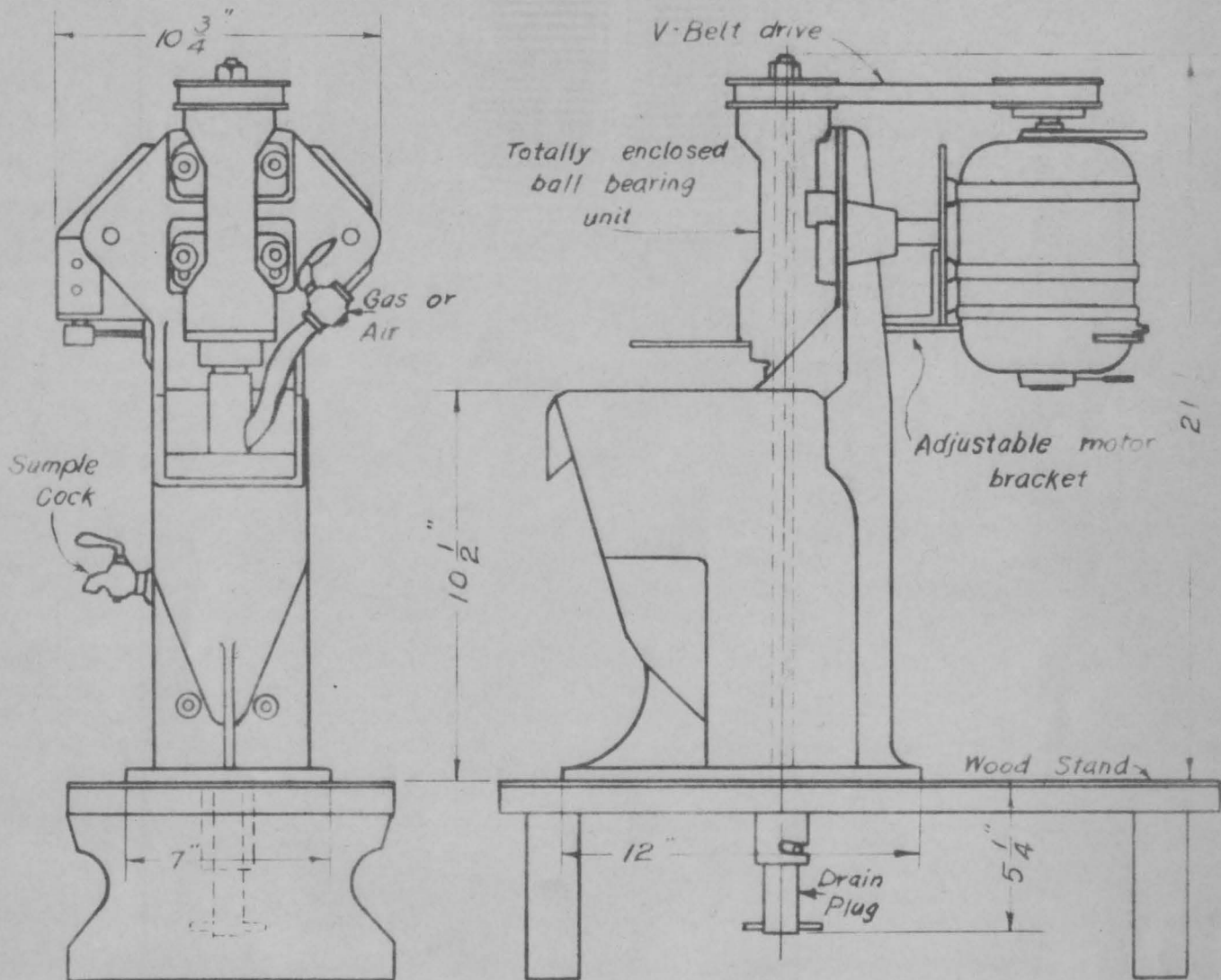
PARTS LIST

500 GRAM LAB. FLOTATION MACHINE

May 26, 1941

H. F. Smith

Figure 1



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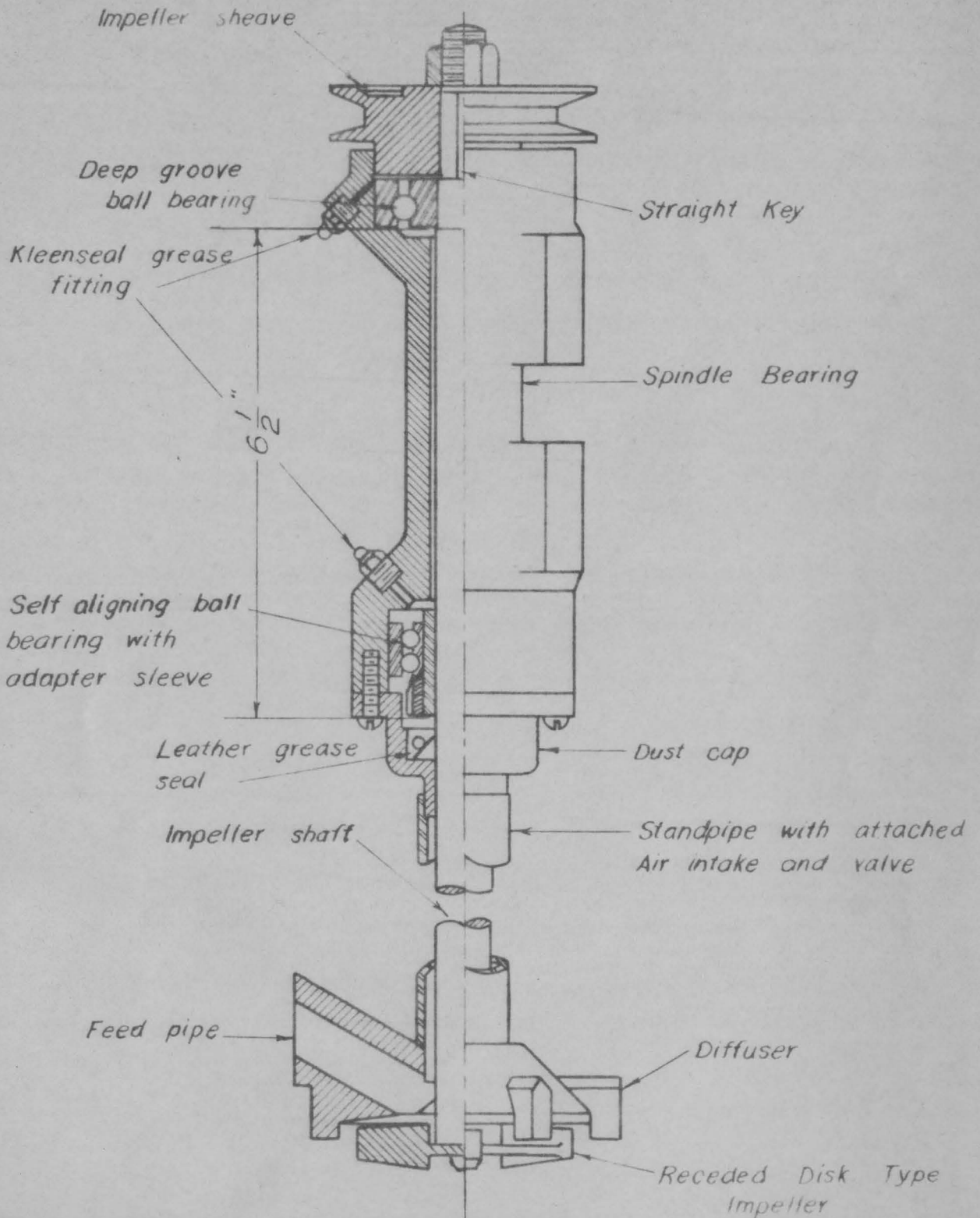
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**GENERAL ARRANGEMENT
500 GRAM LAB. FLOTATION MACHINE**

May 26, 1941

H. F. Smith

Figure 2



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SHAFT ASSEMBLY

500 GRAM LAB. FLOTATION MACHINE

May 26, 1941

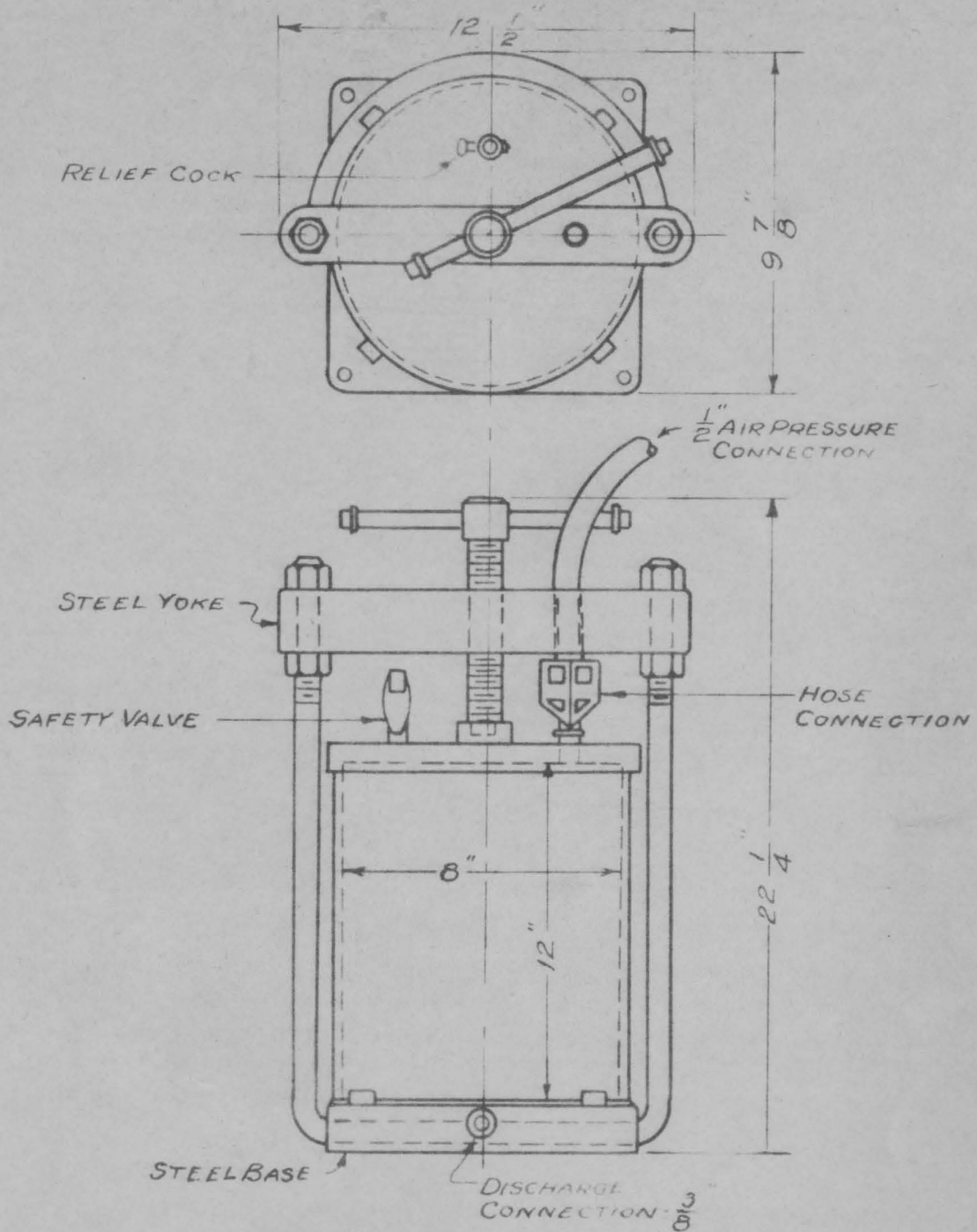
H.F. Smith

Figure 3

in a container. The gangue and unfloated ore particles sink at this point and are recirculated back to the impellor where they are again mixed intimately with the fine air bubbles. The process is continuous. At the end of a flotation run, the motor is stopped, the drain plug (62) opened and the tailings caught in a suitable container.

