FLOTATION OF ZINC SILICATE BY N-OCTYL METHYLENE BLUE

BY
MALVERN FRANK OBRECHT

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1952

FLOTATION OF ZINC SILICATE BY N-OCTYL METHYLENE BLUE

By

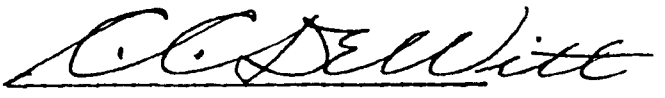
Malvern Frank Obrecht

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

Approved 

FLOTATION OF ZINC SILICATE BY N-OCTYL METHYLENE BLUE

ABSTRACT

The application of n-octyl methylene blue as a collector for the flotation of zinc silicate was investigated. This study was carried out on three zinc silicate ores, namely, (1) Willemite Zn_2SiO_4, (2) Calamine or Hemimorphite, $Zn_2(OH)_2SiO_3$ or $Zn_4(OH)_2Si_2O_7 \cdot H_2O$, (3) A commercial Los Lamentos ore, a tested zinc silicate from Mexico.

The collector was synthesized by preparing a modified dye which was known to mordant zinc salts. The inability to modify methylene blue directly required extensive organic synthesis, including the preparation of ortho n-octyl dimethyl aniline which was used to prepare the compound called n-octyl methylene blue.

The flotation tests were carried out on a feed consisting of from 1% to 6% zinc with the majority of the gangue material being silicious. Reflotation of the concentrate was also investigated. In both studies, a 100 gram batch type flotation cell was employed. Under the test conditions used it was found that n-octyl methylene blue functions as a selective collector for zinc flotation. Reflotation of the concentrate produced an improved cut.

The modified dye appears to offer a new approach to the flotation of zinc silicate. It is theorized that selectivity for zinc silicate of the modified dye is due to the mordant action of the zinc atoms in the atomic lattice of the zinc silicate, further, that the zinc silicate particles are "Enveloped" by the dye molecules.

It is demonstrated that the factors of pH, particle size, and the amount of collector affect the percent zinc in the concentrate, percent recovery of zinc, enrichment of the product, and the improvement factor in the flotation of zinc silicate by n-octyl methylene blue. Certain trends are shown to exist for these factors, and under the conditions of the test "optimums" appear to exist for the zinc silicate ores studied.

The commercial synthesis of n-octyl methylene blue is not practical. However, the approach using this compound as a collector, is fully justified by our present knowledge of dye mordants as well as the presently developed theory of surface chemistry relative to mineral flotation.

ACKNOWLEDGEMENT

The writer expresses his appreciation to Professor Clyde C. DeWitt for his guidance in this investigation of the flotation of zinc silicate by the use of alkyl substituted methylene blue. Many interested engineers in the mineral flotation field have given a full measure of encouragement and interested advice in the opening of what promises to be a confirmation of a new approach to the separation of heavy metal silicates from their gangue materials.

Malvern Frank Obrecht

Candidate for the degree of

Doctor of Philosophy

Final Examination: July 28, 1952, 1:00 P.M., Room 308, Olds Hall

Dissertation: Flotation of Zinc Silicate by n-octyl Methylene Blue.

Outline of Studies

Major Subject: Chemical Engineering
Minor Subject: Metallurgical Engineering
Physical Chemistry

Biographical Items

Born, St. Louis, Missouri

Undergraduate Studies, St. Mary's College, Winona, Minn. 1942-43, Washington University, St. Louis, Mo. B. S. Chemical Engineering 1945.

Graduate Studies, Washington University 1945-46, University of Detroit M. S. in Physical Chemistry 1947, Michigan State College 1947-52.

Experience: Asst. Chem. St. Mary's College 1942-43, Lab. Instr. Washington University 1943-45, Chem. Research and Development Engr. Orchard Paper Co., 1945-46, Techg. Fellowship University of Detroit 1946, Inst. University of Detroit 1946-47, Lec. ibid summer 1947, Asst. Prof. of Chem. and Metall. Engrng. Michigan State College 1947 to date, Adult Extension Lec. in Power Field 1949 to date, Consultant 1947 to date. Member: Am. Inst. of Chem. Engrs., Am. Chem. Soc., Nat. Assoc. Power Engrs., Am. Inst. of Military Engrs., Am. Inst. Engr. Ed., E.S.D., Alpha Chi Sigma, Sigma Xi, Author Engrng. Chemistry of Power Plants and Industrial Water Treatment 1949.

TABLE OF CONTENTS

INTRODUCTION

OBJECT AND SCOPE

The object of this investigation is the flotation of zinc silicate ores by the use of alkyl substituted methylene blue. The modified dye functions as a collector for various zinc silicate ores. Methods for preparation of the modified dyes are not available in the literature, and therefore the synthesis is reported as a part of this investigation.

ZINC SILICATE FLOTATION

Ores rich in zinc content are relatively scarce in the United States. The demands for zinc during World War II emphasized the need for a method of recovering zinc in low-grade zinc silicate ores and tailings from milling operations. There is a need for a collector which can enrich higher grades of zinc silicate ores and thus decrease the cost of producing zinc.

Examination of the literature up to the present indicates that zinc silicate has never been successfully floated either in the laboratory or in the field.

BENEFICATION OF OXIDIZED ORES OF ZINC

Attention has been given to beneficiation of oxidized zinc ores by pyrometallurgical means (56). This type of operation is more costly than flotation and requires a good grade of zinc ore.

High grade zinc ores may be beneficiated by the use of the metallurgical process of volatilization. In this process the ore is decomposed and the zinc vapors mechanically removed by an inert gaseous stream. The decomposition temperature for some ores is 1370°C. (4)

Mineral dressing methods such as jigging and tabling produce little beneficiation of an ore containing hemimorphite, Zn_2SiO_4, and smithsonite, $ZnCO_3$, when the ore is finer than 48 mesh.

The Waelz process of volatilization has been reported to work on oxidized zinc ores with a zinc content of only 6 per cent. However, considerable trouble is encountered in the formation of incrustations on the lining of the kilns. These incrustations require complicated operations to remove them; they also limit the length of the kiln.

Mixtures of quartz gangue and zinc silicate ores, such as willemite and calamine used in this investigation, could be separated by the use of a heavy liquid. The float and sink products of such a process, would probably show a fair separation (78). The general method of heavy liquid separation is described in the Bureau of Mines Technical Paper No. 381. However, according to this authority, this method has not proven practical on the majority of zinc silicate ores. It becomes apparent that a solution to the problem of concentrating these

oxidized zinc ores, especially zinc silicate, by froth flotation, would be a very useful application.

Evidently it is more desirable to float the zinc silicate away from the gangue because it is in much smaller concentration and should require less reagent. However, there may be some merit in first floating the gangue of a zinc silicate ore provided the gangue is essentially quartz. This might be done by the use of amine such as Armour's AM-1120. However, if the gangue is a mixture of the various silicates with quartz, this operation is not successful (17).

Recent patent literature (54) reveals claims by engineers of the International Smelting and Refining Company. They claim a separation of oxidized zinc ores from lead ores by froth flotation. The method used a high concentration of a soluble sulphide and a soluble salt of certain aliphatic amines. In this method it appears that there is first, an adsorption of sulphide. Subsequent metallurgical results have shown that the flotation of oxidized minerals is much more successful with than without sodium sulphide (50). At the present time there is available no laboratory or commercial method of concentrating zinc silicate by froth flotation.

FLOTATION PRINCIPLES (18, 20, 25, 74)

Flotation is a method of wet concentration of ores in which the separation of minerals from gangue is effected by

causing the mineral to float at the surface of the liquid pulp while the gangue remains submerged (28). Since the turn of the century, rapid progress has been made in the flotation of certain sulphide ores. One constantly strives for differential flotation, i.e., the selective flotation of one particular metal ore. In 1902 Froment (37) discovered that bubbles of gas, when passed through an ore mixture, served as a carrier for sulphide minerals. He also discovered that oil helped the bubbles' carrying properties. In 1904 Cattermole was issued a British Patent (10) for a process in which ore, water, and oil were mixed together in order to secure an emulsion of the oil. The emulsified oil coated the sulphide particles and formed gramules which sank. The tailings were allowed to overflow. It should be noted that in early days, large quantities of reagent were used. While working on the Cattermole Process, Sullman, Picard and Ballot found that by using only small amounts of reagent, the granules of sulphide ore floated. Their patent makes the first mention of a soluble frothing agent (70). It was about this time that Hoover (44) developed the modern flotation cell; this cell, as do the more modern flotation cells, used mechanical agitation and compressed air.

The early twenties found much attention being given to the development of organic reagents for differential flotation

of sulphide minerals in ores. The most noteworthy of these are the series of alkali organic dithiocarbonates, commonly known as xanthates, discovered by Keller and Lewis in 1925 (46). Xanthates are now successfully used in the flotation of many non-sulphide minerals. As early as 1905 Schwartz proposed the sulphide filming of oxidized minerals by the use of the various alkali sulphides (66). The mineral dressing literature reveals no success of this method when applied to oxidized mineral of the form of zinc silicate.

Interfaces may exist wherever gases, solids, or liquids come into contact. An interface has length, width and minute thickness. It is an elastic film. The energy connected with this film is referred to as surface or interfacial energy. The scientific fundamentals of flotation have their basis in the work of Gibbs and Helmholtz, Eötvos and van derWaals, on surface phenomena. The structure and nature of interfacial films and the concept of orientation of polar and nonpolar ends of a molecule forming a film on insoluble substances in water was first thoroughly explained by Langmuir in 1916.

FLOTATION REAGENTS

Flotation reagents may be grouped as frothers, modifiers, and collectors. It is desirable in flotation to have a particular chemical function as only one reagent. Thus a frother should only be a frother and not a collector in the same

operation. Many of the chemical characteristics of frothers and collectors are the same. Frequently a collector will function as its own frother and thus eliminate the need for the latter reagent. However, in most commercial flotation operations all three reagents are used.

FROTHERS (3, 29, 36)

Frothers are used to form a stable froth. They function by lowering the surface tension of water. The froth must carry the mineral load to the surface and be stable enough to allow mechanical removal. Frothers are usually organic in nature. One part of the frother molecule is polar, the other nonpolar. The polar end of the frother is in the water phase at the inner surface of the air bubble, the nonpolar part of the frother is in the air interface of the bubble. Good frothers collect at the liquid-air-interface of the gas bubble and give the bubble elasticity. There is less surface energy at the reagent-air-water interface than at the reagent-water interface. Frothers contain one of the following radicals: OH (hydroxyl) CO (carbonyl), $CONH_2$ (amide), COOH (carboxyl), COO (ester) and COC (ether) (75). Commercial frothers are pine oils, cresylic acids and alcohols containing five or more carbon atoms. The amount of frother needed depends on the type of ore being floated. It is usually less than 0.15 pound per ton of ore.

Mineral particles are attached to bubbles when the surface

energy of the air-solid interface is less than that of the solution-solid interface. A tension must exist at the solution-solid-interface; attachment of the particles to the bubbles lowers this tension and establishes equilibrium.

MODIFYING AGENTS

Modifying agents may be classified as pH regulators, cleaning agents, activators, depressants, and dispersants. The same chemical may function as one agent on one ore and as a different agent on another ore. An activator functions by modifying the surface of the mineral so that the collector will be effective. Most activators produce a sulphide surface on the ore, either by chemical means as in the case of copper sulphate or by absorption as when sodium sulphide is used. The majority of the flotation processes require some control of pH. Soda, lime and caustic soda are used to maintain an alkali cycle. The choice of pH regulators is governed by the cost. They should be of such a nature that they will not depress the flotation of the desired mineral.

Depressants are used to prevent the flotation of the undesirable gangues or a particular mineral. These reagents are frequently used in differential flotation. Many sulphide ores are depressed (not floated) by the use of strong oxidizing agents, i.e. the bichromates and permanganates. These oxidizing agents change the sulphides into basic sulphates, oxides,

hydroxides, or thiosulphates. Alkaline cyanides depress the flotation of iron sulphide by reacting with oxidation products to form a protective film of ferrocyanide and complex cyanates. The cyanides also depress flotation in an alkali circuit; in this case it is believed the protective films are hydroxide. The chief use of cyanides is in separating galena from zinc and iron ores like pyrite, pyrrhotite, sphalerite, and marmutite.

Colloidal materials either from slimes or from organic starches and glues are known to depress flotation. This accounts for the necessity of desliming operations in most flotation processes. In the case of organic compounds it is believed the colloids coat the particles; these coated particles selectively attract water and therefore inhibit their flotation. The work of Taggart (71) and associates revealed that the intensity of flotation varies with each reagent and mineral used, and is an inherent property of the ore and reagent system. It is common practice in the separation of two minerals by flotation to attempt to depress the flotation of the one mineral while the other mineral is floated. After this, a promoter reagent is added which destroys the depressant and then the second mineral is subjected to a flotation operation. The amount of promoter depends on the ore, and the amount of the preceding flotation or collector reagent, as well as the optimum pH at which the second mineral may be floated.

COLLECTORS

The alkyl substituted methylene blue, which was used in this investigation, functions as a collector. This collector forms a film or "envelope" around the zinc silicate particles and makes the particles water repellant. Methylene blue was chosen to form the envelope around the zinc silicate particles because it was known that zinc salts are mordants for the ordinary methylene blue dye. However, (8, 33, 34, 38) in order to have flotation by methylene blue, it is necessary to have an aliphatic hydrocarbon chain attached to the dye to produce hydrophilic properties. Also, in order to have flotation, the air bubbles in the presence of water, must have a positive contact angle with the coated particles. The contact angle resulting from the displacement of water by air on the coated zinc silicate particle depends on the nature of the mineral-water, air-water, and water-air interfaces.

One possible mechanism by which alkyl substituted methylene blue renders the zinc silicate particles water repellent is as follows: The polar dye group of the collector is absorbed by the zinc silicate particles. This allows for orientation of the non-polar aliphatic hydrocarbon chain outward from the particles. The aliphatic hydrocarbon chains orient themselves in the air interface of the air bubbles. The bubbles, with their mineral load of the zinc silicate particles, rise to the

surface of the flotation cell where they are removed. It seems entirely reasonable to say the enveloping or anchoring of the dye collectors to the zinc silicate occurs for the same reason that zinc salts, oxides or hydroxides, act as a mordant for methylene blue in textile dyeing. That this is true beyond a reasonable doubt is borne out by data subsequently reported.

Alkyl substituted methylene blue is a cationic collector. Its collecting properties may result from the formation of a positive organic ion. The alkyl-substituted methylene blue positive ion is formed by the loss of a negative chloride ion. In this mechanism, the negative part of the mineral reacts with the positive organic ion. The result, as in the previous mechanism, is the production of an organic hydrophyllic film on the surface of the zinc silicate. Some of the best known cationic collectors are alkyl amines and quaternary ammonium compounds. Whether organic collectors are cationic or anionic compounds is still a field of much theorizing. However, either of these mechanisms give some theoretical mental satisfaction. DeWitt and Ludt (24) in their work on alkyl-substituted triphenyl methane dyes discuss many of the factors effecting cationic flotation.

In cationic flotation, an excess of collector must be avoided (15). In some cases, the frother should be added after the collector to prevent the coating of the particle by the

frother (31), while in other cases, the period of conditioning of the ore affects the degree of flotation.

FLOTATION OF ZINC SILICATE ORES

An exhaustive literature survey reveals no direct work on the flotation of zinc silicate ores. It did however, disclose some investigations on the flotation of oxidized zinc ores. Since zinc silicate belongs to this group of oxidized zinc ores, it is of engineering interest to trace the approaches used in these investigations.

The term oxidized zinc ore or mineral includes the naturally occurring oxygen compounds of zinc such as the oxides, sulphates, carbonates, hydroxides and silicates. Oxidized ores have a tendency to hydrate due to the fact that the oxygen atoms are not completely saturated. This hydration characteristic is not possessed by mineral sulphides. The wettability by water, or hydration, makes flotation difficult. In general, oxidized ores are only slightly more floatable than their accompanying gangue materials which are usually alkaline earth silicates.

The problem of floating oxidized ores is essentially one of changing the surface of the oxidized ores so they are less wettable by water, without making a similar change in the surface properties of their accompanying gangue materials. When this is accomplished, favorable conditions exist for the

froth flotations of the selectively coated particles of the oxidized ore.

Prior to this work two approaches have been used in the investigation reported on flotation of oxidized zinc ores. The first is the sulphidizing of the oxidized surface and subsequent flotation by one of the zinc sulphide mineral collectors. This approach is probably a result of the success obtained in the differential flotation of zinc sulphide by use of the xanthates. Xanthates have been successfully employed as collectors for zinc sulphide for many years. The superficial sulphide coating makes the ore floatable by ordinary zinc sulphide collectors.

An example of this approach (50) is shown in the following investigation on oxidized lead-zinc ores containing 6% lead and 10.5% zinc. In this case, the crude ore was given a batch grind without reagents at 53% solids to approximately 80% - 200 mesh. The pulp was placed in a flotation cell and diluted to about 25% solids. The lead sulphide is floated by using 0.36 pounds per ton of potassium ethyl xanthate, 0.10 pounds per ton of methyl amyl alcohol, and 0.25 pounds per ton of potassium pentasol amyl xanthate. Stage additions of 4 pounds per ton of sodium silicate, 5 pounds per ton of sodium sulphide and 2.5 pounds per ton of potassium pentasol amyl xanthate and subsequent flotation of the oxidized lead ores.

To the lead tailings were added 5.0 pounds of soda ash, 8.0 pounds per ton of sodium sulphide and, .267 pounds per ton of lauryl amine hydrochloride; a five minute conditioning period was used with no air in the cell. This first zinc concentrate is then removed in ten minutes of flotation. To the tailing containing considerable zinc 2 pounds per ton of sodium sulphide was added and a second zinc concentrate was obtained. No tests were run on oxidized zinc ores without first performing an extensive lead separation. These ores apparently contained little zinc silicate and appear to be primary to the other oxidized zinc ores. Results reported on zinc silicate from a silicious gangue were not uniformly good (50).

The explanation of the success on the oxidized lead ores and lack of uniform results on zinc silicate may have its basis in the work of Peterson (57) on sulphidizing. With oxidized ores, the negative part of the mineral containing oxygen may be replaced by sulphur so that the ore is floated in the same way as the corresponding sulphide. This exchange is only possible when the sulphide forming on the surface of the oxidizing ore is more difficulty soluble than the corresponding oxidized compounds, while oxidized zinc may not be sulphidized because zinc sulphide is more soluble than the oxidized zinc ore. In a consideration of the solubility of the sulphide in comparison to the oxidized compound, one

one must always bear in mind that in the first place, sulphidizing apparently forms an amorphous substance, and in most cases, an easily soluble sulphide (58). It thus appears that the solution to the problem of flotation of zinc silicate does not lie in the indicated methods of sulphidizing.

The second approach used in the investigation of flotation of the oxidized zinc ores is in the use of depressants. The most comprehensive investigation using this approach is in the recent work of Bunge, Fine and Legsdin (5). This investigation began with the use of the Rex mine ore which contained smithsonite, zinc carbonate, and hemimorphite or calamine, a zinc silicate. It was pointed out that pure zinc carbonate could be floated by either oleic acid or sodium oleate. The reaction is believed to be $ZnCO_3 + 2C_{17}H_{33}COONa$ --- $(C_{17}H_{33}COO)_2Zn + Na_2CO_3$. However, these reagents also float most of the gangue materials associated with the common zinc carbonate ores. Attempts were made to suppress the gangue flotation by the use of starches and dextrins as depressants.

The depressant reagent was prepared by dissolving the agents in hot caustic solution subsequent to their addition to the flotation pulp. Sodium flouride was used to depress the iron oxide in the ore thus forming a complex ferric ion. Commercial starches of different genera contain unknown amounts of amyloses and unknown carbohydrate constituents. For this

reason, starch was identified only by its trade name. The mechanism of starches and dextrins in flotation is unknown.

Flotation tests were conducted using one pound per ton of starch or dextrin reagent and 0.3 pounds of sodium oleate collector. Three rougher concentrates were taken. 140 Globe pearl starch, 150 Dextrin, 126 Buffalo starch, 52 hydrol, 185/130 Amijel, 152 Dextrin, 186 Mogul brand, cereal binder, 132 Eagle pearl, were tested. It was necessary to perform several cleaning operations on the rougher products. The ore feed contained 20.3% zinc. Best results were obtained using 152 Dextrin as follows: The zinc middling contained 23.6% zinc and the tailings contained 2.9% zinc. The zinc concentrate contained 21.6%. It is interesting to note the conclusions reached by the authors on this ore containing some zinc silicate. These conclusions were: Since the zinc middlings and the tailings contained a fair amount of zinc and were low in carbon dioxide, it was concluded that these products contained the zinc as hemimorphite (zinc silicate), which apparently was either depressed more permanently by the conditioning reagents used or did not respond as readily to the collecting action of the sodium oleate. It was believed that more pertinent information on the depressing reagents on smithsonite or carbonate gangue would be found if the investigation were continued on an ore containing zinc as smithsonite

only. Therefore, the test on the Rex mine ore was discontinued (6). The rest of this investigation was conducted on an ore which was chiefly zinc carbonate.

Andreeva also reports flotation of smithsonite by the preliminary sulfidization at 50-60° followed by flotation at room temperature (1).

8-hydroxqunoline (oxine) has been used in conjunction with terpineol and alkali carbonates or hydroxides in flotation experiments on zinc carbonate with some success (30).

It becomes apparent that these two approaches used in previous investigations seem to offer little promise in flotation of oxidized zinc ores in the form of silicates. The third approach to the flotation of zinc silicate is the development of a collector whose nonpolar molecular part is so large that the hydrophilic action of the zinc silicate is screened by it. The 2-8 tetra diaminothiozonium part of the alkyl substituted methylene blue collector gives a large nonpolar molecular part. When this group is attached to a zinc silicate particle, it should render it hydrophobic. An aliphatic alkyl group of sufficient length attached to this nonpolar group should give the modified dye collecting properties.