Figure 4. (A-102) shows the pressure filter used for the filtration of the concentrate and tailings from the flotation cell. It is also manufactured by the Denver Equipment Company, especially for flotation work. Air pressure applied above the filter bed, which is supported on a wire screen and canvas cloth, forces the water through the filter paper and out of the ore. A safety valve is provided as a precaution against building up excessive air pressures which might burst the filter bed.

Miscellaneous Apparatus. Equipment used in preparing the ore for flotation were the following: Scales for rough weighings, pebble mill and bucking board for grinding the ore, Tyler Standard sieves and Ro-Tap sieve shaker for screen analyses of the crushed ore samples, enameled pans for receiving the concentrate and tailings, and miscellaneous chemical glassware and apparatus.



VIRGINIA POLYTECHNIC INSTITUTE

Dept of Chemical Engineering

Blacksburg, Virginia

PRESSURE
FILTER

May 26, 1941

H F Smith

Figure 4

Methods of Procedure

Ore Preparation. The large allotment of manganese ore from the screens following the log-washers at Paint Bank, Virginia was split into approximately 1000 gram samples and placed in labeled containers. Each of the 1000 gram samples was then ground, either in a pebble mill, or on a bucking board to flotation size. Some samples were ground to finer sizes than others, but in all cases, they were ground through 28 Tyler mesh.

From each ground sample, 100 grams were taken by quartering, and screened through Tyler standard sieves with the aid of the Ro-Tap sieve shaker. Difficulty was experienced in screening samples greater than 100 grams since the fine manganese dioxide tended to coat the screens rather thoroughly. Even with 100 gram portions, it was found necessary to clean the sieves at frequent intervals, during the shaking period. It was possible to duplicate screen analyses by this method with a total shaking time of 15 minutes.

The screen analyses were recorded by weighing the ore retained on each screen, from minus 28 mesh down through minus 200 mesh. The screen analysed sample was then returned to the original sample and thoroughly mixed in.

The 1000 gram samples of crushed, screen-analysed ore were then split into two equal parts by means of a sample splitter. The sample splitter was then used to obtain rep-

representative samples of each 500 gram sample. These small samples were then placed in labeled bottles for future analysis, and the remainder of the ore was placed in containers until needed for flotation tests.

Analysis of Ore. An analytical determination was made for the manganese content of the head or feed sample, the concentrate from the flotation cell, and the tailings or reject from the flotation cell. The procedure, a modification of the Volhard method, was as follows:

The ore was placed in a weighing bottle and dried in an electric oven for one hour at 105° C. following which, it was placed in a dessicator to cool. Approximately one gram of the ore was then weighed out carefully on an analytical balance and placed in a 500 ml. beaker. Just enough hydrochloric acid to completely dissolve the ore was added and the beaker placed on a hot-plate to simmer. When completely dissolved, the beaker was removed from the hot-plate and allowed to cool. The excess acid was then neutralized with a saturated solution of sodium carbonate. A reddish precipitate indicated the neutral point, and just enough dilute sulphuric acid was added to redissolve the precipitate. Roughly 10 grams of zinc sulphate was added and the beaker heated to boiling. Then one gram of zinc oxide was added, and the beaker allowed to cool. When cool, the contents of the beaker were transferred to a 500 ml. volumetric flask and diluted up to the mark. A 100 ml. aliquot was then

withdrawn by means of a pipet and returned to the original beaker. The aliquot sample was then heated to boiling and enough zinc oxide added so that an excess was seen on the bottom of the beaker. This was immediately titrated with a 0.10 N solution of potassium permanganate to a faint pink color. After each addition, the beaker was stirred vigorously and the precipitate allowed to settle. It was not necessary to add acetic acid near the end-point of the titration, since the permanganate had previously been standardized with the Bureau of Standards Ore.

Flotation Procedure. A previously prepared ore sample was weighed and placed in the Denver Sub-A Flotation Cell. An equal weight of distilled water was then added so that the resulting pulp had a dilution of 50 per cent by weight. With the air valve closed, the cell's motor was started, and the first flotation reagent added. Three minutes later, the next reagent was added to the pulp. Other reagents were added in a similar manner, using an eye dropper for liquids and carefully weighed samples for solid reagents. In all cases, three minutes were allowed between additions. When all reagents for the particular test were in the cell, the pulp was allowed to condition for exactly 15 minutes longer. At the end of the conditioning period, a measured amount of water necessary to bring the pulp dilution to 25 per cent by weight was added to the cell.

The air valve was then gradually opened, causing the froth to form and rise, and flotation of the ore started. As the froth rose and flowed towards the lip of the cell, a paddle scraper was used to aid its removal from the cell to an enameled pan placed beneath the cell lip. Flotation was continued until either no more froth rose to the proper level, or the amount of froth became negligible. The time for this to occur was usually 10 to 12 minutes. However, the major portion of the concentrate came over usually in the first five minutes.

The concentrate and tailings were collected in separate enameled pans and filtered in the Denver air pressure filter. Large sheets of filter paper were used to retain the ore, and no difficulty was experienced with the fine ore particles running through the filter paper. The filter cakes were removed from the filter and placed in an electrically heated oven to dry at 120° C.

When dry, the cakes were broken up with a spatula and mixed thoroughly in an enameled pan. After weighing and recording the weights of the concentrate and tailings, the sample splitter was used to cut down the size of the sample in order to get a representative sample for analysis. The sample for analysis was placed in a labeled bottle and stored for future analysis.

The bulk of the sample remaining was then placed in

containers. One container received all the concentrates, and the other received all the tailings from the many flotation tests. These were stored away for future work.

Experimental Data and Results.

Screen Analysis of Ore as Received. A sample of the manganese ore from the Paint Bank Deposit weighing approximately 1000 grams was analysed on Tyler standard screens. The ore was not prepared in any way, but was run as received. Eleven Tyler screens were used ranging from 8 mesh down to 200 mesh. The screening operation was performed with the aid of an electrically driven Ro-Tap Sieve Shaker, and the weight of ore retained on each mesh determined and recorded. The per cent weight and per cent cumulative weight retained on each mesh was also calculated. The data were recorded in Table I.

TABLE I.

Screen Analysis of Paint Bank, Virginia Manganese Ore Fines
from the Log-Washer as Received.

Retained on Tyler Mesh No.	Weight grams	Weight per cent	Cumulative Weight Per Cent
8	164.5	17.60	17.60
10	92.0	9.85	27.45
14	95.0	10.17	37.62
20	104.5	11.18	48.80
28	79.0	8.45	57.25
35	74.0	7.92	65.17
48	76.5	8.19	73.36
65	107.0	11.45	84.81
100	79.5	8.51	93.32
150	36.5	3.91	97.23
200	11.0	1.18	98.41
-200	15.0	1.61	100.02
<hr/>			
Totals	934.5	100.02	-----

Screen Analysis and Distribution of Manganese in Ore

Crushed and Screened Through 14 Mesh. A 1000 gram sample on the manganese ore as received from the Paint Bank deposit was crushed through 14 Tyler mesh and a screen analysis run on the whole sample. Eight Tyler Standard Sieves were used, ranging from 20 mesh on down to 200 mesh. The screening operation was performed with the aid of an electrically driven Ro-Tap Sieve Shaker. Representative samples from each mesh were taken and analysed for the per cent metallic manganese, and the weight of ore retained on each mesh was determined and recorded. The per cent weight retained on each mesh and the per cent cumulative weight was also calculated and recorded. The data are recorded in Table II.

TABLE II.

Screen Analysis and Distribution of Manganese in Ore
Crushed and Screened Through 14 Mesh.

Retained on Tyler Mesh No.	Weight grams	Weight per cent	Cumulative Weight per cent	Manganese per cent
20	175.0	17.32	17.32	34.90
28	152.5	15.09	32.41	32.70
35	124.5	12.32	44.73	34.10
48	130.0	12.86	57.59	23.10
65	213.0	21.08	78.67	14.30
100	68.0	6.73	85.40	11.45
150	62.0	6.14	91.54	15.10
200	39.0	3.86	95.40	22.25
-200	46.5	4.60	100.00	28.42
<hr/>				
Totals	1010.5	100.00	-----	-----

Screen Analysis of Head Samples of Manganese Ore Fines
from the Paint Bank, Virginia Log-Washers. After the ore was ground down to flotation size either on a busking board or pebble mill, a 50 gram sample was taken for screen analysis. Attempts to use more than 50 grams were time-consuming since the fine manganese dioxide tended to clog the fine screens, necessitating frequent cleaning during sieving operations. Even with the smaller sample, it was necessary to clean the screens at intervals. All sieve analyses were run using Tyler Standard Screens, and the sieving accomplished on an electrically driven Ro-Tap sieve shaker. Fifteen minutes was found to be sufficient time to obtain results which could be duplicated. All data are recorded in Table III.

TABLE III.

Screen Analyses of Head Samples of Manganese Ore Fines from the
Paint Bank, Virginia Log-Washers.

Run Number	Per Cent Retained on Tyler Mesh Number					
	35	65	100	150	200	-200
1-A	---	---	---	30.6	30.2	39.2
1-B	---	---	---	30.6	30.2	39.2
2-A	---	10	5	18	42	25
2-B	---	10	5	18	42	25
3-A	---	2	1	28	47	22
3-B	---	2	1	28	47	22
4-A	6	4	6	15	17	52
4-B	6	4	6	15	17	52
5-A	4	12	12	18	14	40
5-B	4	12	12	18	14	40
6-A	3	8	7	11	20	51
6-B	3	8	7	11	20	51
7-A	2	8	10	17	18	45
7-B	2	8	10	17	18	45
8-A	2	5	8	19	18	48
8-B	2	5	8	19	18	48
9-A	18	36	18	10	4	14
9-B	18	36	18	10	4	14
10-A	18	36	18	10	4	14
10-B	18	36	18	10	4	14
11-A	20	36	18	10	4	12
11-B	20	36	18	10	4	12
12-A	16	37	19	10	4	14
12-B	16	37	19	10	4	14
13-A	16	37	17	10	4	16
13-B	16	37	17	10	4	16
14-A	17	37	15	9	3	19
14-B	17	37	15	9	3	19
15-A	16	37	18	10	4	15
15-B	16	37	18	10	4	15
16-A	16	37	18	10	4	15
16-B	16	37	18	10	4	15
17-A	19	36	19	11	4	11
17-B	19	36	19	11	4	11
18-A	19	36	19	11	4	11
18-B	19	36	19	11	4	11

Data and Results of Flotation Tests on Paint Bank.

Virginia Manganese Ore Fines from the Log-Washers. The table shows the separate effects of crude oleic acid, sulphonated tallol, and crude tallol on the flotation of the manganese ore. The effects of sodium silicate, hydrated lime, pine oil, and sulphuric acid are also shown for runs with crude oleic acid and crude tallol. In each run the relative order of addition of the reagents was as follows: 1. hydrated lime, 2. sulphuric acid, 3. sodium silicate, 4. crude oleic acid or crude tallol ore sulphonated tallol, and 5. pine oil.

The ratio of concentration was calculated as follows:

$$\text{Ratio of concentration} = \frac{\text{Weight of feed}}{\text{Weight of concentrate}}$$

The recovery was calculated as follows:

$$\text{Recovery} = \frac{(\text{Weight of concentrate}) (\% \text{Mn in concentrate})}{(\text{Weight of feed}) (\% \text{Mn in feed})} \times 100$$

TABLE IV.

Data and Results of Flotation Tests on Paint Bank, Virginia Manganese

Ore Fines from the Log-Washers.

Run Number	Crude Oleic Acid lbs./ton	Crude Tallol lbs./ton	Sulphonated Tallol lbs./ton	Pine Oil lbs./ton	Sodium Silicate lbs./ton	Sulphuric Acid lbs./ton	Hydrated Lime lbs./ton	pH Number	Manganese in Feed percent	Manganese in Conc. per Cent	Manganese in Tailings per cent	Weight of Conc. per cent	Ratio of Concentration	Recovery per cent	Time for Flotation Minutes	Remarks
1-A	0.2	---	---	0.2	0.2	---	---	6.7	25.30	27.45	23.60	23.7	2.00	25.7	10	Very good froth, difficult to break down.
1-B	0.2	---	---	0.1	0.2	---	---	7.4	24.90	31.90	23.25	18.2	1.89	23.3	10	Excellent froth, difficult to break down.
2-A	0.2	---	---	0.1	0.4	---	---	8.0	24.95	30.10	21.25	27.0	1.82	32.6	5	Good froth, very difficult to break down.
2-B	0.2	---	---	0.1	0.4	---	1.0	8.3	24.85	30.00	23.45	24.9	1.92	30.0	5	Very good froth, easy to break down.
3-A	0.2	---	---	0.1	1.0	---	---	6.2	25.20	26.10	24.25	39.2	1.99	40.6	5	Good froth, very brittle bubbles.
3-B	0.4	---	---	0.1	2.0	---	---	6.1	26.40	30.80	20.40	48.2	1.77	56.2	6	Excellent froth, extremely brittle.
4-A	0.2	---	---	0.1	---	---	---	6.6	24.75	31.00	20.10	30.4	1.74	38.0	5	Uncontrollable froth, very viscous.
4-B	0.2	---	---	0.1	---	3.68	---	4.8	24.75	31.40	23.10	13.6	1.92	17.2	15	Poor froth, uncontrollable and viscous.
5-A	1.0	---	---	---	---	3.68	---	5.5	25.00	36.00	22.65	8.3	1.93	7.8	5	Poor froth, too large bubbles.
5-B	0.2	---	---	0.1	2.0	---	---	6.0	25.00	23.35	25.50	17.8	2.12	16.5	5	Good froth, very easy to break down.
6-A	0.2	---	---	0.1	0.4	1.84	---	5.0	24.05	35.30	22.00	16.7	1.82	24.5	10	Good froth, viscous, difficult to break down.
6-B	0.2	---	---	0.1	---	---	1.0	8.3	24.05	30.10	22.65	26.1	1.88	32.6	15	Excellent froth, but extremely viscous.
7-A	0.2	---	---	0.1	3.0	---	---	6.5	25.70	30.40	22.55	20.9	1.83	22.9	8	Very good froth, very brittle.
7-B	0.2	---	---	0.1	0.4	---	3.0	8.1	25.70	28.15	24.58	23.8	1.94	26.1	5	Good froth, fairly viscous, easily broken down.
8-A	0.2	---	---	0.1	0.4	5.00	---	5.7	23.95	36.00	23.70	6.6	1.95	9.9	5	Poor froth, fairly brittle.
8-B	1.0	---	---	0.1	2.0	---	---	7.5	23.95	27.40	23.40	53.0	1.88	60.6	1	Excellent froth, brittle, easily broken.
9-A	2.0	---	---	0.1	2.0	---	---	7.6	24.95	31.00	23.50	17.5	1.89	21.7	10	Excellent froth, fairly viscous.
9-B	---	---	1.0	0.3	2.0	---	---	7.8	24.95	33.30	25.60	1.7	2.07	2.3	3	Very poor froth, extremely brittle.
10-A	---	0.2	---	0.2	1.0	---	---	7.5	25.00	31.40	25.40	5.9	2.02	7.4	10	Good froth, easily broken down.
10-B	---	0.4	---	0.2	1.0	---	---	7.5	25.00	32.60	24.40	16.3	1.91	21.2	10	Poor froth, viscous, difficult to break.
11-A	---	1.0	---	0.2	1.0	---	---	7.3	25.55	32.20	24.70	8.1	1.96	10.2	10	Very poor froth, large bubbles, brittle.
11-B	---	2.0	---	0.2	1.0	---	---	7.7	25.55	31.40	25.50	5.6	2.01	6.9	10	Good froth, fairly brittle.
12-A	---	1.0	---	0.2	0.2	---	---	7.6	26.50	31.10	26.40	8.7	1.99	10.2	10	Good froth, fairly brittle.
12-B	---	1.0	---	0.2	0.4	---	---	7.6	26.50	34.20	24.90	3.0	1.99	3.9	5	Good froth, slightly viscous, easily broken.
13-A	---	1.0	---	0.2	2.0	---	---	7.9	24.55	32.20	23.80	7.8	1.94	10.2	2	Excellent froth, extremely brittle.
13-B	---	1.0	---	0.2	3.0	---	---	7.8	24.55	32.10	24.50	16.7	2.02	21.8	5	Very good, extremely brittle.
14-A	---	1.0	---	0.2	1.0	---	10.0	12.0	25.80	35.35	23.10	10.6	1.87	14.5	10	Poor froth, uncontrollable, large bubbles.
14-B	---	1.0	---	0.2	1.0	---	5.0	9.9	25.81	33.25	22.60	15.6	1.81	20.1	5	Good froth, slightly viscous.
15-A	---	1.0	---	0.2	1.0	3.00	---	6.5	25.80	34.80	23.70	14.2	1.89	19.2	10	Poor froth, uncontrollable, large bubbles.
15-B	---	1.0	---	0.2	1.0	5.00	---	6.5	25.80	36.35	24.90	7.4	1.93	10.4	10	Poor froth, uncontrollable, large bubbles.
16-A	---	2.0	---	0.4	1.0	---	---	7.4	25.20	30.95	23.40	22.4	1.85	27.6	5	Very good froth, slightly viscous.
16-B	---	2.0	---	0.3	1.0	---	---	7.7	25.20	30.40	25.00	9.2	1.99	11.1	5	Very good froth, slightly viscous.
17-A	---	2.0	---	0.5	1.0	---	---	7.7	25.20	28.80	24.00	26.3	1.90	30.1	5	Excellent froth, slightly brittle.
17-B	---	2.0	---	0.8	1.0	---	---	7.5	25.20	31.40	23.90	22.7	1.87	28.3	5	Excellent froth, slightly brittle.
18-A	---	1.0	---	0.2	1.0	10.00	---	5.7	25.20	35.00	23.60	7.9	1.90	11.0	10	Very good froth, viscous, large bubbles.
18-B	---	1.0	---	0.2	---	---	---	6.5	25.20	32.30	24.20	19.1	1.87	24.5	10	Poor froth, very viscous.