The work on the flotation of copper silicate reported by DeWitt and Ludt (24) led us to believe that a more general approach to the flotation of "oxidized ores" was justified.

For instance, in the process of dyeing, certain inorganic oxides, or hydrated oxides are precipitated in the textile fibre. These substances, necessary to the retention of the dye, subsequently added and adsorbed or reacted with the hydrated oxide in the textile fibre, color the cloth. If the retention of the dye by the textile fibre is due to the presence of the inorganic heavy metal atom, then the dye should, properly reconstituted, act as an enveloping film on a mineral having in its atomic lattice the same metallic atoms as are present in the mordant in the textile fibre as prepared for successful retention of the dye:

In accord with this theory, already well substantiated by both theory and practice in the dyeing industry, the present experimental work on the flotation of zinc silicates is reported. The results obtained thus far are substantially in agreement with the work of DeWitt and Ludt (24). In succeeding data and discussion this point of view will be further developed and amplified.

PROCEDURES

The important experimental procedures are (1) flotation tests, (2) determination of zinc in zinc silicate ore, and (3) synthesis of the alkyl-substituted methylene blue collector.

FLOTATION PROCEDURES

The feed to the flotation cell consists of synthetic mixtures of the zinc silicate ores and sand. Zinc ores used were willemite and calamine. Several cuts of concentrate and the tailings were analyzed for per cent of zinc. These ores were available only in large pieces. The large pieces were passed through a jaw crusher. The product from the jaw crusher was then subjected to a series of roll crushings each of finer setting. This product was then classified in a series of Tyler screens on a rotap machine. Ore retained above the 100 mesh screen is placed in a flint pebble ball mill and dry ground until it all passes the 100 mesh screen. Ore finer than 325 mesh was discarded in order to prevent sliming in the flotation cell. The ores used were relatively pure zinc silicate and required little desliming. The same size sand and ore were used for various runs.

White sand was wet ground in the ball mill, deslimed several times and dried in an oven. The sand was then classified into the same mesh range as the zinc silicate ore.

Flotation feeds were prepared by taking various amounts of the high grade ore and mixing with sand of the same mesh to give a 100 gram sample. Samples ranging from 1% to 20% zinc were used in this investigation. All samples were oven dried before weighing.

Tests were run in a 100 gram batch type flotation cell. Figures 1 and 2 illustrate the workings of the experimental subaeration flotation cell. This type cell has been successfully used in recent flotation investigations (19, 21, 22, 23, 26, 27). These workers used various type ores, feed mixtures, reagents, etc. and illustrated the usefulness of the unit. The lucite cell held about 250 cc. of liquid and had an air inlet at the bottom. The motor driven agitator has its blade directly over the air inlet at the bottom of the cell. Froth is mechanically swept into a Buchner funnel. The funnel is subjected to a continuous vacuum. The filtrate was drawn into a glass bottle. When sufficient liquid is collected the vacuum is broken. The liquid is then allowed to flow by gravity into the supply feed bottle. The supply bottle must always contain some liquid in order to insure a continuous feed into the cell. The rate of liquid feed depends on the rate at which the froth was removed.

TEST PROCEDURE

Measure out 300 cc. of water, add 70 cc. of this water

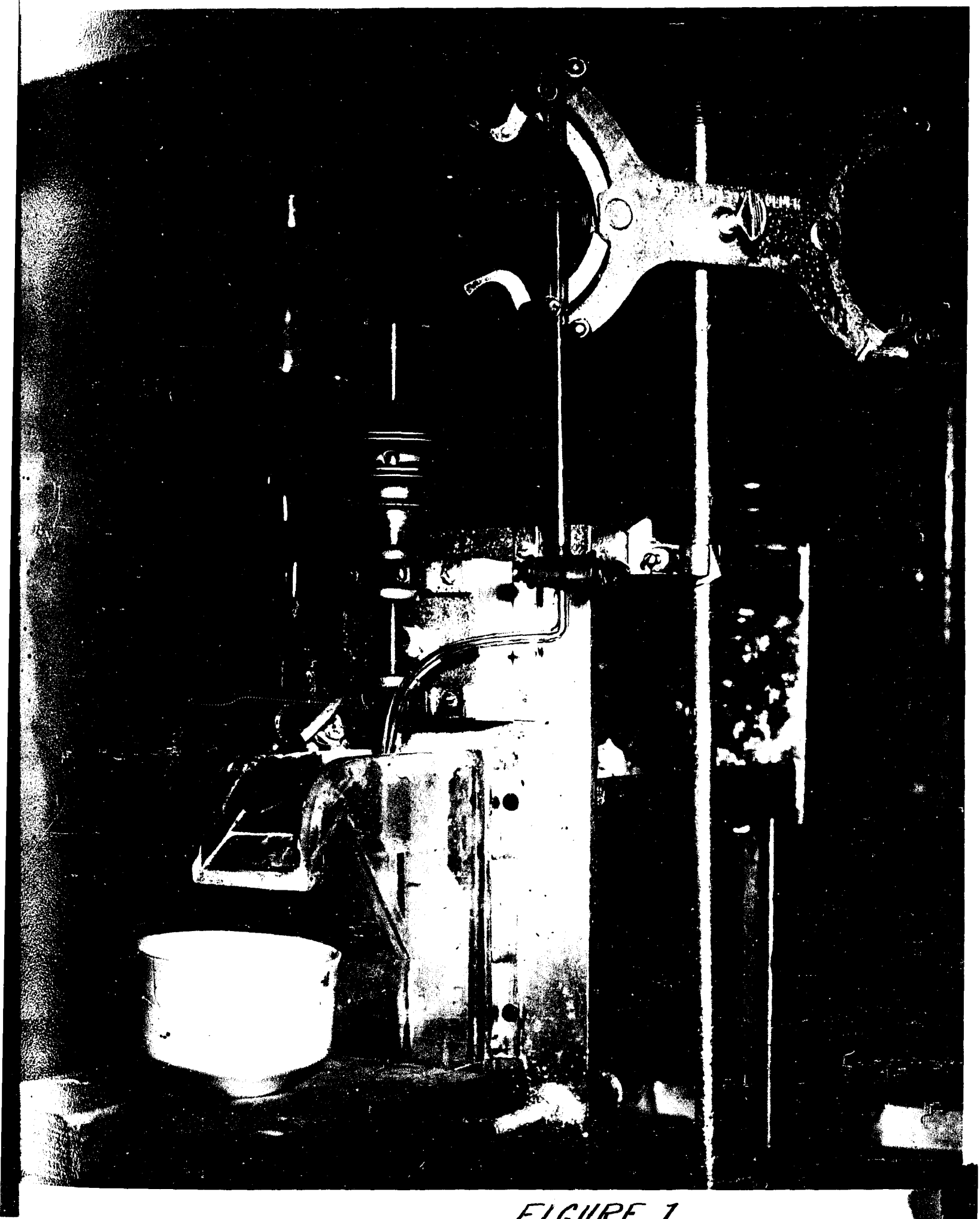
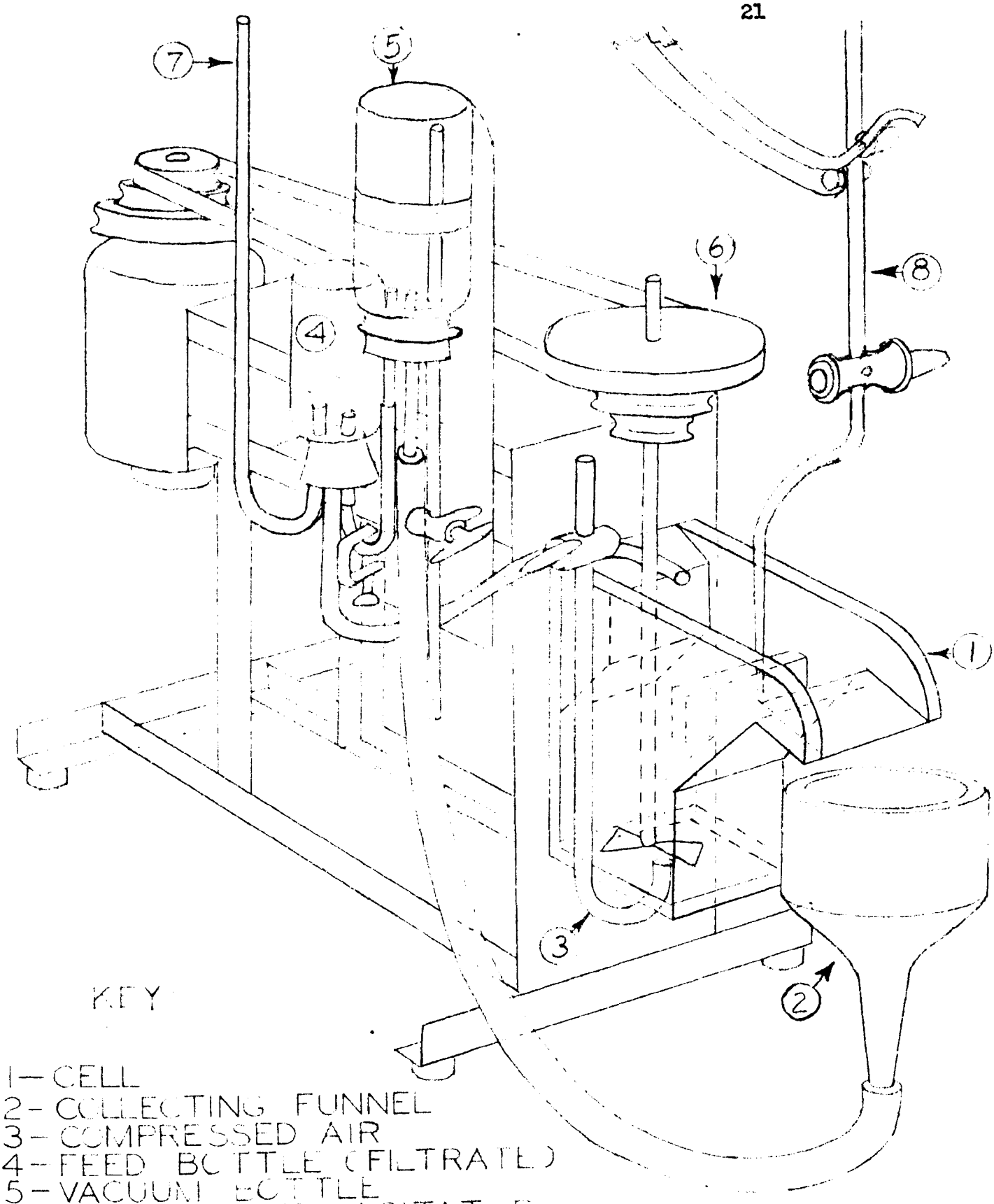


FIGURE 1



BATCH FLOTATION CELL

FIGURE 2

to the cell. Then add the 100 grams of ore mixture with agitation. Place a No. 5 Whatman filter paper in Buchner funnel. Draw 70 cc. of water through the funnel into the supply bottle. Make sure the liquid feed always is closed. Now add the remainder of the water to cell. Adjust the pH and add any modifying agents being employed. Allow the mixture to condition. Add all or part of the collector below the surface again allowing a conditioning time. A measured amount of frother is used and the air flow is adjusted. Water from the supply bottle should be allowed to flow slowly into the cell. As the froth forms in the top of the cell, it is mamually removed by a scraper. On higher grade feeds remove about 10 grams of froth concentrate. A new filter paper is now inserted and another 10 grams sample taken. Be sure that the supply bottle contains liquid at all times. Collector can be added in small amounts over the period of the run. The cell is now drained and a sample of the tailings taken for analysis. Take the pH of mixture on Beckman pH meter or with a Taylor slide comparator. Short range indicating paper can be used during the course of the run. The various concentrates and tailing sample are oven dried at 105-110°C. Record dry weight and determine zinc content of these samples. If necessary more frother can be added during the run. In some cases chemicals can be added during the test to maintain the desired pH.

Water used in these flotation tests was either distilled or Michigan State College well water. This well water has a pH value of 7.4, 2-4 ppm. (parts per million) of suspended solids, a hardness of 333 ppm. as calcium carbonate. The water is high in bicarbonate, 382 ppm. HCO_3. It has a total dissolved solid content of 390 ppm. Some feeds were made using once concentrated ore. This was done because in commercial practice the ores are subjected to a series of concentration operations. Several flotation operations are generally necessary to obtain high grade concentrates and maximum recovery at a minimum cost.

DETERMINATION OF ZINC

From a literature survey it became apparent that precise determination of zinc in a silicate ore is not an easy matter. The Committee on uniformity in technical analysis show in their report (9) that a sample of oxidized zinc ore from New Jersey containing willemite, franklinite and zinc spinels, and having a zinc content of 18.16% was analyzed by forty-two chemists with results varying from 12.20 to 39.22%. Twenty-three of the chemists were or had been in zinc works, three in other works where zinc was frequently determined, eleven were commercial chemists, most of whom made a specialty of zinc, and five were professors or instructors in college. They used eight methods.

The routine method of analysis used in these determinations was an alkaline volumetric solution, an adaptation of

procedure given by Scott (67) and others (32, 64, 78). This method was checked by the gravimetric method of precipitating the zinc sulphide, converting the zinc sulphide to zinc sulphate, and weighing the latter. This gravimetric is reported to be one of the most precise. The details are given in the appendix.

The three ores used in this investigation as well as other test samples, were checked by a polargaphic method. This procedure is shown in the appendix. The apparatus used was the property of Michigan Health Department. It cannot be over emphasized that frequent checks should be made on reagents, etc. to assure accurate analytical results.

METHOD OF ANALYSIS FOR ZINC

From the foregoing it is apparent that the method of analysis for zinc, especially in its ores, must be clearly designated. The following paragraphs exemplify this. The modified alkaline volumetric method used for the analysis of zinc is for reasons stated above, important enough to be given here in detail.

Weigh 4 grams of sample into a 400 cc. beaker, moisten with water and add 25 cc. HCl (Sp. Gr. 1.20). Place beaker on warm plate and evaporate to dryness. Cool, add 25 cc. water, 25 cc. HCl (Sp. Gr. 1.20) and heat to boiling and continue boiling for 2 minutes. Cool, transfer to a 250 cc. measuring flask and dilute exactly to the mark. Filter (1), catching

the filtrate in a dry 600 cc. beaker. Discard the paper and contents (2).

Measure exactly 125 cc. (3) into the original beaker and take to dryness on a warm plate. Cool, add 50 cc. HNO_3 (Sp. Gr. 1.42) and bring to a boil (4). Add about 5 grams $KClO_3$ (5) and boil until solution has a volume of about 20 cc. Cool, transfer to a 500 cc. measuring flask and dilute to the mark. Shake well and filter (6), catching the filtrate in a dry 600 cc. beaker. Discard the paper and contents.

Measure exactly 250 cc. (7) into a 600 cc. beaker, add 25 cc. citric acid solution and 5 cc. (8) iron solution. Neutralize (9) with NH_4OH (Sp. Gr. 0.90) and add 3 cc. (10) in excess. Bring to a boil and titrate at once with standard potassium ferrocyanide solution as described under Standardization.

Calculate the percentage of zinc as follows:

$$\frac{(A - B)}{1} \quad \frac{(F) \times 100}{} = \% \text{ Zinc, where}$$

A is the cc. of $K_4Fe(CN)_6$ solution required for the sample.

B is the cc. of $K_4Fe(CN)_6$ solution required for the blank determination as described under Standardization.

F is the g. of Zn per cc. of $K_4Fe(CN)_6$ solution.

Notes

(1) Use a dry No. 1 Whatman qualitative, 15 cm. filter or similar paper. Carbon must be removed or the manganese will

not be completely precipitated.

(2) The carbon may be filtered out and washed free of chlorides and the insoluble residue used to determine insoluble zinc after ignition and removing the SiO_2 and fusing with $K_2S_2O_7$. Insoluble z inc is usually negligible.

(3) This is equivalent to 2 grams of the sample.

(4) Boil until nitrous oxide fumes have disappeared.

(5) The $KClO_3$ precipitates the manganese. It should be added a little at a time and the watch crystal raised to permit the yellowish gas to escape. This gas is explosive.

(6) Use a dry No. 1 Whatman qualitative, 15 cm. filter or other paper. The manganese is filtered off at this point in the analysis. The first portion of the filtrate should be poured back through the paper if the fine precipitate tends to pass through. The filtrate must be clear and colorless.

(7) This is equivalent to 1 gram of the sample.

(8) The amount of iron to be added depends on the iron in the sample. The solution should contain about .35 g. Fe.

(9) Use litmus paper as the indicator.

(10) The amount of NH_4OH in excess required varies with the per cent of total zinc in the sample. For every 5 cc.

of standard potassium ferrocyanide solution required, an excess of 3 cc. of NH_4OH (Sp. Gr. 0.90) is necessary; for less than 5 cc. the solution should be only slightly alkaline.

Solutions Required

Citric acid Solution -- Dissolve 350 g. citric acid (C.P.) in 1000 cc. of distilled water.

Iron Solution -- Dissolve either ferric nitrate or ferric chloride in distilled water so that 1 cc. contains .035 g. Fe.

Potassium Ferrocyanide -- Dissolve 34.8 g. $K_4Fe(CN)_6$ (C.P.) in 1000 cc. distilled water and standardize against C.P. zinc. Age at least 90 days. See Standardization of Potassium Ferrocyanide given below.

STANDARDIZATION OF POTASSIUM FERROCYANIDE SOLUTION

Weigh .4 to .5 g. of Zn (C.P.) (1) into a 600 cc. beaker and add 50 cc. of water and 10 cc. HNO_3 (Sp. Gr. 1.42). Cover and after solution is complete, boil for five minutes. Cool, dilute to 300 cc. and add 25 cc. citric acid solution and 10 cc. iron solution. Neutralize with NH_4OH (Sp. Gr. 0.90) using litmus paper and add 30 cc. excess. Heat to boiling and titrate immediately with potassium ferrocyanide solution (2). Make a blank determination in a similar manner but adding only 3 drops excess NH_4OH.

Calculate the factor as follows:

$$\frac{C}{A - B} = F \text{ where,}$$

A is the cc. of $K_4Fe(CN)_6$ solution required for the Zn (C.P.)

B is the cc. of $K_4Fe(CN)_6$ solution required for the blank.

C is the weight of Zn in g.

F is the g. of Zn per cc. of $K_4Fe(CN)_6$ solution.

Notes

(1) Zinc Sticks (C.P.) are rolled down to about .10" thick and the surface is cleaned by wiping with gasoline (86° Be')

(2) The solution should be added slowly and stirred vigorously. The end point is determined by transferring 3 drops of solution to a spot plate containing acetic acid (50%). The end point is indicated by a change in color from a yellow to green. The green is caused by the presence of ferric ferrocyanide (Prussian Blue) produced from ferric ammonium citrate and the slight excess of potassium ferrocyanide at the end point in the yellow ferric ammonium citrate.

SYNTHESIS OF COLLECTOR

The exact details of the preparation of n-octyl, 2,8 tetra methyl diaminothiazonium chloride i.e. n-octyl methylene blue is given in the appendix. It appears there in under the titles of 1. Preparation of n-octyl methylene blue, etc. 2. Preparation of ortho-n-octyl dimethyl aniline. The reader

should refer to Tables A and B which gives the complete synthesis of the collector in equation form.

TABULATED RESULTS

AND CURVES

TABLE I

Selective Mordant Action of n-Octyl Methylene Blue
(Reagent: Very Dilute Colored Solution of n-octyl Methylene Blue Approx. 001%)

	Sample	Grams	Mesh	Procedure	Results
Experiment A-7	Washed Ottawa Sand	100	-170 +200	Agitated with reagent.	No appreciable color change.
Experiment B-3	Washed Willemite Ore	10	-170 +200	Agitated with reagent.	Very appreciable color removed.
Experiment B-9	Washed Willemite Ore Ottawa Sand	1 99	-170 +200	Agitated with reagent.	Appreciable color removal.
Experiment D-2	Washed Willemite Ore Ottawa Sand	10 90	-170 +200	Agitated with reagent.	Very appreciable color removal.
Experiment D-7	Washed Calamine Ore Ottawa Sand	5 95	-170 +200	Agitated with reagent.	Appreciable color removal.
Experiment A-3	Washed Calamine Ore	10	-170 +200	Agitated with reagent.	Appreciable color removal.

TABLE II

Flotation of Willemite by n-octyl Methylene Blue

Feed: 100 gm deslimed Willemite-Sand
Feed Size: -170 +200
Water: Distilled pH7
Frother: Pine Oil

Test	Collector #/Ton	Head % Zn	Frother #/Ton	1st Cut Grams	1st Cut % Zn	2nd Cut Grams	2nd Cut % Zn
2-1	0.03	1.0	0.10	9.752	1.92	10.263	1.5
2-2	0.05	1.0	0.10	11.173	2.3	10.502	1.8
2-3	0.06	1.0	0.10	10.765	2.5	11.21	1.9
2-4	0.08	1.0	0.10	9.751	3.91	10.530	3.42
2-5	0.10	1.0	0.10	10.317	4.21	10.720	3.58
2-6	0.20	1.0	0.10	9.271	3.78	10.207	3.16
2-7	0.40	1.0	0.10	9.987	3.68	10.042	3.27

TABLE II A

Flotation of Willemite by n-octyl Methylene Blue
Calculation from Table II

Test	1st Cut % Recovery	2nd Cut % Recovery	Total % Recovery	Avr. % Zn	Imp. Factor
2-1	18.4	15.4	33.8	1.71	57.8
2-2	25.7	18.9	44.6	2.05	91.4
2-3	26.9	21.2	48.1	2.2	105.8
2-4	38.1	36.0	74.1	3.67	271.9
2-5	43.43	38.38	81.81	3.90	318.6
2-6	35.04	32.25	67.29	3.47	233.4
2-7	36.75	32.84	69.59	3.48	242.1

TABLE III

Flotation of Willemite by n-octyl methylene blue vs size distribution

Feed: 100 gm. deslimed Willemite-Sand
Water: Distilled pH7
Frother: Pine Oil approx. 0.10 #/Ton

Test	Collector #/Ton	Head % Zn	Mesh of Feed	Grams Froth	% Zn	Recovery %
3-1	0.09	1.0	100 - 170	12.329	2.9	35.8
3-2	0.09	1.0	170 - 200	11.940	3.8	45.4
3-3	0.09	1.0	200 - 270	12.453	4.25	52.9
3-4	0.09	1.0	270 - 325	11.879	4.01	47.6
			- 325	12.107	3.75	45.4

TABLE IV

Flotation of Willemite by n-octyl methylene blue vs. pH. collector 0.09 #/Ton

Feed Size: -200 +270
Feed: 100 gm. deslimed Willemite-Sand
Water: Distilled
Frother: Pine Oil Approx. 0.10 #/Ton

Test	pH	Head % Zn	Grams Froth	% Zn	% Recovery	Impt. Factor
4-1	4.5	1.0	8.726	4.9	42.8	209.7
4-2	5.0	1.0	11.785	5.2	61.3	318.8
4-3	5.5	1.0	11.048	6.1	67.4	411.1
4-4	6.0	1.0	10.522	5.8	53.7	311.5
4-5	6.5	1.0	10.707	5.1	54.6	278.5
4-6	7.0	1.0	9.698	4.53	43.9	198.8
4-7	7.7	1.0	9.707	4.2	40.8	171.7
4-8	8.2	1.0	10.644	4.18	44.5	186.0

TABLE V

Reflotation of Willemite Concentrates with and without new collector or sand addition

Feed: Various Amounts
Water: Distilled
Feed Size: -200 +270 mesh
Frother: Pine Oil Approx. 0.10 #/Ton

Test	Collector #/Ton	pH	Head % Zn	Total Feed	New Sand	Grams Froth	% Zn	Enrich-ment	% Rec.
5-1	0	7	2.0	100	0	10.256	6.51	3.26	33.0
5-2	0	7	2.0	100	50	9.742	5.8	2.9	28.3
5-1A	0.12	7	2.0	100	0	11.654	9.86	4.93	57.5
5-2A	0.12	7	2.0	100	50	10.431	8.75	4.37	45.6
5-1B	0.12	5.5	2.0	100	0	10.975	12.6	6.3	69.0
5-2B	0.12	5.5	2.0	100	50	11.047	10.97	5.48	60.1

TABLE VI

Flotation of Calamine by n-octyl Methylene Blue

Feed: 100 gm deslimed Calamine-Sand
Feed Size: -200 +270
Water: Distilled pH7
Frother: Pine Oil approx. 0.15 # Per Ton

Test	Collector #/Ton	Head % Zn	Grams Froth	% Zn	% Recovery	Degree of Improvement	Imp. Factor
6-1	0.05	6.0	12.753	9.12	19.4	1.52	29.5
6-2	0.1	6.0	13.147	15.5	34.0	2.58	87.7
6-3	0.15	6.0	12.010	23.15	46.3	3.88	179.6
6-4	0.2	6.0	12.820	25.8	56.4	4.30	242.5
6-5	0.25	6.0	15.382	25.0	64.1	4.16	266.7
6-6	0.3	6.0	12.745	29.0	61.8	4.83	298.5
6-7	0.35	6.0	13.109	29.2	63.8	4.86	310.0
6-8	0.40	6.0	13.102	29.8	65.1	4.96	323.0

TABLE VII

Flotation of Calamine by n-octyl Methylene
Blue vs size distribution

Feed: 100 gm deslimed Calamine-Sand
Water: Distilled pH7
Frother: Pine Oil approx. 0.15 # per ton

Test	Collector #/Ton	Head % Zn	Mesh of Feed	Grams Froth	% Zn	Degree of Improvement	% Recovery
7-1	0.25	6.0	-70 +100	13.295	8.18	1.36	18.1
7-2	0.25	6.0	-100 +200	13.183	17.9	2.98	39.3
7-3	0.25	6.0	-200 +270	14.923	26.4	4.40	65.66
7-4	0.25	6.0	-270 +325	14.279	24.2	4.03	57.59
7-5	0.25	6.0	-325	13.840	18.9	3.15	43.60

TABLE VIII

Flotation of Calamine by n-octyl Methylene Blue vs pH. Collector 0.25 #/Ton

Feed Size: -200 +270 Feed: 100 gm deslimed Calamine-Sand
Water: Distilled Frother: Pine oil approx. 0.15 #/Ton

Test	pH	Head % Zn	Grams Froth	% Zn	% Recovery	Enrich-ment	Imp. Factor
8-1	4.0	6.0	12.514	26.22	54.7	4.37	239
8-2	5.0	6.0	10.421	35.52	61.7	5.92	365
8-3	5.5	6.0	12.276	32.16	65.8	5.36	352
8-4	6.0	6.0	10.738	35.2	63.0	5.87	370
8-5	7.0	6.0	14.207	28.38	67.2	4.73	318
8-6	8.0	6.0	10.933	29.76	54.2	4.96	269
8-7	8.5	6.0	13.133	24.78	54.2	4.13	224

TABLE IX

Reflotation of Calamine concentrate with and without new collector or sand addition.

Feed: Various Amounts — Water: Distilled
Feed Size: -200 +270 — Frother: Pine Oil Approx. 0.10 #/Ton

Test	Collector #/Ton	pH	Head % Zn	Total Feed	New Sand	Grams Froth	% Zn	Degree of Improvement	% Recovery
9-1	0	7.0	18.0	100	0	23.498	34.75	1.93	45.4
9-2	0	7.0	18.0	100	50	25.012	29.0	1.61	40.3
9-1A	0	6.0	18.0	100	0	22.754	38.47	2.14	48.6
9-2A	0	6.0	18.0	100	50	23.741	33.15	1.84	43.7
9-1B	0.3	6.0	18.0	100	0	28.075	41.0	2.28	63.9
9-1C	0.3	6.0	18.0	100	50	27.108	37.61	2.09	56.6

TABLE X

Flotation of Los Lamentos Ore by n-octyl Methylene Blue

Feed: 100 gm deslimed Los Lamentos ore-sand (1% Total Zn)
Feed Size: -270 -325 Water: Distilled
Frother: Pine Oil

Test	Head % Zn	Collector #/Ton	Frother #/Ton	pH	Zn	Recovery %	Imp. Factor
10-1	1.0	0.05	0.10	7	1.69	37.2	63
10-2	1.0	0.15	0.10	7	3.80	68.3	260
10-3	1.0	0.25	0.10	7	4.15	70.2	291
10-4	1.0	0.35	0.10	7	3.65	61.7	225
10-5	1.0	0.25	0.10	4	2.03	53.2	108
10-6	1.0	0.25	0.10	6	4.27	77.1	329
10-7	1.0	0.25	0.10	8	3.16	59.5	188
							Enrichment
10-8*	2.5	0	0.05	7	8.24	56.58	3.3
10-9*	2.5	0.25	0.05	7	7.34	49.21	2.94
10-10*	2.5	0.25	0.05	6	7.95	55.45	3.18

* Reflotation of feed once concentrated

TABLE XI

Flotation of Los Lamentos ore by n-octyl methylene blue

Feed: 100 gm. deslimed Los Lamentos ore (6% Total Zn)
Feed Size: -270 +325 Frother: Pine Oil
Water: Distilled

Test	Head % Zn	Collector #/Ton	Frother #/Ton	pH	Zn %	Degree of Enrichment	Recovery %	Imp. Factor
11-1	6.0	0.05	0.15	7	7.3	1.21	21.2	25.6
11-2	6.0	.15	0.15	7	8.4	1.40	26.3	36.8
11-3	6.0	.25	0.15	7	13.7	2.28	41.5	94.6
11-4	6.0	.35	0.15	7	25.49	4.25	73.1	310.7
11-5	6.0	.35	0.15	4	23.74	3.92	64.1	251.3
11-6	6.0	.35	0.15	6	34.8	5.8	74.0	429.2
11-7	6.0	.35	0.15	8	21.7	3.61	49.6	179.0

AVERAGE PERCENT "WILLEMITE" Zn IN CONCENTRATE VS. POUNDS OF COLLECTOR

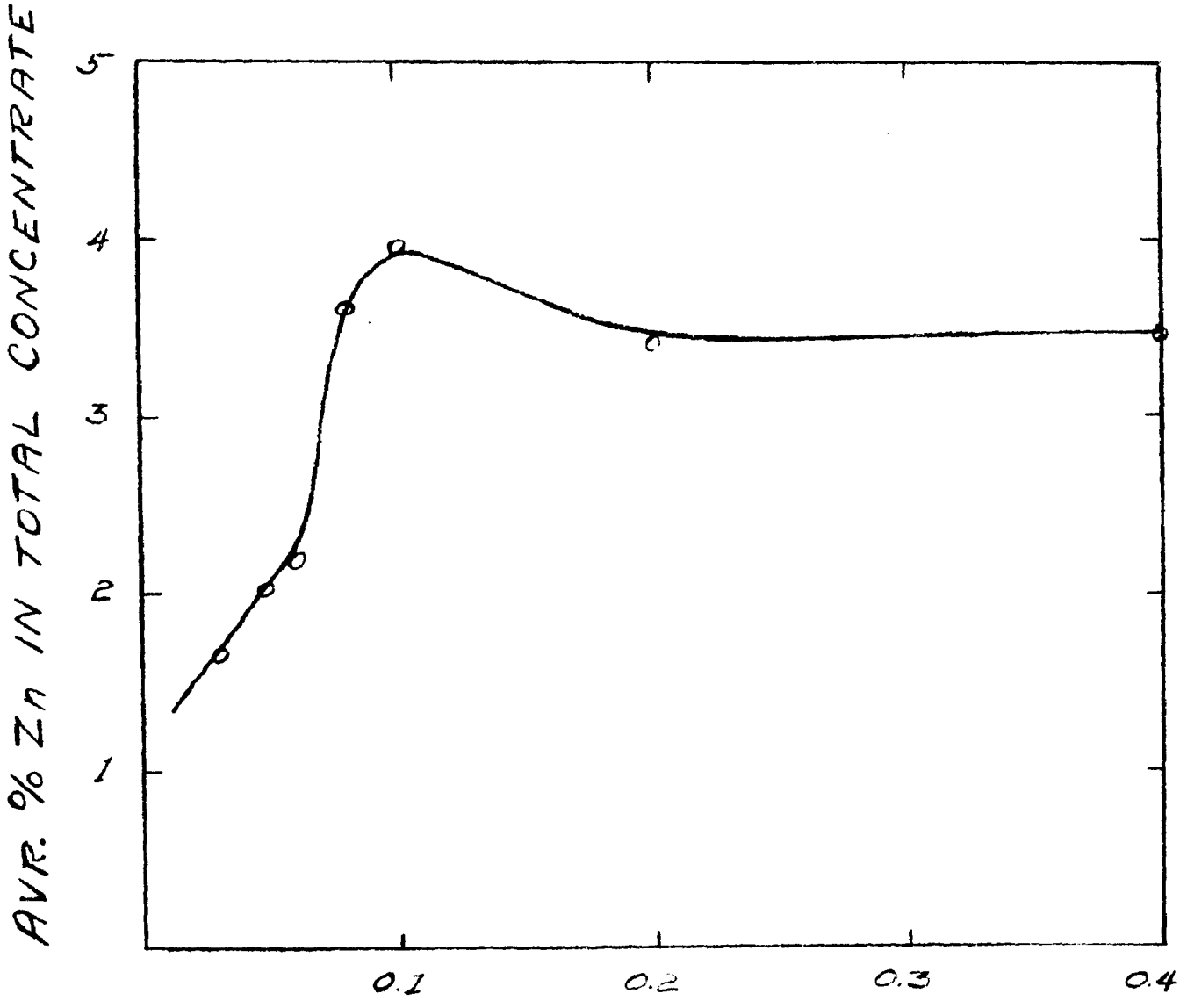


FIGURE 3

TOTAL PERCENT "WILLEMITE" Zn VS. POUNDS OF COLLECTOR

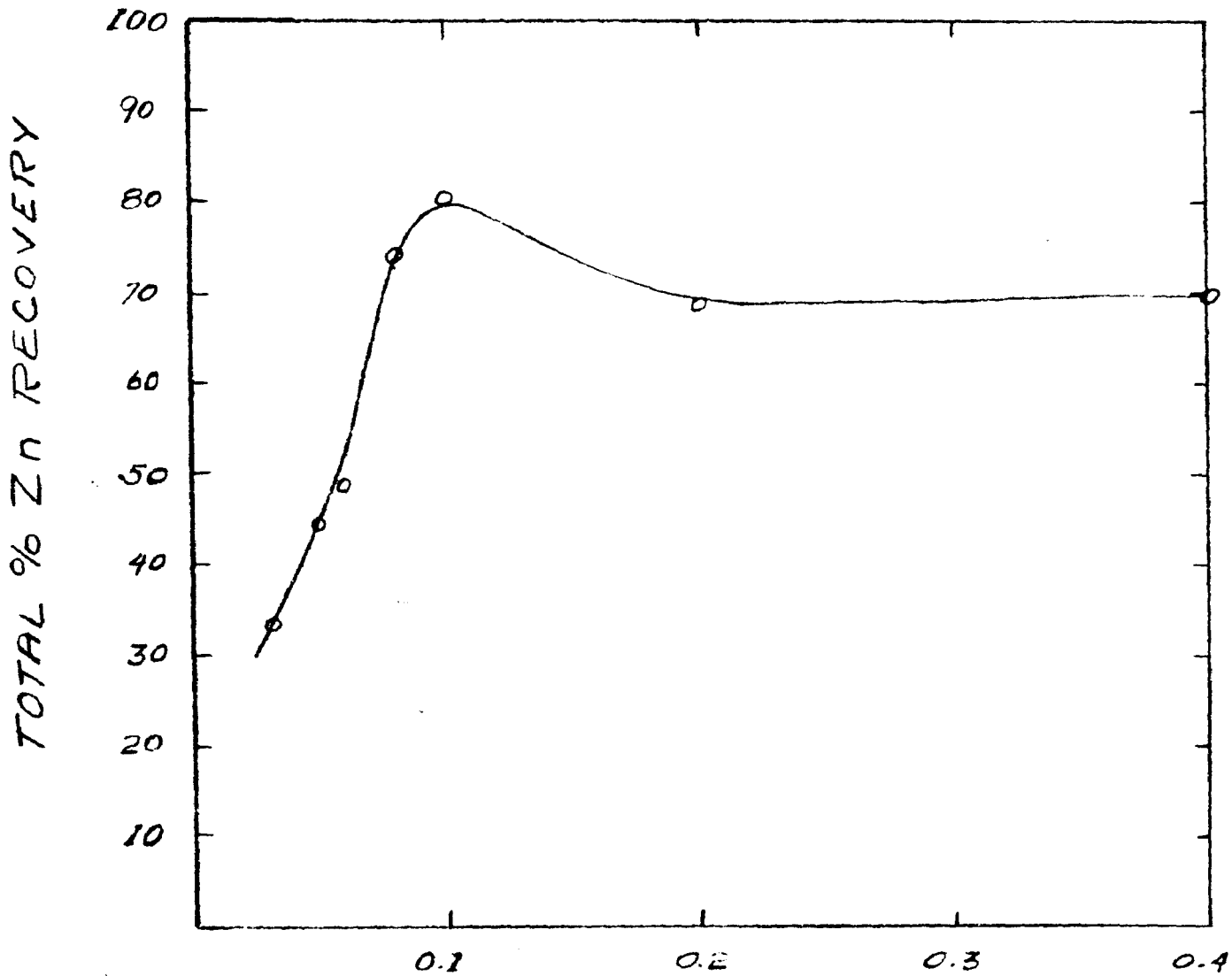


FIGURE 4

IMPROVEMENT FACTOR OF 1% Zn WILLEMITE FEED (-170+200 MESH) VS. POUNDS OF COLLECTOR

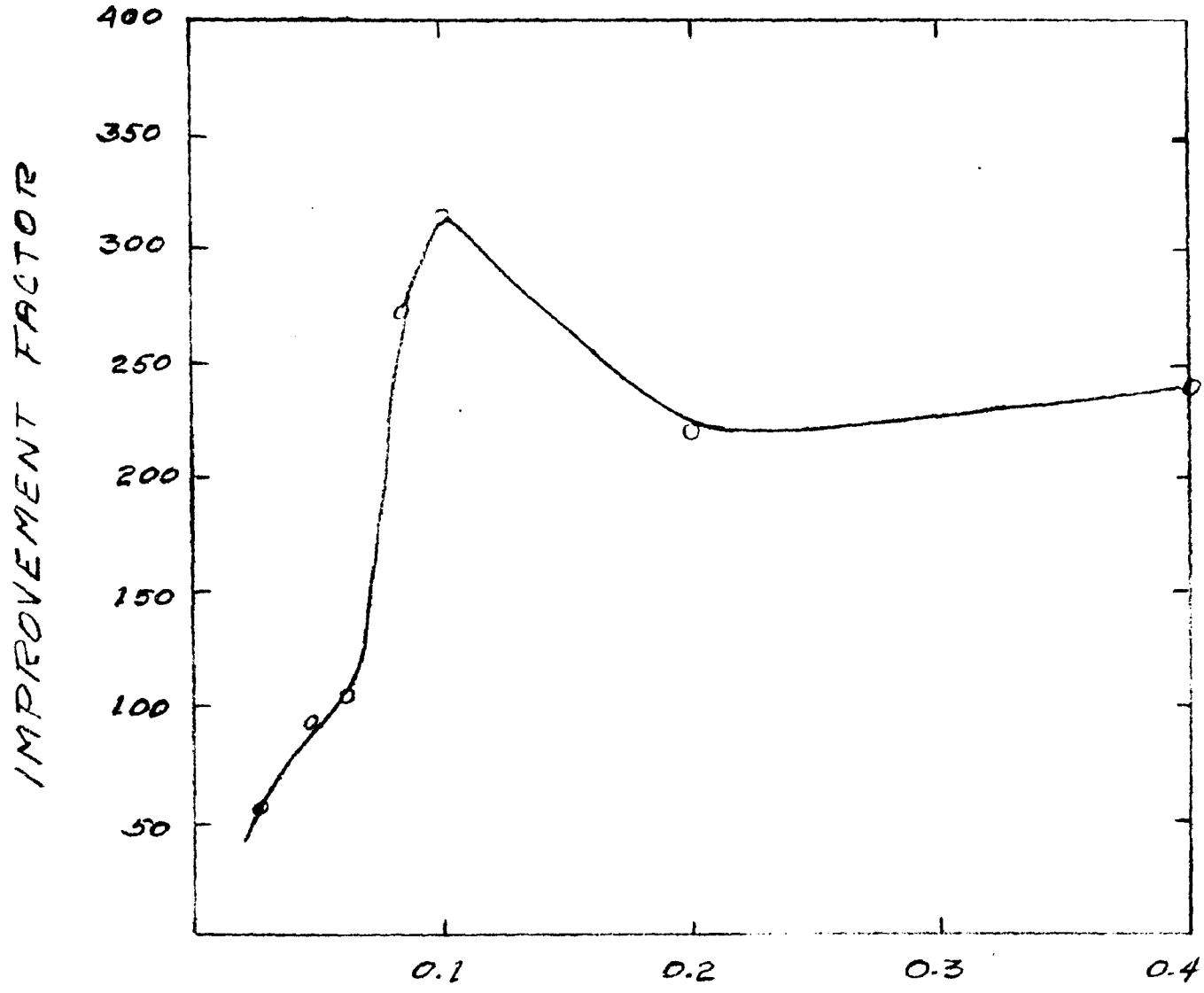
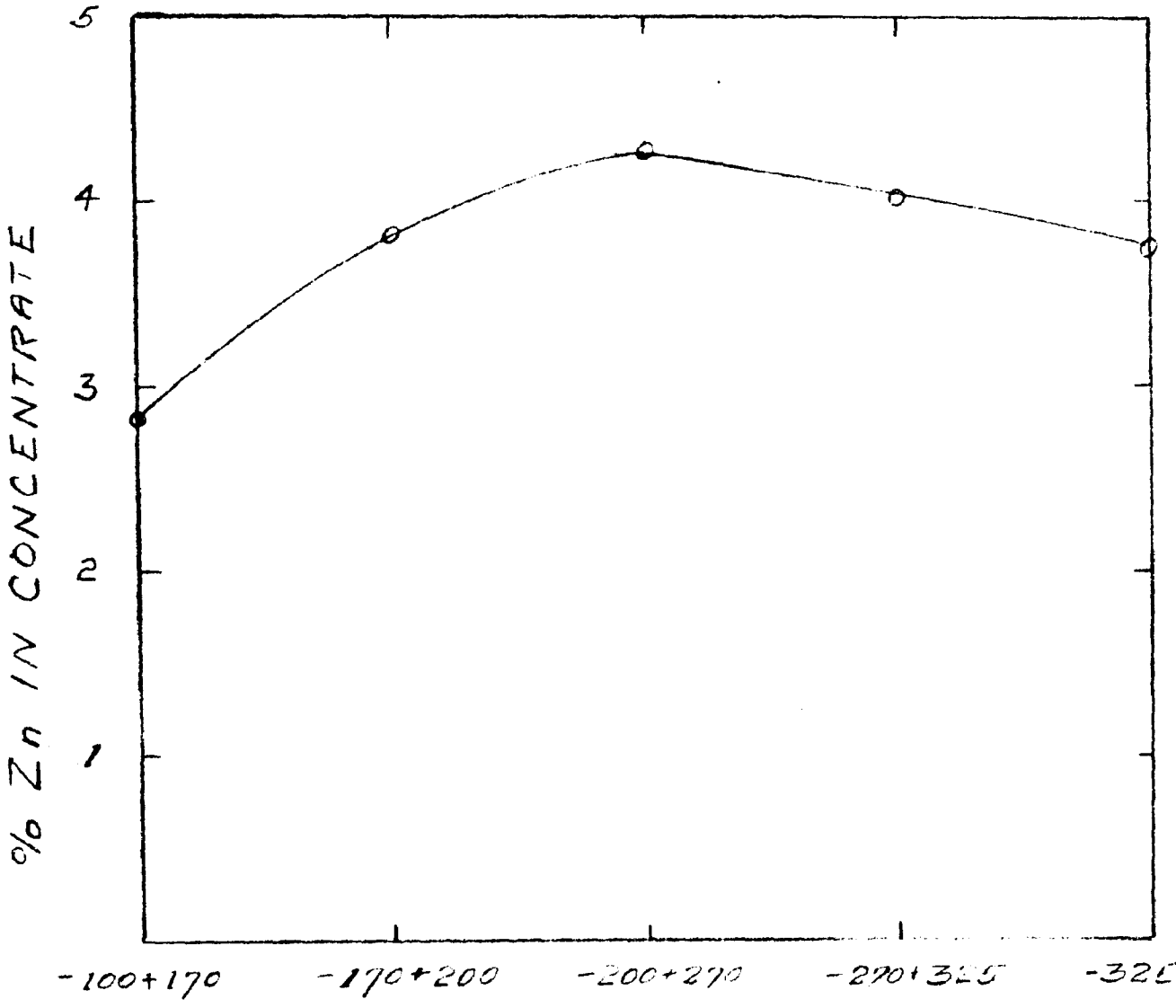