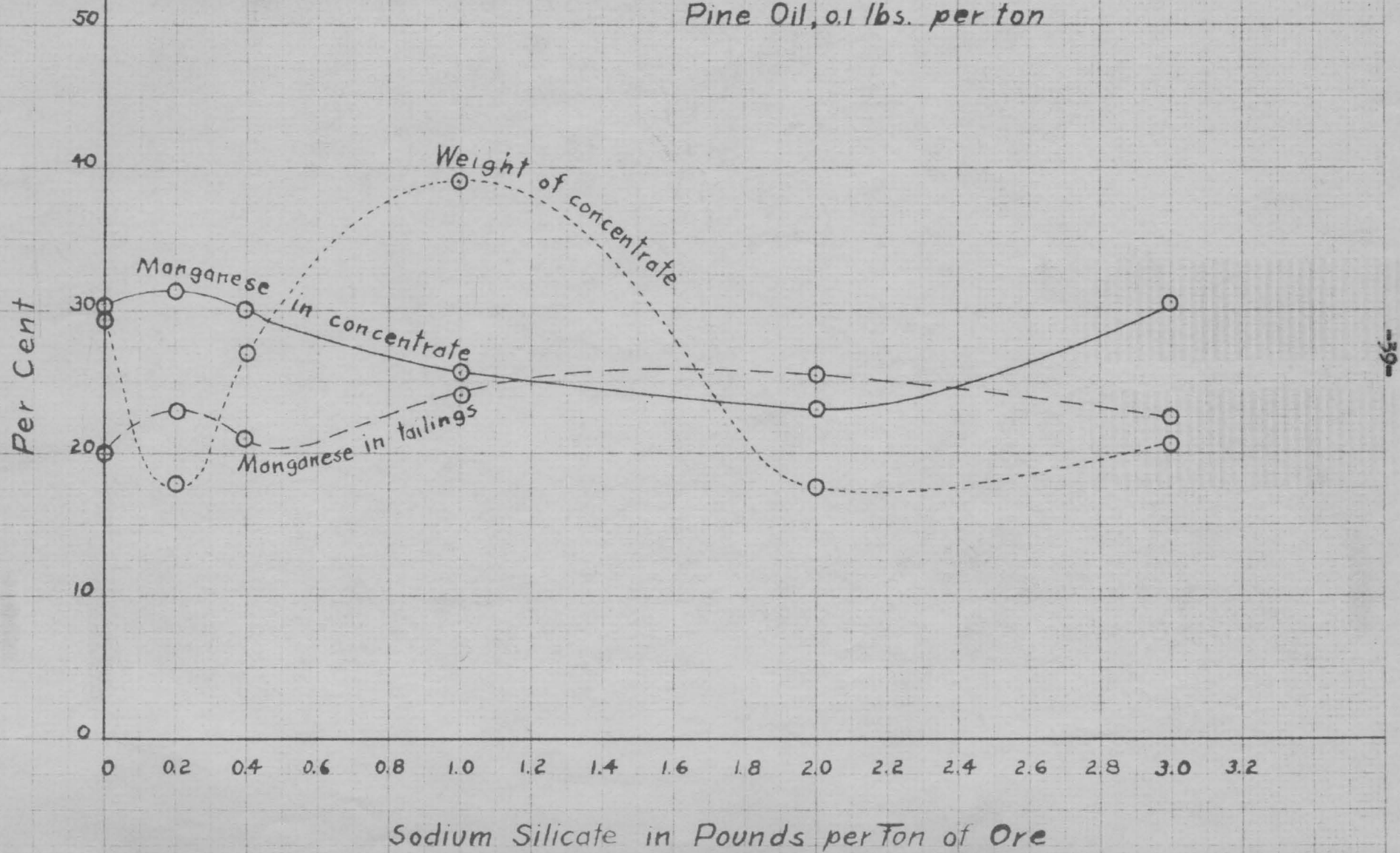
IV. DISCUSSION

Part 1: Crude Oleic Acid as Collector.

Effect of Sodium Silicate. In the flotation tests where the amounts of the collector and frother were held constant, variation of the amount of sodium silicate added to depress the silica produced the curves labeled Graph I. The amount of sodium silicate per ton of manganese ore is plotted against, per cent manganese in concentrate, per cent manganese in the tailings, and per cent weight of concentrate, respectively. The effect of the sodium silicate was not noticeable as regards the degree of separation of the manganese dioxide from the gangue until a concentration of 0.4 pounds per ton of ore was reached. The only effect was in the amount of concentrate recovered. From this point on up to a concentration of 2.0 pounds per ton the per cent manganese in the concentrate became less and less. Addition in excess of 2.0 pounds per ton up to 3.0 pounds per ton had the effect of raising the grade of concentrate. The worst conditions as regards recovery were to be found in the range from 1.0 to 2.0 pounds per ton, where the yield of concentrate was decreasing and the concentrate actually contained less manganese than the original feed or head sample.

The sodium silicate was used as a specific silica de-

GRAPH I
 EFFECT OF SODIUM SILICATE
 Basic Reagents: Crude Oleic Acid, 0.2 lbs. per ton
 Pine Oil, 0.1 lbs. per ton

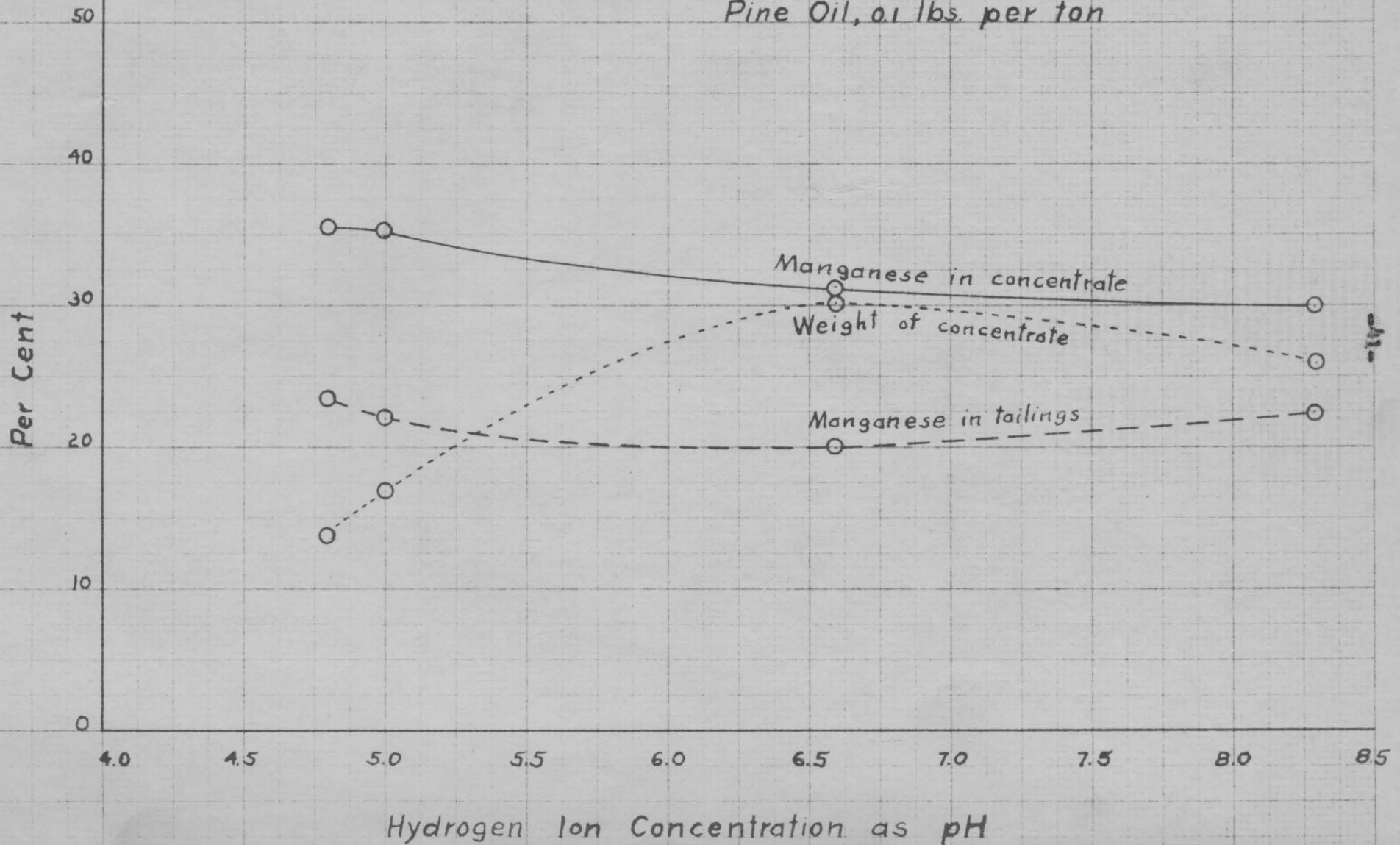


pressor, but it apparently is detrimental to obtaining high grade concentrates. Microscopic examination of a magnetic concentrate from one such run yielded some interesting information. The slide containing the dry powdered ore seemed to be pure manganese dioxide, no silica being visible at all. However, on wetting the same slide and re-examining it was seen that what had seemed to be large manganese dioxide particles were really large grains of silica surrounded or filmed over with much smaller particles of manganese dioxide.

Since the sodium silicate is known to be a silica depressor, it must coat the silica surfaces so as to prevent their floating. But since the silica was floated and not depressed, it may be that the smaller manganese dioxide particles in the flotation pulp adhere to this coating or film. Thus, the silica grains would represent the outward appearance and possess the surface properties of a particle of manganese dioxide, and as such, it would naturally be collected and floated to the surface.

Effect of Hydrogen Ion Concentration. The effect of the hydrogen ion concentration on the flotation with oleic acid is very marked as shown by Graph II. It is evident that an acid pulp medium is conducive to a higher grade concentrate than the alkaline pulp medium. The great disadvantage of the low pH seems to be the extremely low yields of concentrate encountered. Although the alkaline mediums produce a lower grade concentrate, the amount of concentrate is greater. This results in a better over all recovery. Use of an acid process would necessitate the

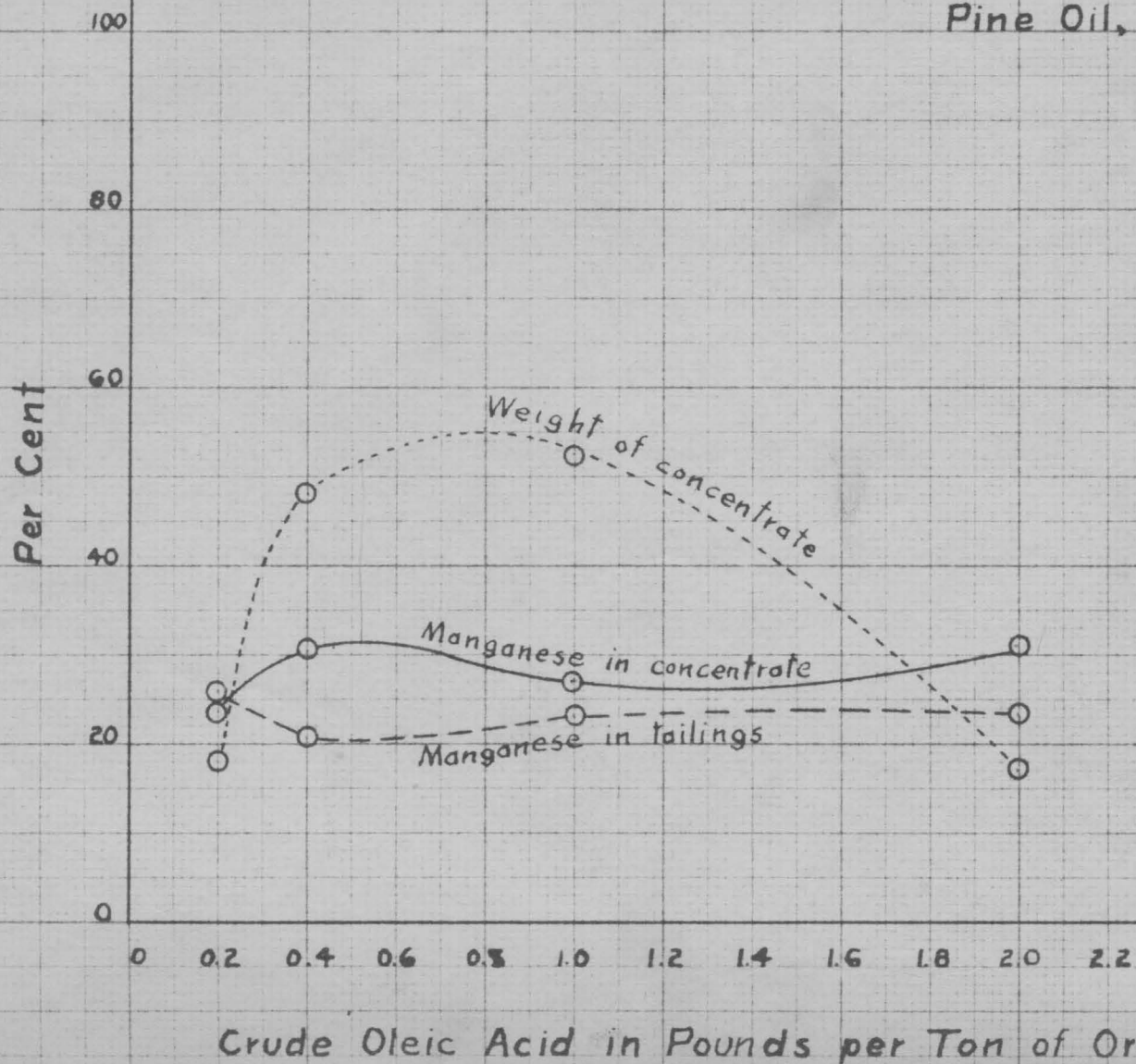
GRAPH II
EFFECT OF HYDROGEN ION CONCENTRATION
Basic Reagents: Crude Oleic Acid, 0.2 lbs. per ton
Pine Oil, 0.1 lbs. per ton