FIGURE 5

PERCENT Zn IN CONCENTRATE VS. PARTICLE SIZE OF 1% Zn WILLEMITE FEED



FEED - 0.09 POUNDS COLLECTOR PER TON

FIGURE 6

PERCENT "WILLEMITE" Zn IN CONCENTRATE VS. pH OF CELL CONTENTS

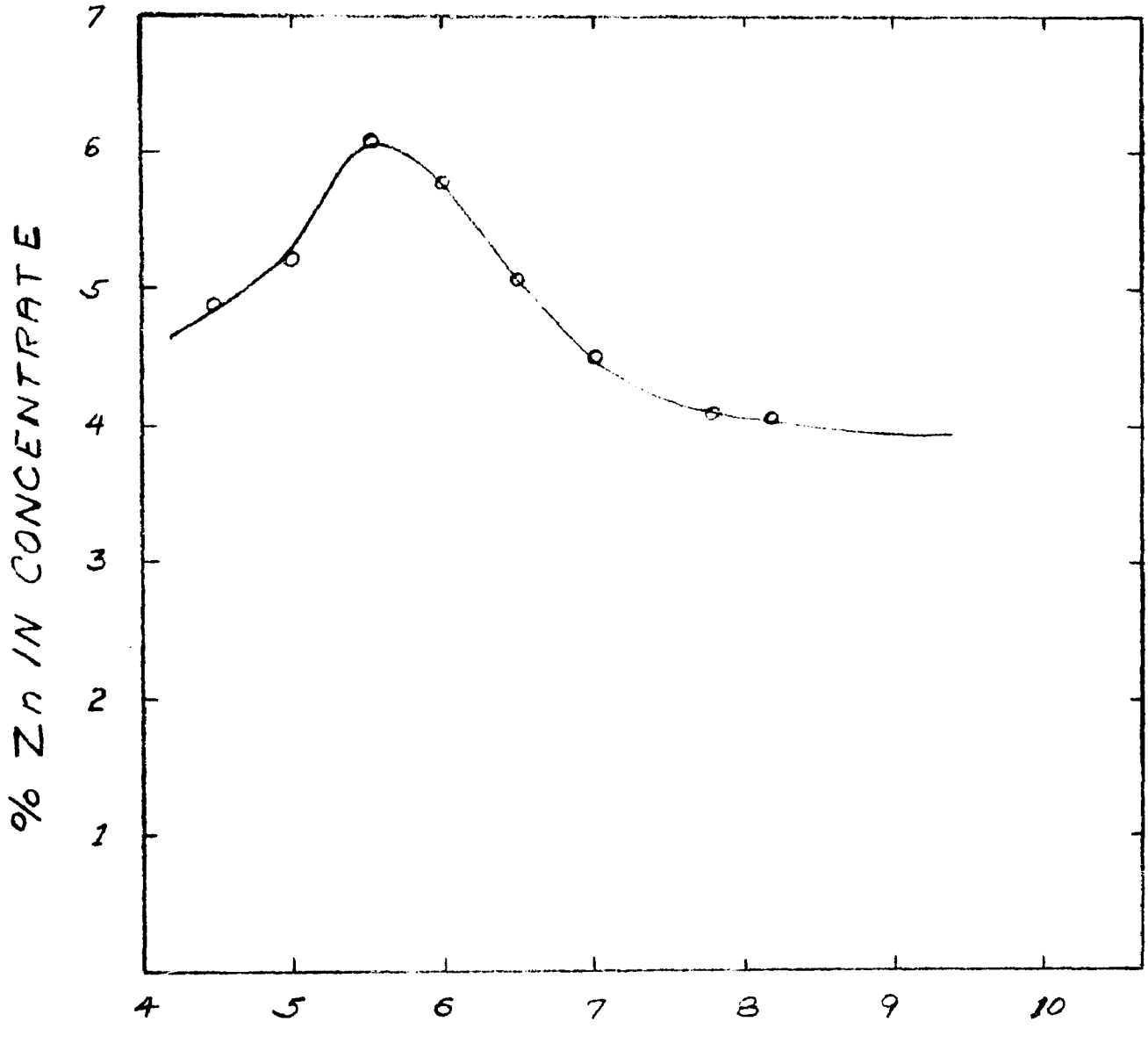


FIGURE 7

IMPROVEMENT FACTOR OF 1% Zn WILLEMITE FEED VS. pH OF CELL CONTENTS

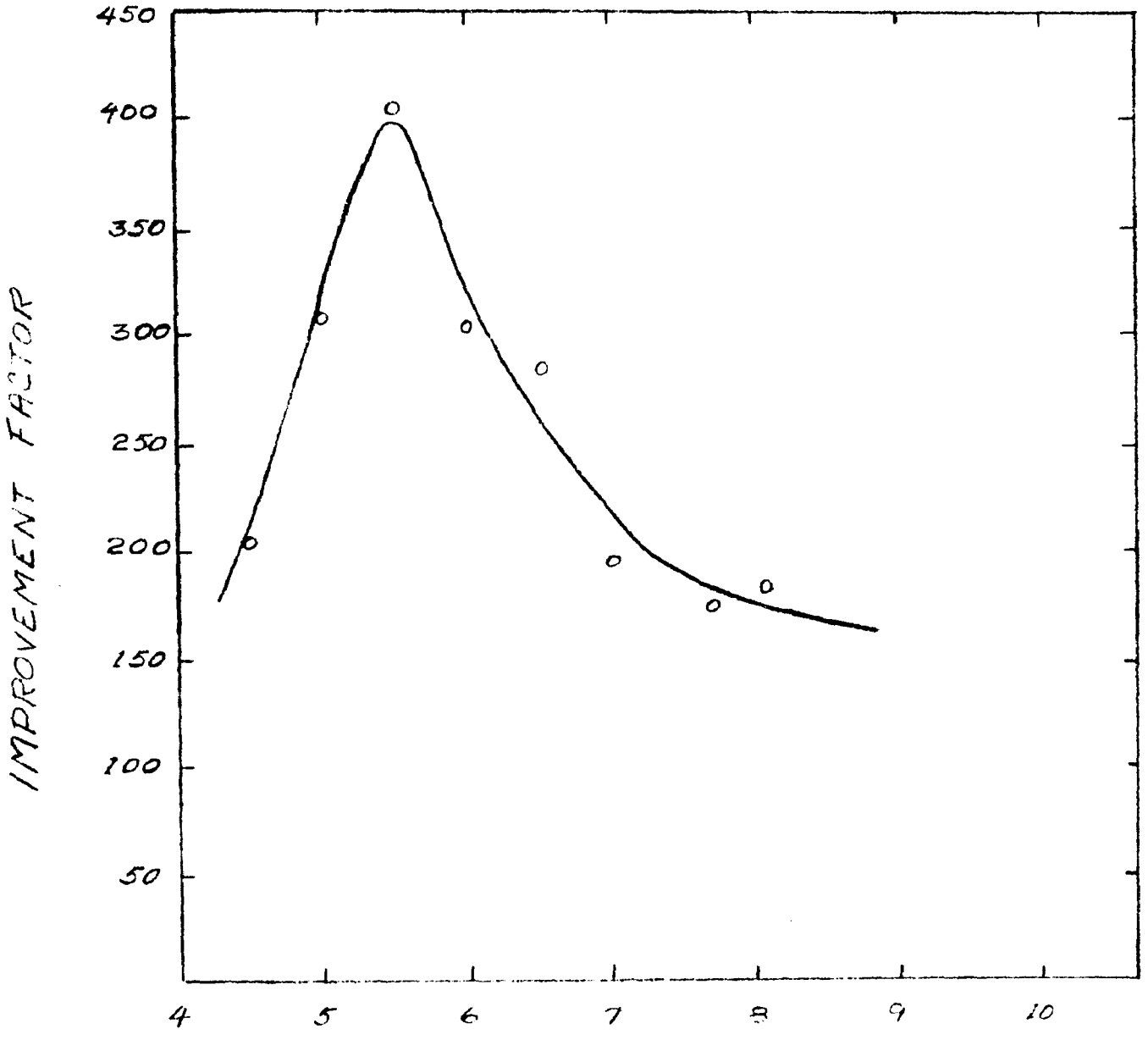


FIGURE 8

PERCENT "CALAMINE" Zn IN CONCENTRATE

VS. POUNDS OF COLLECTOR

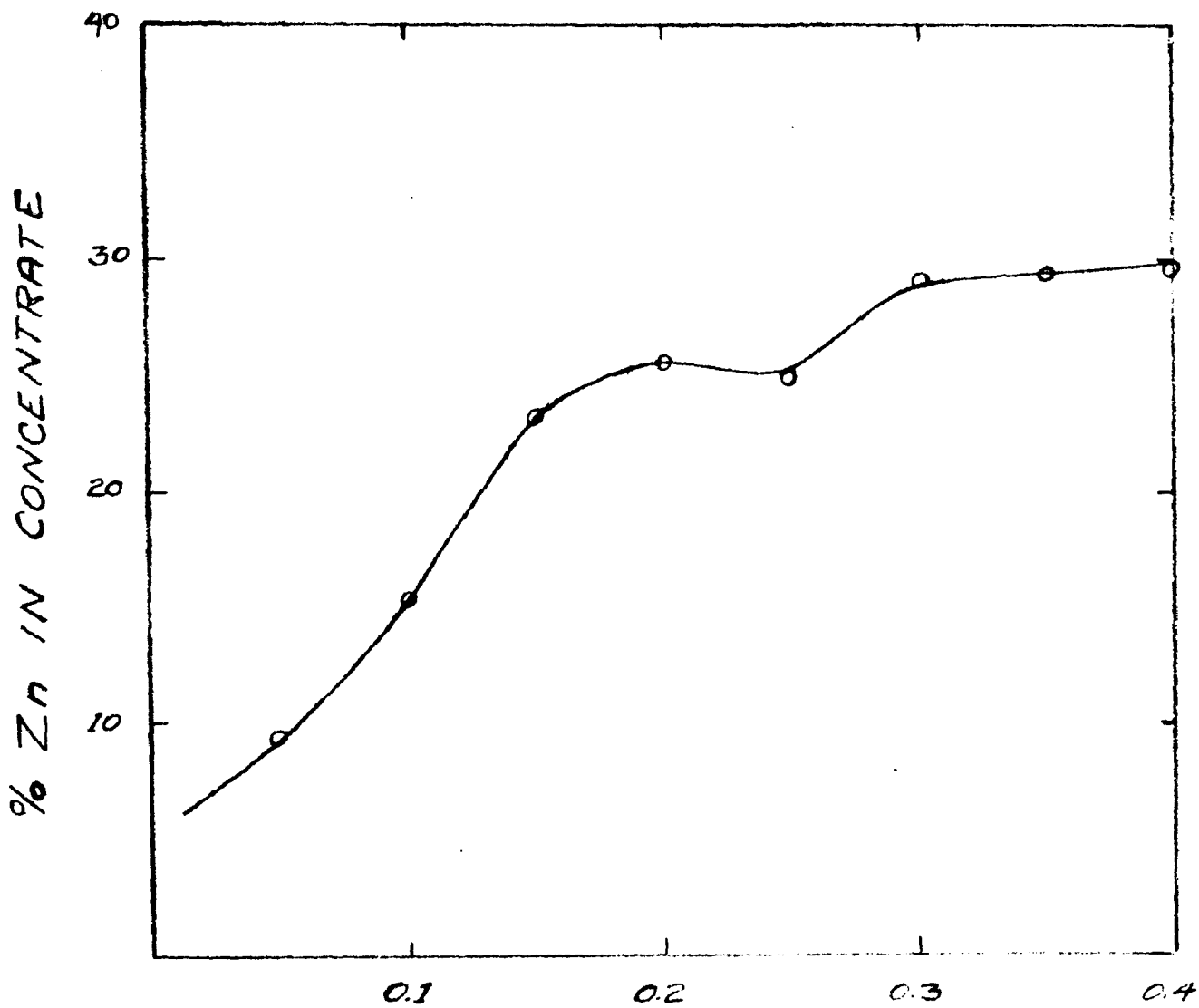
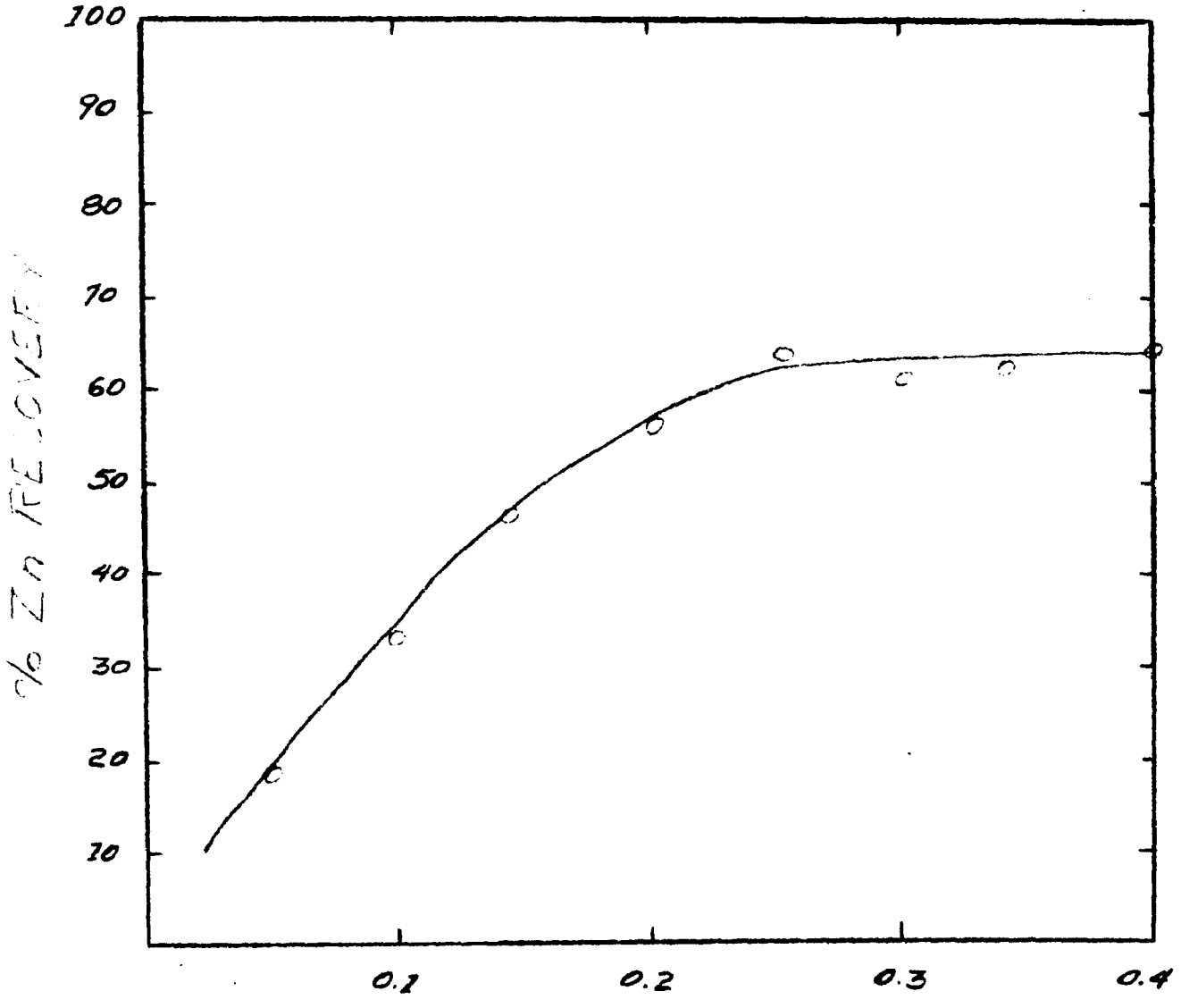