utilization of many more flotation cells than an alkaline process in order to obtain a commercial production volume. The acid process is also said to increase the reagent consumption, and another obvious disadvantage would be the corrosive action on the equipment.

Effect of Crude Oleic Acid. Varying the amount of crude oleic acid used as a collector for the manganese dioxide produced the curves shown in Graph III. No run was made with the collector absent, but starting with a concentration of 0.2 pounds per ton of ore on up to 0.6 pounds per ton of ore, the grade of concentrate became higher. Beyond this point on out to a concentration of 2.0 pounds per ton of ore, the grade of concentrate was slightly lower and tended to remain almost constant. The most noticeable effect of the collector was the amount of concentrate collected. The maximum amount of concentrate recovered was obtained using a concentration of 1.0 pounds per ton of ore, the amount falling off to a minimum on each side of this point. Apparently, the optimum concentration lies in the range from 0.4 to 0.6 pounds per ton of ore where the grade of concentrate is the highest and the amount of concentrate is near its maximum value.

GRAPH III
EFFECT OF CRUDE OLEIC ACID
Basic Reagents: Sodium Silicate, 2.0 lbs. per ton
Pine Oil, 0.1 lbs. per ton



43

Part 2: Sulphonated Tallol as Collector.

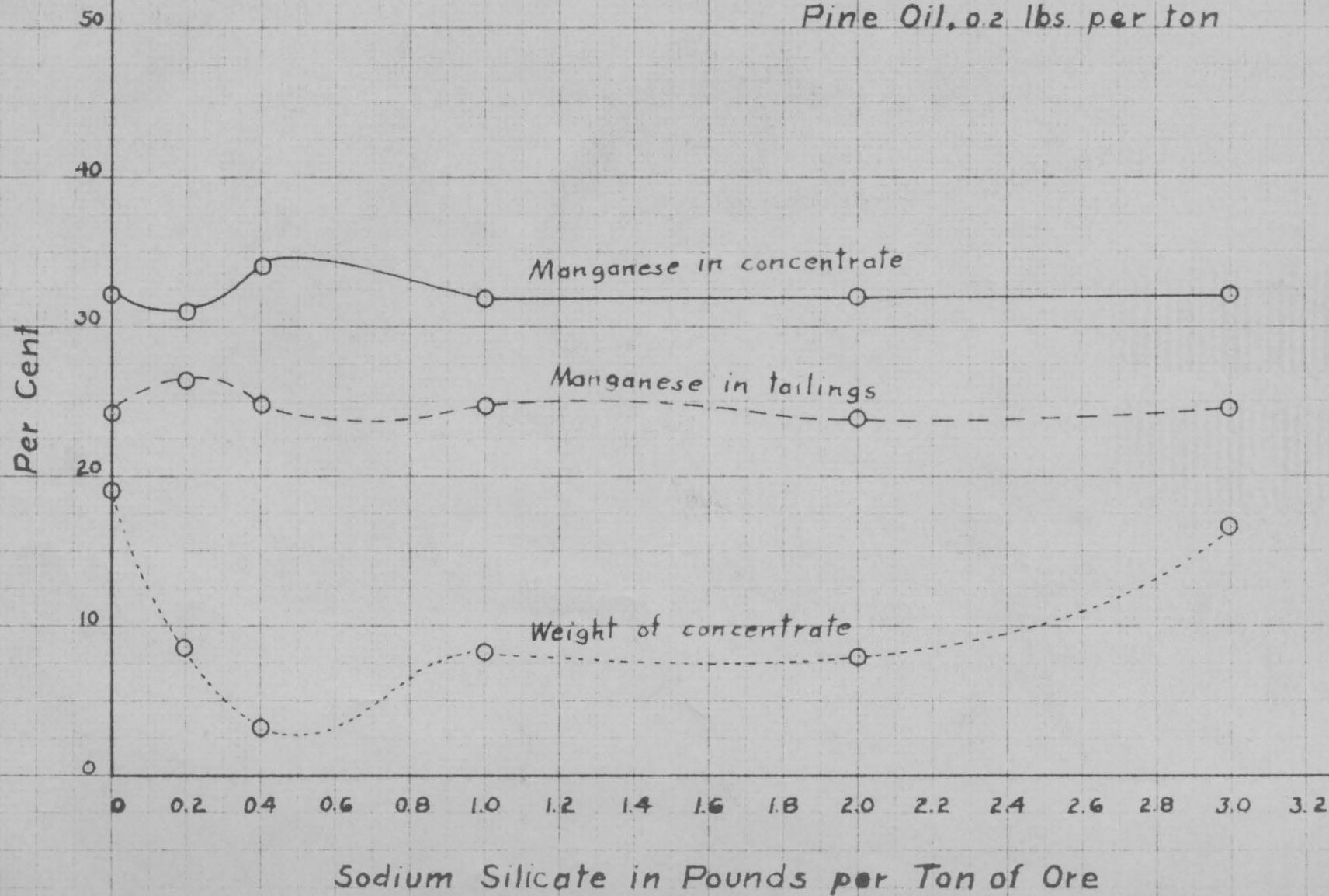
The flotation test of the collecting properties of sulphonated tallol was not encouraging. There was no comparison with the results obtained on crude oleic acid and crude tallol under similar conditions. The grade of concentrate was fairly high, but the yield of concentrate was extremely small. This resulted in a very poor overall recovery. Therefore, it was decided that the sulphonated tallol did not show sufficient promise to justify proceeding with an extensive investigation.

Part 3: Crude Tallol as Collector.

Effect of Sodium Silicate. Runs in which the amount of sodium silicate was varied showed that the reagent had very little effect on the grade of concentrate obtained. A very slight increase was noted in the neighborhood of 0.4 pounds per ton of ore, but it dropped almost immediately after this concentration and remained constant on out to a concentration of 3.0 pounds per ton of ore. The effect of the reagent was more noticeable on the amount of concentrate recovered. Between zero and 3.0 pounds per ton of ore, the addition of the sodium silicate greatly lowered recovery, and since the degree of separation was nearly constant, the overall recovery was the poorest. At concentration of 0.0 and 3.0 pounds of sodium silicate per ton of ore, the overall recovery was identical. In other words, it was possible to effect the same degree of separation by not using sodium silicate as would be obtained by addition of as much as 3.0 pounds per ton of ore.

Effect of Hydrogen Ion Concentration. As in the case of the crude oleic acid, the alkaline pulp mediums were found to give the best overall recovery of the manganese dioxide in the ore as shown by Graph V. Although the acid medium at a pH of 5.7 gave as high a grade concentrate as the alkaline medium at a pH of 12.0, the amount of concentrate was lower. Whereas, in the case of the crude oleic acid, a pH of 6.5 gave the best overall recovery, in the case of the crude tallol, a pH of 10.0 gave the best overall

GRAPH IV
EFFECT OF SODIUM SILICATE
Basic Reagents: Crude Tallol, 1.0 lbs. per ton
Pine Oil, 0.2 lbs. per ton



GRAPH V EFFECT OF HYDROGEN ION CONCENTRATION

Basic Reagents: Sodium Silicate, 1.0 lbs. per ton
Crude Tallol, 1.0 lbs. per ton
Pine Oil, 0.2 lbs. per ton

Per Cent

50

40

30

20

10

0

5.0

6.0

7.0

8.0

9.0

10.0

11.0

12.0

13.0

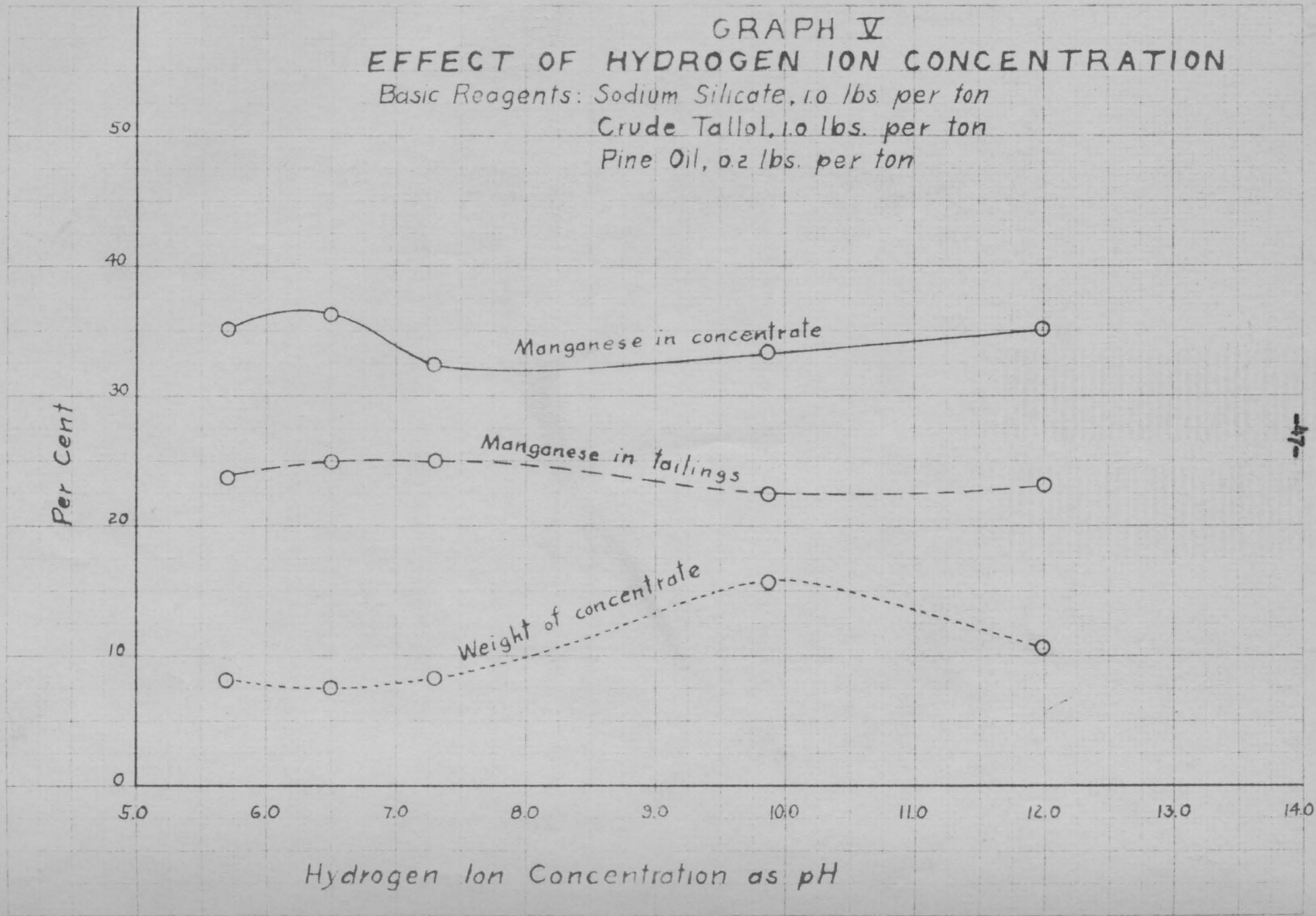
14.0

Hydrogen Ion Concentration as pH

Manganese in concentrate

Manganese in tailings

Weight of concentrate

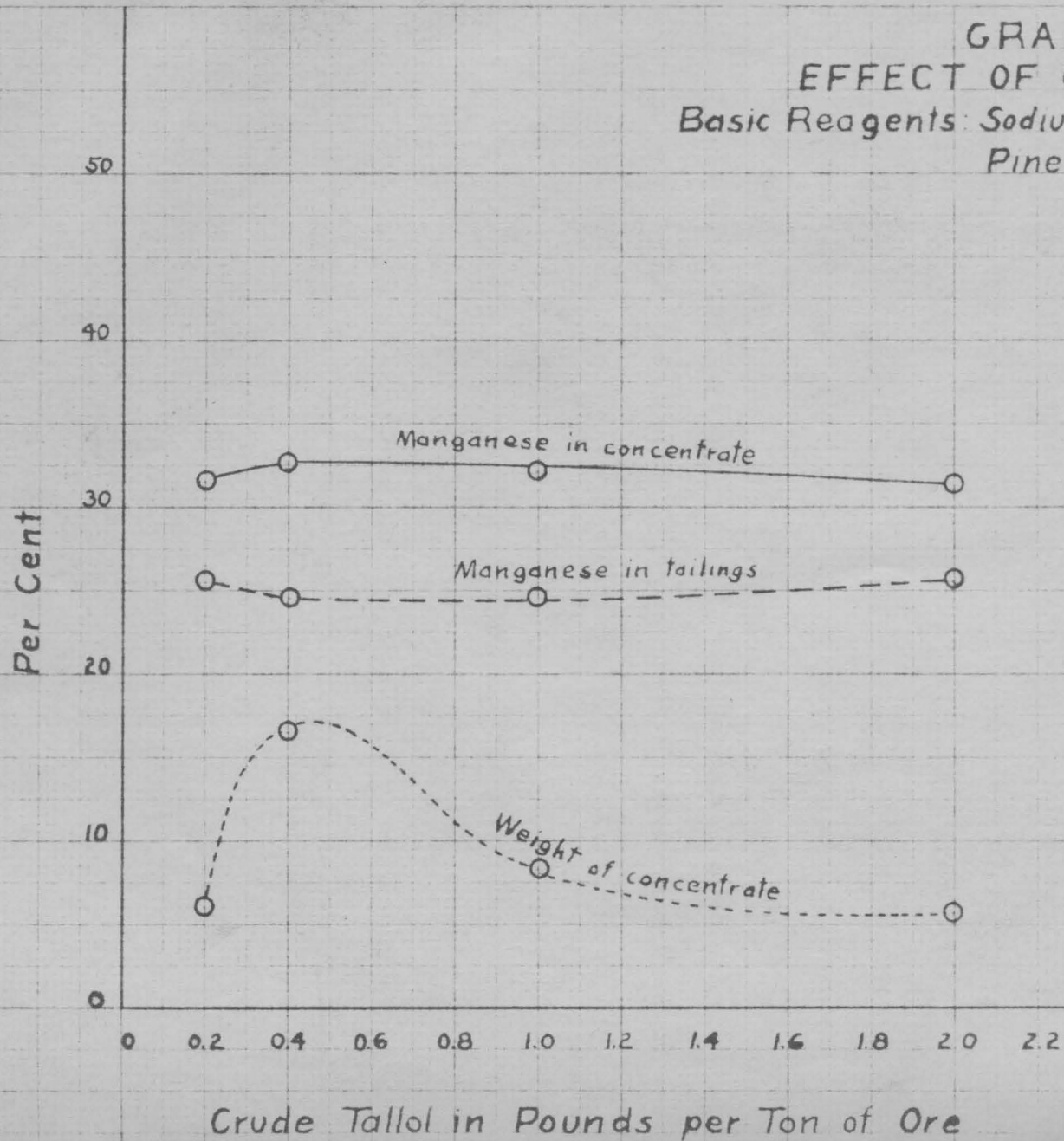


recovery. However, the recovery with crude tallol was only one-third as great as that with crude oleic acid.

Effect of Crude Tallol. The investigation of the collecting properties of the crude tallol indicates that it is not as effective as the crude oleic acid. Flotation runs in which the amount of the crude tallol collector was varied showed that the reagent had practically no effect on the grade of concentrate obtained. It did, however, affect the amount of concentrate obtained materially, as shown by the curves in Graph VI. Starting with a concentration of 0.2 pounds per ton of ore on up to a concentration of 0.4 pounds per ton of ore, the amount of concentrate continually increased. But from this point on to a concentration of 2.0 pounds per ton of ore, the recovery of concentrate steadily decreased. The overall recovery was not comparable to that obtained with the crude oleic acid due principally to the fact that the yield of concentrate was approximately one-third as great.

Effect of Pine Oil. Flotation tests showing the effect of pine oil are shown in the curves on Graph VII. Although the grade of concentrate was little affected by changes in amount of the frothing agent, the amount of concentrate was materially increased by additions up to 0.6 pounds per ton of ore. From a concentration of 0.2 pounds per ton of ore up to 0.6 pounds per ton of ore, the per cent recovery of concentrate increased five-fold, but from this point on to a concentration of 0.8 pounds per

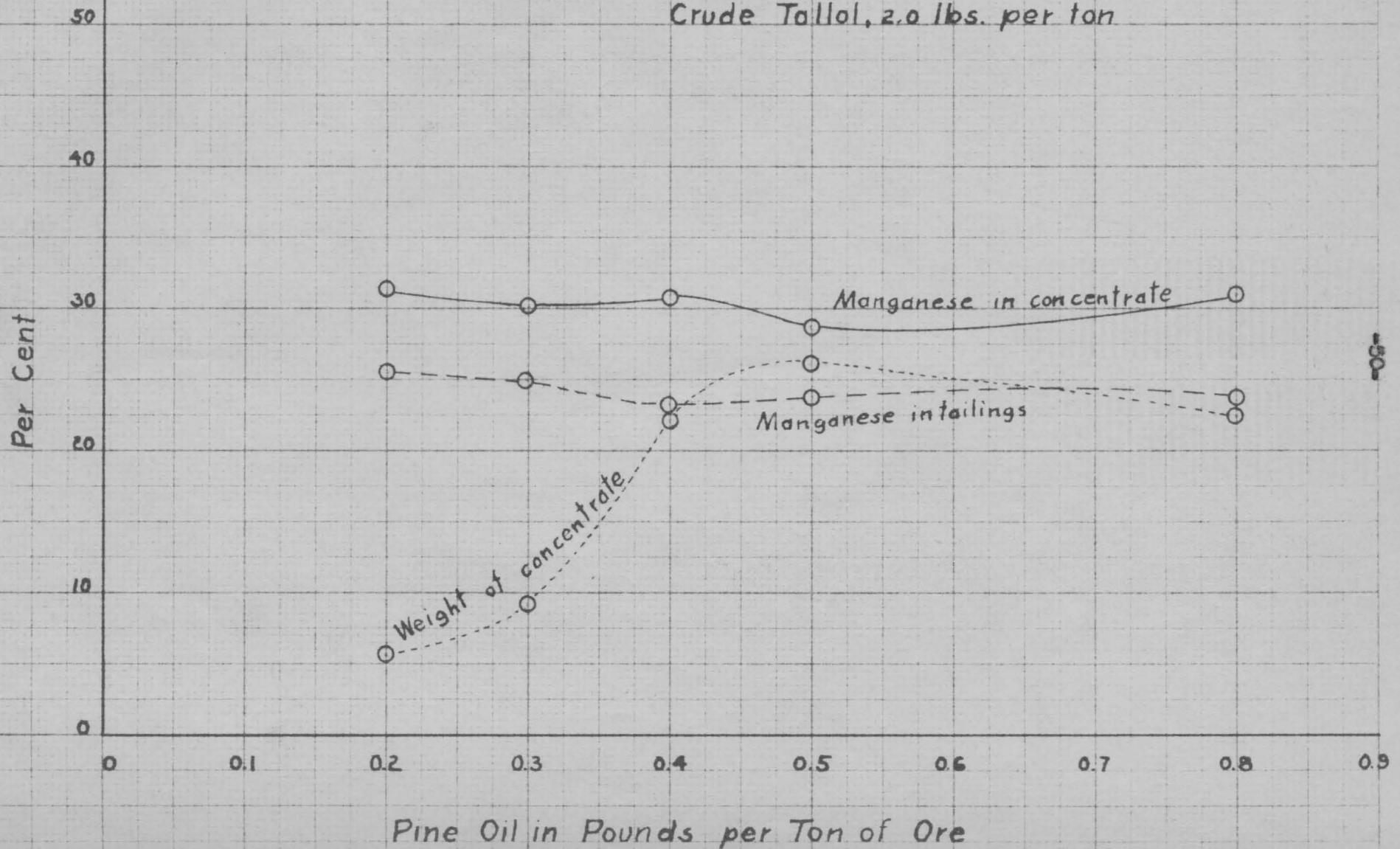
GRAPH VI
EFFECT OF CRUDE TALLOL
Basic Reagents: Sodium Silicate, 1.0 lbs. per ton
Pine Oil, 0.2 lbs. per ton



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GRAPH VII
EFFECT OF PINE OIL

Basic Reagents: Sodium Silicate, 1.0 lbs. per ton
Crude Tallol, 2.0 lbs. per ton



ton of ore, the yield decreased slightly. A complicating factor in such tests on the frothing agent is the fact that both crude tallol and crude oleic acid exhibit frothing properties by themselves. Thus in considering the amount of frother to use the amount of collector must also be taken into account. The investigation has also shown that sodium silicate has a pronounced effect on the froth. In general, the more sodium silicate used, the more brittle the froth will be. The degree of brittleness has a decided influence on the carrying capacity of the froth.