FIGURE 9

PERCENT RECOVERY "CALAMINE" Zn

VS. POUNDS COLLECTOR

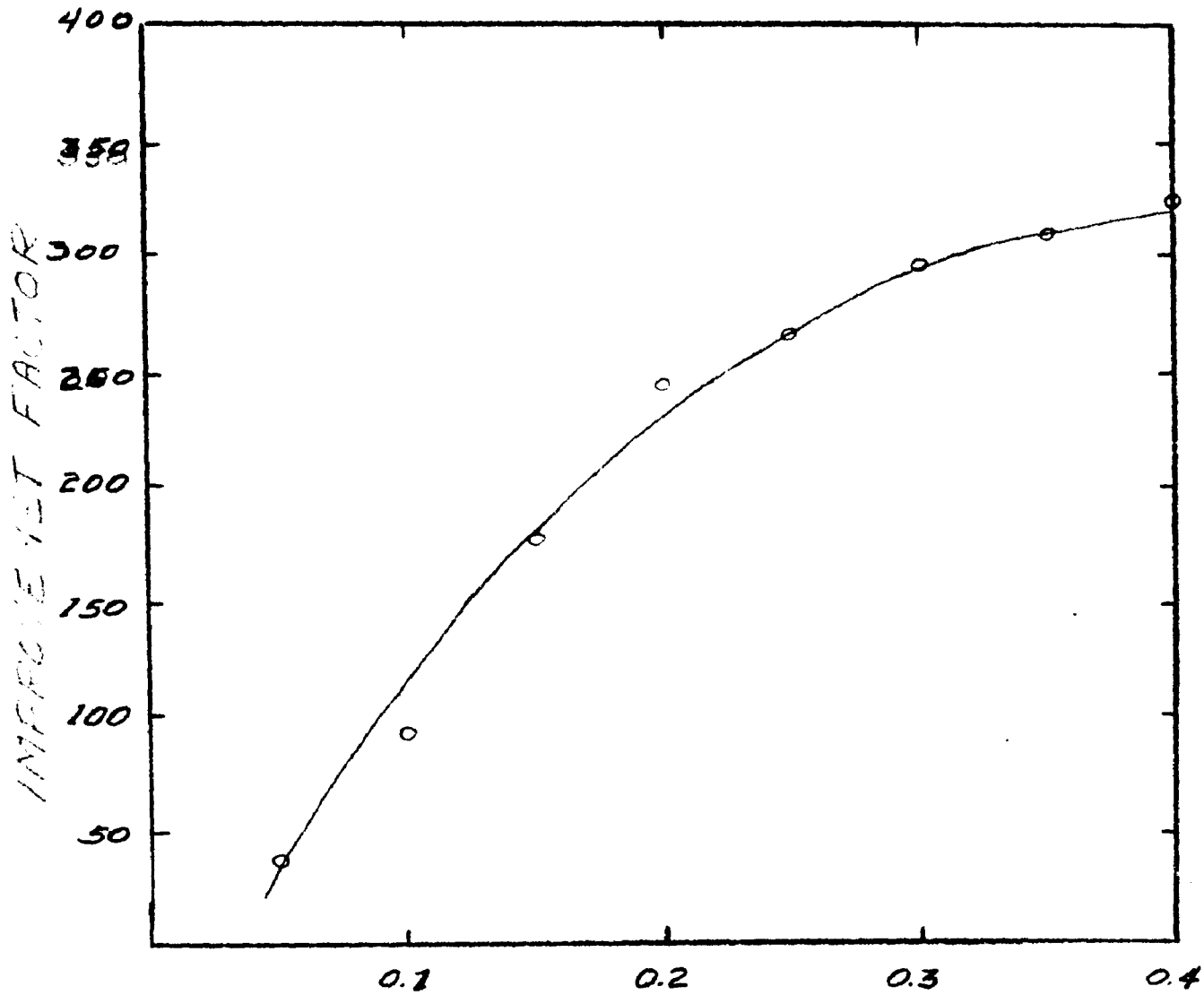


POUNDS n-OCTYL METHYLENE OLEATE

PER TON 6% Zn CALAMINE FEED

FIGURE 10

IMPROVEMENT FACTOR OF 6 % Zn CALAMINE FEED (-200+270 MESH) VS. POUNDS OF COLLECTOR



POUNDS n-OCTYL METHYLENE BLUE PER TON 6% Zn CALAMINE FEED

FIGURE 11

PERCENT Zn IN CONCENTRATE VS. PARTICLE SIZE OF 6% Zn CALAMINE FEED

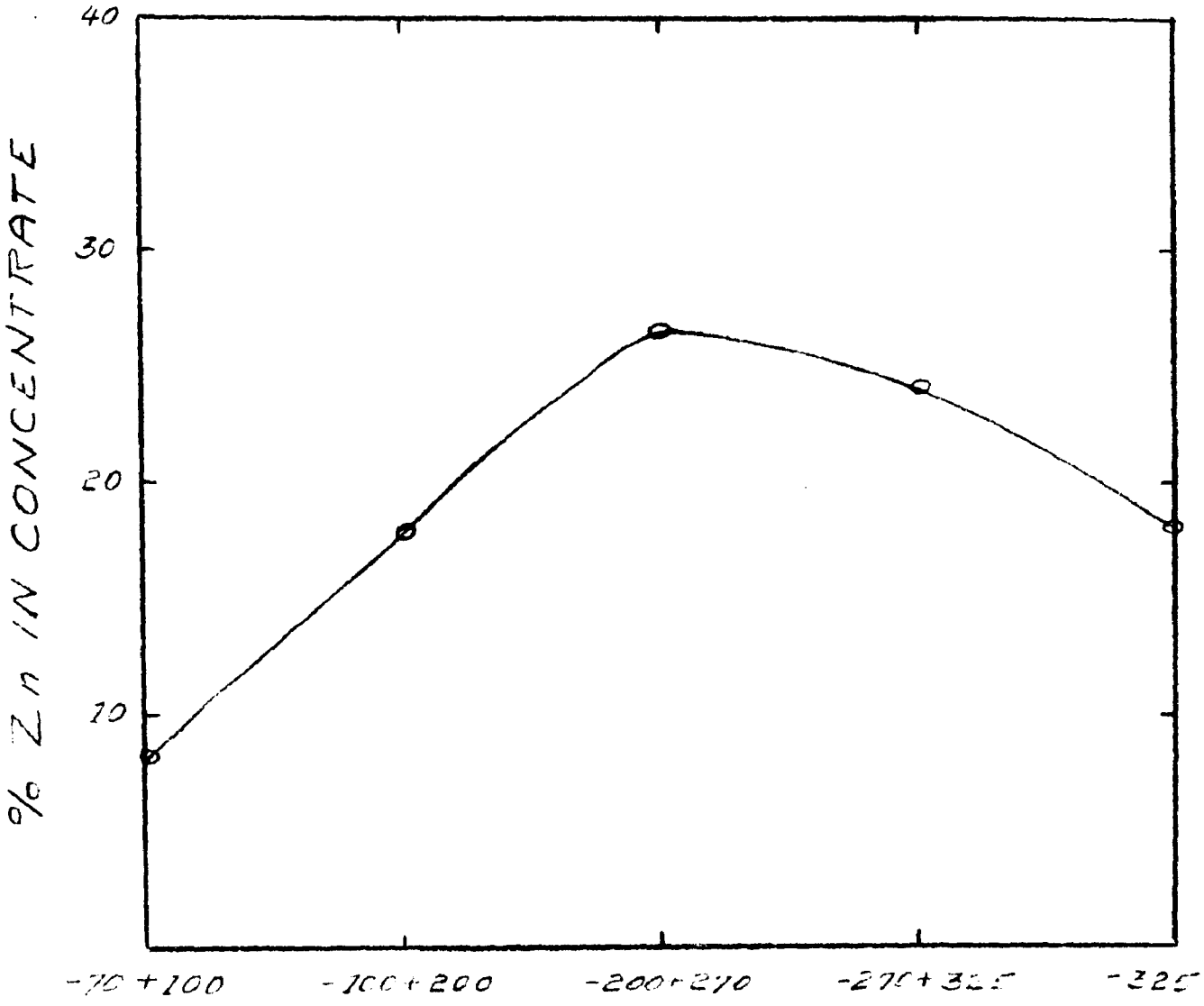
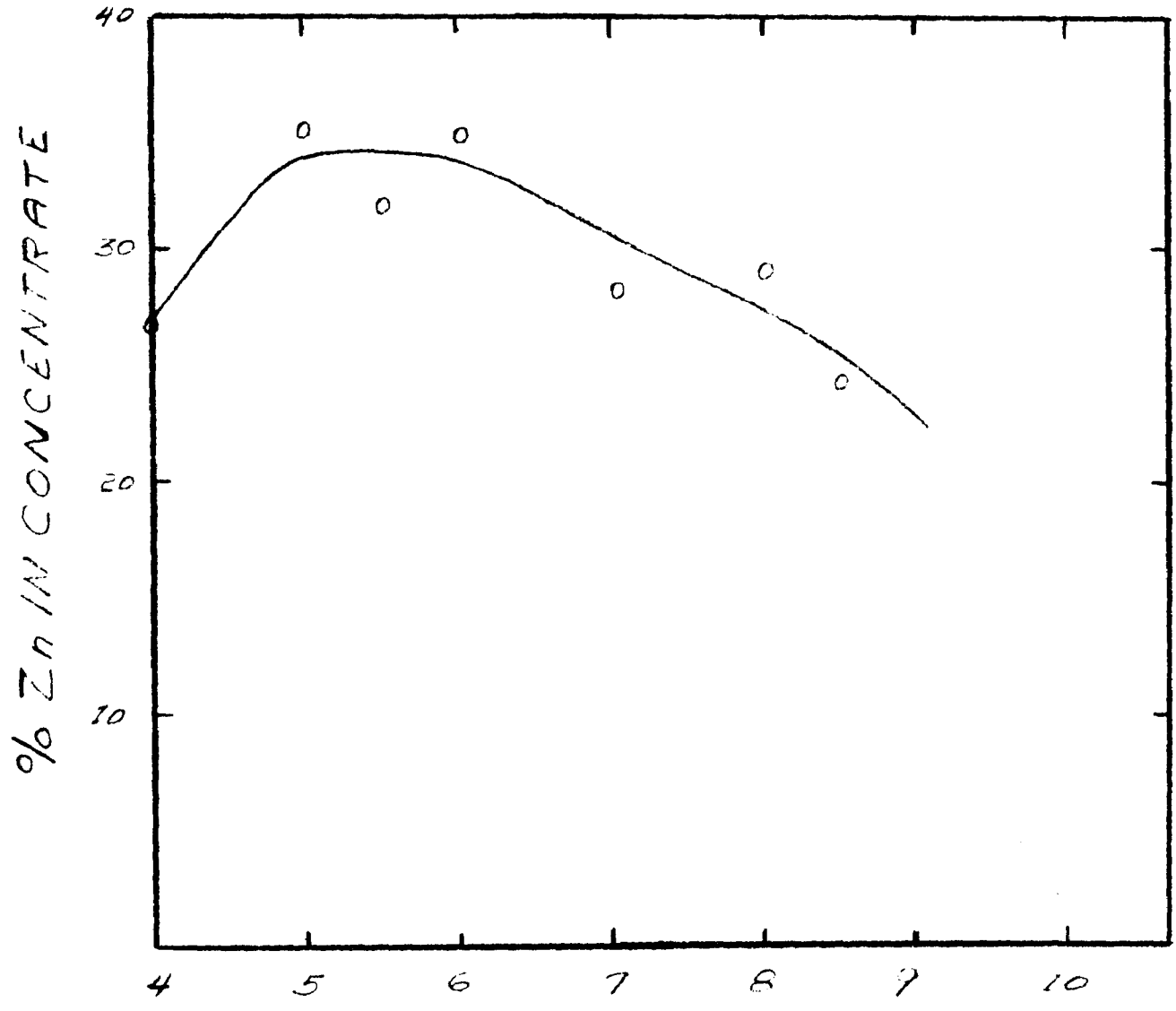


FIGURE 12

PERCENT "CALAMINE" Zn IN CONCENTRATE

VS. pH OF CELL CONTENTS



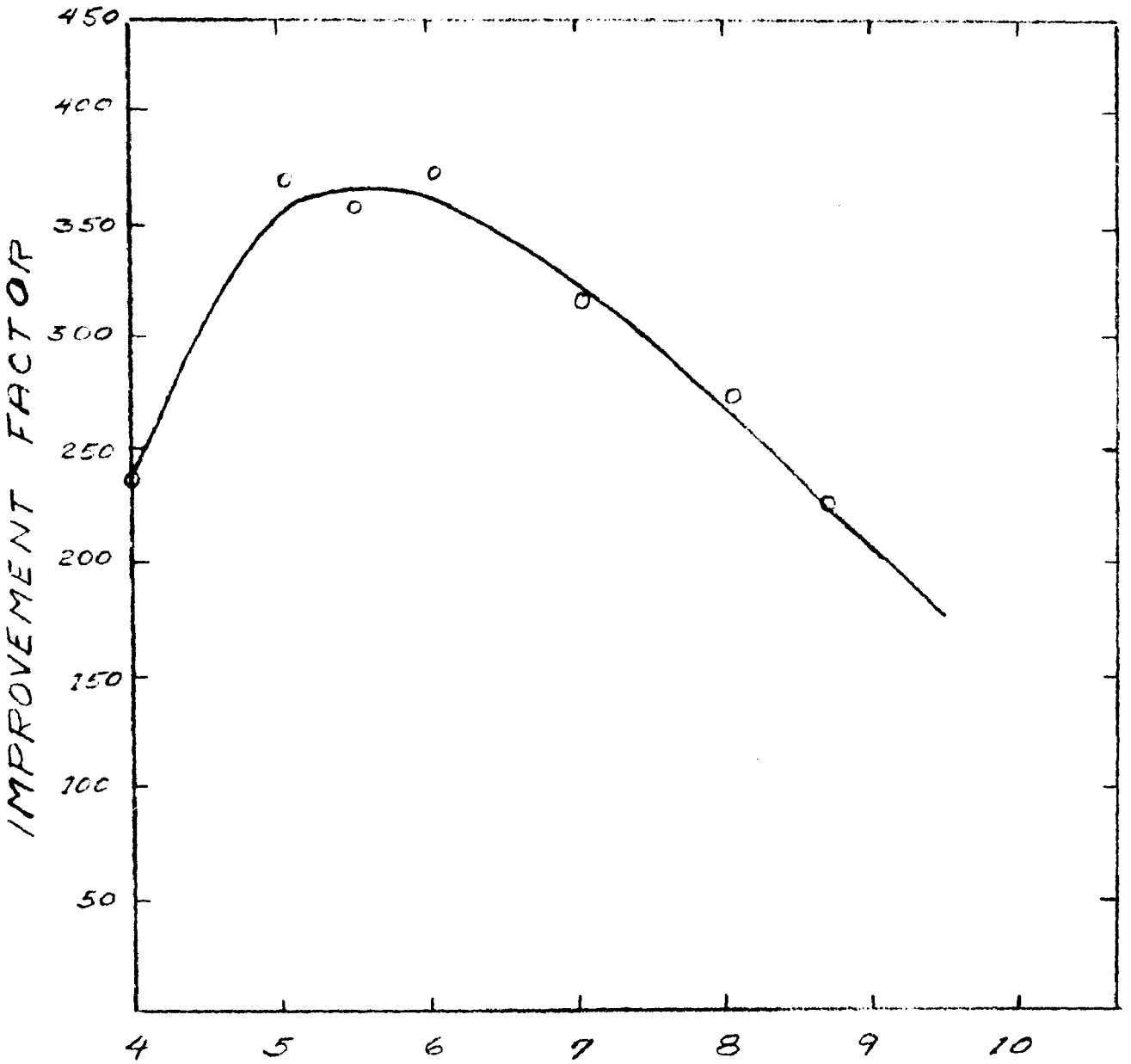
pH OF CELL CONTENTS OF 6% Zn CALAMINE

FEED - 0.25 POUNDS COLLECTOR PER TON

FIGURE 13

IMPROVEMENT FACTOR OF 6% Zn

CALAMINE FEED VS. pH OF CELL CONTENTS



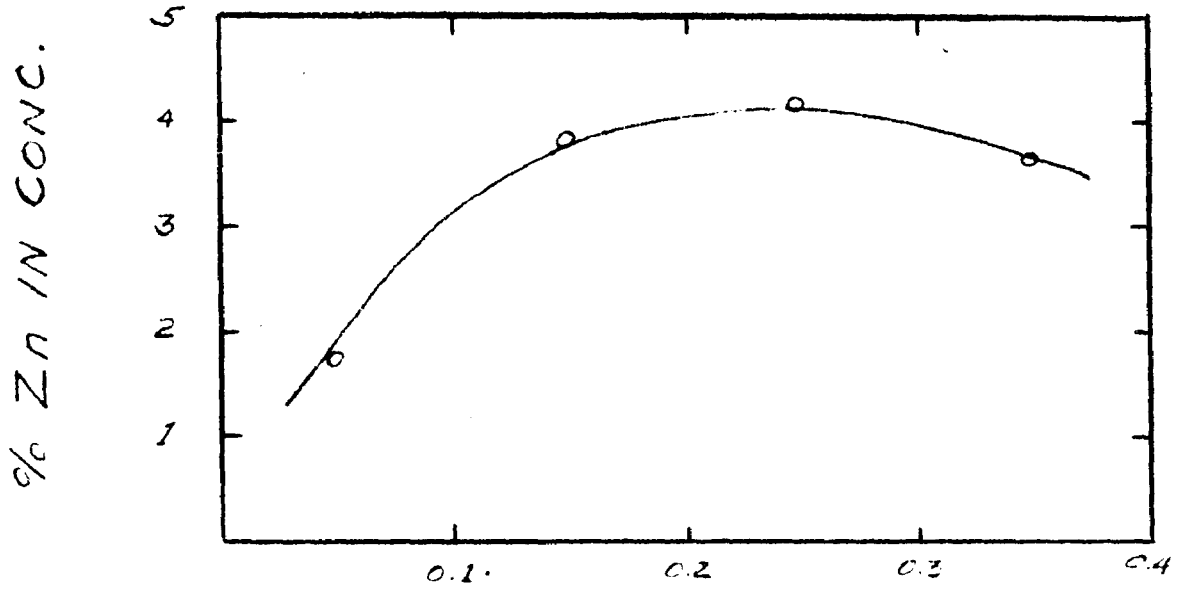
pH OF CELL CONTENTS OF 6% Zn CALAMINE

FEED - 0.25 POUNDS COLLECTOR PER TON

FIGURE 14

LOS LAMENTOS 1% Zn ORE

% Zn IN CONCENTRATE VS. COLLECTOR



IMPROVEMENT FACTOR VS. COLLECTOR

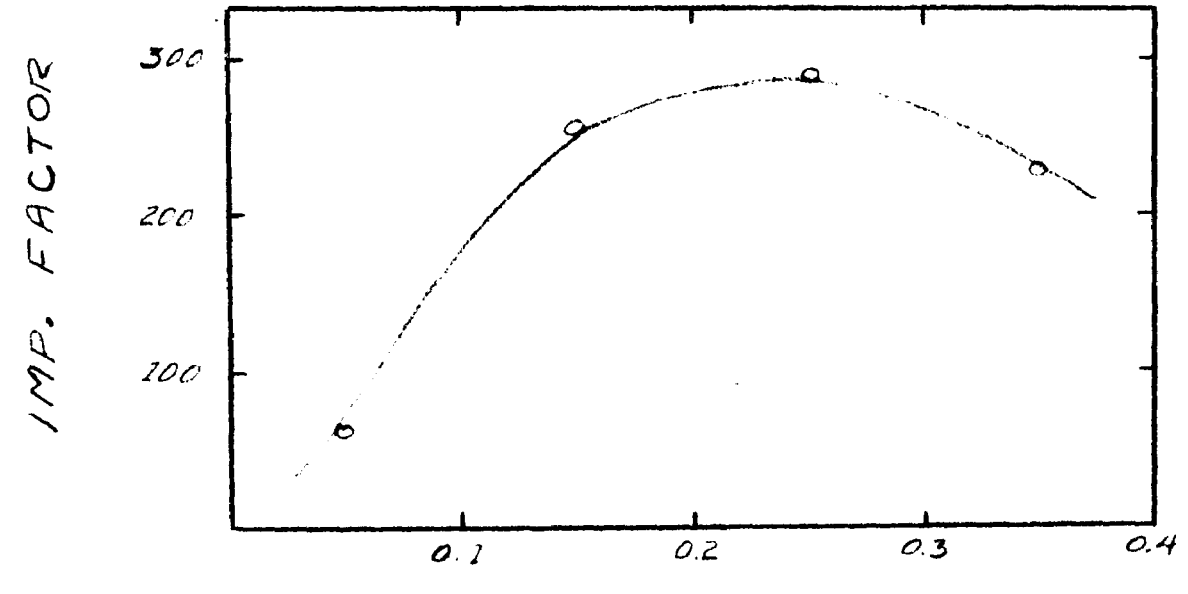
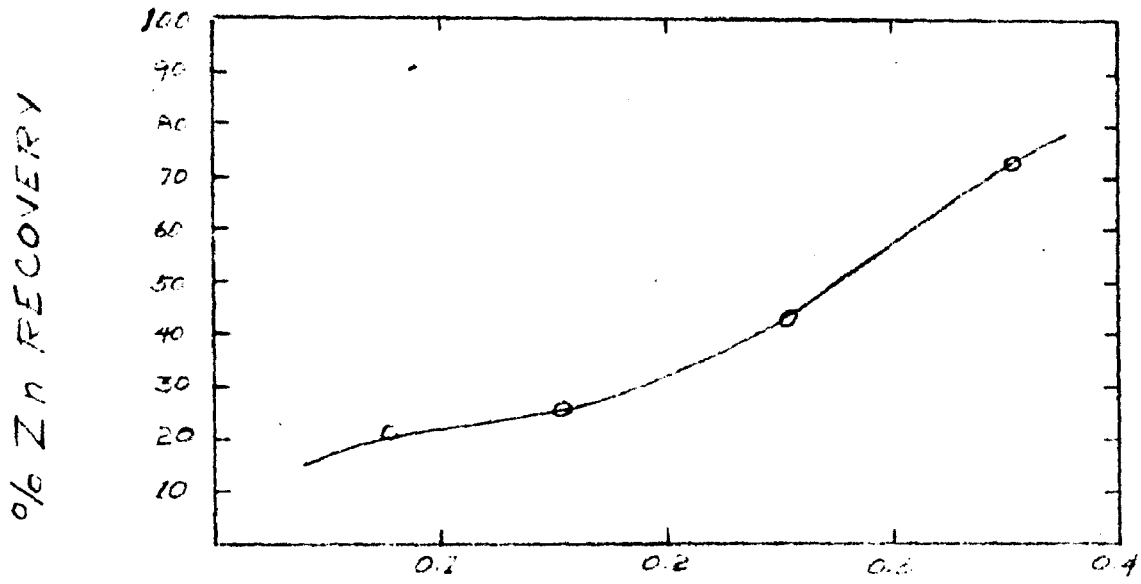


FIGURE 15

LOS LAMENTOS 6% Zn ORE

% Zn RECOVERY VS. COLLECTOR



% Zn IN CONCENTRATE VS. COLLECTOR

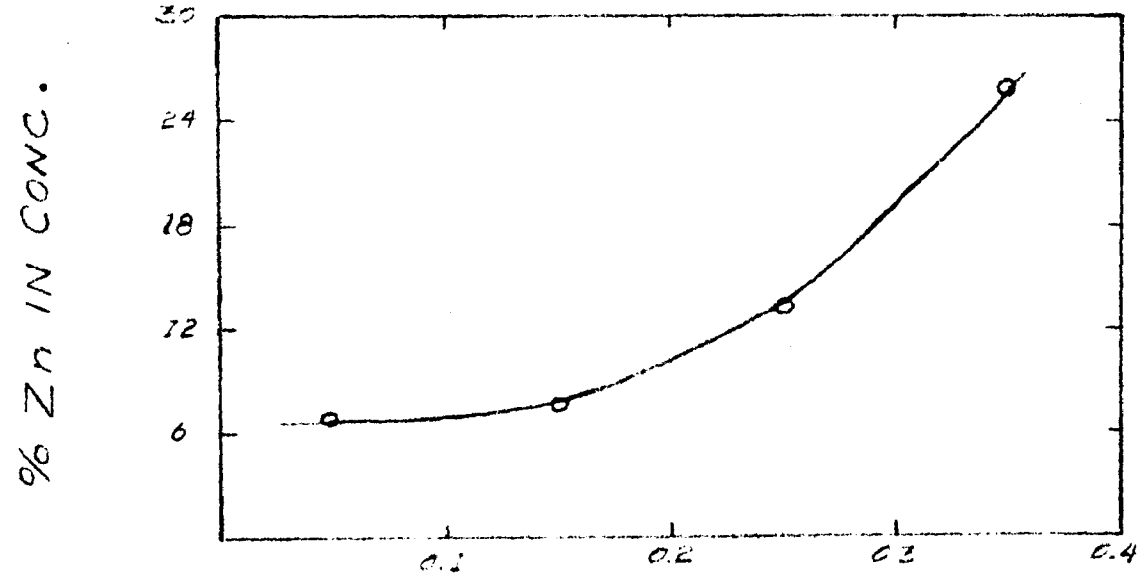


FIGURE 16

DISCUSSION

Examination of the data demonstrates that in every case n-octyl methylene blue functions as a collector for zinc silicate. The experimental data further affords confirmation of the theory that a modified mordant dye will function as a selective collector for the material which it mordants.

The zinc silicate ores tested were (1) Willemite (2) Calamine or Hemimorphite, and (3) Los Lamentos ore. Each showed both enrichment, and improvement when subject to flotation with the modified dye.

In view of the results obtained with these various zinc materials it will aid the discussion to briefly review these silicates. (1) Willemite (12, 51, 59) Zn_2SiO_4 occurs in masses or in crystal; Moh hardness 5.5; sp. gr. 4.1; color, pale yellow when pure; lustre-resinous; translucent on thin edges. Crystal structure; hexagonal prisms, with a 3-sided (rhombohedral) pyramid on the ends. Color when pure is whitish or greenish yellow, but with small amounts of impurities, it may be flesh-red, grayish white or yellowish brown. The Willemite used in this investigation was fairly pure and was greenish yellow. It was obtained from Words Natural Science Establishment, Inc., Rochester, New York. It was subjected to heat and failed to give off water vapor thus indicating

lack of any calamine which it often resembles when massive.

(2) Calamine. (13, 14, 52) $Zn_2(OH)_2SiO_3$ occurs as crystalline linings in cavities, or as stalactitic masses; Moh hardness 5; specific gravity 3.4; color white, sometimes bluish or greenish shade, also yellow to brown. Transparent to translucent. Compositions recorded as $(ZnOH)_2SiO_3$, H_2ZnSiO_5 or $H_2O \cdot 2ZnO \cdot SiO_2$. Water is given off at a red heat unchanged at 340 C. The Calamine used in this investigation was hemimorphite (calamine) of the orthorhombic type. It was obtained from Ward's Natural Science Establishment, Inc. Hemimorphite structural ($Zn_4(OH)_2Si_2O_7 \cdot H_2O$) according to Phillips (60) is orthorhombic pyramidal. The crystals are peculiar in that the two ends are terminated differently. The percentage zinc indicated the presence of impurities.

(3) Los Lamentos Ore: This zinc silicate ore was obtained from the Eagle-Pitcher Company for testing on a commercial ore.

The name of the property from which the ore sample came was Los Lamentos. This mine is located 30 km. West of the town of Villa, Ahumada on the Mexican National Railroad in the state of Chihuahua. It was an old lead producer and a limited amount of zinc silicate ore remains in the old stopes. (11).

This ores' analysis is as follows:

51.3% Zn	---% Cu
1.5% Pb	---% Oz Ag
2.2% Fe	---% Oz Au
.068% Cd	2.42% Ca O

23.0% Insol

Unfortunately, it was not possible to obtain a sample containing less zinc from this source. Tests were therefore conducted in a similar manner as employed on the Willemite and Calamine. The Los Lamentos mine ore was dry ground, deslimed, and classified into various mesh divisions.

Tests were run on this ore in the general range of concentrations used in the fundamental research. Ottawa Sand of the same size distribution was used to dilute the feed to the proper total percentage of Zinc.

THE COLLECTOR

The procedure for preparation of 3 n-octyl 2,8 tetra methyl diaminothiazonium chloride, namely, n-octyl methylene blue, is given in the appendix. Examination of this procedure will indicate the uneconomical feasibility of preparing large quantities of collector for commercial use.

The difficulty of this synthesis was brought about by the inability of finding a reaction or reactions of methylene blue with a compound or series of compounds, which would produce n-octyl methylene blue. A search of the literature

failed to reveal any method for introducing the n-octyl group into the benzene ring of 2,8 tetramethyl diaminothiazonium chloride (methylene blue). All authorities consulted agreed that a direct introduction of a hydrocarbon radical into the benzene nuclei of methylene blue was not feasible and that the structure of dye would probably be altered. In any case, the subsequent separation and purification of a product would be a tedious procedure.

Various reactions were tried in an effort to produce the desired collector by short-cut methods. All failed and/or gave indications of lack of coupling, impossible purifications, rearrangement and apparent distruction of n-octyl chain, which was known to be necessary for flotation. Finally, the reactions used were evolved. See Tables A and B. This method involved the preparation of compounds containing the n-octyl group which could be reacted in final coupling reaction to produce n-octyl methylene blue, and thus assure the minimum danger of side reactions and ease of purification.

Thus, it is reasonably assured that if the coupling of ortho-octyl dimethyl aniline with the thiosulphonic acid of p-amino dimethyl aniline gave a product which possessed the properties of methylene blue, the compound would necessarily have to be alkyl substituted methylene blue. (Reaction 4). The entire procedure was long and tedious because many of the

reactions gave poor yield. For example, reaction C or Table B, is chiefly meta and para directing only a small yield of the required ortho-compound was obtained. Inspection of structure coupling product clearly shows that no reaction to produce the dye should take place with other than the ortho n-octyl compound since the other hydrogens are involved in the coupling reaction.

The final purified material had many of the properties of methylene blue. Description of product is: A pastey material with bluish-red metallic lustre. It was slightly soluble in water, insoluble in ether and benzene, soluble in alcohol. Heated on platimum foil, it gave greenish-violet vapour. It burned with smokey flame, but left no ashes. The lack of ash indicated the compound was zinc free. It dissolved in concentrated sulfuric acid and was unaffected by dilute sulfuric acid. It was not appreciably affected by ammonia. Stannous chloride gave a precipitate. The above properties indicate that the n-octyl methylene blue possesses many of the properties attributed to methylene blue (8).

Finally, a small sample was dissolved in water-alcohol, heated to boiling while carbon dioxide was passed into the flask. Titanium trichloride was added to the solution until it was decolorized. It required approximately two equivalents of iron (in terms of titanium trichloride) for reduction of

one mole of the n-octyl substitute compound (mol. wgt. 331.6). This definitely indicates that this compound was n-octyl methylene blue.

This method is based on the assumption that two equivalents of hydrogen are required for conversion of n-octyl methylene blue into the leuco compound according to the equation:

$$C_8H_{17}C_{16}H_{18}N_3SCl + H_2 \text{ --- } C_8H_{17}C_{16}H_{20}N_3SCl$$

Much work has been done on the volumetric determination of methylene blue and other dyes by this reduction method (35, 39, 47, 48, 68, 69). This method of analysis is very popular in United States dye plants and is considered satisfactory. It is assumed that the conditions of final reaction were such that the n-octyl group remained unchanged and that it did not rearrange. Based on these facts the collector is called n-octyl methylene blue and would chemically probably be 3 n-octyl 2,8 tetra methyl diaminothiazonium chloride.

SELECTIVE MORDANT ACTION

Inspection of Table I will show the results which demonstrate the selective mordant action of n-octyl methylene blue. The washed Ottawa sand removed very little color for colored solution (Test A-7). However, the zinc silicates, Willemite and Calamine, when agitated with the dilute colored solution showed appreciable color removal. (Test B-3, and A-3).

Inspection of the settled material evidenced the fact that mordanting had taken place, the material was dyed. Repeating this procedure with various amounts of calamine, Willemite and sand, produced the same results (Test B-9, D-2, D-7). This demonstrated to the writer that the collector has some degree selective of mordanting for the zinc ore over the silica gangue. This is substantiated by all the data, however, lack of greater selectivity in later tests indicates some reaction at the concentrations necessary to bring about flotation.

FLOTATION OF WILLEMITE-ZINC SILICATE

The results of the flotation test for Willemite by n-octyl methylene blue will be found in Tables II, IIA, III, IV, V, and Figures 3, 4, 5, 6, 7, and 8. For all the work reported on Willemite flotation, a one percent concentration was used. Enough concentrate had to be taken to allow sufficient recovery as well as to give adequate sample for analysis. In all cases, duplicate samples were analyzed (4 grams per sample). Occasionally triplicate samples were run. As pointed out in the procedure, the analysis of zinc silicate is not an easy matter.

It is possible that the amount of material collected might lead one to suppose that possibly some mechanical carry-over gives a concentrate lower in zinc than the feed. This

is due to the fact that the specific gravity of silica is under 2.5. Any mechanical carryover would tend to lower the percentage of zinc in the concentrate, recovery, etc., rather than raise them.

AMOUNT OF COLLECTOR: Inspection of Tables II, IIA give the conditions used in the study of the effect of increased amounts of collector upon the flotation of Willemite. Two cuts were taken for each test run. An attempt was made to take about the same amount in each cut. It is indicated that in all cases, the second cut is lower in percent zinc in concentrate as well as percent recovery of the total zinc in the feed. However, the drop off of concentration in the second cut is not as sharp as one might expect.

Around 0.1 pound collector per ton gave the best concentration in the two cuts. Inspection of figure 3 indicates a sharp increase in concentration to around 4.0%, thence drop off to 3.5% and after that, no appreciable change even with collector amounts of 0.4 pound per ton. An increase of collector on 1% Willemite feed has only a slight depressant effect on the flotation once the maximum is reached.

The percent zinc recovery vs. amount of collector curve reaches a maximum around 0.1 pound collector per ton and is depressed slightly with increased amounts of collector. It then levels off even at 0.4 pounds per ton. At low collector

amounts, very little recovery is obtained. First cuts in all cases show higher recovery than second cuts but, as in the case of percent zinc in concentrate, there is not an extremely sharp drop.

The improvement factor (55, 63) shown in figure 5 reaches a maximum of 318.6. The improvement factor is one of the better methods of demonstrating the effectiveness of flotation. It is obtained in this case by taking the percent zinc in the concentrate times the percent recovery. It actually should be enrichment times the percent recovery. Enrichment is obtained by taking percent zinc in the concentrate and dividing it by percent zinc in the head or feed. It is apparent with 1% feed that percent zinc in concentrate is equal to the enrichment. Often this enrichment is reported as degree of enrichment or as percent enrichment, that is, one hundred times the enrichment.

The percent recovery of zinc is obtained by taking the grams of zinc in concentrate divided by grams of zinc in the head times one hundred. The above methods of calculating are used in the data presented. The improvement factor therefore combines the separating efficiency and the selectivity into one factor. One eliminates "good" results as are often reported in flotation literature and research. Thus, one can have high recovery but very low enrichment or very high enrichment

and very low recovery. The improvement factor presents the final or overall picture.

Since zinc silicate has never been successfully floated in the laboratory or in particularly the commercial field, there exists no criterion for what a satisfactory improvement factor would be. It appears that any improvement factor over two hundred is definitely a step in the right direction.

The improvement factor curve, Figure 5, shows a sharper rise with increased amounts of collector than either the percent zinc in concentrate or the percent zinc recovery curve. The depressant action is also much sharper, dropping improvement factor from 318 to 233 and actually indicating a slight recovery with higher amounts of collector (0.4 pounds per ton).

It thus appears that the amount of n-octyl methylene blue used as a collector for 1% zinc Willemite silicate ore must be critically adjusted for maximum flotation, under conditions used in Table II. It further appears that increased collector depresses slightly the flotation but then holds at a fairly constant improvement factor. We may theorize in this case that a certain amount of collector is necessary to form the "envelopes" or sufficient mordant and that increased collector tends to block the flotation of the "envelopes", but only to a fixed amount.

FEED PARTICLE SIZE: Table III gives the conditions

used to study the effect of feed size on flotation. In this study, only one cut was taken, collector was held constant at 0.09 pounds per ton. As in all tests reported in this investigation, the feed was subjected to a conditioning period with all the collector added before collection was made. This had proven, in preliminary tests, to give better results than a step-wise addition of collector. The results indicate that the minus 200 plus 270 feed gives the highest percent zinc in concentrate as well as the high percent recovery. Examination of curve of percent zinc in concentrate vs. particle size of feed, Figure 6, would lead one to deduce that one must approach a minus 200 mesh particle size to get maximum freedom of zinc containing particles and that subsequent particle size reduction drops the zinc in the concentrate not too greatly. The lack of an appreciable drop is believed to be due to two effects, namely, (1) low concentration of the willemite and (2) the purity of ores used in making the feed. Excessive sliming was not encountered with increased fines as in other cases. However, the drop that does occur appears to be due to sliming.

pH OF CELL CONTENTS: Using the optimum conditions of the minus 200 plus 270 particle size, and the collector concentration of approximately 0.1 pounds collector per ton, the effect of pH changes were studied. An alkali solution could

be controlled by dilute caustic, an acid solution used in conjunction with dilute hydrochloric or sulfuric acid. Inspection of Table IV reveals an interesting fact: as the solution becomes more acid, the percent zinc in concentrate reaches a pronounced maximum at a pH of 5.5, falling sharply on either side of this pH. We should note that the 4.9 percent zinc in the concentrate is only on 8.726 grams of froth and would be lower on a larger cut sample. As the pH was increased the percent zinc in concentrate decreased more or less sharply but the drop appears to level off at a pH of around 8.5.

The plot of percent "willemite" zinc in concentrate vs. pH of cell contents, Figure 7, evidences this drop on either side of the 5.5 pH. It appears that as the pH increases, its effects tend to approach a constant value.

The percent of recovery of zinc in feed has a maximum of 67.4% at the pH 5.2 again dropping on either side. A very sharp drop is noted between the 5 and the 4.5 pH. This can be partially explained by the smaller amount of cut. This should show a less sharp decrease. The increase in recovery between 7.7 and 8.2 is most unusual in light of the fact that inspection of Figure 8 shows that where the discrepancy between the pH's of 4.5 and 5 are corrected in the improvement factor, the discrepancy between 7.7 and 8.2 are not. That is

to say, the improvement factor went from 318.8 at a pH 5 to 209.7 at a pH 4.5, whereas it increased from 171.7 to 186.0 in the latter case. However, the curve of the data taken indicates a gradual drop in improvement factor with increased pH.

It may be reasoned for Table IV that at a pH of 5.5, the maximum collecting action is due to the better "enveloping" of the zinc particles, and/or the depressing of the gangue due to the acid and/or the activation of the zinc particles due to the acid. There was some indication that the use of hydrochloric acid for pH adjustment increased the improvement factor. It may be deduced that under conditions of Table IV the improvement factor is very sharply affected by the pH. This was not so marked in the study of the effect of pH on the flotation of the calamine and Los Lamentos ores. pH may affect more strongly the unhydrated zinc silicate, particularly in terms of the improvement factor.

REFLOTATION: Inspection of Table V reveals several interesting factors which appear to effect the reflotation of once floated ore. Inspection of Test 5-1, 5-1A, and 5-1B, show that (a) reflotation gave an enrichment of 3.26 and a recovery of 33.0 percent, (b) the addition of more collector increased the enrichment to 4.93, and (c) increasing collector and adjusting the pH gave an enrichment of 6.3. Thus, one

concludes that reflotation not only is beneficial, but additional reagent and pH adjustment gives additional improvement. The series of Test 5-2, 5-2A and 5-2B, gives much food for thought. This series used the s ame percent zinc in the feed but was made up by taking 50 grams of new sand, with 50 grams of concentrates to give a final 100 grams of 2 percent zinc. When subjected to the same set of conditions of reflotation as the other set, it gave the same general results but in each case much less degree of enrichment. It thus appears that we have some type of equilibrium between the envelopes particles of gangue and zinc, and solution. This condition seems to be shifted by the introduction of new gangue material.

FLOTATION OF CALAMINE ZINC SILICATE

The results of the flotation test for calamine by n-octyl methylene blue will be found in Tables VI, VII, VIII, and IX and Figures 9, 10, 11, 12 and 13.

In all the work reported here a 6 percent zinc concentration was used. A test on mechanical carryover established again that carryover produces a concentrate lower in zinc than the head.

AMOUNT OF COLLECTOR: In this study slightly more cut was taken but only one cut was made. There is a gradual increase in percent zinc in concentrate with increased amounts of collector. 0.2 pound per ton seems to be the levelling off

point. One notes a slight drop at 0.25 pounds collector per ton, which is attributed in part to the excess cut over the 0.2 and 0.3 pounds collector per ton. Figure 9 which shows the plot of collector vs. zinc in concentrate demonstrates that apparently there is no depressing effect by additional collector, but rather a levelling off above 0.3 pound collector per ton. Comparison with Figure 3 indicates that we do not have a maximum and also that it requires considerable more collector before one reaches the decreasing rate of increasing zinc in concentrate with collector change.

The percent recovery of zinc has a gradual increase with increased amounts of collector. The percent recovery of zinc tends to level off at slightly over 60 percent and has only a slight increase with increased collector after that. The high recovery at 0.25 pound collector is due again to the high cut of concentrate. Comparison of Figure 10 with Figure 4 shows that increased amounts of collector does not produce a sharp maximum and further, apparently does not have any depressant action on the percent recovery of zinc.

This contrast is even more marked when we examine the effect of collector on the improvement factor. A maximum improvement is reached of 323 at the high amount of collector addition. Examination of data in Table VI clearly shows an increase over 0.25 to 0.3 pounds per ton does not greatly

alter the improvement factor, percent zinc in concentrate, or the percent recovery of zinc. Instead of the sharp drop in the improvement factor with increased collector as for Willemite (Figure 5) we have only a steady increase.

One might attribute this to the nature of the calamine zinc silicate and/or the higher concentration of zinc silicate which has a more steady demand. However, the improvement factor comparison leads one to conclude that the modified dye mordants or "envelopes" these particles effectively in both cases. This had been indicated in the work reported in Table I.

FEED PARTICLE SIZE: Table VII and Figure 12 gives the results of effects of particle size on percent zinc in concentrate, degree of improvement and percent recovery of zinc for the calamine feed. It should be noted that the work reported in Table VI was made on minus 200 plus 270 feed. This mesh feed had been used because the work on Willemite indicated this particle size was necessary to free the zinc silicate. This fact is confirmed by the data of Table VII. A slightly coarser feed was used in test 7-1 namely, minus 70 plus 100. In this range, the degree of improvement was only 1.36 with a zinc recovery of 18.1 percent. Apparently the zinc particles were not free enough for flotation. Low results were obtained with the minus 325 feed. Considerable trouble was encountered with this feed in sliming. It appears that the

calamine had considerable impurities in it which gave trouble when released by grinding.

A higher percent of impurities was found in calamine than in the Willemite when the pure ore was analyzed. Of course, this condition of sliming is not improved by the increased concentration used in the studies on calamine.

pH OF CELL CONTENTS: The conditions used for this study and results are given in Table VIII and Figures 13 and 14. The optimums established by the preceding work were employed. The same method of pH adjustment was used, except the pH was adjusted in steps of one-half a pH. The effect of pH on percent zinc in concentrate increases to a flat maximum between 5 and 6. The percent zinc in concentrate has its greatest drop as the pH is increased. It appears from inspection of Figure 13 that the percent zinc in the concentrate is more gradually decreased on the alkaline side than on the acid side. Comparison with the willemite curve, Figure 7, will show that the maximum for calamine is relatively lower and flatter than that of the willemite. Calamine seems less sharply affected by small changes of pH. Here again the acid apparently acts as an activator for zinc silicate particles, allowing more selective mordanting or "enveloping" of zinc particles over the gangue.

Inspection of Table VIII shows that enrichment follows

the same general trend of the percent zinc in concentrate. The percent recovery of zinc shows the same flat maximum between the pH of 5 and 7. However, it is noted that the drop above the pH of 7 is just as pronounced as below the pH of 5. This behavior is different than that of willemite, the latter actually had an increase in percent recovery of zinc as the pH went up.

The improvement factor for calamine reaches a maximum value of 360-370 in the range of pH 5 to 6. It not only has a higher improvement factor than Willemite, but the maximum is much flatter. This would indicate under the test conditions of Table VIII, that (a) the best flotation is obtained on the acid side, (b) that maximum enrichment, percent zinc in concentrate, percent recovery, and improvement factor, exists over a wider range of acid pH than for willemite silicates, (c) that selective "enveloping" is taking place, and (d) that above a pH of 8.5, the flotation is greatly decreased.

One might theorize that the effect of the hydrogen ion (pH) has a marked effect over the "enveloping" of the particles over a wider pH range on the hydrated zinc silicate particles. However, there is undoubtedly some other effect since ordinarily the hydrated ores have a tendency to be more difficultly floated. In fact, one must make the particles water repellent to achieve flotation.

REFLOTATION OF CALAMINE: Table IX shows the results of the reflotation of calamine with and without pH adjustment, new gangue or additional collector. In light of above results, reflotation was attempted with pH adjustment without an additional collector. This is slightly different than the procedure followed for willemite, see Table V.

Test series 9-1, 9-1A, 9-1B, show that reflotation takes place with an enrichment of 1.93 and recovery of 45.4%. Further, that merely adjusting the pH gives improved enrichment and percent recovery of the zinc. However, an enrichment, 2.28 on the 18 percent head, is obtained by pH adjustment and the reconditioning with additional collector.

Test series 9-2, 9-2A, 9-2B, was obtained on a feed of the same final concentration. It was obtained by diluting a more concentrate cut with new gangue (sand). This series of tests shows again that new gangue decreases the effect of reflotation of the once floated material. We obtain only a 1.61 degree of enrichment by reflotation when the new gangue is added, even with the constant amount of head and percentage zinc. Adjustment of the pH before reflotation improves the percent zinc in concentrate and the percent recovery of zinc. However, the improvement is not as great as for test 9-1A. The addition of more collector improves the percent recovery and percent zinc in the concentrate but not as much as in

Test 9-1C. Even additional tests run with more collector added to a 9-1C type sample, failed to give the expected increase in flotation.

One might theorize that the "envelopes" are shifted, blocked, or altered by introduction of new gangue. Further, that due to some equilibrium shift or interexchange between particles, the tendency to "reenvelope" is diminished. It is hard to believe that the gangue would destroy the polar or non-polar group of the modified dye.

FLOTATION OF LOS LAMENTOS ZINC SILICATE

The results of the study on this commercial ore is reported in Tables X and XI and Figures 15 and 16. This investigation was made on feeds having, (a) the same percentage zinc in the feed as in the willemite investigation and (b) the same percentage in the feed as in the calamine investigation.

It was necessary to use a finer size feed to get the maximum release of the zinc. However, sliming was encountered, particularly in the 6% Zn test. Repeated desliming before preparation of feed gave some relief.

ONE PERCENT LOS LAMENTOS FEED: Inspection of Table X shows that the amount of collector necessary to reach a maximum percent zinc in concentrate is higher than for willemite. Further, that once the maximum is reached, very little depressant action takes place. There is nowhere near the drop

in flotation as for willemite feed. The percent recovery of zinc is favorable with that obtained on willemite. The improvement factor reaches a maximum at 291. This maximum is lower than for willemite. The increased collector demand is probably due to (a) the difference in silicate structure, (b) impurities in the Los Lamentos Ore, (c) sliming conditions. Comparison of Figure 15 with Figure 3 and 4 show the less sharp effect of increased amounts of collector in both the pre and pos maximum points.

The effect of change of pH showed the best improvement factor obtained, 329, was at a pH of 6. A drop in percent zinc concentrate, percent recovery of zinc and improvement factor was noted at both the lower and higher pH's. The maximum improvement factor which is lower than for the willemite might be explained by the fact that this ore probably contained some zinc as a hydrated silicate which is not as easily floated as the dehydrated willemite. It is further possible that all the zinc is not in the form of pure silicates and that n-octyl methylene blue is not as an effective collector on the other forms.