Further work should be done on this phase, for the correct amount of frother is an extremely important factor in flotation. The froth should be plentiful, contain many small bubbles, and be in a constant lively state of metabolism. It should not be too viscous since heavy froths tend to hold up or float everything, and do not break down easily after leaving the flotation cell.

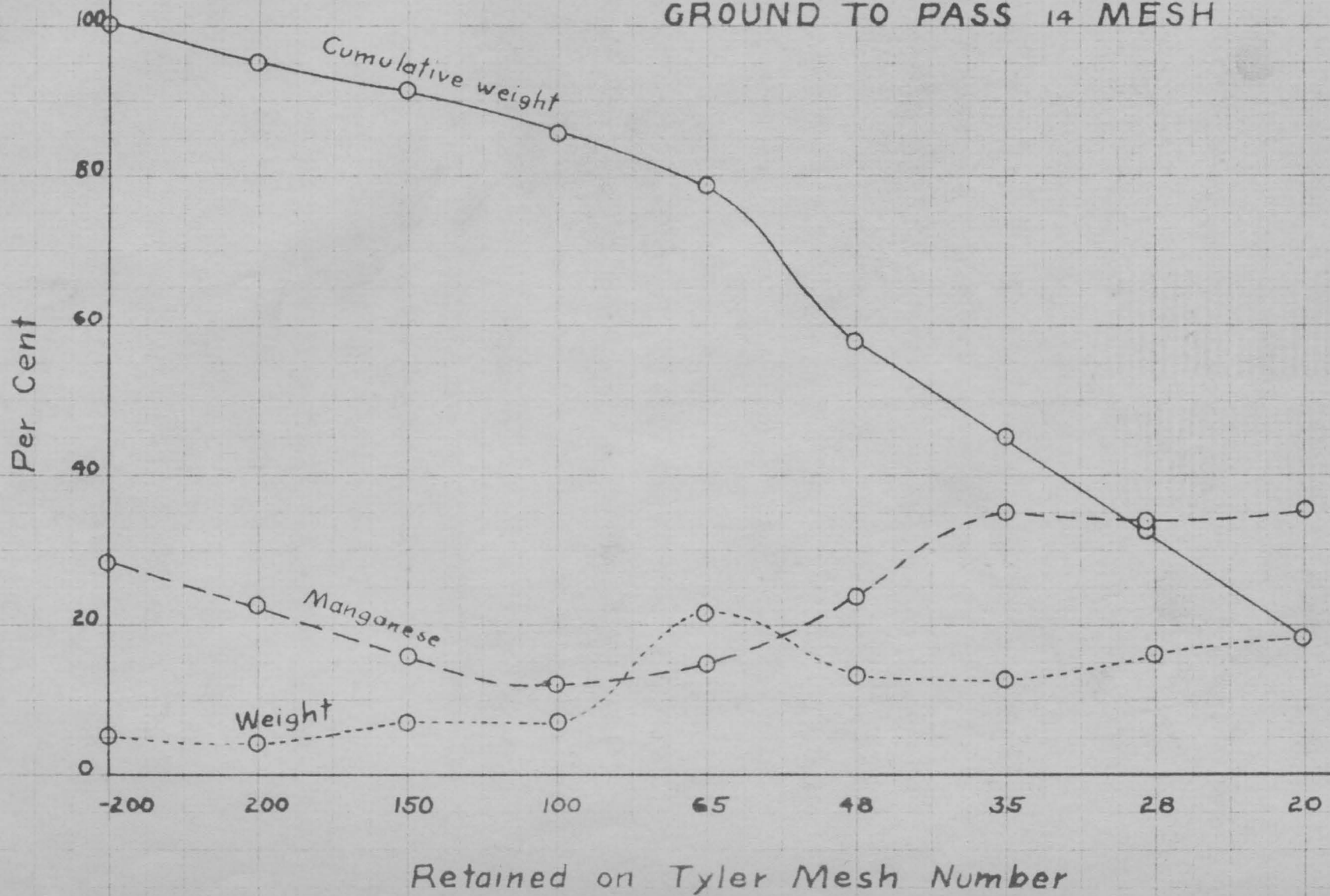
Part 4: Optimum Flotation Size of Ore.

Sieve Analyses and Distribution of Manganese Ore. Analyses of sieve products of the crushed manganese ore are shown by the curves on Graph VIII. It is evident that the greater portion of the manganese is found in the extremely small and the extremely large sizes. This fact alone makes the flotation of the manganese dioxide difficult. A flotation process, which is to be successful, must be capable of floating both extremes of size with equal facility. Some concentration could be effected by flotation of only the larger mesh sizes since the major portion, 80 per cent, of the manganese dioxide is retained on 65 mesh. The flotation tests have indicated, however, that the ore should be crushed at least through 35 mesh, and preferably through 65 mesh, in order to obtain greater recovery. Then too, flotation of only the large sizes would leave much valuable ore to be left in the tailings and lost.

Recommendations for Further Study.

The work completed in this investigation is only a small portion of that which would be needed before the process could be put into commercial operation. For example, the silica depressor used in this investigation, sodium silicate, was not effective in the concentrations used. It seemed to cause the silica grains to become coated with manganese dioxide particles,

GRAPH VIII
SCREEN ANALYSIS AND DISTRIBUTION
OF MANGANESE ORE
GROUND TO PASS 14 MESH



and consequently be floated. A search for other silica depressors should be instigated.

More extensive work should also be done to determine the proper size for flotation. The optimum size would be such as to completely liberate the manganese dioxide from the gangue, and still be not too large for flotation size. Care should be taken not to overgrind the ore, since the manganese ores tend to slime excessively in the sizes smaller than 150 mesh.

A set order of addition of the flotation reagents was followed throughout the tests. Variations of this order should be attempted in order to determine the best sequence of addition. The time between addition of the reagents should also be varied to determine the optimum time. In commercial practice this is important since the time factor is extensively used to determine the number of cells required. For the same reason, the conditioning time should also be varied so as to determine the optimum or shortest time to get complete mixing between ore and reagents.

In order to duplicate commercial conditions as nearly as possible, the manganese ore should not be ground to flotation size until just before flotation. Only freshly ground ore should be used, since surface changes may take place if the ore is allowed to stand for any considerable length of time.

V. CONCLUSIONS.

1. Sodium silicate, specific gravity 1.30, tends to make the flotation froth brittle when used in concentrations of 0.0 to 3.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer, and under each of the following conditions:
(a) with 0.2 pounds per ton of crude oleic acid (Ligro) and 0.1 pounds per ton of Yarmor F pine oil. (b) with 1.0 pounds per ton of crude tallol and 0.2 pounds per ton of Yarmor F pine oil.
2. Crude oleic acid exhibits frothing properties in the flotation of Paint Bank, Virginia manganese ore fines from the log-washer, in concentrations of 0.0 to 2.0 pounds per ton, when used in conjunction with 2.0 pounds per ton of sodium silicate, specific gravity 1.30, and 0.1 pounds per ton of Yarmor F pine oil.
3. Crude tallol exhibits frothing properties in the flotation of Paint Bank, Virginia manganese ore fines from the log-washer, in concentrations from 0.0 to 2.0 pounds per ton, when used in conjunction with 1.0 pounds per ton of sodium silicate, specific gravity, 1.30, and 0.2 pounds per ton of Yarmor F pine oil.
4. Sodium silicate, specific gravity 1.30, is not effective as a silica depressor in concentrations from 0.0 to 0.6 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer, when used in conjunction with 0.2 pounds per ton of crude oleic acid (Ligra) and 0.1 pounds per ton of Yarmor F pine oil.
5. Sodium silicate, specific gravity 1.30, is actually an aid to

silica flotation in concentrations from 0.6 to 3.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer when used in conjunction with 0.2 pounds per ton of crude oleic acid (Ligro) and 0.1 pounds per ton of Yarmor F pine oil.

6. Sodium silicate, specific gravity 1.30, was not effective as a silica depressor in concentrations of 0.0 to 3.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer, when used in conjunction with 1.0 pounds per ton of crude tallol and 0.2 pounds per ton of Yarmor F pine oil.

7. Acid pulp mediums from pH 4.6 to pH 7.0, were conducive to higher grade concentrates than alkaline pulp mediums under the following conditions: (a) with 0.2 pounds per ton of crude oleic acid and 0.1 pounds per ton of Yarmor F pine oil, (b) with 1.0 pounds per ton of sodium silicate, specific gravity 1.30, pounds per ton of crude tallol, and 0.2 pounds per ton of pine oil.

8. Acid pulp mediums from pH 4.6 to pH 7.0, gave lower per cent recovery of the concentrate of manganese dioxide than alkaline pulp mediums under identical conditions of 6(a) and 6(b) above.

9. Yarmor F pine oil in concentrations from 0.2 to 0.8 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer had practically no effect on the grade of concentrate when used in conjunction with 1.0 pounds per ton of sodium silicate, specific gravity, 1.30, and 2.0 pounds per ton of crude tallol.

10. Yarmor F pine oil in concentrations from 0.2 to 0.6 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer increased the per cent recovery of concentrate, reaching a maximum of 0.6 pounds per ton, when used in conjunction with 1.0 pounds per ton of sodium silicate, specific gravity 1.30, and 2.0 pounds per ton of crude tallol.

11. Crude oleic acid (Ligro) had little effect on the grade of concentrate obtained when used in concentrations from 0.2 to 2.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer and in conjunction with 2.0 pounds per ton of sodium silicate, specific gravity 1.30, and 0.1 pounds per ton of Yarmor F pine oil.