Test series 10-8, 10-9, and 10-10 were run on once concentrated Los Lamentos Ore. Reflotation produced an enrichment of 3.3 with a zinc recovery of 56.58. Additional collector and reflotation without pH adjustment gave both enrichment and increased percent zinc recovery. Increased collector and pH

adjustment did not give any improvement over the straight reflotation. This is in contrast to the results obtained with willemite and calamine. However, this contrast, on close analysis, is not so marked. The real change is in test 10-8. That is to say, we apparently reach a fair recovery without the need for additional adjustments before reflotation. The recovery of 56.58% of zinc on Los Lamentos ore vs. 33.3% recovery on the willemite on straight reflotation indicates better chance for improvement of this commercial silicate than for willemite by merely a multiple cell flotation process, without additional collector.

SIX PERCENT LOS LAMENTOS FEED: Inspection of Table XI and Figure 16 will indicate that flotation of this ore is affected by the n-octyl methylene blue. The percent zinc in concentrate is gradually increased with increased amounts of collector and is 25.49 percent with 0.35 pound collector per ton. The rate of change with increased amounts of collector is much lower for this ore than for the calamine (compare Figures 9 with 16). Figure 9 indicates more recovery might be obtained by additional collector.

The percent zinc in the concentrate vs. amount of collector shows a much more gradual increase than with calamine or willemite (compare Figure 16 with Figures 7 and 9). An enrichment factor of 4.25 was obtained with 0.35 pounds of

collector per ton. While the improvement factor went to 310.7.

It may be concluded that under the test conditions of Table X and XI that n-octyl methylene blue functions as a collector for the Los Lamentos ore. Fair amounts of this collector give increases in percent zinc in the concentrate and percent recovery of zinc.

DEPRESSANTS AND ACTIVATORS

Only a few preliminary tests were conducted on the effect of various materials as depressants or activators. No worthwhile success was obtained with any material. Any depressants for silica also tended to retard the flotation of the zinc silicate. The same was true of activator. It is interesting to note in the patent literature (2, 16, 41, 54, 61, 62) certain claims regarding the function of additive materials. For example, one patent (54) claims that sodium sulfide with an aliphatic amines collector containing from 8 to 10 carbons activates flotation of desired material away from a silicious type gangue, while another patent (16) claims the silicious gangue particles can be floated away from the desired material using aliphatic amine having 10 to 18 carbons, using sodium sulfide as a depressant. In both cases, the majority of gangue was silica. Still another patent claims amines with 6 to 16 carbon atoms acts as a collector for

silica without a depressant or activator. However, no literature or patents claims the successful concentration of zinc silicate by floating it or the gangue. The use of various agents should certainly be extensively investigated with the type collector developed in this work. A depressant or an activator appears to offer excellent promise in the pH range between 5 and 7.

ACCURACY AND SUMMARY

The results of this investigation on the three zinc silicate ores by the newly synthesized collector called n-octyl methylene blue should be taken only as trends. The "optimum" conditions given are by no means recommended conditions for commercial flotation of zinc silicate ores. These "optimums" served as guide posts in this investigation in studying the variables, and the behavior of the new collector in a general way.

The results obtained are certainly a direct function of the condition of the various tests to project this new theory of a collector for zinc silicate, and the conditions established is not intended.

It is hoped that the results and "optimums" herein reported and discussed will serve as a guide for future investigation on zinc silicate. It is hoped these results will give encouragement to the pursuit of the new theory of zinc

silicate flotation, that new modified mordant dyes will be prepared and investigated along with the effects of carbon chain length, So that many of the trends can be more fully studied and explored, that answers to such questions as why the pH has such a marked effect on flotation and how its mechanism can be exemplified.

It is strongly believed, based on this investigation, that the solution to successful flotation of zinc silicate lies in pursuit of this new mordant or "envelope" theory, rather than in the past approaches presented in the Introduction.

CONCLUSIONS

Based on the results and discussion herein adduced the following conclusions are made.

A. The synthesized alkyl substituted dye herein designated as n-octyl methylene blue is shown to function as a collector for the zinc silicate ores, willemite, calamine, and Los Lamentos ore, under the conditions tested.

B. This modified dye appears to offer a new approach to the flotation of zinc silicate. It is theorized that selectivity for the zinc silicate is tied in with the mordant action of the dye, further, that the zinc particles are "enveloped".

C. It is demonstrated that the factors of pH, particle size, amount of collector, affect the percent zinc in the concentrate, percent recovery of zinc, enrichment of the product, and the improvement factor in the flotation of zinc silicate by n-octyl methylene blue.

D. That certain trends exist for the factors listed in C. Further, that under the conditions of the tests "optimums" appears to exist for the zinc silicate ores studied.

E. That the commercial synthesis of n-octyl methylene blue is not practical. The approach, using this compound as a collector is however, well justified by our present knowledge

of dye mordants as well as the presently developed theory of surface chemistry as related to mineral flotation.

F. Further investigation on the effects of activators and depressants, and trends reported herein might be conducted.

APPENDIX

APPENDIX

Preparation of n-octyl methylene blue, chemically, 3 n-octyl, 2,8 tetra methyl diaminothiazonium chloride:

This procedure is a combination and modification of several procedures on preparation of methylene blue. (8, 33, 34, 38).

12.2 grams (0.1 mole) of pure dimethylaniline are dissolved in 37.5 grams of concentrated HCL (30%) and allowed to cool. The solution is cooled with ice to 12-15°C. During a one hour period 7.35 grams (.145 mole) of 100% $NaNO_2$ are run in as a 20% solution (delivery tube beneath the surface of the liquid) taking care that the temperature does not rise above 15°C. The nitrosation is completed in four hours.

Add 55 grams of 30% HCI & 100 grams of ice. 17.5 grams of good quality Zn dust is added during a quarter-hour period with mechanical stirring. The temperature must remain below 25°C. (The amount of Zn dust added must be sufficient to completely neutralize the HCI). The solution is now either colorless or a clear red color. Neutralization is complete when Congo paper is no longer turned blue. The solution is filtered and the Zn dust is washed with very little water.

At this point, it is essential that the substances be added quickly and in the correct temperature.

The following solutions are made up at this point:

Solution I = 19 grams pure $Al_2(SO_4)_3$ in 30 cc. H_2O.

Solution II = 26.3 grams crystallized $Na_2S_2O_3$ in 25 cc. of H_2O.

Solution III = 28 grams $Na_2Cr_2O_3$ made up to 45 cc.

Solution IV = 10 grams n-octyl dimethylaniline in 13.5 grams of strong HCl.

Solution V = 12.5 grams very finely powdered manganese dioxide. Made up into a paste with 15 cc. H_2O.

To the p-aminodimethylaniline solution add 2 grams concentrated H_2SO_4 and 50 grams of 50% nonreducing $AnCl_2$ solution. Place the beaker on a felt pad and heat by blowing in steam. Add solution I at the ordinary temperature with good stirring. Add solution II, and after 2 seconds, one-third of solution III. Raise solution temperature to 40°C in one minute by passing in dry steam. Add solution IV and remainder of solution III and heat rapidly to 70°C. Once 70°C is reached, add solution V and heat to 85°C. Hold at 85°C for one-half hour and cool to 50°C. Add 35 grams concentrated H_2SO_4. Cool with ice bath for 36 hours and filter off product with a little 10% brine.

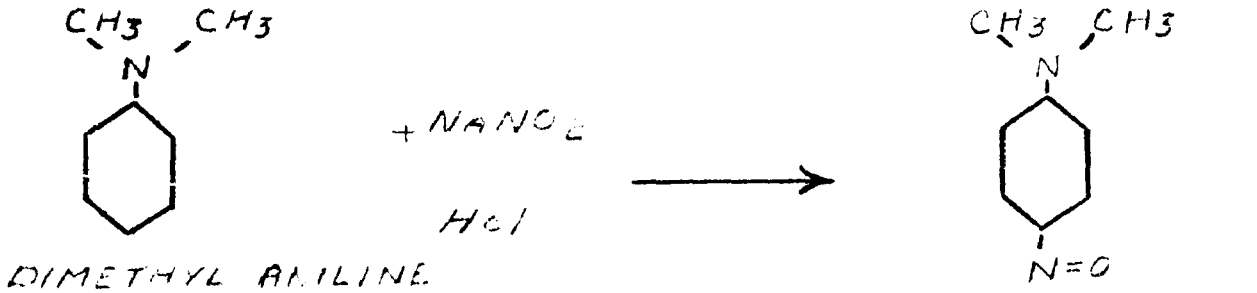
To obtain Zn-free product of n-octyl methylene blue,

dissolve the crude n-octyl methylene blue in H_2O-alcohol mixture and add enough Na_2CO_3 to completely precipitate all the Zn present. Filter the solution. Add 75 grams salt and 25 grams of HCl solution. Let solution stand and cool in salt and ice bath until precipitation is complete and then filter.

The above procedure is given in equation form in Table A. The key to the preparation is equation 4, which yields the n-octyl thiosulphonic acid of indamine. The test and proof of the n-octyl methylene blue is given in the discussion section.

EQUATIONS FOR PREPARATION OF ALKYL-SUBSTITUTED METHYLENE BLUE OR 3 n-OCTYL, 2, 8 TETRA METHYL DIAMINOTHIAZONIUM CHLORIDE

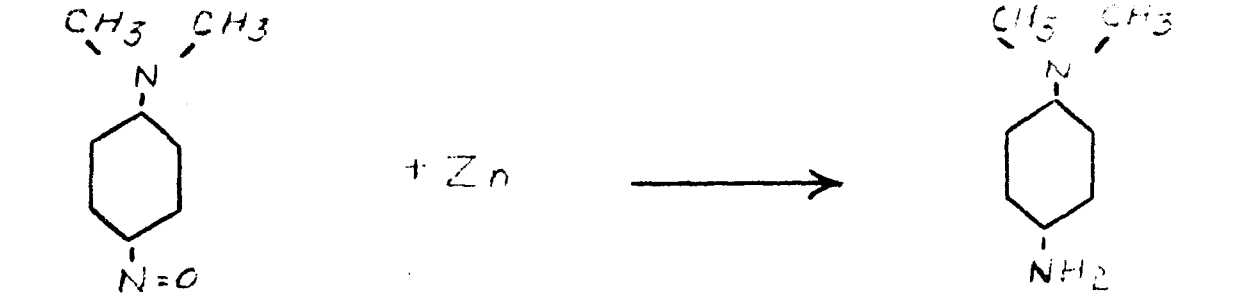
No. 1



DIMETHYL ANILINE

PARA-NITROSO-DIMETHYL ANILINE

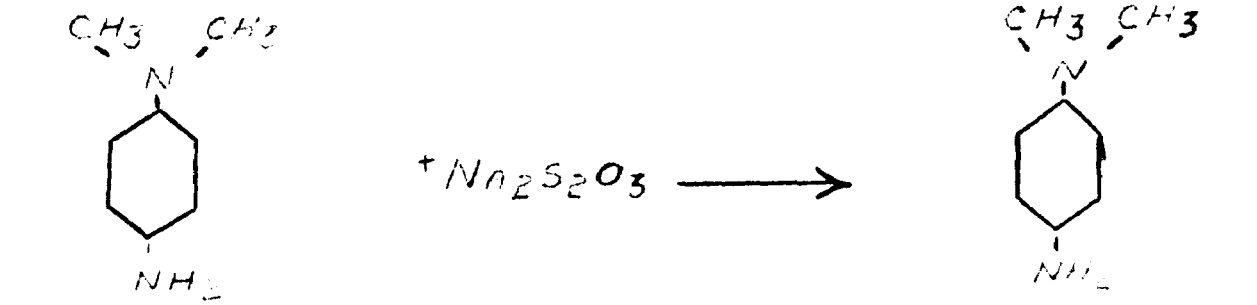
No. 2



PARA-NITROSO DIMETHYL ANILINE

PARA-AMINE DIMETHYL ANILINE

No. 3

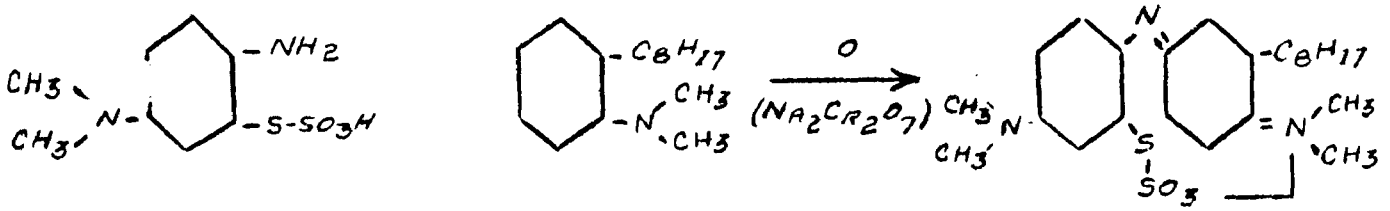


PARA-AMINODIMETHYL ANILINE

P. AMINODIMETHYL ANILINE

TABLE A

No. 4



THIOSULPHONIC ACID OF p-AMINO DIMETHYL ANILINE

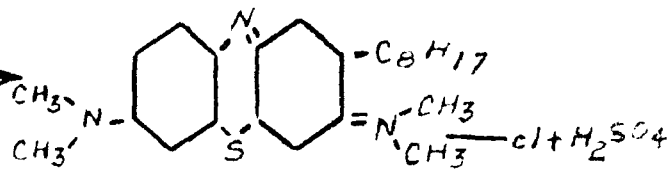
o-OCTYL DIMETHYL ANILINE

n-OCTYL THIOSULPHONIC ACID OF INDAMINE

No. 5

n-OCTYL THIO-SULPHONIC ACID + OF INDAMINE

HCl & $Na_2Cr_2O_7$ (NEUTRAL)

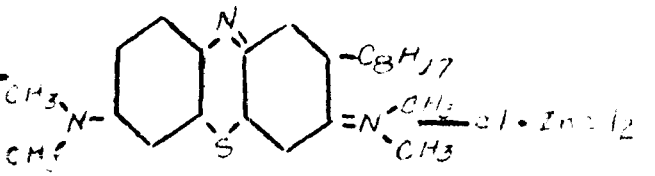


n-OCTYL METHLENE BLUE SOLUTION

No. 6

n-OCTYL METHLENE BLUE + SOLUTION

$ZnCl_2$ & NaCl



ZINC SALT OF n-OCTYL METHYLENE BLUE

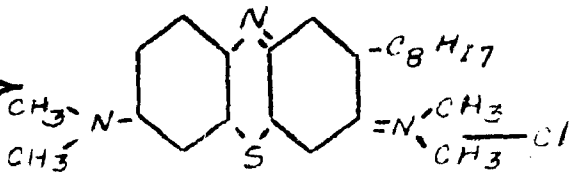
TABLE A

No. 7

ZINC SALT OF METHYLENE BLUE + SOLUTION + Na_2CO_3 & H_2O → $ZnCO_3$ + METHYLENE BLUE IN SOLUTION

No. 8

1-OCTYL METHLENE BLUE SOLUTION + HCl & NaCl →



N-OCTYL METHLENE BLUE, 3 N-OCTYL 2, 8, TETRA METHYL DIAMINOTHIOZONIUM CHLORIDE

TABLE A

The preparation of the 3 n-octyl 2,8 tetra methyl diaminothiazonium chloride depended on the ability of preparing ortho n-octyl dimethyl aniline. Table B gives reactions A to F which show the reactions used to convert benzene into ortho-n-octyl dimethyl aniline.

Reaction A. Benzene to n-heptyl phenyl ketone.

This reaction was brought about by a Friedal-Craft reaction between the benzene and n-capryl chloride.

This chloride (43, 77) was prepared by reacting 2 mols of n-caprylic acid with an excess of thiony chloride (i.e. 3 mols). Equipment used was a three neck flask equipped with reflux condenser, stirring mechanism, dropping funnel and thermometer. After the thionyl chloride was refluxing, the acid was added dropwise. After complete addition, the solution is boiled and allowed to stand for eight hours. The n-capryl chloride is vacuum fractionated and refractionated. The cut was taken at 81-82° at 16 mm. The yield was 72%.

The Friedel-Craft reaction employed was a modification of the method used by Wood & Associates (45). Twenty-five mols of benzene are placed in a three neck flask equipped as for the chloride preparation above. The flask was cooled with an ice-salt mixture and kept at a 10°C while 4.3 mols of aluminum chloride was added. This low temperature was maintained while 1.5 mol of the n-capryl chloride was added over

a three and one-half hour period. The temperature is raised and when hydrochloric acid ceases to evolve the temperature is lowered.

The reaction is kept cool for ten hours, after which time the whole mass is poured on acidified crushed ice. After five hours, the organic layer is separated and the excess benzene distilled off.

The n-heptyl ketone is washed three times with a sodium carbonate solution, and then three times with water, dried and subjected to a vacuum fractionation and refractionation. This reaction gave a yield of 83% of the normal product whose boiling point was 161°F at 20 mm.

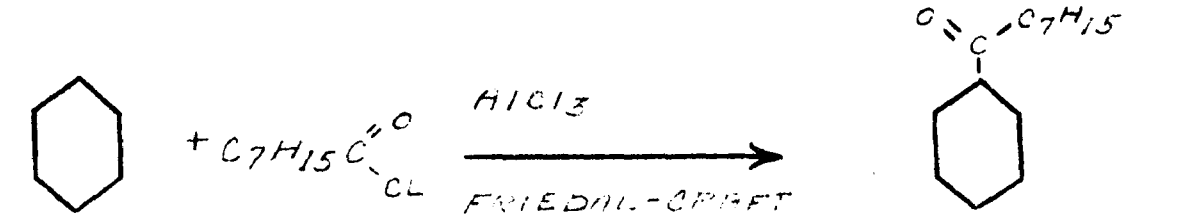
Reaction B. n-heptyl phenyl ketone to n-octyl benzene.

This reaction was carried by the use of a Modification of the Wolff-Kishner Reduction (42). This is an improved procedure over the Clemmensen reduction method (49, 53), the modified procedure consists in refluxing the carbonyl compound in a moderate amount of diethylene or triethylene glycol with 85% hydrazine hydrate and about three equivalents of sodium or potassium hydroxide for one hour, distilling enough water and excess hydrazine to raise the temperature and then refluxing the solution for several hours longer.

In this case, 1.0 mol of n-heptyl phenyl ketone was placed in a round bottom flask to which had been added 120 grams of

EQUATION FOR THE PREPARTION OF ORTHO n-OCTYL AMILINE

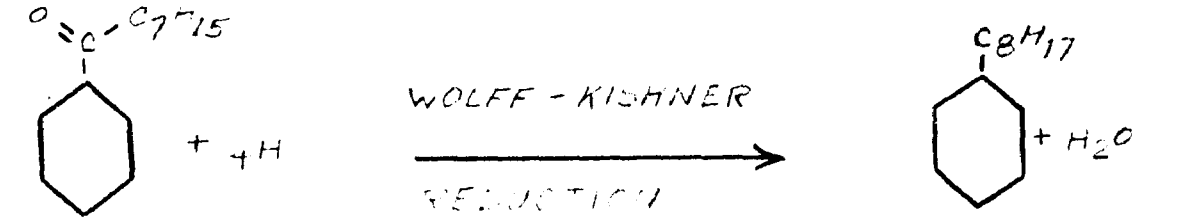
REACTION A



BENZENE

n-HEPTYL-KETONE

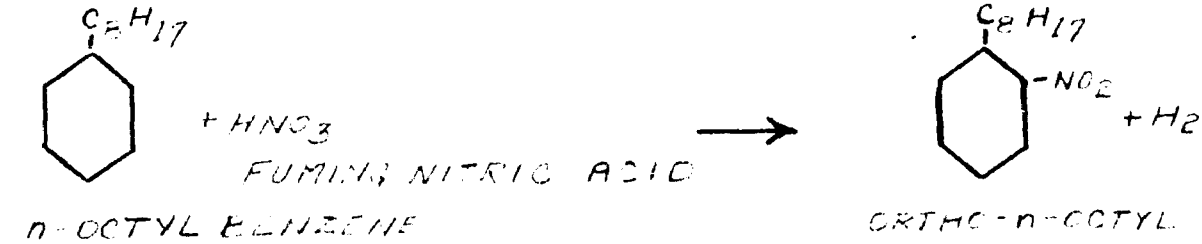
REACTION B



n-HEPTYL-PHENYL KETONE

OCTYL-BENZENE

REACTION C

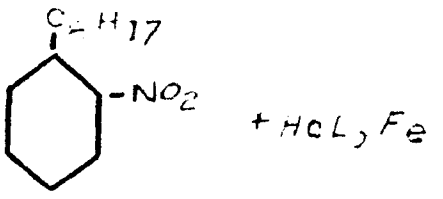


n-OCTYL BENZENE

ORTHO-n-OCTYL NITRO BENZENE

TABLE B

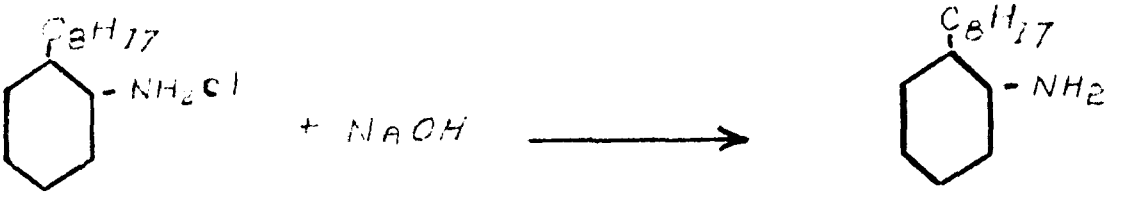
REACTION D



ORTHO-n-OCTYL NITRO BENZENE

ORTHO-n-OCTYL ANILINE HYDROCHLORIDE

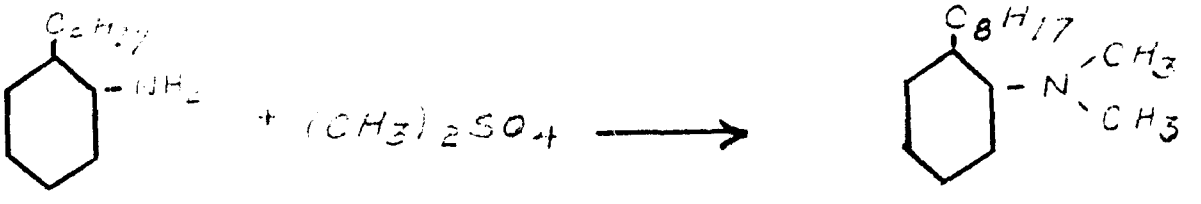
REACTION E



ORTHO-n-OCTYL ANILINE HYDROCHLORIDE

ORTHO-n-OCTYL ANILINE

REACTION F



ORTHO-n-OCTYL ANILINE

ORTHO-n-OCTYL-DIMETHYL ANILINE

TABLE B

potassium hydroxide, 1000 cc. of triethylene glycol and 100 cc. of 85% hydrazine, then the entire mixture was refluxed for two hours.

The aqueous liquor was removed by means of a take-off adapter until the temperature of the liquid rose to 150 degrees. Refluxing was then continued for five hours, after which period the reaction mixture and aqueous distillate were combined, and then extracted with ether and then neutralized. The neutral organic fraction was distilled over sodium. A yield of 60% of n-octyl benzene was obtained, boiling point of 135-137 degrees at 20 mm.

Reaction C. n-octyl benzene to ortho n-octyl nitro benzene.

The production of an ortho nitro group was very difficult, since most nitration methods give substitutions in the octyl group. Furthermore, any method of nitrating n-octyl benzene which places a nitro group on the benzene ring are all chiefly para and meta directing. The method used (65) was the best one found in the literature however, the yield of the pure ortho octyl nitrobenzene was discouragingly low.

One mol of n-octyl benzene was placed in a three necked flask equipped as for capryl chloride preparation. Two hundred fifty cc. of fuming nitric acid is added dropwise while the temperature is held at 10 degrees. The addition takes approximately six hours. The reaction product is poured on

crushed ice and extracted with 400 cc. of benzene. The organic layer is washed three times with sodium carbonate solution and three times with distilled water.

The benzene is distilled over at atmospheric pressure. The remaining material is subjected to vacuum fractionated and refractionation. The yield is only 13% of the ortho compound whose boiling point was 181-182° F at 20 mm.

Reactions D and E. Ortho n-octyl nitro benzene to ortho n-octyl aniline.

In the method used (76) Groggins (40) gives many of the reactions, properties of analine and its derivatives. Two hundred and fifty cc. of methanol are placed in a three necked flask equipped with a stirrer and reflux condenser. To the flask was added 0.5 mol of ortho n-octyl nitro benzene and then 10 cc. of concentrated hydrochloric acid. The entire mixture was refluxed and 90 grams of iron filings were added, 20 grams at a time, refluxing over one-half hour intervals was then continued, for three hours. Potassium hydroxide is used to neutralize the excess hydrochloric acid. The residue can then be filtered hot and the methanol is distilled over. Hydrochloric acid is then added. The mixture is subjected to low temperature and the hydrochloride of the ortho n-octyl aniline can be filtered off. The hydrochloride is changed to the ortho n-octyl aniline by potassium hydroxide.

The ortho n-octyl aniline is extracted with ether. The ether is then distilled off and organic material is subjected to a vacuum fractionation and refractionation. A yield of 65% of ortho n-octyl aniline was obtained its boiling point was 169-171° at 5 mm.

Reaction F. Ortho n-octyl aniline to ortho n-octyl dimethyl aniline.

Dimethylation can be carried out by using methanol and sulfuric acid. However, the modified procedure (7, 73) employed in this case involved the use of dimethyl sulphate which was available. Extreme precautions were necessary due to the severe action upon the mucous membrane.

A three neck flask was used which contained the same equipment as for reaction A. Extra care was taken to insure proper venting of the apparatus. One-half mol of ortho n-octyl aniline was added to the flask along with 0.6 mol of calcium hydrate which is finely powered and thoroughly dried. 0.7 mol of dimethyl sulphate is added slow enough to keep the temperature below 80 degrees. This addition takes about 60 mimutes. The mixture was then refluxed for ten hours and extracted with ether. The excess dimethyl sulphate was fractionated off and the ortho n-octyl dimethyl aniline subjected to vacuum fractionation. The yield was 67% with a boiling point of 181-183° at 10 mm.

This ortho n-octyl dimethyl aniline was used in the preparation of n-octyl methylene blue as given in Table A. It should be pointed out that many of these reactions were carried out numerous times to obtain workable quantities of the desired materials. The yield, etc. or based on the average results. The quantities used were those found by trial and error to give the best amount with the better yields necessary to produce a workable quantity of n-octyl methylene blue.

GRAVIMETRIC DETERMINATION OF ZINC SILICATE ORES (32)

Treat 0.5 g. of the finely ground ore in a covered casserole with 10 ml. of 12 M hydrochloric acid, heating gently until all violent action is over; add 5 ml. of 16 M nitric acid and 5 ml. of 18 M sulfuric acid and digest on the hot-plate until the ore is completely decomposed. Evaporate to copious fumes of sulfuric anhydride in order to expel all traces of hydrochloric and nitric acids, but take care not to go to dryness; allow the solution to cool, and, after estimating the amount of sulfuric acid which remains, add 50 ml. of water and enough more sulfuric acid to make the total concentration of acid about 1.5 to 2 M. Introduce into the solution a piece of sheet aluminum about two inches square and bent up at its corners, and boil for about 10 minutes -- this will usually serve for the complete reduction to the metallic state of any lead, copper, arsenic and antimony

that might be present, but any cadmium or bismuth will be only partially reduced. Filter the solution through a filter paper in which is placed a piece of metallic allumimum, and receive the filtrate in an Erlenmeyer flask. After washing the filter four or five times with small portions of hot water, cool the filtrate and washings to room temperature, add several drops of methyl orange indicator, and neutralize with 15 M ammonium hydroxide; now add enough hydrochloric acid to make its concentration in the final volume equal to 0.3 M, heat the solution to 80° -90°, and pass in hydrogen sulfide to precipitate any cadmium or bismuth and any traces of copper. After the precipitate has settled, filter it off and wash with 0.3 M hydrochloric acid saturated with hydrogen sulfide.

After the precipitate has been filtered and washed with 0.1 M formic acid, which is saturated with hydrogen sulfide, it is transferred to a weighed porcelain crucible and the filter paper is charred, preferably by standing the crucible upon a quartz plate, which is heated strongly by means of a Meker burner. The ignition of the filter paper is very slowly and carefully completed in an oxidizing atmosphere over a Bunsen burner. The reaction should proceed only to the formation of $AnSO_4$ and not to ZnO. If the reaction proceeds to ZnO, the subsequent moistening of the residue with concentrated

sulfuric acid often generates heat enough so that the water which is formed according to the reaction, $ZnO+H_2SO_4---H_2O+ZnSO_4$, is converted into steam, and particles of the precipitate are thrown out of the crucible. After cooling, the precipitate is carefully moistened with a few drops of 9 M sulfuric acid, and the crucible is heated in an air-bath until the excess acid is driven off, then heated over the Bunsen burner to remove any charred material. The precipitate is again moistened with concentrated sulfuric acid and the crucible heated in the air-bath, until the excess of acid is driven off; it is allowed to cool, then weighed; the moistening with sulfuric acid and subsequent evaporation is continued to constant weight, two such treatments usually being sufficient. A blank is run to correct for any impurities in the reagents, and the residue (usually about 0.2 mg) is substracted from the final weight of zinc sulfate.

NOTES ON METHODS OF PRECIPITATION

After the insoluble sulfides of the tin and copper groups have been filtered off, the filtrate can be used for the separation of the zinc from cobalt, nickel, iron and manganese by precipitating the zinc as sulfide after the acidity has been adjusted to a value of pH = 2.1. The procedure is as follows: The filtrate from the hydrogen sulfide precipitation of the copper and tin groups (copper having been previously

removed by electrolysis or electro-deposition) is evaporated to a volume of 125 ml. if the volume is greater than this amount. It is then freed of hydrogen sulfide by boiling in a 750 ml. Erlenmeyer flask until the escaping steam no longer smells of hydrogen sulfide; the solution is cooled to room temperature and 6 M ammonium hydroxide is added until the precipitate which first forms just fails to redissolve. 25 ml. of 1 M citric acid (200 g. citric acid per liter) are added, also a few drops of methyl orange indicator, and then 6 M ammonium hydroxide until the solution is neutral to the methyl orange. If the solution has not been previously cooled, the methyl orange will be rapidly destroyed by the hot solution and its use would be unreliable. The prior removal of the hydrogen sulfide is also essential, as this agent destroys methyl orange. 25 ml. of "formic mixture" is next added, then 20 ml. of 24 M formic acid, after which the volume of the solution is made up to 200 ml. This procedure is necessary in order to establish the right concentration of hydrogen ion for the precipitation and at the same time to provide a buffer to hold the concentration of hydrogen ion sensibly constant during the process of a precipitation.

"Formic mixture" is a solution of the following composition: 200 ml. of 24 M formic acid (Sp. Gr. 1.20), 30 ml. of 15 M ammonium hydroxide, and 200 g. of ammonium sulfate, made

up to one liter with distilled water. The function of the ammonium sulfate is to aid in "salting out" the zinc sulfide in gramular form as recommended by Treadwell in accordance with the work of G. H. Kramers who also showed that ammonium chloride or thiocyanate are equally good for this purpose. Since zinc is usually precipitated as the sulfide from a sulfate solution in the analysis of an alloy or ore, the choice of ammonium sulfate seems to be the preferable one for the "salting out" effect.

The flask containing the solution being analyzed is placed on a wire gauze supported on a tripod and heated to about 60°-70°. Then a two-hole rubber stopper, having each hole fitted with a glass tube which is bent at right angles and which just passes through the stopper, is placed smugly and securely in the neck of the flask. One of the bent glass tubes is connected by means of a piece of rubber tubing to a wash bottle which contains distilled water and is connected in turn with a hydrogen sulfide generator; the other glass tube is equipped with a short piece of rubber tubing to be subsequently closed by means of a pinch clamp. After having introduced the rubber stopper and having observed that the exit tube is open, the hydrogen sulfide is allowed to flow so as to displace the air in the flask and the heating is continued until the solution almost boils. The burner is

removed and the exit tube is closed with a pinch clamp at once, but the hydrogen sulfide supply is kept open and connected with the precipitation flask. The latter is shaken frequently to insure complete saturation. When the solution has cooled to 25°-30°, the supply of hydrogen sulfide may be turned off. The precipitate of zinc sulfide, which should be white in color, will usually settle within thirty or forty minutes and will be ready for filtration. It often happens, in the process of precipitation, especially when the flask has not been thoroughly cleaned, that a layer of zinc sulfide sticks so firmly to the sides of the flask that it cannot be removed. The precipitate adhering to the flask is then dissolved in hot dilute sulfuric acid (2-3 ml. of 18 M sulfuric acid in 25 ml. of water), just neutralized with ammonium hydroxide, or better, neutralized and then made slightly acid with formic acid, saturated with hydrogen sulfide under pressure, heated to boiling to coagulate the precipitate, and filtered through the filter containing the already washed precipitate of zinc sulfide. Further, washing is unnecessary, as any salt or acid present is volatile.

The precipitate of zinc sulfide is filtered through an ashless filter paper and washed thoroughly with 0.1 M formic acid saturated with hydrogen sulfide.

Polarographic Determination of Zinc in Zinc Silicate Ores on FISHER ELECTROPODE (73)

In order to give a basic check on both the volumetric and gravimetric method for analysis of zinc in the various silicate ores, the polarographic method was used. The ore was prepared the same as in the volumetric method up through the addition of $KCLO_3$ and subsequent filtration. (See volumetric method in procedure section). From this point on aliquot portion could be taken and subjected to the following procedure:

Take suitable aliquot to dryness. Cool and add 25 ml. of 0.2 N HCl. Heat just to boiling, and transfer by filtering into 50 ml. volumetric flask containing exactly 5.0 ml. of internal standard which is at a temperature of 25.0°C., and five drops of bromcresol purple. Wash filter paper with repeated portions of distilled water to approximately 45 ml., add 1.0 ml. of gelatine, and make to volume at 25.0°C. Transfer 10.0 ml. aliquot to polarographic cell, add three drops (0.05 ml.) of concentrated ammonium hydroxide and polarize at 1/50 sensitivity (S = 50X) from 1000 x 10^{-3} to 1700 x 10^{-3} volts. The zinc concentration will then be determined from the ratio obtained in plotting this portion of the curve.

Gelatine Maximum Suppressor: A fresh solution containing 1.0 gram of U.S.P. gramular gelatine per 100 ml. of distilled water is prepared. Use 1.0 ml. of this solution

per 50 ml. of solution to be polarized.

Bromcresol Purple Indicator: A 0.1 percent solution is made by mascerating 0.1 gram of dry bromcresol purple powder in a mortar with 18.5 ml. of 0.01 N NaOH and diluting mixture to 100 ml. with distilled water. Use 5 drops per 50 ml. of solution to be polarized.

Oxygen Absorbent for Purification of Nitrogen: Pass nitrogen through a first scrubbingflask containing a solution of 40 ml. NH_4OH, 40 ml. H_2O, saturated with NH_4Cl (approximately 25 grams), and filled with copper gauze, especially in the air spaces; then, through a second scrubbing solution of dilute sulfuric acid (5N).

B I B L I O G R A P H Y

1. Andreeva, A. P., Tsventye Metal, 9, 46-50, (1940).

2. Arnold, G., United States Patent (June 8, 1937).

3. Barsch, O., Kolloid Chem. Beihefte 20, 1 (1924).

4. Barth, O., Die Mellallverfluechtigungsverfonren mit besonderer Beruech suhtigung der Herstullung von Zinkexyd 1935, Wilhelm Knapp, p. 117-147.

5. Bunge, F. H., Fine, M. M. and Legsdin, A., University of Missouri School of Mines and Metallurgy, Bull. Vol. 17, 3, (1946).

6. Ibid., p. 17

7. Cade, I., Chem. and Met. Eng. 29, 319, (1923).

8. Cain, J. C. and Thorpe, J. F., The Synthetic Dyestuffs and Intermediate Products. Charles Griffin & Company Limited, London, p. 289, (1923).

9. Committee on Uniformity in Technical Analysis, J. Am. Chem. Soc. 26, 1648 (1904).

10. Cottermole, British Patent 777,283.

11. Crabtree, E. H. Jr., Eagle-Pitcher Co., Private Communica (1952).

12. Dana, E. S., A Text-Book of Minerology, John Wiley & Sons, Inc. New York, p. 422, (1916).

13. Ibid, p. 466

14. Ibid, p. 360

15. Dean, R. S. and Ambrose, P. M., United States Bureau Mines, Bull. 449, p. 71.

16. DeVaney, F. D., United States Patent 2,410,021 (Oct. 29, 1946).

17. DeVaney, F. D., Picklands, Mather and Co., Private Communica (1950).

18. DeWitt, C. C., Ind. and Eng., Chem. 32, 652, (1940).

19. DeWitt, C. C., and Ashabhai, P. I., 2-4-6 Trihydroxy-phenyl Alkyl Ketones as Flotation Reagents For Manganese Dioxide, M. S. Thesis, Michigan State College, 1951, 30 numb. leaves.

20. DeWitt, C. C. and Botchelder, F. von., J. Am. Chem. Soc. 61, 1247, (1939).

21. DeWitt, C. C. and Brown, M. G., An Alkyl Substituted Triphenylmethane Dye as a Flotation Agent for Stibnite, M. S. Thesis, Michigan State College, 1950, 23 numb. leaves.

22. DeWitt, C. C. and Lenton, P. A., Froth Flotation of Azurite and Maluchite in Alkaline Earth Gangue Material, M. S. Thesis, Michigan State College, 1943, 40 numb. leaves.

23. DeWitt, C. C. and Livingood, M. D., Flotation of Copper Silicate by Selected Alkyl Substituted Pooyhydroxy Nitroso Phenols, Ph. D. Thesis, Michigan State College 1951, 124 numb. leaves.

24. DeWitt, C. C. and Ludt, R. W., The Flotation of Copper Silicate by Alkyl-substituted Triphenyl Methane Dyes, Ph. D. Thesis, Michigan State College, 1947, 95 numb. leaves.

25. DeWitt, C. C. and Makens, R. F., J. of Am. Chem. Soc. 54, 444, (1932).

26. DeWitt, C. C. and Overcash, R. L., Separation of Seeds by Froth Flotation, M. S. Thesis, Michigan State College, 1942, 51 numb. leaves.

27. DeWitt, C. C. and Thakkar, J. L., Alkyl Substituted Wurster's Salts as Flotation Reagents, Thesis, Michigan State College, 1950, 28 numb. leaves.

28. Dow Chemical Co., Flotation Fundamentals 2nd Ed. Dow Chemical Co., San Francisco, P. 7.

29. Edser, E., British Assn. for Adv. of Science. Fourth report on Colloid Chemistry 4, 263 (1922).

30. Erlenmeyer, H., Steiger, J. V. and Theilheimers, W., Helv. Chem. Aeta., 25, 241-5 (1942).

31. Fahrenwald, A. W., Eng. Mining J., 146, 155 (1945).

32. Fales, H. A. and Kenny, F., Inorganic Quantitative Analysis. D. Appleton - Century, N. J., p. 317, (1939).

33. Fierz, David, H. E., Translated by F. A. Mason, Fundamental Processes of Dye Chemistry, J. A. Churchill, London, 1st. Ed. p. 174-177 (1921).

34. Fierz, David, H. E. and Blangey, L., Translated by P. W. Vittum, Fundamental Processes of Dye Chemistry, Interscience Publishers, Inc., New York, 5th Ed., p. 311 (1949).

35. Ibid., p. 392.

36. Foulk, C. W., Koll. Zeitsch, 60, 115 (1932).

37. Forment, A., British Patent, 12778 (1902).

38. Georgievics, G. V. and Grandmougin, E., Translated by F. A. Mason, A Text-Book of Dye Chemistry, Scott, Greenwood & Son, London, p. 201, (1920).

39. Grandnougin, E., Chem. Zeit., XXXVI., 1167, (1912).

40. Groggins, P. H., Aniline and Its Derivatives. D. Van Nostrand Co., New York, (1924).

41. Gutzeit, G., United States Patent 2,125,631 (Aug. 2, 1938).

42. Haung-Minlow, J. Am. Chem. Soc. 68, 2488 (1946).

43. Helferich, B. and Schaefer, W., Organic Synthesis Conant, J. B. ed., New York, John Wiley & Sons, Vol. 9, p. 32, (1929).

44. Hoover, T. J., Mining Magazine, London (1916).

45. Ju, T. Y., Shen, G. and Wood, C. E., Shen, G., Inst. Petr. 514, (1940).

46. Keller and Lewis, United States Patents 1,554,216 and 1,554,220.

47. Knecht, E., J. Soc. Dyers, 6, XIX, (1903).

48. Knecht, E., and Hibbert, E., New Reduction Methods in Volumetric Analysis, 2nd Ed., Longmans, Green, London (1928).

49. Kohmann, E. F., and Johnson, T. B., J. Am. Chem. Soc. 36, 1259, (1914).

50. Lessel, V., Concentration Engineer International Smelting and Refining Co., Private Communica (1950).

51. Loomis, F. B., Field Book of Common Rocks and Minerals. Tenth Impression, G. P. Putnam's Sons, New York and London, p. 67, (1923).

52. Ibid., p. 68

53. Martin, E. E., Organic Reactions, Adams, R. ed., New York, John Wiley & Sons, Vol. 1, p. 167, (1942).

54. McKenna, W. J., Lessel, V. and Peterson, E. J., United States Patent 2,482,859 (Sept. 27, 1949).

55. McDonald, W. T., Eng. Min. J. 126, 679 (1928).

56. Nieto, J. C., Legsdin, A. and Schlechten, A. W., Bull. School of Mines and Metallurgy, Univ. of Mo. Vol. 18, No. 4, p. 3, (1947).

57. Petersen, W., Schwimmaufbereitung, Steinkopff, Dresden and Leipzig, p. 221 (1936).

58. Ibid., p. 228.

59. Phillips, F. C., An Introduction to Crystallography, Longmans, Green and Co., London, New York, Toronto, p. 120 (1946).

60. Ibid, p. 112

61. Ralston, A. W., and Pool, W. O.,United States Patent 2,168,849, (Aug. 8, 1939).

62. Ralston, A. W., and Pool, W. O., United States Patent 2,267,307, (Dec. 23, 1941).

63. Rex, H. J., Eng. Min. J. 149, 69, (1948).

64. Richards, R. E. Asst. Chief Chemist., Tennessee Copper Company, private communica, (1950).

65. Rinkes, I. J., Rec. Tray. Chem. 63, 3, 53, (1944).

66. Schwartz, A. United States Patent 807,501 (1905).

67. Scott, W. F., Standard Methods of Chemical Analysis, D. Van Nostrand Co., Vol. 1, p. 1067, (1939).

68. Siegmund, Monatsh, Chem. XXXIII, 1431, (1912).

69. Sisley, Bull. Soc. Chem., 862, (1901).

70. Sulman and Picard, United States Patent 962,678 (1910).

71. Taggart, A. F., Taylor, T. C. and Ince, C. R., A.I.M.E. Technical Publication 204, (1929).

72. Ullman, F., Diese Berichte 2, 33, 1900, p. 2476.

73. VonFarowe, D., Private Communica, (1950).

74. Wark, I. W., Principles of Flotation, Australasian Inst. Min. and Met., Melbourne, Australia (1938).

75. Weinig, A. J. and Carpenter, C. B., The Trend of Flotation, Quarterly Vol. XXXII No. 4 (Oct. 1937), Colorado School of Mines, p. 21.

76. West, R. J., Chem. Soc. 127, 494, (1925).

77. Weygand, C., Organic Preparations, New York, Interscience Publ., p. 101, (1945).

78. Wilson, L. A., Chief of Testing Dept., New Jersey Zinc, Private Communica, (1950).