12. Crude oleic acid (Ligro) greatly affects the per cent recovery of concentrate in concentrations from 0.2 to 2.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer reaching a maximum per cent recovery around a concentration of 1.0 pounds per ton, when used in conjunction with 2.0 pounds per ton of sodium silicate, specific gravity 1.30, and 0.1 pounds per ton of Yarmor F pine oil.

13. Crude tallol in concentrations from 0.2 to 2.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer had little effect on the grade of concentrate obtained when used in conjunction with 1.0 pounds per ton of sodium silicate, specific gravity 1.30, and 0.2 pounds per ton of Yarmor F pine oil.

14. Crude tallol in concentrations from 0.2 to 2.0 pounds per ton of Paint Bank, Virginia manganese ore fines from the log-washer greatly affected the per cent recovery of concentrate, reaching a maximum per cent recovery around a concentration of 0.5 pounds per ton, when used in conjunction with 1.0 pounds per ton of sodium silicate, specific gravity 1.30, and 0.2 pounds per ton of Yarmor F pine oil.

15. When the Paint Bank, Virginia manganese ore fines from the log-washer is ground in a ball mill for one-half hour, the greater portion of the manganese dioxide is distributed throughout the largest and smallest sizes, the medium sizes containing the least per cent manganese dioxide.

VI. SUMMARY

Low-grade pyrolusite manganese ore from the Paint Bank deposits of Virginia was prepared for flotation by grinding to different degrees of fineness. The coarsest size was 28 Tyler Mesh and the finest was 100 Tyler mesh. Under size products of the grinding were as fine as minus 200 Tyler Mesh.

Flotation tests were run on the ore in a Denver Sub-A Flotation Cell of 500 gram capacity. Each run was made with an amount of ore closely approximating this capacity. The flotation reagents were added in a definite order allowing three minutes between each addition. A conditioning period of fifteen minutes followed the addition of the reagents in each case.

Crude tallol was tested as a collecting agent for the manganese dioxide in the ore, with auxiliary reagents. Runs were made varying the amounts of tallol, pine oil, frother, sodium silicate silica depressor, and the hydrogen ion concentration was varied with either sulphuric acid or hydrated lime.

Crude oleic acid from tallol was also tested as a collecting agent for the manganese dioxide in the ore, with auxiliary reagents. Runs were made varying the amounts of crude oleic acid, sodium silicate depressor, and the hydrogen ion concentration was varied with either sulphuric acid or hydrated lime.

Sulphonated tallol was also tested as a collecting agent, but the preliminary results did not seem to justify continuing with an extensive investigation. The grade of concentrate was fairly high but the yield of concentrate was less than two per cent of the original head sample.

The crude oleic acid was found to be a better collector than the crude tallol, although neither one had much effect on the grade of the concentrate obtained. Sodium silicate had no beneficial action on the grade of concentrate, and with the crude oleic acid, it had a definitely deterrent effect. It was indicated that this was due to its coating the silica with a film of manganese dioxide, thus causing the silica to be collected as a particle of manganese dioxide. The sodium silicate was found to be useful in increasing the per cent recovery of concentrate. Pine oil while not having any effect on the grade of concentrate, was effective in increasing the yield of concentrate. In general, an acid medium was found conducive to obtaining high grade concentrates, but this was more than offset by the low yields encountered. An alkaline medium was found to give the best overall recovery of the manganese dioxide. It was also indicated that the ore should be crushed through at least 35 mesh, and preferably 65 mesh, in order to obtain the greatest recovery.

VII. BIBLIOGRAPHY

1. Anonymous. Concentrating Ores.
Cuban-American Manganese Corp., British Patent 393,607
(1933) Original not seen.
2. Anonymous. Flotation ABC. Bulletin, Great Western Electro-
Chemical Co., Division of Dow Chemical Co., San Fran-
cisco, California. (1940)
3. Arnold, G. Method of Producing a Concentrate of Chrome Ores.,
U. S. Patent 2,082, 817 (1937)
4. Badger, W. L. and McCabe, W. L. "Elements of Chemical Eng-
ineering". P. 592-95. McGraw-Hill Book Co., New
York. 1936. 2nd ed.
5. Basvanov, V. A. Flotation of Manganese Slimes at Chiaturi.
Gorno-Obogatitel Zhur., 3, 11 (1936)
6. Becher, C. Talloil (Liquid Resin) Chem. Zeitung, 60, No.
37, 373-75 (1936) Original not seen.
7. Bergstrom, H. O. V. and Cedarquist, K. N. Dehydrogenation of
Liquid Resin. Swedish Patent 86,321 (1932) Original
not seen.
8. Bohme, H. Th. Improvements in or Relating to Flotation Pro-
cesses. British Patent 410,956 (1934)
9. Coghill, W. H. and Clemmer, J. B. Soap Flotation of Non-
Sulphides. Am. Inst. Min. Met. Eng. Tech. Pub. 445, 18
(1932) Trans Am. Inst. Min. Met. Eng. 112, 449-65 (1934)

10. Crockin, J. M. Separation of Rosin and Fatty Acids From Tall Oil by Selective Sulphonation. Unpublished Thesis. Library, Virginia Polytechnic Institute, Blacksburg, Va. 1940.
11. Dean, R. S. Progress Reports-Metallurgical Div. 12 (1935) Report of Investigations 3306, 39 pp. (1936) Bureau of Mines, Washington, D. C.
12. Dean, R. S. and Clemmer, J. B. and Cooke, S. R. B. Use of Wetting Agents in Flotation. Report of Investigations 3333, (1937) Bureau of Mines, Washington, D. C.
13. DeVaney, F. D. and Clemmer, J. B. Report of Investigations 3045, 9 pp. (1930) Bureau of Mines, Washington, D. C.
14. DeVaney, F. D. and Clemmer, J. B. Concentrating Manganese Ores by Flotation. U. S. Patent 1,591,326 (1934)
15. DeVaney, F. D. and Clemmer, J. B. Floating of Carbonate and Oxide Manganese Ores. Eng. And Min. J., 128, 506-508 (1929)
16. DeVaney, F. D. and Clemmer, J. B. Flotation of Oxide Ores. Eng. and Min. J., 128, 516-18 (1929)
17. DeVaney, F. D. and Coghill, W. H. Preliminary Ore Dressing Tests to Recover Manganese in Rhodochrosite Ores. Report of Investigations 2902, 4 pp. (1928) Bureau of Mines, Washington, D. C.
18. Fahrenwald, A. W. and Staley, W. A. Power Consumed in Stirring Flotation Pulp. Report of Investigations 3006 (1930) Bureau of Mines, Washington, D. C.

19. French, E. H. Production of Pure By-Products from Resin Containing Liquors. U. S. Patent 1,997,171 (1935)
20. Gamelaini, M. Flotation of Manganese Slimes. Gorno-Obogatitel Zhur., No. 1, 37-8 (1938)
21. Gaudin, A. M. "Principles of Mineral Dressing". p. 418. McGraw-Hill Book Co., New York. 1939 1st. ed.
22. Gaudin, A. M. and Behrens, R. H. A Manganese Recovery Problem and Its Solution. Eng. and Min. J. 138, 40-42 (1937)
23. Hasselstrom, T. TAPPI, Special Report No. 52. Forest Products Laboratory, Madison, Wisconsin. 1931
24. Haynes, W. Flotation Process. British Patent 488 (1860)
25. Hegemann, F. Flotation Process German Patent 673,891 (1939)
26. Heisam, E. A. The Status of Research in Ore Dressing Report of Investigations 2669. Bureau of Mines, Washington, D. C. 1925.
27. Hilditch, T. P. Industrial Chemistry of Fats and Waxes. Chapter II. D. Van Nostrand Co., New York. 1927.
28. Keller, A. Flotation Process. U. S. Patent 1,554,216 (1925)
29. Kirby, J. E. Flotation Process. U. S. Patent 2,088,325 (1937)
30. Kirby, J. E. and Werntz, J. H. Flotation Process. U. S. Patent 2,099,120 (1937)
31. Kraft, K. The Original Acids in American Pine Rosins. Ann. 520, 133-43 (1935)

32. Lenker, S. Flotation Process. U. S. Patent 2,012,609 (1935).
33. Lenker, S. Ore Flotation. British Patent 463,261 (1937)
34. Lenker, S. and Gillsons, J. L. Flotation Process. U. S. Patent 2,115,727 (1937)
35. Lenker, S., Gillsons, J. L., and Mentzer, C. T., Jr. Flotation Process. U. S. Patent 2,074,699 (1937)
36. Lewkowitsch, J. Chemical Technology of Oils, Fats, and Waxes. Chapter XII. McMillan Co., London; Vol. I, 5th ed. 1915.
37. McKee, R. H. and Blengali, H. L. Refining of Tall Oil. Paper Trade J. 103, No. 14, 33-4 (1936)
38. Meriss, M. H. Flotation Process. U. S. Patent 2,102,370 (1937)
39. Orelli, A. Flotation Process. British Patent 460,072 (1937)
40. Perkins, W. A. Flotation Process. U. S. Patent 1,364,304 (1921)
41. Pollak, A. Industrial Uses of Tall Oil. Reprint of Paper, American Oil Chemists Society, October 5, 1939.
42. Ralston, O. C. Flotation and Agglomerate Concentration of Nonmetallic Minerals. Report of Investigations 3397. Bureau of Mines, Washington, D. C. (1938).
43. Schmid, W. Liquid Resin and Its Uses. Papier Fabr. 29, Tech.-Wiss. Teil. 1-4 (1931)
44. Shipp, J. B. Pure Products from Tallol. Unpublished Thesis. Library, Virginia Polytechnic Institute, Blacksburg, Va. 1940.
45. Sulman, Picard, and Ballet. Flotation Process. U. S. Patent 836,120 (1906)

46. Taggart, A. F. "Manual of Flotation Processes". pp. 20-30,
McGraw-Hill Book Co., New York, 1921. 1st. ed.
47. Tartaron, F. X. and Duke, J. B. Concentration of Phosphate-
Bearing Minerals. U. S. Patent 2,103,293 (1937)
48. Walloch, J. A. Fatty Acids from Pine Wood. Soap 13, No. 3,
31-3, 73 (1937)
49. Wark, I. W. The Physical Chemistry of Flotation. J. Phys.
Chem. 40, 661-68 (1936)
50. Weed, F. Concentrating Manganese Ores by Flotation. U. S.
Patent 2,014,407 (1936)
51. Weed, F. and Ellis, Concentrating Manganese Ores by
Flotation. U. S. Patent 2,014,406 (1936)
52. Weinig, A. J. Froth Flotation Concentration of Manganese Ores.
U. S. Patent 1,911,865 (1933)
53. Weinig, A. J. and Cuthbertson, K. Concentrating Manganese Ores.
U. S. Patent 1,955,039 (1934)
54. Ziv, Joseph. Tall Oil. German Patent 494,950 (1930)

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